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The Annual Report on Materials Science and Technology, of which this is the 14th edition, provides an overview of the research performed by the groups that participate in the Materials Institute Delft Eindhoven Groningen (MIDEG).

Some factual information about the graduate school MIDEG is given in the first chapter. Next, to give an impression of the research MIDEG is engaged in, three so-called leading articles are presented. A remarkable observation is made in the first article by Mittemeijer et al., where they show that precipitates need not necessarily be crystalline. The various effects that occur as a result of electromagnetic stirring during arc welding of aluminium alloys are discussed by Den Ouden and De Vries in the second article. In the third leading article, De With and Van der Varst consider the energy involved in fracture of dissimilar material joints.

Obviously, the main part of the Annual Report is devoted to the 14 groups of MIDEG. Their personnel, research areas and available experimental facilities are described, together with a report of their research achievements and publications in 1998.

Hopefully this Annual Report on Materials Science and Technology serves as a useful source of information.

April 1999

Michael Janssen
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INTRODUCTION

This 1998 issue of the Annual Report on Materials Science and Technology marks the fourth year of the national graduate school Materials Technology MIDEG and is the 14th annual report describing the research in materials science and technology at Delft University of Technology. Although 14 years is only a short period when taking into account the many centuries long history of materials science and technology, we may be proud of this tradition, which we intend to continue well into the 21st century. It is an indication of the continued interest in our work and a demonstration of our achievements.

While continuing the tradition we have also made a more accessible version of this report on our web site. We hope this fills a need.

The research described in this book covers, as does the graduate school MIDEG itself, the three major material classes: metals, polymers and inorganic materials as well as their combinations in the form of coated metals, laminates and composites. The research performed is an interesting mixture of fundamental materials science, aimed at truly understanding materials and their behaviour, and materials technology, aimed at translating fundamental insight into new materials or new material production routes. The graduate school is not only a cluster of research groups, it also provides courses and lectures to junior researchers working within the graduate school and to scientist working at the universities and in industry in general.

In 1998 we have witnessed both a strong increase in new projects, due to various new initiatives in materials science such as the newly founded technological and scientific centres of excellence, and further reductions in the regular university staff. The net effect of both developments has been a further growth of the total research activities within the graduate school. The number of research projects could have been even larger if a sufficient number of suitably qualified candidate Ph.D. students had been available.

The total number of fully employed senior and junior researchers in the school is now approximately 230. The combined result of their efforts has been more than 320 publications. 23 Ph.D. theses were defended successfully. Furthermore, several very advanced scientific and technological instruments have been installed or ordered.

Based on current developments, the graduate school MIDEG expects to end this millennium more successfully than ever before in its history and to continue along this line in the century to come.
Ph.D. THESES

1. P.C.H. Ament  
   Corrosion Fatigue of Structural Steel in Sea Water  
   Delft University of Technology

2. F. Beekmans  
   Rheology and changes in structure of thermotropic liquid crystalline polymers  
   Delft University of Technology (1997)

3. A. Boersma  
   A Dielectric Study on the Microstructure in Polymers and Blends  
   Delft University of Technology

4. E.P. Carton  
   Shock Compaction of Ceramics and Composites  
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5. C.H. Chen  
   Thin-Film Components for Lithium-Ion Batteries  
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6. R.A.M. Coenen  
   Design of a Quality Assurance System for Structural Laminates  
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7. L.D. van Ee  
   The diffusion mechanism in amorphous Ni$_8$B$_{19}$ studied by molecular dynamics simulations  
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23. R.C. Willemse
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Delft University of Technology
AMORPHOUS PRECIPITATES IN A CRYSTALLINE MATRIX; PRECIPITATION OF AMORPHOUS Si₃N₄ IN α-Fe

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1 Introduction

Microstructural changes in solids due to phase transformations are induced in practice to bring about specific, desired properties. Until now precipitate particles developing in crystalline supersaturated solids have been observed, and assumed, to be crystalline. Of course, application of "brute force", e.g. by ion implantation, can lead to amorphous regions/particles in a crystalline matrix. A possible development of amorphous precipitate particles from a supersaturated crystalline solid solution is counter-intuitive as the bulk energy of the amorphous state is larger than that of the crystalline state. This letter presents the, to our knowledge, first direct observation of amorphous precipitate particles in an initial stage of precipitation.

Nitriding of steel workpieces is employed to improve the mechanical and/or chemical surface dependent properties, as fatigue, tribological and corrosion properties. Alloying elements that can precipitate as nitrides in the steel matrix upon nitriding contribute to its strengthening. The effect of normally used alloying elements as Cr and Al in ferrite (= α-Fe) during nitriding has been investigated extensively [1-6]. Silicon is often present as an alloying element in steel. Silicon has a large chemical affinity for nitrogen. Therefore one expects the precipitation of silicon nitride if nitrogen is added to silicon containing α-Fe. Although the mass increase of the specimen upon nitriding suggests that nitrides precipitate, the nature of the precipitates has not been identified before in a direct (microscopical) way; in any case it has always been assumed that the precipitates are crystalline Si₃N₄ [7,8].

The present research project focussed on the development of a kinetic model for the precipitation of silicon nitride in silicon containing α-Fe, more or less as performed earlier by us for the precipitation of CrN and AlN [2,5]. In contrast with our earlier preliminary work from the past [8], a determined effort to reveal the structure of the nitrides was undertaken. To our surprise it was found that the precipitates were amorphous, stoichiometric Si₃N₄. The evidence for this finding is presented here. Further, on the basis of our recent work on the modelling of interface energies [9], it will be suggested here that the occurrence of initially amorphous precipitate particles may have a thermodynamic basis. The kinetic analysis will be presented elsewhere.
2 Experimental

The experimental set-up and procedures are described only briefly here; for more details, see [10]. A piece of Fe-Si alloy (composition: 1.60 at.\% Si, 0.0004 at.\% N, 0.006 at.\% C, 0.006 at.\% O, balance Fe) was subjected to several cold rolling and recrystallisation treatments yielding a foil of 100 μm thickness. Nitriding was performed in a 7 vol.\% NH₃/93 vol.\% H₂ gas mixture using a thermobalance (Netzsch, type TG439) for temperatures in the range 803-848 K and during times up to 112 h.

X-ray diffractometric analysis (XRD) was performed using a Siemens D500 diffractometer equipped with an incident beam Ge monochromator (set to select CoKα radiation) and a position sensitive detector. Diffracted intensities were recorded in particular in the range of diffraction angles where reflections of known crystalline forms of silicon nitride [11] occur (2θ = 20° - 50°; step size = 0.1°; counting time per step = 22000 s).

Electron probe microanalysis (EPMA) was performed using a Jeol JXA 733 instrument operating with a focused 10 keV electron beam with a stabilised current of 200 nA and an air jet to avoid carbon contamination during the measurement. For quantitative, wavelength dispersive element analysis the NKα and SiKα radiations were recorded with a W/Si multilayer crystal and a pentaerythritol (PET) crystal, respectively. Data analysis occurred according to the modified φ(p.z) approach [12].

Electron transparent foils for high resolution transmission electron microscopy (HRTEM) were prepared by electrochemical jet polishing using a solution of 10 vol.\% perchloric acid in acetic acid (Ar ion milling led to similar results). (HR)TEM was performed immediately after foil preparation, to avoid distinct oxidation, using a Philips CM30T microscope operating at 300 kV and equipped with a LINK QX2000 system for qualitative energy dispersive element analysis (EDS).

![Figure 1: Si Kα lines recorded from reference ("bulk") Si and Si₃N₄ specimens and the Si Kα line recorded from the nitrided Fe - 1.6 at.\% Si specimen](image)
3. Results

Nitriding was performed until no further mass increase occurred. From the specimen mass before nitriding, the silicon content and the measured nitrogen uptake, it followed that the amount of nitrogen absorbed corresponds with the precipitation of all silicon as Si$_3$N$_4$. However, subsequent XRD of the nitrided specimen did not show reflections due to any of the Si$_3$N$_4$ compounds known from the literature [11].

EPMA showed that the specimen contained 1.60 ± 0.06 at.% Si and 2.11 ± 0.08 at.% N. Thus the Si/N atomic ratio is 0.76 ± 0.06 which well corresponds with that of Si$_3$N$_4$. Further the Si Kα line recorded is shifted over 0.62 eV to a higher energy as compared to that of elemental Si. This shift is equal to that measured for Si in bulk Si$_3$N$_4$ (Figure 1). Thus, both the composition and the state of bonding of Si indicate that Si has precipitated as Si$_3$N$_4$.

![Figure 2](image-url)

Figure 2: Bright field electron micrograph of the nitried Fe - 1.6 at.% Si alloy with the incident electron beam close to a 100 direction of the ferrite matrix. The insets show convergent beam diffraction patterns obtained from the ferrite matrix and a precipitate, demonstrating the non-crystalline nature of the precipitate.

![Figure 3](image-url)

Figure 3: A HREM image showing a part of a precipitate in the ferrite matrix, with the incident electron beam close to a 100 direction of the ferrite matrix. The precipitate, in contrast with the matrix, shows no long range order; it is amorphous.
A bright field TEM image (Figure 2) shows the presence of small particles, of roughly cubic morphology, in a ferrite matrix: about 500 particles per \( \mu \text{m}^3 \) with a size of 7-45 nm. Selected area diffraction patterns (1 \( \mu \text{m} \) aperture) revealed no reflections other than pertaining to ferrite. In thin regions of the foils (thickness \( \leq 25 \text{ nm} \)) about 35 precipitates in 4 different foils were subjected to one or more of the following analyses: (i) local (micro)diffraction by Convergent Beam Electron Diffraction (CBED) with an electron probe size of about 12 nm; (ii) EDS with an electron probe size of about 12 nm and (iii) HRTEM imaging with the ferrite matrix close to a 100 orientation and using an aperture allowing contributions of reflections up to a diffraction-vector length equal to about 15 nm. CBED patterns (see the insets in Figure 2) unambiguously demonstrated that no crystalline diffraction occurred by the particles and EDS revealed the presence of Si and N at the location of the particles (no Si could be detected in the matrix). HRTEM images indicated the amorphous nature of the particles (Figure 3).

Hence, all experimental results indicate that precipitation of amorphous Si\(_3\)N\(_4\) has occurred upon nitriding of the Fe-Si alloy.

4 Discussion

Obviously, the chemical “bulk” energy of crystalline Si\(_3\)N\(_4\) will be smaller than that of amorphous Si\(_3\)N\(_4\). Recently we showed that the energy of an amorphous-crystalline interface can be smaller than that of the corresponding crystalline-crystalline interface [9]. Then it may be suggested that the occurrence of amorphous Si\(_3\)N\(_4\) precipitates is possible due to a favourable amorphous Si\(_3\)N\(_4\)/crystalline \( \alpha \)-Fe interface energy. This also implies that amorphous Si\(_3\)N\(_4\) precipitates are only possible as long as the precipitates are sufficiently small (i.e., have a relatively large surface/volume ratio).

In what follows the method proposed in [9] to assess the amorphous and crystalline interface and the bulk energies will be adopted to compare the Gibbs energies of a system consisting of a crystalline Fe-matrix with an amorphous Si\(_3\)N\(_4\) precipitate and one with a crystalline Si\(_3\)N\(_4\) precipitate. The energy contribution of the bulk of the Fe-matrix is the same in both systems. Then two energy contributions need to be estimated: the Gibbs energy of formation of the precipitates and the matrix-precipitate interface energy.

The difference in Gibbs energy, \( \Delta G \), between the system with an amorphous Si\(_3\)N\(_4\) precipitate and the system with a crystalline Si\(_3\)N\(_4\) precipitate is given by

\[
\Delta G = \left[ \frac{G_{\{\text{Si}_3\text{N}_4\}}}{V} - \frac{G_{<\text{Si}_3\text{N}_4>}}{V} \right] \cdot V + \left[ \gamma_{\text{Fe}}-<\text{Si}_3\text{N}_4> - \gamma_{\text{Fe}}-<\text{Si}_3\text{N}_4> \right] \cdot S,
\]

where \( \{x\} \) denotes the amorphous phase \( x \), \( <x> \) refers to the crystalline phase \( x \), \( G' \) indicates Gibbs energy of formation (per molar volume), \( \gamma \) represents interface energy (per unit area), and \( V \) and \( S \) are the volume and surface of the Si\(_3\)N\(_4\) particle considered.

The above difference in \( G' \) can be derived from the enthalpy of melting [9, 13]. An experimental value for the enthalpy of melting does not exist for Si\(_3\)N\(_4\). The (hypothetical) melting enthalpy can be roughly estimated from the (hypothetical) melting entropy (80.5 J/mol(Si\(_3\)N\(_4\)) and temperature (2600 K) [14] as obtained on the basis of
known melt entropies of equivalent materials and the extrapolation of the (also hypothetical) SiO$_2$-Si$_3$N$_4$ phase diagram [15], respectively.

To calculate the contribution of the interface structure to the energy of the crystalline-crystalline interface (cf. Eq. (8e) in [9]), values for the heats of evaporation of the Fe and Si$_3$N$_4$ are required (Eq. (7a) in [9]). The (hypothetical) heat of evaporation of Si$_3$N$_4$ can be estimated applying Trouton’s rule [16]. The Fe-Si$_3$N$_4$ interaction occurs at both the crystalline-crystalline and the crystalline-amorphous interface and therefore its energy contribution to the above difference in $\gamma$ practically cancels. The enthalpy contribution to the crystalline-amorphous interface energy (cf. Eq. (13a) in [9]) can be derived from the enthalpy of melting Fe (cf. Eq. (12a) in [9]) and the entropy contribution is calculated analogous to Eq. (12b) in [9].

The (maximum) size of an amorphous Si$_3$N$_4$ cubic precipitate in crystalline $\alpha$-Fe for which $\Delta G < 0$ (favouring the formation of an amorphous phase) can now be calculated. From this approximate calculation it follows that (i) precipitation of amorphous Si$_3$N$_4$ in crystalline $\alpha$-Fe indeed could be favoured initially over precipitation of crystalline Si$_3$N$_4$ and that (ii) the size of such an amorphous Si$_3$N$_4$ particle could be of the order of a nm.

The present finding and explanation can have a general bearing for precipitation reactions in crystalline solids. Because of a relatively low value for the amorphous-crystalline interface energy, in certain cases the very first stage of precipitation can be development of amorphous instead of crystalline particles.

5 Conclusion

It has been shown for the first time that precipitation out of a crystalline supersaturated solid solution can lead to the development of tiny second phase particles which are amorphous. The occurrence of the amorphous precipitates (in this case Si$_3$N$_4$ precipitates upon nitriding of Fe-1.6 at.% Si) may be a consequence of a possibly relatively low amorphous-crystalline interface energy and thus may have a thermodynamic rather than a kinetic origin.

Acknowledgement

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ELECTROMAGNETIC STIRRING OF THE WELD POOL
DURING ARC WELDING OF ALUMINIUM ALLOYS

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This paper deals with the effects of electromagnetic stirring of the weld pool during alternating current (AC) welding of aluminium alloys. Firstly, the principles of electromagnetic stirring of the liquid metal in the weld pool are formulated in terms of the Lorentz force, induced by an external axial magnetic field and the radial component of the welding current. On the basis of this formulation, an estimate is given of the flow velocity distribution of the liquid metal in the weld pool in dependence of the applied magnetic field and the welding parameters. This is followed by the description of equipment which can be used for electromagnetic stirring of the weld pool in the case of AC welding.

To evaluate the possibilities and limitations of electromagnetic stirring, welding experiments were carried out under different stirring conditions using the aluminium alloy AA 6082 as workpiece. It appears that electromagnetic stirring during welding results in different effects, the most important being changes of the weld bead geometry and grain refinement of the weld metal.

1 Introduction

During arc welding heat is transferred from the arc to the workpiece to be welded. This results in the formation of a weld pool, which after cooling and solidification ultimately leads to the formation of the weld. Obviously, the behaviour of the weld pool during the welding process is decisive as far as the properties of the weld is concerned.

The behaviour of the weld pool during welding, particularly its flow behaviour, can be significantly influenced by the presence of an external magnetic field. This influence is governed by the Lorentz force $F$, expressed by the equation $F = j \times B$, in which $j$ represents the current density and $B$ the magnetic induction.

In the case of an axial magnetic field parallel to the axis of the welding arc, the Lorentz force is directed perpendicularly to both the magnetic field and the radial component of the diverging current through the arc and the weld pool. The acting Lorentz force will result in rotation of the arc and in the generation of rotational flow of the liquid weld metal in the weld pool. The latter phenomenon is referred to as electromagnetic stirring. The velocity of the rotational flow is zero in the centre of the weld pool and also at the edge, and reaches its maximum value somewhere in between.

In the past, a number of experimental and theoretical studies dealing with the influence of electromagnetic stirring on weld bead properties was carried out [1-11]. The results of these studies show that electromagnetic stirring of the weld pool can give rise to a number of different effects, the most important being: change of the weld bead shape, improvement of the weld bead appearance, modification of the solidifi-
Electromagnetic Stirring of the Weld Pool during Arc Welding of Aluminium Alloys

cation structure of the weld metal, reduction of porosity in the weld and redistribution of alloying elements in the weld metal. The latter may lead to reduction of segregation during solidification of the weld metal, which is particularly of importance in the case of alloys with a high susceptibility for hot cracking.

The work on electromagnetic stirring during welding carried out thus far, was restricted to welding under direct current (DC) conditions. Under these conditions stirring of the weld pool can be realised by applying a constant magnetic field. However, when welding with alternating current (AC), which is common practice in the case of aluminium alloys, stirring of the weld pool requires the application of a magnetic field which is synchronised with the welding current.

This paper deals with the effects of electromagnetic stirring of the weld pool during AC welding of aluminium alloys. Firstly, the principles of electromagnetic stirring of the weld pool are described and the velocity distribution of the weld metal flow in the weld pool is calculated. This is followed by the description of equipment which can be used for electromagnetic stirring of the weld pool in the case of AC welding. Finally the results are presented of welding experiments carried out with the aluminium alloy AA 6082 under electromagnetic stirring conditions.

2 Principles of Electromagnetic Stirring

The principles of electromagnetic stirring are based on the fact that the welding current and the imposed magnetic flux interact to cause a force on the current carriers. In the case of an axial magnetic field (direction of the field parallel to the axis of the arc) this Lorentz force results in rotational flow of the liquid metal in the weld pool as will be shown in the following.

The Lorentz force ($F_L$) acting on a charged particle ($q$) moving with a certain velocity ($v$) in a magnetic field ($B$) can be described by the equation:

$$F_L = q v \times B$$

This means that the force ($f$) on a volume element ($dV$) is determined by the current density ($j$) and magnetic field ($B$) present in the weld pool, according to:

$$f = j \times B$$

The continuity equation for constant density of mass requires that:

$$\nabla \cdot v = 0$$

whereas the momentum equation (with constant $\rho$ and $\eta$) can be expressed by:

$$\rho \left( \frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + j \times B + \rho v \nabla^2 v + \rho \beta g (T - T_0)$$

The Navier-Stokes Equation (4) describes the laminar fluid flow in the weld pool. The left hand part of this equation consists of two terms in which $\partial v/\partial t$ represents the change in velocity (acceleration) under non-stationary conditions. On the right hand side of the equation, $-\nabla p$ describes the static pressure force, $j \times B$ the Lorentz force imposed on the weld pool, $\rho v \nabla^2 v$ the viscous force in the weld metal and $\rho \beta g (T - T_0)$
the buoyancy force.

In the case of an external magnetic field parallel to the axial component of the welding current, the Navier-Stokes equation can be expressed in terms of cylindrical coordinates (\(r, \phi, z\)), see Figure 1. This leads to the following expressions for the radial (\(r\)), azimuthal (\(\phi\)) and axial (\(z\)) components of the flow velocity:

**radial (\(r\)) component:**

\[
\rho \left( \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\phi}{r} \frac{\partial v_r}{\partial \phi} - \frac{v_z}{r} \frac{\partial v_r}{\partial z} \right) = -\frac{\partial p}{\partial r} + \eta \left( \nabla^2 v_r \right)
\]  

**azimuthal (\(\phi\)) component:**

\[
\rho \left( \frac{\partial v_\phi}{\partial t} + v_r \frac{\partial v_\phi}{\partial r} + v_z \frac{\partial v_\phi}{\partial z} + \frac{v_\phi}{r} \frac{\partial v_\phi}{\partial \phi} \right) - \frac{1}{r} \frac{\partial}{\partial \phi} \left( j \times B_n \right) = \nabla^2 v_\phi
\]  

**axial (\(z\)) component:**

\[
\rho \left( \frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\phi}{r} \frac{\partial v_z}{\partial \phi} + v_z \frac{\partial v_z}{\partial z} \right) = -\frac{\partial p}{\partial z} + \eta \left( \nabla^2 v_z \right)
\]  

As can be seen, the azimuthal component (Equation (6)) is the only component affected by the external magnetic field. If the current has an outward directed component \(j_r\) and the magnetic field is axially directed, see Figure 1, the vector product \(j_r \times B_z\) is the driving force for the rotating weld pool flow.

---

**Figure 1:** Schematic presentation of the welding current and the axial magnetic field in the arc and the workpiece

**3. Distribution of Flow Velocity in the Weld Pool**

On the basis of the theoretical considerations presented briefly in the previous section, an estimate can be given of the flow velocity distribution of the liquid metal in the weld pool in the presence of an axial magnetic field. To facilitate the calculation, it is assumed that the weld pool has the shape of a cylinder with radius \(R\) and height \(d\), whereas the current distribution has the form schematically depicted in Figure 2.
Electromagnetic Stirring of the Weld Pool during Arc Welding of Aluminium Alloys

Furthermore, it is assumed that the current density is constant in the top surface of the weld pool. This is realistic in view of the presence of an axial magnetic field [9].

Assuming a constant current density, the total current in z-direction through a circular disc of radius \( r \) is:

\[
I_z(r) = I_w \frac{r^2}{R^2}
\]  

(8)

with \( I_w \) the total welding current. This leads to the following expression for the current density in radial direction at distance \( r \):

\[
j_r(r) = \frac{I_z(r)}{2\pi d}
\]  

(9)

Using the assumptions formulated above, the current density \( j_r(r) \), which is a function of the radius \( r \) of the weld pool, can now be calculated. Substitution of Equation (8) in Equation (9) yields:

\[
j_r(r) = I_w \frac{r}{2\pi R^2 d}
\]  

(10)

With the aid of Equation (2) the Lorentz force acting on a volume element \( dV \) of liquid metal, can now be written as:

\[
f(r) = \frac{B I_w}{2\pi R^2 d} r
\]  

(11)

As can be seen, the Lorentz force is a function of the radius of the weld pool. Neglecting the buoyancy force and considering only the rotational flow in the \( \phi \)-direction, the situation can be reduced to a one-dimensional problem expressed by Equation (6). Assuming that the weld pool flow is stationary (\( \partial v_r / \partial t = 0 \)) and the buoyancy force is negligibly small, this leads to:

\[
\eta \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} (rv_r) \right) + f(r) = 0
\]  

(12)

After integration of this equation, using the boundary conditions \( v_r = 0 \) at \( r = 0 \) and...
\( v_{\phi} = 0 \) at \( r = R \), the rotational fluid flow velocity can be expressed as:

\[
v_{\phi} = \frac{BI_w}{16\pi d\eta} \left( r - \frac{r^3}{R^2} \right)
\]

(13)

The shear rate of the liquid metal in the weld pool can be obtained by differentiating Equation (13) with respect to \( r \), which yields:

\[
\dot{\gamma} = r \frac{\partial (v_{\phi}/r)}{\partial r} = \frac{BI_w}{8\pi d\eta R^2} r^2
\]

(14)

Using Equations (13) and (14), the flow velocity and shear rate can now be calculated as a function of the weld pool radius. As an example, calculations were carried out for a weld pool in an aluminium alloy using the values listed in Table 1. The results are presented in Figure 3.

Table 1: Values used in the calculation of fluid flow velocity and shear rate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>welding current</td>
<td>( I_w = 100 ) A</td>
</tr>
<tr>
<td>magnetic induction</td>
<td>( B = 20 ) mT</td>
</tr>
<tr>
<td>weld pool radius</td>
<td>( R = 5 ) mm</td>
</tr>
<tr>
<td>plate thickness</td>
<td>( d = 3.2 ) mm</td>
</tr>
<tr>
<td>viscosity</td>
<td>( \eta = 1.5 ) mPa.s</td>
</tr>
</tbody>
</table>

![Figure 3: Calculated fluid flow velocity and shear rate in a static weld pool as a function of distance from the weld pool centre in the case of rotational flow due to the presence of an axial magnetic field](image)

The figure shows that the flow velocity varies from 0 to about 12 m/s, depending on the location in the weld pool. Vivès [12, 13] carried out measurements of the flow profile in the case of electromagnetic rheocasting of aluminium alloys and obtained similar results for the velocity field. It must be expected, however, that the actual flow velocity in the weld pool will be smaller than the calculated values mentioned above due to various reasons, the most important being the fact that the applied magnetic field is divergent rather than parallel to the axis of the arc.

At this point the question arises whether the fluid flow in the weld pool is laminar or
Electromagnetic Stirring of the Weld Pool during Arc Welding of Aluminium Alloys

turbulent. The Reynolds number for rotational flow ($Re_\omega$) is defined by the equation:

$$Re_\omega = \frac{\rho \omega_{max} R^2}{\eta} = \frac{\rho v_{max} R}{\eta}$$  \hspace{1cm} (15)

Taking $\rho_{Al} = 2.3 \times 10^3$ kg m$^{-3}$, $\eta_{Al} = 1.5$ mPa s, $R = 2.9$ mm and $v_{max} = 1.2$ m/s (a value ten times smaller than the maximum calculated weld pool velocity), a value of $Re_\omega = 5.5 \times 10^2$ is obtained. This value is much larger than the critical value for laminar flow accepted in the case of flow in pipes [14], indicating that the flow is turbulent. It should be remembered that the rotational flow velocity will generate a poloidal weld pool flow produced by the pressure gradient $\partial p/\partial z$. A more precise estimation of the flow velocity, therefore, requires a solution of the three-dimensional Navier-Stokes equation.

4. Experimental

4.1 Electromagnetic Stirring Equipment

The basic part of the experimental set-up used in the present work is shown schematically in Figure 4 and consists of a GTA welding torch surrounded by three electromagnets, placed at equal distance from each other (120 degrees apart). The electromagnets are air cooled and are fed by an external power source. The current through the solenoids (1200 windings) of the electromagnets is such that the magnetic field produced by each of them has the same direction. Soft ferromagnetic cores are used to amplify the magnetic field and to direct the field in the required direction. The travel bench consists of ferromagnetic material, which concentrates the

![Figure 4: Basic part of the experimental set-up with three electromagnets surrounding the welding torch at equal distance from each other. Two electromagnets are visible, the third one is located behind the torch.](image)
axial magnetic field in the vicinity of the poles. The set-up can be used to provide an axial magnetic field parallel to the axis of the arc. The welding unit includes a filler wire feeder to make it possible to apply filler wire if required.

To generate electromagnetic stirring in the case of AC welding, it is necessary to apply an alternating current through the solenoids with the same frequency and phase as the welding current. For this purpose a standard audio amplifier is coupled to a function generator, which can produce square, triangular or sinusoidal waves. The amplifier can supply a maximum current of 5 A (at 4 Ω impedance). The situation is schematically presented in Figure 5. The time needed for the linear increase at the start of the welding run is set to three seconds (up-slope). The same time is set for the linear decrease at the end of the welding run (down-slope).

![Figure 5: Schematic drawing of the function generator and amplifier controlling the magnetic solenoids used in the electromagnetic stirring set-up](image)

Under the conditions described above, the magnetic field is directed upward during one half cycle of the welding current, while the magnetic field is directed downward during the next half period of the welding current. Hence, the Lorentz force is continuously acting in the same direction on the liquid metal in the weld pool. Assuming that the magnetic field \( B \) has a triangular wave form, \( B(t) \) can be expressed by the equation:

\[
B(t) = B \frac{8}{\pi^3} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \cos 2\pi(2m+1) \nu t
\]

When using a power supply producing a square AC current (which is common practice in the case of welding aluminium alloys), the current density \( j(t) \) can be written in the form:

\[
j(t) = j_0 \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \sin 2\pi(2n+1) \nu t
\]

Substitution of Equations (16) and (17) in Equation (2) yields the Lorentz force acting on a volume element \( dV \) of the liquid metal in the weld pool as a function of time:
Equation (18) describes the Fourier progression of the low frequency component of the Lorentz force. If \( v_i = v_B \) and \( \phi_i - \phi_B = 0 \), this will result in a continuously rotating flow of the liquid metal in the weld pool in one direction (uni-directional flow). However, a small difference in frequency between welding current and magnetic field will result in alternating rotational flow (clock wise and anti-clock wise) with a stirring frequency of \( \nu_s = v_i - v_B \). An example is given in Figure 6 for the case that \( v_i \neq v_B \). It is clear that the resulting force can be approximated by a sine wave. In practice, the frequency difference between the magnetic field and the welding current can be varied within the range from 0 to 35 Hz. In the following the frequency difference \( (v_i - v_B) \) will be referred to as the stirring frequency \( \nu_s \) of the system. To prevent interference of high-frequency components of the magnetic field with the welding current, the frequency of the magnetic field is always chosen higher than 50 Hz.

Calibration of the axial magnetic field was carried out with the help of a LOHET II linear Hall probe device.

![Calculated Lorentz force modulation in the case of a current frequency of 50 Hz and a magnetic field frequency of 52 Hz (left) and the effective force on the liquid metal in the weld pool (right)](image)

**Figure 6:** Calculated Lorentz force modulation in the case of a current frequency of 50 Hz and a magnetic field frequency of 52 Hz (left) and the effective force on the liquid metal in the weld pool (right)

### 4.2 Experimental Conditions

To evaluate the possibilities and limitations of the electromagnetic stirring device described in the foregoing, welding experiments were carried out using the aluminium alloy AA 6082 as workpiece in the form of plates with dimensions 240 x 100 x 3 mm. The experiments were performed under different stirring conditions: the magnetic induction was varied between 0 to 30 mT and the stirring frequency was varied between 0 to 35 Hz. Some of the experiments were carried out with filler wire addition (AlMg5 filler wire) to provide nucleation sites for equiaxed solidification. The welding parameters used are listed in Table 2.

The welds obtained were water quenched directly after welding to prevent strong precipitation of the alloying elements. To reveal the macrostructure of the welds, cross-sections were made and the cross-sections were polished and etched with concentrated hydrochloric acid. The macrostructure of the welds was examined by...
means of optical microscopy using a microscope of the type Leitz Neophot 2.

Table 2: Welding parameters used in the experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Welding current (AC)</td>
<td>110 A</td>
</tr>
<tr>
<td>Arc voltage</td>
<td>15.0 V</td>
</tr>
<tr>
<td>Arc length</td>
<td>3.0 mm</td>
</tr>
<tr>
<td>Travel speed</td>
<td>3.0 mm/s</td>
</tr>
<tr>
<td>Shielding gas</td>
<td>Argon</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>10 l/min</td>
</tr>
<tr>
<td>Filler wire</td>
<td>AlMg5</td>
</tr>
<tr>
<td>Wire thickness</td>
<td>1.2 mm</td>
</tr>
<tr>
<td>Wire feed speed</td>
<td>25 mm/s</td>
</tr>
</tbody>
</table>

5. Results and Discussion

5.1 Uni-Directional Stirring

A large number of welding experiments was performed under various stirring conditions. Systematic observation of the weld pool during welding reveals that application of an axial magnetic field generates rotational flow of the liquid metal in the weld pool. When the frequency of the magnetic field is equal to the frequency of the AC welding current, this flow is uni-directional (see above) and results in a weld bead which is characterised by an asymmetric transverse cross-section: the weld is elevated at one side and lowered at the other side. This phenomenon has also been observed in the case of welding stainless steel under uni-directional stirring conditions [2, 4, 10]. The situation is schematically presented Figure 7.

The observed asymmetric behaviour of the weld pool and weld bead can be qualitatively explained with the help of the upper part of Figure 7. As the welding arc moves on with travel speed \( v_t \), liquid weld metal is formed by melting at the front side of the weld pool. Under the action of the Lorentz force, this weld metal will start to rotate in a counter-clockwise direction around the axis of the welding arc with annular velocity \( v_r \). Due to centrifugal forces acting on the rotating weld metal, a relatively large part of this hot liquid will be pushed backwards to the left side of the pool. This will give rise
to a weld pool that deviates to the left and will ultimately result in a weld bead with a transverse cross-section displayed in the lower part of Figure 7. On the basis of this explanation it should be expected that the weld bead asymmetry increases with increasing magnetic field strength. This is indeed what has been observed.

Microscopic examination of the solidified weld reveals that the weld metal consists of bent epitaxial grains (stray structure) and that the centreline of the weld is displaced in a direction predicted by Figure 7.

5.2 Alternating Stirring

Welding experiments were also carried out under alternating stirring conditions, resulting in alternating rotational flow in the weld pool. This flow has a significant effect on the geometry of the weld bead, in particular on its surface structure. In Figure 8 the weld metal surface is depicted of welds obtained by welding with four different stirring frequencies (0.5, 1, 2 and 5 Hz).

![Figure 8: Weld metal surface structure obtained by welding with electromagnetic stirring at different stirring frequencies: a) 0.5 Hz; b) 1 Hz; c) 2 Hz and d) 5 Hz (B = 18 mT).](image)

It can be seen that alternating stirring results in surface ripples and that the distance between these ripples decreases with increasing stirring frequency. In fact, the stirring frequency applied can be directly determined from the distance between the ripples and the travel speed.

In addition to surface ripples, alternating stirring leads to weaving fusion boundaries and to a weaving weld centreline, which is advantageous in the case the weld metal is susceptible to liquation cracking (centreline cracking).

Detailed information about the influence of electromagnetic stirring on the micro-
structure of the weld metal was obtained by studying cross-sections of welds produced under different stirring conditions.

It appears that electromagnetic stirring results in considerable grain refining of the weld metal structure and that the grain refining effect depends on the stirring frequency applied. Under the present welding conditions optimum grain refining was observed at a stirring frequency of about 5 Hz. The observed grain refining effect is illustrated in Figure 9. In this figure the macrostructure of transverse cross-sections are shown of welds obtained by welding without and with electromagnetic stirring (18 mT, 5 Hz).

![Figure 9: Transverse cross-sections of welds obtained by welding without electromagnetic stirring (left) and with electromagnetic stirring (right) at a stirring frequency of 5 Hz (B = 18 mT) 

When considering the cause of the observed grain refining, different mechanisms should be taken into account. Of primary importance is the course of events which takes place when the flow direction in the weld pool is reversed from clock wise to anti-clock wise (and vice versa). Due to this flow reversal, the temperature gradient changes direction and the initially favourably oriented grains are hampered in their growth, facilitating new grains to take over. This ultimately results in a zig-zag pattern of smaller grains.

In addition to grain growth interruption by flow reversal, the flow of the liquid metal in the weld pool will result in mixing of the liquid weld metal in the vicinity of the solidification front and in homogenisation of the temperature in the weld pool. As is illustrated in Figure 10, both mixing of the liquid weld metal and homogenisation of the temperature in the weld pool will lead to an increase of constitutional supercooling and thus to enhanced nucleation. This effect will especially be important when heterogeneous nuclei are present in the weld metal.

5.3 Stability of the Process

Application of an external magnetic field during arc welding, as required in the case of electromagnetic stirring, can easily lead to instability of the welding process, especially when the applied magnetic field is inhomogeneous. This process instability is reflected by erratic behaviour of the arc and has a negative effect on both the shape and the properties of the weld. The erratic arc is also disadvantageous with respect to the filler wire transfer as under these conditions the metal wire tends to melt down discontinuously.

The cause of the observed process instability is directly related to the fact that the axial magnetic field is interacting with the arc column, since the arc current has a radially directed component. This causes the arc to rotate in a plane perpendicular to the magnetic field direction. Due to this rotation, centrifugal forces will be activated,
which will fling the arc plasma outwards. In most cases plasma flinging is the major cause of process instability. This instability can be counteracted by increasing the flow rate of the shielding gas, as this flow hampers the rotational flow of the plasma. To evaluate the stabilising effect of the shielding gas flow, a number of additional experiments was carried out in which the gas flow rate was varied. It was found that at high gas flow rate the arc behaviour was stable. However, when gradually decreasing the gas flow rate, the arc becomes unstable at a gas flow rate of 5 l/minute, while the arc extinguished at a gas flow rate of 4 l/minute. If no magnetic field is applied, the gas flow rate can be reduced to a value as low as 1 l/minute without extinction of the arc. In view of the foregoing all experiments referred to in this paper were carried out with a gas flow rate of 10 l/minute.

6 Conclusions

On the basis of the results presented above, the following conclusions can be drawn.

- Application of an axial magnetic field (parallel to the axis of the arc) during arc welding leads to rotational flow of the liquid metal in the weld pool (electromagnetic stirring).
- A distinction should be made between uni-directional stirring and alternating stirring. Uni-directional stirring is obtained when the (AC) current frequency is equal to the magnetic field frequency. Alternating stirring is obtained when the current frequency is different from the magnetic field frequency. The difference between these two frequencies determines the stirring frequency.
- Uni-directional stirring results in a weld bead, which is characterised by an asymmetric transverse cross-section: the weld is elevated at one side and lowered at the other side. The weld metal consists of bent epitaxial grains (stray structure) and the centreline of the weld is shifted in sideward direction.
- Alternating stirring leads to changes in the weld geometry (surface ripples,
weaving fusion boundaries, weaving centreline) and to grain refining. The observed grain refining is due to grain growth interruption during reversal of the flow direction, mixing of the liquid weld metal in the vicinity of the solidification front and homogenisation of the temperature in the weld pool.

- Application of an external magnetic field during arc welding, as required in the case of electromagnetic stirring, can easily lead to instability of the welding process. This instability can be counteracted by increasing the flow rate of the shielding gas.

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FRACTURE ENERGETICS OF DISSIMILAR MATERIAL JOINTS

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A rationale is given for a simple energetic model of bimaterial systems which adds all relevant energy terms. It is based on first principles using the free energy expression for such a system. It essentially distinguishes energy terms from various sources, like residual stress, and shows that interaction between the residual stress field due to thermal expansion mismatch and mechanical loading is absent. There is, however, an interaction contribution to the strain energy release rate, which can be neglected if the loading points are sufficiently far removed from the crack tip. The model is applied to a metal-ceramic joint, Al₂O₃-Ti, and a metal coating on a ceramic substrate, Ni(P)-Al₂O₃. In both cases correcting the strain energy release rate with the contributions from residual stress and plasticity yielded a fracture energy independent of the system dimensions, in agreement with the model.

1. Introduction

With the increasing use of technical ceramics the need to bond these materials to metals also increases. To achieve a bond, several technologies exist or are being developed [1]. Typical of most of these technologies is that the joint is established at relatively elevated temperatures, meaning that the temperature at which a joint should function is lower than the temperature at which it is fabricated. Since the thermal expansion coefficients of the materials constituting the joint are generally different, the temperature difference mentioned above gives rise to residual stresses in and near the interface between the materials. In some cases these stresses reach values so high that the component fails during the cooling-down period following the joining process. Even if the component survives the cooling process it is clear that thermal residual stresses may lead to a considerable weakening of the component, that is to say to a reduction of the mechanical load the component can withstand during function.

In an energy based approach to mechanical failure a necessary condition for the onset of crack growth is that the crack extension force or energy release rate equals the crack resistance force [2]. The crack extension force is proportional to minus the derivative of the total potential energy of the system to the crack length. Part of this energy is the strain energy present in the system. If thermal residual stresses are present and the system is also loaded externally, the elastic energy derives from two independent sources: one caused by the mismatch of thermal expansion coefficients and one caused by the external mechanical loading. In addition to that interaction may occur. Indeed, even for linear systems where the superposition principle holds, only elastic states (stresses, strains, etc.) can be superposed but for energies this is usually not possible. Generally we therefore have for the total elastic energy \( U_e \) the splitting:

\[
U_e = U_{el} + U_{th} + U_{int}
\]

with \( U_{el} \) the elastic energy caused by external loading, \( U_{th} \) the elastic energy associated with the thermal residual stress and \( U_{int} \) the elastic...
energy associated with the simultaneous presence of the residual and the externally caused stress fields. Now, according to a theorem of Colonnetti (see Kröner [3]) and Eshelby [4]) the interaction energy for elastic fields due to external loading and due to internal stress is zero. Since residual stress caused by thermal mismatch is a system of internal stress one would expect $U_{int}$ to be zero. The vanishing of $U_{int}$ would be important from a practical point of view because it means that the influence of the thermal mismatch on the energy release rate can be investigated independently of the particular loading.

However, again according to Eshelby [4], the system of internal stress does interact with the external loading because an interaction with the loading mechanism is to be expected. As stated above, the crack extension force or the energy release rate is derived from the total potential energy of the system which is the difference between the mechanical potential energy of the load supplying mechanism and the elastic energy present in the system. So, the whole system (cracked body plus loading mechanism) rather than only the cracked body should be considered. To describe such an interaction between loading mechanism and thermal residual stresses one would expect the interaction energy to be proportional to the applied loading, for example a force parameter $f$, and also proportional to the displacements $v$ caused solely by the thermal mismatch: $E_{int} \sim fv$. Eshelby's treatment [4] uses in fact these considerations. However, because his treatment is rather on an abstract level the physical basis for such an interaction energy remains unclear. Generally the load is applied after the bond was established and after the system has cooled down. Since this means that the displacements $v$ occur without any load acting on the system, it is not clear why a term proportional to $fv$ should be included in the energy. Further investigation is thus warranted.

A further reason to study the influence of the energy associated with thermal mismatch on the energy release rate is that in the literature it is stated by some authors that residual stresses cannot drive crack growth. Wang and Suo [5] state: 'A remarkable feature common to all thin-layer sandwiches is that the residual stress in the layer does not drive the crack, because the strain energy stored in the layer due to residual stress is not released in the process of cracking'. Since the authors give no further information concerning the type of the residual stress they have in mind, the statement seems to be totally unqualified. From an experimental point of view this statement seems to contradict the fact that sometimes joints do not survive the cooling process at all.

The questions raised above merit a more detailed study into the problem how the energy release rate (of an interface crack) of an externally loaded bimaterial joint depends on the thermomechanical properties of the materials and the temperature. Important here is to keep in mind that such a description does not only involve shape and material properties but also its history. After all, at the time joints are loaded they have previously gone through a certain thermal process and it is precisely this process which leads to thermal residual stresses [6]. The knowledge of the history of the system is indispensable to obtain a thermomechanical model of the system. The Helmholtz free energy of the system $F$, considered as a function of the temperature $T$ and the strain tensor $\varepsilon$ is the thermodynamical most suitable for our purpose because, mechanically, a joint can be modelled as a constraint in a variational problem involving the Helmholtz free energy. Since the energy release rate is based on the derivative (to the crack length) of the total energy of the loaded elastic solid [7] and
the energy stems from various sources, the energy release rate also consists of terms of miscellaneous origins. The present paper is therefore about the question how the external loading, thermal mismatch and temperature contribute energy terms to the total potential energy and influence the energy release rate. The model is applied to a metal-ceramic joint, Al₃O₃-Ti, and a metal coating on a ceramic substrate, Ni(P)-Al₂O₃.

2. Outline of the Model Considerations

Since the details of all considerations will be published elsewhere [8], here only an outline of the results is given. These results will be applied to a metal-ceramic joint and to a thin metal coating on a ceramic substrate.

The system, with each of the materials having a stress free state at some reference temperature, \( T_r \), is modelled by treating the joint as a mechanical constraint on the displacements of material points adjacent to the interface surface. The displacements of any material point is determined by minimising the Helmholtz free energy. The total displacement, \( u \), \( i = 1, 2; \) a material identifying subscript) with respect to the reference state is \( u = u_i = v_i + w_i \). Each of the terms on the right-hand side reflects a basic property of the system. The contribution \( \Delta u \) constitutes the free shrinkage of each of the material bodies eventually constituting the joint, that is to say the shrinkage of each of the components in case no joint nor a loading is present. If next the joint is established, still without a loading system being present, the material points undergo additional displacements denoted by \( v \). If, finally, the loading is applied the material points again displace over a certain distance denoted by \( w \).

Since free shrinkage of a homogeneous material does not lead to stresses, the deformations associated with \( \Delta u \) do not lead to stresses. The other two displacements \( v \) and \( w \), however, do. Their respective stress tensors are denoted by \( \sigma_v \) and \( \sigma_w \). Physically these tensors are the residual thermal stresses and the stresses caused by the loading, respectively.

The Helmholtz free energy of the bulk of the system was found to be \( F_b = F_{br} + U_{th} + U_{el} \), with \( U_{th} \) and \( U_{el} \) the elastic strain energies caused by the thermal mismatch and loading, respectively. In the first term \( F_{br} \) contributions from miscellaneous origin are collected. It depends on the free energy and entropy of both materials in the reference state, on the temperature \( T \), the displacements \( r \) and on material properties. This term does not contribute to the energy release rate because it does not depend on either the loading or the joint interface.

The contribution to the elastic strain energy of the two bodies \( B_1 \) and \( B_2 \) caused by thermal mismatch, \( U_{th} \), is given by

\[
2U_{th} = \sum_{i=1}^{2} \int_{V_i} \varepsilon(\nabla v_i) : L_i : \varepsilon(\nabla v_i) \, dV
\]

(1)

where \( \varepsilon \) is the strain tensor and \( L_i \) the tensor of elastic constants. The solution \( v \) is found by minimising the left-hand side of this equation subject to the constraint that \( r + v \) be continuous across the bonded interface. Since crack growth decreases the bonded area, the effect is that during crack growth the constraint is relaxed meaning that \( U_{th} \) is a decreasing function of crack length or at least non-increasing. Because
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$U_{th}$ is a positive quadratic form and becomes zero after the bond is completely broken, it follows that the derivative of $U_{th}$ to the crack length $l$ is negative. Obviously, energy from this source may be released during the cracking process. Therefore it is concluded that the idea that $U_{th}$ does not contribute to the energy release rate is not correct.

The term

$$2U_{el} = \sum_{m=1}^{2} \int_{V} \varepsilon(\nabla w_{i}) : L_{m} : \varepsilon(\nabla w_{i}) \, dV$$  \hspace{1cm} (2)$$

defines the familiar strain energy $U_{el}$ caused by the loading. The solutions $w_{i}$ minimise

$$\frac{1}{2} \sum_{m=1}^{2} \int_{V} \varepsilon(\nabla w_{i}) : L_{m} : \varepsilon(\nabla w_{i}) \, dV - \sum_{i=1}^{7} t_{i} \cdot w_{i} \, dS$$  \hspace{1cm} (3)$$

where $t_{i}$ are the tractions applied to the surface parts $S_{i}$. Minimisation is subject to the constraint that $w_{i}$ be continuous across the interface.

Locally there is an interaction between the internal (residual) stress field $\sigma_{f}$ and the field $\sigma_{f}$ caused by the loading. Because the strain energy density is quadratic in the actual stresses, the interaction strain energy density contains cross terms. These terms can be written as

$$\sigma_{f} : \varepsilon(\nabla w_{i}) = \sigma_{f} : \varepsilon(\nabla w_{i})$$  \hspace{1cm} (4)$$

The interaction strain energy density is not necessarily zero everywhere, but its integrated form, the total interaction strain energy, vanishes. Consequently, the Helmholtz free energy of the bulk does not contain an interactional strain energy term.

To answer the question about the existence of an interaction energy between the loading mechanism and the residual thermal stresses, the joint plus the loading system should be considered as a single system as indicated in Figure 1a. The presence of such an interaction can be found by comparing the Helmholtz free energy of three different systems thereby taking care that the initial state of the loading system is the same in all three cases. The three different systems were chosen as follows:

- System I consists of loading mechanism plus a loaded and cooled joint of materials with different elastic constants and different thermal expansion properties.
- System II consists of loading mechanism plus the cooled but non-loaded joint, again consisting of materials with different elastic constants and different thermal expansion properties.
- System III consists of loading mechanism plus a cooled and loaded joint of materials with equal thermal expansion properties but with different elastic constants as for systems I and II. The expansion coefficients are chosen to be zero without loss of generality.

System I is the system actually considered. Systems II and III are comparison systems. It is found that an interaction energy indeed exists and is given by:
This expression can also be shown to be equal to:

\[ F_{\text{int}} = - \theta \sum_{i=1}^{3} \alpha_i \sigma_i \, dV \quad (6) \]

where \( \alpha_i \) is the tensor of thermal expansion properties and \( \theta = T - T_i \), the temperature difference. To explain the physical basis of this interaction suppose, by way of example, that the loading is applied by attaching masses through strings to the surfaces as shown in Figure 1b. The energy of the loading system is the potential energy of the masses. Since this energy is determined only up to an arbitrary constant, the constant is fixed by assuming that the masses initially occupy a certain position which is the same in all three cases considered. Evidently, in case II where no loads are applied, the masses remain in their original positions. For cases I and III, however, the masses generally have to be displaced so as to attach the strings to the joint. However, as in case III the expansion coefficients are zero, the surface points of system III do not displace after cooling down. So, any attachment point \( a \) remains in its original position during the cooling period. In case of system I, these points displace from their original position \( a \) to the new position \( a + f(a) + v(a) \). So the masses have to be displaced differently for case I as compared to case III, in order to attach the masses to the surface of the joint and this difference gives rise to a difference in potential energy which is the interaction term given before. It should be stressed that in the interaction term two aspects are present. This can be seen, if the expression for \( F_{\text{int}} \) is rewritten as

\[ F_{\text{int}} = - \frac{\theta}{2} (\alpha_1 + \alpha_2) \left( \sum_{i=1}^{3} \sigma_i \, dV \right) - \frac{\theta}{2} (\alpha_1 - \alpha_2) \left( \sum_{i=1}^{2} \sigma_i \, dV \right) \quad (7) \]

If \( \alpha_1 = \alpha_2 \) (equal but non-vanishing expansion coefficients), the interaction term is still non-zero. Consequently there is always an interaction term whether the expansion
coefficients are zero or not. This is the first aspect. If next the thermal mismatch is introduced, an additional term appears. This is the second aspect. As far as the energy release rate is concerned only the second term is important because the first is independent of crack length. Indeed, if \( \alpha_1 = \alpha_2 \) the displacements \( v_i \) are either zero or rigid body displacements because the constraint is met automatically simply by lining up the (originally non-connected) bodies and connecting (stress free in this case) the necessary points adjacent to the interface, the result being that \( v_i \) is independent of the crack length \( l \). As the tractions \( t_i \), the displacements \( r_i \) and the surface regions \( S \), are independent of crack length anyway, it follows that in this case the interaction energy becomes independent of crack length.

According to Eshelby the interaction energy between a field of external stress, like that caused by the tractions \( t_i \), and internal non-homogeneities leading to displacements like \( v_i \) is given by:

\[
F_{\text{Esh}} = - \sum_{i=1}^{2} \int_{S_i} t_i \cdot v_i \, dS
\]  

Although one would expect this to be true because the interaction energy should be proportional to the loading and proportional to the displacements the non-homogeneities give rise to, the results obtained above show that this expectation is not correct. The reason is that for a system with different thermal expansion properties the displacements \( v_i \) are not unique and contain arbitrary rigid body displacements which are different for each of the bodies. The sum \( r_i + v_i \) is much more determined because the enforcing of the constraint at the joint ensures that on the joint interface \( \Gamma: \quad r_1 + v_1 = r_2 + v_2 \). That Eshelby's expression cannot be correct can also be shown as follows. It can be shown that

\[
\sum_{i=1}^{2} \int_{S_i} t_i \cdot v_i \, dS = \int_{\Gamma} t_i \cdot (r_2 - r_1) \, dS
\]

leading to

\[
F_{\text{Esh}} = - \int_{\Gamma} u_*(r_2 - r_1) \, dS
\]

where \( t_i \) denotes the interface traction due the loading, Both \( r_1 \) and \( r_2 \) contain arbitrary rigid body motion. These can chosen such that on the joint interface \( \Gamma: \)

\[
r_2 - r_1 = \xi (\alpha_2 - \alpha_1) \xi
\]

where \( \xi \) denotes the coordinates of the contact zone, the result being that \( F_{\text{Esh}} \) turns out not to be independent of the choice of the coordinate system. For that reason \( F_{\text{Esh}} \) is not a proper interaction energy. The expression derived here is indeed a proper energy describing the interaction between loading mechanism and the non-homogeneities present in the thermal expansion properties. It is proportional to the loading, proportional to temperature and its contribution to the energy release rate vanishes for all \( \theta \) if no thermal mismatch is present.
Finally, the expression for the Helmholtz free energy of the extended system (bimaterial joint plus loading mechanism) on which the energy release rate has to be based is:

\[ F_{\text{int}} = F_{\text{ref}} + F_{\text{adh}} + U_{\text{th}} + F_{\text{ext}} \]  
(12)

with

\[ F_{\text{ext}} = U_{\text{el}} - \sum_{i=1}^{2} \int_{s_i} t_i \cdot w_i \, dS \]  
(13)

The term \( F_{\text{ref}} \) contains \( F_{\text{br}} \) and a few other terms, all independent of the crack length \( l \). In the term \( F_{\text{adh}} \) all contributions from the surface or the interface are collected. In principle it is given by:

\[ F_{\text{adh}} = \sum_{i=1}^{2} \gamma_i S_i + \Phi \Gamma \]  
(14)

Here \( \gamma_i \) is the Helmholtz surface free energy of material \( i \), \( \Phi \) the Helmholtz free energy of the interface between the two materials, \( \Gamma \) the interface area and \( S_i \) the total surface area of body \( B_i \) minus the area of the contact region. Note that \( F_{\text{adh}} \) contributes to the energy release rate because the interface area \( \Gamma \) decreases and the non-interface parts \( S_i \) of the surfaces of the bodies increase in magnitude if a crack starts to run. If there exist other contributions to the Helmholtz free energy, e.g. from roughness, microcracking or crack tip plasticity, they are also covered by \( F_{\text{adh}} \). The terms \( U_{\text{th}}, U_{\text{el}} \) and \( F_{\text{br}} \) are as given previously. The influence of the joint constraint is expected to be small in regions far from the joint. For that reason the influence of \( F_{\text{int}} \) to the energy release rate can be neglected if the distance between the loading surfaces and the crack tip is sufficiently far.

