PRECIPITATION PHENOMENA IN ALUMINIUM-BASED METAL MATRIX COMPOSITES:
EFFECTS OF REINFORCEMENT ON KINETICS AND MISFIT ACCOMMODATION

PRECIPITATIE VERSCHIJNSELEN IN ALUMINIUM METAAL MATRIX COMPOSITEN:
INVLOED VAN VERSTERKende DEELTJES OP KINETIEK EN MISPASSINGSACCOMMODATIE
P recipitation phenomena in aluminium-based metal matrix composites: effects of reinforcement on kinetics and misfit accommodation

Proefschrift

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6. M.J. Starink and P. van Mourik: 'Cooling and heating rate dependence of precipitation in an Al-Cu alloy', accepted for publication in Materials Science and Engineering

7. M.J. Starink, P. van Mourik and B.M. Korevaar: 'Lattice parameter variations resulting from precipitation and misfit accommodation in a quenched and aged Al-Cu alloy with silicon particles', to be submitted for publication

8. M.J. Starink, V.M.F. Abeels and P. van Mourik: 'Lattice parameter and hardness variations resulting from precipitation and misfit accommodation in a particle reinforced Al-Si-Cu-Mg alloy', to be submitted for publication
CHAPTER I

GENERAL INTRODUCTION

Nowadays, aluminium is a metal widely used in various applications. The worldwide consumption of aluminium is second only to iron. Aluminium has reached this position fairly recently: a little more than one century ago, aluminium was an exotic, expensive metal mainly used as ornament or decoration.

After conventional casting, the mechanical properties of aluminium are generally worse than of most steels, which are also cheaper. For this reason aluminium was initially not used for structural applications. In the first part of this century various developments contributed to the rise in aluminium consumption. First, due to the invention of the production of aluminium via an electrolytic route between 1886 and 1888, the price of aluminium came down. Secondly, new applications like in aviation and other transport sectors, demanded low density materials. (Aluminium has a very low density; of the most common metals only magnesium has a density lower than aluminium.) Thirdly, due to new inventions it became possible to produce aluminium alloys with better mechanical properties. One of these new inventions was precipitation hardening.

Precipitation hardening is possible when aluminium is alloyed with elements which have a high diffusivity and high solubility in the Al-rich phase. In these alloys, a heat treatment consisting of solution treatment, quenching and subsequent ageing can lead to the formation of (semi-) coherent phases which increase the strength of the alloy. Well known alloying elements which give rise to precipitation hardening are copper, magnesium and zinc.

After the second world war the demand for aluminium initially shrunk. This was mainly due to the decreased demand from defence industries (for instance the aviation industry). In the second part of this century non-metallic materials like plastics became important competitors for various applications. With this new competition the demand for improved aluminium alloys increased. Within the last few decades two main developments took place which improved the mechanical properties of aluminium-based alloys.

Rapid solidification of aluminium alloy leads to extended solid solubility of alloying elements in the Al-rich phase and refinement of the structure of the alloy. Rapid solidification can be achieved for instance by melt spinning (see for instance Ref. 1), gas atomisation (2) or the Osprey process (3). In all cases a further consolidation process (for instance hot extrusion or hot isostatic
pressing) is necessary to produce a fully densified product (4). Since rapidly solidified aluminium powders generally contain fairly high amounts of hydroxides and adsorbed moisture, a degassing treatment prior to consolidation may be necessary (5). Although much of the initial extended solubility and some of the refinement of the structure is lost during consolidation (see for instance Ref. 6), rapid solidification processing (RSP) can increase some of the mechanical properties of classical aluminium alloys. More important is that via RSP completely new alloys can be produced. With RSP it is possible to increase the percentage of iron and nickel up to about 10 % in weight (due to the formation of course intermetallics, conventional aluminium alloys contain only a few tenths of a percent of these elements), and so produce new heat resistant aluminium alloys (4, 7, 8, 9). RSP also made it possible to produce alloys with a high percentage (about 20 volume percent) of finely dispersed silicon particles (10). These high silicon alloys posses an improved wear resistance and reduced thermal expansion, which makes them attractive for applications like parts of combustion engines.

Another important development of the last few decades is the development of aluminium-based metal matrix composites (MMCs). A metal matrix composite is an alloy which consists of particles or fibres embedded in a metallic matrix. Typically about 20 volume percent of particles or fibres are used. For these inclusions ceramic materials like aluminium oxide (Al₂O₃) and silicon carbide (SiC), but also carbon and boron fibres are used. The main advantages of aluminium-based MMCs over monolithic aluminium alloys are: low thermal expansion, high wear resistance, high elastic modulus and high strength at elevated temperatures. There are also disadvantages attached to MMCs: they are difficult to machine, inspect and recycle, they have low ductility and toughness, and whiskers can be a health hazard. This, combined with the higher production costs (about 2 to 10 times the cost of producing conventional aluminium alloys, depending on production route, see Ref. 11), will cause aluminium-based MMCs to be attractive only for certain special applications. Currently MMCs are used in combustion engines and in sports equipment. Other applications in the automotive, aircraft, defence and space industries are under investigation.

In an MMC, many of the physical properties of inclusion and matrix are very different. Some of these differences impart desired properties to the MMC. The high stiffness of ceramic inclusions, for instance, imparts a high stiffness to the composite. Other properties of composites are linked in a quite complex way to the properties of the constituting materials. The yield strength of a ceramic inclusion is generally much higher than the yield strength of the
matrix. In many cases the strength of the composite does not increase continuously with increasing volume fraction of inclusions: reduced precipitation strengthening due to the introduction of reinforcing particles, bad interfacial strength and detrimental surface reactions can spoil the mechanical properties of MMCs.

Precipitation in Al-based MMCs is in many cases different from the precipitation in the monolithic alloy. In some cases these differences are caused by chemical interactions between matrix and inclusion during the production process. It is for instance well known that at elevated temperature SiC reinforcements react with aluminium to form aluminium carbide (see 12):

\[ 4 \text{Al} + 3 \text{SiC} \rightarrow \text{Al}_4\text{C}_3 + \text{Si} \]

The formation of aluminium carbide degrades the mechanical properties of the MMC. The silicon which is released by this reaction can (partly) dissolve in the aluminium matrix and, in case the matrix is age hardenable, interfere with precipitation processes. As a result precipitation kinetics might be altered or cause the formation of silicon-containing precipitates which do not form in the monolithic alloy. An example of the latter is the Al-Cu-Mg alloy reinforced with SiC (see Ref. 13). When this MMC is produced by conventional casting or rheocasting Al_5Cu_2Mg_8Si_6 particles are formed around the SiC. When the same MMC is produced by spray deposition or by mixing in the solid state followed by extrusion, this intermetallic phase is not detected. This result can be explained from the available interaction time and the interaction temperature, which are both high in the casting methods, thus favouring the formation of aluminium carbide. Another example for chemical interaction is the reaction between a magnesium containing matrix and an aluminium oxide reinforcement:

\[ 3 \text{Mg} + \text{Al}_2\text{O}_3 \rightarrow 3 \text{MgO} + 2 \text{Al} \]
\[ 3 \text{Mg} + 4 \text{Al}_2\text{O}_3 \rightarrow 3 \text{MgAl}_2\text{O}_4 + 2 \text{Al} \]

Both reactions cause a depletion of the Mg content of the matrix, and thus diminish age hardening by magnesium-containing precipitates (see for instance Ref. 14).

Apart from chemical interactions also stresses due to misfit of the reinforcing inclusions can alter precipitation kinetics. Temperature changes, for instance during quenching or during cooling after casting or after thermo-mechanical processing, cause the matrix and the inclusion to shrink. The coefficient of thermal expansion (CTE) of aluminium is however, much larger than the CTE of the ceramic reinforcements most generally used in MMCs (SiC, Al_2O_3, graphite, boron, Si). (The effect of alloying elements on the thermal expansion coefficient of aluminium is only a few percent (see Ref. 15), and in
these cases negligible.) Thus temperature changes cause misfit. This misfit is accommodated partly by elastic deformation of matrix and inclusion and partly by plastic deformation of the matrix. Accommodation by plastic deformation significantly increases the tensile yield strength of MMCs (16). Both elastic deformation and plastic deformation can influence the precipitation in age hardenable matrices. An example of an MMC in which elastic deformation influences precipitation is the Al-1.7at%Cu alloy reinforced with SiC. In this alloy both the density and the orientation of the 0' precipitates (0' precipitates are semi-coherent, plate-shaped particles) strongly depends on the elastic stresses around the SiC particle (17). The dislocations created during plastic deformation of the matrix can annihilate part of the excess vacancies which are introduced by quenching (18). Excess vacancies increase the rate of formation of various precipitates, either by enhancing the rate of diffusion of alloying elements or by providing nucleation sites. Thus accommodation of misfit by plastic deformation can reduce the rate of formation of precipitates which formation depend on the availability of excess vacancies. On the other hand plastic deformation can also enhance the formation of certain precipitates. This is the case for precipitates which nucleate on dislocations. An example of these mixed effects is found in reinforced Al-Cu alloys (see for instance 19, 20). In these alloys the formation rate of GP-zones is severely reduced, while the formation of 0' phase precipitates is enhanced. Since the peak hardness during artificial ageing is associated with the presence of fine 0' phase precipitates, the time required to reach peak hardness is reduced by the addition of ceramic particles.