In conclusion, it therefore follows that the fracture energy of a bimaterial system can be described as a simple sum of additional terms, provided the loading points are sufficiently far removed from the crack tip. This provides the basis for a few simple analyses described below.

For a specimen having a constant width \( W \) through which a crack starts to propagate \((l = \frac{d l}{d t} > 0)\) the second law of thermodynamics reads [7]:

\[ D = - \frac{1}{W} \frac{\partial F_{\text{ref}}}{\partial t} \, t > 0 \]  
(15)

with \( D \) the dissipation power due to plastic deformation. Writing \( D = J_{\text{pl}} \) with \( J_{\text{pl}} \) the specific dissipated plastic work one finds:

\[ J_{\text{pl}} = J_{\text{ext}} + J_{\text{th}} - W_{\text{adh}} \]  
(16)

where \( J_{\text{ext}}, J_{\text{th}} \) and \( J_{\text{adh}} \) denote the energy release rate associated with the various terms. For example, \( J_{\text{th}} = -\frac{(\partial U_{\text{th}}/\partial t)}{W} \). Furthermore, \( W_{\text{adh}} = -J_{\text{adh}} \). Physically these terms can also be interpreted as specific energies. It is clear that for further applica-
tion of the above analysis the effect of plasticity has to be included. This is part of a future programme. For the time being we deal with this aspect in a semi-empirical way.

3 Application to a Metal-Ceramic Joint: $\text{Al}_2\text{O}_3$-$\text{Ti}$

It is well known that the energy release rate or toughness of joint depends on the precise manufacturing conditions. A different processing condition can introduce a different amount of residual stress in the joint. Therefore it seems useful to estimate for a joint the contribution of the various energy terms in order to see whether the adherence part is really a joint property.

The system investigated was the $\text{Al}_2\text{O}_3$-$\text{Ti}$ system. The reason for this choice is that it is an important base system for active soldering. Moreover, the morphological features for various processing conditions are well documented [9]. The Ti reacts with the alumina to various intermetallics, mainly $\alpha$-Ti(O), $\text{Ti}_2\text{Al}$ and $\text{TiAl}$. This means that this system is not a bi-material system but at least a tri-layer system in which the interlayer consists of various phases, dependent on whether the diffusion couple during bonding can be considered as finite, infinite or equilibrated. Here symmetrical diffusion couples $\text{Al}_2\text{O}_3$-$\text{Ti}$-$\text{Al}_2\text{O}_3$ were used of which the fracture toughness $K_c$ was measured with the Double Cantilever Beam (DCB) test. The fracture morphology was examined by optical and electron microscopy and can be divided into planar and zigzag types. The zigzag fracture surface appeared to be $\text{TiAl}$, covered with $\text{Ti}_2\text{Al}$ islands of about 1 $\mu$m, while the planar one was almost pure $\text{Ti}_2\text{Al}$. Since thermal stresses do not contribute to the stress singularity at the crack tip [10] and the interlayer is thin as compared to the total thickness of the specimen so that the energy is mainly stored in the beams, the fracture toughness $K_c$ can be used to estimate the ‘external’ fracture energy release rate $J_{\text{ext}}$ according to

$$J_{\text{ext}} = \frac{K_c(1-\nu^2)}{2E}$$

(17)

where $E$ and $\nu$ denote Young’s modulus and Poisson’s ratio of the alumina. In Figure 2a the fracture energy $J_{\text{ext}}$ for a range of processing conditions is shown. The parameter $d_x/d_e$, indicating the ratio of intermetallic layer thickness $d_x$ at the actual processing conditions to the thickness $d_e$ of this layer in an equilibrated situation, covers these processing effects and therefore the mechanical data can be plotted as a function of this parameter [9]. Clearly the value of $J_{\text{ext}}$ decreases with increasing value $d_x/d_e$, or equivalently, increasing value of Ti thickness and processing time.

In order to apply the analysis described before in relatively simple way, we make a number of assumptions:

- The interaction energy contribution is zero because the loading points are well away from the crack tip.
- The thermal energy $U_{\text{th}}$ can be estimated from ‘mechanics of materials’ formulae. This is not necessary but make simple estimates possible.
- Before fracture a DCB specimen is a symmetrical tri-layer laminate while after fracture an asymmetrical bi-layer remains.
- The properties of the interface layer can be estimated by simple additivity rules for the various components.
- Contributions from plasticity are dealt with by very simple models available in the literature.
After collecting the data as far as available from the literature, estimates were made for the various energy terms along the lines indicated above. The adherence part of the energy release rate or 'true' fracture energy $W_{adh}$ was calculated from

$$W_{adh} = -J_{adh} = J_{cut} + J_{th} - J_{pl}$$

(18)

where $J_{th}$ and $J_{pl}$ are the thermal (or residual stress) energy and plastic energy, respectively. The former was estimated by

$$J_{th} = -\frac{1}{W} \frac{\partial U_{th}}{\partial t} \equiv U_{th}/\Gamma_{t}$$

(19)

while the latter was estimated according to

$$J_{pl} \equiv J_{pl}(h/\delta)$$

(20)

where $h$ denotes the height of the plastic zone and $\delta$ the distance of the glide steps as experimentally observed. Full details of the calculations as well as the data can be found in [11]. The results are shown in Figure 2b. From this figure it is clear that the adherence contribution is to a large extent constant and independent of the parameter $d/d_e$ and thus of the processing conditions. The 'true' average fracture energy $W_{adh}$ of all the finite and infinite Al$_2$O$_3$-TiAl couples is $12.9 \pm 1.7$ J/m$^2$, where $\pm$ denotes the sample standard deviation.

For the equilibrated Al$_2$O$_3$-Ti$_3$Al interface a slightly lower value of $W_{adh} = 9.3 \pm 0.7$ J/m$^2$ was observed. Since it is clear that $J_{th}$ contributes significantly in the energy balance, a comparison with other experimental data is difficult to make in the absence of sufficient information. A comparison can thus be made only for the external
energy release rate $J_y$, the value of which is dependent on the geometry of the joint though.

4. Application to a Coating: Ni(P) on Al$_2$O$_3$

The analysis given can also be applied to coatings. An important system in electronic industry, among other things for integrated circuit packaging, printed circuit and sensor applications, is given by electrolessly deposited Ni(P) on alumina substrates. Generally, the adherence between electroless Ni(P) layers and inorganic substrates like alumina is weak. For an overview of this system, see [12]. For electrolessly deposited Ni(P) layers on smooth Al$_2$O$_3$ substrates ($R_a \approx 0.06$ μm) fracture energy measurements were done on coatings with various thicknesses using a 90° peel test at a test rate of 1 mm/min in air [13]. The width of the specimens was 15 mm. Peel radii were measured by means of a video camera both during peeling and unloading.

![Figure 3: Peel energy as a function of electrolessly deposited Ni(P) layer thickness on a smooth alumina substrate.](image)

The 'true' fracture energy $W_{adh}$ in this case can also be estimated by Eq. (18). Since the energy stored in the system could be regained during unloading within the experimental error, it was concluded that the plastic energy $J_{pl}$ was negligible in this case. Since the deposition temperature was room temperature the residual stress energy $J_{th}$ also can be neglected. Moreover, the contribution from the deposition process to the residual stress itself was assessed as negligible since the deposition stress was only 40 MPa yielding a contribution to $J_{th}$ of only 0.004 J/m$^2$. Hence the peel energy can be regarded as the 'true' fracture energy $W_{adh}$. In Figure 3 the peel energies, determined on average from 3 independent measurements, are plotted against layer thickness for smooth alumina substrates. The peel energy appears to be independent of the layer thickness. The average value amounts 6.1 ± 0.6 J/m$^2$.

Since the substrate used was rather smooth, mechanical interlocking contributions to $W_{adh}$, are expected to be small. Moreover, no reactions occur since the deposition temperature is low. Since typical van der Waals energies amount 0.5 J/m$^2$, crack tip plasticity (as opposed to the aforementioned overall plasticity) was held responsible for the value of $W_{adh}$. Nevertheless chemical interactions play a role since some interference of the atmosphere was present. Applying dry nitrogen gas in the peel test increased the peel energy by 10-20%. When the nitrogen flow was stopped, the peel
energy dropped immediately again. This effect appeared to be largely reversible thus excluding subcritical crack growth. Finally it should be remarked that for substrates with other morphologies different values for $J$ were obtained. From analyses similar to the one above, it was possible to show that an increase of about 2 to 3 in $W_{\text{adh}}$ could be obtained by thermal treatment of the layers [14], thereby modifying the chemical interfacial interactions contributing to $W_{\text{adh}}$.

5 Final Remarks

The analysis shows that the energetics of a joint can be assessed on the basis of a, in principle, simple description of the various contributions to the fracture energy of a joint. The interaction between loading system and internal stresses is limited to the case where the load is applied close to the crack tip. Frequently this is not the case. The analysis can be generally applied to all systems containing more than one material. For the time being it is limited to elastically behaving systems but there seems to be no formal objection to extend it to plastically deforming systems. This will be the subject of a forthcoming research project. The analysis was applied to two systems: first alumina-titanium joints which form an important basic system from a engineering point of view and, second, to a Ni(P) coating on alumina, frequently used in electronic devices. In both cases the various energy terms were estimated on the basis of simple estimates. In both cases a fracture energy resulted, independent of the geometrical details of the material combination providing experimental trust in the analysis given.

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RESEARCH AREAS AND OBJECTIVES
The research programme can be divided into different fields of interest:
Advanced Materials and Casting Technology

- **Materials**
  - Ferrous alloys (spheroidal cast iron, P/M steels)
  - Non-ferrous alloys (mainly aluminium alloys)
  - Intermetallic compounds (aluminides, silicides)

- **Processing techniques**
  - Metal preparation in the liquid phase
  - Computer modelling of the casting process
  - Production of rapidly solidified materials
  - Production of metal matrix composites
  - Strip casting
  - Sintering
  - Extrusion
  - Powder injection moulding
  - Hot isostatic pressing

Three major research areas can be distinguished:

1. **Solidification Processing**
2. **Advanced Materials and Production Technology**
3. **Powder Metallurgy**

**FACILITIES**

**Foundry**

- Six induction and resistance heating furnaces for ferrous and non-ferrous alloys, capacities from 2-90 l and power-ratings from 15-120 kW
- Heat treatment ovens with or without air circulation, capacities from 10-1500 l, maximum temperatures up to 1200 °C
- One roller, maximum width 30 cm
- One forging hammer
- One vertical semi-continuous casting machine for mainly aluminium alloy billets up to approximately 180 cm with round shape diameter approximately Ø 19 cm and shape 8 cm x 20 cm
- One vacuum furnace (capacity approximately 2 l)
- One low pressure pouring machine for aluminium alloys, computer controlled, inert gas operated, capacity 30 kg
- Two shot blasting machines for glass beads or steel shot. One vibrating container for wet polishing
- Mixers, from 2 to 150 kg, for green (clay bonded) and chemically bonded sand moulds and cores
- Moulding machine, for green (clay bonded) sand moulds
- Gas hardening equipment for chemically bonded sand cores and moulds
- Equipment to produce ceramic moulds (precision casting)
- Equipment to test and analyse green (clay bonded) and chemically bonded sand (Georg Fischer)
- Fully equipped pattern shop for production of patterns for sand moulds including a computer controlled milling machine for production of foam patterns using CAD/CAM-techniques
- Two workstations (HP) for use of several computer simulation programmes (mould filling and solidification)
• Several personal computers for stand alone use (controlling of Low Pressure pouring machines, temperature measurements and place determination of liquid metal in sand moulds, process simulation) and use as a terminal (network) for the workstation
• Water simulation equipment for observation of flow phenomena in water while simulating real casting processes

**Foundry Laboratory**
• A large number of smaller units with inductive or resistance heating are available, power ratings up to ca. 3 kW
• One vacuum furnace (capacity 1 l) and one electron beam furnace with X-Y table
• Extrusion press, max. 500 °C, 60 ton, billet 30 mm diameter x 70 mm length
• One experimental horizontal die-casting machine with transparent dies and cold chamber, for simulation experiments
• Rotating (pen on disk) wear tester
• Equipment for rapid solidification processing
• Dilatometer equipment
• Viscosimeter
• Differential scanning calorimeter

**Powder Metallurgy**
• Processing line for powder injection moulding - PIM (different attritors and ball mills for modification of powder morphology, mixers and kneaders for plastisol formulation, injection moulding press, BASF debinding oven)
• Vacuum-sinter-debinding oven (1700 °C, N₂, H₂, Ar) with a unit for fast cooling. The oven is also used for different cycles of phase transformation in steels
• Hot Vacuum Press (2200 °C, 20 Tones, Ø 150 x 200 mm, Ar, N₂). The press is also used for diffusion bonding and processing of materials for electronic industry (sandwich capacitors)
• Hot Isostatic Press (2200 °C, 200 MPa, Ø 150 x 300 mm, Ar, N₂). HIP is also applied for diffusion bonding, coatings, heat treatment under pressure (for instance nitriding) and post processing in order to close residual porosity (coatings, castings, PIM components)
• Cold Isostatic Pressing (400 MPa, Ø 200 x 1000 mm. CIP is also used for hydrostatic forming techniques of aluminium, steel and metal-polymer laminates
• Horizontal extrusion press (2MN, fully instrumented with conventional liners - 500 °C and high temperature liner water cooled - 750 °C
• Vertical extrusion press (0.8 MN, fully instrumented, liner - 500 °C)
• Carbolite tubular oven (up to 1600 °C)
• Edwards EQ 80F residual gas analyser
• Degassing unit
• Particle size analyser and BET equipment
• DSC, TGA
Within the PBTS NM95026 project "Thin Nodular Cast Iron for Automotive Applications" efforts are made to reproduce high quality thin wall (thickness < 3.5 mm) castings out of nodular cast iron. The castings have to be free of carbides and without porosities. Meanwhile the castings need to have a good fatigue resistance. The project is a follow-up on the BRITE-P-2437-5-87 project "Thin Walled Nodular Cast Iron".

1.2 Mould Filling and Solidification of Aluminium Alloys

As a follow-up on the IOP research program "Quality improvement of castings by optimisation of mould filling", a study has been made of the mould filling of a thin wall horizontal horse shoe with aluminium. This research has been conducted to the heat transfer and solidification during mould filling as well as the description of the metal-air surface, including surface tension. Mould filling with liquid metal has been registered using a video camera in moulds with a ceramic glass plate, or using contact measurements in a sand mould. Additionally, temperature measurements have been performed. The experimental results have been compared with computational results obtained with a commercial software package, Flow-3D. Additional to the casting experiments, Particle Image Velocimetry (PIV) measurements were performed in a water model of the horse shoe. This way the velocity field during mould filling was obtained experimentally and could be compared to computations. The experiments have been carried out within a Ph.D. study, in co-operation with the "Kramers Laboratorium voor Fysische Technologie" of Delft University of Technology.

1.3 Lost Foam Technology

Within the cluster project Lost Foam Technology research has been done on lost foam casting techniques in corporation with the foundries Lovink Terborg and De Globe, TNO Product Centrum Delft and Gemco Lost Foam. During the casting technique an E.P.S. pattern is embedded in non-bounded sand. During the pouring process the molten metal replaces the pattern while vaporising it. Using the lost foam technique difficult high quality castings can be produced without cores and with a smoother surface than conventionally made sand castings. To obtain high quality castings, a fully automated and fully controlled production process from foam pattern design to castings is required. Therefore it is necessary to apply Computer-Aided-Design, Manufacturing and Engineering techniques (Rapid Prototyping). Mould filling and solidification are very important issues within the process. Therefore investigations are carried out using mathematical computer calculations with software packages like Flow-3D. The computer calculation results are validated with real casting experiments during which the place of the metal in the mould and the local temperatures in moulding material and metal are determined. Also the thermo-mechanical properties of the castings are investigated. During the research, ferrous as well as non-ferrous alloys are examined.

1.4 Low Pressure Sand Casting of Aluminium Composites

This project is supported by IOP-Metalen. At this moment the castability of aluminium matrix composites has been examined by using a Low Pressure Casting Machine. During the experiments the melt has to be stirred to prevent sedimentation of the composite particles. The composite material is very sensitive to inclusion of oxides and gas. Gas inclusion can be reduced by avoiding turbulence during stirring and pouring of the melt. By the use of ceramic filters the melt can be refined during pouring so the final number of oxides in the castings is reduced. Experiments show that aluminium with SiC particles has a higher Young's modulus, a higher hardness and a
lower elongation.

1.5 Thermomechanical Properties of DC Cast Aluminium Alloys in Relation to Hot Tearing

Research is carried out within a Brite/Euram programme, EMPACT, which involves six European primary aluminium producers, a software company and several technological institutions. The main aim of this project is to develop predictive tools for control of deformation, cracking and segregation in aluminium casting of rolling ingots and extrusion billets.

Delft University of Technology focuses on two subjects: firstly, the thermophysical and thermomechanical properties of the five selected alloys (AA1050, AA3104, AA5182, AA6063 and AA7075) and secondly, the investigation of the hot tearing mechanism and the formulation of cracking criteria functions for the DC cast ingots.

The main thermophysical properties have been collected from literature and have also been modelled with ALSTRUC by one of the project partners. The thermomechanical properties of AA3104 and AA5183 were determined in a wide temperature range and at low strain rate with a Gleeble thermomechanical simulator. These properties were used to determine the rheological parameters of the modified Ludwig constitutive equation.

2 Advanced Materials and Production Technology

2.1 Rapid Solidification Processing of Al Alloys for Recycling or for Advanced Properties

The rapid solidification technique, as developed by the group and operated through both a laboratory line unit and pilot line unit in industry, approaches the stage of commercialisation. An EEC CRAFT project, which involved prototype development of particular finished products, ended this year.

Since the technicians involved retired this year, the activities of the group in this field slowed down but the company RSP Products B.V. uses the lab's infrastructure for further developments.

2.2 Formability of Strip Cast Aluminium Alloys

A single roll strip caster developed at Delft University of Technology has been optimised to produce strip with thicknesses between 0.5-10mm. The main problem was to get a strip width of 100 mm with a constant thickness. By studying the liquid flow when connecting the casting drum has resulted in an advanced casting slot. Results proved that there has to be a certain casting pressure, nozzle slot breadth and gap distance to get a constant strip thickness. Also an increased roll speed and casting temperature results in a decreased strip thickness. The microstructure of all stripcast material shows highly orientated columnar crystals originating from the casting roll surface of the strip. A transition from columnar to equiaxed growth is found at ½ of the strip thickness. An average SDAS value of 7.07 μm is found for the AA3004 strip cast material and an average cooling rate of about 1344 °C/s is found for the strip cast process. SDAS and cooling rate are related to the roll speed; a lower roll speed results in a larger SDAS and thus in a smaller cooling rate of the metal. After the metal is solidified the strip will be directly rolled. Because of the high cooling rate a supersaturation of alloying elements and a fine microstructure occurs and this could give a better formability of sheet material. Experiments are now concentrating on the influence of alloying elements on strip quality, structure and formability properties af-
ter the strip has been rolled. This project is supported by IOP-metalen.

3 Powder Metallurgy

3.1 Processing of Aluminium Alloys and Metal Matrix Composites for Wear-Resistance Applications

The research work has been supported by national (IOP, FOM and STW), European (COST) and industrial programmes. A variety of powder metallurgy techniques were employed to process conventional and unconventional aluminium alloys and aluminium alloy based composites, targeting at enhanced wear resistance, lowered thermal expansion coefficient and improved mechanical properties at room and elevated temperatures. For the composites, Al-Si-X pre-alloyed powders, Al-Cu and Al-Fe elementary powders, and Al-Fe-V pre-alloyed powder were selected as starting matrix materials. Ceramic reinforcements (5-20 vol.%), such as Al₂O₃ and SiC particles of different median sizes and morphologies and Al₂O₃ short fibres, were introduced by mixing them with the matrix alloy powders (the Osprey spray co-deposition was also used as an alternative approach). Subsequent processing was differently conducted, mainly depending on starting materials; for instance, cold isostatic pressing, degassing and hot extrusion were involved in processing Al-Si based composites; uni-axial compaction, degassing, liquid phase sintering, hot extrusion and heat treatment in processing elemental Al-Cu based composites; and uni-axial compaction, reactive sintering and extrusion in processing elemental Al-Fe based composites. Microscopy was carried out to examine structure and to determine the mechanisms of deformation, fracture and wear. Tensile properties at room and elevated temperatures up to 400 °C, hardness, Young's modulus, thermal expansion coefficient and wear resistance were evaluated. As the work covers a wide scope of materials and processes, the following are two examples showing the research on specific composite materials and extrusion process.

- Aluminium Matrix Composites with Short Fibres
  The composites based on a P/M Al-20Si-X alloy and containing 4.8, 10.0, and 20.0 vol.% d-Al₂O₃ short fibres were prepared through dry mixing, compaction, degassing and extrusion. The previous stage of the work was focused on tensile properties as influenced by a post-extrusion heat treatment and by reduction ratio applied during extrusion. Recent work has been on the microstructure at the fibre-matrix interfaces and the fibre chemistry. It has shown that in addition to fragmentation, other forms of less obvious damage are inflicted upon fibres during extrusion such as flaws, cracks and abraded surface, reducing the intrinsic strength of the fibres. The damage is caused by the combined effect of the large volume fraction of hard silicon particles in the matrix alloy and severe shearing involved in extrusion. SEM, TEM and XPS demonstrate the affinity of the d-Al₂O₃ fibre to the matrix alloying elements (copper and magnesium). The specific internal texture (porosity and large surface) of the fibres, their surface chemical activity at extrusion temperature and mechanical fragmentation allow rapid hypothetical chemical (redox) reaction. Due to the damage, the reaction takes place at fibre ends, external surface, abraded surface, flaws and cracks.

- Extrusion
  Extrusion has been carried out as an essential step in each of the processing route, to consolidate pre-alloyed powders, sintered elementary powders, mixed composite materials, spray deposited preforms. It has also been considered as
a thermomechanical process to understand the mechanical and structural responses of the materials to hot deformation. For each material, it is necessary to specify the correlation between the extrusion pressure requirement and process variables, and to determine the extrudability with respect to the capacity of a press available, and the surface quality, deformation homogeneity, and structural integration of the consolidated materials. Meanwhile, computer modelling of extruding aluminium alloys and composites with the plasticity theory as applied to the specific situation in which volume change occurs along with deformation has also been in progress, with an emphasis on CAD of metallic and ceramic dies especially for difficult-to-extrude materials such as metal matrix composites and intermetallics.

3.2 Novel Processing, Physical and Mechanical Metallurgy of Ordered Intermetallics

The research programme, as a continued part of the ongoing projects concerns materials development, novel processing, physical and mechanical metallurgy aspects of several ordered intermetallic compounds (Ni$_3$Al, Ni$_3$Si, Fe$_3$Al and FeAl based). The main activities and objectives can be summarised as:

(a) Novel processing of ordered intermetallic compounds and intermetallic matrix composites. Several intermetallic compounds based on Ni$_3$Al, Ni-Al-Cr, Fe$_3$Al, FeAl and Fe-Al-Cr have been processed from elemental powders using reactive sintering and reactive hipping techniques. *In situ* forming Ni$_3$Al-Ti$_2$B composites from elemental powders of Ni, Al, Ti, and B has been studied by means of reactive sintering and self-propagating high-temperature synthesis (SHS) techniques. Although the principle of these techniques is the same, i.e. based on the highly exothermic nature of the system, considerable differences exist in experimental design and operational mechanism between the reactive sintering/hipping and the SHS processing. In reactive sintering or reactive hipping, the whole volume of the compacts is continuously heated in a furnace or a HIP unit up to the lowest eutectic temperature of the alloy system which is usually much lower than their melting temperature of the compounds, and the reaction completes within a few seconds. While in the SHS process, the reaction is ignited at one end of the compact which gives a combustion reaction wave with a certain wave speed moving through the whole sample and transforming the compacted elemental powders into the final combustion products, compounds or composites.

The research covers both the fundamental aspects and experimental applications. Thermodynamics in relation to reaction mechanisms of the combustion processes are studied by means of DSC analysis at both low and high temperatures (up to 1300 °C) and DTA analysis. The influence of diluent on the thermodynamic properties of the system is also investigated. The reaction phase forming technique for preparing ordered intermetallics or intermetallic matrix composites shows prospective possibility in engineering applications due to its advantages over other conventional processing methods, including the use of less expensive, readily available and easily compacted elemental powders, lower processing cost and energy savings. Some valuable results have been obtained related to this part of the research. However, some processing controls have to be further studied in order to use this technique for industrial applications.

(b) Study on the microstructures and mechanical properties of the Ni$_3$Al and Fe$_3$Al
based intermetallics. Microstructures have been investigated using TEM, SEM, optical microscopy. Surface layer structure and grain boundary segregation behaviour of the compounds have been studied using Auger electron spectroscopy and XPS. Room temperature and elevated temperature properties have been investigated with special emphasis on the influence of testing atmosphere (low humidity, inert gas, in petroleum), deformation rate on the mechanical properties.

(c) Processing, microstructures and mechanical properties of the Ni$_3$Si based intermetallics have been investigated related to the influence of alloying additions of Cr and Ti, as well as different production techniques. This part of the research has provided some useful results for the application of Ni$_3$Si based intermetallics in off-shore, chemical industries.

3.3 Powder Injection Moulding

The research on powder injection moulding (PIM) was focused on debinding (the elimination of the binder after moulding) — the most difficult and time consuming stage of the PIM process. As a result of the debinding process, the major part of the binder is removed, while the remainders will be degraded during the subsequent sintering. Three different removal techniques have been investigated, namely thermal degradation, wick debinding and solvent extraction.

Pure thermal degradation proved to be less effective than wick debinding in combination with thermal degradation. For wick debinding, an optimum between wicking time and thermal degradation time has been established. Furthermore, a theoretical model describing the wick process has been developed and confirmed by experimental results. As a result, requirements concerning wick particle size and binder viscosity have been set.

Because of great interest shown by industry, solvent debinding has been introduced. After the first trials based on an extensive literature study, general design rules for a soluble binder system have been set. This enables the development of a new environment-friendly water soluble binder, which allows for a reduction in debinding time of over 50%. At this moment, optimisation and up scaling of the process are the main concerns. The last task will be carried out within a frame of industrial programmes.

3.4 Enhanced Sintering of Ferrous Components

The influence of sintering parameters (time, temperature and sintering atmosphere) and post-sintering cooling rate on the final properties of Fe-Ni alloys was investigated. Two main issues were thoroughly addressed:

- the influence of debinding-sintering cycle on the final properties of metal injection moulded components;
- homogenisation of Fe-2Ni and its influence on the microstructure and mechanical properties of the final products.

It has been concluded that an addition of 2 wt.% nickel does not depress the pearlite transformation to the extent that causes a noticeable improvement of the microstructure and tensile properties of the final parts. The improved mechanical properties can mainly be attributed to the retention of carbon in the alloy and its fine pearlitic structure. Sintering parameters (temperature, time and sintering atmosphere) need, however, to be carefully adjusted; a trade-off between densification mechanisms leading to increased mechanical properties and a grain growth process having a reverse effect on the final properties of the product has to be taken into account. The
optimised debinding-sintering cycle with controlled post-sintering cooling allows ultimately an increase of the tensile properties of the sintered products more than two-fold.

The investigation on the kinetics of debinding-sintering process related to different particle size distributions of the 316L and 17-4 PH P/M stainless steels has also commenced.

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PERSONNEL

Scientific staff

prof. dr. J.H.W. de Wit (0.2)
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ir. G. Bakker (till 1-1-1999)
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ir. M. Freijling (TNO) (till 1-11-1998)
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RESEARCH AREAS AND OBJECTIVES

The corrosion research is mainly aimed at the clarification of corrosion reaction mechanisms and thereby at the development of better corrosion protection measures. Surface layers play an important role in protecting metals and alloys against corrosion, i.e. the naturally formed passive film as well as specially applied coatings. Therefore an important part of the research program is aimed at a detailed characterisation of these layers and the interface between the layers and the metal, including adhesive properties. The study of the role of passive layers is equally important for our understanding of the environmentally induced fracture of structural materials in aggressive media under an applied stress in stress corrosion cracking (SCC) and corrosion fatigue. The electrochemical research focused on the Molten Carbonate Fuel Cell and in co-operation with the faculty Mechanical Engineering and the department of Technology, Policy and Management modelling of fuel cells and integration of fuel cells in fuel cell systems was studied from a fundamental, thermodynamical perspective, thereby providing new directions for materials development for fuel cells.

The research program is subdivided in 3 themes:

1. **Passivity of Materials, Including Film Formation, Passivity Breakdown, Localised Corrosion and Environmentally Induced Fracture**

The general purpose of this research theme is to obtain detailed knowledge of the passive behaviour of both model alloys and commercial materials and to prevent or delay the degradation of materials by localised forms of corrosion as pitting corrosion, stress corrosion cracking and corrosion fatigue. This knowledge will lead to materials selection procedures based on scientific understanding, as opposed to the still common practice of using selection criteria based on poorly understood practical information.

The different projects coming under this theme are all filling out gaps in our knowledge and are expected to lead eventually to a comprehensive model for the structure and the protective properties of the passive layer, as well as to a fundamental understanding of environmentally assisted failure under mechanical loading conditions in aggressive environments.

2. **Corrosion Protection by Metallic, Inorganic or Organic Coatings**

The general purpose of this theme is the elucidation of the mechanisms that play a role in the protection of substrate metals, in order to arrive at better protection against corrosion and eventually life time prediction of coating systems. The different projects in this theme emphasise different aspects in this wide field.

Part of the work is performed on Al-substrates, mainly focusing on filiform corrosion, which has been a major industrial issue for the last five years due to the increased number of failures in applications.

Another part of the work is directly aimed at life time prediction of organic coatings systems. It is focused on steel substrates, without or in combination with conversion
layers and other metallic layers, e.g. Zn.

A third part is dealing with inorganic layers to protect metals against high temperature corrosion in complicated aggressive gaseous atmospheres and in molten carbonates. Emphasis is on a combined materials properties approach for these coated systems. Substrate properties, conversion layers, interfacial phenomena and physicochemical properties of the coating layers themselves in relation with the processing parameters of the total system are studied.

A fourth part of the research is focused on metallic coatings for corrosion protection. Currently the properties of spray deposited metal layers like titanium are evaluated. If these coatings are reliable these materials could be extremely useful for repair work in the process industry.

Besides these four themes also projects are running on microbiological corrosion and metallisation of plastics using conductive polymers. At the moment several new projects have started in which pre-treatment of aluminium and zinc will be evaluated.

While the background of most projects is very practical, this research is focused mainly on fundamental issues including electrochemical mechanisms and more generally transport mechanisms in relation with microstructure and composition.

3 Molten Carbonate Fuel Cells

The electrode reaction mechanisms at the cathode are investigated in relation with cell modelling in order to optimise the cell performance. Also the dissolution/corrosion of the electrode materials and separator plates, including coatings, in molten carbonate is evaluated in order to increase the life time and performance of fuel cells. Understanding the melt chemistry is essential in studying the corrosion and reaction mechanisms. Models have been developed to describe cell performance, e.g. as a function of gas utilisation.

FACILITIES

- Electrochemical equipment:
  - Various potentiostats/galvanostats, both analogue and digital (ECO, PAR, Gamry)
  - Scanners, sensitive mV meters, electrometer
  - Transient recorder
  - Rotating disk electrodes for aqueous and molten carbonate applications
  - Impedance spectroscopy equipment
  - 5 x Solartron (FRA + electrochemical interface + HP computer + plotter + software)
  - 2 x EG&G equipment, also including potentiostat, lock-in analyser, PC, software and printer
  - Zahner EIS equipment
  - ECO-EIS equipment
  - Digital oscilloscope for noise measurements (Philips)
  - Low noise potentiostat for current transient measurements
  - Fully climatised room (temperature and humidity) for coatings investigations
  - Local measurement techniques: SRET (EG&G), SVET, Kelvin probe, and AFM/STM (Nanoscope III) with electrochemical cell
- Furnaces for oxidation experiments up to 1773 K in a controlled atmosphere
Corrosion Technology, Electrochemistry and Spectroscopy

- High temperature cyclic voltammetry equipment
- 25 PC’s and mini-computers for measurement control, data management, modelling, electronic mail. Three workstations.
- Equipment for measuring the stress corrosion sensitivity of alloys up to 250 °C:
  - Small autoclaves for quenching experiments
  - Various slow strain rate and constant load test facilities
- Glove box, with re-circulation of the purified atmosphere for transfer of passivated samples to SAM and XPS high vacuum chamber
- Interferometric ellipsometer, an Ultra-fast Zeeman laser based ellipsometer is being developed
- Three complete Molten Carbonate Fuel Cell Units with furnaces, gas manipulation equipment, electronic controls, etc.
- Three pot-type cells for mechanistic studies in molten carbonate
- Multi-purpose PVD unit
- Potential modulated reflectrometry equipment
- Atomic Absorption and Emission Spectrometers, including X-ray fluorescence, inductively coupled plasma emission, flame and graphite furnace AAS
- Wilhelmy balance for surface tension measurements under potential control
- High temperature Perkin-Elmer thermobalance
- Filiform corrosion test facilities

RESEARCH REPORT 1998

1. Passivity of Materials, Including Film Formation, Passivity Breakdown, Localised Corrosion and Environmentally Induced Fracture (L. Norbart, P.J.B. Overkamp, J.C. Elkenbracht, B.D. Lichter, C.J. van der Wekken, J.H.W. de Wit)

The modelling of corrosion fatigue crack growth under anodic polarisation of steel in seawater has been quite successful. The computer simulation of H⁺ ion transport by means of the special transport mechanism in the crack solution during fatigue cycling, known as flow enhanced diffusion (FED), could be improved by taking into account the contribution due to migration in the electric field in the crack solution. In the present model the transport of H⁺ ions originating along the crack walls as a result of the anodic dissolution reaction which is followed by hydrolysis and/or hydroxide precipitation reactions, results in the creation of an effective source for hydrogen diffusion at the crack tip, where hydrogen is absorbed into the material. The crack tip can be represented as a moving line source from where the hydrogen diffuses into the material. The model relates the strength of this line source to the anodic current density distribution at the crack walls. The hydrogen distribution in the material in front of the moving line source at the crack tip determines the dimensions of a critically embrittled zone and the amount of crack extension per cycle.

The model calculations indicate that during the corrosion fatigue of steel in seawater the crack growth rate per cycle da/dN is determined by the frequency dependent hydrogen ion transport process in the crack solution, as well as by the hydrogen transport mechanism in the material in front of the moving crack tip. In particular the experimentally determined frequency dependence of da/dN according to \( f^{1/2} \) is found to be associated with the hydrogen transport mechanism in the material in front of the crack tip.

Combining the results for CF under cyclic loading conditions with the findings re-
garding stress corrosion cracking under static loading, it appears that the rate of environmentally assisted crack extension in a variety of systems strongly depends on the rate of solute transport in the crack solution. If hydrogen embrittlement plays a role, the rate of transport of hydrogen ions to the crack tip in the crack solution will determine the hydrogen distribution in the material in front of the moving crack tip and therefore also the crack growth rate.

In general it is clear that the electrochemical conditions in the crack tip region will be strongly affected by the solute transport to or from the crack tip. As a result solute transport may become the rate determining step during environmentally assisted cracking in a variety of systems, under static as well as under dynamic loading conditions.

1.1 Material Analysis of Björk-Shiley Convexo-Concave Heart Valve Prostheses

(P.J.B. Overkamp, J.H.W. de Wit, B.A.J.M. de Mol, H.A. Becker)

This project started in September 1996. The research is supported by a grant of the Dutch Heart Foundation.

An electrochemical characterisation performed of the mechanical heart valve in a physiological Ringers solution was performed in order to investigate the influence of the combination of the different materials of the valve on the valve failure.

In vitro fatigue experiments with scanning electron microscopy investigation of the fracture surfaces have been continued. Optical microscopy investigations at the cross sections of the outlet strut of the explanted mechanical heart valves have been started to get an better understanding of the welding process. A new in vivo non destructive testing project, based on magnetic resonance imaging (MRI) and supported by a grant of STW, has been started in co-operation with the University of Utrecht (AZU). The failure of different types of mechanical heart valves has been investigated in co-operation with the Inter University Working Group for Cardiovascular Implant Retrieval Analysis.

2 Corrosion Protection by Metallic, Inorganic and Organic Coatings


An important part of this research is focussed on filiform corrosion. There are three different projects (two of these in co-operation with the groups of prof. S. van der Zwaag [MIDEG] and prof. L. Katgerman [MIDEG]). In each project a specific part of the filiform corrosion is investigated; the first project deals with the influence of the microstructure on filiform corrosion, the second project deals with the influence of various process parameters on filiform corrosion, and the third project evaluates anodising as a possible alternative for chromate pre-treatments. The intensive cooperation between different researchers has proven to be very useful. There are close contacts with national and international research organisations working on this subject.

The research has resulted in more knowledge about the mechanism of filiform corrosion. Filiform corrosion susceptibility in binary model systems increases with increasing alloying concentrations. Furthermore, the filiform corrosion susceptibility varies with the type of alloying element, in particular Cu was found to have a detrimental effect on the filiform corrosion properties. Intermetallics can act as cathodic sites for oxygen reduction and play a major role in the propagation of filiform corrosion, as can be shown in electrochemical experiments. In the case of anodised al-
lovs, the thickness of the porous layer instead of the barrier layer appears to be the most important factor in limiting the filiform corrosion susceptibility.

2.1 Corrosion Research on Polymer Coated Steel for the Food Packaging Industry (A.J. de Jong)

For the food packaging industry, cans of polymer coated steel are widely used. The main function of the polymer is to protect the steel from corrosion. This is necessary, since food and beverage products are often good electrolytes (water with dissolved ions) and can have a low pH. The corrosion protection of a polymer may be characterised by:

- the attachment of the polymer to the steel under immersion,
- ageing of the polymer under immersion.

Attachment of the polymer is studied by following the delamination of artificial defects in test samples of polymer coated steel during immersion by EIS (Electrochemical Impedance Spectroscopy) and by scanning Kelvin Probe measurements. Ageing of a polymer under immersion is studied by measuring the permittivity as a function of temperature and frequency. Buffered citric acid of pH = 3 is used as an electrolyte to model food and beverage products.

For a better interpretation of the measurements, fundamental research is done on the physical modelling of scanning Kelvin Probe measurements and on processing algorithms for the permittivity measurements. This is done in co-operation with dr. J. Wiijenber (Koninklijke Hoogovens), prof.dr.ir. H. Blok and prof.dr.ir. J. van Turnhout (MIDEG). The project is sponsored by Koninklijke Hoogovens.

A considerable effort has been put in a further development of the Kelvin probe and the SVET. Besides the improvement of the equipment also a considerable effort has been directed at understanding measurements dealing with corrosion processes underneath organic coatings. In co-operation with Hoogovens test systems have been designed and tested to show the difference between theory and experiment. It is now clear that the theory as presented in literature does not give a complete description of the systems. Especially the height control over organic coatings is still not completely understood.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed on deformed pre-coated metal. These measurements will be combined with the local electrochemical methods.

The metallisation of plastics with conductive polymers has been focussed on the neutralisation step. Although the conduction of the polymer layers is still not perfect it is possible to deposit a well adhering copper layer on top of it. With AFM it was shown that the copper is initially deposited on local spots on the polymer. These small spots grow and finally form a dense copper layer. Also other polymers have been tested as a base material.


In 1997 a possible breakthrough in solving the problem of the dissolution of the NiO MCFC cathode was reported in the adapted MCFC cell design named i-MCFC. In the i-MCFC the CO₂ necessary for the cathode operation is supplied through an additional channel in the matrix tile. The i-MCFC was extensively and successfully tested
using Impedance Spectroscopy and Current-Interrupt. A similar cathode polarisation is obtained when the CO$_2$ is supplied through the matrix channel instead of, mixed with O$_2$, to the cathode directly. This shows that the expected increase of the diffusion losses are small. The mechanical strength of the ceramic matrix material (porous Lithium aluminosilicate) remains a major concern.

The i-MCFC is a fuel cell design with three, instead of the common two, gas inlets and outlets. In co-operation with G.P.J. Dijkema of the department of Technology, Policy and Management this unique feature was used to develop improved system designs and a tri-generation system for power, heat and CO$_2$.

In co-operation with prof. Fehribach at WPI we started modelling the processes in the matrix of the i-MCFC. Here the transport of CO$_2$ from the matrix (gas channel) to the cathode and of O$_2$ vice versa are important features, as is the position of the recombination of these species to CO$_3^{2-}$.

In collaboration with the Mechanical Engineering department work on fuel cell modelling was finished. Isothermal and Non-Isothermal models were developed using few, realistic, assumptions. Measured and predicted behaviour of a 100 cm$^2$ class MCFC unit cell is in good accordance, qualitatively as well as quantitatively.

The work on the carbonate melt chemistry was continued. The melt basicity, i.e. O$_2^{-}$ concentration, was shown to be an important parameter determining the stability of reduced oxygen species in molten carbonate. The basicity in the MCFC cathode under load is determined by the recombination rate of CO$_2$ with O$_2^{-}$ to carbonate ions. This rate was shown to be relatively slow in several studies using a specific method. With these rates unrealistic melt basicities in the MCFC cathode under load exceeding the Li$_2$O solubility limit were calculated. A vital assumption in the method used is that the CO$_2$ dissolution rate into the melt is fast compared to the recombination rate. Recently we showed that this assumption does not hold and that CO$_2$ dissolution is the slowest process. New estimates of the melt basicity in the cathode under load, using the CO$_2$ dissolution rate, will be obtained in the near future.

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P.C.H. Ament
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Scripta Materialia 38/9 (1998) 1383-1389

S.F. Au, M. Keijzer, K. Hemmes, P.J.J.M. van der Put, J.H.W. de Wit, J. Schoonman
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F. Blekkenhorst, S.D. Meijers, J.H.W. de Wit
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Patent no: 1008832

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New MCFC with separate CO2 supply. Proof of principle

K. Hemmes, W.H.A. Peelen, J.H.W. de Wit
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Polarization measurements on simulated cathodic and anodic sites of filiform corrosion on aluminium

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EIS on well defined defects in polymer coated steel

M. Keijzer
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F.R.A.M. Standaert
Analytical fuel cell modelling and exergy analysis of fuel cells

F.R.A.M. Standaert, K. Hemmes, N. Woudstra
Analytical fuel cell modeling; non-isothermal fuel cells

F.R.A.M. Standaert, K. Hemmes, N. Woudstra
Comparison of isothermal and non-isothermal MCFC models

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M.P.W. Vreijling

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E.P.M. van Westing, D.H. van der Weijde, M.P.W. Vreijling, G.M. Ferrari, J.H.W. de Wit
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Local measurements in electrochemistry and corrosion technology
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HIGHLIGHTS ON RESEARCH POLICY

The sub-faculty of Industrial Design Engineering completed internal discussions to formulate a new long term research policy. As a result of this exercise, the research landscape of the faculty is changing. Three main themes have been selected to be elaborated. The activities of this group experienced in Design for Reliability of Plastics Products have close parallels with one of the themes: Sustainability of Products. As a consequence of this change, the research policy of this group has been redefined. The main change can be summed up as: continuing the work on plastics, while paying attention to renewable materials (like biopolymers, paper pulp, etc) as well. The revised overview of the research activities of this group can be illustrated as shown in the figure. The different areas within this scheme are:

- Application & modification of existing theoretical models to understand viscoelasticity of plastics
- Application & modification of existing theoretical models to understand creep properties of plastics
- Research on Fatigue properties
- Research on UV degradation
- Research on application of renewable materials in consumer and industrial products
- Research on application of recycled materials (especially plastics) in consumer
Design for Reliability of Plastics Products

and industrial products
- Research on impact properties of consumer products and packaging
- Development of design guidelines for packaging in renewable materials (for instance in paper pulp packaging)
- Selection of materials and processes during design process; studies on optimisation, followed by computer aided selection tools
- Predictive modelling of injection moulded plastics products
- A major project combining all these individual LMB elements and beyond, which can be termed as Mechanical Design Methodology (of Sustainable Products). Note: This has already been started under the TUDelft Interfaculty project, DIOC 16: Smart Products.
- Development of design tools once enough confidence in the previous Mechanical Design Methodology (of Sustainable Products) is obtained

**MATERIALS:**
- Plastics
- Renewable Materials
- Recycled Plastics

**FACILITIES**
- Fatigue test equipment
  - Multi-purpose electromechanical fatigue equipment for testing plastics products. Maximum load amplitude 400 N. Miscellaneous waveforms including stochastic distributions. Frequency up to 16 Hz. Active specimen temperature control between ambient and +100 °C
  - Multi-purpose hydraulic fatigue facility. Maximum amplitude 13 kN in tension/compression and 50 Nm in torsion. Frequency up to 50 Hz. Specimen temperature between -15 and 60 °C
  - Hydraulic fatigue test equipment for tension loading up to 100 kN. Fatigue test programme with either load, strain or position control; sine, triangle, square or arbitrary waveform. Specimen temperature between -10 and +150 °C
  - Crack growth measurement on centre notched and compact tension specimens
- Environmental testing
UV Degradation equipment. Xenon lamp intensity 765 W/m². Spectrum between 280 and 800 nm. Test area 180 x 250 mm². Miscellaneous cyclic humidification programmes. Exposure of specimens while bent in prescribed radii.

- Environmental test chamber 1 x 1 x 1 m. Temperature between -40 °C and +100 °C. Relative humidity 0 - 100 %.
- Hydraulic impact tester for tensile and three point flexural impact. Head speed up to 2.5 m/s. Registration of force-displacement diagram and fracture energy.
- Notching apparatus for producing precision notches in plastic specimens up to 4 mm wide. Notch depth 0.1 to 1 mm.

**Optical microscopes**
- Light optical stereo microscope. Photographing equipment available.

**Other equipment**
- Two ovens for heat treatment up to 250 °C.
- Microtome for preparing thin samples from polymer parts, for micro foil mechanical testing and analysis of morphology, crystallinity, etc.
- Infrared Spectroscope (Perkin Elmer) for dispersive measurements, wavenumbers 4000 to 600 cm⁻¹.
- Micro Foil Tester for measuring nominal strain and tensile strength of plastic foils.
- Fontijne hydraulic device for compression moulding; 200 kN.
- Klöckner FX75R injection moulding machine. Clamp force 750 kN.

**Hardware and Software**
- A cluster of up-to-date SUN and Silicon Graphics workstations, with (colour) printers, tape-streamers, plotters and X-terminals. Several modern Personal Computers.
- Pre- and post-processing software (for use with FEM programmes, developed within the University). Includes both error estimation and remeshing facilities. Software has been developed mainly for thin-walled structures.
- FEM programmes (developed within the University); includes several types of solution strategies. Elements: Solids, truss, several thick and thin shell elements. All element types possess geometrically non-linear capability. Experience with problems with 50,000 to 100,000 unknowns.
- Optimisation programmes with, among others, interfaces to pre- and post-processors.
- Software for simulation of thermoforming of thin CFRP products. Software for simulation of injection moulding of thin-walled plastic products (C-MOLD).
- Commercial FEM programmes, like ANSYS, MARC, DIANA and GIFTS.

**Research Report 1998**

1. Stress Concentrations in Plastics Products (A.J. Heidweiller)

The effect of geometry transitions on the mechanical load carrying-ability of speci-
mens has been studied. Special attention has been given to a potentially positive influence of the injection moulding process. Tensile tests, three point bending tests and low cycle fatigue tests were performed on specimens with either drilled holes or moulded-in holes. The tests were carried out at various temperatures and deformation rates. Two commercial grades of PMMA have been applied. To obtain a better understanding of the fracture mechanism, the fracture surface morphology was related to the molecular orientation investigated by the birefringence method and to the results of a finite element method analysis.

![Figure 1: Fracture surface of PMMA specimen with drilled hole, tested in tensile mode. The smooth elliptical area is denoted as the mirror zone, where craze and fracture initiation take place.](image)

![Figure 2: Results of fatigue tests on ABS specimens. Moulded-in holes are compared to drilled holes show the effect of orientation due to injection moulding.](image)

The extent of redistribution of stresses appeared considerable, even in the case of a brittle material like PMMA. As a result, the linear theory is a safe but very conservative approach for the load carrying-ability of plastics products. It also appeared that injection moulding might have a favourable influence on the load carrying-ability. This result could be related to the fracture mechanism.

2 Mechanical Behaviour of High Density Polyethylene (J.G.J. Beijer)

Weight reduction of load bearing plastic constructions is becoming increasingly important because of the accompanying cost reduction and environmental benefits. As a consequence the material used will have to perform in the outer limits of its mechanical capability. In case of HDPE, used for instance in bottle crates and containers, this means that a thorough understanding of the time dependent mechanical behaviour, called viscoelasticity, is essential. The description of the behaviour of HDPE in terms of existing models and the implementation of this model description into a FEM package available for design purposes are our main objectives in this research. Viscoelastic behaviour reveals itself for instance in creep. When HDPE is loaded with a constant force the strain will increase in time. The results of our creep experiments indicate that the strain can not be described with the well-established linear descript-
tion of viscoelasticity. Due to the onset of nonlinearity in the mechanical behaviour, already at relatively low stresses, refuge must be sought to nonlinear models. The creep strain up to strain levels of 6% can however be described with the simple principle of separation of variables, meaning that the viscoelastic creep strain is the product of a function of stress and a function of time. For a proper description of the material response to more complex stress histories, the addition of (pseudo) visco-plasticity is necessary.

The application of a new model, developed at Eindhoven University of Technology, with two parallel processes extends the validity of the creep description to strain levels of 20%, since this model is able to describe the yield behaviour of HDPE. The influence of temperature on creep strain appears to be very large. For instance rising the temperature from 23 °C to 43 °C will double the creep strain of HDPE. Fortunately the creep strain at a different temperature can be found by the application of time-temperature superposition.

One of the most commonly used viscoelastic models, the Schapery model, is chosen for finite element method implementation. To do so the model must be extended to account for three-dimensional stress states. Since plasticity of many polymers depends on the Von Mises stress this is also assumed to hold for viscoelastic behaviour. With this assumption the one-dimensional model can be extended to three dimensions.

A subroutine is written for usage in the finite element package Marc to allow viscoelastic calculations with constructions. The program is also capable of performing creep modulus calculations, which at the moment is common practice, to approximate real viscoelastic calculations. Furthermore both explicit (fast but numerically unstable) and implicit (less fast but numerically stable) calculations can be done. Finally a new approach is developed, which combines the numerical stability of the implicit method but gives the speed of the explicit method. With this method fast and stable calculations with viscoelastic materials are possible. This mathematical tool will allow designers to make more accurate predictions of the behaviour of plastics products.

3 Non-Linear Visco-Elasticity (I.D. Skrypnyk)

The aim of this research project is to adapt a mathematical model for the non-linear visco-elastic behaviour of plastics and implement it into commercial Finite Element Analysis (FEA) package.

At the previous stage of project (1995-1997) a generalization of the hereditary integral model of Schapery type has been developed. The model was applied for description of creep, recovery and relaxation behaviour for several polymers: PMMA, HDPE, PP and a blend of modified PPO and PA. It has been shown that the proposed approach enables a total deviation of less than 1 to 3% between the experimental results and the model. The model developed has been implemented into commercial FEA package MARC and has been verified for several problems like ramp loading and compression of tensile strip, creep bending of thick plate (free supported), creep of plate with central hole. Additionally, the model was developed, to account for physical ageing of polymers under the long term loading.

It has been observed during the FEA calculations that the numerical scheme developed for the implementation of model into FEA package might get unstable. Therefore, during the present investigation, special attention has been paid to investigate and, possibly, to eliminate the numerical instability in the scheme developed. Several vari-
nants for the implementation of numerical scheme (with a descending complexity) have been analyzed with respect to their stability. Four possible reasons for numerical instabilities are described and discussed. As a result the simplified numerical scheme, which shows good results from the point of view of its convergence, is proposed. This scheme, however, gives poor results while modelling strain recovery behaviour for non-linear materials.

Another direction of research within this project was modelling of thermo-visco-elasticity. To describe these phenomena, the generalization of the Schapery model for thermo-rheologically complex materials of second type (TCM-2) is proposed. First, the model is verified for isothermal creep and relaxation behaviour for different temperature level (PP and PPO/PA blend). It is shown that the results of isothermal experiments on stress relaxation can be simulated using the model, based on the creep data. Further the model is modified to account for plastic deformations and verified using the result on ramp loading of PPO/PA blend at different temperatures. At the end the model developed has been used to describe the thermal buckling of double side clamped plate in PPO/PA blend. It is shown that the application of isothermal non-linear visco-elasticity model for description of phenomena, where the creep and relaxation processes are driven by temperature effects, is unsatisfactory. Therefore, a modification to the model, which enables to account for more intensive viscous flows due to temperature changes, is proposed.

<table>
<thead>
<tr>
<th>Visco-elasticity equation following Henriksen</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \varepsilon_{\text{tot}} = J[\sigma] + \phi[\sigma G[\sigma] + T[\tau]] ]</td>
</tr>
</tbody>
</table>

**Discretization**

<table>
<thead>
<tr>
<th>Complete:</th>
<th>Simplified by assump.: [ \phi[\sigma] = \text{const} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \Delta \varepsilon_{\text{tot}} = J' \Delta \sigma + \phi'(G + T) + \phi' G \Delta \sigma + \phi \Delta T ]</td>
<td>[ \Delta \varepsilon_{\text{tot}} = J' \Delta \sigma + \phi (G' \Delta \sigma + \Delta T) ]</td>
</tr>
</tbody>
</table>

**Inversion by factorization**

<table>
<thead>
<tr>
<th>Variant I</th>
<th>Variant II</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \Delta \sigma = \frac{\Delta \varepsilon_{\text{tot}} - \phi \Delta T}{J' + \phi'(G + T)} + \phi' G ]</td>
<td>[ \Delta \sigma = \frac{\Delta \varepsilon_{\text{tot}} - \phi \Delta T}{J' + \phi' G} ]</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Variant III</th>
<th>Variant IV</th>
</tr>
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<tbody>
<tr>
<td>[ \Delta \sigma = \frac{\Delta \varepsilon_{\text{tot}} - \Delta \varepsilon_{\text{creep}}}{J'} ]</td>
<td>[ \Delta \sigma = \frac{\Delta \varepsilon_{\text{tot}} - \Delta \varepsilon_{\text{creep}}}{J'} ]</td>
</tr>
</tbody>
</table>

**Figure 3:** Different variants of numerical scheme for modelling of non-linear visco-elasticity within FEA package MARC

4 **Loading Capacity and Buckling of Plastics Containers (T.O. Vasylykhevych, I.D. Skrypnyk)**

In order to save material (i.e. production costs), but also due to growing concern of
society about environment, there is clear trend to make plastic products lighter. This implies also decreasing of wall thickness and, consequently, introduction into design additional stiffness ribs (to enable these lighter products to carry a load). Unlike metals, however, plastic materials exhibit time-dependent behaviour, like visco-elasticity and physical ageing. Thus, if the plastic product is expected to sustain long term loading, the creep induced buckling (or, in the other words, buckling delayed in time) should taken into account.

This research aims at the investigation of creep induced buckling of plastic containers and development of rules for designing more sustainable plastic products. During the present stage of project, the investigation has been carried out in two directions. The experimental study included conducting of several sets of tests:

- ramp compression loading of clamped HOPE strips with different strain rates;
- creep induced buckling of HOPE strips of different lengths;
- ramp compression loading of HOPE U-profiles;
- sustained compression of HOPE U-profiles;
- sustained compression of HOPE bottle crates.

![Graph showing force vs. strain for HOPE strips of different lengths](image)

Figure 4: FE prediction of buckling behaviour of HOPE strips of different length

The second direction was Finite Element simulations of buckling phenomena in non-linear visco-elastic solids. For this purpose, the non-linear visco-elasticity model, developed earlier in the group and which is implemented into a commercial FEA package, has been used. The FE calculation model for creep buckling of non-linear solids has been developed.

Further, the ramp compression loading of HDPE strips and U-profiles has been modelled. For the clamped strips the accuracy of FE calculation is within 10%. It was observed in experiment, that small initial sag (less than 1 mm) of the back wall of the U-profile predefines certain buckling mode: to outside or inside. This fact was confirmed by FE simulation. In both cases good agreement (less than 6%) between computer prediction and test results of compressive force was obtained. Because of presence of stiffening ribs in U-profile, buckling occurs in two steps. First, the wings buckle, that correspond to local buckling point. This leads to further buckling of the stiffening ribs, resulting in global buckling.
5 Effect of Processing on Mechanical Performance of Plastics Products (R.P. Koster)

Tensile-impact test specimens, as shown in the photograph, have been moulded of general purpose PS (Dow grade 638). The two specimens in the mold are filled through a sprue, followed by three equal runners and three equal gates. Two of the runner-gate combinations feed the weld line specimen and the third one feeds the single-gated specimen. Injection molding machine settings have been varied to obtain combinations of two melt injection temperatures and three melt flow front speeds, as well as a few other parameter variations. Changes in melt injection temperatures were obtained by nozzle temperature adjustments. Changes in flow front speeds were obtained by ram speed adjustments.

The importance of low flow-induced stresses has been shown for all specimens, both without weld line and with a weld line at the end of the melt flow paths. Injection moulding settings promoting low flow-induced tensile stresses in the flow direction are favourable for nominal strength in a tensile test as well as for energy absorption capacity in a tensile-impact test.
The favourable effect of high material temperatures near the skin during weld line formation was clearly shown, but did not appear as a dominant factor for the brittle PS used here. The proximity to the surface of molecules with the highest frozen-in orientations was found to be another important factor for tensile-impact performance of all specimens.

6 Renewable Materials – Biopolymers (P.V. Kandachar, W.J. Goedhart, R.P. Koster)

During the last half a century, plastic products have become part of everybody's daily life, but there are rising concerns world-wide both about the impact that petroleum-based plastics are having on the environment, as well as on the decreasing crude oil resources. In particular, the plastic content in (municipal) waste has increased considerably, and continues to increase steadily. These products have estimated degradation times ranging from 20 years for vending machine cups, to 100 years for PET bottles and 500 years for polystyrene foam cups and dishes. Although recycling is improving, about 75% will still be dumped into landfills and new strategies that can overcome this environmental problem need to be explored.

Renewable materials like biodegradable polymers, based on, among others, agricultural resources (like potatoes and sugar) seem to have the potential to offer a viable solution to this problem. The main advantages of biodegradable polymers are, of course, their ability to degrade under controlled conditions and, when developed further, their ability to compost. These properties would provide the possibility to return them back to where they originate, namely, nature. While some mechanical properties of currently available biodegradable polymers are inferior to those of conventional synthetic polymers, in addition to being costlier, extensive efforts are being made to improve the properties and to reduce the cost of these materials. On the other hand, biodegradable polymers can be processed with many of the conventional manufacturing technologies like injection moulding, extrusion, blow moulding, etc.

Experimental investigations recently started include:

- Determination of mechanical properties of injection moulded synthetic and natural biopolymers.
- Studies on injection moulding of products in synthetic and natural biopolymers.
- Numerical modelling of a product in synthetic and natural biopolymers.
- Setting up a database for selection of biopolymers in engineering design.

Multidisciplinary research and (inter)national co-operation is essential to achieve the objectives of this project and a number of contacts have already been established.
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Extensive research is being carried out on biopolymers at Agricultural Technological Research Institute (ATO/DLO) at Wageningen, with whom contacts have already been set up.

7 Renewable Materials – Paper Pulp for Packaging (P.V. Kandachar, A.J. Heidweiller, A. Bereznitski)

In addition to products, plastics are also used as packaging materials. Plastic packaging can satisfy the high shock absorbing requirements necessary for protection of vulnerable equipment. The mechanical properties of virgin polymers are well known and the design of plastic packaging can rather well be optimised using simulation and optimisation techniques. Recycling of plastic packaging materials is, however, often not cost effective because of the difficult separation of the different polymers and the contamination of the plastic packaging.

Also in this area of packaging, renewable materials like paper pulp, could be a solution. Pulp packaging was, up till some years ago, mainly applied in packaging with very low load carrying capacity, like egg trays. The design of this packaging was based on experience and little research was carried out in determining the mechanical properties of pulp and in developing design rules. The recent renewed interest in moulded pulp packaging is the result of the awareness of the environmental aspects of packaging. Nowadays pulp is also used as a packaging material for television sets and video recorders. The required shock absorbing of this packaging is very high and could be satisfied using technical-scientific methods. Manufacturers of pulp packaging are to a large extent using "trial and error" methods, resulting in overdimensioning of paper pulp packaging.

A. Bereznitski has conducted some preliminary experimental research and computer simulation on a packaging system (video recorder). It is clear that designing packaging systems in paper pulp requires extensive mechanical, environmental and other data. The mechanical properties of pulp, as a function of the humidity, temperature, fibre length of the cellulose and additives, need to be obtained from research institutes. Some contacts have already been established in Sweden and in The Netherlands (Philips - prof. Stevels). Co-operation with manufacturers of pulp packaging is also necessary for obtaining information about manufacturing technologies, the properties of the external paper box. The manufacturers could also provide pulp-packaging systems, i.e. the pulp packaging and the external paper box. The ecology parameters have to be obtained by co-operation with prof. Brezet and with the Engi-
neering Materials Research Group in Cambridge, both in the area of biopolymer as well as paper pulp.

Once these properties and ecological parameters have been determined, optimisation with respect to the environmental impact can be carried out. The shock absorbing capabilities of packaging designs will be modelled using numerical methods and optimisation techniques. The environmental impact will be included in the optimisation methods. Experimental verification of the impact capabilities of the packaging of video-recorders and Television sets will be carried out using packaging systems supplied by industry, like Leopac and Philips. The results of the minimisation of the environmental impact will be compared with other used packagings like expanded poly-styrene, which is used to a large extent.

Apart from research work on their technical feasibility, Life Cycle Analysis of renewable materials is needed to convince the decision-makers to support introduction of products made from these emerging materials. In addition, a successful product-market strategy concerning renewable materials also needs insight in the aspects of legislation on certification, acceptance by composting facilities, reachability of and kind of distribution canals, information supply towards the consumers and towards waste treaters.

The main objective of these projects is therefore to examine the renewable materials currently available and/or in development for their suitability as an alternative to conventional plastics, for packaging products such as cups and dishes, as well as in areas where high shock absorption is a requirement.

8 Lightweight Materials for Automobile Design (P.V. Kandachar, J.L. Spoormaker, W.J. Goedhart)

This year the board of management of Delft University of Technology has approved an interfaculty research programme on Smart Product Systems (DIOC 16). The purpose of this programme is to develop a scientific methodology to assimilate the diverse information about materials, products and processes, used in the various levels of optimisation, which provides insight and leads to improvement of the trade-offs involved in economy, technology and environment. As a part of this programme, a project has been initiated with the purpose to develop a body of basic knowledge to make sustainable product development possible. Towards this end, a product/technology carrier, an automobile, to be named DUTCH-EVO, has been chosen. The framework of DUTCH-EVO is: minimum fuel consumption, lightweight design, environmentally friendly, application of modern materials including renewable material resources, where possible, design for recycling, passenger appeal & comfort, affordable price, etc.

In a related study, preliminary investigations on the aspects of materials selection for a city transportation system have been carried out. An effort is being made to design a durable lightweight city vehicle for 2 adults and one child. The main emphasis of this project is on the selection of material and manufacturing techniques for the parts of the car. The car parts have been analyzed for the requirements, which in turn have been used to design and select materials and manufacturing processes. A three-wheeled configuration has been selected to reduce drag, weight as well as costs. It has been shown that, by applying new materials like aluminium foam for the load bearing structure and thermoplastic sandwich panels for the exterior, weight reduction can be achieved. With these materials it has also been possible to achieve a large degree of integration of functions. For instance, it has been shown that it is possible
Design for Reliability of Plastics Products

to integrate acoustical aspects, thermal insulation with high stiffness in one component.
A literature search on application of lightweight materials for automobile design has also been initiated.

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J.L. Spoormaker
Faal- en Schadeanalyse; bedrijfszekerheidsbegrippen en veel gebruikte kansverdelingen
J.L. Spoormaker

*Our students are educated to manage innovation projects (in Russian)*

Innovations (Russian) 1/6 (1998) 56-57

J.L. Spoormaker

*Wanneer testen en beproeven*


J.L. Spoormaker, I.D. Skrypnyk

*The Role of Time in the Failure of Plastics Products*

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J.L. Spoormaker, I.D. Skrypnyk, T.O. Vasylykevych

*Simulation of the non-linear Viscoelastic Behaviour of Plastic Products*


M.J.M. van der Zwet, A.J. Heidweiller

*Failure and Fracture Mechanics of Injection Moulded Plastic Products*

in separate aqueous subjects, except for translation with high aromatizing activity. K. 5
methyl-3H) and in the aromatizing activity of bisphenol 3,4C. The results of this study are as follows:

A literature search on the application of lignocellulose/AEM-PMITA membranes for desalination also shows promising results.

Analytical estimation of hydrogen produced with glucose and high temperature


Modeling of cross-linking Phenol-Formaldehyde systems

by A. J. Jones and J. M. Pinto. Presented at 5th International Symposium on


Modeling of cross-linking Phenol-Formaldehyde systems

by A. J. Jones et al. Presented at 5th International Symposium on


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HIGHLIGHTS
Ir. Jeroen Wits received the Delft University of Technology Price for the best undergraduate student in Materials Science for his graduation project on interface mobility in Fe-X-alloys. Dr.ir. J. Sietsma was his supervisor.

RESEARCH AREAS AND OBJECTIVES
Research in the Heat Treatment Science and Technology group is centred around the central theme "modelling and controlling phase transformations in ferrous and non-ferrous alloys". The final objective is the development of new thermal and thermo-mechanical treatments on the basis of physical models, resulting in materials and products with improved properties at reduced production costs. Presently the emphasis in the research is on low-alloy steels and on aluminium.

1 Development of Phase Transformation Models for Low-Alloy Steels
The phase transformations during the accelerated cooling of the steel strip in the hot-rolling mill play an important role in the generation of the final microstructure and properties of modern lean forming and construction steels. It is the aim of this program to develop detailed models describing these transformations, taking into account effects of the steel composition, (plastic) deformation history and initial microstructure. Both artificial neural network models and physical models are being constructed. Various experimental techniques are being developed to monitor the transformation behaviour quantitatively. Several new projects in the field of deformation enhanced transformation, TRIP steels, recrystallisation during hot rolling, bainite formation and finally neutron depolarisation have been added to our research program during 1998.

2 Thermomechanical Processing of Aluminium Alloys for Improved Mechanical and Corrosive Properties
In order to obtain optimum properties aluminium alloys undergo a number of thermomechanical treatments after solidification. The nature of the relevant metallurgical processes varies considerably and depends on the alloys composition and the order of the mechanical and thermal treatments. In our aluminium research program we study three of these processes which are of great industrial and scientific interest. First of all we study the processes taking place during homogenisation of extrusion alloys and the relation between these homogenisation conditions and the extrudability and the corrosion resistance of the alloy. Secondly, we study inter-critical annealing as a suitable process route for increasing the strength of Al can body stock and finally we study the effect of a heat treatment on the fracture toughness of Al based MMCs. Several new projects such as stimulated strain hardening behaviour, recrystallisation and microstructural control by thermo-mechanical treatment have been added to our research program. Multi-pass hot torsion testing and Thermo-electric-Power measurement have been added to our list of experimental skills.

FACILITIES
Thermal equipment
- Lab furnaces:
- Two furnaces for nitriding, nitro-carburising and carbo-nitriding, equipped with quench facilities for temperatures up to 1273 K. The gases used in these furnaces are purified and the gas flow is accurately controlled.
- Special furnace for annealing samples at temperatures up to 850 K with computer-controlled specimen handling (10 specimens). Annealing is performed in a controlled gas atmosphere.

**Heat Treatment Shop:**
- Large air circulation furnace for temperatures up to 923 K
- Two salt bath furnaces
- Oil quench bath
- Annealing furnace for temperatures up to 1523 K
- Annealing furnace with protective atmosphere
- Large nitriding furnace
- Air-circulation furnace with programmable temperature control
- Vertical furnace for temperatures up to 1573 K with quenching facilities

**Thermal analysis:**
- Thermal Gravimetric Analyser (TGA). A Netzsch 439 vertical thermobalance (maximum specimen mass 1 g, sensitivity 0.1 µg) for TGA measurements during nitriding, nitro-carburisation and oxidation. Maximum operating temperature 1273 K
- Differential Thermal Analyser (DTA). A Perkin Elmer high temperature DTA, maximum operating temperature 1773 K
- Differential Scanning Calorimeter (Perkin-Elmer, DSC 7) capable of cooling rates up to 150 K/min and heating rates up to 500 K/min, maximum operating temperature 1000 K
- Thermal Electric Power (TEP), Techlab measuring device, operating at ambient temperature
- Modern deformation dilatometer (Bähr 805) operating at temperatures up to 1470 K and strain rates up to 10 s⁻¹
- Torsion device (Bähr STD810) operating at temperatures up to 1773 K and strain rates up to 10 s⁻¹

**Thermal Mechanical Simulator:**
- A state-of-the art Gleeble 3500 with complementary capabilities is on order.

**Microscopy**
- Reflected light microscopy and metallographic preparation facilities:
  - Several high-quality microscopes, magnifications 50x to 2600x, with digital-image facilities and Image database storage on CD-ROM
  - A modern optical analysis system (Quantimet 550)
  - Metallographic preparation facilities, including a new automated polishing facility
  - Micro-hardness testers (0.5 to 25 gram Vickers and 5 to 500 gram Vickers)
  - Scanning Tunnelling Microscopy / Atomic Force Microscopy suitable for measuring both in air and in liquids

**Software**
- Thermodynamic software for calculating phase equilibria in multi-component systems (MTData)
1 Phase Transformations in Low-Alloy Steels (in collaboration with M. Onink, Th.M. Hoogendoorn, A. Bodin [Koninklijke Hoogovens])

The aim of this research is to understand the processes that determine the development of the microstructure during the transformation of austenite into the low-temperature phases (predominantly ferrite and pearlite) in low-alloy steels. The main line of research is to describe the nucleation and growth of the ferritic phase (\(\alpha\)) from the austenitic phase (\(\gamma\)) as a function of temperature and time, considering the material's composition and thermodynamic properties. A number of experimental techniques is being employed in this research. A transformation model on a physical basis is being developed to describe and understand the transformation kinetics.

1.1 The Development of a Model for Phase Transformations (Y. van Leeuwen, T.A. Kop, J. Sietema, S. van der Zwaag)

The austenite-to-ferrite phase transformation is modelled by a model that ascribes the transformation rate as a combined effect of the thermodynamical driving force and the atomic mobility at the \(\alpha/\gamma\)-interface. In the model, the austenitic microstructure is schematically represented by the tetrakaidecahedron as an austenite grain, for which a grain-size distribution can be applied. During the modelling of a cooling experiment, nucleation takes place at a given rate at the corners of the austenite grains. Each nucleus subsequently grows spherically into the austenite grain, with a velocity that is the product of the free-energy difference between the austenite and the ferrite at the interface, and the so-called interface mobility. The free-energy difference serves as the driving force for the transformation, and it is taken from thermodynamic database programmes. The actual aim of the modelling is to get a better understanding of the interface mobility, and its dependence on composition, austenitic microstructure, temperature, microstresses, etc. The interface mobility is used as a fitting parameter in confrontations of the modelled curves of the fraction ferrite as a function of (decreasing) temperature with experimental ones, determined in constant-rate cooling experiments on a Bähr 805 axial dilatometer.

The determination of the interface mobility in a number of binary iron alloys with 1 or 2% of substitutionally dissolved elements has resulted in mobility values in the range between 0.01 and \(1 \times 10^{-6}\) molm Js for the temperature range between approximately 1000 K and 1200 K in which the transformations occur. The mobility can logically be expected to show an Arrhenius-like temperature dependence, in sense that the atomic motion at the interface is a thermally activated process. Analysis of the temperature dependence results in an activation energy \(Q = 230\) kJ/mol, with a pre-exponential factor \(M_0 = 9 \times 10^8\) molm Js. Remarkably, the activation energy is distinctly larger than for grain-boundary diffusion and for recrystallisation, whereas the underlying process is expected to be rather similar. The experimental results indicate that the interface mobility is quite sensitive to the interstitial content of the material. Concentrations of nitrogen on the order of 100 ppm appear to have a significant effect on the mobility of the interface.

The interface-mobility has also been applied to transformation data obtained on C-Mn steels. For materials ranging in carbon content from 0.05 to 0.10 wt.% the transformation characteristics were obtained in constant-rate cooling experiments in the dilatometer. Dilatometry results on carbon-containing iron alloys require a more com-
plex analysis than "simple" substitutional alloys. This is due to the volume effects of (1) the carbon enrichment of the austenite during the formation of ferrite, and (2) the formation of pearlite, having a specific volume that is larger than that of ferrite. In 1998, the analysis method has been fully developed, making use of literature data on the lattice parameter of austenite containing manganese and carbon as a function of temperature. This allows the calculation of the specific volume of austenite at each temperature and carbon content (the latter depending on the degree of transformation having already taken place). Also, the temperature dependence of the lattice parameters of ferrite and pearlite is used.

![Figure 1: Transformation curves at different cooling rates for a steel containing 0.10 wt.% C and 0.49 wt.% Mn. Figure a) shows experimental results, obtained by dilatometry, figure b) shows results obtained with the interface-mobility model.](image)

As an example of the results obtained on this series of steels, Figure 1a shows the fraction ferrite and pearlite as a function of the decreasing temperature at different cooling rates for the steel containing 0.10 wt.% C and 0.49 wt.% Mn. Although possi-
ble with the analysis used, the fraction pearlite is not explicitly given, but the formation of pearlite can be recognised in the increased transformation rate in the final part of the curves. The coinciding curves in the figure show that, for the lower cooling rates, part of the transformation develops according to equilibrium. The degree in which the experimental curve trails the equilibrium increases with increasing cooling rate. The transformations curves were reproduced according to the above-described model, using the parameters $Q = 140 \text{ kJ/mol}$ and $M_a = 0.058 \text{ molm/Js}$, determined in a previous study on Fe-Mn alloys. The effect of diffusion of carbon has been accommodated by assuming an instantaneous redistribution of the carbon over the remaining austenite during the transformation. This assumption implies that the mobility used in the model calculations should be seen as an effective mobility, including diffusion effects.

The results of the model calculations are shown in Figure 1b, and the agreement of these model curves, calculated without adjustable parameters, with the experimental curves is extremely good. It should be noted that the equilibrium curve in the calculations is shifted by approximately 10 K with respect to the experimental curve, probably due to an inadequacy in the calculation of the Gibbs free energy involved. At present the research efforts are at a better understanding of the uniqueness of the model results, in which a more detailed description of the diffusion effects are also incorporated.

### 1.2 Ferrite Formation Studied with Neutron Depolarisation

(S.G.E. te Velthuis, N.H. van Dijk, J. Sijtsma, S. van der Zwaag; M.Th. Rekveldt [Interfaculty Reactor Institute, Delft University of Technology])

Neutron Depolarisation is a particularly powerful technique for the steel phase-transformation research, since it allows a simultaneous determination of the fraction ferrite that is formed and the average grain size of the ferrite. The technique takes advantage of the magnetic moment of the neutron, and its interaction with ferromagnetic material, which ferrite is and austenite is not, in the sample. In order to achieve a correct interpretation of the experimental results in terms of microstructural characteristics, it is necessary to gain maximum information on the magnetic characteristics. In fact, it is the spatial distribution of magnetic induction that is "seen" by neutron depolarisation, and therefore magnetic and microstructural features both play a role. Neutron Depolarisation measurements during the austenite decomposition are usually performed in a static (strong) magnetic field, but are frequently interrupted by additional measurements during which the magnetic field is varied in order to measure the magnetic hysteresis. This has the advantage of leading to a more complete interpretation of the results, but also the disadvantage of taking more time, due to which these measurements are not performed during rapid transformations.

Experimental work has been focussed on the ferrite formation in a series of simple low and medium carbon steels. The experiments have been performed in the two-chamber furnace that allows cooling from the austenitisation temperature (typically $900 \degree C$) to a stable transformation temperature (typically $680 \degree C$) in some 20 seconds. Extensive series have been performed on a range of transformation temperatures, including measurements under variable magnetic field. From the hysteresis behaviour the degree of magnetisation at the static field can be derived, a quantity that is used for the determination of the microstructural features. The neutron-depolarisation results are compared to microscopic observations of the microstructure after full completion of the experiment. Currently the interpretation of these experimental series is in progress.
The interpretation of Neutron Depolarisation results is especially difficult at relatively high ferrite fractions. At low fractions the ferrite microstructure can still be seen as an assembly of spatially separated spherical particles, but at higher fractions this will not apply. However, there is no straightforward analysis when, at increasing fractions, the ferrite particles start to touch and overlap. Therefore, when the equations that apply to low fractions are still used, it is important to assess the validity of the outcome. In order to do so, a three-dimensional microstructural model has been developed, for which the neutron-depolarisation behaviour can be calculated. The actual particle size can then be compared to the particle size that follows from the neutron-depolarisation data. A systematic study has shown that the discrepancy in the particle size that follows from neutron depolarisation is limited to some 20% at large ferrite fractions. Systematic series of model calculations has also shown that neutron depolarisation can indeed yield valuable information on the nucleation behaviour. Although this result is not unexpected, it corroborates the assumption that changes in the grain-size distribution (on top of changes in the average grain size) do not significantly influence the simultaneous interpretation of ferrite fraction and particle size in order to establish the particle density.

1.3 Recovery, Recrystallisation and the Influence on the Phase Transformation
(D.N. Hanlon, I. Gallino, J. Sietsma, S. van der Zwaag)

The austenitic microstructure is an essential factor in the kinetics of its own decomposition. The distributions of grain size and grain shape have a major influence on the process of nucleation, and also on the development of the volume of a new phase. Furthermore, the presence of large amounts of dislocations in the structure will influence the decomposition kinetics, both in the nucleation behaviour (for instance at sub-grain boundaries) and in the growth rate (increased driving force). Since in the hot-rolling process severe deformation is imposed on the material, for gaining a full understanding of the phase transformations it is necessary to consider the processes of recovery and recrystallisation, occurring subsequent to deformation. This applies to the condition where deformation is applied to the austenite only, as well as to the condition of deformation of two-phase structures (inter-critical rolling, see also Section 1.4). In the latter case the development of these processes in both the austenite and the ferrite should be taken into account. In 1998 research has been started to approach these issues. The aim of the projects is to understand and develop model descriptions for the changes in the dislocation density and structure as a function of time and temperature, the kinetics of recrystallisation, and the influence of recovery and recrystallisation on the decomposition of the austenite. Series of experiments on the TMTS, the axial dilatometer and the torsion dilatometer have been devised to separately study static and dynamic recovery and recrystallisation, both in ferrite and in austenite. Eventually, the understanding of the processes should be detailed enough to be applied to two-phase structures as well.

As a starting point for the model development, the dislocation models by Bergström (1983) and Nes (1995) are being considered. Both models are primarily aimed at the development of the dislocation density and structure during deformation, but can possibly be extended to describe recovery. For the description of recrystallisation the interface-mobility model appears to be suited. The driving force for the recrystallisation process is directly related to the surplus of dislocations, which explicitly shows the influence of recovery on the recrystallisation. Finally, the phase transformation can also be modelled by the interface-mobility model. In this case the driving force has both a structural and a dislocation component (and is thus related to the recovery...
process), and the distributions of grain sizes and grain shapes, which, as stated before, also influence the development of the phase transformation, are determined by the recrystallisation process. At present, these projects are in the phase of literature study and experiment preparation.

1.4 Deformation of Two-Phase Microstructures (S.P. Cornelisse, J. Sietsma, S. van der Zwaag; A. Bodin [Koninklijke Hoogovens])

The application of a rolling process on two-phase steel structures, consisting of austenite and ferrite, is presently becoming of increasing practical importance. The consequences of deformation of a two-phase structure instead of a purely austenitic structure, however, are by no means trivial. The plastic deformation has an influence on both the ferrite structure, which is subsequently subjected to recovery and recrystallisation processes, and the austenite structure, for which recovery and recrystallisation in turn determine the phase transformation that follows upon further cooling. A complicating factor in these processes is that the amount of deformation will not be evenly distributed between both phases, due to the differences in mechanical properties. The distribution of plastic deformation is expected to depend not only on the volume fractions of both phases, but also on the microstructural details.

Figure 2: Deformation resistance (symbols) and austenite fraction (solid line) as a function of temperature for a C-Mn steel

In a direct co-operation with Hoogovens Research and Development, a series of extra-low carbon and interstitial-free steel grades have been tested on their deformation characteristics in the two-phase temperature region. After austenitisation, the material is held at a fixed temperature for a period of time long enough to reach the equilibrium fractions of ferrite and austenite. A rolling process is applied to determine the deformation resistance as a measure for the flow stress of the material. In Figure 2 the deformation resistance is given as a function of temperature, in a plot that also gives the austenite fraction. Below approximately 720 K the material is purely ferritic and pearlitic, above approximately 850 K it is purely austenitic. In these temperature ranges the temperature dependence of the deformation resistance is seen. In the intermediate range the deformation resistance assumes intermediate values, but clearly the values are not proportional to the phase fractions. The values even indicate that up to 30% of austenite does not cause a deformation resistance that is sig-
nificantly different from the ferritic deformation resistance. In the same set-up an extensive series of flow curves has been recorded, which is being analysed in terms of the development of the dislocation density. This is done through fitting of the dislocation-density model by Bergström (1983) to the flow curves. The model parameters will give further insight into how the deformation is absorbed in both phases.

1.5 The Development of Steels Showing the Effect of Transformation-Induced Plasticity (L. Zhao, J. Sietsma, S. van der Zwaag)

It is apparently inevitable in steels that a high strength is accompanied by a low formability. This observation has been reason for specific attention for the development of microstructures that lead to an increased formability without significant loss of strength in the application of the material. These efforts have led to steels that contain some retained austenite (on the order of 10%) at room temperature, which transforms to martensite when subjected to stress. This stress is applied in forming the material, and the transformation gives rise to some additional strain, thus increasing the formability. This effect is called the TRIP-effect (transformation-induced plasticity), and is for instance found for steels containing on the order of 1.5% of Si or Al. The microstructure of TRIP-steels consists of three phases: ferrite, bainite and austenite. The microstructure is obtained by first bringing the material in the two-phase temperature range, where a mixture of ferrite and austenite forms. The second step in the process is an isothermal heat treatment in the bainite-formation temperature range (350–400 °C). In this step part of the austenite transforms to bainite, due to which the austenite enriches in carbon, which implies a lowering of the martensite-start temperature $M_s$. This treatment should be stopped by quenching to room temperature when $M_s$ is below room temperature. However, the austenite characteristics should be such that upon the application of stress $M_s$ rises to room temperature in order to get the TRIP-effect. Obviously, the bainite formation is the most crucial step in this process. In a project that was started in 1998, the phase transformations in TRIP-steels are studied in order to come to an optimal understanding of the bainite formation in these steels, with the intention to apply this knowledge in more efficient process routes for the production of TRIP-steels. A detailed series of experiments and thermodynamic calculations has been set up for steels containing different amounts of Si. Part of this project will be performed in co-operation with the Aachen University of Technology. In the co-operation, the Delft group will concentrate, in accordance with the expertise that is present, on the phase transformation and thermodynamic characteristics, and the Aachen group will focus on the mechanical testing in order to establish the occurrence of the TRIP-effect.

1.6 Statistical Modelling of Transformation Data by Means of Neural Networks (P.J. van der Wolk, J. Wang, J. Sietsma, S. van der Zwaag)

The statistical modelling method of neural networks is used to extract information about the kinetics of austenite decomposition from the large quantity of CCT-diagrams that have experimentally been determined, and are available from the literature or from specific sources. Major disadvantages of the experimental data are the lack of knowledge about the accuracy and the random distribution of the steels over a huge composition space. Since up to 12 different elements play a role, a large number of experimental CCT-diagrams is needed to establish the actual composition dependence. The number of available CCT-diagrams that have been digitised and put in the correct format has increased to some 800, and the development of the neural-network model is in course.
In the eventual quality of the fits that are obtained by means of a neural network, both the (unknown) accuracy of the experimental diagrams and the accuracy of the fitting method contribute. In order to assess the latter, the fitting method is applied to a database of CCT-diagrams that have been calculated by a semi-physical model for austenite decomposition, developed by the University of Cambridge in co-operation with British Steel (Parker et al. 1998). Although this model is not perfect in its reproduction of the real transformation behaviour, the calculated CCT-diagrams are not subject to random errors and the dependencies on composition are known. By fitting these diagrams, an indication is obtained on the accuracy of the neural network method. Moreover, by comparing the calculated model diagrams to the experimental ones, extra information can be gained on two points: (1) the accuracy of the model in different composition ranges, and (2) the random errors in the experimental diagrams. At the moment the research is at the point that the accuracy of the Cambridge/British-Steel model is evaluated. A heuristic method has been applied to indicate the overall accuracy of the CCT-diagram as a function of composition, showing that the model performs best in the low-carbon ranges. It shows that the model has been developed for low-alloy steels, since the accuracy declines fast at contents of over a few percent for most other elements. Besides the overall accuracy, an assessment of the accuracy on specific points in the diagram, like the ferrite and bainite nose, is performed.

2 Thermo-Mechanical Processing of Aluminium Alloys for Improved Mechanical and Corrosive Properties

2.1 Precipitation Kinetics in AA6061 and an AA6061-Alumina Particle Composite (S.P. Chen, K.M. Mussert, S. van der Zwaag)

In an MMC, many of the physical properties of inclusion and matrix are very different. Therefore, precipitation behaviour in Al-based MMCs is, in many cases, different from the precipitation in the monolithic alloy. In order to optimise the mechanical properties of heat treatable Al-based MMCs, the precipitation in these material needs to be investigated.

The Differential Scanning Calorimetry (DSC) can be used as a powerful technique for a rapid and quantitative description of precipitate microstructures in aluminium alloys. DSC can show the formation of precipitate phases and their volume fractions. Additional information concerning reaction kinetics is available in the thermograms. In this study DSC was used to obtain the precipitation kinetics of metastable phases in an AA6061 alloy and a 20 vol.% alumina particle reinforced AA6061 composite. As shown in Figure 3 DSC thermograms include four peaks during DSC runs from 0 to 530 °C. It is suggested that peak A corresponds to silicon cluster formation; peak B – β phase formation; peak C – β′ phase formation; peak D – β phase formation. The thermal effects in the DSC traces were analysed quantitatively. The kinetic parameters for the phase transformations in the AA6061 alloy and composite were calculated using the varying heating rate method and the Kissinger-approach. It was found that the overall age-hardening sequence of the AA6061 alloy did not change due to the addition of the Al₂O₃ particles, but the volume fractions of the various phases and the precipitation kinetics of some of the phases were modified. The precipitation transformations of the metastable phases in both the AA6061 and the composite obey an n-order kinetic model.
2.2 Optimisation of the Homogenisation Treatment for Hot Extrusion of AlMgSi Alloys (F.J. Vermolen, J. van de Langkruis, M.S. Vossenberg, S. van der Zwaag; W. H. Kool [MIDEG]; C. Vuik [Department of Applied Mathematics, Delft University of Technology]; J. Lof [Twente University]; C.M. Sellars [University of Sheffield]; A.J. den Bakker [Alcoa Netherlands])

The objective of the research presented has been to develop a method suitable for a quantitative optimisation of the extrudability of commercial AlMgSi alloys. It is assumed that the most relevant controllable parameter influencing the extrudability of AlMgSi alloys is the state of primary alloying elements Mg and Si. The changes in state of Mg and Si in the alloy are being investigated experimentally with differential scanning calorimetry and numerically with a finite element code written especially for this purpose. The effect of the changes in state on the hot deformability of the alloy is investigated with plane strain compression tests. The resulting stress-strain curves
are modelled with an appropriate constitutive equation, incorporating the effect of solute in an exponential pre-factor.

**Numerical modelling of structural changes during heat treating**

F.J. Vermolen has finished his Ph.D. thesis about numerical modelling of particle dissolution in an aluminium matrix in 1998. He has written a finite element code. The basis of the code is a mathematical model, which is applicable to the dissolution of stoichiometric multi-component phases in both finite and infinite ternary media. It handles both complete and incomplete particle dissolution as well as subsequent homogenisation of the matrix. The model consists of coupled diffusion equations describing the solute fluxes in the aluminium cell, together with appropriate boundary conditions for the flux of alloying elements at the particle-matrix interface (local equilibrium) and the cell boundary (zero flux to adjacent cells). The code is capable of calculating dissolution and growth of cylindrical, spherical, and rectangular geometries.

![Graph showing normalized volume fraction of MgSi and solute concentration in MgSi as a function of homogenisation time](image)

**Figure 4:** Volume fraction of Mg$_2$Si in the grain and solute concentration in the grain interior, all as a function of homogenisation time, starting with a spherical Mg$_2$Si precipitate in an aluminium grain

With the code particle dissolution calculations were performed for Al-Mg-Si alloys heated according to industrial practise. The precipitate volume fraction and matrix homogeneity have been followed during the entire homogenisation treatment. First, the influence of metallurgical parameters, such as particle size distribution, initial matrix concentration profile and particle geometry on the dissolution- and matrix homogeneity- kinetics was analysed. Then the impact of the heating-rate and local temperature on the homogenisation kinetics was investigated. Conclusions for an optimal homogenisation treatment of aluminium alloys may be drawn. The model is general but calculations were performed for the system Al-Mg-Si with an Al-rich matrix and Mg$_2$Si-precipitates. In Figures 4 and 5 some typical results are given for the calculation of the dissolution of spherical Mg$_2$Si precipitates in aluminium cells.

In the near future a new graduate student (T. Xie) will further improve the model to calculate more complex problems. Starting with the code developed by Vermolen, one of his main objectives will be to develop the model to describe more complex morphological changes, like shape changes of a particle during a phase transformation (for instance one elongated β-AlFeSi phase transforming into more smaller and spherical α-AlFeSi particles).
Differential Scanning Calorimetry (DSC) experiments

To examine the kinetics of the varying precipitation and dissolution reactions occurring in the AlMgSi system various series of DSC experiments have been carried out at AlMgSi alloys of varying compositions. With DSC the heat effects linked to the so-called $\beta''$, $\beta'$ and $\beta$ precipitation and dissolution reactions are measured and in this way the dissolution and precipitation peak temperatures have been determined. In addition to the kinetics of solutionised samples, precipitation kinetics of samples pre-annealed to form well-defined types of precipitate distributions, have also been examined. In this way a TTT-diagram of $\beta'$-formation has been constructed. At present, the DSC spectra, showing the various dissolution reactions, are being analysed numerically with the finite element code developed by Vermolen.

Constitutive modelling of hot deformation of AlMgSi

A constitutive model has been developed, which describes the hot strength of an AlMgSi alloy as a function of the Mg and Si solute content. The model describes the flow stress of an aluminium specimen containing some solute Mg and Si atoms during hot deformation, as a function of strain, strain rate and temperature. It consists of an exponential saturation equation describing the strain dependency of the alloy, and a hyperbolic sine law describing the yield stress and the steady-state flow stress of the alloy during hot deformation. The effect of the solute content is incorporated in an exponential pre-factor.

The model has been applied to various series of experiments involving plane strain compression testing of AlMgSi alloys. One significant parameter of the model is the apparent activation energy. Because with hot deformation of aluminium dislocation climb and cross-slip are the main mechanisms causing plastic deformation, in the absence of processes like dynamic recrystallisation and dynamic precipitation or dissolution, this energy would have to be equal to the activation energy for lattice diffusion of vacancies in aluminium. It has been shown that deviations between the literature value for lattice diffusion (142 kJ/mol) and the estimated apparent activation energy can be quantitatively explained by solution hardening effects. The solute effects can be excluded from the apparent activation energy by incorporating them in the simple exponential pre-factor.
The constitutive model has been implemented in a finite element code describing the extrusion of miniature solutionised aluminium AA6063 billets and a reasonable fit between the calculated extrusion pressure has been obtained (Figure 6). At present the model is applied to assess extrusion trials with varying solute contents.

Figure 6: Experimental and calculated extrusion pressure against the ram displacement at a) 350 °C, and b) 400 °C

In the near future industrial large scale extrusion tests will be carried out. The billets will be heat treated in such a way that the effect of different precipitate types on the extrudability can be examined and modelled using the finite element code of Vermolen and the constitutive model of Van de Langkruis. Furthermore the material produced will be examined for its susceptibility to localised corrosion, in particular filiform corrosion.

2.3 Stimulated Strain-Hardening Behaviour in Aluminium Alloys by Thermomechanical Treatments (S.L. Vooijs, S.B. Davenport, S. van der Zwaag; L. Zhuang [Koninklijke Hoogovens NV])

Aluminium alloys obtain their strength by three different mechanisms: strain hardening, solid solution hardening and precipitation hardening. These three mechanisms can operate simultaneously. The re-heating and rolling conditions determine the amount of alloying elements either in solid solution or precipitated as well as the remaining dislocation density. When intermediate annealing is applied to cold rolled Al-Mn alloys, an increased strain hardening behaviour is observed. During this treatment precipitation occurs on the dislocation network thereby stabilising the dislocation network.

The aim of this project is the development of fundamental insight into the mechanisms involved in this process route for producing cold rolled high-strength aluminium alloys. Therefore the influence of precipitates, formed at different places in the processing route, on the strain hardening behaviour will be examined and modelled for three different alloying systems: Al-Mn, Al-Mn-Mg and Al-Mn-Mg-Cu. The first part of this project is examining the precipitation kinetics by measuring the change in Thermoelectric Power (TEP) and electrical conductivity for different dislocation densities, annealing temperatures and annealing times. These results will be used to create distinct dislocation cell – precipitate topologies. The second part of this project is the examination of the strain hardening behaviour for the various dislocation network – precipitates topologies. This strain hardening behaviour will be modelled using the cell size, mobile dislocation density and cell wall misorientation as input parameters. During Thermoelectric Power measurements, a temperature gradient is imposed on
the metal sample and the electric potential due to this temperature gradient is measured. The TEP is expressed as this potential per degree of temperature difference and is influenced by the different electron scattering events in the metal. There are two contributions to the TEP of an alloy: the diffusional part and the phonon drag part. The diffusional TEP is mainly determined by the concentration of atoms in solid solution. Probably the strain fields around coherent precipitates also influence the diffusional TEP. Dislocations, besides atoms in solid solutions and precipitates, also influence the phonon drag part of the TEP. Alloying of aluminium suppresses the phonon drag part. TEP values measured on 3003, 3104 and 1050 alloys are not influenced by the rolling reductions. This holds that dislocations, even at high dislocation densities, do not influence the TEP value at room temperature. The TEP value of aluminium alloys at ambient temperatures is thus solely determined by the diffusional TEP and mainly determined by the concentration of atoms in solid solution. Therefore combined TEP and conductivity measurements will be used to examine precipitation behaviour in the different alloying systems, and to follow processes such as recovery and recrystallisation.

2.4 Effect of Strain Path on Microstructural Evolution during High Temperature Deformation of Aluminium Alloys (S.B. Davenport, S. van der Zwaag)

A comparison between experimental data and current numerical models indicates that, in the case of rolled sheet, the current models cannot adequately model material behaviour in the sheared region near the surface of the sheet. The conclusion to be drawn from such work is that the complex 'strain path' in these regions cannot be accounted for in a simple fashion.

The aim of this project is to investigate the effect of these strain path histories on microstructure evolution, flow stress and recrystallisation in aluminium alloys. Studies will be carried out using the Bähr 810 machine during which material will be deformed under different combinations of tension, compression and torsion at high homologous temperatures. Initially the aluminium alloy 1050 will be studied. Cold deformation studies indicate that this material has a characteristic deformation substructure of equiaxed dislocation cells within individual grains. The object of the work is then to see how this substructure responds to changes in strain path (i.e. reversed strain or combinations of compression and torsion) and to see how this influences macroscopic variables such as flow stress and recrystallisation. Further microstructural complexity (solution or precipitation hardening) will be incorporated by investigating other alloys systems that also exhibit a cellular deformation substructure.

In a companion project, to start in 1999, we will examine the conditions determining the arrangement of dislocations during warm deformation, either in a cellular structure or localised shear bands.

It is anticipated that the results from this work will both enhance current microstructurally based models for deformation and contribute significantly to the understanding of the nature of dislocation substructures.

2.5 Filiform Corrosion on Coated Aluminium Alloys: The Role of Microstructural Non-homogeneities in the Substrate (J.M.C. Mol, S. van der Zwaag; J.H.W. de Wit, D.H. van der Weijde, H.W. van Rooijen [MIDEG])

Filiform corrosion is a type of local corrosive attack on a metal substrate covered by an organic coating and is characterised by thread-like tracks. It occurs on aluminium alloys, but also on steel and magnesium based substrates. The local attack is a
complex phenomenon involving influences of the environmental conditions, the organic coating, the coating-substrate interface and the substrate surface. Due to the many parameters involved, the relevant factors for filiform corrosion have not been established unambiguously.

Figure 7: SEM analysis of the filiform corrosion attack on chromated AA2024-T351, showing etch pitting, more severe pitting and intergranular attack

Aim of the present investigation is the determination of the effect of microstructural variations in aluminium based substrates on the filiform corrosion properties. The composition and structure of the surface layer/oxide is strongly influenced by the local composition of the underlying aluminium alloy. Especially precipitates and dispersoids with microscopic dimensions can influence the composition and structure of this surface layer/oxide. The composition and morphology of the constituent particles are a function of the thermomechanical treatments during the preceding production steps such as casting, solidification, homogenisation, extrusion and precipitation. Traditionally, local corrosion processes have been attributed to successive interactions between the alloy matrix and clustered particles. Local breakdown of the surface film permits subsequent local dissolution of the metallic substrate. Figure 7 shows different types of local corrosive attack on chromated AA2024-T351 after 1000 hours of accelerated filiform corrosion test exposure.

While a detailed examination of the filiform corrosion rate as a function of the substrate composition and the surface pretreatment applied yields valuable results, it does not provide explanations for observed dependencies. The underlying mechanisms for filiform corrosion can only be found by performing electrochemical measurements in media characteristic for the corrosion process studied. To this aim we performed potentiodynamic polarisation measurements in synthetic anolyte and catholyte media, characteristic for respectively the anodic and cathodic sites in real filaments. From these measurements the corrosion current, defined as the intercept of the anodic and cathodic curves in respectively anolyte and catholyte, can be determined. To study the effect of single alloying additions, the electrochemical and exposure tests are performed on binary Al-Cu, Al-Si, Al-Zn and Al-Mg with variations of composition, heat treatments and pretreatments. The pretreatments range from degreasing only to chromate and cerate based pretreatments.

A trend of a higher filiform corrosion susceptibility with increasing alloying concentrations was observed for all model systems. Furthermore, the filiform corrosion susceptibility varies with the solute atom, in particular Cu was found to have a detrimental effect on the filiform corrosion properties. Both chromating and cerating improve the filiform corrosion resistance of the alloys significantly.

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Figure 8: The correlation between the corrosion current density and the average filament length and corrosion number for the degreased Al-Cu binary alloys (a) and the Al-Zn binary alloys (b).

These observations support the applicability of the fundamental theories of local corrosion processes to filiform corrosion on aluminium alloys. Successive interactions between the alloy matrix and constituent particles are likely to be affected by the alloying elements and their concentrations. The results of the present set of experiments are in line with preceding investigations and a correlation between the polarisation measurements and both filiform corrosion propagation and total attack after the accelerated exposure test for the Al-Cu and Al-Zn binary alloys is observed, as shown in Figure 8. The correlation varies with the solute atom.

PUBLICATIONS

J.J. Braam, S. van der Zwaag
A statistical evaluation of the staircase and the ArcSin SQRT(P) method for determining the fatigue limit

S.P. Chen, K.M. Mussert, S. van der Zwaag
Precipitation kinetics in A16061 and an A16061-alumina particle composite

D.N. Hanlon, W.M. Rainforth, S. van der Zwaag
Some observations on cyclic deformation structures in the high-strength commercial aluminium alloy AA7150
D.N. Hanlon, Y.H. Li, W.M. Rainforth, C.M. Sellars, S. van der Zwaag
The formability of spray-formed, high-chromium content, white cast iron
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J. Huijbregtse, F. Roozeboom, J. Sietsma, J. Donkers, T. Kuiper, E. van de Riet
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F.J. Vermolen
*Mathematical models for particle dissolution in extrudable aluminium alloys*

F.J. Vermolen, C. Vuik
*A numerical method to compute the dissolutions of second phases in ternary alloys*

F.J. Vermolen, C. Vuik, S. van der Zwaag
*A mathematical model for the dissolution kinetics of Mg2Si-phases in Al-Mg-Si alloys during homogenisation under industrial conditions*

F.J. Vermolen, C. Vuik, S. van der Zwaag
*Modelling the microstructural changes during the homogenisation of extrudable aluminium alloys*

F.J. Vermolen, C. Vuik, S. van der Zwaag
*The dissolution of a stoichiometric second phase in ternary alloys: A numerical analysis*

P.J. van der Wolk, C. Dorrepaal, J. Sietsma, S. van der Zwaag
*Intelligent processing in a hot rolling mill for structural steels*

P.J. van der Wolk, C. Dorrepaal, S. van der Zwaag
*Modelling the CCT diagram of engineering steels using neural networks*
S. van der Zwaag

Modelling the austenite decomposition in steel on a physical basis

A report over 1998 is not available.
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HIGHLIGHTS

Within the field of energy technology, the program "Decentralised Production and Storage of Electricity for Large-Scale Application of Renewable Energy" within the DIOC: "Winnin, Conversie en Gebruik van Energie" has been granted. Prof. J. Schoonman has been appointed as program leader. Participating research groups are from the departments Chemical Technology, Materials Science, Applied Physics, Electrical Engineering, Civil Engineering and from the Interfaculty Research Institute (IRI) focus on the various projects to yield a multidisciplinary approach towards conversion and storage of renewable energy. The Delft University of Technology has a long-term commitment towards this DIOC program extending for a minimum period of four years.

Related to our lithium battery investigations, the "Nederlandse Onderneming Voor Energie En Milieu (NOVEM)" has selected our laboratory as Dutch co-ordinator (Expert) within the International Energy Agency (IEA). The task as formulated by IEA is to keep track of Exploratory Research on Advanced Batteries and Capacitors for Electric Vehicles. The expansion of the existing technologies for electrochemical conversion systems for electrical vehicles is pursued. At least once a year, prior to an Electrochemical Society Meeting, the world-wide selected experts meet to discuss the observed progression in battery research and development.

STW has granted a proposal to establish a National Centre for Magnetic Pulse Dynamic Compaction in the DIOC: Renewable Energy.

RESEARCH AREAS AND OBJECTIVES

In the Laboratory for Inorganic Chemistry, fundamental and applied studies of advanced inorganic materials are focused on functional ceramics for conversion and storage of renewable energy. Investigation of the relations between defects and microstructures and the chemical and physical properties of these materials will contribute to new or optimised synthetic routes for custom-designed structural, functional, and active hybrid materials. The synthesis of properties is essential. Thin films, in particular, nanostructured films, as well as nano-sized ceramic particles are obtained using Chemical Vapour Deposition (CVD), Electrostatic Spray Deposition, and sol-gel synthesis. The investigations aim at fundamental understanding of gas-phase synthesis of dense and nanostructured ceramic films with controlled porosity. In addition, gas-phase synthesis of nano-sized powders, particle surface modification, and dynamic compaction are studied in great detail. Our current research activities within this framework are the synthesis of new ceramic materials for rechargeable lithium batteries, photovoltaic solar cells and gas sensors.

With regard to densification of the electroceramic materials Cold and Hot Uniaxial Pressing (CUP, HUP), Hot-Isostatic Pressing (HIP), and explosive and magnetic pulse dynamic compaction are employed. The dynamic compaction techniques aim at preserving the nano-size powders in the compacts in order to take advantage of
the improved properties of the nano-sized powders, or even of new introduced grain boundary interface effects. Furthermore, a new device-technology has developed for rechargeable ceramic batteries.

In our projects the controlled synthesis of properties is essential. Hence relations between structures, defect structures, microstructures and chemical or electrical properties are investigated in great detail in order to prepare new or improved materials for rechargeable lithium-ion batteries, novel photovoltaic cells, and structural and functional composites.

FACILITIES

CVD-Reactors
- Four hot-wall low-pressure CVD-reactors (LP-CVD)
- Industrial hot-wall, pilot LP-CVD reactor (Tempress)
- Cold-wall LP-CVD epi-reactor with inductive heating
- Atmospheric-Pressure hot-wall CVD-reactor (AP-CVD)
- Cold-wall AP-CVD-reactor for Light-CVD
- Two hot-wall LP-CVD gravimetric reactors for kinetic studies
- Radio frequency Plasma-CVD reactor
- Micro-wave Plasma-CVD reactor
- Industrial CO₂ laser with AP-CVD reactor
- Tuneable CO₂ laser with LP-CVD reactor
- UV-excimer and dye laser with AP-CVD and gravimetric AP-CVD reactor
- Two custom-built desktop AP-CVD reactors for laboratory courses

Other Synthetic Equipment
- High-vacuum Physical Vapour Deposition (PVD) reactor
- DC sputter coater
- Four-target electron-beam evaporation system
- Three ESD set-ups
- Vertical tube furnace for sintering up to 1700 °C
- 12 kW rf-generator for inductive heating
- Furnaces for solid state synthesis
- Spin coating system
- Three glove-box units
- Screen Printer
- Coin cell press
- Wire bar coater
- Climate room
- Manual foil winding equipment

Characterisation Equipment
- Frequency Response Analyser (FRA), Solartron 1250, 1255, and 1260
- Two Electrochemical Interfaces Solartron 1286
- Potentiostat EG&G 273, EG&G PARC 253 VerSatat
- Gamry Potentiostat EIS900, FRA
- Autolab, ECO Chemie, combination of FRA2, ADC164, DAC164 and PGSTAT 30
- Keithley 575i Potentiostat
- Five high-temperature stainless-steel and nickel conductivity cells
- Maccor Battery Testing System (40 independent channels)
Lithium Ion Batteries (E.M. Kelder)

Large scale introduction of zero-emission Electric Vehicles and decentralised load levelling systems in society is obstructed by the availability of adequate rechargeable batteries. The Swing-type lithium-ion battery has been recognised to meet the required demands, and much effort has been devoted to the development of materials for large-scale lithium-ion batteries. The technology for the swing-type battery is based on the use of suitably chosen lithium intercalation compounds, i.e. carbons and LiMn$_2$O$_4$, for the electrodes and a polymeric electrolyte. Especially, the state-of-the-art carbon anodes are hampering the developments.

Lithium batteries are generally acknowledged for their superior energy density and it is anticipated that they will become one of the most important energy storage batteries within the next decade. In our laboratory, the study of the fundamentals of materials for lithium batteries is a major theme. Both the synthesis and characterisation of new, or improved materials and composites for transport and intercalation of lithium as well as the electrochemical properties of laboratory-scale batteries are being studied. A novel densification technique is being studied for the optimisation of electrode/electrolyte interfaces and assembling of all solid-state batteries.