From the above it becomes evident that in most cases the solution treatment and ageing treatments used for the monolithic alloy need to be modified in order to obtain the maximum benefit of age-hardening in the corresponding reinforced alloy. In order to optimise the mechanical properties of heat treatable Al-based MMCs, the precipitation in these alloys needs to be investigated.

In this thesis several articles are brought together which focus on the influence of dispersed particles on the precipitation in aluminium alloys. As dispersed particles, silicon and aluminium oxide particles were studied. The matrix of the alloys studied consisted of Al-Cu, Al-Cu-Si, and Al-Cu-Mg-Si. The articles concerning the first two alloys make up Part 1 of this thesis. The work on Al-Cu-Mg-Si alloys is compiled in Part 2. Precipitation was studied by differential scanning calorimetry (DSC), X-ray diffraction and hardness measurements. Besides the study of precipitation kinetics, X-ray diffraction
also enables the study of lattice parameter shifts induced by elastic and plastic deformation, both of which are important for the precipitation kinetics.

References

Part 1. Precipitation in Al-Cu and Al-Si-Cu alloys

Chapter II  A comparative study on heat effects in an Al-Cu alloy reinforced with silicon particles and in a binary Al-Cu alloy

Chapter III  Cooling and heating rate dependence of precipitation in an Al-Cu alloy

Chapter IV  A calorimetric study of precipitation in an Al-Cu alloy with silicon particles

Chapter V  Lattice parameter variations resulting from precipitation and misfit accommodation in a quenched and aged Al-Cu alloy with silicon particles
CHAPTER II

A COMPARATIVE STUDY ON HEAT EFFECTS IN AN AL-CU ALLOY REINFORCED WITH SILICON PARTICLES AND IN A BINARY AL-CU ALLOY

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Abstract

To investigate the enhanced precipitation kinetics in metal matrix composites, a comparative study of precipitation phenomena in a solid-quenched Al-Cu alloy reinforced with silicon particles and in a solid-quenched binary Al-Cu alloy was performed using differential scanning calorimetry. An Al-1.3at%Cu-19at%Si alloy was produced by melt spinning and subsequent extrusion. A binary Al-1.65at%Cu alloy was produced by conventional casting. Both alloys were investigated after solution treatment and subsequent water quenching (=WQ) and after slow cooling (~10 K/min) from 793 K to room temperature. The following striking differences were observed: i. Only in the WQ Al-Cu alloy GP-zone formation occurred, whereas in the WQ Al-Cu-Si alloy no appreciable GP-zone formation was observed; ii. The temperature range of the formation of $\theta'/\theta$ phases in WQ Al-Cu-Si was situated at lower values as compared to the WQ AlCu alloy; iii. After slow cooling at 10 K/min no precipitation heat effects were observed for the Al-Cu-Si alloy, whereas the Al-Cu alloy showed a heat effect due to precipitation of $\theta'/\theta$ phases. The above results indicate that the copper precipitation from the supersaturated Al-rich phase is influenced by the presence of silicon. Hence, to obtain optimal mechanical properties of MMCs, specific heat treatments different from the ones normally used for the corresponding unreinforced alloys are necessary.
1. Introduction

Advanced aluminium alloys often consist of an aluminium-rich matrix reinforced with ceramic particles. Such metal matrix composites (MMCs) possess a high wear resistance and high ratios of Young's modulus to density and of strength to density. The matrix of an MMC can play an important part in the optimisation of the mechanical properties, for instance via precipitation hardening.

An Al-Cu-Si alloy with about 20 vol% silicon can be considered as a model system for MMC heat treatment studies as it combines the possibility of precipitation with the presence of reinforcing particles. It has recently been shown by differential scanning calorimetry (DSC) that copper and silicon (both dissolvable in the Al-rich matrix) precipitate simultaneously in a quenched Al-Cu-Si alloy with 21 vol% silicon particles (1). It appeared that copper atoms precipitated in either the intermediate $\theta'$ phase or the equilibrium $\theta$ phase, whereas silicon atoms always precipitated directly as silicon phase (1).

It is generally accepted that in quenched binary Al-Cu alloys the precipitation proceeds via intermediate phases according to a temperature dependent sequence. At sufficiently low temperatures (below approximately 450 K) the following scheme applies (GP I/II stands for Guinier-Preston zones): supersaturated solid solution $\rightarrow$ GP I/II $\rightarrow$ $\theta'$ $\rightarrow$ $\theta$.

DSC studies on Al-Cu alloys generally reveal this sequence (2, 3, 4). It should be noted that in practice $\theta'$ and $\theta$ precipitation show overlap. Thus, for quenched Al-Cu alloys separated effects of $\theta'$ and $\theta$ precipitation are not observed during DSC experiments.

The presence of reinforcing particles changes the precipitation kinetics in quenched MMCs as compared to the precipitation in the quenched corresponding alloy without reinforcing particles (5-9). In order to gain more insight in the effects of reinforcing particles it was decided to perform a comparative study of precipitation in quenched Al-Cu alloys with and without reinforcing silicon particles using DSC.
2. Experimental procedures

2.1 Production routes

To obtain an Al-Cu-Si alloy with a size distribution of reinforcing particles comparable to the one in MMCs, the following production route was chosen. An Al-1.3 at%Cu-19.1 at%Si alloy was produced by melt spinning from 99.998 wt% Al, 99.99 wt% Si and 99.9 wt% Cu (for a detailed description of the melt-spinning process, see Ref. 10). Melt spinning yielded ribbons with the following typical dimensions: thickness 50 μm and width 3 mm. Chopped ribbons (flakes) were dried for 24 hours at 380 K to eliminate moisture that might be attached. The flakes were precompacted, preheated inside the liner of the extrusion press (20 min at 650 K) and subsequently extruded with a reduction ratio of 20:1. A binary Al-1.65 at%Cu alloy was produced by conventional casting from 99.998 wt% Al and 99.9 wt% Cu (the composition was chosen such that the equilibrium copper fraction of the Al-rich matrix at the homogenization temperature applied is equal for both alloys). After casting, the Al-Cu alloy was homogenized at 773±5 K for 48 h. Final treatment of both alloys consisted of homogenizing at 793±2 K for about 5 minutes followed by a water quench.

2.2 Differential scanning calorimetry

The DSC apparatus used was a Dupont type 910. As a reference pure aluminium (99.99%) with a mass close to that of the specimen was used. Both reference and specimen were enclosed in an aluminium pan sealed with an aluminium cover. A protective gas atmosphere of pure argon was employed. The following heating rates were applied: 0.5, 2, 5, 20, 40 K/min. Runs were recorded between 300 and 791 K. The first run started 1 hour after quenching in water and will be referred to as the H+WQ run (after Homogenizing and Water Quenching). After the first run, the specimen was maintained at 791 K for 2 minutes, subsequently it was allowed to cool freely inside the DSC apparatus for 200 min. The cooling of all specimens after the first run was identical and nearly exponential; the cooling rate on passing the copper solvus at 750 K was 22 K/min and on passing 550 K the cooling rate was 6.5 K/min. At the end of the cooling room temperature was reached. Subsequently, a second run, at the same heating rate as the first run, was performed. This second run will be referred to as the H+SC run (after Homogenizing and Slow Cooling).

Baselines reflect the heat flow due to the difference in heat capacity of specimen and reference in the absence of reactions. In view of the linearity of the heat capacity of pure aluminium, silicon and copper in the temperature
range studied (see (11)) and in view of the Kopp-Neumann rule, it is assumed that the heat capacities of the alloys studied depend linearly on temperature in the temperature range studied. Hence, baselines are considered to be straight lines. Baselines were constructed by extrapolating the straight part of DSC curves at low temperatures to higher temperatures. Only for the Al-Cu alloy it was necessary to perform a third run after extremely slow cooling (0.5 K/min) to obtain a straight part to be extrapolated. The very slow cooling assured a complete copper precipitation before the third run started. The DSC curves presented are corrected for the heat flow due to the differences in heat capacity between specimen and reference. Then, the lines representing the absence of reactions, are flat horizontal lines.

3. Results

In Figs. 1 and 2 typical examples of the H+WQ runs (heating rates 5 K/min) are shown for the Al-Cu and the Al-Cu-Si alloy. For all heating rates studied the following observations were made:

![DSC curve of the H+WQ run of the Al-1.65 at%Cu alloy.](image)

Fig. 1: DSC curve of the H+WQ run of the Al-1.65 at%Cu alloy.
1. The DSC curves of the Al-Cu alloy show two exothermic (indicated by I and III) and three endothermic (indicated by II, IV and V) effects.

2. The DSC curves of the Al-Cu-Si alloy show only one exothermic and one endothermic effect. The endothermic effect can be subdivided in two subeffects. The endothermic effect is not completed within the temperature range studied.

3. The temperature ranges of the main exothermic effect (effect III) for the Al-Cu alloy are situated at higher temperatures than those of the exothermic effect in the Al-Cu-Si alloy.

4. The effect II, observed for the Al-Cu alloy, is absent for the Al-Cu-Si alloy.

\[ 5 \text{ K/min} \]

\[ 5 \text{ J/K.mol} \]

Fig. 2: DSC curve of the H+WQ run of the Al-1.3 at\%Cu-19.1 at\%Si alloy.

In line with results from literature (2, 3, 4), the effects displayed by the DSC curves of the H+WQ run of the Al-Cu alloy are attributed to the following reactions: I. GP-zone formation, II. GP-zone dissolution, III. \( \theta' \)\( /\theta \) formation, IV. \( \theta' \) dissolution, and V. \( \theta \) dissolution (see also Chapter III). An exothermic transformation of \( \theta' \) to \( \theta \) phase in the final stages of effect IV might be included in the analysis of the observed heat effects. As DSC curves known from literature (2, 3, 4) never show clear indications of an exothermic effect in this
temperature region, it is assumed that during heating of the Al-Cu alloy at a constant rate this transformation does not occur. The exothermic effect in the DSC scans of the Al-Cu-Si alloy (Fig. 2) is attributed to the combined precipitation of silicon and copper, the latter as θ' or θ phase, whereas the endothermic effect is related with the dissolution of the copper containing phases and of silicon (1). In comparing Fig. 2 with Fig. 1 it is observed that i. GP-zone formation/dissolution is absent in the Al-Cu-Si alloy and ii. in the Al-Cu-Si alloy the dissolution of the θ' and θ phases does not result in clearly separate endothermic effects.

In Figs. 3 and 4 typical examples of the H+SC runs (heating rates 5 K/min) are shown for the Al-Cu and the Al-Cu-Si alloy. From a comparison of Fig. 3 with Fig. 1 it is observed, that in the DSC curve of the H+SC run of the Al-Cu alloy GP-zone formation/dissolution is virtually absent, whereas the magnitude of the θ'-phase dissolution effect had decreased strongly in comparison with the θ-phase dissolution effect. Comparing Fig. 4 to Fig. 3 yields that clearly no θ'/θ precipitation (nor silicon precipitation) occurs during the H+SC run of the Al-Cu-Si alloy. This was observed for all heating rates applied.

![Graph showing DSC curve of the H+SC run of the Al-1.65 at%Cu alloy.](image-url)

**Fig. 3:** DSC curve of the H+SC run of the Al-1.65 at%Cu alloy.
The copper solvus for both the binary and the ternary alloy is situated at about 750 K (12, 13). This is clearly related with the sharp decrease in endothermic effects around this temperature observed for both alloys studied (cf. Figs. 1-4). The temperature of maximum silicon solubility however, is situated beyond the DSC end temperature used in this study (13), thus for the Al-Cu-Si alloy the end of silicon dissolution is not observed in Figs. 2 and 4.

In Table I the peak temperatures of the (main) precipitation effect in the H+WQ runs for the Al-Cu and Al-Cu-Si alloy and in the H+SC runs for the Al-Cu alloy are given as a function of heating rate. It is observed that for all heating rates the peak temperatures increase in the following sequence: H+WQ run of Al-Cu-Si, H+WQ run of Al-Cu, H+SC run of Al-Cu.

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Fig. 4: DSC curve of the H+SC run of the Al-1.3 at%Cu-19.1 at%Si alloy.
4. Discussion

The main differences between the Al-Cu-Si and the Al-Cu alloys studied are:

1. For the H+WQ Al-Cu-Si alloy no appreciable GP-zone formation/dissolution occurs, in contrast with the Al-Cu alloy.

2. The temperature range for the (main) precipitation effect is situated at lower temperatures for the H+WQ Al-Cu-Si alloy than for the H+WQ Al-Cu alloy, the difference being about 70 K (see Table I).

3. During the H+SC run no precipitation takes place for the Al-Cu-Si alloy, whereas for the Al-Cu alloy a clear precipitation effect is observed.

From these differences it is concluded that for the H+WQ Al-Cu-Si alloy GP-zone formation is suppressed, whereas the kinetics of the precipitation of copper containing intermediate (θ') and equilibrium (θ) phases are enhanced. Note that after H+SC for the Al-Cu-Si alloy nearly complete precipitation has occurred, whereas for the Al-Cu alloy the Al-rich matrix is still supersaturated (cf. Fig. 3 to Fig. 4).

<table>
<thead>
<tr>
<th>Heating Rate (K/min)</th>
<th>Peak Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al-1.3at%Cu-19.1at%Si</td>
</tr>
<tr>
<td></td>
<td>H+WQ ±3K</td>
</tr>
<tr>
<td>0.5</td>
<td>488</td>
</tr>
<tr>
<td>2</td>
<td>514</td>
</tr>
<tr>
<td>5</td>
<td>538</td>
</tr>
<tr>
<td>20</td>
<td>566</td>
</tr>
<tr>
<td>40</td>
<td>600</td>
</tr>
</tbody>
</table>

After homogenizing and quenching, the Al-rich matrix of the Al-Cu-Si alloy is supersaturated with copper (1.65 at%; all copper dissolves at the homogenizing temperature, see Ref. 13) and silicon (1.05 at%, using the ternary phase diagram (13)). Most of the silicon in the ternary alloy is present as second phase silicon particles (18.2 at%, corresponding with about 22 vol%). After homogenizing and quenching, the Al-1.65at%Cu alloy has only one phase. Hence, the Al-rich phases of both alloys are equally supersaturated with copper atoms. From the Al-rich corner of the of the Al-Cu-Si phase diagram (13) it is
known that silicon has nearly no influence on the solid solubility of copper in aluminium and vice versa. Thus, the interaction between silicon and copper atoms in the Al-rich matrix is small and it is unlikely that the presence of silicon dissolved in the Al-rich matrix can cause the large difference in precipitation kinetics observed.

As a result of the production by melt spinning and extrusion (essentially a powder metallurgy route) the Al-Cu-Si alloy possesses a much finer grain size and a higher oxide content than the conventionally cast Al-Cu alloy. Compared to the observed differences between the peak temperatures of the H+WQ Al-Cu-Si and the H+WQ Al-Cu alloy (see above and Table I) Papazian (5) reported only small differences in peak temperatures for aluminium alloys produced via a casting and a powder metallurgy route. Hence, it is unlikely that the observed differences in peak temperatures are related with the different production routes as such.

On quenching the Al-Cu-Si alloy, misfit occurs due to the large difference in coefficient of thermal expansion between the reinforcing silicon particles and the surrounding matrix; just as is the case for a quenched particle-reinforced MMC. This misfit is partly accommodated by plastic deformation of the matrix and partly by elastic deformation (14). The suppression of GP-zone formation and the enhancement of precipitation of the intermediate (θ') and equilibrium (θ) phases, as observed in this study, was also reported for various Al-Cu based MMCs (5, 6, 7, 8). The explanation of these phenomena is generally given as follows (5, 6):

1. at low temperatures the misfit dislocations (formed on quenching, see above) annihilate excess vacancies;
2. as GP-zone nucleation and formation requires excess vacancies and as GP zones are thought not to nucleate on dislocations (15), GP-zone formation is suppressed by a lack of vacancies;
3. as the intermediate and equilibrium phases do nucleate on dislocations, the misfit dislocations present in quenched MMCs enhance the precipitation of these phases (see also Ref. 7).

In the above explanation it is assumed that the excess vacancies are annihilated at low temperatures and consequently are no longer available for precipitation of the intermediate/equilibrium phases at elevated temperatures. However, from an activation energy analysis of the peak temperature of the main precipitation effect for the H+WQ Al-Cu-Si alloy, an effective activation energy was derived of $E_A = 1.00\pm0.07$ eV (1), which is lower than the activation energies for silicon and for copper diffusion in aluminium (16). As precipitation of copper and silicon atoms from a supersaturated Al-matrix can
only proceed via the vacancy mechanism, this low value indicates a vacancy-enhanced precipitation. The quoted result indicates that in the H+WQ Al-Cu-Si alloy excess vacancies are retained at elevated temperatures*.

*Apparently, even the much smaller matrix grain size in the H+WQ Al-Cu-Si alloy compared to the H+WQ Al-Cu alloy, resulting from the different production routes (see Section 2.1), does not introduce a remarkable loss of vacancies.

It is thought that the observed changes in precipitation kinetics for the H+WQ Al-Cu-Si alloy can be explained as follows. On quenching the Al-Cu-Si alloy the misfit between the Al-rich matrix and the silicon particles is partly accommodated plastically (misfit dislocations) and partly elastically. Then, on average, the matrix is left in a condition of hydrostatic tensile stress (17). As Al-Cu GP-zone formation is related with a decrease in average atomic volume, these hydrostatic tensile stresses contribute an extra elastic strain energy to the GP-zone formation energy. Zahra et al. (18) showed that, in absence of a hydrostatic stress, the contribution of elastic strain energy to the total formation energy of zones is already significant. Thus, the presence of hydrostatic stresses in the matrix may effectively hinder the formation of GP zones in the Al-Cu-Si alloy studied. Then, in absence of GP-zone formation excess vacancies may remain available and allow an enhancement the precipitation of copper and silicon atoms, thus lowering the apparent activation energy for precipitation (see preceding paragraph).