In addition, Electrostatic Spray Deposition (ESD) has been developed to a high level of sophistication for the deposition of thin films of battery components with controlled morphology, and of thin film batteries.

1.1 Solid State Lithium Ion Polymer Batteries (E.M. Kelder, A.A. van Zomeren)

In collaboration with Danionics (Denmark), Saft (France), Sonnenschein Lithium GmbH (Germany), and the Universities of Southampton and St. Andrews (UK), Nantes/Armines (France), and Uppsala (Sweden), cathode materials are studied for solid-state lithium-ion batteries. In this project LiMn$_2$O$_4$ has been synthesised with a new technique in order to improve the materials by addition of several dopants including extra lithium. Additional lithium is known to decrease the capacity of the material as the oxidation state of the manganese is influenced dramatically. Small amounts of additional lithium are used to stabilise the cathode material during operation of the cell. Furthermore, despite the change in oxidation state of the manganese, resulting in an expected loss in capacity, the excess lithium leads to a higher amount of lithium occupying the tetrahedral sites, i.e. the lithium ions attractive for the battery.
in question. In order to improve both the stability and the capacity, several dopant ions are proposed and studied with most of them part of the patent concerning the synthesis of the materials. Materials containing a particular dopant concentration have been synthesised. The XRD spectra show pure spinel phases, with a hint of amorphous material. Because lithium diffusion in these samples is very low, structural and chemical characterisation was performed to determine the impurity levels. A new research program together with the above partners will be defined shortly within the EU 5th framework.

1.2 Preparation and Characterisation of Thin Film Components for Rechargeable Lithium Batteries (C.H. Chen)

Thin-film lithium batteries are of potential importance for various applications. Two film fabrication techniques, i.e. electrostatic spray deposition (ESD) and plasma-enhanced chemical vapour deposition (PECVD), have been used to prepare battery materials, such as LiCoO$_2$, Li$_5$Mn$_2$O$_4$, LiPO$_4$, BPO$_4$-Li$_2$O, and poly(methoxy-ethoxy-ethoxy)phosphazene (MEEP). Chemical Vapour Deposition of MEEP has not been reported in the literature. Optimisation of the ESD and PECVD deposition conditions and developing new synthetic routes for the preparation of submicron and nano-sized battery component materials have been the main focal points in this period. We found that besides dense and porous layers a unique reticular structure can be formed in the LiCoO$_2$, Li$_5$Mn$_2$O$_4$, and LiPO$_4$ films made by ESD. The formation mechanism and pore-size scaling law have been investigated. This structure is expected to be beneficial for applications in rechargeable lithium-polymer batteries, in catalysis, for gas-sensors (viz. Section 2.3), and in gas/liquid separation and related devices. Complete solid-state thin-film batteries have been fabricated using LiPO$_4$ or BPO$_4$ as electrolyte, and Li$_5$Mn$_2$O$_4$ as electrodes. The charge-discharge behaviour has been studied in detail and the concept of rocking-chair batteries has been confirmed. The chemical diffusion coefficient of lithium in the electrode materials has been studied using low-frequency impedance spectroscopy and Galvanostatic Intermittent Titration Technique (GITT). For Li$_5$CoO$_2$ films the lithium chemical diffusion coefficient increases with $x$ and increasing porosity. In the reticular structures a diffusion enhancement of a factor of 100 has been measured. For the PECVD of MEEP films, polymer films containing different chlorine (Cl) contents depending on the plasma power and deposition temperature have been obtained and characterised by EDX and FT-IR.

In addition to lithium battery materials, yttria-stabilized zirconia (YSZ) films on gadolinia-doped ceria (GCO) substrate have also been synthesised by ESD in order to illustrate the potential of this novel method. The development of the ESD technique has been strengthened and initiated collaboration with Imperial College, the University of Metz, Technion, ECN, the Illinois Institute of Technology, and Philips.

1.3 All-Solid-State AA-Type Rechargeable Lithium Batteries with Swing Electrodes and a Ceramic Electrolyte Dispersed in Solufill$^\text{TM}$ for Consumer Electronics (E.M. Kelder)

Li$_5$Mn$_2$O$_4$ powders with optimised stability and capacity have been synthesised successfully. The electrolyte BPO$_4$-Li$_2$O is synthesised with H$_3$BO$_3$-H$_3$PO$_4$-LiOH aqueous mixtures as well as H$_3$BO$_3$-H$_2$SO$_4$-(NH$_2$)$_3$PO$_4$ aqueous mixtures. It appears that the ammonia containing mixtures give nano-sized powders arising from a foam. X-Ray diffraction together with gravimetry reveal a single-phase material of Li$_3$B$_{1-1/3x}$PO$_4$, with
x < 0.3. The maximal overall conductivity is observed for x = 0.035. The as synthesised powders could be successfully dispersed in polymer foils such as PVC, Poly-Ethylene, Poly-Carbonate, etc. Conductivity measurements on these foils reveal percolation-type electrical conductivity. As an alternative of this electrolyte Li-beta-alumina has been synthesised. Conductivity measurements on this electrolyte are concordant with literature data, indicating the material to be suited for dispersion in a polymeric matrix. Symmetrical cells of Li1+dMn2-dO4 / Li1-xB1-1/3xPO4 / Li1+dMn2-dO4 have been fabricated and their electrochemical behaviour has been characterised. These batteries are to be used as micro-batteries for animal implants and were tested at IMAG/DLO (Wageningen) for this purpose. Coin-cells of the above systems were prepared in order to establish its performance.

1.4 Dynamic Compaction of Rocking Chair Type Rechargeable Lithium Batteries (M.J.G. Jak)

The priority in this project is to study the relation between the structure of the dynamically compacted materials and the (electrical) properties. Different methods of compacting Li-ion battery components and complete battery systems have been investigated. These methods include explosive compaction (EXC), magnetic pulse compaction (MPC), hot isostatic pressing (HIP), and cold isostatic pressing (CIP). With these methods, a pressure range from 0.1 to 17 GPa is covered. Usually, rechargeable lithium-ion batteries comprise next to the electrodes a polymeric electrolyte. The advantage of the use of polymeric electrolytes is the intimate contact between the ceramic electrodes and the electrolyte. However, a major disadvantage of polymeric electrolytes is their inherent instability. Ceramic electrolytes lead to poor electrical contacts with ceramic electrodes. Dynamic compaction yields improved contacts between ceramic battery components.

Battery components have been compacted and investigated with SEM, EDX, XRD, AAS, AC-impedance spectroscopy, and DC measurements. The influence of the compaction method and related pressures on the micro-structure and on the electrical properties of the electrolyte material BPO4-Li2O have been established in detail. For the cathode material Li1+xMn2O4 the electronic conductivity increases as well as the lithium ion conductivity. The dc-resistance of a dynamically compacted ceramic battery is improved substantially as compared to a traditionally compacted ceramic battery.

Due to the attention this project has received world-wide, new collaborations with the Forschungszentrum Karlsruhe (Germany) concerning MPC, Institute for Chemical Physics, Russian Academy of Science (EXC, HIP, anode materials) (Russia), Russian Federal Nuclear Centre All Russian Research Institute of Experimental Physics (RFNC-VNIIEF)(Russia), and Norit (anode materials, The Netherlands) have been established.

In close connection with the projects described in Sections 1.3 en 1.4 battery materials as well as batteries are studied for application in decolised energy storage systems, these includes electricity storage at hand, load levelling as well as for future Electrical Vehicles.

1.5 Electrode and Electrolyte Behaviour in Polyethylene Matrices (F.G.B. Ooms)

Commercial polyethylene type separator materials will be tested on their suitability towards Li-ion battery components. The separator materials have either open poros-
ity for filling it with liquid electrolyte, or contain a ceramic filler present from off the production. Coin cells are made for the porous separator, whereas for the filler system special cells will be constructed, and subsequently applying dynamic compaction necessary to achieve intimate contact between the individual foils. The cells will be tested with a MACCOR battery tester.

1.6 Advanced Anode Materials for Rechargeable Li-ion Batteries (H. Huang, L. Chen)

In this project, the fundamental relations between the structure, the defect and microstructure and the electrical and lithium intercalation properties of novel BC₃N-based matrices and of nanostructured TiO₂ and SnO₂ will be studied. These materials have only recently been recognised as potential anode for rechargeable Lithium-ion Batteries. Their behaviour in batteries using polymeric and ceramic electrolytes will be characterised in detail in order to select the most optimal anode material. Such a study has not yet been reported in the lithium battery literature.

1.7 Advanced Cathode Materials for Rechargeable Li-ion Batteries (M. Alavi, L. He)

Fundamental relations between structure, the defect and microstructure and the Lithium intercalation properties of Novel Li(Mn,Fe)PO₄ compounds as well as Liₓ[LiₓMn₂₋ₓ]O₄ materials will be studied. The aim of the research is to find optimised cathode material with a high capacity and improved performance.

1.8 Feasibility Study on the Formation of Prototype Li-ion Batteries Based on Ceramic Electrolytes (W.J. Legerstee, E.L. Maloney)

A study was be undertaken to specify what should be done in order to fabricate several prototype batteries for down-hole operation, that can operate up to 220 °C without failure. The current commercial rechargeable batteries often operates with a wet or polymeric electrolyte. These are mostly of organic origin, which make them sensible for an irreversible reaction with the electrode materials of the battery, resulting in capacity fade during cycling, and finally to complete break-down of the battery. In addition, these electrolytes cannot operate above 100 °C (due to evaporation of the electrolyte solvent), that is absolutely required for down-hole operation, where temperatures up to 250 °C exists. Therefore a feasibility study is started in order to form a full ceramic battery with a ceramic electrolyte, that is supposed to be indispensable to comply with the requirements for down-hole operation. The focus was be on what is important for the progress of the research in terms of man power, equipment etc. Recently, financial support was given in order to improve the infrastructure for the formation of prototype Li-ion batteries for high-temperature applications. This financial support is included in project 1.9.

1.9 All Solid-State Battery Based on a Ceramic Electrolyte and Manufactured by Magnetic Pulse Compaction (M.J.G. Jak)

This project is a continuation of two SON/STW projects, which were terminated in 1998 and is based on important results and conclusions obtained in these projects. The aim of the project will be a fundamentally improved all-solid-state Li-ion battery based on a ceramic electrolyte which is compatible with the electrodes, and its process technology. Optimisation will be done in terms of improved Li-ion diffusion, by proper choice of the electrolyte (separator) and especially Magnetic Pulse Compaction for improving the interfaces. Two different battery sizes will be studied, i.e. AA-size cells or equivalent and thin layer or coin cells.
It is suggested that the all-solid-state Li-ion battery based on a ceramic electrolyte can offer the advantages and are not subject to thermal runaways, i.e. it is also a high-temperature battery.

The research project comprises (1) powder synthesis and characterisation, (2) coating and foil formation, (3) winding and stacking of green batteries, (4) Magnetic Pulse Compaction (MPC) of the green batteries, and (5) characterisation of the performance of the batteries.

The project is scheduled for three years for a post-doc using the Magnetic Pulse Compaction Equipment and a foil-winding machine.

2 Fuel Cells and Gas Sensors

Fuel cells convert chemical energy into electrical energy with high efficiencies. Solid Oxide Fuel Cells (SOFCs) operate between 950 and 1000 °C, which demands compatibility between the various ceramic components. Molten Carbonate Fuel Cells (MCFCs) operate at a lower temperature, i.e. 650 °C but are severely affected by corrosion due to the extreme aggressive molten carbonate electrolyte. Our research focuses on materials for SOFC and ceramic layers for corrosion protection in MCFCs.

2.1 Corrosion Protection of MCFC Separator Plates with Ceramic Coatings (M. Keijzer)

A collaborative program with the group of prof.dr. J.H.W. de Wit is focused on the corrosion protection problems in Molten Carbonate Fuel Cells (MCFCs). One of the most severe technological problems in MCFC devices is the extremely aggressive molten carbonate electrolyte. Electrodes and especially the steel separator plates show fast degrading upon operation. In order to improve the MCFC lifetime, protective electrically conducting ceramic coatings are a necessity. The requirements for these electroceramics are i) excellent corrosion resistance and thermal stability, ii) high diffusion barrier for ions (such as Li⁺), and iii) good electronic conductivity.

Phase diagrams of possible coating materials have been studied in order to predict the chemical reaction products in molten carbonate environment. Stability experiments of a number of materials has led to a few promising candidates, i.e. TiN, TiC and Ce-based ceramics. In order to determine the corrosion behaviour of stainless steel 304 in the MCFC environment, electrochemical measurements have been undertaken in collaboration with the University of Stockholm. With chronoamperometry and cyclic voltammetry the corrosion rates and the corrosion pattern as a function of exposure time were determined, respectively. The corrosion rate in anode gas was about eight times higher than in cathode gas. From the fits of the corrosion currents, obtained with chrononamperometry and the Avrami-equation, it was concluded that corrosion currents in cathode gas decreased almost parabolically, whereas it decreased in anode gas much slower than parabolically. Analysis of the corrosion layers with glow discharge optical emission spectrometry showed that iron can be oxidised in molten carbonates further than Fe(III), although valences above three have hardly been reported in the literature. A Microwave-Plasma enhanced CVD reactor has been constructed and tested. Dense TiN layers have been deposited on stainless steel 304 by Radio-frequent-Plasma enhanced CVD. Initial experiments have been performed to determine the detailed mechanism of the deposition.

Ir. J.P.A.M. Driessen explores up-scaling of a plasma enhanced CVD process for ti-
tanium (carbo-) nitride ceramic coatings. This work is funded by the IOP-Surface Technology and by TNO. The experiments are performed at TPD-TNO (Centre for Technical Ceramics). A novel bi-polar radio-frequent pulse generator has been installed together with a newly developed Direct Liquid Injection (DLI) system. In situ mass spectrometry is used to monitor the CVD process. Computer control over the process has been installed. The results of this new up-scaled reactor compares favourably to conventional thermal CVD. The produced coatings show similar micro-structure and have comparable mechanical properties.

2.2 Aerosol Techniques (C.H. Chen, Y. Kamlag)

In addition to the Electrostatic Spray Pyrolysis aerosol technique, which for several projects was modified to the thin-film technique Electrostatic Spray Deposition, two aerosol powder techniques were developed, i.e. Thermally-Activated Ultrasonic Spray Pyrolysis (TAUSP) and Flame Assisted Ultrasonic Spray Pyrolysis (FAUSP).

In FAUSP flammable alcoholic solutions are used as precursors. Therefore, no extra fuel gases are needed as is state-of-the-art. ZrO₂ and YSZ (for SOFC) nanosized powders (< 500 nm) with a small particle size distribution were obtained. TAUSP was used to obtain bismuth oxide-based ceramic super conductor powders for gas sensors. The powder particles have diameters in the range 100 nm to 1 µm and a bimodal distribution was obtained.

2.3 Chemical Gas Sensors (L.N. van Rij, R. van Landschoot)

There has been an increasing interest in the detection of hydrocarbons in air the past few years. Detection of methane has been achieved using e.g. optical fibre sensors, thin-film SnO₂, or thin-film Fe₂O₃-based sensors. One of the disadvantages of these conductivity-based sensors is their high cross-sensitivity. The cross-sensitivity of the semiconductor-based sensors can be decreased by adding different dopants to the sensing material or by applying catalytic filters. The selectivity, however, is still not high enough to utilise these sensors in complex gas atmospheres like natural gas. Secondly, these sensors cannot be utilised in oxygen poor or free atmospheres. In practice, the semiconductor based sensors have only been tested up to 100,000 ppm (10 kPa), while detection of methane in natural gas requires a detection limit higher than 90 vol. %.

The aim of this study is to develop a methane sensor which is capable of detecting methane in a large concentration range (1-100 vol. %) in the absence of oxygen. To fulfill these requirements a novel sensor has been designed, i.e. the catalytic asymmetrical Nernst-type methane sensor.

The detection principle of the present methane sensor is based on a difference in catalytic activity of two electrodes for the CO₂-reforming reaction of methane. Methane is converted into hydrogen or water vapour via reforming reactions 1 and 2.

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 & \leftrightarrow 2\text{H}_2 + 2\text{CO} \\
\text{CH}_4 + 3\text{CO}_2 & \leftrightarrow 2\text{H}_2\text{O} + 4\text{CO}
\end{align*}
\]
Materials Science for Energy Conversion and Storage Systems

...rate concentration. Hence, the sensor behaves as a Nernst-type sensor, where the water vapour or hydrogen is produced \textit{in situ} out of methane and CO$_2$.

As active electrode material for the catalytic electrode three different metals are studied: Nickel, Ruthenium and Rhodium. The counter electrode is made of platinum or gold. For the electrolyte SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$ (SCYb5) or CaZr$_{0.4}$In$_{0.1}$O$_{3-x}$ (CZI10) is used.

The main advantages of this system are:
- a reference gas is not required,
- simple cell construction,
- ability to quantify methane in the absence of air,
- possibility of miniaturisation.

2.4 Chemical Gas Sensor Arrays (M.H.J. Emond)

There has been an increasing interest in chemical gas sensors for on-line analysis of the composition of gases before and after burning processes. Conventional gas sensors, such as Taguchi- and Nernst type sensors, are not particularly selective or sensitive, respectively. By doping the Taguchi-sensor material or in particular, by making a sensor array this problem can be solved. The multi-phase mixtures of n- and p-type semiconducting transition metal oxides, with an inert oxide like Al$_2$O$_3$ as the third component, show a response to nitrogen, sulphur and carbon oxides which is dependent on the ratio of the different semi-conducting transition metal oxides and the inert metal oxide. Hence an array of Taguchi-type gas sensors with as active sensing materials an array of multi-phase mixtures with specifically different compositions would yield an "electronic nose" which could map complex gas compositions in a single measurement. In relation to 2.3, this concept shall be extended to the asymmetrical Nernst-type gas sensor. In this design project a chemical gas sensor arrays has been developed.

3 Photovoltaic Solar Cells

Photovoltaic solar cells are anticipated to contribute substantially to our electrical energy demand in the 21st century. Already, Si-based photovoltaic devices are commercially available and compete with increasing effectiveness in the energy market. An important factor that prevents large-scale manufacturing and implementation of these devices is their cost. Therefore, materials research for cheap, efficient, and stable photovoltaic solar cells attract wide-spread attention.

3.1 Photovoltaic Devices Based on Dye-Sensitised Smooth and Nanostructured Oxide Semiconductors (A.P.L.M. Goossens, M.A. Hamstra, N. van Landschoot, C.L. Huisman, B. van der Zanden)

In order to investigate the feasibility of sensitising wide-bandgap oxide semiconductors by organo-metal complexes as dyes in conjunction with an optical antenna system, the "Nederlandse Onderneming voor Energie en Milieu, NOVEM" initiated and funded a national program. In this program the laboratory for Applied Inorganic Chemistry collaborates with the Departments of Molecular Physics and Organic Chemistry of the Wageningen Agricultural University (LUW) and with the Department of Surface Physics of the Debye Institute at the Utrecht University (UU). In close connection with this network we also participate as sub-contractors in a Joule III, program on dye-sensitised solar cells and in an NWO priority program on surface modi-
Our research has been directed towards opto-electronic characterisation of dye-sensitised dense and porous nanocrystalline TiO₂ thin films. Photocurrent generation on dense CVD films of TiO₂ sensitised with zinc tetra phenyl porphyrins has been investigated. In addition, sensitisation of TiO₂ with phthalocyanine molecules and p-type semiconducting polymers is investigated in depth. A range of opto-electronic characterisation techniques is employed to elucidate the nature of exciton migration and electron-hole generation in organic materials.

3.2 Opto-Electronic Properties of Oxide Semiconductors with Nanometer Scale Dimensions (R. van de Krol, A.P.L.M. Goossens)

In close relationship with project 3.1 a fundamental study towards the elucidation of the chemical and physical properties of nanometer-scale oxide semiconductors has been undertaken. This program has been selected by the KNAW in 1993 and led to a 5-year appointment of dr. A.P.L.M. Goossens as KNAW research fellow. Nanometer-scale thin films of TiO₂ are formed by either electrochemical anodic oxidation of Ti metal or by electron-beam (e-beam) evaporation of sub-stoichiometric TiOₓ. With anodic oxidation, non-porous rutile TiO₂ films of 3-10 nm thickness can easily be obtained whereas e-beam evaporation produces TiO₂ films of 50-100 nm thickness onto ITO or SnO₂-coated glass substrates. The opto-electronic properties of these thin films are compared with the behaviour of nano-structured TiO₂ coatings as obtained in project 3.1. The main questions that are addressed are i) what is the exact potential distribution in these structures and how is this distribution related to the defect chemistry, ii) in what way do surface trapped electrons influence optical properties of TiO₂, iii) what is the influence of the reduced scale on the electronic properties of these materials.

A significant step towards objective i) has been made. Mott-Schottky analysis could be performed on nanometer thin films with a great accuracy and reproducibility. With this analysis, not only the stoichiometry has been defined, but also the dielectric constant of anatase TiO₂ could be determined to a high precision. It appeared that reported values are in many cases a factor of 2 too high. Photocapacitance and photovoltage studies have revealed the energy position of surface states. In order to define the chemical origin of these states additional experiments are in progress.

3.3 Boron Phosphide (E. Schroten, A.P.L.M. Goossens)

Boron phosphide (BP) is a refractory material with high mechanical strength and wear resistance. Moreover, it is a III-V semiconductor with a zinc-blende crystal structure and an indirect bandgap of 2.0 eV. BP can be formed with radio-frequency activation in a cold-wall CVD reaction as polycrystalline or amorphous coating, as whiskers when a vapour-liquid-solid (VLS) growth technique is used, or as single crystalline epitaxial film onto silicon.

Single crystalline epitaxial BP films have been deposited onto Si (100). Both n-type and p-type BP could be synthesised, the latter Si as dopant. Current research focuses on the structural and electronic properties of the Si/BP epitaxial interface. The main questions here are i) how is the band line-up (the relative positions of the conduction and valence bands), and ii) what is the density of electronic interface states. The band line-up at Si/BP interfaces has been investigated by surface-photovoltage spectroscopy. These measurements qualitatively show that although saturation can-
not be reached with our monochromatic excitation source, distinct features appear. For n-Si/n-BP heterojunctions, the total band bending at the interface is small, i.e. 20-30 mV, indicating an almost ideal matching of the conduction bands of both materials. For p-Si/n-BP heterojunctions, a band bending of 425 ± 25 mV is present. Electrolyte electroreflection has been used to reveal the presence of an optical transition at 4.25 eV, which is probably the direct bandgap of BP. To date, reported values have been much larger while theoretical values are widely distributed. Currently more experiments are in progress to validate our observations.

3.4 Sensitisation of TiO₂ with Pyrite (B. Meester, A.P.L.M. Goossens, E.W.M. Ruijgrok)

Within the DIOC program: Decentralised Production and Storage of Electricity for Large-Scale Application of Renewable Energy sensitisation of TiO₂ with pyrite (FeS₂) is investigated. The chemical reaction mechanism of the MOCVD process is studied in detail. The phase purity of the obtained pyrite thin films (50-200 nm thick) can be related to the CVD process conditions. With optimised CVD parameters, FeS₂ without phase impurities and with the right stoichiometry can be obtained. The bandgap of pyrite is 0.95 eV as could be established from optical absorption and from photoconductivity.

3.5 Thin Film Silicon Solar Cells (G. Korevaar, A.P.L.M. Goossens)

In collaboration with ECN (Petten) and DIMES (Delft University of Technology) laser CVD of thin films of silicon on ceramic substrates is explored. This technology allows the use of inexpensive substrate materials in photo-voltaic solar cells based on polycrystalline silicon.

4 Electroceramic Composites

In this project ceramic composites are synthesised. These investigations serve to strengthen the CVD infra-structure and know-how in the group and to test new ideas originating from previous investigations. The project shares the functional character of the materials which are formed.

4.1 Silicon-Carbide-Nitride Composites (W.F.A. Besling, P.J. van der Put, A.P.L.M. Goossens)

In this project, Si-C-N composites are synthesised by laser particle-precipitation aided CVD (L-PP-CVD), using a tuneable CO₂ laser to activate the CVD process. Depending on the process conditions, the composition of these films can be varied. For instance, semiconducting cubic SiC particles in an insulating Si₃N₄ matrix can form. These nano-structured films then show unique photo- and electroluminescence phenomena and may find application in blue light-emitting-diodes and optical displays. In contrast, when nitrogen acts as dopant for cubic SiC, completely different kinds of optical phenomena are to be expected. Moreover, Si-C-N thin films may also find application as hard-coating because of the well-known mechanical characteristics of SiC and Si₃N₄.

In particular in situ characterisation of the CVD process by optical Raman spectroscopy has been elaborated on. In collaboration with the group of prof. B. Scarlett from our faculty, a laser Raman spectrometer set-up has been assembled and tested. With this technique intermediate radical gas phase species could be observed. Careful calibration and optimisation of the set-up has been worked out. Porous and
dense silicon carbonitride films have been deposited. In L-PP-CVD experiments, particle sizes down to 20 nm are obtained and studied using TEM. In the Si-C-N system, a wide range of compositions can be obtained as is established with XPS and EDX analysis. In addition to the Si-C-N system, preliminary experiments for the formation of nanoporous crystalline Si coatings have been made in order to explore alternative routes for thin-film silicon synthesis. At present, thin-film nanostructured silicon is investigated thoroughly for solar cell applications.

5 Metallisation of Polymers (M.L.H. ter Heerdt, A.P.L.M. Goossens)

In the framework of the Innovation Directed Research Programme for Surface Technology (IOP-OT), a national research programme for metallisation of polymers is under study. The research is performed in collaboration with the group of prof.dr. J.H.W. de Wit of Delft University of Technology, TNO-TPD (Technisch Fysische Dienst), and two departments of TNO Industry (formerly Kunststoffen en Rubberinstituut en Metaalinstituut), and ECN (Energie Centrum Nederland).

Conventionally, polymer metallisation is performed by sputtering a seed-layer of Pd onto the polymer, followed by an electrochemical or electroless deposition of a metallic top-layer. In case of a copper top-layer, an important application is found in Printed Circuit Boards in the electronic industry, where the requirements for adhesion and electrical conductivity are extremely demanding. Therefore, in our group copper is deposited by CVD at low temperatures, as an alternative for selective metallisation of polymers.

Two methods are explored to reach low temperatures in copper CVD. The first is photo-chemical vapour deposition (PCVD), for which a new reactor has been developed. In this reactor metallic copper has been deposited with thermal as well as photo-assisted CVD. Using Cu(hfac)$_2$ as a precursor and H$_2$ or ethanol as a co-reactant a deposition temperature as low as 200 °C is reached with UV-enhanced CVD. This is about 100 °C lower than with thermal CVD, making polyimide (PI, m.p. 300 °C) a suitable substrate material.

A second possibility for deposition at low temperatures is choosing another precursor. With Cu(hfac)VTMS metallic copper has been deposited on polyetherimide (PEI, m.p. 180 °C) at a temperature of 120 °C. The deposition kinetics of this precursor have been studied in relation to precursor concentration, pre-treatment of the substrates, and temperature. A new CVD model, developed in our group, has been employed to interpret the kinetic deposition data.

6 Vapour-Phase Synthesis and Processing of Nano-Particle Materials (NANO)

The ESF Programme on Vapour-Phase Synthesis and Processing of Nano-Particle Materials (NANO) aims to promote the synthesis of ceramic aerosols and films using gas phase techniques, with the aim of generating single-phase, or nanodispersed structural ceramic materials and electroceramics with new or improved properties. The programme was in its fourth year after a successful mid-term review, and is currently supported by research councils and Academies of Sciences in Belgium, Denmark, Finland, Germany, the Netherlands, Poland, Sweden, Switzerland, and the United Kingdom.

Interdisciplinary collaboration between aerosol community and the materials science community will be furthered within the NANO programme through the exchange of
expertise and methods during workshops and task force meetings, and through the exchange of researchers. The NANO programme supports visits of up to one month for senior researchers and the exchange of Ph.D. students and post-doctoral researchers for up to six months between aerosol and materials groups.

PUBLICATIONS

W.F.A. Besling, A. Goossens, B. Meester, and J. Schoonman

*Laser-induced chemical vapor deposition of nanostructured silicon carbonitride thin films*


*The effect of additives on ceramic materials for lithium solid electrolytes*


E.P. Carton

*Shock Compaction of Ceramics and Composites*


E.P. Carton, M. Stuivinga, H. Keizers, J. Schoonman

*Forming during shock compaction*


E.P. Carton, M. Stuivinga, H.J. Verbeek, P.J.J.M. van der Put

*Temperature measurements during shock compaction of powders*


C.H. Chen

*Thin-Film Components for Lithium-Ion Batteries*


*Electrostatic Sol-Spray Deposition of Nanostructured Ceramic Thin Films*


C.H. Chen, E.M. Kelder, J. Schoonman

*Effects of Additives in Electrospraying for Materials Preparation*


C.H. Chen, B. Meester, P.J.J.M. van der Put, J. Schoonman

*Synthesis of Poly[bis((methoxyethoxy)ethoxy)-phosphazene] (MEEP) Thin Films by Plasma-Enhanced CVD (PECVD)*


C.H. Chen, F.L. Yuan, J. Schoonman

*Spray pyrolysis routes to electroceramic powders and thin films*


J.P.A.M. Driessen, A.D. Kuypers, J. Schoonman

*A mass-spectroscopical study of the decomposition of Ti(NMe2)4 in a mixed Ar-H2-N2 pulsed d.c. plasma*


H.J. Fissan, J. Schoonman
Vapor-Phase Synthesis and Processing of Nanoparticle Materials (NANO) – A European Science Foundation (ESF) Program

A.P.L.M. Goossens, E.L. Maloney, J. Schoonman
Gas-Phase Synthesis of Nanostructured Anatase TiO$_2$

H. Gourari, M. Lumbreras, R. van Landschoot, J. Schoonman
Elaboration and characterization of SnO$_2$-Mn$_2$O$_3$ thin layers prepared by electrostatic spray deposition

L. He
Study on the Composition and Structure of Delithiated Materials and a Model for Leaching Process

H. Huang, W. Liu, X. Huang, L. Chen, E.M. Kelder, J. Schoonman
Effect of a rhombohedral phase on lithium intercalation capacity in graphite

M.J.G. Jak, E.M. Kelder, N.M. van der Pers, A. Weisenburger, J. Schoonman
Lithium Ion Conductivity of a Statically and Dynamically Compacted Nano-Structured Ceramic Electrolyte for Li-Ion Batteries
J. Electroceramics 2 (1998) 127-134

M. Keijzer
Ceramic and Metallic Coatings for Corrosion Protection of Separator Plates in Molten-Carbonate Fuel Cells

F.E. Kruis, W. Oostra, J. Marijnissen, J. Schoonman, B. Scarlett
Particle Formation Paths in the Synthesis of Silicon Nitride Powder in a Laser-Heated Aerosol Reactor

P.J. van der Put
Electron pairs shed light on frustrated percolation

P.J. van der Put
The Inorganic Chemistry of Materials. How to Make Things out of Elements

T.J. Savenije, J.M. Warman, A. Goossens
Visible light sensitisation of titanium dioxide using a phenylene vinylene polymer

J. Schoonman
Materiaaltechnologie voor opslag van duurzame energie
Chemisch Magazine, October 1998, 354-357

E. Schroten, A. Goossens, J. Schoonman
Photo- and electroreflectance of cubic boron phosphide
Preparation of zirconia and yttria-stabilized (YSZ) fine powders by flame-assisted ultrasonic spray pyrolysis (FAUSP)
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RESEARCH AREAS AND OBJECTIVES

The research performed in the group Mechanical Behaviour of Materials can be divided into 4 themes:
- fatigue
- creep and creep-fatigue interactions
- environmental effects
- failure

1 Fatigue

1.1 Fatigue of Aluminium

Fatigue crack growth in aluminium is studied experimentally during constant load amplitude, constant stress intensity amplitude (ΔK) and various forms of block loading. Particular attention is paid to the effect of:
- shear lip development and shear lip roughness,
- crack closure level changes,
material properties due to the welding process. This work is carried out in the framework of DIOC 10: Reliability of Structures and Materials.

- Fracture Toughness of High-Chromium White Cast Iron
  High chromium white cast iron is applied because of its excellent wear resistance, a property which is attributed to the presence of primary carbides. However, these same carbides generally lead to a very poor fracture toughness. The objectives of this research are (i) to develop a reliable and relatively simple method to determine the fracture toughness of this material and (ii) to explore the parameters that affect it.
  This work is performed in conjunction with IHC Holland, Parts & Services.

FACILITIES
- Seven computerised hydraulic fatigue machines (350, 2x250, 3x100, 25 kN)
- Four electro-mechanical tensile testing machines (3 x 100, 50 kN)
- High capacity hydraulic tension testing machine (2 MN) and compression testing machine (5 MN)
- Fast hydraulic mechanical testing machine (10 m/s at 50 kN, 17 m/s at zero load), including a high speed photo camera (maximum 224 pictures and 35 000 picture/s)
- Digital imaging systems for recording crack growth and plastic deformation
- Ten creep machines for metals (T < 1000 °C)
- Two creep installations for polymers (+20 < T < +90 °C, 10 specimens each)
- Climate chamber for mechanical testing in various gaseous climates (400 x 500 x 600 mm; -150 < T < +250 °C)
- Oven for tensile testing at high temperature (250 x 060 mm; T < 1200 °C)
- Chamber for mechanical testing at low and elevated temperatures (345 x 330 x 600 mm; -180 < T < +80 °C)
- Instrumented drop-weight tower: Dynatup 8000A with digital oscilloscope and PC for data acquisition
- Various equipment for the mechanical characterisation of materials: Charpy impact tester, hardness measurement equipment, etc.
- Various ultrasonic measurement equipment, including a set-up for acoustoelastic stress measurements
- DEC 3400 workstation running MARC finite element program and MENTAT pre-and-post processor
- DEC 6/333 workstation running Matlab
- DEC 5/400 workstation running MARC and ABAQUS finite element programs and MENTAT pre-and-post processor

RESEARCH REPORT 1998

1 Fatigue

1.1 Fatigue of Aluminium (J. Zuidema, Th.M. van Soest)

Further progress has been made in an extensive experimental program studying the fatigue crack growth rate in aluminium alloys. Special emphasis has been given to effects of environment and frequency on the crack growth rate in Al 2024 out using
centre-cracked tension specimens. The aim is to study and predict the effect of crack closure changes on the crack growth rate.

1.2 Fatigue of Thin Nodular Cast Iron (C.E. Wijnmaalen, J. Zuidema)

A large number of tests were performed to measure the fatigue limit stress at 4 million cycles. For this purpose the stair case procedure was used. An important issue is the geometry of the specimens, since this can affect the initiation of fatigue cracks, and therefore the resulting fatigue limit, significantly. Relevant aspects are crack initiation at corners or at the cast skin.

Furthermore “normal” S-N curve testing is performed in order to obtain an overall impression of the stress dependence of the fatigue life.

Additionally, crack growth experiments under constant amplitude loading were performed and threshold values, $\Delta K_p$, were measured. The tests were performed on three specimen thicknesses with approximately the same amount of carbon, but different sizes of the graphite nodules. The defect square root area theory of Murakami is applied to predict the fatigue limits.

2 Creep and Creep-Fatigue Interactions

2.1 Crack Growth in Asphalt (M.I. Arbouw, J. Zuidema; R.L. Krans [Dienst Weg- en Waterbouwkunde, Rijkswaterstaat, Delft]; F. Tolman [Netherlands Pavement Consultancy])

The study is continued on the fatigue crack growth rate behaviour of asphalt with a special emphasis on the creep-fatigue interactions in this material. Fatigue and creep crack growth experiments in sand asphalt specimens have been carried out in centre-cracked tensile set-ups at 0 °C. Specimen thickness, frequency and $R$-value (load ratio) have been varied. Most of the tests were constant load experiments, but a constant $\Delta K$ experiment was carried out also.

Paris law, relating crack growth rate $\frac{da}{dN}$ and $\Delta K$, describes the results well. Results of tests at different frequencies $f$ can be reduced to a single scatter band by plotting $\frac{da}{dt} = f \frac{da}{dN}$ instead of $\frac{da}{dN}$ versus $\Delta K$. It is concluded that the dominant crack growth mechanism in this type of asphalt and under the investigated circumstances is creep for positive $R$-values. A model has been successfully developed for the prediction of creep-fatigue interactions as a function of the (positive) stress ratio $R$ and the frequency $f$. For negative values of $R$ the explanation of the results is more complicated. The reason is that now also a real fatigue component of crack growth exists. A preliminary model is developed to describe crack growth under combined fatigue and creep mechanisms of crack growth.

The tests are performed on two kind of asphalt materials: fine sand asphalt material (with 2 mm stones max.) and dab 08 (with 8 mm stones).

3 Environmental Effects

3.1 Hydrogen Embrittlement in Steel (A.H.M. Krom, A. Bakker; R.W.J. Koers [Shell Research, Amsterdam])

This project was terminated in 1998 and led to the Ph.D. thesis of A.H.M. Krom

4 Failure

4.1 Fracture Toughness of Thin Nodular Cast Iron (C.J. Boone, M. Janssen)
The $J$-$R$ curve was determined for nodular cast iron with different nodule morphologies, i.e. different nodule sizes and relative distances. These differences were obtained by varying the wall thickness and thus creating different solidification conditions. Table 1 gives an overview.

<table>
<thead>
<tr>
<th>Material thickness [mm]</th>
<th>Nodule morphology density [mm$^{-2}$]</th>
<th>Nodule morphology spacing [μm]</th>
<th>Nodule morphology size [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>400-650</td>
<td>54</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>1300 - 1650</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>5500 - 7200</td>
<td>16</td>
<td>14</td>
</tr>
</tbody>
</table>

The tests on the 7 and 4 mm thick material were performed with standard 3-point bend specimens (SENB). As was already reported last year, it was necessary to use a non-standard test geometry for 2 mm thick material, i.e. the Single Edge Notched Tensile specimen (SENT). The results for this geometry were validated by testing 4 mm thick specimens also.

In Figure 1 the fracture surfaces are shown of the stable crack extension in the SENT specimens. From these surfaces the original nodule morphology can still be recognized; many nodules are even still present and intact. The material surrounding the nodules shows strong deformation indicating coalescence of the cavities in which the nodules are present.

Since graphite can hardly withstand tensile stresses, it seems reasonable to assume that in the crack tip region the mechanical behavior of nodules resembles that of voids. Rice and Johnson developed an approximate model for describing plastic deformation at a crack tip under plane strain conditions. They used this, among other things, to calculate the critical crack tip opening displacement ($\Delta a$) at the moment a crack extends to a void with diameter $2R_o$ at a distance $X_o$ straight ahead of the crack tip.

This model is used to make predictions for the current three nodule morphologies. $J_c$ values are calculated from $\Delta a$ values by using the relation

$$J_c = 2\sigma_y \Delta a,$$

where $\sigma_y$ is the yield strength which is equal to about 350 MPa. For $X_o$ and $2R_o$, values are assumed equal to the nodule spacing and nodule size respectively given in

Figure 1: Stable crack extension in 4 and 2 mm thick SENT specimens (---l = 20 μm)
Table 1. In Table 2 the predicted $J_c$ values are shown along with the (average) experimentally determined values.

<table>
<thead>
<tr>
<th>Material thickness</th>
<th>$J_c$ [N/mm]</th>
<th>$J_{lc}$ [N/mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 mm</td>
<td>35</td>
<td>20.7</td>
</tr>
<tr>
<td>4 mm</td>
<td>20</td>
<td>19.6</td>
</tr>
<tr>
<td>2 mm</td>
<td>8.4</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Although the experimental and predicted values clearly differ, the tendency is the same, namely a decreasing fracture toughness for smaller nodules which are closer to each other.

In 1998 this project was terminated, at least for the time being.

4.2 Fracture Behaviour of Metal Matrix Composites (K.M. Mussert, A.C. van Gorp, A.H.C. Duwel, M. Janssen, A. Bakker; S. van der Zwaag [MIDEG])

Fracture in an AA 6061 based metal matrix composite (MMC) containing 20 vol.% $\text{Al}_2\text{O}_3$ particles is modelled using an axisymmetrical finite element model and a statistical approach for calculating the strength of reinforcing ceramic particles via the Weibull model. Data obtained from these calculations is used to model damage evolution using the modified Gurson damage model.

The continuum is considered to consist of a periodic assemblage of hexagonal cylindrical unit cells approximated by circular cylinders, which allows for a simple axisymmetrical calculation whereby the finite element mesh consists of 350 isoparametric quadrilateral 4-node elements, see Figure 2. The MMC is modelled with a matrix of AA 6061 ($E = 69$ GPa, $\nu = 0.33$, $\sigma_{ys} = 276$ MPa) and $\text{Al}_2\text{O}_3$ particles with a diameter of 4 $\mu$m ($E = 393$ GPa, $\nu = 0.27$, $\sigma_{ys} = 2000$ GPa, this is a fictitious high value to prevent plastic deformation in the particle). To keep triaxiality constant during the loading history, the ratio $\rho = \sigma_{11}/\sigma_{zz}$ has to remain constant.

In case of a uniform stress distribution, the survival probability, $S$, of a ceramic particle volume, $V$, is governed by:

$$S = \exp \left[ \frac{V}{V_0} \left( \frac{\sigma}{\sigma_0} \right)^m \right]$$

where $\sigma$ is the stress in the particle, $\sigma_0$ and $V_0$ are two constants with dimensions of stress and volume respectively, and $m$ is the Weibull modulus. This equation can be
rewritten, allowing a straight line representation with slope $m$, when $\ln \ln (1/S)$ is plotted against $\ln \sigma$:

$$\ln \ln \frac{1}{S} = \ln \frac{V}{V_0} + m \ln \sigma - m \ln \sigma_0$$

By plotting the calculated survival probability of an $\text{Al}_2\text{O}_3$ particle versus the macroscopic axial stress applied on the whole MMC, the applicability of Weibull statistics on these type of new materials is checked, see Figure 3.

![Figure 3: The survival probability $S$ as a function of macroscopic axial stress $\sigma_{zz}$ for a particle with a diameter of $4 \mu m$ with loading histories $\rho = 0, 0.1, 0.3, 0.5$ and $0.7$ ($m = 15, \sigma_0 = 350 \text{ MPa}, \sigma_{yy} = 276 \text{ MPa}$ and $n = 14.94$)](image)

It can be concluded that in case of $\rho = 0.5$ and $0.7$, the survival probability of the ceramic particle is governed by a Weibull distribution, whereas for $\rho = 0, 0.1$ and $0.3$ this is no longer the case from the point where curvature starts.

Using the cell model described above, damage evolution in terms of the description of the failure probability of individual particles is analysed. To investigate the role of particle-particle interactions and the spread of damage in MMCs, a more Gurson-like approach is used, which is based on spherically symmetric deformations around a single spherical void. To take the interaction of neighbouring ceramic particles into account, it is assumed that a certain volume fraction of broken particles is present in the MMC and that the percentage of broken particles is equal to the failure probability of an individual particle. A disk shaped compact tension specimen (which is also used for experimental testing) is modelled. This finite element mesh (Figure 4) consists of 2368 plane strain quadrilateral 4-node elements.

![Figure 4: Finite element mesh used for calculations](image)

Since the software does not yet support the implemented void nucleation model.
properly, this forced us (for the time being) to a rigorous simplification, assuming that all particles in the vicinity of the crack tip are fractured from the beginning. For the composite with 20 vol.% of Al₂O₃ particles, the computations were therefore performed with an initial void volume fraction of 0.20. The critical void volume fraction, \( f_c \), was set at 0.25, as derived from a void cell model computation for \( p = 0.7 \) and the failure void volume fraction \( f_F \) was 0.35. In Figure 5, the calculated load and J-integral are plotted versus the displacement of the nodes where the load is applied, *i.e.* the load-line displacement.

![Figure 5: The calculated load and J-integral as a function of the load line displacement](image)

It is observed that both the load and the J-integral 'collapse' at the same time. According to a manufacturer of an MMC consisting of an AA 6061 matrix reinforced with 20 vol.% Al₂O₃ particles, the fracture toughness value, \( K_{IC} \), of this material should be approximately 20 MPa√m. The matching \( J_c \)-value (with \( E = 108 \text{ GPa} \)) is 3.3 N/mm, which is almost the value at which the calculation starts to diverge.

4.3 **Prediction of Fracture Initiation using Local Fracture Criteria (G. Pape, A. Bakker)**

The failure behaviour of dynamically (transient) loaded welded steel structures can be assessed if the fracture initiation behaviour of the material is known. An important aspect in this assessment is the effect of high strain rates on the fracture initiation process. The different material properties of the weld and heat-affected zone have to be taken into account also.

High rate tensile tests will be performed on specimens taken from the steel plate, the weld material as well as the heat affected zone. The resulting data will be used as input for finite element calculations. In these calculations use will be made of a local fracture criterion which accounts for the accumulated damage during deformation. Using this local fracture criterion, a prediction can be made of the initiation of fracture.

In order to verify the used local fracture criteria model, the laboratory experiments (tensile tests) will also be simulated and the results compared. Another verification follows from predicting failure in (scaled down) structural components that will be tested experimentally.
Previously experiments were performed on smooth tensile specimen tested at different strain rates. During these experiments the load was measured using a piezoelectric transducer. However, at high loading rates (up to testing velocities of approximately 6 m/s) severe oscillations were measured. To verify whether these oscillations actually occur in the specimen, the load was also measured on the elastic part of the specimen (see Figure 6). For this purpose two strain gages were used at both sides of the specimen, thereby eliminating possible bending strains from the results. It was also verified that both the strain gages and the amplifiers provide sufficient bandwidth to produce reliable strain signals.

A typical example of the results is shown in Figure 7. Clearly, oscillations that occur in the piezoelectric load signal, are not visible in the strain gage measurements. Apparently these oscillations do not have a mechanical nature or at least do not affect the actual stresses occurring in the specimen. Therefore, to eliminate oscillations in the piezoelectric load signal, it is filtered with a moving average technique. Although the filtered signal still shows some low frequency oscillations, it is in good agreement with the strain gage signal.

In future tests the signal from the piezoelectric transducer, after elimination of harmonic oscillations, will be used to provide the load data. The deformations will be derived from high speed film pictures using image analysis software. Combining the load and deformation data the flow curve for the material can be derived and fitted into a constitutive model. This will provide the material data input for finite element calculations.

Attempts will be made to account for the effect of adiabatic heating of the specimen during high rate plastic deformation. After the materials constitutive behaviour has been derived from experiments, the fracture initiation behaviour will be examined experimentally. By using different notch geometries the triaxiality of the stress state is...
varied and the effect on the fracture initiation behaviour can be determined.

![Graph showing load history during high rate tensile test](image)

**Figure 7**: Loading history during high rate tensile test. PZ = Piezoelectric load transducer, SG1 and SG2 = Strain gage load signals

4.4 **Micromechanical Based Critical Flaw Size Prediction** (C.H.L.J. ten Horn, A. Bakker; G. den Ouden, E. van der Giessen [MIDEG]; R.W.J. Koers, J.T. Martin [Shell Global Solutions])

Due to a welding process, material properties are influenced by the temperature history. However, material properties are also affected by plastic deformations that occur. These phenomena, which both can cause residual stresses to build up, are closely linked, providing a large amount of complexity. Therefore a two-step approach is used.

As a first step it was chosen to only evaluate the effect of plastic deformations and the associated residual stresses on the material properties, while eliminating the effect of the temperature history. A practical problem which is considered to be representative for this case, is the reeling process of pipelines.

![Diagram of pipeline reeling process](image)

**Figure 8**: The stages during the reeling process of a pipeline

In the oil and gas industry, pipeline is manufactured and welded off location. However, to enable transport the initially straight pipeline has to be reeled. In Figure 8 a schematic overview is given of this reeling process. Four stages can be identified. During the first stage the initially straight pipeline is reeled onto a drum. In the second stage the pipeline is unreeled by pulling it from the drum onto the aligner. In the third stage, the pipeline is aligned to obtain a constant radius of curvature for the pipe. This stage also positions the pipe at the right angle for laying the pipe. Finally the pipeline is straightened. As a consequence of the reeling process the pipeline will be
subjected to cyclic plastic deformation.

In this research a pipeline is considered with a diameter of 168 mm and a wall thickness of 19 mm. During the reeling process the outer fibre of the pipeline is subjected to deformations up to 2.5%. In previous studies it has been found that the reeling process affects the mechanical properties of the material. In particular the yield strength and the fracture toughness of the material seems to be reduced. Also the brittle to ductile transition temperature shifts to higher values.

Since the main objective is the prediction of critical flaw sizes, the drop in fracture toughness due to the reeling process was investigated first. Finite element simulations of the reeling process were performed using the Gurson – Tvergaard damage model. This model implements void nucleation, growth and coalescence in a finite element model. The first preliminary results show a significant reduction in fracture toughness of reeled material compared to virgin material.

For the verification of the finite element results, it is intended to also simulate the reeling process experimentally. These experiments should show the drop in fracture toughness and yield strength and the shift in transition temperature.

With regard to the effect of temperature history and associated residual stresses on the material properties, a separate assessment will be made using a finite element model. Ultimately the results of both assessments will be combined into a single model to predict the critical flaw size.

4.5 Fracture Toughness of High-Chromium White Cast Iron (M.B. van Leeuwen, M.Janssen; M.F. Mendes de Leon [IHC Holland, Parts & Services, Kinderdijk, The Netherlands])

A preliminary investigation is performed in how to quantify the fracture toughness for this very brittle material. A relatively simple way of obtaining fracture toughness information of a material is the use of the Charpy Impact test (ASTM E 23). However, besides the fact that the conditions are not well defined from a fracture mechanics point of view, this test does not yield any information about the strength of the material under dynamical loading. This drawback can be overcome by using instrumented test equipment so that the forces that act on the specimen can be measured. Therefore tests were performed with an instrumented drop-weight tower.

Manufacturing specimens of high-chromium white cast iron is very cumbersome and expensive. For the drop-weight tests U-notched Charpy specimens were manufactured using electric discharge machining. However, questions that still need to be answered, relate to the most convenient specimen shape and size and to the position and orientation of the specimen relative to the casting-mould.

An investigation with a tentative nature which was also initiated is to roll slabs of cast iron to different reduction percentages at a relatively high temperature. This is an attempt to improve the fracture toughness by breaking-up the network of primary carbides. Due to experimental problems the results are not yet available.

PUBLICATIONS

P.C.H. Ament
Corrosion Fatigue of Structural Steel in Sea Water

S.P. Chen, K.M. Mussert, S. van der Zwaag
Precipitation kinetics in Al6061 and in an Al6061-alumina particle composite

C.H.L.J. ten Horn, A. Bakker
Fracture toughness evaluation using circumferentially cracked cylindrical specimens

M. Janssen (ed.)
Research in Materials Science and Technology - Annual Report 1997

M. Janssen, C.J. Boone
Fracture toughness of thin nodular cast iron

A.H.M. Krom
Numerical modelling of hydrogen transport in steel

K.M. Mussert, M. Janssen, A. Bakker, S. van der Zwaag
Modelling fracture in aluminium based metal matrix composites using a statistical approach

G. Pape, A. Bakker
High rate deformation behaviour during explosion loading of steel

L. Varkoly, J. Zuidema, B. Varkolyova, M. Chalupova
Fatigue Failure of Materials, theory & solved examples
University of Zilina, Zilina (1998) 235

C.J. van der Wekken, P.C.H. Ament, M. Janssen, J. Zuidema
Predicted and experimental corrosion fatigue crack growth rates of anodically polarised steel in deaerated sea water

J. Zuidema, J. Schulte, R.L. Krans, F. Tolman
Creep-fatigue interactions during crack growth in a fine-sand asphalt concrete mixture
In this research, a popliteal a. cond. 2531. in the situs region of the aorta, was subjected to a cyclically changing strain of 30% in the longitudinal direction. The aorta was subjected to 60 cycles of strain during the test. During the cyclic loading, the aortic wall thickness increased by 2.5%. In previous studies, it has been shown that the aortic wall thickness increased by 1.5% after 10 cycles of strain. The increase in wall thickness was attributed to the formation of aortic plaques. The present study confirms this finding.

Since the main objective is the prediction of clinical flow states, the strain-stress-strain relationships of the aortic wall were performed using a finite element model. This model incorporates the effects of viscoelasticity and anisotropy. The results of this model show a good agreement with experimental data. The model also predicts the effects of temperature on the aortic wall properties. The model is capable of predicting the effects of aging on the aortic wall properties.

4.5. Artificial Intelligence Techniques in Medicine

A preliminary investigation of the use of artificial intelligence techniques in medicine was conducted. The results of this study show that artificial intelligence techniques can be used to improve the accuracy of medical diagnosis. The artificial intelligence techniques used in this study included neural networks and fuzzy logic. The results of this study show that these techniques can improve the accuracy of medical diagnosis. The study also shows that artificial intelligence techniques can be used to improve the efficiency of medical diagnosis.

PUBLICATIONS

P.D. Ansell
Commen dent of Brudicic Schlo in Bioe Sci
Ph.D. theel, Delt University of Technology, Delh University Press, Delt (1990), 197
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dr. B.-N. Nguyen (from 1-12-1997)
dr. S.M. Schloegl (from 1-5-1997)
dr. D.M. Weygand (since 1-11-1998)

Graduate students
A.A. Baqi, M.Sc.
ir. H.H.M. Cleveringa
ir. P.R. Onck
drs. K.G.W. Pijnenburg (since 1-3-1997)
ir. M.G.A. Tijssens

HIGHLIGHTS

Dr. ir. P.R. Onck was granted a research fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW).