In the above explanation it is assumed that the copper and silicon atoms in supersaturated solid solution behave totally independent (see second paragraph of this Section). Further it should be noted that the increased number of nucleation sites as offered by the high dislocation density in the quenched Al-Cu-Si alloy cannot account for the low value of the apparent activation energy, as the latter only reflects a diffusion controlled process.

Nevertheless, the increased number of nucleation sites in the Al-Cu-Si alloy (due to the presence of misfit dislocations and a small matrix grain size) as compared to the Al-Cu alloy explains why during slow cooling the precipitation in the Al-Cu-Si alloy can fully proceed, whereas the precipitation in the Al-Cu alloy proceeds only to a small extent. Thus, the DSC curve for the H+SC run of the Al-Cu-Si alloy does not reveal any precipitation, while the H+SC curve for the Al-Cu alloy shows a marked precipitation effect. Due to a combined lack of vacancies and nucleation sites (both resulting from the slow cooling before this run) this precipitation effect is situated at the highest temperature range observed (cf. Figs. 1, 2 and 3).
5. Conclusions

1. Hydrostatic tensile stresses in particle-reinforced Al-Cu based MMCs may effectively hinder GP-zone formation.

2. In quenched particle-reinforced Al-MMCs the precipitation of intermediate and equilibrium phases is enhanced by misfit dislocations as well as by retained excess vacancies.

References

CHAPTER III

COOLING AND HEATING RATE DEPENDENCE OF PRECIPITATION IN AN AL-CU ALLOY

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Abstract

Differential scanning calorimetry and X-ray diffraction was used to study the cooling and heating rate dependence of precipitation in an Al-1.66 at% Cu alloy. After homogenizing, cooling at a rate of 22 K/min (SC22) is sufficient to retain all copper in solid solution. GP-zone formation during subsequent heat treatment is hindered. This is ascribed to an insufficient amount of (excess) vacancies. After a water quench (WQ) a large amount of GP zones is formed during a subsequent one-hour storage at room temperature. The heat content of the GP-zone dissolution effect can quantitatively be described in terms of the heat of precipitation of GP I zones and the solid solubilities as derived from the GP I-zone solvus. The heat content of the combined $\theta'/\theta$-phase precipitation effect appeared to be proportional to the amount of copper atoms precipitated, yielding an average value for the heat of copper precipitation of 36 kJ/mole copper. The activation energy for $\theta'$-phase formation is 0.75 eV for SC22 specimens and 1.10±0.10 eV for WQ specimens. The differences in reported activation energies for $\theta'$-phase formation are discussed in terms of mobility of dissolved atoms (related to the vacancy concentration), interfacial energy and direction of growth (normal or perpendicular to the $\theta'$-phase plate).
1 Introduction

Recently it was shown that the heat of precipitation in a solid-quenched Al-Cu alloy reinforced with silicon particles could quantitatively be described in terms of the heats of precipitation of both alloying elements and of solid solubilities of the constituting binary alloys (1). Further it appeared that copper precipitation depends on the heating rate: at low heating rates (≤ 20 K/min) copper precipitated mainly as the metastable θ' phase, whereas at high heating rates (≥ 40 K/min) copper precipitated mainly as the equilibrium θ phase.

Although the precipitation from a supersaturated Al-rich phase in binary Al-Cu alloys during non-isothermal ageing has often been studied (2, 3, 4), the relation between precipitation effects and the heating rates applied has, to our knowledge, not been investigated until now. The full precipitation sequence in quenched Al-Cu alloys is usually given as follows:

supersaturated solid solution → GP I → GP II → θ' → θ  \[ (1) \]

where GP I/II stands for Guinier-Preston zones*, θ' is a transition phase having a structure which is a tetragonal distortion of the CaF₂ structure and which has a composition Al₂Cu and θ is the equilibrium phase having a body centred tetragonal structure with the same chemical composition as θ' (5). According to Nakamura et al. (6) the so-called X phase would occur between GP II and θ'. This phase should be responsible for the peak hardness during ageing of quenched Al-Cu alloys. The X phase has, however, not been identified by X-ray or TEM analysis.

* Until recent publications, discussion about the nature of GP I and GP II zones has persisted (7). GP II zones are considered to be a slightly modified (multi-layered) form of (predominantly mono-layered) GP I zones, or to be a different phase (then the indication θ'' phase instead of GP II zones is usually preferred). In this paper the indication GP II is used. In any case, GP II is subsequent to GP I.

In this paper the results of a study on the influence of the heating rate on the precipitation effects in a conventionally cast Al-Cu alloy are presented. The quench sensitivity of the precipitation reactions was investigated by variation of the cooling conditions after the homogenizing treatment: water-quenching and cooling at a rate just fast enough to keep copper in solid solution. As copper precipitation from an Al-rich matrix is associated with enthalpy changes large enough to allow differential scanning calorimetry (DSC), this technique was applied. In addition, X-ray diffraction was used for the identification of DSC effects and to obtain, via the determination of the Al-rich phase lattice parameter, information about the average copper content of the Al-rich phase.
Experimental procedures

2.1 Specimen Preparation and Heat Treatment

A binary Al-1.66 at%Cu alloy was produced by conventional casting. After casting, the Al-Cu alloy was homogenized at 773±5 K for 48 h. Chemical analysis showed the following composition of the alloy: 1.66 at% Cu, 0.01 at% Si, 0.012 at%Fe, 0.001 at% Ti, 0.001 at% Zn, 0.005 at% Mg, balance aluminium.

After homogenizing, cylindrical specimens (height about 0.5 mm, diameter about 6 mm) were machined from the ingots. These specimens were subjected to a solution heat treatment, consisting of homogenizing at 793±2 K for 10 minutes followed by a quench into water at room temperature. The specimens were stored at room temperature for one hour before further investigation (mostly a DSC experiment). These specimens will be referred to as WQ (water-quenched) specimens. Part of the WQ specimens were reheated to 790±3 K inside the DSC apparatus, kept at this temperature for 2 minutes and subsequently cooled to room temperature inside the DSC apparatus. For one set of specimens the cooling was free and hence determined by the heat conduction from the DSC cell to the surroundings, the cooling of each specimen in this set was identical and nearly exponential (the cooling rate on passing the copper solvus at 760 K was 22 K/min and on passing 550 K it was 6.5 K/min). These specimens will be referred to as the SC22 (slowly cooled at 22 K/min) specimens. For other specimens, the initial cooling rate was set at fixed values: 12, 8, 6, 5, 4, 2, 1 and 0.5 K/min. However, the heat conduction from the DSC cell to the surroundings was in all cases too low to maintain the set cooling rate over the whole temperature range. For each set value, it appeared that from a certain temperature downwards, the cooling was identical to the free cooling of the SC22 specimen. The specimens with a set initial cooling rate will be referred to as the SC12, SC8 etc. specimens.

It appeared that for the SC22 specimens nearly all copper was kept in solid solution (see Section 4.1). In order to study possible GP-zone or X-phase formation, the SC22 specimens were aged at temperatures between 423 and 523 K. Cooling of these specimens took place inside the DSC apparatus. Subsequently, these specimens were investigated by DSC.

Also WQ and SC22 specimens heated at a constant heating rate to the end temperature of the main precipitation peak (see Section 3.1) were prepared. For this, DSC scans at heating rates 0.5, 2, 5, 20 and 40 K/min were interrupted at the end temperatures of the main precipitation peaks. After interruption of the scan, the specimens were immediately (within 10 seconds) removed from the
DSC apparatus and quenched into water at room temperature. These specimens will be indicated as WQ\textsubscript{DSC} and SC\textsubscript{DSC} specimens, followed by the heating rate.

2.2 **Differential Scanning Calorimetry**

The DSC apparatus used was a Dupont type 910. A protective gas atmosphere of pure argon was employed. The calibration and baseline correction methods are described elsewhere (8). For the WQ specimens the following heating rates were applied: 0.5, 2, 5, 20 and 40 K/min, for the SC22 specimens 0.5, 2, 5, 10, 20, 40, 60 and 80 K/min were applied. For the SC specimens cooled at rates lower than 22 K/min, only the heating rate 5 K/min was used. For the SC22 specimens aged at temperatures between 423 and 523 K, DSC runs were performed at 40 K/min. Runs were recorded between 298 and 791 K. Unless stated otherwise, the accuracy of the measurement of peak temperatures is within about ±2 K, the accuracy of the measurement of other characteristic temperatures is within about ±3 K, and the accuracy of the determination of heat contents is within about ±5%.

2.3 **X-ray Diffraction**

To study the composition of the Al-rich phase at the end temperature of the main precipitation peak (see Section 3.1), the lattice parameters of WQ\textsubscript{DSC} and SC\textsubscript{DSC} specimens were determined by X-ray diffraction. These experiments were performed on filings of the DSC specimens by the Debije Scherrer (DbS) method (see for instance Ref. 9). X-ray diffraction started within three hours after quenching of the original DSC specimen. Exposure time was 6 hours. Copper radiation filtered by a Nickel filter was used. The temperature inside the DbS camera at a point close to the specimen was measured and recorded. Temperatures were between 294 and 297K. Temperature variations during single experiments were typically in the order of 0.5 K. Film type and film development procedures were identical for all experiments. The Al-rich phase lattice parameter was determined by using the so-called Nelson-Riley extrapolation (see Ref. 9). The lattice parameters were corrected for the average temperature during the measurement, adopting the linear expansion coefficient of pure aluminium (23.5 \times 10^{-6}, see Ref. 10). All lattice parameters presented in this work are corrected to 298 K.

To investigate the influence of filing on the Al-rich phase lattice parameter the following experiment was performed. Firstly, an SC22 specimen was heated to 673 K, kept isothermal for 2 min and then cooled very slowly (at rates between 0.1 and 0.5 K/min and interrupted for isothermal ageing at 473 and
423 K for 10 hours) down to room temperature. From filings of this specimen, the Al-rich phase lattice parameter was determined, yielding 0.40488±0.00002 nm. Then, these filings were subjected to exactly the same heat treatment as described above, and again the lattice parameter was determined, now giving 0.40490±0.00002 nm. In both cases only the Al-rich phase and the \( \theta \) phase was detected.

For phase identification, an additional X-ray diffraction experiment was performed on a WQ specimen using a high-temperature Guinier camera. The diffraction pattern of Cu K\( \alpha_1 \) radiation transmitted through a thin (~ 70 \( \mu \)m) specimen was recorded on a water-cooled film during heating the specimen from 293 to 773 K at 0.5 K/min.

2.4 Optical Microscopy

Jena Neophot optical microscopes were used to characterize the microstructures of WQ_{DSC} and SC_{DSC} specimens. Polished specimens were etched with a 1:1 mixture of Keller and Wilcox reagent and 5% Nital.
3 Results

3.1 Differential Scanning Calorimetry

Fig. 1 shows a DSC run of a WQ specimen taken at 5 K/min. Five effects (two exothermic and three endothermic) are discerned. The effects are numbered I to V. In line with results from literature (2, 3, 4, 11, 12), the effects observed in the DSC curves of the WQ run of the Al-Cu alloy are attributed to the following reactions (see also Sections 3.2 and 4.2):

I. GP-zone formation,
II. GP-zone dissolution,
III. \(\theta'/\theta\)-phase precipitation (main precipitation effect),
IV. \(\theta\)-phase dissolution,
V. \(\theta\)-phase dissolution.

![DSC Run of a WQ Specimen](image)

Fig. 1: DSC run of a WQ specimen.

In Fig. 2, a DSC curve of an SC22 specimen taken at 5 K/min is shown. The effects are interpreted analogously to the effects in the WQ specimen (Fig. 1) and are numbered accordingly. Comparison of Fig. 2 with Fig. 1 yields the following observations:
- the GP-zone formation effect (effect I in Fig. 1) is absent in the SC22 specimen
- the GP-zone dissolution effect (effect II in Fig. 1) is very small for the SC22 specimen
- the magnitude of the main precipitation effect (effect III) is smaller for the SC22 specimen than for the WQ specimen
- the end temperature of the main precipitation effect is higher for the SC22 specimen than for the WQ specimen
- the θ'-dissolution effect (effect IV in Fig. 1) is less pronounced for the SC22 specimen than for the WQ specimen.

![DSC run of a SC22 specimen](image)

Fig. 2:  DSC run of a SC22 specimen.

Table I gathers the experimental data obtained for effects I and II (absent for the SC specimens). All characteristic temperatures increase with increasing heating rate, whereas the heat contents generally decrease with increasing heating rate. From Fig. 1, it is observed that effect II seems to consist of two subeffects. For higher heating rates ($\geq 20$ K/min), two endothermic peaks are discerned in the temperature range of effect II.

In Table II, the experimental data obtained for effect III for the WQ and SC22 specimens are gathered. Clearly, all characteristic temperatures increase with
increasing DSC heating rate, whereas the heat content of effect III decreases with increasing heating rate. Further, it is noted, that for a constant DSC heating rate, the characteristic temperatures for the SC22 specimens are always higher than those for the WQ specimens. For a constant heating rate the heat contents of effect III for the SC22 specimens are generally lower than those for the WQ specimens.

Table I: The end temperature ($T_c$), peak temperature ($T_p$) and heat content of Effect I and the heat content of effect II for WQ specimens as a function of DSC heating rate.

<table>
<thead>
<tr>
<th>Heating rate (K/min)</th>
<th>Effect I</th>
<th></th>
<th>Effect II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_p$ (K)</td>
<td>$T_c$ (K)</td>
<td>heat content (J/mole)</td>
</tr>
<tr>
<td>0.5</td>
<td>*</td>
<td>378±5</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>347</td>
<td>388</td>
<td>*</td>
</tr>
<tr>
<td>5</td>
<td>363</td>
<td>393</td>
<td>17</td>
</tr>
<tr>
<td>20</td>
<td>372</td>
<td>398</td>
<td>18</td>
</tr>
<tr>
<td>40</td>
<td>389</td>
<td>415</td>
<td>17</td>
</tr>
</tbody>
</table>

* Could not be estimated due to low heat flow

The temperature of minimum absolute heat flow between effect IV and effect V in the WQ specimens increases with increasing heating rate from 670 K at 0.5 K/min to 745 K at 40 K/min. The peak temperature of effect V is almost identical for SC and WQ specimens. It appeared to be nearly insensitive to variations in the heating rate, although for high heating rates ($\geq$ 20 K/min) it shifted to slightly higher values.

DSC runs on the very slowly cooled specimens were performed at 5 K/min. The DSC curves obtained did not show any heat effects below 520 K. The DSC curves for the SC5, SC6, SC8 and SC12 specimens strongly resemble the DSC curve for the SC22 specimen (Fig. 2). Fig. 3 shows the DSC curves of the SC4, SC2 and SC1 specimens; for comparison the curve of the SC22 specimen is also shown. It is observed that the heat content of effect III (the main precipitation effect) decreases with decreasing cooling rate. For a cooling rate of 0.5 K/min no precipitation effect is observed during the subsequent DSC experiment at a heating rate of 5 K/min (DSC curve of SC0.5 is not shown). The end temperature of effect III decreases with decreasing cooling rate. For cooling rates $\leq$ 4 K/min, the magnitude of effect V decreases with decreasing cooling rate. For these low cooling rates a new effect, situated in the temperature range 730-790 K, appears.
(see Fig. 3). The magnitude of this new effect, denoted effect VI, increases with decreasing cooling rate.

Fig. 3: DSC curves of SC1, SC2, SC4 and SC22 specimens.

The total heat release during a DSC scan (i.e. the integral of the heat flow from room temperature to end temperature of the scan), is directly related to the amount of copper atoms precipitated during the cooling before the scan. The total heat release during a DSC scan, \( \Delta Q_{\text{tot}} \), was obtained by integration of the DSC curves between 520 and 789 K (before 520 K no heat effect occurs). In Fig. 4, \( \Delta Q_{\text{tot}} \) (which is always endothermic) is given as a function of the cooling rate. The accuracy of these measurements is within \( \pm 30 \) J/mole. It is observed that \( \Delta Q_{\text{tot}} \) increases slightly when the cooling rate is decreased from 20 to 2 K/min. When the cooling rate is decreased further, \( \Delta Q_{\text{tot}} \) increases rapidly to about 500 J/mole. This is higher than the values obtained for the heat release during the main precipitation effect (see Table II).

SC22 specimens were isothermally aged at 423, 443, 463, 483, 503 and 523 K for fixed times. The DSC runs of SC22 specimens aged at 423 K for more than
480 min show an endothermic effect in the temperature range 460 to 570 K (see Fig. 5). After 2000 min ageing the heat content of this effect equals 220±10 J/mole. DSC runs of SC22 specimens aged for up to 2000 min at temperatures between 443 and 523 K do not show any heat effect below 580 K. Above 580 K either the main precipitation effect (effect III), or the endothermic θ'-dissolution effect (effect IV) was observed.

<table>
<thead>
<tr>
<th>Heating rate (K/min)</th>
<th>peak temperature (K)</th>
<th>end temperature (K)</th>
<th>heat content (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WQ</td>
<td>SC22</td>
<td>WQ</td>
</tr>
<tr>
<td>0.5</td>
<td>546</td>
<td>563</td>
<td>578</td>
</tr>
<tr>
<td>2</td>
<td>586</td>
<td>601</td>
<td>618</td>
</tr>
<tr>
<td>5</td>
<td>603</td>
<td>629</td>
<td>638</td>
</tr>
<tr>
<td>10</td>
<td>648</td>
<td></td>
<td>685</td>
</tr>
<tr>
<td>20</td>
<td>638</td>
<td>660</td>
<td>673</td>
</tr>
<tr>
<td>40</td>
<td>658</td>
<td>670</td>
<td>693</td>
</tr>
<tr>
<td>60</td>
<td>*</td>
<td></td>
<td>713±5</td>
</tr>
<tr>
<td>80</td>
<td>*</td>
<td></td>
<td>718±5</td>
</tr>
</tbody>
</table>

* Could not be estimated due to low heat flow

### 3.2 X-ray diffraction

The results of the Al-rich phase lattice parameter determinations by are gathered in Table III. The DSC experiments on filings of specimens quenched from the end temperature of effect III (see Section 2.3) enabled the identification of phases present at this temperature. The phases detected are also given in Table III. As a minimum amount of a diffracting phase should be present in order to surpass the detection threshold, the absence of diffracted lines from a certain phase does not imply the absence of that phase.