RESEARCH AREAS AND OBJECTIVES

1 Plasticity of Metals

The objective is the development of a class of models that provides a quantitative link between the structure of the material and, ultimately, its macroscopic elastoplastic behaviour. Models are considered at several length scales. Metallic foams are considered at the length scale of the foam cells. Polycrystal behaviour is formulated on the basis of so-called crystal plasticity models which describe the elastoplastic response of individual crystals. These models are based on a description of slip on discrete slip systems, and provide a solid and natural basis for accounting for microstructural phenomena as e.g. texture development. On a smaller scale, models are explored to describe plasticity on the basis of discrete dislocations. These models serve as "input" for the crystal plasticity models, but also provide a means to study small-scale plasticity problems where a continuum description of dislocations breaks down.

1 Part of the work reported here has been carried out within the "Onderzoeksschool Polymeren PTN" or in the "Onderzoeksschool Engineering Mechanics".
2 Deformation and Fracture of Polymers and Blends

Within this theme, a number of projects are concerned with the deformation and fracture of polymers (including rubbers and polymer blends). As far as deformation behaviour is concerned, current emphasis is on the viscoplastic behaviour of amorphous polymers and of semicrystalline polymers. In addition, the development is studied of failure in these polymers and associated polymer blends by crazing in competition with plasticity.

3 High-Temperature Failure of Polycrystalline Materials

Fracture of polycrystalline metals, alloys and ceramics at elevated temperatures often occurs by the nucleation, growth and coalescence of microscopic cavities at grain boundaries. A comprehensive micromechanical model of creep rupture is being developed, which aims at quantitatively relating microstructural properties on the scale of cavities or grains to the macroscopic creep fracture parameters. In addition to creep conditions, cyclic loading and the influence of the environment (e.g., hydrogen) is studied.

4 Failure of Brittle Materials and Coatings

Fracture in materials that are inherently brittle, like ceramics, or that behave in a brittle manner under certain conditions, is often much more complicated than the simple textbook notions assume. As a rule, brittle fracture is characterised by the occurrence of micro-cracking and strongly serrated crack propagation paths, involving crack branching, crack kinking etc. In the case of coatings, these features interact with other failure mechanisms, such as delamination along the interface with the substrate. In this field, we are interested in the physical factors controlling these fracture features, their mechanistic description and the resulting overall characteristics.

FACILITIES

- a cluster of workstations: Silicon Graphics Indy's, Challenge M, Indigo2 Extreme and O2's;
- a five-node Silicon Graphics Challenge L server;
- a four-node Silicon Graphics Origin 200.

RESEARCH REPORT 1998

1 Plasticity of Metals

1.1 Discrete Dislocation Plasticity (H.H.M. Cleveringa, D.M. Weygand, E. van der Giessen; A. Needleman [Brown University]; D. Srolovitz [University of Michigan]; J.Th.M. De Hosson [MIDEG])

In this work, plastic deformation is studied at length scales of the order of microns. At this length scale a continuum plasticity theory involving a smeared out description of dislocations may no longer be appropriate. Therefore we have developed a model to treat dislocations as discrete entities. The collective behaviour of these dislocations determines the plastic flow. The difference of this model with other models describing plastic flow using discrete dislocations is that this model allows for the solution of boundary value problems. The boundary conditions are accounted for by means of a
finite element discretisation of the elastic continuum in which the dislocations are embedded. To simulate realistic behaviour of dislocations we introduce rules for creation and annihilation of dislocation, for pinning at obstacles and their subsequent release. The motion of the dislocations are governed by a linear drag relationship. This year we finalised a study of bending of a small single crystalline strip using this type of discrete dislocation plasticity model. Cases with multiple slip systems and with a single slip system are presented. The bending moment versus rotation relation and the evolution of the dislocation structure are outcomes of the boundary value problem solution. The effects of slip geometry, obstacles to dislocation motion and specimen size on the moment versus rotation response are considered. Also, the evolution of the dislocation structure is studied with emphasis on the role of geometrically necessary dislocations. The dislocation structure that develops leads to well-defined slip bands, with the slip band spacing scaling with the specimen height. Size effects and slip band spacing are features of bending that have been observed in experiments but that are not accessible by continuum theories.

Figure 1: Dislocation distribution for a mode I crack problem after some amount of crack propagation. The curve below the horizontal axis shows the crack profile.

The big advance during this year was the completion of a framework to model the discrete dislocation plasticity in the neighbourhood of a mode I crack. We consider symmetry around the crack plane. To model propagation of the crack we introduce a cohesive surface in front of the crack tip. This cohesive surface is governed by a traction–separation law that mimics the separation of atomic planes. We assume small-scale yielding which means that dislocation activity is confined to a region close to the crack tip. Compared to previous discrete dislocation studies, we use a different
approach to describe the stress and strain fields of a dislocation. We developed an analytical formulation to describe edge dislocations in a half-space. In this half-space dislocations feel a traction-free surface at the symmetry plane. The dislocations can move on two types of slip systems which are located symmetrically with respect to the crack plane. Sources and obstacles are distributed randomly on these slip planes. A main focus in this kind of study is the brittle-ductile transition in the material. In the simulations we see a strong interaction between the crack tip and the dislocation structure. When the stress state at the crack tip is high enough for the crack to propagate, this propagation does not occur in a smooth manner, but in spurts. The crack moves until the dislocation structure forms a lock in front of the crack tip. When we increase the density of the obstacle structure we see a transition from a more ductile behaviour to a more brittle behaviour. Figure 1 shows the dislocation structure in a region very near to the crack tip for a case that revealed rather brittle behaviour. The curve below the horizontal axis shows the profile of the crack. The initial crack tip was located at (0,0).

Other applications of the same technique are explored in the group of prof. J.Th.M. De Hosson (MIDEG) in relation to high-rate localised shearing; this work will be reported in the Chapter elsewhere in this Report.

1.2 Mechanics of Metal Foams (P. R. Onck; E. W. Andrews, L. J. Gibson [MIT]; J. W. Hutchinson [Harvard University])

Recent development of cost-effective processing techniques of metal foams has increased their potential for use in a wide range of applications, such as structural sandwich panels, energy absorption devices and acoustical damping panels. For these materials to be used in a given structural application, the designer must have knowledge of basic mechanical properties like stiffness and strength. Standard tests are currently being developed to evaluate the mechanical properties of these materials. An important issue in this is the effect of specimen size on the measured properties. Size effects arise when macroscopic dimensions of the specimen become of the order of the material's microstructure. Though absent in testing of most dense materials, size effects must be addressed for foams due to their relatively large material length scale (the cell size).

We have studied the effect of specimen size on the mechanical properties of aluminium foams. Size effects have been investigated experimentally for uniaxial compression, shear and indentation. While the stiffness and strength decrease with decreasing specimen size for uniaxial compression, they increase with decreasing specimen/indenter size for shear and indentation. To interpret the experimental results, a two-dimensional hexagonal honeycomb has been adopted as a model material. Using classical tools from structural mechanics, the microstructural origin of the different size effects have been traced back and related to the constraints imposed by the boundary conditions.

2 High-Temperature Fracture

2.1 Creep Rupture in Polycrystalline Materials (P. R. Onck, B.-N. Nguyen, E. van der Giessen)

Polycrystalline materials at elevated temperatures under creep conditions are often subject to intergranular cracking. The relevant damage mechanisms at the micro-scale are viscous grain boundary sliding, nucleation, growth and coalescence of
cavities leading to microcracks while the linking-up process of microcracks leads to a macroscopic crack.

Last year, a small-scale damage microstructural approach proposed previously was explored to investigate the creep crack growth from an initial sharp crack as well as from an initial blunt crack (Ph.D. thesis of P.R. Onck). In this approach, the polycrystal is represented by a process window situated at the crack tip and discretised by so-called grain elements connected by interface elements which incorporate these damage mechanisms. The process window is surrounded by a standard creeping continuum submitted to remote boundary conditions corresponding to a HRR field representing the crack-tip field in a steadily power-law creeping material.

This year, our attention was focused on the crack-tip constraint effects on creep fracture. At first, we established a formulation of higher-order crack-tip fields in creeping solids which can be derived from an asymptotic development analogous to that for elasto-plastic bodies. These fields are controlled by three parameters: $C^*$, $A^*_n$ and $\sigma_{\text{eq}}$. The latter govern the magnitude of the higher-order fields, and thus account for the constraint effects due to geometry and loading configuration. Furthermore, by carrying out simulations of steady-state creep we evidenced significant deviations of the near-tip fields with respect to the HRR creep solution in some selected specimens (with different crack depths). To investigate the role of crack-tip constraint effects on creep crack growth, we again used the above-mentioned microstructural modelling approach but imposed higher-order fields as remote conditions. The results issued from this study showed that a negative value of $A^*_n$ tends to reduce the diffuse damage above the crack tip. On the overall behaviour, its effect in ductile cases is to delay the crack advance and to decrease the growth rate, while it has an almost negligible effect on more brittle crack growth. Finally, with the use of higher-order fields, we could also partially explain the specimen size effect observed experimentally: at the same value of $C^*$, crack growth in a smaller specimen is slower than crack growth in a larger specimen.

2.2 Hydrogen Attack (S.M. Schlögl, E. van der Giessen)

Hydrogen attack (HA) is a phenomenon occurring in steels exposed to high pressures of hydrogen at elevated temperatures. During this process, the dissolved hydrogen reacts with the carbides of the steel to form methane in grain boundary cavities. The methane pressure inside these cavities depends on the microstructure of the used steel which consists of a ferritic matrix and alloy carbides such as $M_7C_3$, $M_{23}C_6$, $M_6C$ and $M_2C$.

We developed a thermodynamic model where we described the different phases in the multicomponent system Fe-Cr-Mo-V-C with the sublattice model. Their Gibbs energies were then used to calculate the equilibrium methane pressure in dependence of the microstructure. Figure 2 shows the equilibrium methane pressures at 720 K calculated for various carbides found in standard 2.25Cr-1Mo steel when they are exposed to different hydrogen pressures. Among the four different carbide types, $M_7C_3$ is found to be the most unstable one, leading to a methane pressure of 210 MPa at a hydrogen pressure of 20 MPa.

Furthermore, we developed a finite element code for HA in a welded reactor. The axisymmetric finite element accounts for the four main microstructural regions: the weld metal (WM), the coarse grained heat affected zone (CGHAZ), the fine grained heat affected zone (FGHAZ) and the base metal (BM). These differ in grain size, carbide type and carbide composition, and they possess different creep properties. Most damage is predicted for the FGHAZ, somewhat less for CGHAZ, followed by WM
while BM shows the least damage. The computations also reveal that the damage process is accompanied by severe stress redistribution, especially in FGHAZ and CGHAZ. The redistribution can be so strong that compressive stresses develop in the FGHAZ at the inner radius. Evidently, this has a dramatic consequence on the predicted time to coalescence, and amplifies earlier suggestions that lifetime predictions in these situations cannot be based on stress states corresponding to steady creep.

![Figure 2: Computed equilibrium methane pressure $P_{CH}$ for carbides found in standard 2.25Cr-1Mo steel at 720 K in dependence of the hydrogen pressure $P_{H}$. The ferrite contains 1.7% Cr and 0.3% Mo.](image)

3 Deformation and Fracture of Polymers

3.1 Failure of Polymer-Rubber Blends (K.G.W. Pijnenburg, E. van der Giessen; R.J. Gaymans [Twente University])

Many brittle glassy polymers are toughened by way of blending in small rubber particles. The basic mechanism is that when the material is deformed, plasticity is initiated at the rubber particles and takes place in a larger volume, increasing the energy dissipation. The deformation mechanisms and the relation of particle properties and toughening efficiency has been the subject of many studies, but still the precise mechanisms are not well understood. Moreover, a quantitative description of the deformation processes at a micro scale is lacking. The objective of this project is to investigate the deformation processes in well-defined blends of styrene-acrylonitril (SAN) with various core-shell rubber particles following a combined experimental-modelling approach.

Last year we studied the behaviour of a polymer-rubber blend using a 2D unit cell model under shear deformations. This model has been expanded during this year to incorporate more general types of deformation, but this time for a cavitated blend. We find that all important characteristics of the shear deformation are also found in more general loading conditions. In particular we always see a shear band initiating in the ligament between two particles. With continued deformation the material in this shear band locks, which causes the band to propagate outward. The existence of a shear band that connects two adjacent rubber particles enables the material to deform macroscopically and a decrease in overall stress is observed.
The simulations also revealed a rather surprising finding. The maximum stress level reached during the deformation may be regarded as a yield point on a macroscopic scale. The location of these yield points in stress space, as a function of deformation type, defines a yield curve. We have found that the yield curves do not depend on the void volume fraction directly, but rather on the size of the ligaments in between the particles. Because of this, standard models for porous materials, such as the Gurson model, will not describe the behaviour of the polymer blend correctly. In fact, they tend to substantially overestimate the actual macroscopic yield curve. While the Gurson model has been more or less validated for porous metals, its limited success for polymeric porous materials is due to (1) the different plastic flow characteristics and (2) the significantly higher yield strain.

3.2 Fracture of Polymers under Impact Conditions (R. Estevez, E. van der Giessen; R.J. Gaymans [Twente University])

The objective of this project is to predict the macroscopic fracture or crack growth characteristics in terms of appropriate macroscopic constitutive models, involving plasticity through the 'shear yielding' mechanism, crazing, and possibly cavitation of blends, all in dependence of the local temperature and strain-rate. In particular, the purpose is to give an explanation for the unexpected toughening phenomena at high strain-rates observed experimentally.

Work during this year has been devoted to the extension of a previous study on the development of the plasticity around a crack tip for a mode I loading by analysing the competition between shear yielding and crazing in glassy polymers, for isothermal conditions. Having established the link between the particular plastic zone shape and the specific stress-strain response (especially to the softening immediately following upon yield and subsequent orientational hardening), we now accounted for crazing by embedding Cohesive Surfaces in the continuum. The model for this has been developed in collaboration with the project to be described in Section 4.1. The crazing mechanism is thought to proceed in two stages: (1) initiation and (2) widening of crazes by drawing in new polymer material from the craze-bulk interface. To model the mechanical response of the crazes, we use the Sterstein and Myers criterion (1973) to define a critical stress state (a combined tensile and hydrostatic stress) for craze initiation, and a visco-plastic formulation of the widening process. To complete the description, we assume a critical extent of craze widening corresponding to a critical length for craze fibrils before their break down. From these mechanical craze characteristics, one is able to obtain the corresponding traction-opening law for the Cohesive Surfaces.

A qualitative parameter study shows that once crazing initiates, all the deformation becomes concentrated at the craze front leading to rapid failure when fibrils start to break down. Depending on the parameters in the initiation criterion, crazing initiates for different stress state levels and two situations can be distinguished: (i) Crazing takes place at the crack tip if craze initiation occurs in the elastic regime (prior to material yielding); (ii) otherwise, crazing nucleates in the bulk material where the maximum Mises effective stress is located. Some plasticity is developed around the crack tip in the latter case. Both phenomena have been observed in experiments. A relevant feature is that once crazing initiates, this mechanism becomes dominant in terms of damage and deformation localisation, and leads to unstable crack propagation. Thus, craze initiation is the signal of the material's failure, with the fracture toughness being controlled mainly by the sensitivity of craze initiation to hydrostatic stress vs. Mises effective stress.
4  Failure of Brittle Materials and Coatings

4.1  Discrete Decohesion Modelling of Brittle Fracture (M.G.A. Tijssens, E. van der Giessen; L.J. Sluys [Faculty of Civil Engineering, Delft University of Technology])

Polymers typically exhibit two types of failure: shear yielding and crazing. In contrast to shear yielding, which results in relatively high energy dissipation, crazing is often the precursor to brittle fracture. Under special conditions, such as compressive loading, both thermoplastics and thermosets can be made to shear yield, but under tension many polymers fail in a brittle manner. Polymer blends are systems in which a dispersion of small rubber particles has been added with the intend to toughen the material by suppressing crazing and promoting shear yielding. In many blends, such as HIPS (high impact polystyrene) and ABS (acrylonitrile-butadien-styrene), crazing and shear yielding occur simultaneously. In these materials as well as in composites, multiple crazing occurs and is controlled by the microstructure. The way in which crazing initiates and propagates through these heterogeneous systems is however largely unknown.

The basic idea in the current project is to use separate discretisations of the continuum and the cohesive surfaces and the use of a large number of cohesive surfaces immersed in the continuum to incorporate sufficient freedom for cracks to develop. This approach avoids that the crack path has to be specified a priori. During this year we have developed the cohesive surface model for crazing in collaboration with the project described in Section 3.2. We have applied it, amongst others, to crazing around a hole in a plate under tension where crazes develop in a rather diffuse manner. It has been shown that the model is capable of capturing in a qualitative sense, the rate and temperature dependence of craze development, i.e. the polymer appears more brittle as the temperature decreases or the loading rate increases. It was also shown that the finite element results for these kind of calculations converge and do not suffer from mesh dependency.

4.2  Adhesion of Brittle Coatings on Ductile Metallic Substrates (A.A. Baqi, E. van der Giessen; J.Th.M. De Hosson, G. de With [MIDEG])

Brittle coatings on ductile substrates are used for protective or wear resistance purposes. Failure of these coatings can occur by a number of mechanisms including delamination, cracking or buckling. This project is part of a programme that aims at developing techniques to characterise the adhesion of such systems by means of indentation.

We have so far been carrying out pure indentation calculations for a ductile material coated by a brittle thin film. The aim of these computations is to study the stress distribution generated by the indentation process in the coated system. Special attention is given to the stresses at the surface of the film and at the film/substrate interface. Such stresses are of interest because of their role in coating failure.

The system we have studied is composed of an elastic-perfectly plastic substrate coated by an elastic thin film indented by a spherical or conical rigid indenter. Perfect sticking and perfect sliding conditions at the contact area have been investigated, but it was found that the stresses are only sensitive to the contact condition in the contact area. Therefore, perfect sticking has been assumed throughout the simulations. Because of the axisymmetry of both loading and geometry, an axisymmetric formulation is used. All calculations are done numerically using a finite strain, finite element method.
Stress distributions and the load-indentation depth data are the outcome of our current calculations. Depending on the depth of indentation, large tensile radial stresses occur at the surface of the coating outside the contact area and this may lead to a mode-I ring cracks. High shear stress is also seen at the surface, which might cause splitting of the indented part of the film. The interfacial stress component normal to the interface is of obvious importance for delamination when it is tensile, and this indeed occurs, outside of the contact area.

Force $F$ versus indentation depth $h$ data were also obtained. It was shown that at small indentation depths compared to the film thickness, the response is more of a Hertzian type, where $F \propto h^{5/2}$. At large indentation depths, $F \propto h$ for the spherical indenter which is caused by bending of the film and plasticity in the substrate. A conical indenter gives rise to a response at larger indentation depth that scales roughly with $h^2$.

**PUBLICATIONS**

M.W.D. van der Burg, E. van der Giessen, V. Tvergaard  
*A continuum damage analysis of hydrogen attack in a 2.25Cr-1Mo pressure vessel*  

H.H.M. Cleveringa, E. van der Giessen, A. Needleman  
*Discrete dislocation modeling of plastic flow processes*  

H.H.M. Cleveringa, E. van der Giessen, A. Needleman  
*Discrete dislocation simulations and size dependent hardening in single slip*  
Journal de Physique IV **8** (1998) P4/83-92

B.N. Nguyen, P.R. Onck, E. van der Giessen  
*Creep Crack Growth: From the Microscale to the Continuum Solid*  

A. Roos, J.Th.M. De Hosson, H.H.M. Cleveringa, E. van der Giessen  
*A computer simulation methodology of metal perforation*  

A. Roos, J.Th.M. De Hosson, H.H.M. Cleveringa, E. van der Giessen  
*Shear deformation at high strain rates using fast-moving dislocations: a computer simulation methodology*  

S.M. Schlögl, E. van der Giessen  
*Local versus global decarburization during hydrogen attack in a vessel*  

A.C. Steenbrink, E. van der Giessen
Micromechanics of Materials

Strain localization and void growth in polymers
A.C. Steenbrink, E. van der Giessen, P.D. Wu  
Studies on the growth of voids in amorphous glassy polymers
M.G.A. Tijssens, E. van der Giessen, L.J. Sluys
Micromechanically-motivated cohesive surface modelling of crazing in polymers
In: S.N. Atluri, P.E. O'Donoghue (eds.), Modeling and Simulation-based Engineering,  
P.D. Wu, K.W. Neale, E. van der Giessen
Effects of Strain Paths on Sheet Metal Limit Strains
P.D. Wu, K.W. Neale, E. van der Giessen, M. Jain, A. Makinde, S.R. MacEwen
Crystal Plasticity FLD Analysis of Rolled Aluminium Sheets
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HIGHLIGHTS

Dr. R. Benedictus was granted the Hoogovens Research Prize for his research "Thermodynamics and Kinetics of Solid State Amorphization", performed in our group.

RESEARCH AREAS AND OBJECTIVES

1 Thin Surface Layers and Interfaces
   1.1 Microstructure of, Stress Development, Diffusion and Phase Transformations in Multilayer Systems
   1.2 Formation, Microstructure and Internal Stresses of Surface Layers
   1.3 Structure of Grain Boundaries in Ordered Alloys

2 Phase Transformations in Iron-Based Interstitial Alloys
   2.1 Ageing and tempering of iron-based interstitial martensites
   2.2 The Austenite-Ferrite Transformation in Fe-C Alloys

3 Microstructural Imperfections and Diffraction-Line Broadening

4 High Resolution Electron Microscopy for Structural Analysis

FACILITIES

- Scanning electron microscope (Jeol, JSM 6400 F) equipped with a field emission gun and provided with a large specimen analysis chamber. This microscope is also equipped with an energy-dispersive X-ray microanalysis system (Noran Voyager III).
- Electron probe X-ray microanalyser (Jeol, JXA-733) equipped with four wavelength-dispersive spectrometers and one energy-dispersive system. This instrument is provided with Noran Systems TN5500 and TN5600 for instrument control, data acquisition and data analysis.
- Fully automated equipment for scanning Auger electron spectroscopy (PHI 4300 SAM). The system offers the possibility of Auger depth profiling, secondary electron imaging, back-scattered electron imaging and scanning Auger microscopy.
- Fully automated equipment for X-ray photoelectron spectroscopy (PHI 5400 ESCA). The instrument is provided with a dual anode X-ray source and an ion-gun for depth profiling. The system offers the possibility of small area analysis, angle-resolved photoelectron spectroscopy and low energy Ion Scattering Spectrometry (ISS).
• HP/Apollo workstations (DN 3500) for instrument control, data acquisition and
data analysis of the PHI 4300 SAM and the PHI 5400 ESCA systems.
• An UHV specimen processing chamber coupled to the PHI 5400 ESCA system.
  This chamber is provided with an ion-gun, two quadrupole mass spectrometers,
a specimen heating device and a unit for controlled admission of reactive
gases. One quadrupole mass spectrometer (Balzers QMG 112) is used for
control and analysis of the gas composition. The other quadrupole mass spec-
trometer (Balzers QMG 422) is used for Secondary Ion Mass Spectrometry
(SIMS).
• A Philips CM30T high-resolution transmission electron microscope (HREM)
equipped with a twin lens. It can also be used in scanning mode (STEM) and
quantitative X-ray micro-analysis (LINK system) can be applied.
• A Philips CM30UT-FEG 300 kV high-resolution transmission electron micro-
scope equipped with an ultratwin lens and a field emission gun (FEG). Quanti-
tative X-ray analysis (LINK system) Electron Energy Loss Spectroscopy
(PEELS of Gatan) can be applied. Both an off-axis CCD camera (for real time
image acquisition) and a slow scan 1024 x 1024 pixel camera (for high quality
image and diffraction acquisition) are present.
• EM400 transmission electron microscope (TEM) equipped with a twin lens. It
can also be used in the scanning mode (STEM) and quantitative X-ray micro-
analysis (Tracor system) can be applied.

Table 1: The most important properties of the microscopes at the NCHREM (Delft).

<table>
<thead>
<tr>
<th></th>
<th>CM30T</th>
<th>CM30UT-FEG</th>
<th>EM-400</th>
<th>CM200-FEG available in 2001</th>
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<tr>
<td>maximal voltage</td>
<td>300</td>
<td>300</td>
<td>120</td>
<td>200</td>
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<tr>
<td>point resolution (nm)</td>
<td>0.23</td>
<td>0.17</td>
<td>-0.4</td>
<td>0.19</td>
</tr>
<tr>
<td>tilt possibilities</td>
<td>±45°</td>
<td>±28°</td>
<td>±45°</td>
<td>±28°</td>
</tr>
<tr>
<td>information limit (nm)</td>
<td>0.20</td>
<td>0.10</td>
<td>-0.2</td>
<td>0.10</td>
</tr>
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<td>boron</td>
<td>boron</td>
<td>boron</td>
<td>boron</td>
</tr>
<tr>
<td>probe size for EDS</td>
<td>1.5</td>
<td>0.7</td>
<td>10</td>
<td>0.2</td>
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<tr>
<td>STEM probe size (nm)</td>
<td>1.0</td>
<td>-</td>
<td>-3</td>
<td>0.10</td>
</tr>
<tr>
<td>EELS resolution</td>
<td>800 meV²</td>
<td>800 meV¹</td>
<td>-</td>
<td>50 meV³</td>
</tr>
<tr>
<td>energy filtered imaging</td>
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<td>-</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td>probe size for EELS (nm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2 nm²</td>
</tr>
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<td>Gatan</td>
<td>Gatan off-axis</td>
<td>-</td>
<td>1024 x 1024</td>
</tr>
<tr>
<td>video camera</td>
<td>Gatan</td>
<td>Gatan off-axis</td>
<td>-</td>
<td>Gatan off-axis</td>
</tr>
</tbody>
</table>

• On-line and off-line image processing facilities (TIETZ system, Macintosh, IBM)
are available for both CM30 microscopes.
• An IBM RS6000 58H computer is used for the collection and processing of
  through focus series of images and for structure reconstruction from electron
diffraetograms and HREM images.
• An advanced system to prepare and manipulate specimens, and to bring
  specimens into the microscope under a controlled atmosphere.
• Electrochemical polishing equipment (Struers) for specimen preparation.

² a PEELS system will be mounted by Philips on either CM30T or CM30UT
³ 0.2 nm at 500 meV, 2 nm at 50 meV
• Ion-mills (Gatan, Barna, Baltec) for the preparation of TEM samples.
• Automated X-ray powder diffractometers: two Siemens D-500 (one with a scanning position sensitive detection system; both D500's will be replaced in the near future), one D5005 theta-theta diffractometer, and a Siemens D5000 with Eulerian cradle. The present X-ray powder diffraction software is the Siemens Diffrac AT program package and rather comprehensive packages written in our laboratory for data collection, stress determinations and line profiles analysis (size-strain analysis). Most of the software will be updated along with the replacement of the diffractometers.

RESEARCH REPORT 1998

1 Thin Surface Layers and Interfaces

1.1 Microstructure of, Stress Development, Diffusion and Phase Transformations in Multilayer Systems

1.1.1 Growth Conditions, Microstructure and Stress Development in Multilayer Systems (H. Yang, A.J. Böttger, E.J. Mittemeijer; group of J.-E. Sundgren [Linköping University, Sweden]; O. Thomas [Université de Marseille, France]; B. Chenevier [Ec. Nat. Sup. de Grenoble, France]; F. Roux [Ion Beam Systems, Grèasque, France]; D. de Boer [Philips, Eindhoven])

The residual (growth) stresses of thin metallic (multi)layers has been measured by means of X-ray diffraction or by curvature measurements (Univ. Marseille). In addition X-ray diffraction line profile analysis (LPA) is used as a tool for studying crystal imperfections, in particular grain size and microstrains.

On the basis of compositional analysis (electron probe micro analysis), glancing incidence X-ray diffraction (Philips Natlab) and profile fitting of the superlattice peaks, the overall composition and the sublayer thicknesses were analysed. These results were used to establish the dependency of the deposition rate on the sputter pressure. For Ag and Ni the deposition rate is decreasing linearly with increasing Kr pressure when the deposition voltage is kept constant.

All pure Ag, Ni films (200 nm thickness) and Ag/Ni multilayers under investigation show a strong \{111\} fibre texture. This enables the application of XRD sin²θ method to different \{hkl\} reflections coming from the \{111\} family to determine the residual stress inside the material. To enhance the accuracy, Bragg peak positions were obtained by profile fitting after background subtraction, and systematic error in the peak positions (2θ) is corrected by measuring a reference ZnO specimen. Application of curvature and XRD methods yield comparable results for the overall stress in the (multi)layers.

Analysis of stresses in Ag (200 nm) and Ni (200 nm) single layers produced using 1, 5, 8 and 12 mTorr Kr sputtering pressure was performed. The results from pure Ni films strongly suggest an influence of sputtering gas pressure (between 1 and 12 mTorr Kr) on stress and microstructure of the film. The stress undergoes a transition from tensile to compressive stress with the decrease of the sputtering pressure. This is not the case for the pure Ag films which are in a tensile state of stress regardless the sputtering pressure used. LPA analysis, however, shows that sputtering pressure does alter the microstrain and grain size. An increase of sputtering pressure will lead to a smaller grain size and an increase of the microstrain.

Stress analysis of Ag/Ni multilayers (200 nm, 10-period, identical Ag and Ni sublayer
thickness) produced using 1, 5, 8 and 12 mTorr Kr sputtering pressure, shows that the sputtering gas pressure, although it drives the stress reversal in pure Ni film, does not affect the stresses in the pure Ag film and the Ag/Ni multilayers. The Ag and Ni sublayers are both in a tensile state of stress. Also the stress-free lattice parameters of Ag and Ni for the specimens under investigation is independent of the sputtering pressure.

Analysis of stresses in two sets of Ag/Ni multilayers (total thickness about 200 nm, 10-period, Ag sublayer thickness varied, namely 2.5, 5, 10, 15 and 17.5 nm) sputtered at 1 and 2 mTorr Kr gas pressure, respectively showed that: the sublayer thickness affects both the state of stress and the stress-free lattice parameter. An increase of the sublayer thickness (Ag or Ni) leads to a decrease of stress for that type of sublayers (Ag or Ni). The stress-free lattice parameter of Ag decreases with a decrease of the Ag sublayer thickness, whereas the stress-free lattice parameter of Ni increases with decrease of Ni sublayer thickness. This hints to some intermixing of Ni and Ag atoms at the Ni/Ag interfaces.

A set TiN/AlN multilayers (thickness about 150 nm) deposited on either MgO<001> or Si<100> substrates is investigated. The stress in the TiN layer is strongly related to the configuration of the TiN/AlN multilayers. The TiN layer of multilayers deposited on Si wafers possess a tensile stress, whereas those of multilayers sputtered on MgO substrates possess a compressive stress regardless the TiN-sublayer thickness (between 5 nm and 15 nm). In specimens of fixed TiN sublayer thickness (5 nm) and varying AlN sublayer thickness the stress in the TiN layers decreases with increasing AlN sublayer thickness. At an AlN sublayer thickness of about 3 nm the films are almost stress-free. This is tentatively attributed to a phase transformation of AlN from hexagonal to cubic structure occurring at about this thickness.

1.1.2 Microstructural Control of Multilayers. (J.F. Jongste, A.J. Böttger, E.J. Mittelmeijer)

Thin layers and coatings have found widespread application in practice for a variety of reasons. For example metallic (multi)layers are used for their electric, magnetic or diffusion-barrier properties in the microelectronics industry. Such multilayer systems are characterised by the extreme density of interfaces. The physics and chemistry of such interfaces is related to unusual and new phenomena of both fundamental and practical interest.

Phase transformations occurring at interfaces can not be understood on the basis of bulk thermodynamics, i.e. taking into account the interface energy contributions is imperative. Control of the microstructure of such systems is difficult at present because the parameters that control the microstructure are poorly understood. A particular interesting phenomenon is the presence of extremely high compressive macrostresses that can occur in sputtered layers (stresses up to -10 GPa do occur). Not only the macrostress is important for the properties of the multilayer e.g. adhesion to substrate but also the so-called microstresses varying on a local scale can be of decisive importance. An average value of the microstrain as high as 1% has very recently been observed in thin films. This may be a consequence of the very high interface density in association with the presence grown-in defects in the (sputtered) layers.

In this project the Cu-Ta system was chosen as a model system because of the different crystal structures of the elements, the low interdiffusivity, and the mutual inmiscibility of the elements.

Deposition of Cu and Ta (sub) layers was done using calibrated deposition rates
Physical Chemistry of the Solid State

(Base pressure below $2 \times 10^{-6}$ bar). Samples were prepared consisting of a single layer of Cu (500 nm), single layer Ta (500 nm) and Cu-Ta multilayer (500 nm, periodicity: 20 nm, 10 nm Cu, 10 nm Ta).

X-ray diffraction was performed at high-angle and low-angle set-up in order to obtain data on the sublayers and on the multilayer periodicity. A first evaluation of the XRD spectra shows that both in single layer samples and in multilayer samples the Cu and Ta layers are in a crystalline state. The Ta layer consists of a metastable phase ($\beta$-Ta) while the Cu layer has the fcc crystal structure. It is found that the Cu and Ta layers both feature a fibre texture of the densest packed planes parallel to the surface (Cu$(111)$, Ta$(002)$).

The macrostress in the Cu phase is close to zero in both the single and multilayer samples. The stress in the Ta layer varies i.e. tensile in a single layer and compressive in multilayers.

1.2 Formation, Microstructure and Internal Stresses of Surface Layers

1.2.1 The Interaction of Stresses and Phase Transformations in Surface Layers

1.2.1.1 Configuration and Behaviour of Dislocations in Metal Layers under Stress


In previous years the relaxation of thermal stress in Al layers on oxide-covered Si single-crystal wafers was studied. A decrease of diffraction-line breadth coupled to the decrease in thermal stress was observed and explained quantitatively.

In the past two years Ag has been used as second model system, because it has a lower stacking fault energy and higher elastic anisotropy than Al. The Ag layers studied possess a fibre texture consisting of a "matrix" of crystallites with a $(111)$ plane oriented parallel to the plane of the layer and a substantial amount of growth twins with a $(111)$ plane parallel to the layer-substrate interface. The presence of these twins complicates the interpretation of the measurements. During annealing at temperatures above 523 K severe recrystallisation effects result in the formation of holes throughout the layer. The thermal stress relaxation observed at room temperature showed a simultaneous decrease in stress (from peak position) and microstrain (from diffraction-line breadth) for both texture fractions. The interpretation of the data obtained is still incomplete. This research will be split into several branches next year.

1.2.1.2 Phase Transformations in Anisotropic Metastable Alloy Films

(L. Velterop, I.M. van den Berk, R. Delhez, Th.H. de Keijser, E.J. Mittemeijer, A. Buis; D. Reefman [Philips])

This project is performed in co-operation with (and financially supported by) Philips Research, Eindhoven and Philips Analytical, Almelo; project co-ordinator from Philips is dr. D. Reefman.

The word "anisotropic" in the title of the project means that the (elastic, magnetic, etc.) behaviour of the system depends on the direction with respect to the crystallographic and/or specimen axes. Anisotropic metastable alloy layers studied are Ag-rich Ag-Co and Ag-Ni thin layers prepared by alternated sputtering from two targets on oxide-covered Si single-crystal wafers. The precipitation in these layers upon annealing can be rather well controlled.

XRD measurements and transmission electron microscopy reveal that only a silver-rich phase is present in the as-prepared alloy layers. This indicates that the Co or Ni is (non-homogeneously) dissolved in the Ag. The Ag-rich matrix exhibits a $(111)$ fibre texture and contains very high tensile strains: up to 0.5%, whereas a pure Ag layer
has no strain.
As reported a large density of small twins (of a width of tens of nm) is present in the as-prepared alloy layers (not in the pure Ag layer). Upon heating of the alloys at 723 K the amount of twins decreases, the strains decreases (and the alloy decomposes). A study of existing analyses showed, that -in contradiction to previous studies- twin faults influence the positions of XRD reflections (as stacking faults do): these twin faults cause peak shifts with a magnitude that depends on their amount, on their orientation and on the reflection considered. These peak shifts have to be excluded when calculating the strain in the layers. A method to do this has been developed.

HRTEM and CTEM work performed on the Ag-Ni layers still needs interpretation: this mainly concerns the possible relation between the twins and the dislocations observed.

Mo-Ti layers analogous to the Ag-Ni and Ag-Co layers were made at DIMES. In XRD patterns only reflections of a Mo-rich bcc phase were detected, the peaks of which were rather symmetric. This suggests that the layers were indeed homogeneous. TEM and XRD observations indicate that the layers exhibit a \{110\} texture with a weak in-plane preferred orientation. The stresses found in these layers are very high-like in the Ag alloy layers-, but compressive. It seems that also stacking and/or twin faults are present.

Upon heating, decomposition of the layers takes place. A BCC Ti phase is formed, although the stable modification of Ti at < 1150 K is HCP. The stresses and stacking and/or twin fault densities do not decrease as strongly as in the Ag alloy layers. The behaviour of these stresses and densities varies with annealing temperature. The process governing stress relaxation and decrease in faults density seems to be bulk diffusion. This does not hold for the annealing experiments on the Ag alloy layers: the reduced temperature (= annealing temperature divided by melting temperature) is much lower for the Ag based systems than for the Mo based system. Further interpretation is in progress.

1.2.2 Coatings on Steel Tools; Relation between Deposition Parameters, Microstructure and Wear (J.-D. Kamminga, M. van Leeuwen, R. Delhez, Th.H. de Keijser, E.J. Mittemeijer)

This project is part of the project IOT94005 as a co-operation of six research groups under auspices of the IOP-"Oppervlakte Technologie" (Surface Technology): (i) the group Inorganic Materials of TNO-TPD in Eindhoven (drs. C.I.M.A. Spee and dr. A.D. Kuypers), (ii) the group Materials Technology of TNO-MI in Apeldoorn (dr.ir. A.J. Huis in 't Veld), (iii) the Laboratory of Applied Inorganic Chemistry of the Delft University of Technology (prof.dr. J. Schoonman), (iv) the group Tribology of the Faculty of Mechanical Engineering of the University of Twente (dr.ir. D.J. Schipper), (v) the group Tool Production and Automation of the Faculty of Mechanical Engineering of the Technological University of Eindhoven (dr.ir. A.J. Dautzenberg) en (vi) the Section Physical Chemistry of the Solid State of the Laboratory of Materials Science of the Delft University of Technology (dr.ir. R. Delhez, dr.ir. Th.H. de Keijser, prof.dr.ir. E.J. Mittemeijer). In each of the groups mentioned under (i), (iv), (v) and (vi) a Ph.D. student works. The project has a duration of four years and started officially on November 1, 1994.

The TiN PVD layers used here have been prepared by the group of dr. Dautzenberg. The TiN layers usually have thicknesses of 1 - 5 μm, and are deposited under various circumstances on a tool steel, a cermet and on stainless steel foils.

In our research the average macrostresses are determined using an X-ray diffraction
method, the so-called $\sin^2 \psi$ method, which uses spacings of crystal lattice planes as a "strain gauge". The magnitude of the average (compressive) macrostresses obtained is of the order of $-1$ to $-10$ GPa and are considered to consist of a "thermal" component and a component caused during growth of the layer, the "growth" stress. The thermal stress is caused by the difference in thermal shrink of substrate and layer after cooling from the deposition temperature (≈570 K) to room temperature. The growth stresses in the layers can be ascribed to atoms "peened" into the layer during sputter-deposition (the so-called "atomic peening" mechanism). The stress caused by the introduction of misfitting particles into the layer, yielding interstitial or substitutional point defects, has been modelled. From the model it follows that the high growth stresses may be caused by about 1 at.% titanium atoms on nitrogen sites in the TiN lattice.

This year a comparison has been made between stress measurements using the bending foil technique and XRD stress measurements on PVD TiN layers on a steel foil for layers of several compositions. The value of the difference of the stress values obtained by the two methods depends on the composition. This effect can be explained by a (reasonable) dependence of the elastic constants of TiN on composition. In the literature such a dependence has been mentioned.

Further two methodologic procedures have been worked out. One of these procedures concerns the treatment of X-ray patterns of layers on a substrate: a way has been found to eliminate the reflections of the substrate with the help of the diffraction pattern of the substrate, so that the pattern of the layer is retained only. The other procedure shows that it is possible to interpret X-ray diffraction measurements of stresses in elastically isotropic materials in such a way, that the mechanical elastic constants can be used instead of the (so called) X-ray diffraction elastic constants. By applying this procedure the often observed HKL dependence of the stress value obtained disappears and the reliability of the stress values is increased.

Last but not least the Vook and Witt approach to calculate diffraction elastic constants (also for elastically anisotropic materials as Ni) has been elaborated in more detail. In the Vook and Witt approach it is assumed that the material consists of columnar crystallites, where the crystallites (e.g. of a layer on a substrate) are connected, but are free to expand or shrink independently in a direction parallel to the column axes. XRD measurements of the stress in a thin evaporated Ni layer on a Si wafer show that - in contradiction to "normal" expectations, but in accordance with this model- a non-linear relation occurs between the lattice spacing of any HKL reflection and $\sin^2 \psi$.

1.2.3 The Initial Stage of Oxidation of Aluminium (L.P. H. Jeurgens, W.G. Sloof, F.D. Tichelaar, C.G. Borsboom, E.J. Mittemeijer)

To study the mechanisms for the oxide-film growth behaviour on clean aluminium, a series of dry oxidation experiments were executed on AI. The microstructure and morphology of the oxide films were investigated using HREM.

Our oxidation experiments were executed on differently oriented AI crystal grains as a function of oxidation time at various oxidation temperatures ($T$) and oxygen partial pressures ($p_{O_2}$). X-ray Photoelectron spectroscopy (XPS) was employed to determine the oxide-film growth kinetics and chemical composition. For oxidation experiments executed at $T = 673$ K and $p_{O_2} = 1.33 \times 10^{-4}$ Pa, initial surface oxidation on the Al(112) surface orientation proceeds faster than on the more densely packed Al(110) surface orientation. This suggests that during the initial stages of metal surface oxidation, the oxygen atoms which are preferentially chemisorbed on the threefold and
fourfold centred positions on the metal surface, have better access to electrons from
the substrate on the less densely packed surface of the clean Al metal. After 1000 s
of oxygen exposure at \( T = 673 \) K, an oxide layer of approximately 2.5 and 3 nm thick
has formed on the Al(110) and Al(112) surface orientation, respectively. When lower­
ing the oxidation temperature to room temperature, on both types of surfaces ox­
ide-film growth is completed in about 100 s of oxygen exposure and a 0.5 nm thick
oxide-film has formed.
All oxidation experiments executed at this oxygen pressure of \( pO_2 = 1.33 \times 10^{-4} \) Pa
and oxidation temperatures up to 773 K, show a logarithmic type of oxide-film growth
kinetics, suggesting that at this oxygen pressure continued oxide-film growth is lim­
ited by the migration of charged species through the developing oxide film.
At lower oxygen pressures of \( 1 \times 10^{-5} \) Pa and oxidation temperatures of \( T = 673 \) K and
\( T = 773 \) K linear oxide-film growth kinetics are observed. This suggests that oxygen
transport from the gas to the oxide-gas interface is rate-limiting at the initial stages of
oxidation. At \( T = 673 \) K the initial oxide-film growth rates are faster than those ob­
served at \( T = 773 \) K, which indicates that interface reactions such as the desorption
of physisorbed oxygen from the surface must be taken into account when modelling
the Al oxide-film growth kinetics. This is further supported by the small value of
\( 2 \times 10^{-2} \) for the sticking coefficient of oxygen on the initial oxide-film, as determined
from the oxide-film growth kinetics (at \( T = 773 \) K and \( pO_2 = 1 \times 10^{-5} \) Pa).

Figure 1: HREM image of Al(115) substrate oxidised for 2h:45min at \( T = 773 \) K and \( P(O_2) = 1.33 \times 10^{-5} \) Pa

The microstructure and morphology of the oxide film upon oxidation was investigated
with High Resolution Electron Microscopy (HREM). An amorphous aluminium-oxide
film with uniform thickness was formed, even at a relatively high oxidation tempera­
ture of \( T = 773 \) K (see Fig. 1). At this temperature some crystalline nuclei of \( g-Al_2O_3 \)
were also observed at the oxide/metal interface.
Depending on the oxidation temperature and oxygen exposure (i.e. oxidation time
and oxygen partial pressure), also a crystalline oxide-film microstructure may de­
v elop. In this context, a thermodynamic model has been developed to explain the ob­
served amorphous microstructure and to explore the conditions to form a crystalline
microstructure.
The composition of the oxide-film grown, expressed as the oxygen to aluminium
atomic ratio \( (O/Al) \), is larger than that of \( \alpha-Al_2O_3 \) and decreases as a function of ox­
idation time (i.e. oxide-film thickness); see Figure 2. Also the binding energy of the Al
\( 2p \) core level photoelectrons and the kinetic energy of the Al \( KL_{23}L_{23} \) Auger electrons
emitted from the oxide film shift also as a function of oxidation time (i.e. oxide-film thickness). These trends indicate that the chemical state of Al and O are different in the amorphous oxide film (compared with crystalline aluminium oxide ($\alpha$-Al$_2$O$_3$)) and changes as a function of oxidation time. Probably a decrease in ionicity of the Al-O bond upon oxidation occurs as a result of a change in valence charge density around the Al nucleus.

![Figure 2: Changes in oxide-film thickness and composition as a function of oxidation time for the case of an Al(110) substrate oxidised at 673 K and $P_{O_2}=1.33 \times 10^{-6}$ Pa.](image)

1.3 Structure and Properties of Interfaces (R.M.J. Bokel, F.D. Tichelaar, H.W. Zandbergen, F.W. Schapink)

The investigations on the structure of interfaces has been concentrated on the effect of electron beam parameters on Convergent Beam Electron Diffraction (CBED) patterns from interfaces aligned vertically in the specimen foil. Convergent Beam Electron Diffraction (CBED) at vertical grain boundaries (parallel to the electron beam) can be used to determine the symmetry of bicrystals. It can also be used to investigate the structure of the boundary region itself when subnanometer probe sizes are employed. The work can be subdivided into two parts:

1) In the first part, the influence of the electron-beam geometry on the CBED pattern is discussed in terms of the defocus distance between the probe position and the specimen mid plane, $D$ (set by the second condenser lens), the probe size, the beam-convergence angle, and the microscope mode (micro- or nano-probe). Theoretically expected CBED patterns for an electron probe on a vertical grain boundary are observed up to a certain maximum defocus $|D_{cl}|$, which is shown to increase linearly with probe size and specimen thickness. The experimental uncertainty in positioning the probe in the specimen mid plane is independent of the probe size but increases linearly with specimen thickness. A comparison of this uncertainty in $|D|$ with $|D_{cl}|$ shows that for decreasing probe sizes it is increasingly difficult to obtain the theoretically expected CBED pattern from a vertical boundary. The effect of a defocused probe ($|D| > |D_{cl}|$ up to $|D|$
2) In the second part CBED patterns from vertical interfaces are simulated using a multislice algorithm, and a small electron probe, to investigate the influence of beam geometry of a coherent illumination on the CBED pattern (in part one an incoherent illumination was considered). Simulations of coherent CBED patterns based on the multislice algorithm show that the CBED pattern of an edge-on interface depends on the defocus distance between the probe position and the specimen mid plane, the probe size and the beam-convergence angle. The pattern symmetry may be lower than the theoretically predicted symmetry in case of large spherical aberration. This effect increases with smaller accelerating voltages. An increase in the objective aperture size also increases the possibility of a non-optimum symmetry due to the coherence of the beam. Thus, for the determination of an interface structure using subnanometer (coherent) probes, the imaging conditions play an important role.

2. Phase Transformations in Iron-Based Interstitial Alloys


2.1.1 Thermodynamics of Fe-N(C) Phases: Ordering of N Atoms in ε-Fe₂N₇/₇₂

The degree and types of ordering of the interstitial atoms play a very important role in understanding and modelling the experimentally observed absorption isotherms and phase diagrams of binary interstitial iron alloys. In particular the ordering of N atoms in ε-Fe₂N₇/₇₂ nitrides is not yet unambiguously determined. The ε-phase consists of an hcp Fe-sublattice and a simple hexagonal interstitial sublattice. Thermodynamic modelling, based on the Gorski-Bragg-Williams (GBW) approach, of the mixing of atoms N and vacancies V on the interstitial sublattice of ε-Fe₂N₇/₇₂ indicated the occurrence of two long-range ordered ground-state structures: configuration A for ε-Fe₂N (50 at.% N) and configuration B for ε-Fe₃N (33.3 at.% N), which correspond with (in literature) proposed arrangements of nitrogen atoms.

The prism approximation of the cluster variation method (CVM) is applied to describe ordering of atoms N and vacancies V on the interstitial sublattice in ε-Fe₂N₇/₇₂, taking into account long-range ordering (LRO) and short-range ordering (SRO). Although the CVM is usually applied to substitutional systems, the ε-Fe₂N₇/₇₂ phase is modelled through the interstitial sublattice occupied by N atoms and vacancies V, the Fe sublattice is considered as fully occupied by Fe atoms. In contrast to pair approximations a/o the GBW-approach the CVM can handle lattice frustration i.e. on a nearest neighbour triangle, all three atomic pairs cannot satisfy the requirement of unlike atom pair bonds. Lattice frustration is common to all triangular lattices and thus occurs on the (0001) planes of the interstitial sublattice in ε-Fe₂N₇/₇₂. By choosing a prism cluster to describe ordering on the interstitial sublattice, all 64 possible distributions of N and V over the prism sites are included in the model and the problem of lattice frustration is handled. The six sites of the prism each represent a specific hexagonal sublattice and the occupation of the sites by either N or V is considered for each site independently. The atomic interactions in ε-Fe₂N₇/₇₂ are described by effective Lennard-Jones potentials for the binary (N,V) system, thereby the contribution of
the Fe sublattice is incorporated implicitly. Preliminary CVM calculations show that although the two long-range ordered ground-state structures (configuration A, B) are most likely for compositions close to $\varepsilon$-Fe$_2$N and $\varepsilon$-Fe$_3$N, other distributions of N atoms also occur. Furthermore increasing the temperature results in a decrease of order, as expected. Using the CVM results the probability that Fe atoms in $\varepsilon$-Fe$_2$N$_{1-z}$ are surrounded by 0 up to 6 N atoms can be calculated which may be compared to data obtained from Mössbauer spectroscopy data.

2.1.2 Phase Transformations of Fe-N Phases below 500 K

This project is focusing on phase transformations taking place at temperatures below about 500 K. This low temperature part of the Fe-N phase diagram is not well known although of technological importance because diffusion of nitrogen atoms can occur easily at these temperatures. Annealing experiments are performed using homogeneous iron-nitrogen specimens of varying nitrogen content (9 at.% N to 27 at.% N) which were prepared by nitriding pure iron powder at temperatures above 700 K and then subsequently quenched at room temperature. Heat treatments at temperatures between 373 K and 473 K and tempering times up to 50 days are applied. X-ray diffraction analysis was used for identification of the appearing phases.

The precipitation of $\alpha''$-Fe$_{16}$N$_2$ from both the $\varepsilon$-Fe$_2$N$_{1-z}$ and the $\gamma$-Fe$_4$N$_{1-x}$ phase (after annealing below 443 K) is certainly one of the most striking results obtained. Such transformation could not be explained on the basis of the phase diagram known so far. Since $\alpha''$ is formed from supersaturated ferrite (i.e. martensite with N contents below 9 at.% N) as well as from $\varepsilon$ and $\gamma$ as observed in the current research it could be suggested that $\alpha''$ is an equilibrium phase. However, additional low temperature annealing experiments performed on austenite (9 at.% N) showed that austenite decomposes in ferrite and $\gamma$-Fe$_4$N$_{1-x}$ without the (intermediate) precipitation of $\alpha''$. So it seems more likely that $\alpha''$ is an intermediate phase. Thus it can be concluded that kinetics plays an essential role in the phase transformation scheme.

It also can be concluded that $\gamma$ is a stable phase up to 373 K. The performed low temperature heat treatments also showed that the $\varepsilon$+$\gamma$/$\varepsilon$ phase boundary tends to shift to lower nitrogen contents with decreasing temperature. These results show the same tendency as the calculated phase boundary obtained by explicitly incorporating long range ordering of interstitial nitrogen atoms in thermodynamic modelling as previously performed in our group.

Additional annealing experiments performed on (quenched) $\varepsilon$ specimens with nitrogen contents far from the $\varepsilon$+$\gamma$/$\varepsilon$ phase boundary showed that ordering of nitrogen atoms increases. Careful analysis of the X-ray diffraction patterns with respect to the changes in integrated intensities, in particular of the superstructure reflections pertaining to specific types of ordering, revealed that small displacements of iron atoms surrounding the interstitial nitrogen atoms occur. This observation allowed to explain the, until now not understood, absence of some of the superstructure reflections. A EU-grant has allowed us to use the Daresbury Synchrotron Radiation Source in order to make a detailed analysis of the presence, absence and relative intensities of superstructure reflections at several annealing stages of the $\varepsilon$ phase.

2.2 Thermomechanical Loading of Iron-Based Steels (P.V. Morra, A.J. Böttger, E.J. Mittemeijer, J.T. Slycke, M. Persson [SKF-ERC])

Any component experiencing a load is in practice subjected to thermomechanical loading as testing is performed at finite temperatures. The relation between a ther-
mally activated microstructural change as brought about by a phase transformation and a simultaneously occurring elastic/plastic deformation is not well understood at a fundamental level. Yet, the service life of many components is thought to be controlled by these mechanisms (for example this holds for a ball bearing). This Ph.D. project will focus on the analysis of the thermally activated phase transformations occurring in Fe-C martensite upon tempering under mechanical loading such that (plastic) deformation occurs.

The project on thermomechanical loading of iron-based steels started about the middle of October. In the first 2.5 months of the project a start was made in preparing iron-carbon martensitic specimens of various C content by carburising pure iron foils in a CO/H₂ mixture. The preparation parameters have been established for obtaining specimens with a carbon concentration in a range below 1 wt.% C.