From Table III it is observed that all measured Al-rich phase lattice parameters are lower than the lattice parameter for pure aluminium (0.40496 nm, see Ref. 13). Both for the WQ and the SC specimens, the Al-rich phase lattice parameter increases with decreasing DSC heating rate.

During the initial part of the heating in the high-temperature Guinier camera experiment on a WQ specimen only the Al-rich phase is detected. Lines
related to the metastable $\theta'$ phase appear at 400 K and disappear at 640 K. Lines related with the $\theta$ phase appear at 570 K and disappear at 750 K (the precision of these temperature determinations is within about $\pm$ 15 K).

![Diagram](image)

**Fig. 4:** Total heat consumed during the DSC run of SC specimens, $\Delta Q_{\text{tot}}$, as a function of the cooling rate.

### 3.3 Optical Microscopy

Figs. 6, 7 and 8 show optical micrographs of the $\text{SC}_{\text{DSC}2}$, $\text{SC}_{\text{DSC}20}$ and $\text{WQ}_{\text{DSC}5}$ specimens, respectively. All micrographs show the presence of $\theta'$-phase and $\theta$-phase precipitates. The $\theta'$-phase precipitates can be distinguished by their characteristic plate-like structure. It is apparent that the amount of precipitates is smallest in the $\text{SC}_{\text{DSC}20}$ specimen. Further it is observed, that the length of the $\theta'$-phase plates is about 5 $\mu$m in the $\text{SC}_{\text{DSC}2}$ and about 0.5 $\mu$m in the $\text{WQ}_{\text{DSC}5}$ specimen. The grain size of the Al-rich phase in the $\text{SC}_{\text{DSC}2}$, $\text{SC}_{\text{DSC}20}$ and $\text{WQ}_{\text{DSC}5}$ specimens is about 400 $\mu$m.
Table III: The results of the X-ray diffraction analysis.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>DSC end temperature (K)</th>
<th>phases detected</th>
<th>Al lattice parameter (nm) ±0.00002</th>
<th>( x_{Cu} ) (at%) ±0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC22</td>
<td>600</td>
<td>( \alpha )</td>
<td>0.40421</td>
<td>1.57</td>
</tr>
<tr>
<td>SC2S0.5</td>
<td>638</td>
<td>( \alpha, \theta', \theta )</td>
<td>0.40478</td>
<td>0.38</td>
</tr>
<tr>
<td>SC2S2</td>
<td>668</td>
<td>( \alpha, \theta', \theta )</td>
<td>0.40464</td>
<td>0.67</td>
</tr>
<tr>
<td>SC2S5</td>
<td>698</td>
<td>( \alpha, \theta', \theta )</td>
<td>0.40447</td>
<td>1.03</td>
</tr>
<tr>
<td>SC2S20</td>
<td>707</td>
<td>( \alpha )</td>
<td>0.40430</td>
<td>1.38</td>
</tr>
<tr>
<td>SC2S40</td>
<td>707</td>
<td>( \alpha )</td>
<td>0.40422</td>
<td>1.55</td>
</tr>
<tr>
<td>WQ</td>
<td>618</td>
<td>( \alpha )</td>
<td>0.40417</td>
<td>1.68</td>
</tr>
<tr>
<td>WQS2</td>
<td>638</td>
<td>( \alpha, \theta' )</td>
<td>0.40467</td>
<td>0.61</td>
</tr>
<tr>
<td>WQS5</td>
<td>638</td>
<td>( \alpha, \theta' )</td>
<td>0.40455</td>
<td>0.86</td>
</tr>
<tr>
<td>WQS20</td>
<td>673</td>
<td>( \alpha, \theta', \theta )</td>
<td>0.40436</td>
<td>1.26</td>
</tr>
<tr>
<td>WQS40</td>
<td>693</td>
<td>( \alpha, \theta )</td>
<td>0.40426</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Fig. 6: Optical micrograph of a SC22 specimen heated at 2 K/min to 638 K.
Fig. 7: Optical micrograph of a SC22 specimen heated at 20 K/min to 698 K.

Fig. 8: Optical micrograph of a WQ specimen heated at 5 K/min to 638 K.
4.1 The fraction of dissolved Cu atoms of the Al-rich phase

The Al-rich phase lattice parameter of binary Al-Cu alloys shows a linear dependence on the copper fraction, $x_{\text{Cu}}$, of that phase (5). Using data from Refs. 14, 15 and 16 the following relation between the Al-rich phase lattice parameter (at 298 K) and $x_{\text{Cu}}$ is obtained:

$$a_{\text{Al}} = a^0_{\text{Al}} - x_{\text{Cu}} \times 0.0477 \text{ nm}$$  \hspace{1cm} (2)

where $a^0_{\text{Al}}$ is the lattice parameter of pure aluminium. This equation is valid in case the average macrostress in a specimen is zero. Although filing causes broadening of diffracted lines, lattice parameters obtained from filings reflect in good approximation the "unstrained" lattice parameter (17).

![Diagram](image)

Fig. 5: DSC run of a SC22 specimen aged for 2000 min at 423 K.

The close correspondence between the Al-rich phase lattice parameter of the overaged and subsequently filed specimen and the Al-rich phase lattice
parameter of the filed and subsequently overaged specimen (see Section 2.3) further evidences this. Thus, the Al-rich phase lattice parameters obtained from filings can be safely used in Eq. 2 to obtain values of $x_{\text{Cu}}$, which are gathered in Table III.

### 4.2 Identification of DSC effects.

The identification of the heat effects occurring in DSC runs of WQ and SC22 specimens (see Section 3.1) was discussed previously (8). For most of the DbS experiments on $\text{WQ}_{\text{DSC}}$ and $\text{SC}_{\text{DSC}}$ specimens as well as for the high-temperature Guinier experiment on a WQ specimen heated at 0.5 K/min lines due to the $\theta'$ and $\theta$ phase have been observed at the end temperature of effect III (see Section 3.2). These observations confirm that effect III is caused by the formation of $\theta'$ and $\theta$ phases. For the SC22 specimen heated at 40 K/min, a significant heat evolution (16±1 J/mole, see Table II) during the main precipitation effect is observed. However, the DbS X-ray diffraction on the $\text{SC}_{\text{DSC}40}$ specimen detected only the Al-rich phase. Clearly DSC can detect smaller amounts of precipitating $\theta'/\theta$ phase than DbS experiments can. Hence, although for some WQ$_{\text{DSC}}$ specimens no $\theta'$ or $\theta$ phase is detected (Table III), the presence of these phases in these specimens can not be ruled out. This is also indicated by the amount of copper dissolved in the Al-rich phase after completed precipitation ($x_{\text{Cu}}$ in Table III), which is lower than the Cu content of the alloy.

Except for effect VI, the heat effects observed in the DSC runs of the SC specimens cooled at rates lower than 22 K/min are attributed to the same reactions as the ones observed in the DSC run of the SC22 specimen. Effect VI is discussed in Section 4.3.

The temperature range of the endothermic effect between 460 and 570 K in DSC runs of the SC22 specimen aged for 2000 min at 423 K (see Fig. 5) corresponds well with the endothermic GP II-zone dissolution effect for a, GP II-zone containing, Al-1.7at%Cu specimen (18). The temperature range for the dissolution of GP I zones is about 50 K lower than the temperature range for GP II-zone dissolution (2, 18). This indicates that the observed endothermic effect is caused by the dissolution of GP II zones. In addition it is noted that in water-quenched Al-1.7at%Cu specimens aged for 2000 min at 423 K the formation of GP II zones and the dissolution of GP I zones are both close to being completed, while the amount of $\theta'$ phase formed is still negligible (19).

According to the metastable solvs of the X-phase (see Ref. 6), X-phase dissolution should occur in a temperature range about 50 K higher than GP II-
zone dissolution. The endothermic effect between 460 and 570 K in the SC22 specimen aged for 2000 min at 423 K is attributed to GP-II zone dissolution. SC22 specimens aged for up to 2000 min at temperatures between 443 and 523 did not show any dissolution effects below 580 K. Thus it is concluded that no X-phase formation had occurred in the isothermally aged SC22 specimens. Also during the X-ray diffraction experiments no Cu-containing phases except for the θ' and θ phases were observed. So the occurrence of the X phase, which was reported by Nakamura et al. (6), cannot be confirmed.

4.3 The influence of cooling rate on copper supersaturation and on copper precipitation/dissolution

Since precipitation during cooling involves θ-phase formation (see for instance TTT diagrams of quenched Al-Cu in Ref. 2), the amount of copper precipitated during cooling, Δx, can be estimated from (see also next Section):

$$\Delta Q_{\text{tot}} = \Delta x \Delta H^\theta$$  \hspace{1cm} (3)

in which $\Delta H^\theta$ is the heat of precipitation of θ phase, 44 kJ per mole copper in the θ phase. The amount of copper atoms precipitated during cooling at a rate of 22 K/min can be estimated from either $\Delta Q_{\text{tot}}$ (using Eq. 3) or from the Al-rich phase lattice parameter (using Eq. 2). The two determinations agree within experimental error, and it follows that about 3% of all copper atoms had precipitated. So all or nearly all copper remains in solid solution. At cooling rates below 22 K/min, the amount of copper atoms remaining in solid solution decreases with decreasing cooling rate. At cooling rates below 2 K/min the amount of copper atoms precipitated during cooling increases strongly. With Eq. 3 follows that during cooling at 0.5 K/min, about 70% of the copper atoms precipitate.

The endothermic effect VI is present after cooling at very low rates, for which the amount of θ phase strongly increases (see above). Thus the effect VI is attributed to dissolution of θ-phase precipitates formed during the slow cooling prior to the DSC-analysis. The θ phase formed during slow cooling (at low undercooling) will be coarser than the θ phase formed in effect III during heating (at large undercooling). Since, due to longer diffusion paths, dissolution of coarse precipitates takes more time, dissolution of the coarse θ-phase precipitates formed during cooling will proceed beyond effect V (dissolution of θ-phase precipitates formed during effect III). This is indeed observed (see Fig. 3).

For cooling rates ≤ 22 K/min, nearly no traces of GP-zone formation or dissolution are observed in the subsequent DSC runs. This is explained as follows. Slow cooling from the homogenizing temperature results in a
reduction of the excess vacancy concentration. Since vacancies are needed for a quick start of GP-zone formation, GP-zone formation during subsequent heat treatment is retarded. Especially for the very low cooling rates (≤ 1 K/min) also the reduced supersaturation due to θ-phase precipitation during cooling might prevent GP-zone formation.

4.4 Heat contents of precipitation/dissolution effects

4.4.1 Introduction

The heat produced during the precipitation of a certain phase can quantitatively be described in terms of the (metastable) solid solubility after precipitation and the heat of precipitation of the phase involved (1). For this description it is assumed that the end of precipitation is reached when the driving force, the difference between the average amount of atoms dissolved in the Al-rich phase and the (metastable-) solubility, becomes zero. The total heat of precipitation per mole alloy, ΔQ, is then given by (see Ref. 1):

$$\Delta Q = \Delta H \frac{x_{Cu}^0 - x_{Cu}^*}{1 - 3x_{Cu}^*}$$  \hspace{1cm} (4)

in which ΔH is the heat of precipitation per mole copper, $x_{Cu}^0$ is the atomic fraction of copper initially dissolved in the Al-rich phase (in our case the gross copper content), $x_{Cu}^*$ is the (metastable-) solid solubility at the end temperature of the precipitation effect. As $x_{Cu}^* < x_{Cu}^0 \leq 1$, the $(1-3x_{Cu}^*)$ term can be neglected.

Values of the heats of precipitation of GP I zones, GP II zones, θ' phase and θ phase can be obtained from the slope of the straight line through the data points of the plot of the logarithm of the (metastable-) solid solubility versus the reciprocal temperature (1, 20). Table IV gathers values for the heat of precipitation obtained from literature.

For GP zones, the interfacial energy and the energy related to elastic strains around the zones can have a significant influence on the total energy of the formation of the zones (21). Since both the creation of strains and interfaces require an energy input to the specimen, both strain and interfacial energy lower the total amount of energy associated with the formation of zones. The importance of these contributions is determined by the average size of the zones: the total formation energy of small zones contains relatively large strain and interfacial energy contributions. For GP zones formed at room temperature (the average diameter of these zones is about 3 nm, see Ref. 21) the total energy of the zones and elastically deformed matrix around them, is about 13 kJ per mole copper in the zones (21).
Table IV: Heats of precipitation of GP zones, stable and metastable phases in Al-Cu alloys.

<table>
<thead>
<tr>
<th>Phase/Zone</th>
<th>( \Delta H ) (kJ/mole)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP I</td>
<td>22±3</td>
<td>6, 21</td>
</tr>
<tr>
<td>GP II</td>
<td>31±5</td>
<td>6</td>
</tr>
<tr>
<td>( \theta' )</td>
<td>34±4</td>
<td>1</td>
</tr>
<tr>
<td>( \theta )</td>
<td>44±1</td>
<td>1, 6</td>
</tr>
</tbody>
</table>

From the above follows that after formation of GP zones during a DSC run has been completed, at least two reactions can occur on continued heating: GP-zone dissolution and GP-zone coarsening, resulting in endothermic and exothermic effects, respectively. Further it is expected that coarser GP-zones dissolve at higher temperatures and produce an increased heat effect as compared to the finer zones. Thus, effect II in DSC runs on WQ specimens is dominated by dissolution of GP zones but it also comprises GP-zone coarsening. This explains the complicated, heating rate dependent shape of effect II (see also Ref. 21).

4.4.2 Heat content of effect I and II.

For the WQ specimens, the heat evolution during the DSC run caused by the formation of GP zones (about 17 J per mole alloy, see Table I) is one order of magnitude lower than the heat of dissolution of the zones (about 100 to 190 J per mole alloy). This indicates that about 90% of the GP zones are formed during the one-hour storage at room temperature between quenching and the start of the DSC run. So, it is justified to approximate the heat of formation of the zones by the heat of GP-zone formation at room temperature: 13 kJ per mole copper in the zones (see previous Section). Since the heat evolution during the room temperature storage was not measured, it is not possible to obtain the total heat evolved during the formation of the zones. However, since reversion of GP zones in Al-Cu is complete (21), the heat dissipation during the GP-zone dissolution effect (heat effect II) equals the total heat evolved during the formation of the zones. It is now possible to apply Eq. 4 to the heat dissipation during the dissolution of GP zones. For the solvus of GP I zones the formula given by Nakamura et al. (6) is used. The results of the calculations are gathered in Table V. A good agreement between calculated and measured values is observed.
The endothermic heat effect in the SC22 specimen aged for 2000 min at 423 K (see Fig. 5) is attributed to the dissolution of GP II-zones (see Section 4.2). Since GP II zones form by coarsening of previously formed GP I zones (see Ref. 22), the amount of copper atoms in GP II zones is determined by the GP I solvus. In applying Eq. 4, we must thus take \( x_{\text{Cu}} \) equal to the solvus of GP I zones at 423 K (about 0.91 at%). This leads to a value of 230±40 J/mole for the dissolution of the GP II zones, which corresponds well with the measured value (220±10 J/mole).

### Table V:
Comparison of the measured and theoretical heat content \( \Delta Q_{\text{meas}} \) and \( \Delta Q_{\text{theor}} \) of the GP-zone dissolution effect (effect II) as observed in the DSC runs of the WQ Al-Cu alloy as a function of DSC heating rate. Also the copper solubility at the end temperature of the GP-Zone formation effect \( (x_{\text{Cu}}) \) as obtained from the GP I-zone solvus is given.

<table>
<thead>
<tr>
<th>Heating rate (K/min)</th>
<th>( x_{\text{Cu}} ) at%</th>
<th>( \Delta Q_{\text{theor}} ) (J/mole)</th>
<th>( \Delta Q_{\text{meas}} ) (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.43</td>
<td>160</td>
<td>190±40</td>
</tr>
<tr>
<td>2</td>
<td>0.51</td>
<td>150</td>
<td>140±30</td>
</tr>
<tr>
<td>5</td>
<td>0.56</td>
<td>140</td>
<td>130±20</td>
</tr>
<tr>
<td>20</td>
<td>0.61</td>
<td>140</td>
<td>130±15</td>
</tr>
<tr>
<td>40</td>
<td>0.81</td>
<td>110</td>
<td>100±10</td>
</tr>
</tbody>
</table>

### 4.4.3 Heat content of effect III

On the basis of the same assumptions as given in Section 4.1.1, the heat content of effect III can be calculated. In this case two possible modes of precipitation should be considered, and two values for the heat evolution during precipitation are obtained: one for \( \theta' \)-phase precipitation \( \Delta Q^{\theta'} \) and one for \( \theta \)-phase precipitation \( \Delta Q^{\theta} \). The respective values of \( x_{\text{Cu}} \) are derived from the \( \theta' \) and \( \theta \)-phase solvus lines as given by Murray (5). From Eq. 4 follows that the end temperature can be regarded as the determining variable for the heat content of effect III. Hence, Fig. 9 gives the theoretical estimates for \( \Delta Q^{\theta} \) and \( \Delta Q^{\theta'} \), as well as the experimental values for the heat content of effect III, \( \Delta Q \), as a function of the experimental end temperature of effect III. The values of \( \Delta Q \) are always intermediate between \( \Delta Q^{\theta} \) and \( \Delta Q^{\theta'} \). This again confirms that effect III is caused by the combined \( \theta'/\theta \)-phase precipitation. All data points in Fig. 9 are well represented by one single line, i.e. the end temperature of effect III is, in
this case, solely related with the experimentally observed heat content of effect III.