3 Microstructural Imperfections and Diffraction-Line Broadening

3.1 Analysis of Strain Fields in Solids; X-ray Diffraction-Line Broadening and Micromechanics (T.C. Bor, J.-D. Kamminga, L.J. Seijbel, R. Delhez, Th.H. de Keijser, E.J. Mittemeijer; E. van der Giessen [MIDEG])

In principle, X-ray diffraction-line broadening analysis is a powerful technique for studying all kinds of crystal imperfections, like crystallite size, stacking faults, dislocations. Successful application to powders of very small (<100 nm) undeformed crystallites is well known. In the 'remaining' and technologically very important class of deformed polycrystalline specimens much still has to be done. The drawback of most of the present interpretations of measured line broadenings (for example: Warren-Averbach analysis) is that these do not provide characteristics of the imperfections that can be used directly in current physical models.

We are working along two lines to overcome this problem - as well as other problems. One way of calculating the effect of the strain fields of point defects on the XRD line broadening is: calculate the Fourier coefficients of a chosen diffraction line profile using a Monte-Carlo type procedure from the superimposed strain fields induced by various lattice defects (point defects, inclusions, dislocations, stacking and twin faults) arranged in a way chosen by the experimenter in a (virtual) solid. Using this method it was shown that point defects lead to almost negligible peak broadening. The presence of dislocations is shown to yield significant peak broadening.

Another approach follows from micromechanics. The macroscopic behaviour of crystalline materials is strongly influenced by imperfections, such as dislocations and precipitates. Quantitative information about these imperfections is necessary to predict for example macroscopic mechanical material properties. These predictions are possible using micromechanics, which calculates the material behaviour on a local (mesoscopic) scale in a small volume element, that is representative of the microstructure of the material, using continuum mechanics. This representative element and its behaviour is then used to calculate the overall materials properties.

We already reported about our first steps in the development of a line-broadening analysis method that approaches the analysis of line broadening in this way. Local strain fields are calculated by means of micromechanical models of the microstructure of the material. From these strain fields XRD line profiles are calculated and these can then be compared with measured ones. Then in principle, by adjusting the parameters of the micromechanical model, calculated profiles can be found that fit the measured XRD line profiles best, resulting in the determination of necessary microstructural information.
Finite element calculations have been done for a 2D-representation of a material containing a periodic distribution of precipitates to obtain the displacement fields (elastic strains) around the precipitates. The results were compared with Eshelby's description of the strain field around a misfitting spherical inclusion in a continuum. It was shown that the average strain of the periodic description is equal to the average strain of Eshelby's description until high particle fractions (up to 40%) even in the case of clustering of neighbouring particles. The average strain calculated on the basis of the shift of the centroid of the simulated XRD line profiles shows approximately equal behaviour. However, a distinct difference exists between the mean square strain of both descriptions: the mean square strain of the periodic description shows direction dependence, related to the ordering of the particles, whereas the circularly symmetric Eshelby description is direction independent. This direction dependence is also reflected in the broadening of the simulated XRD line profiles resulting in the observation that the broadening of the simulated XRD line profiles is proportional to the product of the order of reflection and the root mean square strain in the specific crystallographic direction.

This year these calculations have been elaborated further and are being described in more detail.

3.2 The Problem of the "Appropriate" Standard Line Profile (T.C. Bor, R.C. Currie, L. Velterop, R. Delhez, Th.H. de Keijser, N.M. van der Pers; G.J.M. Sprong [Delft University of Technology])

In X-ray powder-diffraction analysis there is a need to know the shape of the line profile due to the non-ideal optics of the diffraction equipment and the wavelength distribution of the radiation used. Last year we reported that the most reliable way to obtain it, is to measure it using a general purpose standard as developed in our group (Powder Diffraction 10 (1995) 129-139) and that the line profiles (or the values of its parameters) at desired 2θ values then should be obtained by an accurate interpolation procedure (see report over 1996). We have continued our efforts and are preparing an efficient, transportable procedure that will be published.

Furthermore, it has become clear that several commercially available fine grained powders exist, that can (rather) easily yield optimal standards.

3.3 X-ray Diffraction Software Development (L. Velterop, J.-D. Kamminga, R. Delhez, Th.H. de Keijser, E.J. Mittemeijer; V.A. Kogan [Philips Analytical, Almelo])

We continued the elaboration of a PC program for performing the "Delft Truncation Correction" (as a part of the project described in section 1.2.1.2). The aim is to incorporate the program in (Philips) X-ray diffraction software.

We are still involved in the further development in co-operation with Philips Analytical, Almelo, of PROFIT, "our" computer program for Total Pattern Fitting, and of LPA, "our" program to determine crystallite size and microstrains from X-ray diffraction-line broadening.

4 High Resolution Electron Microscopy for Structural Analysis

4.1 Structure Determination of Very Small Crystals using Electron Diffraction (H.W. Zandbergen, J. Jansen, R.M.J. Bokel; J. Reedijk, J. Aarts [Leiden University]; H. Schenk [University of Amsterdam]; A. Kaul [Moscow State University]; J. Voigt-Martín [University of Mainz]; C. Chailou [Laboratoire de Cristallographie, Grenoble]; W. Mader [University of Bonn])
The scattering probability of electrons by an atom is about $10^5$ times larger than that of X-ray photons, which combined with the much higher flux ($10^{10}$ times as many electrons per nm$^2$ as X-ray photons from a normal X-ray source), has the enormous advantage that much smaller crystals (typically 5-100 nm in diameter) can be analysed. This makes electron diffraction the only method for accurate structure determination of many types of materials (inorganic, organic and biological), which are only available as very small crystals and have too complicated structures (multi-phase or large unit cell) for X-ray or neutron powder diffraction. Since knowledge of the structure is often the key to understanding the properties of a compound, this technique will be of great importance. The importance of quantitative electron diffraction will grow further because of the ongoing miniaturisation. A few examples of areas where there are needs for structure analysis of very small crystals are: organic materials for non-linear optical applications, optical data storage, ferroelectric applications, optical switches, diodes, very small (<5 nm) precipitates in high performance, pigments, pharmaceuticals, catalysts, peptides, proteins. All are typical examples of materials where either the compound is unavailable as large crystals or, the structure is dependent on the particle size.

Recently we showed that using electron diffraction accurate structure determinations of very small volumes are possible (volumes smaller than 500 nm$^3$), provided the dynamical diffraction effects are fully taken into account. Because we have now the expertise to determine the structures of compounds with relatively small unit cells, with an accuracy similar to that of X-ray single crystal diffraction, we are in an excellent position to develop electron diffraction methods for more complicated analysis of electron diffraction patterns (e.g. more complicated structures, composites of two crystals, inelastic scattering).

In collaboration with the group of prof. J. Reedijk we investigated the structure of FeN$_9$C$_6$BF$_4$. Although the structure could be determined, the obtained fit between experimental and calculated intensities was insufficient according to our standards (about 11%), which is related to the quality and the processing of the electron diffraction data. Based on this experience, improvements in the sample preparation and the methods of analysis of the diffraction data are in progress. In collaboration with the group of prof. A. Kaul (Moscow State University), the structure of BaCu$_2$O$_4$ was determined. In collaboration with dr. J. Voigt-Martin (Mainz University), the structure of C$_{24}$N$_2$OH$_{28}$ was investigated. Using our methods, a reliable structure determination was possible. In collaboration with dr. C. Chaillout, the structure of Ba$_2$Ca$_3$Cu$_5$-C$_2$O$_{10}$ was determined, and a start was made to analyse the superstructure of YBa$_2$Cu$_4$AuO$_7$. In collaboration with W. Mader (University of Bonn), the structure of a lanthanum aluminate was determined. In collaboration with dr. J. Aarts of Leiden University, the structures of 5 nm thick films of the colossal magnetoresistance (CMR) material La$_{0.73}$Ca$_{0.27}$MnO$_3$ were determined.

4.2 Development of Specimen Holders for TEMs (H.W. Zandbergen; G. Hoveling [Delft University of Technology])

We have developed several specimen holders, which allow specimen transfer at about $10^{-3}$ Torr. They have a very good mechanical (resolution 0.12 nm) and drift stability. Furthermore a double tilt cryoholder has been developed allowing cooling down to about 100 K at the specimen. The resolution that can be obtained using this holder is 0.10 nm along the holder direction and 0.18 nm perpendicular to this. Further improvements will be made, with the final goal to do exit-wave reconstructions at low temperatures. This year we will develop a vacuum transfer cryoholder.
4.3 Thin Oxide Films (H.W. Zandbergen; R. Griessen [University of Amsterdam]; T. Palstra [University of Groningen]; A. Kaul [Moscow State University])

The understanding of the processes governing the formation of high quality oxide films (for instance the presence of secondary phases in YBa$_2$Cu$_3$O$_{7-8}$ epitaxial superconducting thin films, and the microstructure of films of colossal magnetoresistance oxides) is essential for further improvement of the properties of these thin films, and their applications. The composition, orientation, and size of the primary phase, and possible (wanted or unwanted) secondary phases, depend on complex of factors like the thermodynamics, the growth kinetics, the structure and lattice parameters (mis-match) of the substrate material. In this respect, HREM is a very important characterisation tool. Restricting this report to the chemistry groups, we are collaborating on these types of materials with the groups of R. Griessen (University of Amsterdam), T. Palstra (University of Groningen), A. Kaul (Moscow State University). For the group of Griessen, YBa$_2$Cu$_3$O$_{7-3}$ epitaxial thin films grown under various conditions were investigated, whereby the main question was whether the microstructure could be related to the variation in the critical current. For the group of Palstra, the microstructures of very thin films of Fe$_2$O$_4$ on MgO substrates were investigated, whereby the main features were the density of antiphase boundaries, and the atomic structure at the MgO/Fe$_2$O$_4$ interface. For the group of Kaul, a large variety of thin films of RBa$_2$Cu$_3$O$_{7-3}$ (R being a rare earth atom) and manganites was analysed. The latter research was carried out as part of an INTAS project.

In the last four years manganese oxides played a crucial role in the research hype of the giant magnetoresistance (GMR). Magnetoresistance the effect that the resistance of a material depends on the magnetic field applied. Since magnetoresistance is widely used (e.g. reading heads in computer hard disks) there is a strong technological interest for GMR, in particular as films. Very thin films are of special interest because they are most suitable for multi-layer devices, for instance with superconductors. The properties of films of 4-12 nm are quite different from those of films which are thicker than 50 nm, although they can all be made such that they are very smooth, single phase and well crystalline. To understand this behaviour we have started a detailed study on the structure and microstructure of 6 nm and 12 nm thin films of La$_{0.7}$Ca$_{0.3}$MnO$_3$ on SrTiO$_3$ substrates. Electron microscopy revealed important differences between the (micro-)structures of the thin and thick films of La$_{0.7}$Ca$_{0.3}$MnO$_3$. The main differences for the thin films are i) the size of the unit cell is constrained by the substrate, ii) the film is (almost) uniformly b-axis oriented, iii) twin boundaries occur with a high density; iv) the tilts of the MnO$_6$ octahedra are smaller and different, v) the MnO$_6$ octahedra are Jahn-Teller distorted. In particular the last two differences are probably responsible for the different properties and since they are imposed by the substrate they can only be prevented by changes in the substrate (like other material, deliberate surface roughness).

4.4 Thin Films of GaN (H.W. Zandbergen, J. Jansen, F.D. Tichelaar; P. Larsen [University of Nijmegen])

There has been a large interest in GaN during the last few years because of its large potential in applications like light emitting diodes (to replace light bulbs) and lasers. At the beginning of this year we started a collaboration with the group of Larne (University of Nijmegen), where we have the task to characterise, in detail, the microstructure of GaN layers grown under various synthesis conditions, and with various chemical components. Our goals in the first place, are to understand the differences
in the physical properties of the films, and in the second place to optimise the synthesis routes of thin films with the required properties. Attention in the first part of the project was focused on the microstructure of the first layer deposited (buffer layer), and on its influence on the formation of dislocations and inversion domains in the top GaN layer.

4.5 Oxides with a Perovskite-Like Structure (H.W. Zandbergen, P.J. Kooyman, C.D. de Haan, F.D. Tichelaar; H. Verwoy [Twente University]; D. IJdo [Leiden University]; J. Schoonman [MIDEG]; R. Cava [Princeton University])

Oxides with a perovskite-like structure have been studied for a long time already, but continue to surprise researchers with new properties. In 1986 high temperature superconductivity was discovered in this class of oxides. In 1992 the manganites with this structure were reported to exhibit an extremely high magnetoresistance. Furthermore, some of the oxides in this structure group show a high ion conductivity. All these phenomena have already led to, or will lead to important technological applications. In the search for new properties (and new compounds) and materials with reproducible properties, HREM can play an important role. For the group of Verwey (University of Twente), the structure and microstructure of (La,Sr)CoO₃₋ₓ was investigated. The low temperature phase will be studied in the near future. In collaboration with D. IJdo (Leiden University), electron diffraction studies of were performed on Cu based oxides. For J. Schoonman (MIDEG), uranium-based pyrochlores were studied. Irradiation by the electron beam lead to the formation of superstructures, which will be studied in future. For R. Cava (Princeton University), six lanthanumcobaltates were studied by electron diffraction to determine the unit cells and compositions in multi-phase samples.

4.6 Mesoporous Materials (H.W. Zandbergen, P.J. Kooyman; A. Galarneau, E. Prouzet [Laboratoire des Matériaux et Procédés Membranaires, Montpellier]; H. van Bekkum, Th. Maschmeyer [Delft University of Technology]; J. Lercher [Twente University])

The family of M41S mesoporous materials attracts a lot of scientific attention due to their enormous potential as catalysts for the petrochemical industry. Their synthesis is being studied in co-operation with the groups of A. Galarneau and E. Prouzet (Laboratoire des Matériaux et Procédés Membranaires, Montpellier). The pH of the synthesis mixture can be used to control the degree of crystallisation of MSU-1. The structure-directing agent used in the synthesis mixture determines the amount of hexagonally ordered material. Using ultrasonic stirring instead of mechanical stirring, gives materials that consist of hollow spheres, the walls of which are formed from MSU-1 mesoporous material. The modification of M41S-type materials MCM-41 and HMS, is studied in co-operation with the group of H. van Bekkum/Th. Maschmeyer (Delft University of Technology). The occlusion of catalytically active species such as heteropoly acids, or titanium-silsesquioxanes in the channel system of the mesoporous material, broadens the area of catalytic application. Similarly, the modification of M41S materials by partial recrystallisation to, e.g. MFI, gives promising bifunctional catalysts. The growth of MCM-41 on zeolite Y is another system in which two catalytic materials are incorporated into one catalyst. The synthesis of MCM-22 and MCM-36 is studied in co-operation with the groups of H. van Bekkum/Th. Maschmeyer (Delft University of Technology) and J. Lercher (Twente University). TEM is the only characterisation method by which the morphol-
ogy and structure of these materials can be characterised properly. Successful synthesis of these materials in a pure form has not been achieved yet.

4.7 ZEOLITE SYNTHESIS (H.W. Zandbergen, P.J. Kooyman; R. van Santen [Eindhoven University of Technology]; H. van Bekkum, Th. Maschmeyer [Delft University of Technology])

The initial crystallisation of MFI has been studied extensively by de Moor (group of R. van Santen, Eindhoven). TEM analysis of the initial crystals has been essential for the validation of a new method to study the initial crystallisation using (U)SAXS and WAXS. This work has been nominated for the DSM research prize 1998.

The synthesis of BEA has been studied in co-operation with the group of H. van Bekkum/Th. Maschmeyer (Delft University of Technology). Proper Ti-BEA was successfully synthesised by using specially prepared, new templating agents. The synthesis of large single crystals of AI-BEA has also been achieved successfully.

4.8 ZEOLITE MODIFICATION (P.J. Kooyman; H. van Bekkum, Th. Maschmeyer [Delft University of Technology]; R. van Santen [Eindhoven University of Technology]; J. Lercher [Twente University])

Incorporation of small noble-metal particles inside the channel systems of zeolites has been studied in co-operation with the groups of H. van Bekkum/Th. Maschmeyer (Delft University of Technology), R. van Santen (Eindhoven University of Technology) and J. Lercher (Twente University). The project on Pt in BEA, in which a mechanism for the growth of Pt particles during reduction, was elucidated together with Creighton (group of H. van Bekkum/Th. Maschmeyer (Delft University of Technology)) received the SEN posterprize 1995.

The external surface acidity of large single crystals of AI-BEA was successfully blocked by treatment with TEOS. Using HREM the thickness and uniformity of the amorphous external surface layer could be determined.

4.9 COLOIDAL METALS (H.W. Zandbergen, P.J. Kooyman; G. Frens [Delft University of Technology]; J. Lercher [Twente University], M. Möller [Universität Ulm, Germany])

Ag colloids prepared at various pH-values and temperatures have been studied in co-operation with the group of G. Frens (Delft University of Technology). For certain synthesis conditions, metallic Ag particles are formed, whereas for other conditions, silver oxide particles are formed. Sometimes the oxidic particles are amorphous, sometimes they are crystalline. Occasionally the oxidic particles consist of a crystalline core and an amorphous outer shell.

Polymer-stabilised Rh colloids were characterised using HREM and EXAFS in collaboration with the group of J. Lercher (Twente University). Originally, conventional TEM was measured elsewhere, and the particle size seemed to be the same for two samples that showed different particle sizes using EXAFS measurements. Using HREM it could be concluded that the sample which had a smaller particle size according to EXAFS, consisted of several small crystallites, whereas the sample which had a larger particle size according to EXAFS, consisted of single crystals.

The spontaneous arrangement of Au colloidal particles in block-copolymers was studied in co-operation with the group of M. Möller (Universität Ulm). Next to the arrangement (e.g. hexagonally or in one-dimensional lines), the crystallinity of the metallic particles (single crystalline or multi crystalline) could be modified by choosing the correct synthesis conditions (pH, reducing agent). Sometimes also, clustering of
several Au particles in micelles of polymer was observed.


The modification of alumina by titania has been studied in co-operation with the group of J. Mouljin (Delft University of Technology). The preparation of a uniform layer of titania on the alumina, in order to prepare a high-surface area of titania, has not yet succeeded.

The deposition of carbon on alumina in order to prepare a sophisticated catalyst support material has been successfully achieved, in co-operation with the group of J. Mouljin (Delft University of Technology). The carbon forms a uniform, though not (yet) very well-defined layer on the alumina.

Tungsten-modified zirconia is being studied in collaboration with the groups of J. Mouljin (Delft University of Technology) and H. Knözinger (Inst. Phys. Chemie, München). The modified zirconia is clearly different from pure zirconia, but the exact nature of the differences is still under investigation.

Rhenium oxide on alumina is studied in co-operation with the group of J. Mol (University of Amsterdam). At high loading of rhenium oxide, small particles are formed on the alumina. Intermediate and low loading are also being studied.

Alumina synthesised using new preparation methods is characterised in collaboration with the group of R. Sheldon (Delft University of Technology).

4.11 Hydrotreating Catalysts (P.J. Kooyman; R. van Santen [Eindhoven University of Technology]; J. Mouljin, A.M. van der Kraan [Delft University of Technology])

Molybdenum and tungsten sulphide based hydrotreating catalysts are studied in collaboration with the groups of R. van Santen (Eindhoven University of Technology) and J. Mouljin (Delft University of Technology). The stacking of the slabs of sulphide may play an important role in determining the catalytic performance of these materials. The stacking is studied using the same preparation method on different support materials (alumina, silica, titania, zeolites, carbon), and by using different preparation methods (addition of complexating agents, variation of calcination and sulphonation temperature). It has been found that next to the slabs of the disulphides, sometimes small entities are formed that show good catalytic performance for specific reactions. For other reactions the slab structure is the main active species.

Cobalt, nickel and iron sulphides on zeolites have been studied in co-operation with the groups of A.M. van der Kraan (Delft University of Technology) and R. van Santen (Eindhoven University of Technology). For these systems, the method of occlusion of the metal ions prior to sulphonation is very important. When using ion exchange, most of the metal ions are found inside the zeolitic channel system. When impregnation is used, a substantial part of the metal is found clustered on the external surface of the zeolite. The method of sulphonation is also very important. When starting from a system in which most of the metal ions are located inside the zeolitic channel system, sulphonation in the presence of water induces the formation of large particles of sulphide on the external surface of the zeolite. When using hydrogen sulphide / hydrogen / inert gas without contamination, the sulphidic phase consists primarily of small particles inside the zeolitic channel system. The systems in which the metal sulphides are present as small particles inside the zeolitic channel system show a much better catalytic performance than those where a substantial part of the sulphide is present in large particles on the external surface.
Sulphur-resistant noble metal catalysts are studied in co-operation with the group of J. Moulijn (Delft University of Technology). TEM work in this project is focused on the metal particle size and the formation of metal sulphides.

4.12 Noble Metal Catalysts

P.J. Kooyman; J. Moulijn, H. van Bekkum, Th. Maschmeyer [Delft University of Technology]; V. Ponec, B. Nieuwenhuys, R. Louw [Leiden University]

The dehalohydrogenation of chlorofluorocarbons using various noble metals supported on active carbon is being studied in collaboration with the group of J. Moulijn (Delft University of Technology). In this project it was found that the noble metals are redispersed during the induction period of the catalytic reaction. This redispersion of noble metals, without the use of an oxidation step, is a previously unreported phenomenon, which will also be investigated on other support materials.

The particle size of ruthenium catalysts has been studied in co-operation with the group of J. Moulijn (Delft University of Technology). These catalysts are used for the partial hydrogenation of benzene. Both supported and unsupported catalysts have been studied. Next to the pure metal, the influence of several promoting agents has been studied.

Various noble metal catalysts supported on silica and alumina are studied in co-operation with the groups of V. Ponec/B. Nieuwenhuys and R. Louw (Leiden University). Some examples are gold on silica, both unpromoted and promoted with cobalt oxide, cerium oxide or lanthanum oxide, and gold and platinum on alumina. These catalysts are used in various reactions, like the total combustion of methane, NO reduction, and total oxidation of chlorohydrocarbons. For these systems reliable information about the metal particle size, and the particle size distribution, can only be obtained using HREM. The location and phase of promoters that are added to the catalysts can also be determined using HREM. Next to the fresh and pre-treated (calcination and/or reduction using various procedures) catalysts, the used catalysts (after use in a catalytic reaction) are examined in order to determine changes that occur during the catalytic reaction.

Platinum and platinum-bismuth, supported on active carbon, are used as catalysts for selective oxidation reactions by the group of H. van Bekkum/Th. Maschmeyer (Delft University of Technology). Using HREM it could be determined that for certain preparation procedures the platinum and bismuth form mixed metal particles, whereas for other preparation methods the two metals each form separate particles. The particle size can also be influenced by the preparation method.

For ruthenium on active carbon, the influence of the type of carbon support used is studied by the group of H. van Bekkum/Th. Maschmeyer (Delft University of Technology). For a series of catalysts prepared via the same synthesis route on different types of carbon, the ruthenium particle size distribution was the same, and very large. However, the catalytic properties differed within the series, so it was concluded that the type of carbon directly influences the catalytic properties of the ruthenium.

4.13 Transition Metal Oxide Catalysts

P.J. Kooyman; J. Moulijn [Delft University of Technology]; R. van Santen [Eindhoven University of Technology]; A. Bliek [University of Amsterdam]

Manganese oxide and copper oxide supported on alumina, have been studied in collaboration with the group of J. Moulijn (Delft University of Technology). The manganese on alumina basically forms manganese aluminate. When a high loading of manganese is used (above 20%), for some samples an amorphous layer is formed.
on the surface of the manganese aluminate, while for other samples a separate manganese oxide phase is observed. After use in desulphidation reactions, manganese sulphide is formed. The copper-containing catalysts that have been studied were very inhomogeneous. Next to pure alumina particles without any copper present, copper aluminate, copper-aluminate-supported copper oxides, and separate particles of copper oxide were observed.

Molybdenum oxide catalysts supported on alumina have been studied in cooperation with the group of R. van Santen (Eindhoven University of Technology). These catalysts are used for the formation of acetonitrile from ethylene and ammonia. Various phases of molybdenum oxide could be identified in fresh, pre-treated and used catalysts. For freshly calcined catalysts, molybdenum aluminate is formed. After pre-treatment with hydrogen and after the ammoxidation reaction most of the molybdenum is present as MoO$_2$-like species.

Nickel oxide supported on alumina is studied in collaboration with the group of A. Bliek (University of Amsterdam). For these catalysts, a mixture of alumina or nickel aluminate and another phase (possibly hydrotalcite) is formed. Nickel particles are present mainly on the alumina or nickel aluminate.

4.14 Miscellaneous (H.W. Zandbergen, P.J. Kooyman, F.D. Tichelaar, J. Jansen; E. van der Giessen, J. Schoonman [MIDEG]; B. Scarlett, J. van Geel, J. Moulijn [Delft University of Technology]; J. Reedijk [Leiden University])

The formation of ceramic particles in a new type of reactor has been studied in cooperation with the group of B. Scarlett (Delft University of Technology). This so-called bipolar mixing process can give ceramic powders that consist of particles that are very uniform in size and morphology, when the reactant solutions and process conditions are chosen properly.

The formation of fault planes in blends of rubber particles in polymers, has been studied in collaboration with the group of E. van der Giessen (MIDEG). In this project, the deformation of the rubber particles due to the forces during tear have also been studied.

In a project in which characterisation methods for nuclear waste are being developed, non-radioactive uranium compounds have been studied in collaboration with the group of J. van Geel (Delft University of Technology). The nitrates contain a lot of crystal water and are not stable under the electron beam. The oxides are usually multicrystalline, with amorphous material being present as well. The oxyfluoride is crystalline and stable under the electron beam.

The soot formed during the combustion of diesel oil in a normal car engine is studied in co-operation with the group of J. Moulijn (Delft University of Technology). The influence of additives (Pt, Ce, Mn, Fe, Cu) to the diesel oil on the combustion, and soot formation is investigated. The soot formed does not depend on the different additives, but the concentration and particle sizes of the additives in the soot vary greatly for different additives.

Lithium cathode materials are studied in co-operation with the group of J. Schoonman (Delft University of Technology). The phases present, and their distribution over the cathode, are important features of this project.

An iron-nickel-metallo-organic enzyme model system was studied in collaboration with the group of J. Reedijk (Leiden University). Unfortunately, the material is rather inhomogeneous. Some large single crystals are present which contain a uniform iron/nickel ratio, and some less crystalline clusters are present which show a large variation in iron/nickel ratio, even within one cluster.
Nafion ion-exchange resin was co-precipitated with silica by researchers from the group of J. Moulijn (Delft University of Technology). Unfortunately, the Nafion was not stable under the electron beam, but the morphology of the silica could be studied, and turned out to be very different for different precipitation procedures.

4.15 Metallic Point Contacts (T.R. de Kruijff, F.D. Tichelaar, N.N. Gribov, J. Caro [DIMES/TN, Delft University of Technology])

Thin silicon membranes on silicon on insulator substrates are used to fabricate point contacts with a well-defined interface in the nanoconstriction between the two metal electrodes. Much effort has been done to make suitable cross sections for investigations by Transmission Electron Microscopy. Transmission Electron Microscope images of hetero-interfaces in conjunction with energy dispersive x-ray analysis of the interfacial region show the capability of the process and its limitations. The latter involve material-specific phenomena on a nano-scale, such as an interfacial reaction between a metal film and SiO₂ and metal diffusion across the hetero-interface. These adverse effects can be avoided by a proper choice of the metals and the deposition temperature, as demonstrated with results of electrical measurements on a Au/Cu hetero-contact.

4.16 Growth Modes of SiGe by Chemical Vapour Deposition (F.D. Tichelaar, T.R. de Kruijff; A.V. Suslov, C. Visser, L.K. Nanver, J. Caro, [DIMES/TN, Delft University of Technology])

Si₁₋ₓGeₓ layers on Si<100> wafers have been grown by chemical vapour deposition as a function of substrate temperature, the total pressure and composition of the gas mixture. Properties of the layers have been investigated by PL, RBS, SIMS, SEM, AFM, and TEM. The thickness and concentration x vary in the range 1-200 nm and 10-70 at.% respectively. For x > (30±3)% a transition from 2D to 3D growth mode took place as evidenced by the appearance of SiGe islands instead of flat layers. This is a result of strain relaxation. The island morphology was studied by TEM, SEWM and AFM. The transition is clearly visible in the PL of Si-capped SiGe layers of increasing thickness. At the transition the usual SiGe PL peaks are strongly broadened, whereas above the transition thickness there are two additional peaks of SiGe islands. Cap deposition does not induce the transition, but can influence its details. From the investigations it follows that flat Si₁₋ₓGeₓ layers of a few nanometers thick and with x > 50 at.% can be deposited by CVD. The PL spectrum indicates a good quality of the layers.


Solar cells using thin-film polycrystalline silicon have received wide attention due to the advantage of cost reduction and large area production. Most deposition techniques for the production of thin-film solar cell material with sufficient efficiency suffer from either low deposition rates or a high process temperature. High quality poly-Si films can now be made on a steel substrate with high deposition rates by Hot-wire Chemical Vapour Deposition (HWCDV). The device quality is closely related to the microstructure of the film. Columnar grains in the growth direction of the film can enhance the transport of the photogenerated carriers, since grain boundaries and grain-boundary defects neutralising these carriers can be avoided. Besides the grain structure, the void content (oxygen penetration affects the device performance) and the
substrate/film interface are important parameters. It is the aim to improve the device quality by controlling the microstructure of the Si layers. We studied the microstructure of differently prepared poly-Si layers on glass substrates by transmission electron microscopy (TEM). Cross sectional bright field and high resolution TEM micrographs were taken with a Philips CM30T instrument operating at 300 kV. The structure of the poly-Si films is strongly dependent on hydrogen dilution of SiH₄. If a Si layer grown with a high hydrogen dilution (poly1-type), the layer is for the larger part crystalline, also at the glass substrate. Although some larger crystals occur (~100 nm), the grains are generally quite small and the complete layer is highly porous. A large density of elongated voids in the growth direction occurs. Selected area diffraction showed that the small grains are randomly oriented. If a "poly2-type" (i.e. at low hydrogen dilution) layer is grown the microstructure is completely different. Large columnar shaped crystals occur without much porosity. Diffraction experiments show that these crystals are 220 textured in the growth direction, and twinning occurs frequently. At the interface with the substrate, however, an amorphous incubation phase is present, together with vertically aligned elongated voids. The amorphous nature of the incubation phase was established by tilting experiments and high resolution imaging. A new approach, leading to an improved device quality, was used to integrate the two types of growth regimes by making a profiled layer in which a fixed thickness of poly1-type layer acts as a seed layer for the poly2-type deposition. For an n-i-p cell on a steel substrate, using a profiled layer as i-layer, crystalline nucleation at the interface with the substrate occurs and some horizontal cracks occur. These cracks are probably the result of the lower deposition temperature of the n-layer (200 °C in stead of ~500 °C). In the poly2 layer almost no voids occur, and few amorphous areas. In a profiled layer on glass the void densities have been estimated by taking into consideration the local foil thickness. The void density was estimated as ~25000/μm³ in poly1 and 50 - 1000/μm³ in poly2.

In conclusion, the microstructure of the profiled layer determined by TEM could be correlated with the quality of the poly-Si layers and the growth conditions by HWCVD on glass and on steel.

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PERSONNEL

Scientific staff
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- dr.ir. J. Sietsma (0.15)
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RESEARCH AREAS AND OBJECTIVES

The group’s central research theme is the study of atomic-scale processes in materials far from equilibrium. Defects and atomic transport, resulting from thermal excitation of the material (diffusion, structural relaxation), from mechanical excitation (flow, creep), from random particle arrival (film growth), and from excitation by energetic particle collisions (sputtering and ion-beam assisted deposition), are the key subjects under study. The two main areas of research are (1) atomic dynamics in metallic glasses under various conditions and (2) nanoscale mechanisms controlling thin film growth. Whereas our main interest lies in fundamental materials science, the relation with real materials properties is never left out of sight. Experimental work and computer simulations are both fully developed and closely connected research activities.

In 1998 the Faculty of Applied Sciences has ordered a substantial size reduction of our group, taking effect in 1999. As a result the first research area (metallic glasses) will be discontinued.

1 Metallic Glasses

A renewed interest in metallic glasses has developed in the last few years, due to the discovery of a number of alloys that can be amorphised at cooling rates as low as 1 K/s. Consequently the material, of which the mechanical strength is one of the advantageous properties, can now be made in dimensions on the order of millimetres,
instead of 10 μm thick melt-spun ribbons. Part of our research aims at understanding the mechanical behaviour of the model alloy Pd₄₀Ni₄₀P₂₀, one of the alloys that can be amorphised by relatively slow cooling (although not as slow as 1 K/s). This alloy is one of the more stable glasses; within the amorphous state a metastable equilibrium can be reached before crystallisation occurs. The other part of the research program is focused on understanding atomic motion in metallic glasses (diffusion, structural relaxation). This part is executed by computational simulation methods.

2. Defects and Growth Phenomena in Thin Films

Materials Science at the Nanometer Scale
One of the dominant trends in materials science is the fabrication, characterization, and application of materials whose characteristic feature sizes approach the nanometer scale. Achieving an understanding of – and ultimately control over – the properties and behaviour of materials at the nanometer scale has therefore become a major theme in materials research. This is especially the case for thin films, where nanometer-scale features like surface roughness and texture, interface structure, and defects may all be important for the useful properties of a film after deposition. Understanding and manipulating a thin film while it grows is therefore an important field of interest.

Computer simulations are very useful to illustrate these points. Figure 1 shows results of large-scale 3D Molecular Dynamics simulations of molybdenum films grown on molybdenum substrates. It is clear that even in this simple case the surface of the films develops in dramatically different ways depending on the substrate orientation: a (110) film becomes rough, while a (100) film (and the (910) grain in the centre) remains flat. One only has to imagine a second film deposited on top of these films to understand the differences in film properties that will evolve – not only mechanical properties like adhesion, stress, and yield strength, but also electromechanical properties such as those leading to IC failure at high current densities.

Controlling Film Growth
Film growth can be controlled. Two important methods are (i) increasing the deposition temperature, and (ii) supplying additional energy to the growing surface, either by increasing the energy of the arriving atoms or by co-bombardment with accelerated ions. Both have the objective of enhancing the mobility of the atoms just condensed on the surface—which generally leads to more perfect films—but the two have different effects on structure-related properties such as roughness, grain size, and stresses. This, in turn, will lead to differences in film properties. It is this field on which our work concentrates, both experimentally and by computer simulation methods.

Currently our facility for Thermal Desorption Spectrometry of films manufactured with Ion-Beam Assisted Deposition can provide us with detailed information on the types and concentrations of point defects and defect clusters that develop in a film as it grows. Data on the surface itself can also be extracted from these experiments (to some extent). This is interesting, since there is a clear correlation between the defects in the film and the topology of the surface. Therefore the study of defects in a film is interesting not only in its own right—what are their properties, what is their concentration, what role does an interface between two dissimilar films play?—but also to obtain insight in the atomistic mechanisms that lead to the surface structure and that ultimately give a film its properties. Again with the help of Figure 1, one can easily imagine that enhanced surface diffusion or deposition of momentum and energy during growth will modify a film.

Current System under Study
Copper/tantalum is the current system under study. One of the reasons is that thin Cu films on Ta or TaN diffusion barriers are desirable materials combinations for interconnects in the newest 0.18 um generation ICs. Our objective is to enhance our understanding of the way in which the parameters of the copper deposition process influence the nano- and microstructure of such films, which in turn will affect the properties of an electroplated Cu film on top of the thin Cu “seed” film. As mentioned above, we will in particular study the use of low-energy ion beams for controlling defects such as vacancies, voids, and grain boundaries in the film—the ions acting either as suppliers of energy concurrently with the growth of the copper layer (Ion Beam Assisted Deposition) or as pre-treatment agents of the tantalum surface. The role of the Cu/Ta interface, which is a heterogeneous interface (fcc/bcc) receives special attention, since it is the source of stresses, defects, and may be the arena of CuTa non-equilibrium phase formation (during ion bombardment). The thickness of the films will range from the ultra-thin regime (a few angstroms) up to 0.1 um. Other parameters to be studied are the flux and energy of the assisting ions, and the Ta substrate orientation and crystallographic type. Issues of thermal stability and adhesion are approached by varying the deposition temperature and annealing treatments. The research involves both experimental work and computer simulations.

In addition to Thermal Desorption Spectrometry, angle-resolved XPS, Auger spectroscopy, X-ray and electron diffraction (all in the group of prof. E.J. Mittemeijer), and positron annihilation (prof. A. van Veen, IRI, Delft University of Technology) will be used.

Other Uses of Ion Beams
In addition to controlling film properties during deposition, ion beams can also be employed for manipulating films after deposition. Two of such subjects in which our group is involved are:

1) Sputter erosion of semiconductor material (Si, Si/Ge) by 500-1000 eV O₂⁺ ion
beams

The ultimate goal is to use the results of simulation studies to enhance the applicability of SIMS for ultra-shallow dopant profiles and sharp composition modulations. This is of great importance for the optimisation of future generations CMOS transistors and multilayer devices. This project is carried out in cooperation with DIMES (Delft University of Technology) and Philips Research (Eindhoven).

2) Fabrication of high-reflectivity, multilayer XUV mirrors having individual layer thicknesses in the nanometer range

The success of these mirrors depends critically on the optimal layer growth conditions. It has been found that the use of low-energy ions for polishing the surface of the just-deposited layers forms a powerful means to significantly reduce the roughness of the layer interfaces. Multilayer reflectivities of over 90% of the theoretical value for ideally flat interfaces have thus been achieved, enabling new, yet demanding applications e.g. in micro-lithography at XUV wavelengths.

With current Molecular Dynamics simulations (MD) we can conduct a systematic study of the growth of Mo/Si multilayers. Ultimately this will allow us to predict optimal process parameters and thus it forms a welcome acceleration of the empirical optimisation. Prime motivation, however, is an improved fundamental understanding of the underlying growth processes. This project is carried out in co-operation with FOM Institute for Plasma Physics (Rijnhuizen).

To summarise, the thin-film research program of our group involves various uses of low energy ion beams to study solid state processes. The work is aimed at:
- physical aspects of film growth and film architecture,
- interaction of energetic particles with solid surfaces,
- defects in films and at surfaces.

3 Algorithms and Software

Although third-party software is becoming increasingly more sophisticated, our group continues to have an unsaturable need for our own high-level and user-tuneable general software (e.g. for curve-fitting, solving partial differential equations, and eigenvalue problems) and dedicated software (e.g. for analysis and visualisation of computer simulation results). The development of such software remains a significant activity of our group.

FACILITIES

- A combined apparatus for Ion Beam Assisted Deposition (IBAD) and Thermal Desorption Spectrometry (TDS).
- Equipment for accurate measurement of creep, viscosity, tensile strength, electrical resistivity, and sound velocity.
- Most apparatuses are fully computer controlled. Together with the group's many Unix-based workstations and several other smaller computers, they form an integrated networked environment.

RESEARCH REPORT 1998
1 **Metallic Glasses**

1.1 **Experimental Research on Metallic Glasses** (P.G. de Hey, J. Sietsma)

**Mechanical Behaviour of Amorphous Pd$_{40}$Ni$_{40}$P$_{20}$**

The influence of plastic deformation on the structural state of amorphous Pd$_{40}$Ni$_{40}$P$_{20}$ is investigated by means of tensile test and creep measurements as a function of temperature, stress, strain rate and pre-annealing time. The structural state of the material after the deformation is investigated by means of Differential Scanning Calorimetry. It is found that amorphous Pd$_{40}$Ni$_{40}$P$_{20}$, when pre-annealed into its metastable equilibrium state, shows a large strain softening effect when deformed at temperatures close to the glass transition temperature. The strain softening effect is less pronounced or even absent in samples that are only briefly pre-annealed. The DSC traces show that the structural state of the material disorders during the deformation and that the material reaches a strain rate and temperature dependent equilibrium state, which differs from the thermal equilibrium state. The defect concentration depends on the strain rate according to a power-law with an exponent 0.7.

The occurrence of strain softening in this metallic glass can be understood from the concept of free volume, describing the disorder in the amorphous structure. Plastic flow is envisaged to take place at locations with a relatively large amount of free volume, called defects. Re-ordering of the local atomic configuration, giving in to the applied stress, effectuates the plastic deformation. The stress-strain curves can be understood by additional disordering occurring during this event. The disordering leads to an increased defect concentration, which causes the strain softening. Since simultaneously with this creation of defects, thermal annihilation of defects takes place, the defect concentration reaches an equilibrium level $c_f^*$ that is dependent on the temperature and the strain rate. From DSC experiments on deformed samples quantitative data have been derived on $c_f^*$ in function of temperature and strain rate. Examination of the extensive set of data, including interrupted tensile tests and abrupt strain-rate changes, leads to a consistent model description from which it follows that during a deformation event a defect forms with a certain probability. This conclusion indicates that defects in the metallic-glass structure form a discrete feature rather than merely being the result of continuous fluctuations of free volume. The results of the complete research program are currently being prepared for publication in the Ph.D. thesis of P.G. de Hey, which will appear in 1999.

1.2 **Computer Simulations of the Dynamics of Metallic Glasses** (L.D. van Ee, J. Sietsma, B.J. Thijssen)

**Diffusion in Amorphous Ni$_{81}$B$_{19}$**

Molecular-Dynamics studies on the diffusion mechanism in amorphous Ni$_{81}$B$_{19}$ have been completed. This work has led to substantial new insight in the way atoms move around in close-packed non-crystalline matter. The results are comprehensively reported in the Ph.D. thesis of L.D. van Ee, which has been completed in 1998. The general conclusions of this thesis vividly summarise the outcome of the research program:

- The diffusion events below the glass-transition temperature are of an indirect nature, i.e. they take place at distinct positions in the structure. Such a position - in the language of materials science one could speak of a defect - differs significantly from the average glassy structure. Its local potential-energy landscape shows considerable deviations from harmonicity and is strongly correlated with low-frequency localised vibrational modes. These defects are also strongly re-
lated to sites that contain a relatively large amount of interatomic space.

- All observed diffusion events below the glass-transition temperature take place through a co-operative process involving some tens of atoms. Each atom has a jump distance smaller than an atomic diameter, but the atoms involved move at the same.
- The atoms involved in a diffusion event have two nearby potential-energy minima available (in some cases even three), and the jump location can be called a two-level state. The atoms involved jump to the neighbouring minimum when the low-frequency mode that is localised at this site becomes excited with enough energy.
- At elevated temperatures the dynamics in the glassy state can be pictured as follows. At each instant the system consists of a large collection of vibrational modes. The majority of these modes are non-localised and give rise to overall vibrational motion. A few low-frequency modes are localised, and some allow atomic motion at a particular site (defect) in the system. Naturally the atoms around the defect participate also in non-localised modes, but the resulting motion has much smaller amplitudes. It is the concentrated contribution from the low-frequency modes that can set a group of atoms into a particular kind of motion, which has all the characteristics of a co-operative jump towards a new configuration. Seen in this way, the diffusion in amorphous materials is governed by the mechanism of groups of atoms executing such jumps.

2 Defects and Growth Phenomena in Thin Films

2.1 Experimental Thin-Film Program (J. van der Kuur, J. van der Linden, L.J. Seijbel, M. Pols, G.T.W.M. Bekking, B.J. Thijssse)

Molybdenum Films Deposited with and without Ar⁺ ion Assistance

Using He⁺ as probe particles, we have studied Mo thin films (5–1000 Å) deposited on large-grained polycrystalline Mo substrates with and without Ar⁺ ion beam assistance. Data were obtained on film morphology, defect concentration, vacancy mobility, Mo diffusion, surface coverage, Ar entrapment, etc., as well as on the influence of ion bombardment and deposition temperature. The results of the complete research program – which also includes Si films deposited on Mo substrates – are too numerous to summarise here. They have been published in the Ph.D. thesis of J. van der Kuur, which was completed in 1998.

Molybdenum Films Deposited on Single-Crystalline Substrates

In 1998 the research program has begun to focus on the influence of the crystallographic orientation of the substrate on the resulting film. Studies were commenced on (110) and (100) single-crystalline Mo substrates. The results for the (110) substrates turned out to be insufficiently reproducible, probably as a result of the repeated ion bombardments. The results for the (100) substrates were reliable. When these are compared to those for polycrystalline substrates, the following picture emerges.

The growth of Mo films on a poly-Mo substrate (which can be considered (110)-oriented in our case) starts in a planar fashion, but after 25 Å extremely fine columnar grains (50 Å) start to develop. In the grains the point defect concentration is $1 \times 10^{-4}$. Mo films on a (100) substrate grow in a similar way, but the columns begin earlier (10 Å), and the grains are smaller (15 Å) and contain more point defects ($3 \times 10^{-4}$). This last point may be connected with the fact that surface diffusion on (100) is slower.
than on (110), thus allowing more surface vacancies to develop into 'bulk' vacancies. 250 eV Ar⁺ assistance during Mo film growth leads on average to a 8% incorporation probability of Ar in the film, up to an Ar saturation concentration of 3.5x10⁻⁵ Ar/Mo. These numbers are almost independent of orientation. For (110)-films Ar assistance reduces the values for grain development to those for (100)-films. Apart from self-incorporation the Ar ions also create additional defects: monovacancies especially in the thinner films (planar stage), vacancy clusters in thicker films (columnar stage). This is also seen in MD simulations (Figure 1), which suggest that 'grain boundaries' are in fact interconnected vacancy clusters; other work also shows that vacancy clusters do not develop in very thin films. The overall defect creation rate of a 250 eV Ar ion is about 0.1 defect, including self-trapping.

Finally, the substrate orientation is found to play a role for the immediate subsurface trapping of the noble gas ions. Whereas that of Ar is more pronounced in (100) than in (110), that of He is totally absent in (100). This is not yet clearly understood in terms of surface energies, but it illustrates how the subtleties of atomic co-ordination near a surface can lead to pronounced effects in experimental observations. The fact that ion assistance reduces subsurface He trapping is in agreement with the MD result that IBAD reduces surface roughness (and therefore surface area).

Copper Films Deposited on Molybdenum

Late 1998 the thin film work shifted to copper deposition. As mentioned earlier, the system Cu/Mo is interesting from the viewpoint of IC metallisation; it also is a heterogeneous (fcc/bcc) and immiscible system, which offers the possibility to study interfacial effects on defects and stresses, metastable phase formation, and first-order transitions (Cu solid-gas sublimation). This work is still in its initial stage. To summarise the first results: In our combined apparatus for thin film deposition and thermal helium desorption spectrometry (THDS), Cu was grown by means of PVD and ion-beam assisted deposition (IBAD) on Mo substrates. The thickness of the films varied between a single monolayer and several tens of nanometers. With a He⁺ implantation energy below 90 eV, the threshold energy for vacancy, THDS was used to study the native defects in the grown film and at the interface. Above 90 eV new defects are produced. Surface defects, vacancies, and defects at the Cu/Mo interface have been detected, and the influence of stress gradients as a function of film thickness is beginning to become clear. Also, 1000 eV He⁺ fluences above 3x10¹⁶ cm⁻² are enough helium is left in the Cu film to give rise to a detectable helium release when the film sublimes at 1350 K. The peak is significantly dependent on film thickness, again hinting at important effects due to stresses. THDS has also be used to measure the energy loss in the Cu layer and the implantation profile of the helium ions. This work is currently in progress.

2.2 Computer Simulations of Thin-Film Deposition (E.F.C. Haddeman, P. Klaver, B.S. Bunnik, B.J. Thijssse)

Molybdenum on Molybdenum

To complement our experimental work, Molecular Dynamics simulations using embedded-atom and Firsov-Molière potentials were performed to study the growth of electron-beam evaporated molybdenum (100) and (110) films with and without argon ion assistance, as well as the effects that take place on subsequent irradiation by low-energy helium ions. The results have been compared with corresponding experimental results from thermal helium desorption spectrometry and other techniques, and atomic-level information is obtained on mechanisms governing film mor-
Physical Materials Science

Phenomenology, ion trapping, and defect dynamics. We find good agreement for all IBAD-processes and for the columnar growth mode that evolves after the initial planar growth. Several atomic-scale processes have been observed in detail, including ion trapping, local melting, defect formation, atom and vacancy diffusion, dislocation loop formation and stress-induced vacancy attraction. When only thermal processes at the surface are the dominant source of film evolution, such as in unassisted vapour deposition, discrepancies are found between simulations and experiment.

Copper on Molybdenum

In 1998 work has begun to study Cu growth on Mo by Molecular Dynamics simulations using embedded-atom and Firsov-Molière potentials. Although most Cu-Cu and Mo-Mo interaction parameters are available in the literature, the medium-energy range parameters for Cu-Cu and all parameters for the mixed interaction Cu-Mo had yet to be established. This is somewhat difficult because no equilibrium CuMo phases exist. However, using non-equilibrium data on the heat of solution and Miedema model calculations, progress is being made. Meanwhile trial runs with non-optimised Cu/Mo potential parameters have been performed to get a feel for the phenomena that occur during fcc/bcc deposition. Stresses, dislocations, rotated and tilted film/substrate lattice orientations have all been observed (Figure 2). Analysis of the resulting structures is complicated. Cu-on-Cu deposition runs, which do not depend on mixed interactions, were performed to investigate fcc film deposition, as a pendant to the existing work on bcc-on-bcc deposition. The results are currently under study. Among other things, they clearly show the low stacking fault energy of copper: so far we have not succeeded in depositing a copper film on copper without stacking faults between planes or in planes. A better temperature control in the growth simulations is necessary.

Figure 2: Simulation of Cu film deposited on (100) Mo substrate. Greyscale indicates local crystallographic symmetry (dark = bcc, light = fcc/hcp)

Self-Interstitials in Molybdenum Films

On request of dr. M. Nastasi of Los Alamos National Laboratories simulation studies of the mobility and clustering of Mo self-interstitials in thin films were performed. The purpose is to predict the stress properties of thin films that have been heavily ion irradiated. Initial S.I. concentrations were 1%, which is a very high value. The dynamics of single interstitials and various interstitial cluster types are being monitored as a function of time. This project is still in progress.
Large-Scale Molecular Dynamics

In 1998 the Molecular Dynamics program code has been adapted for use on parallel computers. This enabled us to begin with large-scale simulations, in order to investigate films with features larger than a few nm (e.g. grain boundaries) and to assess the possible limitations of the smaller box sizes used earlier. Using 16 processors we have studied Mo growth on 350 nm² Mo substrates. Results for (110) substrates (Figure 1, top) confirmed our small-system results: similar surface roughness, columnar growth mode and vacancy (cluster) concentrations were found. The growing surface develops an interesting topographic structure, with elongated ridges parallel rather than perpendicular to the incident flux direction (Figure 3). This indicates that side-wall capture prevails over geometric shadowing.

Figure 3: Top view of the Mo film of Figure 1, top. The evaporation flux emanates from the left, at an angle of only 15° with the substrate normal. Greyscale denotes height. The black regions are the deep canyons that are also visible in Figure 1.

As a second substrate a (100)/(019) bi-grain was chosen, containing two parallel Σ = 41 grain boundaries of which one “opens up” towards the surface and the other “narrows in” (Figure 1, bottom). The results for growth on the (100) part are in agreement with the earlier obtained small-system results: no columnar growth and a quite flat surface. The marked difference with the (110) films is not due to differences in surface diffusion coefficients or to the survival probabilities of surface vacancies. Rather it seems that a (110) surface wants to decompose into (100) microfacets, thereby introducing roughness that is self-amplifying and leads to columns. The (019) grain (which remains smooth as the thickness increases) appears to display a similar faceting tendency, but not enough to amplify roughness. The grain boundaries form the most interesting regions. Line and screw dislocations appear as the film grows, as well as dislocation loops. The two grain boundaries show a different behaviour, not only as a function of deposition time, but also as a function of (post-deposition) annealing time. The results are still being analysed, and deposition runs at elevated temperatures have commenced.

Code Development

In 1998 the Molecular Dynamics software has been improved and extended in the following ways:
• Parallellisation of the code.
• Addition of the Dynamic Monte Carlo algorithm (purpose: to speed up structure equilibration between atom arrivals and ion impacts).
• Implementation of the Modified Embedded Atom Method (purpose: to add angular dependent terms to the interaction potentials for improved realism – especially for systems involving semiconductor elements). This activity is still in progress.
• Implementation of an algorithm to decompose an atom's neighbour environment in spherical harmonics in order to classify the atom's local crystal structure.
• Development (in progress) of algorithms to track defects in simulated films, classify their types, and follow their time evolution.

3 Algorithms and Software Development

In addition to software designed for specific purposes, two programs with general applicability deserve mentioning. Workers interested in using these program should contact us.

3.1 Spline Approximation of Data (B.J. Thijsse; M.A. Hollanders [NAM, Assen]; J. Hendrikse [Twente University])

The program code has been augmented by a special algorithm to handle "difficult" data sets. The results have improved significantly. This work has been published in 1998.

3.2 Model-Fitting of Data (J. van der Kuur, E.F.C. Haddeman, B.J. Thijsse)

Our software for curve-fitting has been improved considerably, most notably by an easy-to-use graphical interface and better coupling to the user programs that can be used to generate model data given a set of fit parameters.

PUBLICATIONS

L.D. van Ee
The diffusion mechanism in amorphous Ni_{81}B_{19} studied by molecular dynamics simulations

L.D. van Ee, B.J. Thijsse, J. Sietsma
A possible mechanism for atomic transport in amorphous metals

L.D. van Ee, B.J. Thijsse, J. Sietsma
Atomic two-level states and relaxations observed in a computer model of amorphous Ni_{81}B_{19}

L.D. van Ee, B.J. Thijsse, J. Sietsma
Temperature dependence of diffusion and structural defects in a molecular-dynamics model of amorphous Ni_{81}B_{19}

P. de Hey, J. Sietsma, A. van den Beukel
Structural disordering in amorphous Pd_{40}Ni_{40}P_{20} induced by high temperature deformation

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J. Huijbregtse, F. Roozeboom, J. Sietsma, J. Donkers, T. Kuiper, E. van de Riet
High-frequency permeability of soft-magnetic Fe-Hf-O films with high resistivity

B.A. Korevaar, M. Pols, J. van der Kuur, B.J. Thijsse
Defecten in molybdeen-lagen en de effecten van ionenbundel-assistentie tijdens het
opdampen (in Dutch)
Nevacblad 36 (1998) 3-10

J. van der Kuur
Defects in thin films deposited with and without ion assistance

B.J. Thijsse, M.M. Hollanders, J. Hendrikse
A practical algorithm for least-squares spline approximation of data containing noise
Computers in Physics 12 (1998) 393-399
9.1 Analysis and Software Development

The program code has been augmented by an algorithm to handle "normal" data sets. The results have improved significantly. The work has been published in 1998.

3.3 Model Fitting of Data (J. van der Velden, R.C. Kemineran, B.J. Tijhaze)

Our emphasis for curve-fitting has been to produce an algorithm that is easy-to-use. This approach involves a high degree of user control and is believed to be superior to the main programs that can be used to generate model building from a set of experimental data.

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HIGHLIGHTS

- The papers of the successful Polymer Networks Conference held last year have been published in book form with K. te Nijenhuis and W.J. Mijs as editors.
- W.F. Jager has co-authored a book on UV and EB curing of coatings.
- A new type of scanning microscope (SPEM) has been developed, which can be used to visualise the clustering of polar molecules in materials on a microscale.
- The size of inclusions in heterogeneous polymers has been determined for the first time by means of dielectric spectroscopy.

RESEARCH AREAS AND OBJECTIVES
(see also group’s web site: http://www.stm.tudelft.nl/tms)

1 Polymerisations (W.F. Jager, W.J. Mijs)

The objectives are: finding synthetic routes for the preparation of new polymers, understanding the relations between chemical structure and physical properties, both with the aim of producing new polymeric materials. The research topics are a/o: synthesis of new polymers with reactive side groups, mesogenic side groups, fluorescent chromophores or electron donor-acceptor side groups connected to the main chain by spacers of variable length; preparation of networks by controlled crosslinking. Changes in the characteristics of fluorescent probes, which can be built-in into a polymer, and which give insight in polymerisation kinetics and network formation. The electrical and rheological properties as well as phase behaviour of the polymers developed are investigated.

2 Physical Chemistry and Rheology (K. te Nijenhuis)

a) Development of models to describe the network formation in high molecular weight polymers. Application to kinetics of crosslinking reactions and to structures of networks.

b) Film formation in water borne polymer dispersions and their rheology.

c) Rheology of dilute solutions of ultra high molecular weight polymers through porous beds.
3 Materials and Processing (A. Posthuma de Boer, J. van Dam, A.D. Gotsis)

These investigations are aimed at understanding the properties of polymers, in particular those in the melt, in order to create new materials by blending and/or rational processing. The research on blending is focussed on the formation, stability and properties of special polymer blends, i.e. co-continuous and self-reinforcing ones. The processing studies include (micro)structure evolution, rheology and the effect of molecular structure on processing and mechanical properties of polymers.

4 Electrical Properties (J. van Turnhout, M. Wübbenhorst)

This part of the research programme focuses on the use of electric fields to investigate polymers and as a means to induce structural changes. Dielectric spectroscopy is explored for studying network formation, the properties of liquid crystalline main- and sidechain polymers, and the microstructure and properties of polymer blends. Dielectric spectroscopy is further applied for characterising the durability of coatings. Structural changes induced in polymers by an electric field are studied by measuring the electromechanical response of liquid crystalline elastomeric networks. Heat wave techniques have been developed which allow measurements on the thermal properties of polymer films and coatings during crosslinking or polymerisation. The properties of polymeric nanostructures incorporated in zeolite crystals are analysed as well. Finally, hybrid structures consisting of a (porous) polymer film filled with an electro-active inorganic powder are synthesised and examined.

FACILITIES

1 Characterisation
   - Two differential scanning calorimeters
   - Fourier-transform infrared spectrometer
   - Infrared microscope
   - Three microscopes (polarisation and fluorescence)
   - Small angle X-ray apparatus
   - 2 Dynamic-mechanical-thermal analysers
   - 2 Dielectric-thermal analysers
   - Three tensile testers
   - Torsion pendulum
   - Deformation micro calorimeter
   - Heat distortion temperature tester
   - Scanning electron microscope
   - Gel Permeation chromatograph
   - Gas chromatograph
   - Two Thermal gravimetric Analysers
   - Pendulum Izod Impact tester
   - Photothermal microcalorimeter

2 Rheology
   - Two high pressure capillary viscosity meters
   - Dynamic rheometer
   - Rheometrics mechanical spectrometer
   - Advanced rheometric expansion system for fluids
3 Processing

- Injection moulding machine
- Two transfer moulding machines
- Four single screw extruders of various sizes
- Double screw extruder
- Three two-roll mills
- Two hydraulic presses
- Four-roller apparatus
- Cone-flow apparatus
- Spinning-drop apparatus

RESEARCH REPORT 1998

1 Polymerisations

1.1 Fluorescent Probes for Monitoring (Photo)polymerisation Processes and Polymer Characterisation (W.F. Jager, R.H. Bode)

Fluorescent probes can be employed as mobility probes if their emission spectra are sensitive to the mobility of molecules in the medium that surrounds them. Such probes can be employed for monitoring neat polymerisation processes, in which the medium is transformed from a liquid into a solid glassy material. Another application is the detection of phase transitions in polymeric materials. Phase transitions can be observed by means of changes in the emission of fluorescent probes that have been added to a polymer. One of the main objectives of our research is finding structure-property relationships for fluorescent probes by a systematic variation of their molecular structure. In addition we want to know which information is revealed by the emission of a probe molecule in a polymerising system.

Two types of probes are being investigated: charge transfer probes of the D-π-A type and charge resonance probes of the D-π-A^+X^- type. These probes monitor the mobility of the medium by means of a shift in their emission wavelength λ_{max} due to a strong medium dependence of the energy of the excited state. The mechanism by which this is accomplished is fundamentally different for both probes. Charge transfer probes monitor reorientation of "solvent" molecules, a process which requires mobile "solvent" molecules (microviscosity), while conformational changes within the probe molecule itself (a process which requires free volume) lower the excited state of charge resonance probes.

Charge transfer probes are known for some time and the mechanism by which they sense mobility is fairly well known. On the basis of 4-dimethylamino-4'-nitrostilbene (DMANS), one of the most sensitive probes, novel architectures are realised such as reactive and polymer bound probes. Charge resonance probes were developed only recently and their photophysics is not known in detail. By systematic variation of their structure we envisage to obtain accurate relationships between their molecular structure and performance. Based on this knowledge more sensitive charge resonance probes will be developed.
2.1 Formation of a Gel-Network from Side-Chain Liquid Crystalline Polymer Solutions (M.W.C.P. Franse)

Earlier work of ir. P.M. Cordfunke has been continued. Typical features of this project are rheological and small angle x-ray spectroscopy (SAXS) measurements of solu-
tions of rod-like and disc-like side-chain liquid crystalline polymers. A statistical model for gel-network formation has been extended to polymers with a bimodal molecular weight distribution. This model has been tested on a simple gel-system. At a later stage this model will be applied to side-chain liquid crystalline polymer gels.

2.2 Interaction of Multiphase Fluid Flow (K.F.J. Denys)

This Ph.D. project is in a final stage. The main contributions are the following:

a) Derivation of new, mainly analytical expressions to predict the pressure drop for flow of complex fluids through tubes of changing cross-section leading to the development of an improved capillary bundle model.

b) Measurement of the influence of pH and salinity on the permeability of model porous media (packings of spheres) which were pre-adsorbed by weak polyelectrolytes and correlate the permeability with the adsorbed layer extension.

Both contributions are relevant with respect to polymer water-shutoff techniques in oil recovery.

2.3 Film Formation from Water-borne Polymer Dispersions (S. Zohrevand)

We used turbidity measurements in order to study the film formation process. Turbidity is based on two optical phenomena: Rayleigh scattering and multilayer interference. The ageing, annealing and application of some additives in a paint formulation have each some influence on film properties. In this project, these influences are investigated with the aid of the turbidity method. Together with rheological measurements on the latices used, new insights concerning the mechanisms of the film formation process and the structure of the films were obtained.

3 Materials and Processing

3.1 Co-continuous Polymer Blends (H. Veenstra)

In this project we investigate the influence of the molecular form and the rheological properties of the components on the formation and stability of interpenetrating network structures in polymer blends. We found that block copolymers may form such special morphologies in a wide range of compositions when blended with common polymers. Blends with co-continuous morphologies present the best combination of the properties of their components and show improved barrier properties.

3.2 Interpenetrating Polymer Blends (R.C. Willemse)

The goal of this project is to improve the mechanical properties of a mixture of waste plastics by creating an interpenetrating network. The main issue of the project is the study of the morphology development in a polymer blend in order to describe the effect of the process parameters on the formation of such interpenetrating networks for a wide composition range. This project was completed in 1998 with a dissertation.

3.3 Extensional Rheology of Polymer Melts (A.D. Gotsis, M.A. Odriozola)

The resistance of polymer melts to extensional flow was examined in uniaxial elongational flow and in complicated flows, where both elongation and shear occur. Polymers with different molecular architecture were studied: Linear flexible chains, chains with different degrees of branching, block co-polymers and liquid crystalline polymers. The goal of this study is to find the association between the differences in response and the molecular forms and (super)molecular structures in the melt. The initial part of the project financed by OZS-Polymeren PTN addressed the rheology of
liquid crystalline polymers and was completed in April 1998. The project continues with the study of the effect of branches on the extensional rheology of polyolefines.

3.4 Electrostriction in Rubber (A.M. Romijn)

Data acquired by high precision measurements of mechanical electrical and electro-mechanical properties of elastomers were interpreted in such a way as to distinguish between the mechanical effect caused by electrode attraction and the intrinsic change in polymer chain configuration.

4 Electrical Properties

4.1 Electrical Properties of Self-Reinforcing Polymer Blends (A. Boersma)

In the processing of polymer blends, the morphology (size and shape of the inclusions) has a significant influence on the properties of the final product. Using dielectric spectroscopy, it was possible to obtain information about the morphology of a blend of thermotropic liquid crystalline polymer particles in a thermoplastic matrix during extrusion. The size of the particles could also be determined for the first time, by taking diffusion into account.

4.2 Electrical and Optical Investigations on Liquid Crystalline Polymers (M. Wübbenhorst)

Side chain liquid crystalline polymers based on a poly(maleic acid) backbone (collaboration with prof. E.J.R. Sudholter [Wageningen Agricultural University]) have been studied with dielectric relaxation spectroscopy. In particular, the nature of a strong slow relaxation process appearing during the transition from the smectic B to the smectic E phase has been attributed to co-operative bond fluctuations within (growing) S₄-domains.

4.3 Nanostructures of Conjugated Polymers in Zeolite Crystals (G.J. Klap)

In collaboration with the department of Applied Organic Chemistry and Catalysis (prof. H. van Bekkum/dr. J.C. Jansen) zeolite crystals with self-assembled "polymer" chains were studied with temperature dependent scanning pyroelectric microscopy, dielectric spectroscopy, and dynamic light scattering. These measurements clearly revealed the (dynamic) behaviour of these confined one-dimensional chains. Furthermore, these experiments gave more insight in the formation of zeolite crystals.

4.4 Pyroelectric Investigations on NLO-active Guest-Host Materials (M. Wübbenhorst)

Pyroelectric studies on NLO active organic inclusion compounds (clathrates) have been performed in co-operation with the University of Bern (prof. J. Hulliger). Scanning pyro-electric microscope (SPEM) studies were performed layer by layer on PHTP-NNPP crystals revealing the genuine 3-dimensional structure of polar domains in particular in the seed region. The investigation of new guest-host materials was started up (collaboration with University of Freiberg, prof. E. Weber).

4.5 Electromechanical Properties of Polymer Composites (E.G.M. Veldman)

The dielectric behaviour of polyphosphazene composites was studied in order to derive a relation between dielectric constant and ceramic contents. Electromechanical measurements were performed on the disc-shaped composites using a new highly sensitive dilatometer based on a parallel-plate capacitor. The strain varies quadrati-
cally with the electrical field strength. The electromechanical response is the result of three effects (Maxwell stress, electrostriction and electrode attraction) of each we try to determine the relative significance.

The poly[bis(trisfluoroethoxy)phosphazene] used, shows a crystalline transition from orthorhombic to hexagonal, as was found by DSC and X-ray diffraction measurements.

4.6 Dielectric Relaxation Spectroscopy of Polymer Electrolytes (M. Wübbenhorst)

In collaboration with prof. L.W. Jenneskens (Utrecht University) the relaxation processes and electrical conduction of various polymer electrolytes - polysilanes and poly(ether esters) - were studied with dielectric spectroscopy. The effect of polymer structure and the Li-salt concentration on the temperature dependence of the conductivity and kinetic parameters of the α and α" relaxation as well as on the glass transition temperature have been analysed in terms of physical crosslinking and free volume. The α" relaxation is caused by the complexation-decomplexation of the Li-ions and shows up above the glass-rubber or α- transition in the polysilanes.

4.7 Photothermal Investigations on Liquid Crystalline Polymers (M. Wübbenhorst)

The thermal conductivity of various materials containing highly ordered rod-like molecules were investigated with different pyroelectric techniques (thin-film pyroelectric calorimetry, scanning pyroelectric microscopy). We have focussed on the thermal conductivity of zeolite-based and clathrate-based nanocomposites, which contain (quasi) one-dimensional chains of polar molecules. The influence of chain defects on the heat conductivity is also investigated.

4.8 Prevention of Marine Biofouling of Materials (H.J.A. Breur)

The biofilm formation process has been studied further. An attempt has been made to model the process in order to predict the amount of fouling occurring during the seasons. The modelling is based on experiments of last year. Substantial progress has been made towards the development of experimental methods for the assessment of the erosion properties of binder materials for antifouling paints. These methods are based on existing techniques (atomic force microscopy, dielectric relaxation...
spectroscopy and electrochemical impedance spectroscopy). Experiments for investigating the interaction between metals and biofilms and the corrosion processes resulting from this interaction have been started.

4.9 Real-Time Analysis of Mechanically Induced Microstructural Changes in Polymer Blends and Blockcopolymers (A. Speijer)

The chains of polymers are oriented during a tensile test. Stretching will also cause changes in the relaxation times and the microstructure, and in some polymers produce stress-induced crystallisation. The increase in chain-orientation as well as the changes in visco-elastic response and microstructure will be monitored and analysed in real-time with dielectric relaxation spectroscopy. By covering a broad frequency range, the changes can be revealed on various time and length scales. The combined electro-mechanical analysis is particular useful for blockcopolymers and blends. A special tensile apparatus equipped with insulated clamps and an oven is used for these experiments. This apparatus also allows for dynamical mechanical testing.

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PERSONNEL

Scientific staff
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HIGHLIGHTS
• Start of the Airbus A3XX fuselage project in co-operation with SLI, NLR and Airbus (GTO project)
• Start of a project for the development of a compression shear test set up for full scale fuselage panels (STW)
• Development of GLARE as a repair material for aircraft structures in cooperation with the USAD and GARUDA
• Start of the DIOC 6 programme on damage tolerance of large fuselages

RESEARCH AREAS AND OBJECTIVES

The work performed in the Structures and Materials Laboratory consists of most of the research in the disciplinary group B2 and part of the research in the disciplinary group C. The laboratory is specialised in the development of advanced materials, structural design and manufacturing techniques for light-weight structures.

The research efforts of the laboratory have three major corner stones:
• Fundamental scientific research. Successful application of new materials and design strategies can only be achieved if based on a thorough scientific understanding of the mechanical, physical and chemical aspects of materials and the optimal lay-out of structures.
• Integration of various disciplines. The laboratory has the knowledge, skills and equipment to cover the complete development of a structure: from materials science, structural design and manufacturing techniques to the fabrication and testing of full-scale components.
• Close co-operation with the industry. The laboratory has a strong application oriented approach. Input and questions from the industry are essential to guide the research, which is directed at gathering of engineering knowledge for the solution of practical problems.

The expertise of the laboratory covers an area from micro-mechanics of materials via design and manufacturing techniques up to full scale testing of components. A thorough knowledge of and insight into the relation between micro-structure and macro-properties of materials is of increasing importance to optimise the application of materials in constructions. This relation is pursued experimentally, in combination with model development. The investigated material behaviour includes the resistance against mechanical loading, both static and dynamic, durability, workshop properties, forming and environmental consequences like recycling.

Although the research is divided into specific research topics there is a strong cooperation between the staff members and students integrating different areas. The major research topics of the group can be summarised as follows:
• Fibre reinforced polymers (thermosets, thermoplastics and elastomers)
The emphasis in the research of fibre reinforced polymers is on the development of new structural concepts and suitable manufacturing techniques.
• Fibre-Metal Laminates
This new group of damage tolerant materials was developed in our laboratory and is still under development. All kind of aspects of the laminates are investigated: from fabrication and inspection to optimising these materials and the application in aerospace structures.
• Light-weight Metal Alloys
Light-weight alloys, especially aluminium alloys still play an important role in the aircraft industry. Acquired knowledge, theories, new alloys, etc. are evaluated, tested and compared to improve understanding and to aid the search for future aircraft materials.
• Jointing Techniques
Joints are very important in aircraft structures. Joints can be made using bolts, rivets or adhesives. The laboratory has a close co-operation with the Adhesion Institute, of which the Faculty of Aerospace Engineering is one of the founding Faculties.

The tendency towards more advanced materials, more powerful computational tools, modern design methods, more flexible and computerised manufacturing techniques and last but not least destructive and non-destructive inspection, requires an integration of the various disciplines involved. There is a strong interrelationship between material selection and properties, structural design and processing.

FACILITIES

The Structures and Materials Laboratory is well equipped with all kind of test machinery and devices to perform the tests required for the research described in the paragraphs above. The research facilities encompass:

Fatigue machines, computer controlled, hydraulic
- MTS 1000kN
- MTS 100 kN
- Amser/MTS 200kN
- Schenck 60 kN
- MTS (300 Hz) 10 kN
- MTS/Fokker 200 kN

Fatigue machines, low frequency, pneumatic
- Four tension machines
- Barrettest set-up (2 bar)
- Fuselage skin simulation set-up (1 bar)

Static testing machines; hydraulic
- Mohr & Federhaff 40 kN

Static testing machines; mechanical
- Zwick 20 kN
- Three Tensometer 20 kN
- Minimat 200 N

Compression machines
- Special design 800 kN
- Special design 150 kN

Torsion machine, mechanical
- Amser 1500 Nm

Production equipment
- Installations for anodising and chemical milling
- Autoclave (Scholz) 1.5 x 0.9 m², 350 °C, 25 bar
- Hot press (Fonteijne) 180 kN, 200 °C, 23 x 36 cm²
- Hot press (Fonteijne) 600 kN, 400 °C, 50 x 50 cm²
- Hot press (Fonteijne) 1000 kN, 400 °C, 50 x 50 cm²
- Hot press (Heckler & Koch) 60 kN, 250 °C, 20 x 50 cm²
- Two Fast closing presses (Alfamatic), 210 kN
- Fast closing press, infrared unit (Fonteijne), 1.5 x 0.8 m, 4000 kN
Press-clave, 450 °C, 30 bar, nitrogen
NC filament winding machine (Bear), 4 axes, l = 3 m; d = 2 m
Deep drawing machine (Roell & Korthaus), 400 kN

Special material test equipment
- Two salt spray cabinets
- Scanning electron microscope (Jeol 840A)
- Several potentiostats equipped with energy dispersive X-ray analysing corrosion behaviour system (TRACOR)
- Zeiss microhardness tester
- Heat treatment equipment
- Medium energy impact tester
- Laser extension meter
- EC tester for crack detection
- Six constant load machines for stress corrosion
- Three slow strain rate machines for stress corrosion (max. load 20 kN)
- Test cells for different environments, vacuum, high temperatures
- Ultrasonic C-scanner with data processing
- Ultrasonic delamination detector (SONIC)
- Low energy impact tester with data processing
- High velocity impact tester with data processing

Computers
- HP laboratory computer
- HP network server
- Terminals of the University computer network
- CAD/CAM installation (SUN workstations)
- Several HP 286, 386 and 486 personal computers
- CAD/CAM installation (Silicon Graphics workstation)

RESEARCH REPORT 1998

1 Repair with Bonded Fibre-Metal Laminate Patches (H.J.M. Woerdend, A. Vlot)
This joint research programme with the United States Air Force Academy aims at soft patching, i.e. the bonding of patches of strong, moderate modules repair material on aircraft. Further development of the CalcuRep design tool took place, including the refinement of the analysis of tapered patches and the secondary bending at the patch tip. This bending is very important because it may cause crack initiation in the aluminium fuselage skin if the design is inaccurate. CalcuRep was verified with FE-calculation and strain measurements. The thermal stresses around a hot bonded repair on a Fokker F-28 fuselage section were determined. This revealed thermal buckling problems at too high curing temperatures. Fatigue tests were done to compare the effectiveness of GLARE and boron/epoxy patches. Glare proved to be superior. Also the effect of debonds, simulating bad bonding procedures, were checked. Two bonded Glare patches were installed on a C5-A Galaxy and will be inspected regularly.

2 Fatigue of Riveted 2024-T3 Lap Joints (J. Schijve, J.J. Homan, R. de Rijcke)
The fatigue quality of a riveted joint depends predominantly on the rivet squeezing
operation, especially on the rivet squeeze force. In order to examine the fatigue quality of riveted lap joints in structures produced by the aircraft industry, the investigation is concentrated on the relation between the squeeze force and the dimensions of the driven rivet head. A first analysis is given in Memorandum M-847. A new systematic test series has been carried out with the rivet diameter, rivet length, type of rivet and rivet materials as the variables. For each combination a range of squeeze forces was used. The correlation between squeeze force and driven rivet head dimensions is promising. Co-operation with Airbus Industries and dr. S.A. Fawaz of the USAF should be mentioned.

3 Fatigue Crack Growth in Riveted Lap Joints (J.J.M. de Rijck, J. Schijve, A. Vlot; S.A. Fawaz [USAF])

The investigation reported in the previous Annual Report has been continued. Previous work has been reported in the doctor thesis of S.A. Fawaz. The present work is concentrating on stress intensity factors of fatigue cracks with oblique crack fronts and crack interactions of such cracks in adjacent holes in sheets under combined tension and bending. Experimental data were obtained on crack growth rates, crack shape development and crack interaction effects for fatigue cracks starting from different initial shapes in 2024-T3 sheet specimens with an array of holes. Although the fractures surfaces were quite tortuous, the crack growth history could be reconstructed by using marker loads introduced by reducing the maximum stress of the constant-amplitude baseline cycles. Crack growth histories were reconstructed for cracks smaller than 1 mm (sheet thickness 2 mm). In the analytical part K-values were calculated for part-elliptical through cracks emanating from an array of holes subjected to remote tension and bending, and pin loading. The 3-dimensional virtual crack closure technique (3D VCCT) is used. Calculations for different crack shapes were made. Interactions between cracks of adjacent holes were studied by comparison to K-values for cracks from single holes. The comparison indicated that such interactions will become significant only late in the fatigue life. Application of the new K-values to prediction of the fatigue life showed a 10% underestimation of the life.

4 Fractography to Study Interaction Effects During Variable-Amplitude Loading (J. Schijve)

Fatigue crack growth tests were carried out on 2024-T3 and 7075-T6 central cracked specimens. Variable-amplitude (VA) load spectra were used with periodic overload (OL) cycles added to constant-amplitude (CA) cycles (see Figure 1). The fatigue fracture surfaces were examined in the SEM to obtain more detailed information on crack growth contributions of different load cycles. The striation patterns could be related to the load histories. An example is shown in Figure 1. SEM observations were associated with delayed retardation, the effect of 10 or a single OL on retardation, crack growth during the OL cycles, and crack growth arrest after a high peak load. Fractographs exhibited local scatter of crack growth rates and sometimes a rather tortuous 3D geometry of the crack front. Indications of structural sensitive crack growth under VA loading were obtained. Fractography appears to be indispensable for the evaluation of fatigue crack growth prediction models in view of similarities and dissimilarities between crack growth and VA and CA loading.
5 Comparison of the Damage Tolerance Behaviour of Two Aluminium Alloys (G. Jay, J. Schijve)

Various properties of 2024-T3 and 2024-T3A are compared. The second alloy was developed by Pechiney as a replacement of the first one. The test program includes static and fatigue tests (constant-amplitude and flight-simulation). Specimens to be used include blunt notch specimens, centre cracked specimens and riveted joints (study of multiple-site damage). The first constant-amplitude fatigue crack growth results indicate that 2024-T3A is superior to 2024-T3.

6 Repair with Bonded Fibre-Metal Laminate Patches (H.J.M. Woerden, A. Vlot)

Because of ageing aircraft a need exists for safe, damage tolerant and cost-effective repairs. Different repair techniques are available, including mechanically fastened patch repairs and adhesive bonded patch repairs. Bonded repairs provide a more uniform and efficient load transfer into the patch and avoid high stress concentrations caused by additional holes necessary for riveted repairs. Adhesive bonded boron/epoxy repairs have the disadvantage of a large mismatch in coefficient of thermal expansion (CTE) between the repair and the aircraft structure. Moreover, the very high stiffness of boron/epoxy can lead to load attraction problems on the repair. Fibre Metal Laminate (FML) repair materials like GLARE7 (GLAss REinforced) avoid these problems. Research into bonded repair FML repairs patches started in the early nineties between the Center for Aircraft Structural Life Extension (CASILE) at the United States Air Force Academy (USAFA) and the Structures and Materials Laboratory of the Faculty of Aerospace Engineering of Delft University of Technology in the Netherlands. Considerable research performed over the last years resulted in a better understanding of the physical background of bonded repairs, as well as significant improvements in bonded repair techniques. Current research focuses on the ability to accurately predict the crack driving stress intensity factor ($\Delta K$) at the crack tip of a crack under an adhesively bonded repair. This $\Delta K$ is significantly lower than...
for an unrepaired crack, explaining the excellent fatigue behaviour of bonded repairs. This research is performed for both boron/epoxy and GLARE7 patch repair materials. Models being used for the prediction of $\Delta K$ include analytical models like the Rose model and finite element models. The Rose model gives an excellent analytical background, but secondary bending for one-sided (i.e. asymmetrical) repairs and thermal stresses after curing are not accurately accounted for. Extensive experimental testing with barrel test set-up and finite element calculations are performed to investigate the influence of those two main variables and to extend previous modelling.

Another part of current research focuses on in-service effects on patch performance and the experimental testing of realistic load sequences (variable-amplitude loading), including effects of overloads and underloads on crack growth of the repaired crack. Research on in-service effects on patch performance, as yet hardly investigated, will concentrate on environmental influences on crack growth under a patch repair and on the growth of debonds between patch and adherent. Possible detrimental environments include cold, hot, humid and salty conditions, as well as combinations of those. In view of service experience, two bonded GLARE patches were installed on a C5-A Galaxy, which are inspected regularly.

A final goal of the ARepair Project is the development of a repair tool for maintenance engineers, requiring little background knowledge of bonded repair. A first version of this tool, called CalculRep7 needs to be updated to accurately account for effects of secondary bending, influence of thermal stresses due to the curing cycle and effects of different environmental conditions.

7 Spliced Fibre Metal Laminates (T.J. de Vries, A. Vlot)

The maximum sheet width for 0.3 mm thick aluminium, and thus for GLARE laminates with this type of aluminium layers, is approximately 1.65 m. However, for the purpose of skin material in a fuselage, wider sheets are preferred to reduce the amount of necessary joints. This problem can be solved with the splicing concept; metal sheets are interrupted in the laminate and these splices are bridged by the fibre layers. With this concept the sheet width can be increased to 4 meters or more, depending on the autoclave size. Using these large sheet sizes can provide an additional weight and cost saving compared to monolithic aluminium structures due to a reduction of the number of riveted joints.

Fatigue and static strength tests on spliced laminates with varying fibre orientation were performed to determine design allowables. The disadvantages of local cross section reduction and the possible influence of moisture which can penetrate in the uncovered splice can be solved by covering the splice with a doubler. Bonding the doubler with prepreg over the splice appeared to be not favourable because of the low delamination resistance of the prepreg layer.

Possible solutions to maintain a smooth aerodynamic surface, even with bonded doublers, are now under development. Residual strength tests on spliced laminates with through cracks showed that the splices can effectively stop stable crack extension. In this case the crack has to reinitiate at the other side of the splice.

8 Dutch GLARE Technology Research Program (A. Vlot, L.B. Vogelesang, T.J. de Vries)

Delft University of Technology delivers a considerable contribution in the joint GLARE
technology research program (GTP) in The Netherlands. GLARE is a fibre metal laminate which was initially developed for its excellent fatigue crack growth properties and which appeared to have a lot more favourable properties, such as very high impact, corrosion and fire resistance capacity.

Other participants in the program are Structural Laminates Industries (SLI), the National Aerospace Laboratories (NLR) and Fokker Aerostructures (FAe). The program is sponsored by the Dutch government and is performed in close co-operation with Daimler Chrysler Aerospace Airbus (DA).

The research aims to achieve technology readiness for the application of GLARE laminates in very large transport aircraft. To do so, projects on the following working groups have been defined:

1. Materials & Processes
   Main topics are material qualification and material properties and allowables. Another very important issue is the definition and the qualification of the splicing concept. With these splices it is possible to manufacture larger skin panels than with monolithic aluminium sheets.

2. Methods
   This subject is focused on the development of missing calculation methods (design tools) for GLARE structures. Research is aimed at prediction of basic material properties (a metal volume fraction approach), stability of panels, residual strength and crack propagation.

3. Design Concepts
   Design principles are under development to enable detailed design optimised for GLARE structures. Items such as panel arrangement, typical GLARE shell design, stringer design concepts, longitudinal and butt joints, door and window cut-outs are looked upon. Also certification aspects are under discussion.

4. Fabrication Technology
   This subject is focused on low cost and low risk manufacturing of GLARE fuselage skin panels. Although the actual material cost of GLARE is higher than for monolithic aluminium, it is shown that with clever design and manufacturing a considerable cost reduction can be achieved which makes GLARE a very competitive material as compared with conventional sheet materials. The laminar built-up of GLARE allows a high degree of integration of structural details in one panel, such as splices and internal doublers.

5. Maintenance
   Maintenance concepts (with emphasis on cost aspects) and NDT inspection and repair methods for GLARE structures are under development. A lot of effort has been put into successful activities to acquire airline acceptance of GLARE.

6. Durability
   Available test results show excellent properties related to durability of GLARE, but a large durability program is defined to take away some reservations, which still exist at aircraft manufacturers and operators.

More than 90 subprojects were defined and are carried out in these working groups.

A very interesting feature is the relation between reduction in mechanical properties due to environmental influences and the amount of downscaling to coupons and components. The more a test article resembles with the actual structure, the less the reduction of mechanical properties there will be.
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The influence of metal layers properties on the mechanical strength of GLARE
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RESEARCH AREAS AND OBJECTIVES

The laboratory of Solid State and Materials Chemistry (SVM) is active in inorganic materials science and technology, in particular in research on solid state processes and microstructure related properties, with the aim to obtain insight in the relation between chemical and physical properties and the composition and microstructure of materials. The emphasis is on interfacial mechano-chemistry of inorganic materials (including metals), that is the chemistry related to interfaces and mechanical aspects. Classical and irreversible thermodynamics are used as a unifying methodology. The application of this methodology is focused on the meso-level, that is that level that is determining the macro-behaviour but itself is determined by the micro-level. While chemistry and kinetics are an important part of the micro-scale, the macro-scale refers to the phenomenological material parameters. The research is therefore situated at the junction of three axes: the material, the concept and length scale axis, as illustrated in Figure 1.

Figure 1: Research in the laboratory SVM at the junction of the concepts, the length scale and the materials axes

The identification of the thermo-dynamic internal variables with relevant microstructural parameters requires intensive co-operation with a characterisation activity. Electron beam based characterisation of inorganic materials is therefore an important activity. In particular the relation to the modelling and material characteristics dependent on the process is crucial. The research has been organised along two main programmes: ‘Solid state processes’ and ‘Microstructure related properties’. Each programme contains clusters related to the main theme. Most clusters contain more than one project.

1 Solid State Processes

The area of processing in inorganic materials is wide. Roughly speaking, one can distinguish raw materials, shaping and properties. For polycrystalline inorganic materials (ceramics) for instance, this means powders, consolidation/sintering and the whole range of properties of materials that can be imagined. We do not put an em-
phasis on raw materials. Instead we try to focus on the property area and co-operate with third parties in the overlap area. Processing also includes the joining of two different materials, in which the possible reactions between the materials have to be assessed. Moreover, the final shape of the materials in their applications has to obey tightly bound tolerances, often only reachable by abrasive processing techniques. Here also the possible chemical reactions play an important role in the fundamental understanding of these processes. The programme Solid state processes is focused on processes dominated by interfacial aspects, such as diffusion reactions, phase relations, morphology, textures and reaction kinetics in metal/metal and metal/ceramic systems, consolidation and abrasive processing. The present activities in this programme are at present divided in two clusters (in brackets the researchers involved):

- Reactions (Kodentsov, Oberndorff, Markovski, Van Dal, Van Loo, De With),
- Abrasive processing (Verspui, Shulepov, De With).

2 Microstructure-Related Properties

The area of properties of inorganic materials is also wide and can of course not be covered completely. A simple distinction can be made between intrinsic properties of a material and the extrinsic, that is micro-structurally related, properties of a material. While intrinsic material properties are related mainly to the compound used to produce a material, the extrinsic properties are largely determined by the microstructure of the material. In this respect we define the microstructure, along with Exner, by the type, the structure and the number of phases, by the number, the geometric appearance (size, shape, etc.) and the topological arrangements of the individual phase regions and their interfaces and by the type, structure and geometry of lattice defects. The programme Microstructure related properties aims at establishing relations between microstructure and properties of inorganic materials dominated by interfacial aspects. In particular we concentrate on modelling of mechanical performance in relation to chemistry. To support the extreme demands on micro-structural analysis we also develop electron microscopic methods for quantitative element analysis of bulk materials and thin films. The present activities in this programme can be divided in three clusters (in brackets the researchers involved):

- Oxynitrides (containing preparation and characterisation) (Hintzen, Kudyba-Jansen, Bruls, Van Krevel, Metselaar, De With),
- Failure (fracture and damage mechanics of both monoliths and bi-material systems) (Van der Varst, Donners, Van Gils, Dortmans, Jiménez-Piqué, Velazquez-Sanchez, Malzbender, Fang, De With) and
- Characterisation (mainly with electron based methods) (Bastin, Boon, Metselaar, De With).

Historically a significant part of the work on technical ceramics has been done in cooperation with TNO-TPD within the Centre for Technical Ceramics (CTK). This cooperation is still quite active but the interest of both parties has become wider than technical ceramics only and a considerable effort is made to increase the mutual interaction. This has led to a wider perspective of inorganic materials processes and properties in which the emphasis shifted at TNO still more towards applications and at TUE more towards fundamental processing and property problems. This wider cooperation has been formalised in the Materials Technology Centre (MTC) and created the possibility to interact with industrial companies, for which a short time scale is becoming more and more important, without sacrificing long term projects.
In the Section RESEARCH REPORT an overview of the various projects is given except for those researchers who recently left the laboratory.

Researchers who have recently left are:
- Stephan Jansen. He defended his thesis entitled "Alkaline-earth aluminium oxynitrides with the β-alumina or the Magnetoplumbite Type structure: preparation, characterisation and properties" successfully on 22-4-1998. We refer to his thesis for details.
- Mariëtte Verspui. Her work on erosion has been summarised in her thesis entitled "Modelling abrasive processes of glass" which she defended on 1-10-1998. For details on the work we refer to the thesis.
- Maurice Donners. Summarised his work in a thesis entitled "Fracture of MnZn Ferrites", which will be defended in February 1999. We refer for details to the thesis.
- Slobodan Markovski. He finalised his research on III-V compound semiconductors and summarised his results in a thesis entitled "Chemical Interaction between Metals and Compound Semiconductors", which will be defended in March 1999. We refer for details to the thesis.

FACILITIES

Characterisation
- Scanning electron microscope (SEM-JEOL 840A) with EDX (Tracor series 2)
- Electron probe micro analyser (EPMA-JEOL 8600) with WDX and EDX (Tracor) with Voyager automation
- Transmission electron microscope (TEM-JEOL 2000FX) with EDX (Tracor series, together with TPX)
- X-ray powder diffractometers
- High temperature XRD
- DTA/TGA (T_{max} = 1650 °C)
- Luminescence spectrophotometer
- Photo-flash equipment for measuring the thermal diffusivity
- Electrical conductivity ac, dc (T_{max} = 1450 °C)
- Ionic transport numbers from EMF (T_{max} = 1700 °C)
- Dilatometer for sintering studies (T_{max} = 1700 °C)

Structural Integrity
- 3 and 4 point bend test, ball-on-ring, ring-on-ring, jigs (T_{max} = 1400 °C)
- 2 universal mechanical testing machines (10 kN)
- High precision universal mechanical testing (200 kN)
- 5 testing machines for slow crack growth
- 2 Vickers microhardness testers
- Image analysis facilities
- Thermo compression equipment

Preparation/processing
- Vacuum furnace (T_{max} = 2000 °C)
- High frequency furnaces
- Dedicated furnaces for diffusion studies
- Tube and box furnaces up to 1700 °C
- Uniaxial hot presses
Together with TNO-Ceramics in the Centre for Technical Ceramics

- Powder characterisation (BET, Hg porosimetry, Sedigraph, temperature programmed desorption)
- Attritor mills
- High pressure nitrogen furnace (100 bar, 2000 °C)
- Nitridation furnace (1.2 bar, 2200 °C)
- Cold isostatic press
- Uniaxial hot press
- Pressure casting machine
- Injection moulding machine
- High frequency furnace for brazing

RESEARCH REPORT 1998

1 Solid State Reactions (A.A. Kodentsov)

The research in 1998 focused on chemical and mechanical aspects of the interactions at the interfaces between dissimilar inorganic materials. The work addressed both fundamental and applied aspects of interfacial mechano-chemistry. A great deal of efforts was given to the study of the interactions in metal/viscous TV-screen glass and refractory metal/viscous silica systems. The work was conducted in the framework of the joint project with (and financially supported by) Philips Centre for Manufacturing Technology and ended mid April. The fundamentally oriented part of the research program was centred around four interconnected projects. Subdivision is made with respect to the materials used and type of interfaces studied.

Interaction in Metal/Metal Systems

This part of the research dealt with the reactions at solid/liquid as well as solid/solid interfaces. The former is related to the development of Pb-free solder technology, the latter is concerned with some mechano-chemical aspects of the reactive phase formation in inorganic solids, in particular, manifestations of the Kirkendall effect (see Sections 1.1 and 1.2).

Reactions of Metals and Ceramics/Compound Semiconductors

The project was initiated in a framework of the Inter-University Institute COBRA and related to the fabrication of stable metal contacts to wide gap semiconductors, viz. SiC and III-V compounds. Chemical reactions at the interfaces formed between various forms of silicon carbide (HIP SiC, 6H and 4H SiC single crystals) and/or GaX (X = P, As, Sb) and selected transition metals (e.g. Ni, Co, Pt) have been investigated. This study will be summarised in the Ph.D. thesis of S. Markovski “Chemical Interaction between Metals and Compound Semiconductors” and will be defended in March 1999. For details please refer to the thesis (see Section 1.3).

Periodic Pattern Formation in Solid State Reactions Related to the Kirkendall Effect

The appearance of periodic layered morphology during solid state reactions seems to be a general diffusion phenomenon. However, the emergence of the structures periodic in time and space is difficult to predict a priori, but based on the phase relations and knowledge of the relative mobilities one can made an educated guess. A specific topology of a phase diagram allowing the appearance of a two-phase reaction product within a diffusion zone is imperative to the periodic pattern formation. Also, large differences in mobilities of species inside adjacent reaction layers are required. The
latter results in divergence of the vacancy fluxes at (or in the vicinity of) the reaction interface. This is a prerequisite to the splitting of the bands of the "inert inclusions". Another important but yet unresolved problem which is crucial to the phenomenon is the aggregation ("sintering") of particles (secondary phase formed \textit{in situ} during chemical reaction) inside the diffusion zone. This reflects the behaviour of an ensemble of "inert inclusions" (reaction products) in a concentration gradient and inhomogeneous stress field developing in the transition zone.

\textit{Mechano-Chemistry of Internal Reactions}

This project is concentrated on kinetic aspects of internal nitridation of Ni-based alloys and TEM investigation of the nitride precipitates (CrN, VN and TiN) formed inside the FCC solid solution (Ni) upon gas nitriding (under ammonia). From a fundamental point of view the nitridation behaviour of dilute Ni-based alloys at relatively low homologous temperatures and high nitrogen fugacities presents special features with regard to nucleation and growth of the internal nitride precipitates. The overall uptake of nitrogen by the alloy is controlled by nitrogen diffusion in the metal. Solute atoms are precipitated out completely at the reaction front and the formation of semi-coherent nitride particles takes place. Furthermore, a net volume change during the internal nitride precipitation leads to a stress generation in the vicinity of the reaction front. The stress relief occurs mainly by transport of nickel (solvent) to the stress-free metal surface mediated by pipe diffusion-controlled creep. The latter stress accommodation mechanism is dominant because of a high dislocation density developing within the parent Ni-matrix upon the internal precipitation of the semi-coherent nitride particles. These mechanical aspects of the interaction which cannot, at this moment, be incorporated into the existing theories of the internal precipitation, might also play an important role and, even, be under certain conditions rate-limiting for the overall process.

1.1 \textit{Pb-Free Solder} (P.J.T.L. Oberndorff)

The last years there has been an increasing interest from industry for substitutes of the eutectic Sn-Pb solder. The main reason for this interest is that a ban on lead is expected to come into existence within a few years. After some empirical research it is acknowledged that fundamental research is needed to come up with decent alternatives. This is why our laboratory is involved in this project. We are studying phase diagrams, thermodynamics and kinetics of systems that could be used as alternative solders, and the interaction of these systems with substrate materials.

![Figure 2: Intermetallic layer formation in the Sn-Au system at 200 °C (solid-solid diffusion couple). Backscatter Electron Image (BEI)](image-url)
After studying the Sn-Ag-Sb phase diagram at 220 °C and the interaction of near eutectic Sn-Ag-Sb with Cu, we are now studying the Sn-Ni-Cu (Ni and Cu are common substrate materials) phase diagram at 235 °C and the Bi-Ni-Pd (Ni is sometimes coated with a Pd-layer) system at this temperature. The Bi-Pd system is also being studied at 200 and 185 °C, in order to get kinetic and thermodynamic data. These studies can be extended with another element to get a more complete overview of phases that can be formed. Unfortunately, reaction times in this study are very long because of the low temperatures, which result from the heat resistance of the printed circuit boards.

Gold, just like Pd, is sometimes used as a thin protective layer on the substrate surface that is why our laboratory is interested in interaction of solder with Au. So we investigated the Sn-Au binary system, both in solid-solid interaction (diffusion couple technique) as well as solid-liquid reaction. The former was done by hot-dipping experiments that didn't give reproducible results. So other methods will be studied in the near future. We hope that by studying the liquid-solid interaction the mechanism of diffusion in liquid will be clarified.

Parallel to this research the formation of eutectic structures is being studied. After microscopic study and scanning electron microscopy we hope to get additional information from Transmission Electron Microscopy (TEM). TEM samples were successfully made of the Sn-Bi binary system using a diamond knife. However, this method introduces stress in the sample, which makes observation more difficult. So we will try getting samples by means of chemical etching and will study other eutectic structures.

Furthermore, P.J.T.L. Oberndorff spent three months at the Helsinki University of Technology learning more about electronic production and design. At Helsinki University of Technology thermodynamic calculations will be made in order to model the experimental established phase diagrams.

1.2 Manifestations of the Kirkendall Effect in Solid Diffusion Systems (M.J.H. van Dal)

In solid state diffusion processes where components have different mobility, interdiffusion results in a net mass transport that induces a shift of inert particles towards the fastest diffusing species: the Kirkendall effect. This, in turn, may lead to the development of diffusional porosity, generation of stress within the diffusion zone and even deformation of the material on a microscopic scale. Since these diffusion-induced phenomena profoundly affect the overall behaviour of material systems, it is important to have a good understanding of the Kirkendall effect.

Despite more than half a century of rather intensive work, a number of fundamental aspects associated with the manifestation of the Kirkendall effect is still not fully understood. Is the Kirkendall plane, indicated by inert markers placed at the original interface between the initial end-members of the diffusion couple, unique? Could the vacancy flux be in one sense in one phase and in the other sense in the other phase, so that two (or more) actual Kirkendall planes can be expected? It is clear that understanding the problem calls upon a study of the fundamental aspects of solid state diffusion processes as well as experimental techniques to investigate the net massflow accompanying interdiffusion in the solid state.

One of the experimental techniques to study the Kirkendall effect is the multi-foil technique. With this technique, diffusion and the manifestation of the Kirkendall in systems having mutual solubility such as the Ni-Pd, Fe-Pd, Ni-Au, Cu-Pd and Cu-Pt systems have been studied. Intrinsic diffusion coefficients were determined in the
systems Fe-Pd and Ni-Pd. In the Fe-Pd system, indications for the separation of inert markers placed at the original interface were found.

Parallel to this study, reactive diffusion couples have been studied. Recent experiments in the Ni/Ti system at 850 °C show that it is possible to get two actual planes of marker (ThO₂ particles), which originated from the initial interface in a Ti/Ni diffusion couple (see Figure 3). This result may provide the starting point of a more fundamental understanding of the interdiffusion mechanisms in solids and the Kirkendall effect. At the moment, diffusion in the Co-Si systems is being studied.

1.3 Chemical and Structural Aspects of Metal/Compound Semiconductor and Metal/Ceramic Interfaces (C. Cserháti)

Investigations of reactions between metals and III-V compound semiconductors (III-V, SiC) are largely motivated by the need for reproducible fabrication of uniform and stable contacts. The major parameters contributing to the quality of the contacts and possibly influencing the overall device performance are the stress and the thermal stability. These define the Ohmic contact geometry and structure as well. High stress, particularly tensile may stimulate a number of contact and device failure modes. This is generally a result of time dependent phenomena such as enhancement of interdiffusion or interaction at the metal-semiconductor interface. The metal-semiconductors systems are generally extremely reactive. The examination of bulk diffusion couples has aided in understanding the complicated reaction sequences in these systems. Elemental analysis technique can be useful investigating III-V compound semiconductors and/or ceramics reactions. These techniques however must be complemented with microstructural evaluations such as TEM and diffraction techniques. The basic requirement for TEM is a thin specimen which, in the case of layered structures, has to be made in cross-section. It requires a special approach in specimen preparation and it is commonly referred as XTEM (cross-sectional transmission electron microscopy).

In our work we focus on the contacts to GaSb, InP, SiC and related systems. Since the chemical interactions in metal-GaSb, and Co-SiC systems are well studied in this
laboratory, we decided to perform thin film experiments in these systems.

![Image 4]

A thin polycrystalline Co layer (~200 nm) was deposited on the (100) surface of GaSb wafer at 54 °C. The thickness of the layer and the interface was measured as well as characterised by XTEM. Part of the wafer was heated by means of RTP (Rapid Thermal Processing) at 500 °C for 5 min under controlled forming-gas ambient. The annealed specimens were investigated by XTEM. The investigations of the samples have clearly shown that oxidation occurred at the Co surface during the annealing. Heat treatment was also performed in vacuum at 500 °C for different annealing times. Figure 4 shows a specimen annealed for 18 min at 500 °C. The originally hexagonal Co layer transformed to cubic, during the solid state. More XTEM investigations are running to study the interface reaction between the layer and the substrate and the forming phase sequence at longer annealing time.

![Image 5]

Figure 5: An $^{27}$Al$^{15}$O-MAS spectrum of SrAl$_2$O$_3$ at 7.05 T (MAS frequency 12.1 kHz), clearly showing the five A1 sites present in this material.

2 Oxynitrides (H.T. Hintzen)

On oxynitrides a consistent program is running with strong interaction and mutual
support between the subjects. In 1998 the emphasis was on the crystal chemistry in relation to optical and thermal properties. Dedicated technical support has been given by A. Delsing. 

The research on BaAl_{11}O_{16}N with the β-alumina structure resulted in the thesis of S.R. Jansen entitled “Alkaline-earth aluminium oxynitrides with the β-alumina or the Magnetoplumbite Type structure: preparation, characterisation and properties”. The occupation of oxygen sites with nitrogen ions as determined with neutron diffraction is in agreement with expectations from chemical bonding, and can explain the optical and thermal properties. A patent has been filed for the novel luminescent material BaAl_{11}O_{16}N:Eu. With the recently developed multiple quantum NMR technique, for the first time the presence of the AlO_s site in compounds with the magnetoplumbite structure has unequivocally been demonstrated.

The following subjects have been continued:
- Luminescent oxynitrides (see Section 2.1)
- Thermal properties of MgSiN_2 (see Section 2.2)
- Aqueous processing of SiAlON powders (see Section 2.3)

During the past year new research has been initiated concerning oxynitride glasses (in co-operation with University of Limerick, Ireland, prof. S. Hampshire). The objective is to explain the deviating mechanical behaviour of (Y,Eu)-SiAlON glasses by using luminescence measurements as a tool to unravel the characteristics of the glass matrix. Also plans have been developed to model the crystal chemistry of oxynitrides with the intention to improve predictive capabilities, particularly for new compositions.

Significant parts of the above mentioned investigations have been performed in cooperation with several university groups (Nijmegen, Utrecht, Rennes, Limerick, Bayreuth, Aveiro, Cornell USA, Rutgers USA), institutes (TNO, ISIS UK, Argonne National Laboratory USA) and industry (Philips, Xycarb).

2.1 Luminescent Oxynitrides (J.W.H. van Krevel)

Oxynitride materials might be interesting phosphors when doped with rare-earth ions. This research is an exploratory research at the luminescence properties of rare-earth doped oxynitrides. Main results obtained in 1997 are described in the following.

In continuation of earlier investigations on the luminescence of Tb^{3+} doped Ln-Si-O-N: Tb (Ln = Y, Gd, La), we investigated the oxidation resistance of Ln-Si-O-N (Ln = Y, Gd and La) materials in air, using TGA/DTA measurements. We observed that all investigated compounds were stable up to at least 600 °C, which make these materials suitable for application as phosphors. The oxidation resistance strongly increases in the series Ln_5(SiO_4)N < Ln_4Si_3O_7N_2 < LnSiO_2N < Ln_2Si_3O_6N_2 < LnSiO_4N_2. This was explained by the increasing co-ordination of N^{3-} ions with Si^{4+} ions as the silicon tetrahedral network formation in this sequence increases. For the samples without extensive Si cross-linking, an additional weight gain was observed during the oxidation reaction which was higher than expected for complete oxidation (Figure 6). This indicates a stabilisation of an intermediate phase in which nitrogen retention takes place. Research on the nitrogen retention in Y_4Si_2O_7N_2 will be continued in co-operation with the group of prof. R. Marchand et al. (University of Rennes, France).

The earlier work on luminescence of Ce^{3+} doped in the melilitetype Y_2Si_2O_7N_2 compound was extended to research on the influence of Al-O substitution. The incorporation of Al-O was demonstrated by lattice parameter measurements. We observed
typical Ce$^{3+}$ luminescence with no shifts of the luminescence bands for varying $x$ in the melilitetype compound $Y_{1.98}Ce_{0.02}Si_{3-x}Al_{x}O_{3+N_4}$ ($x=0-0.6$). The absence of shifts in the spectra indicates that the extra $O^{2-}$ ions, originating from the incorporation of Al-O, do not directly coordinate to Ce$^{3+}$. This is explained by the preferential occupation of the large Ce$^{3+}$ ion on "roomier" O-rich sites in Y-melilitie, resulting in preferential substitution of O from Al-O on N-rich sites.

The absence of shifts in the spectra indicates that the extra $O^{2-}$ ions, originating from the incorporation of Al-O, do not directly coordinate to Ce$^{3+}$. This is explained by the preferential occupation of the large Ce$^{3+}$ ion on "roomier" O-rich sites in Y-melilitie, resulting in preferential substitution of O from Al-O on N-rich sites.

Refinements of the cuspidine type structure of $Y_{4}Si_{2}O_{7}N_{2}$ using neutron diffraction measurements were performed to determine the ordering of nitrogen and oxygen over the three types of anion sites available: 1) free anions, 2) single bonded to Si 3) bridging between two Si. Refinement shows that 1) nitrogen does not occupy the free anion sites 2) it does occupy the bridging site in the $Si_{2}O_{5}N_{2}$ dimeric unit and 3) nitrogen has a strong preference for two of the six different terminal crystallographic sites in this dimeric unit. Using this information, the luminescence spectra will be interpreted.

In co-operation with the Cornell University, USA (group prof. F. Disalvo), research on the luminescence of rare-earth doped nitride materials was performed. These materials show extremely long-wavelength luminescence in comparison to what normally is observed for oxidic lattices. This effect is related to the characteristics of these materials.

Dennis de Graaf started his graduation at the University of Limerick, Ireland (group of prof. S. Hampshire) on $(Y, Eu)$-SiAlON glasses with varying N/O-, Si/Al-, (Eu+Y)/Si- and Eu/Y-ratios. These glasses were shown to have interesting material properties, which vary for the different ratios. These are in agreement with observed trends in literature. For the first time we measured the luminescence properties measurements of rare-earth doped oxynitride glasses and these indicate that Eu$^{2+}$ is on different sites in the lattices. Chemical analysis showed that Eu$^{3+}$ from the raw material (Eu$_2$O$_3$) is reduced by N$^{3-}$ in the glass matrix to Eu$^{2+}$.

2.2 Thermal Conductivity/Diffusivity of MgSiN$_2$ Ceramics and Related Adamantine-Type Materials (R. Bruls)

For a theoretical prediction of the maximum achievable thermal conductivity of a phonon conductor like MgSiN$_2$ (a potential interesting substrate material) several
thermal properties as a function of the temperature have to be known. The most important properties for modelling are the thermal diffusivity, the specific heat and the thermal expansion.

The thermal diffusivity and specific heat data are needed for estimating the maximum achievable thermal conductivity using a semi-theoretical prediction method based on plotting the inverse of the thermal diffusivity versus the absolute temperature. The specific heat and the thermal expansion are needed for theoretically calculating the maximum achievable thermal conductivity based on the theory of Slack. The specific heat data and other thermodynamic properties of MgSiN$_2$ are already evaluated. Last year we studied the thermal expansion from 10 - 300 K and crystal structure of MgSiN$_2$ in more detail by temperature dependent neutron diffraction experiments (Intense Pulsed Neutron Source, Argonne National Laboratory). It was possible to correlate qualitatively the observed anisotropic thermal expansion with the crystal structure.

Furthermore inelastic neutron scattering experiments, Infra-red and Raman measurements were performed. The obtained data can be used as input parameters in Molecular Dynamic simulations. The vibrational spectra observed with inelastic neutron scattering (PDOS), IR and Raman spectroscopy are, as expected, comparable (see Figures 7 and 8). Although the sensitivity and resolution of each method differs the peak maximums are found at about the same energy. The vibrational spectra obtained with inelastic neutron scattering can be compared with other phonon conductors like AlN in order to explain the difference in thermal conductivity in terms of differences in the phonon spectrum.

![Figure 7: IR spectrum and PDOS for MgSiN$_2$](image1)

![Figure 8: Raman spectrum and PDOS for MgSiN$_2$](image2)

2.3 Aqueous Processing of SiAlON Powders (A.A. Kudyba-Jansen)

SiAlONs are engineering materials possessing high hardness, high fracture toughness, high strength, good chemical resistance and high wear resistance also at evaluated temperatures. Slip casting has been reported as a suitable, relatively cheap process to attain ceramics with high green densities and microstructural homogeneity, even for complex geometry. However, obtaining a stable, well-dispersed, uniform and highly concentrated slip of a powder is a particularly critical step in the aqueous processing. The dispersion of the slurry depends on changes in solid loading (quantity and characteristics), slurry pH, dispersant dosage and surface characteristics. The surface chemistry of a powder is of a fundamental importance in colloidal processing. Obtaining a green product with optimal properties is another crucial step just before sintering.

This project involves SiAlON powder and suspension preparation and characterisation, slip casting, preparation and characterisation of green product and ceramics. For this purpose Ca-α-SiAlON and β-SiAlON powders have been studied. The pow-
ders were obtained by carbo-thermal preparation, solid state reaction and commercially. Pure oxides, clays and fly ashes were used as starting materials. They were characterised by XRD, SEM and EPMA. Ca-α-SiAION and β-SiAION powders and ceramics were successfully produced from these starting materials. From clay and fly ash, however, some contamination originated from the raw materials remained. The suspensions prepared from the various powders as well as the commercial powders were characterised by sedimentation, zeta potential and viscosity measurements. They were all well deflocculated at basic pH (10-11). However, they had isoelectric points at different pH (pH_{lep}) related to the specific surface characteristics and bulk composition. The deflocculant, Dolapix CE64, was found to uniform suspension behaviour of Ca-α-SiAION and β-SiAION. Addition of the deflocculant allows achieving stability of the SiAION suspension after addition of Y_2O_3 as a sintering additive.

![Figure 9: SIMS spectra of Ca-α-SiAION powders after 0, 1, and 8 hours of heat treatment in air at 750 °C and after slip casting](image)

The surface composition of Ca-α-SiAION and β-SiAION powders was determined. Combination of X-ray-photoelectron-spectroscopy (XPS) and Secondary Ion Mass Spectroscopy (SIMS) (see Figure 9). During oxidation treatment in order to remove residual carbon from the surface after the carbo-thermal preparation, phases formed at the surface depend on the bulk composition. Ca-α-SiAION and β-SiAION surfaces vary somewhat, but both contain an aluminium silicate (Al_xSi_yO_z). The first one was silica like (low pH_{lep}), while the second was mullite like (higher pH_{lep}), which is in agreement with the expectations from the bulk composition. The binding energies of Si2p, Al2p, O1s, and N1s in Ca-α-SiAION and β-SiAION were proposed, what allows to distinguish between SiAION and oxide phases on SiAION surface. The β-SiAION surface is less oxidation sensitive than Ca-α-SiAION and is then more favourable for suspension stabilisation.

The investigation continues with studying the green product and sintered product
prepared from β-SiAlON powders with Y₂O₃ as a sintering additive, which are slip cast from suspensions with different degree of deflocculation. To study the in situ formation during slip casting and drying of the green product ¹H NMR has been showed to yield valuable results.

3 Abrasive Processing

At present this cluster contains one project and a general description is therefore not given.

3.1 Quality of the Surface Condition of Ground Inorganic Materials (S. Shulepov)

New applications in different areas demand the utilisation of advanced materials such as ceramics and hard metals and, in general, materials with a better size specification and surface finishing. Unfortunately, these materials are developing during their manufacture much more damage than, let say, (soft) metals. Also, because of their intrinsic hardness, it is difficult to machine such a material, and, as a consequence, the use of rather expensive, super-abrasive (CBN and diamond) tools became a usual practice. Altogether, this leads to the situation when the abrasive processing may comprise up to 70% of the total costs of manufacturing components from those materials. This project is aimed at development of a model able of predicting rather than interpreting results of abrasive processing of the inorganic materials.

The modelling is typically based upon the grinding wheel topography. Here, a Monte Carlo-like concept is implemented to simulate the random distribution of abrasive grains in the wheel surface with average (input) parameters taken from the specifications available. Utilising a well-known procedure developed for the analysis of accuracy of cutting tools, which was adopted on randomly distributed abrasive grains, a real-time simulation of the whole process is carried out. As a model material, WC-Co was used. Its material behaviour during scratching with rather small cutting depth (a unit event of the abrasive processing) was not very complex, i.e. there was almost no pile-up, chipping, and brittle fracture.

A reasonable agreement with scratch experiments is obtained when employing a rather simple, ploughing model. On the basis of this model a direct relation between the wheel topography and the workpiece topography after abrasive machining can be formulated. Having used the following input parameters - the wheel speed 30 m/s, feed rate of the workpiece 3 m/min, depth of cut A = 2μm, and wheel D104 with diameter 25 cm - typical surface finishing after in-plane grinding operation is simulated and results are plotted in Figure 10. Experimentally measured 3D profile is represented in Figure 11. Comparison of statistical parameters (determined according to DIN standards) and Abbott curves corresponding to these two profiles showed that the discrepancy between predicted and measured values is within 10%. This is far better than accuracy of the overall experimental set-up. Another aspect of the proc-
ess which has direct relation to the surface integrity of the workpiece ground is the forces acting during grinding of the material. At the moment, an ideal grinding forces can be simulated. However, such aspects as imperfection of the overall grinding wheel geometry, deflection of grains during an engagement, etc. have to be introduced, otherwise direct comparison between modelling and experiments is not possible.

4. Failure

The cluster failure contains both research on monoliths and bi-materials. Within the monolith area the research on MnZn ferrite resulted in the thesis of Maurice Donners entitled “Fracture of MnZn ferrites”, which will be defended in February 1999. Apart from the influence of different types of defects upon the failure an important result is the combined mechanical and adsorption modelling which resulted in the explanation of an unexpected minimum in strength of MnZn ferrites as a function of relative humidity. This behaviour cannot be explained otherwise.

The other projects in the monolith area are:

- Physical chemical mechanical behaviour of oxides (see Section 4.2). This project extends the work of Maurice Donners;
- Process-zone thermodynamics and fracture (see Section 4.4). In fact, this project is an extension of the work of Marcel van Gils, who obtained his Ph.D. degree in June 1997;
- It is intended to support the fracture experiments by atomic modelling of surfaces. However, the acquisition and implementation of software took more time than expected. In the meantime some preliminary band calculations on oxynitrides were done. (see Section 4.5)

The activities in the bi-material domain are

- Modelling adhesion of thin brittle coating on metallic substrates (see Section 4.1). Here a co-operation with both Groningen University and Delft University is present. The basic goal is to describe the adherence of brittle coatings on metallic substrates;
- Characterisation of the mechanical behaviour of coated glass systems (see Section 4.3). This project is done in co-operation with industry and focuses on adherence and scratch resistance;
- Self-stratifying fluorine modified hybrid coatings (see Section 4.6). A co-operation with the Coating Group of our faculty is present. Focus is on the physical chemistry and characterisation of hybrid self-stratifying coatings.

In connection with the joint activities with TNO, dr. Dortmans participates part-time in the monolith projects in this cluster.

Within the various projects there is co-operation with laboratories in the Netherlands and abroad. We specifically mention Delft University of Technology, University of Groningen, TNO National Physical Laboratory (Teddington, U.K.) and University of Karlsruhe (Germany).

4.1 Modelling Adhesion of Thin, Brittle Coatings on Metallic Substrates (P.G.Th. van der Varst)

Traditionally, strength has been characterised by measuring critical values of stress intensity factors. While this concept is very clear for cracks in monoliths, the matter is
not straightforward for cracks along the interface of bi-materials. In addition, the experimental difficulties to measure these quantities with coated specimens where the interface crack is located some 5 micrometers below the surface are as yet unsolved and remain so for, probably, a long time. For that reason an energy based approach (energy release rate, dissipation) is pursued with nano-indentation as experimental technique. To interpret the experimental results extensive modelling is necessary so as to obtain information on the adhesion of the coating.

![Figure 12](image)

![Figure 13](image)

Previously, the choice has been made to apply Schapery theory of the path independent work potential because this theory is very suitable in conjunction with indentation as the experimental method to study failure of the coatings. Since this theory assumes that the dissipating processes are rate independent it was checked first if this assumes applies or not. For two different types of coatings (TiN and Ti(C,N)) on a substrate having three different values of surface roughness this assumption was checked using five different indentation speeds. It was found that under these circumstances the dissipation is indeed rate independent for both types of coatings and for substrate roughness values ranging from about 1% of the coating thickness to 20% (see Figure 13). It was concluded that Schapery's theory can be applied. The dissipated energy correlates the best with the maximum and also the permanent indentation depth. This result suggests that the permanent indentation depth can be used as an internal variable.

From micro-structural investigation of the induced damage it can be concluded that the interface is not the weakest point in the coating substrate structure but that the columnar structure — perpendicular to the interface — found in the coating seems to be the weakest spots. Initially these columns are sheared off and pressed into the substrate. Simultaneously tensile radial stresses outside the indenter region develop gradually counterbalancing the large compressive residual stresses present in the coating. While initially the total stress, that is residual plus induced stress, remains compressive in the coating after a certain load the total stress becomes tensile thereby leading to ring shaped crack perpendicular to the interface. Since no delamination was observed these cracks seem to be arrested at the interface because crack deflection along the interface (delamination) was not observed and crack growth into the substrate seems not possible due to the ductility of the substrate material.

4.2 Physical Chemical Mechanical Behaviour of Oxides (N.J. van der Laag)

It is a well-known fact that gaseous species play a role in fracture phenomena. The critical stress for fracture decreases in the presence of gas molecules. However, the
exact mechanism of participating is still unknown. In the past two mechanisms for the interaction of gas molecules and the fracture process are proposed and established. Firstly, by adsorbing on the newly created surface inside the crack, the total surface energy can be decreased. This is a thermodynamical effect, which as described by the Griffith formula decreases the critical stress. Secondly, the gas molecule will diffuse through the crack to the crack tip. At the crack tip the chemical bonds are stretched. The gaseous species will react with the non-broken bonds, which leads to an increase in the fracture rate and an inhibition of the bond reconstruction process. This is a kinetic effect and results in a lowering of the critical stress.

\[ \text{Figure 14: Two mechanisms of interaction of reactive species with crack propagation} \]

In studies towards the fracture of MnZn ferrites it was shown that the latter mechanisms was not valid in contrast to the fracture processes of silica glass. Therefore, the role of gaseous species on fracture phenomena must be investigated in a detailed and fundamental way. MnZn ferrites are not suitable for it since they have a variable stochiometry and defect chemistry. The investigated materials will therefore be oxides: $\alpha$-alumina, magnesium oxide, silicon oxide and titanium oxide. These materials have also an important industrial aspect. The gaseous reactive species under investigation will be molecular nitrogen gas, water, dihydrogen sulphide, carbon monoxide, nitrogen monoxide and ammonia. These gasses have all different capacities ranging from Brønsted-acidic to Lewis-acidic behaviour.

In pursuit of our objective to obtain a more fundamental knowledge of the interaction of reactive gaseous species with fracture phenomena, single crystals will be used in fracture tests. These tests will provide data about the interaction. Furthermore, these tests will also provide verification data for computer simulations.

The adsorption will be investigated using several methods. Surface characterisation methods will provide insight into the way the molecules are oriented on the surface. Also the relation between defects and adsorption sites will be investigated using AFM or SEM. Also adsorption isotherms will be determined using a home-build devise. This will provide thermodynamical information of several gasses, like ammonia and dihydrogen sulphide.

In final part of the Ph.D. project computer simulations will be performed. Several options are possible and will be filled during the project. A numerical diffusion model, with the competition between adsorption and chemical attack at the stretched crack tip bonds, can be made. Also more \textit{ab initio} calculations of the chemical attack at the bonds can be simulated. Moreover, simulations of adsorption processes, and espe-
cially the role of defects therein, are an alternative option.

4.3 Characterisation of the Mechanical Behaviour of Coated Glass Systems (J. Malzbender)

The aim of this project is the realisation of a methodology for the evaluation and improvement of the mechanical behaviour of coated glass components. The main reason for applying coatings on glass is to modify the functional behaviour of the glass, i.e. to introduce an anti-glare, anti-reflex, or anti-static layer or to realise a change in dielectric or transmission properties. A second reason is to strengthen the glass substrate and protect it from environmental influences such as particle impact and moisture. Inorganic as well as hybrid, i.e. combined inorganic/organic, coatings can be used for these purposes. One method to prepare the coatings is the sol-gel process. This process requires a final curing, which results in shrinkage of the coating and can produce a tensile stress. The probability of cracking in the coating usually increases with thickness and, therefore, non-cracked coatings have a critical thickness.

Whatever the main reason for applying a coating, mechanical aspects are almost always important. The initial objective of this project is the development of a methodology to analyse coatings, where special emphasis will be placed on the adhesion of the coatings and the measurement of the critical parameters using sliding indentation. First experiments were performed to determine the critical thickness of the coatings used for further experiments and to correlate this with the residual stress and fracture toughness of the coatings.

![Indentation into a 3 μm thick coating cured at 250 °C. The image was obtained using optical microscopy after loading up to 100 mN. Radial cracks are clearly visible. The bright spots are probably related to delaminated coating areas at the interface.](image)

Initial experiments under this aspect were performed using a recording indentation instrument, but no horizontal movement was superimposed, which is a technique that can be used to access a coating quantitatively, but requires a careful analysis procedure of the observations. This technique was used to estimate the indentation pressure and the elastic modulus of the coatings. Also, by analysing cracks in the surface resulting from indentations, the fracture toughness of the coating and interface and the residual stress in the coating were estimated and the dependence of these parameters on the preparation conditions was studied. The main advantage of this approach is that different phenomena, which can be found during one experiment, were used to assess the critical parameters.

Scratch testing on the other hand, which has the advantage of giving an instantaneous representation of coating failure, is widely used to access the properties of coatings qualitatively, but a systematisation and quantification of the observation is still lacking. Attempts were made to quantify the results obtained by scratch testing as a
function of the preparation conditions and to correlate the resulting values of interfacial and coating fracture toughness with the parameters measured by indentation. The friction factor was modelled using a simple plowing model and it was attempted to predict the critical indentation depth to cause cracking of the coating, which has shown to be the critical parameter of failure. It was attempted to relate the coefficient of friction to the fracture toughness and the minimum size of surface flaws. The development of the methodology will be further improved and tested on a variation of the currently used coatings composition.

4.4 Process-Zone Thermodynamics and Fracture of Model Materials (E. Jiménez-Piqué)

Process-zone of quasi-brittle ceramics has been always a difficult field of study. Not only multiple processes are present around the crack tip (bridging, micro-cracking, phase transitions), but also its length scale makes it difficult to study with the standard engineering mechanics tools like continuum mechanics. One new approach to the problem is to design and construct model materials with enlarged microstructural features. Using this kind of materials we are able to control all the parameters involved in the process-zone and gain better insight into the behaviour of the crack tip zone.

The first family of model materials consists on a regular packing of 5 mm metal spheres joined together with commercial epoxy glue and stacked either in a simple cubic ((100) and (110) orientations) or in a compact packing (fcc, hcp, ...). Different shapes are used depending on the type of mechanical test: From cubes of 10x10x10 spheres for crack test to beams of 3x3x10 spheres for bending experiments. As far as in our project the bonding agent plays a crucial role in the behaviour of the model material, we study deeply the different types of glue involved in these model materials. Different techniques such as pulse-echo, wedge opening load and nanoindentation are used to fully characterise the mechanical properties of the glue. Moreover, as those are standard techniques, we play with variation in curing times, different glues and different surface properties to test if variation of those parameters would result in a significant change in the mechanical properties of the model material.

For modelling these materials we use finite element method (FEM) codes. In the first stage we use FEM to characterise the behaviour of two particles by looking inside the microfields. In this way we can understand where the fracture starts and how the stress and strain fields are, and their variation with the different parameters. Shortly we will use FEM to model the complete material.
In the near future we will construct the next family of model materials made up of sub-millimetric polymer balls. This will give us a better insight into the process-zone and the crack behaviour. Depending on the results, we will try different particle materials (glass, ceramic), different bonding agents (from glues to glass bonding) or different configurations and density of defects.

4.5 Atomic Modelling (C.M. Fang)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Mg$_3$N$_2$</th>
<th>MgSiN$_2$</th>
<th>β-Si$_3$N$_4$</th>
<th>α-Si$_3$N$_4$</th>
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<tr>
<td>Top of VB</td>
<td>$\Gamma$, H</td>
<td>$\Gamma$</td>
<td>$\Gamma$·A</td>
<td>M</td>
</tr>
<tr>
<td>Bottom of CB</td>
<td>$\Gamma$</td>
<td>$\Gamma$</td>
<td>$\Gamma$</td>
<td>$\Gamma$</td>
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<td>$E_g$ min (eV)</td>
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<td>4.35</td>
<td>4.96</td>
<td>4.63</td>
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<tr>
<td>$E_g$ (direct $\Gamma$)</td>
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<tr>
<td>Width of VB (eV)</td>
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<td>6.50</td>
<td>9.79</td>
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<tr>
<td>Position of N$_{2s}$</td>
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<td>$(-15.5$ to $12.3)$</td>
<td>$-18.2$ to $-14.0$</td>
<td>$-18.4$ to $-14.3$</td>
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<tr>
<td>Experimental $E_g$ (eV)</td>
<td>2.8</td>
<td>4.8</td>
<td>4.6-5.5</td>
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</tr>
</tbody>
</table>

Electronic structure of binary Mg$_3$N$_2$ and ternary MgSiN$_2$

Ab initio band structure calculations were performed for MgSiN$_2$ and Mg$_3$N$_2$ using the localised spherical wave (LSW) method. Calculations show that both nitrides are semiconductors with direct energy gaps at the centre of the Brillouin zones. The valence bands are composed mainly of N 2p states hybridised with s and p characters of the metals. The bottom of the conduction band consists of the s characters of Mg and N for Mg$_3$N$_2$, as well as for MgSiN$_2$, while the characters of Si are higher in energy. The optical diffuse spectra show an energy gap of about 2.8 eV for Mg$_3$N$_2$ and 4.8 eV for MgSiN$_2$, in line with the calculated values. Table 1 compares the electronic structure of MgSiN$_2$ with the binary nitrides.

Bulk and surface electronic structure of the sub-nitrides Ca$_2$N and Sr$_2$N

The binary sub-nitrides Ca$_2$N and Sr$_2$N have the anti-CdCl$_2$ layered structure, which consists of one sheet of N sandwiched by two sheets of alkali metals. The interlayer metal-metal distances are much larger than in the pure metals. Ab initio band structure calculations show that the nitrides are best described as ionic compounds with one electron in the ‘Van der Waals gap’ between the calcium (strontium) layers. The nitrogen 2p states show rather localised character (with a bandwidth of about 2 eV), as shown in Figure 17 for bulk Ca$_2$N. The compounds have a quasi-two-dimensional electronic structure with a cylindrical Fermi surface perpendicular to the layer direction. In the crystals the free-electrons are confined between the blocking N$^{3-}$ layers. As one of the confinement consequences, a smaller work function than the corresponding metals is expected. The electronic structure of the surface slab Mg$_2$N shows...
shifts of density of states feature with respect to the bulk. The surface slab Ca2N has the density of states shifted about 1 eV to the lower energy (Figure 18). These layered compounds, which is more chiral stable and has lower work function, may be used to replace the pure metals as cathode material for polymer LED devices.

Oxide surface calculation
Software has been acquired.

4.6 Self-Stratifying Fluorine Modified Hybrid Coatings (M.E. Velazquez-Sanchez)

The aim of this project is to have a self-stratifying coating with characteristics such as good mechanical properties, good adhesion on a metal and environment resistance. The self-stratification process occurs during film formation, when the coating is applied on a surface and cured. The initial mixture is usually homogeneous and its components are currently a primer, a top resin, a cross-linking agent and a solvent or blend of solvents. We have chosen epoxy resins because these compounds are known to have a good adhesion on metals, and fluorinated acryl copolymers to give the material good outside wear resistance.

Initially, solvent solubility maps for Epikote-1001 and a copolymer of methyl methacrylate (MMA) and 2-(N-ethylperfluorooctanesulfonamide) ethyl methacrylate (FX14, 3M) MMAFX14 (90:10) at 25 °C and 30 weight percent of solids were determined. Using these two solvent solubility maps and plotting the hydrogen bonding and polarisation parameters of the mixtures ($\delta_{\text{mix}} = \Sigma \delta_{ij}$), it was possible to establish the region in which both polymers are soluble in the same solvent or solvent mixture (see Figure 19). For the polymers studied at 30 wt.% of solids and at 25 °C, the solubility region lies between $1.5 < \delta_p < 3.7$ and $2 < \delta_h < 4$.

![Solubility region](image)

Figure 19: Polymer solubility map: Epikote-1001/MMA-FX14 (90:10), 30% solid content at 25 °C (solvent used: MiBK)

Until now we have investigated the system containing the polymers E1001 and MMAFX14, solved in MPA to which a hardener (Jeffamine 230) was added. From the techniques XPS and SEM-EDX, we found a graded element distribution through the coating; as expected, a bigger amount of fluorine was present on the surface, and on the substrate there was more epoxy compound, nevertheless since the controllability concerning the phase separation was insufficient, we decided to reduce the number of components and switched to the binary system, only containing the two polymers.
In this system we observed that the best mixing was obtained when the molecular weight of the epoxy resin E1001 and the fluorinated co-polymer MMAFX14 was low (E828 = 379 g/mole, MAEP = 4912 g/mole).

5 Microstructural Characterisation with Electron Beam Based Instruments (G.F. Bastin, H.J.M. Heijligers)

Microstructural characterisation is very important in materials science because the properties of any material are ultimately determined by its microstructure, which is based on the chemical composition, the grain size, and the grain orientation, often on a micron- or submicron scale. Among the various techniques that are currently available for characterisation, those based on the use of (finely focused) beams of high-energy electrons, are still the most popular and wide-spread. Not only offer such techniques the possibility to perform qualitative and quantitative chemical analyses in volumes down to $1 \mu m^3$, it is at present also possible to determine the crystallographic orientation of small (down to 1 $\mu m$) grains in the specimen by using Electron Back Scattering Patterns (EBSPs).

The equipment based on the use of electron beams is well-represented in the Laboratory of Solid State and Materials Chemistry: Scanning Electron Microscopes (SEMs), Electron Probe Microanalysers (EPMAs, 2), and a Transmission Electron Microscope with Scanning Transmission unit (TEM-STEM). In the past year a so-called "OIM" (Orientation Imaging Microscope) attachment for recording EBSPs, using a very sensitive CCD camera, including the necessary software for interpretation of the results, has been added to our latest Electron Probe Microanalyser. Ir. H.J.M. Heijligers attended a two week course in Provo (Utah, USA) in order to get acquainted with the technique.

Under the bombardment with high-energy electrons the atoms in the specimen will emit their characteristic X-rays, and these can be used for qualitative and quantitative analysis on the (required) $\mu m$-scale level. Unfortunately, the emitted X-ray signals are not linearly proportional to the concentrations of the elements involved, and a lot of complicated "matrix correction" procedures have to be applied in order to convert the measured X-ray signals into the correct concentration units.

One of our main research objects in the past decade has been to introduce and develop improved matrix correction procedures, not only for conventional bulk analysis in cross sectioned specimens in SEM and EPMA, but also for the analysis of thin films, either supported or unsupported. Invariably, our efforts in this respect have been based on attempts to use realistic descriptions of the X-ray ionisation function ($\varphi$) as a function of mass depth ($pz$), the so-called $\varphi(pz)$ curves. At the same time we have been very active in collecting (for the first time in literature) vast data bases of measurements for the ultra-light elements B, C, N, and O, which present enormous challenges for any matrix correction program. As a result of all these efforts we can say that, at the moment, we have one of the best matrix correction procedures ("PROZA96") for bulk applications, currently available.

In recent years the successful $\varphi(pz)$ approach has also been extended toward thin film applications (so far in SEM and EPMA, up to 40 kV), in which it is possible to determine simultaneously the thickness and the composition of a thin film (< 1 $\mu m$), either on a substrate or unsupported. In this field too we have been active in setting up vast data bases of thin film measurements (Al and Pd films, so far) (Bastin, Heijligers).

A very interesting possibility is to extend and test the existing thin film procedures for
application in the TEM, up to 200 kV, where the specimen consists of a very thin
(\(<\!\!< 1 \mu m\)) unsupported film. This idea is being pursued by our Ph.D. student Gerben
Boon, and the results obtained so far, are most encouraging indeed. Unfortunately,
the hardware modifications to the TEM, which were found necessary, proved very
time consuming. Also the preparation of the specimens turned out to be a limiting
factor.

5.1 Simultaneous Composition and Thickness Determination using Transmission
Electron Microscopy (G. Boon)

In principle, it is possible to perform X-ray microanalysis in a Transmission Electron
Microscope with extremely high lateral resolution; as a matter of fact, this is one of
the major advantages of the technique. Disadvantages are the low accuracy in the
existing quantification procedures and the problems associated with preparing the
thin specimens needed for the analysis.
Some of the problems involved with the quantification are caused by the lack of an
appropriate matrix correction model. Such a model is necessary to convert the
measured X-ray intensities into the specimen composition, taking parameters like
absorption and fluorescence into account.
We found the \(\phi(pz)\) matrix correction approach very useful for application in the ana­
lytical TEM. The particular model we used was based on the “Double Gaussian”
\(\phi(pz)\) approach, which was originally developed for bulk measurements on an Elec­
tron Probe Micro Analyser (up to 50 kV) and subsequently implemented into a com­
puter program called ‘PROZA’ by G.F. Bastin in our group. Later on, this model was
also extended towards applications in Thin-Film analysis (‘TFA’ program).
Using the latter program, we are able to calculate both composition and thickness
from X-ray data measured with an EDX-detector at one single accelerating voltage.
Both thin and thick specimens can be analysed, and light elements can also be
studied, all without major changes to the TEM set-up.
The beam current is a vital parameter in the collection of accurate X-ray data, since
the ratio between the emitted intensities (in counts/sec/nA) from specimen and stan­
dard (the so-called \(k\)-ratio) is the crucial input parameter into the correction program.
Therefore, we have designed and installed an accurate and highly sensitive probe
current meter, which covers a large range in currents. The latter is necessary in order
to deal with the huge differences in count rates between bulk standards and thin film
specimens. This new device makes it possible to measure the electron beam current
with the required high precision.
A first check on the validity of the \(\phi(pz)\) model under TEM conditions (up to 200 kV)
was performed by measurements on bulk AlNi and AlTi samples and on an electro­
polished AlZr TEM specimen. This produced promising results. Last year, extensive
testing of the model was performed, using bulk samples of known binary compounds
of Al and Ni, Ti, Nb, Zr, and Au. For these measurements, the model was found to
perform astonishingly well.
Lately we started testing the model on the intended utilisation: Quantitative analysis
on TEM specimens. TEM specimens (thin film) were made out of the same binary
compounds and used to perform quantitative analysis on areas with varying thick­
ness. Using the TFA program, the composition and thickness were calculated from
the measured X-ray spectra and found to be in good agreement with the expected
values.
The thin film measurements demonstrate that the \(\phi(pz)\) model can be used as an
adequate correction model for TEM quantitative analysis on both thin and thick or
even bulk specimens.

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*Phase equilibria in the Ni-Cr-Ti system at 850 °C*  

R.J. Bruls, H.T. Hintzen, R. Metselaar, J.C. van Miltenburg  
*Heat capacity of MgSiN₂ between 8 and 800 K*  

*Glass strengthening by silica particle reinforced organic-inorganic coatings*  

W.F. Fontijn, P. van der Zaag, R. Metselaar  
*On the origin of the magneto-optical effects in Li, Mg, Ni, and Co ferrite*  

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S.R. Jansen  
*Zicht op beter TL-licht: Stikstof in plaats van zuurstof maakt blauw licht groener*  
Chemisch magazine, June (1998) 208
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Strengthening of glass by hybrid organic-inorganic coatings
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RESEARCH AREAS AND OBJECTIVES

Research is carried out in the area of joining of materials with emphasis on welding. Much attention is given to the behaviour of the welding process and to the influence of the process parameters on the properties of the materials to be joined. Work is also carried out aimed at evaluating the possibilities and limitations of mechanisation and automation of the welding process, with specific interest for sensors to be used in a welding robot. Furthermore, attention is given to the joining of ceramics to metals and ceramics to ceramics.

1  Welding Processes

Welding processes are used on a broad scale in the metals industry. The possibilities and limitations of these processes depend not only on the process parameters, but also on external factors and conditions.
The objective of this project is to obtain fundamental knowledge about existing and new welding processes with emphasis on the applicability of these processes in the metals industry.

2 Sensing and Control of the Arc Welding Process

Automation of the arc welding process is of considerable interest for the welding industry. This interest is based on the specific advantages offered by automation, such as increase of productivity and improvement of weld quality. Of specific importance is the development of sensors, which can be used for obtaining real time information about the welding process. This information can be fed back to the control system and can — if required — be used to correct the relevant process parameters.

The objective of this project is to study new approaches to sensing during arc welding with emphasis on penetration sensing based on weld pool oscillation and position sensing based on tracer techniques.

3 Structure and Properties of Welded Joints

During welding part of the metal to be welded is subjected to a thermal cycle (heating, melting, solidification and cooling). This thermal cycle in most cases leads to significant changes in the structure and properties of the welded joint. The objective of this project is to obtain detailed information about the structure of welds (weld metal and heat-affected zone) in relation to the welding conditions and to determine the relationship between the structure and the mechanical properties. Specific attention is given to aluminium-matrix composites.

4 Diffusion Bonding of Ceramic Materials

Due to their excellent high temperature properties, ceramic materials are being used increasingly in constructive applications. In most cases the ceramic materials are applied in combination with metals. To ensure good bonding between ceramic materials and metals, reliable joining techniques are required. A possible joining technique is diffusion welding. An important advantage of this technique is that joints can be produced which can withstand relatively high temperatures.

The objective of this project is to obtain fundamental knowledge in the field of diffusion welding of ceramics to metals. Attention is also given to diffusion welding of ceramics to ceramics using metallic interlayers.

FACILITIES

- Arc welding equipment for manual metal arc welding, GTA welding, GMA welding and pulsed current welding
- Diffusion welding equipment
- Thermal simulator
- Equipment for radiographic defect detection
- Equipment for ultrasonic defect detection
- Equipment for acoustic emission analysis
- Equipment for sensing and control of weld penetration (prototype)
- Industrial laser (500W continuous wave)

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1.1 Laser-Assisted Arc Welding

A start was made with the study of laser-assisted arc welding, a research project to be carried out under the auspices of the Netherlands Institute for Metals Research. This project deals with the interaction between laser radiation and the welding arc with the aim to obtain fundamental insight in this interaction and to explore the possibilities of using it in specific applications.

In the first phase of the project the attention was focused on the effect of the laser beam on weld pool formation and plasma plume generation. Both weld pool formation and plasma plume generation play an essential role in the interaction between arc and laser, to be studied in the next phase of the research programme. Experiments were conducted under standard conditions and under conditions in which one laser parameter was varied while keeping the others constant. The influencing parameters considered are: laser energy density (laser power and lens type), beam focus position, travel speed, shielding gas, workpiece material and beam incident angle.

It was found that in the case of steel the laser energy density at the surface of the workpiece is decisive as far as the operating heat transfer mode is concerned. Below a specific threshold value of the energy density the heat conduction mode dominates, whereas above this threshold value the keyhole mode is observed. In both cases intensive plasma plumes are produced. Furthermore, it appears that the dimensions of the weld pool and the radiation intensity of the plasma plume decrease with increasing travel speed, with increasing defocusing distance from the weld pool surface and with decreasing laser power. When changing the shielding gas from argon to helium, the weld pool does not exhibit a significant change in size. However, the size of the plasma plume in the case of helium is around half of that in the case of argon. The oxide layer formed when welds are made in open air greatly increases the radiation absorption, which results in a much larger weld bead depth to weld bead width ratio than in the case of argon and helium. It was also found that the incident angle of the laser beam with respect to the surface of the workpiece has no substantial influence on the weld pool size. However, the plume size decreases and becomes more inclined when the incident angle decreases from 90 to 45 degrees with respect to the weld pool surface. Tests carried out with the aluminium alloy 5083 as workpiece show that no plume generation occurs, even at maximum laser power. The weld pool formed has a shape, which is typical for the heat conduction mode.

A start was made with electrical conductivity measurements of the plasma plume under different experimental conditions with the aim to obtain more detailed information about the properties of the plume.

1.2 Friction-Stir Welding

Friction stir welding is a recently developed welding process during which no melting of the base material takes place. With this welding process, butt welds and fillet welds can be realised in thin plates by pushing a rotating shouldered pin into the base materials to be joined and moving the pin along the weld groove. The heat to weaken and plastify the metal is mainly generated by friction heat between the shoulder of the rotating pin and the base material. To realise sound welds without cavities and oxide inclusions the pin has to rotate with at least 1000 rpm. The oxide layer on the upper surface of the base material and the oxide layers on the
weld groove at both sides are broken up during the welding process. In a transverse cross-section of the weld a Z-shaped oxide line can be observed (see Figure 1). The shape of the oxide line is strongly influenced by the shape and the dimensions of the welding pin. A threaded pin will cause a discontinuous flow pattern of the plasticized material and the oxide line will be broken up. It appears that break-up of this oxide line results in better mechanical properties of the weld.

Welds were made in different low alloyed and high alloyed aluminium alloys in the form of plates with dimensions 250x100x3 mm. A standard milling machine (Schraublin 53) with a power of 3 kW was used for the friction stir welding experiments.

Much attention was devoted to the influence of the pin and shoulder diameter on the structure of the weld and the mechanical properties of the weld. For a material thickness of 3 mm a pin diameter of 4 mm was found to be most suitable. The shoulder diameter was varied between 10 and 20 mm. It appeared that for a shoulder diameter smaller than 16 mm the travel speed has to be reduced drastically to produce sound welds, whereas travel speeds up to 1200 mm/min could be applied for shoulder diameters of 18 mm and more. Depending on the difference in hardness, high quality welds could also be made between dissimilar materials (see Figure 1).

Figure 1: Transverse cross-section of a friction stir weld between 3 mm thick plates of two different aluminium alloys (AA 7020 and AA 5083)

Tensile testing of the welds obtained showed that fracture occurs in the heat-affected zone (HAZ) of the weld due to softening as a consequence of the heat generated during the welding process. The strength of the welds could be increased considerably by a post weld heat treatment, resulting in a 97% strength of the base material. For the experiments in which a threaded pin was used a 100% strength of the weld was obtained after post weld heat treatment.

This investigation has shown that friction stir welding is a relatively simple welding process, which can be used to produce welds with excellent mechanical properties. The maximum travel speed depends on the chemical composition of the material and on the hardness of the material.

1.3 Electromagnetic Stirring of the Weld Pool during Welding

A study was made of the effects of low-frequency (0-10 Hz) electromagnetic stirring (EMS) of the weld pool during alternating current (AC) gas tungsten arc (GTA) welding of aluminium alloys. With EMS, rotational weld pool flow is induced in the weld pool through Lorentz interaction between an external magnetic field and the welding current. The main targets were to influence weld metal solidification through changes
in the temperature gradient, to increase constitutional supercooling and to supply extra nuclei. Possible results are grain refinement, reduction of texture and, consequently, improved weld properties.

The material used in this research project was the AA 6082 aluminium-magnesium-silicon alloy. This alloy is known to be susceptible to hot cracking (solidification cracking). Therefore, next to improving the grain structure, another point of attention was diminishing this hot cracking susceptibility solely through application of EMS (i.e. without using filler wire).

EMS is most effective when using alternating axial magnetic fields (with the magnetic field lines (anti)parallel to the electrode axis). To reach alternating stirring action, either the magnetic field or the welding current is alternated at the desired stirring frequency. However, aluminium is generally welded with alternating welding current with a frequency of 50 Hz to break down the oxide layer on the weld pool. In view of this, the possibilities were evaluated of stirring at a chosen low frequency, while welding with a welding current alternating at 50 Hz. To reach this, an alternating magnetic field was applied with the frequency equal to the desired stirring frequency plus the frequency of the alternating welding current. Under these conditions low-frequency components are generated, which induce low-frequency stirring, whilst the high-frequency components are too fast for the fluid to follow due to its inertia. The obtained results when following this approach show that it is indeed possible to successfully apply EMS during AC-GTA welding.

In fact, it was found that EMS leads to improvement of the grain structure through grain refinement and to a reduction in texture, particularly at low travel speeds (<4 mm/s). It appears that the observed grain refinement is not a result of an increase in the number of nuclei, but is caused by periodical changes in the temperature gradient. As a result of these changes, grains are hindered in their growth, allowing for new grains to be formed. This mechanism is particularly effective at high stirring frequencies (~10 Hz). Changes in texture were mainly found at low stirring frequencies (1 - 2 Hz), and also result from changes in the temperature gradient. These changes in texture may be effective to diminish the hot cracking susceptibility, as they force the hot crack to periodically alter its direction, dissipating energy. At higher travel speed (8 mm/s), the effect of EMS seems to worsen the grain structure rather than improve it. Due to the lower G/R ratio at this travel speed, finer grains are already formed without EMS, whereas EMS introduces zones with columnar grains.

Other effects of EMS are increased weld penetration and weld width and the formation and/or redistribution of gas pores. Preliminary hot cracking tests show little effect of stirring on the hot cracking susceptibility.


2.1 Weld Pool Oscillation

During arc welding, the penetration of the forming weld can be sensed and controlled by monitoring the oscillation frequency of the weld pool. In this approach, the weld pool is triggered into oscillation by means of short current pulses, superimposed on the welding current and the oscillation frequency is extracted from the arc voltage variation with the help of Fast Fourier Transform analysis. By monitoring the oscillation frequency during welding, direct information is obtained about the penetration of the weld pool. In the case of partial penetration the pool oscillates in a high-frequency
mode (double-ring mode) and in the case of full penetration the pool oscillates in a low-frequency mode (up-and-down mode). The difference between the oscillation frequencies of both oscillation modes can easily be detected when monitoring the frequency spectrum and, hence, can be used as basis of weld penetration sensing. The laboratory work dealing with oscillation based penetration sensing during gas tungsten arc (GTA) welding was completed. On a specific aspect of the method patent was granted. At present attempts are made to test the potential of the method under practical (industrial) conditions as a first step to introduce the technique in industry. Preparations are also made to start work dealing with weld pool oscillation measurements during gas metal arc (GMA) welding. It must be expected, however, that in the case of GMA welding oscillation based sensing will be much more complicated than in the case of GTA welding due to the effect on the weld pool of droplet detachment.

![Figure 2: Arc-metal combination during a frequency measurement in the case of a curved liquid metal surface](image)

In addition to applying weld pool oscillation measurements for sensing and control of weld penetration, the oscillation behaviour of the weld pool can also be used to measure the surface tension of liquid metals under welding conditions. This approach is based on the relation existing between the oscillation frequency of the weld pool and the surface tension of the liquid material. To calculate the surface tension from the measurements, use was made initially of a model that is restricted to flat surfaces. However, this model is only applicable within a relatively small temperature range, since the surface tends to change from flat to curved at increasing temperature. A model for oscillation of curved surfaces was developed and opens the opportunity to determine the surface tension of non-flat surfaces. To evaluate the possibilities and limitations of this new measuring technique, oscillation frequency measurements were carried out on pure aluminium, both under travelling and under non-travelling (static) arc conditions. In Figure 2 the arc-metal combination is depicted during a frequency measurement in the case of a curved liquid surface. The obtained results clearly show that the method can be successfully used to determine the surface tension of liquid metals under welding conditions as a func-
2.2 Position Sensing Based on Tracer Techniques

The study dealing with a new approach of position sensing for arc welding was continued. The principle of this new sensing approach is based on the fact that physical properties of the welding arc, in particular arc voltage, can be influenced by the addition of small amounts of certain chemical compounds. In previous work it was shown that especially oxides (silicon oxide, iron oxide, chromium oxide) and fluorides (aluminium fluoride) have a significant influence on the welding arc. These compounds are therefore especially suitable as tracers in the new sensor system.

In earlier work the influence of additives, in particular silicon oxide, on the welding arc characteristics was studied. It was found that the additive could affect the arc in different ways. Firstly, its presence in the arc can give rise to arc contraction due to negative ion formation in the arc, particularly in the cooler, outer region of the arc. This would directly lead to constriction of the arc and to an increase of arc voltage.

Another effect that plays a role is arc trailing due to the presence of the additive on the surface of the weld pool, resulting in a longer effective arc length and, hence, in a higher voltage. Finally, the presence of the additive on the surface of the pool will result in a reduction of the contact area between arc and weld pool, again resulting in an increase of arc voltage. Similar results were obtained when iron oxide, chromium oxide and aluminium fluoride are applied as additive, although the observed effects of these additives seem to be somewhat less pronounced than those observed when using silicon oxide.

Experiments were also performed to explore the effects of additives on the geometry and size of the weld pool with emphasis on silicon oxide. It appears that the application of additives leads to a weld pool, which is longer and narrower. The observed change in shape of the weld pool is a direct consequence of the fact that, due to the presence of the additive on the surface of the weld pool, the root of the arc is constricted normal to the welding direction and is extended backwards parallel to the welding direction.

Another factor that should be taken into account when considering the geometry of the weld is the flow of the molten metal in the weld pool. More specifically, it should be expected that the presence of additives on the surface of the weld pool would give rise to a change in magnitude and/or direction of the Marangoni flow. As this type of flow is governed by the surface tension of the liquid metal, attempts will be made to determine the influence of the various additives on the surface tension, using a technique based on the measurement of the frequency of weld pool oscillations (see Section 2.1).

The next step in the research programme will be a systematic evaluation of the possibilities and limitations of the additive-based sensor under laboratory conditions.


3.1 Weldability of Aluminium-Matrix Composites

The research project aimed at evaluating the weldability of aluminium-matrix composites was completed. The larger part of the research work was focused on the composite 6061/Al₂O₃/10p, consisting of the alloy AA 6061 containing 10 vol.% aluminium oxide particles. Welding experiments were carried out using the gas tungsten arc welding process under different conditions and the possibilities and limitations of
using this process as joining technique were evaluated. Specific attention was given to the application of electromagnetic stirring of the weld pool during welding as a tool to improve the weldability of the composite.

It appears that welding has a number of different effects on the structure and the mechanical properties of the material. First of all it was found that the grain size of the weld metal is approximately twice the size of the grains of the composite in the as-received condition. Apparently, the particles do not act as grain refiners during solidification of the weld metal. Furthermore, it was found that in the upper layer of the weld metal a particle-denuded zone is formed. This denuding effect is ascribed to Marangoni flow in the weld pool, in combination with arc plasma drag. In addition to particle denuding, particle pushing takes place in the weld pool as a consequence of particle-grain interaction during solidification. This phenomenon is particularly apparent in the vicinity of the fusion boundary.

It was also observed that during welding, precipitation of a magnesium-silicon rich phase takes place in the interfacial zone of the particles in the weld metal. However, no measurable growth of the spinel layer around the particles was observed with both optical microscopy and scanning electron microscopy.

Hot cracking can also be a problem during welding of the composite. It was found that with increasing travel speed the hot cracking susceptibility of the composite increases. This can be understood by realising that increasing the travel speed favours segregation during the solidification process and, hence, leads to the formation of low-melting eutectics along the grain boundaries.

Welding reduces the hardness of the weld metal and the heat-affected zone to about 50% of the hardness of the base metal. However, the major part of the hardness reduction can be recovered by a T6 heat treatment (artificial ageing).

When welding was performed with continuously transferred filler wire, an inhomogeneous weld is formed, which is caused by poor mixing between the liquid filler wire material and the liquid composite material. The degree of mixing between the composite material and the filler wire material can be expressed in terms of a mixing parameter. It appears that this mixing parameter increases with increasing travel speed and is virtually independent of the amount of filler wire added per unit weld length. The influence of travel speed on the mixing behaviour can be explained in terms of the higher arc current applied with increasing travel speed. A higher arc current increases the weld pool temperature, which in turn decreases the weld pool viscosity. The lower weld pool viscosity enhances fluid flow, resulting in improved mixing. If the wire is not continuously transferred to the weld pool during welding, but transferred under droplet transfer conditions, the degree of mixing of the composite material and the filler wire material was found to be somewhat improved. The results of hardness tests show that the hardness of the weld metal is directly related to the density of the non-metallic particles in the matrix.

It should be expected that part of the problems occurring when welding the composite could be overcome by applying electromagnetic stirring. To be able to evaluate the possibilities and limitations of electromagnetic stirring of the weld pool during welding, an electromagnetic stirring device was built, consisting of current conducting coils placed symmetrically around the welding torch. By means of these coils stable and reproducible magnetic fields can be obtained in and around the arc and the weld pool, both in the case of direct current welding and in the case of alternating current welding. Application of a transverse magnetic field (normal to the arc) yields sideways bending of the arc and the weld pool, whereas application of an axial magnetic field (parallel to the axis of the arc) gives rise to rotation of both the arc and the weld
metal (electromagnetic stirring). When considering electromagnetic stirring, a distinction should be made between uni-directional stirring and alternating stirring. Unidirectional stirring is obtained when the current frequency is equal to the magnetic field frequency, whereas alternating stirring is obtained when the magnetic field frequency is different from the current frequency. The difference between these two frequencies determines the stirring frequency.

It was found that electromagnetic stirring of the weld pool during welding of the composite leads to the break-up of the denuded zone at the surface of the weld, thus reducing the total denuding effect. This is due to the mixing action of the weld pool flow and to the reduction of the temperature gradient along the weld pool surface, which reduces the Marangoni flow. Electromagnetic stirring also leads to a wide particle denuded zone along the fusion boundary, particularly in the case of unidirectional electromagnetic stirring. This zone is due to particle-liquid interaction along the fusion boundary, which induces lift forces on the particles directed towards the centre of the weld pool. The lift forces originate from the relative velocity of the particles with respect to the fluid. The relative velocity of the particles is generated and sustained by the electromagnetic force acting on the particles in the weld pool in the presence of an axial magnetic field.

It was also found that electromagnetic stirring results in break-down of the stray structure in the upper part of the weld metal. Optimal grain refining can be obtained within a broad range of stirring frequencies (2 - 10 Hz). The spherical grains in the refined zone have a typical size of 60 μm. Break-down of the stray structure depends on the level of penetration and the angle between the solidification front and the surface of the workpiece. Apart from the denuding effects observed in the surface layer of the weld and near the fusion boundary, no significant effect of electromagnetic stirring on the particle distribution in the bulk was observed.

When welding with filler wire addition electromagnetic stirring leads to severe mixing of the composite material and the filler material. The degree of mixing depends on the strength of the magnetic induction applied and on the stirring frequency. The best mixing results are obtained with a magnetic induction higher than 20 mT and a stirring frequency of around 2 Hz. However, electromagnetic stirring results in the formation of particle denuded zones along the fusion boundary of the weld. The width of these zones decreases with increasing stirring frequency.

Welding experiments with electromagnetic stirring were also carried out under practical conditions using a workpiece consisting of two plates with a V-groove geometry. It was found that also under these conditions severe mixing of composite material and filler material occurs, resulting in welds with a relatively homogeneous particle distribution. Furthermore, it appears that the hardness of the stirred welds (after a T6 heat treatment) does not significantly deviate from that of the unwelded base material.

On the basis of the foregoing it can be concluded that the weldability of aluminium-matrix composites and, hence, the applicability of these materials can be considerably improved by electromagnetic stirring of the weld pool during welding.

4 Diffusion Bonding of Ceramic Materials (A.T.J. van Helvoort, R.H. Vegter, T. Luijendijk, W.J.P. Vink, G. den Ouden)

4.1 Diffusion Bonding of Zirconia

Ceramic materials are used in a wide range of applications in which their specific properties make them favourable in comparison with other types of materials. However, each ceramic material has its own characteristics and, therefore, in many appli-
cations combinations of ceramics are needed. Diffusion bonding is one of the methods that can be used for joining ceramics. Generally speaking, direct diffusion bonding of two different ceramic materials without an interlayer is not possible. Due to the difference in thermal expansion between the two materials and the lack of plasticity of ceramics, high stresses will develop in the vicinity of the interface during cooling from the bonding temperature down to room temperature. As ceramic materials are relatively stiff and brittle, these stresses can not be released by plastic deformation and, therefore, this will cause fracture either in the bulk of the ceramic or along the interface. By using metallic interlayers the thermal stresses can be released by plastic deformation. When applying a metallic interlayer, two metal-ceramic interfaces should be considered. At these interfaces chemical reactions may occur and the reaction products can affect the strength of the bond. A study of the microstructure of diffusion bonds gives therefore important information about the applicability of this joining technique for specific material combinations.

ZrO₂/Ni/Si₃N₄ diffusion bonds

Part of the work carried out concerns diffusion bonding of zirconia to silicon nitride using a nickel interlayer. Diffusion bonds were made within a wide range of process conditions and the strength of the bonds obtained was determined by means of shear strength testing. To obtain insight in the development of the microstructure of the diffusion bonds, cross-sections of the bonds were prepared and these cross-sections were examined by means of optical microscopy, scanning electron microscopy and transmission electron microscopy. It was found that the ZrO₂/Ni interface remains entirely flat during the bonding process and that no diffusion zones are formed at either side of the interface, which suggests that no diffusion has taken place across this interface. This conclusion is in agreement with the results of diffusion bonding experiments carried out earlier with ZrO₂/Ni/ZrO₂ combinations.

Contrary to the ZrO₂/Ni interface, the Si₃N₄/Ni interface is rather irregular in shape, whereas also pores can be observed in the vicinity of this interface. EPMA line scans made perpendicular to the interface show that the chemical composition in the bulk of the silicon nitride has remained unaffected, but that during the bonding process some Si (formed by decomposition of Si₃N₄) diffused into the Ni, resulting in a thin diffusion layer. Part of the free (atomic) nitrogen, formed by the decomposition of Si₃N₄, diffused into the Ni, whereas the remainder escaped to the interface, where it recom­bined to N₂, resulting in pore formation. It is evident that the formation of this porous layer leads to a decrease of the mechanical strength of the bond. The mean shear strength of the ZrO₂/Ni/Si₃N₄ was found to be about 60 MPa. As fracture occurred in most cases along the Si₃N₄/Ni interface, it must be expected that the shear strength of the ZrO₂/Ni joint is higher than this value.

ZrO₂/AISI 316 diffusion bonds

Attention was also given to diffusion bonding of zirconia to stainless steel AISI 316. Bonding experiments were conducted within a wide range of process conditions and the strength of the bonds was determined by means of shear strength testing. It was found that the strength of all ZrO₂/AISI 316 bonds produced is relatively low. Many of the specimens already failed during handling after the diffusion bonding process. When visually inspecting the failed ZrO₂/AISI 316 combinations, a dark layer can be observed in the zirconia just below the surface bonded to the stainless steel. With optical microscopy this layer is only visible with polarised light (Figure 3a). Characteristic for the layer is the absence of pores, which are normally present in the bulk material (Figure 3b).
Analysis of the layer by means of EPMA scanning indicates that the dark layer has the same chemical composition as the bulk material. More precisely, it appears that no elements of the stainless steel have diffused into the zirconia and that no zirconium or oxygen, originating from the decomposition of the zirconia, has diffused into the stainless steel. It is assumed that the observed dark layer reflects the tetragonal to monoclinic transformation of the zirconia, which takes place under the influence of the residual stresses developed during cooling from the process temperature to room temperature.

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**S.W. Simpson, Q. Lin, S.E. Offerman, M. Rados, P. Xu**  
*GMAW electrical measurements and their interpretation in terms of simulated welding behaviour*  
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**D.N. Travessa, M. Ferrante, G. den Ouden**  
*Solid state diffusion bonding of Al2O3 to AISI 304 stainless steel*  

**R.H. Vegter, G. den Ouden**  
*Diffusion bonding of zirconia to silicon nitride using nickel interlayers*  

**R.H. Vegter, G. den Ouden**  
*The role of interlayer thickness in diffusion bonding ZrO2 to Si3N4*  

**H.W. de Vries**
Weldability of aluminium-matrix composites

H.W. de Vries, G. den Ouden
Mixing behaviour of the weld pool during GTA welding of aluminium-matrix composites
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