In Fig. 10 the average composition of the matrix at the end temperature of the main precipitation effect is given as a function of that end temperature. Again, as was also observed for the heat evolved during the main precipitation effect, there is virtually no difference between the average matrix composition after the main precipitation effect for the SC and the WQ specimens at a fixed end temperature of the precipitation effect.

![Graph showing heat evolved during main precipitation effect as a function of end temperature](image)

Fig. 9: The heat evolved during the main precipitation effect as a function of its end temperature. Calculated values (using Eq. 4) for the case of $\theta$ precipitation and for the case of $\theta'$ precipitation and measured values for the main precipitation effect in SC and WQ specimens are given.

From the value of the atomic copper fraction of the Al-rich phase at the end temperature, $x_{Cu}^{\text{Tend}}$, and the atomic copper fraction of the Al-rich phase at the start of the DSC run, $x_{Cu}^{0}$, the amount of copper atoms precipitated, $\Delta x$, can be calculated as $\Delta x = x_{Cu}^{0} - x_{Cu}^{\text{Tend}}$. In Fig. 11, the experimentally observed heat content
both for WQ and SC22 specimens, are well represented by a single straight line through the origin, the slope of which gives the average heat of precipitation of the copper atoms which are present in a precipitate at the end of effect III, $\Delta H$: $\Delta H = 36 \pm 1$ kJ per mole copper.

This value is intermediate between the heats of precipitation for $\theta'$ and $\theta$ phase (34 and 44 kJ/mole, respectively), and thus in agreement with the attribution of effect III to $\theta'$ and $\theta$ phase precipitation.

![Graph showing precipitate composition at various temperatures.](image)

**Fig. 10:** Average matrix composition at the end temperature of the main precipitation effect as a function of the end temperature of the main precipitation effect. Solid solubilities for $\theta$ and for $\theta'$ phases (obtained from Ref. 5) and measured values for the main precipitation peak in SC and WQ specimens are given.

### 4.5 Activation energy analysis

The activation energy of a reaction occurring during heating at a constant heating rate can in some cases be obtained by a Kissinger analysis or variants thereof (23). Such an analysis can only be performed in cases where heat effects are caused by a single precipitation process. For non-isothermal annealing
with a constant heating rate, $\dot{\Phi}$, (i.e. the case of DSC experiments) it can be shown, that in good approximation the following relation between the temperature for a fixed stage of transformation, $T_f$, and the heating rate, $\dot{\Phi}$, holds (23):

$$\ln \frac{T_f^2}{\dot{\Phi}} = \frac{E_A}{k_B T_f} + \ln \beta_f$$

where $\beta_f$ is the state variable fully determining that fixed state of transformation, $E_A$ is the activation energy of the process and $k_B$ is Boltzmann's constant. Thus, the activation energy can be obtained from the slope of straight lines through the data points of the plots of $\ln(T_f^2/\dot{\Phi})$ versus $1/T_f$.

Fig. 11: The heat evolved during the main precipitation effect as a function of the amount of copper precipitated.

It was decided to obtain effective values for the activation energy only for the beginning stages of effect III, where it can safely be assumed that only $\theta'$-phase formation is taking place (see results of the X-ray diffraction experiments, Section 3.2). It follows from Eq. 3 that a fixed amount of heat developed, $Q_f$, corresponds to a fixed amount of precipitated $\theta'$ phase. Two transformation
stages were chosen: for $Q_f = 28$ J/mole and $Q_f = 55$ J/mole. In order to assure that the temperature of the fixed stage of transformation, $T_f$, was always lower than the peak temperature of effect III, only values of $T_f$ equal to or below 656 K were considered. The lowest temperature included in the analysis was 526 K. The values thus obtained do not depend significantly on the stage chosen. The average values for the apparent activation energy of $\theta'$-phase formation are:

for the WQ specimen: 1.10±0.10 eV,
for the SC22 specimen: 0.75±0.15 eV.

In Table VI activation energies for $\theta'$-phase formation obtained from literature are gathered. Most of the data concern the overall kinetics of $\theta'$-phase formation. Only Aaronson and Laird (24) observed differences in the kinetics of thickening and lengthening of $\theta'$-phase plates in a solid-quenched and aged Al-1.7at%Cu alloy. For the thickening, the rate dependent step appeared to be ledge formation of the broad surface of the $\theta'$-phase plates, whereas for the lengthening, the rate dependent step was found to be pipe diffusion. The thickening was described by a linear time-dependency, whereas the lengthening was described by a square-root time-dependency. The activation energy for thickening was found to be 1.20±0.13 eV, and the activation energy for lengthening was found to be 1.02±0.02 eV. Chen and Doherty (25) also studied the rate of thickening. They proposed a square-root time-dependency of the thickening during isothermal ageing. Combining their data (as presented in Figs. 1 and 2a of Ref. 25) and the data by Aaronson and Laird, and using this square-root time-dependency, results in an activation energy for thickening of 1.25±0.09 eV.

Table VI: Activation energies for $\theta'$ phase formation. (WQ=water quench, IWQ=ice-water quench, I=isothermal, NI=non-isothermal)

<table>
<thead>
<tr>
<th>homogenizing temperature (K)</th>
<th>cooling</th>
<th>heat treatment</th>
<th>Cu content (at%)</th>
<th>$E_A$ (eV)</th>
<th>kinetics studied</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>798</td>
<td>WQ*</td>
<td>I</td>
<td>473-548</td>
<td>1.7</td>
<td>1.1</td>
<td>overall</td>
</tr>
<tr>
<td>821</td>
<td>WQ</td>
<td>I</td>
<td>473-573</td>
<td>1.7</td>
<td>1.02</td>
<td>lengthening</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.20</td>
<td></td>
<td></td>
<td>thickening</td>
</tr>
<tr>
<td>813</td>
<td>IWQ</td>
<td>I</td>
<td>543-683</td>
<td>1.3</td>
<td>0.89</td>
<td>overall</td>
</tr>
<tr>
<td>793</td>
<td>WQ</td>
<td>NI</td>
<td>526-644</td>
<td>1.7</td>
<td>1.10</td>
<td>overall</td>
</tr>
<tr>
<td>790</td>
<td>SC22</td>
<td>NI</td>
<td>527-656</td>
<td>1.7</td>
<td>0.75</td>
<td>overall</td>
</tr>
</tbody>
</table>

* followed by a reversion treatment
The activation energy for $\theta'$-phase precipitation in the SC22 specimen is significantly lower than activation energies reported in the quoted studies (see Table VI). It is also much lower than the activation energy for $\theta'$-phase formation in the WQ specimens. This can be accounted for by: i. difference in lengthening and thickening kinetics, ii. excess vacancies, and iii. interfacial energy. These will be discussed below.

i. **lengthening and thickening kinetics.** The optical micrographs of precipitate structures (Figs. 6, 7 and 8) show that the $\theta'$-phase plates in the SC$_{DSC}$ specimens are generally much longer than those in the WQ$_{DSC}$ specimens (about 5 and 0.5 $\mu$m, respectively). This strongly suggests that lengthening is relatively more important for $\theta'$-phase formation in SC22 specimens than for $\theta'$-phase formation in WQ specimens. Since the activation energy for lengthening is about 0.2 eV lower than the activation energy for thickening (see above), this can, at least partly, explain the observed difference between the activation energy for $\theta'$-phase precipitation in SC22 specimens and the activation energy for $\theta'$-phase precipitation in the WQ specimens.

ii. **excess vacancies.** All apparent activation energies for the $\theta'$-phase precipitation (see Table VI) are lower than the activation energy for copper diffusion in aluminium and self diffusion in aluminium (both about 1.4 eV, see Ref. 10). As copper diffusion can only proceed via a vacancy mechanism, this indicates that in all these specimens significant amounts of excess vacancies are present.

iii. **interfacial energy.** Interfacial energy acts to increase apparent activation energies obtained from Arrhenius analysis (28). According to Berkenpas (28), this effect increases with decreasing temperature. This can explain why the activation energies obtained from studies at relatively low temperatures (around 530 K) are higher than the ones obtained from studies at higher temperatures (around 600 K) (see Table VI).
Conclusions

For an Al-1.66 at%Cu alloy it is found that:

- During cooling from the homogenizing temperature at rates lower than 22 K/min, significant amounts of copper atoms precipitate. For cooling rates higher than 22 K/min, all copper atoms remain in solid solution.
- After cooling at a rate of 22 K/min, the copper atoms are nearly completely retained in solid solution. The GP-zone formation during subsequent heat treatment is hindered. This is thought to be due to an insufficient amount of (excess) vacancies.
- After a water quench (i.e. in the presence of a large amount of excess vacancies) a large amount of GP zones is formed during a subsequent one-hour storage at room temperature.
- The heat content of the dissolution of GP zones (effect II) can quantitatively be described in terms of the heat of precipitation of GP I zones and the solid solubilities as derived from the GP I-zone solvus.
- The heat content of the combined $\theta'/\theta$-phase precipitation effect appeared to be proportional to the amount of copper atoms precipitated, yielding an average value for the heat of copper precipitation of 36 kJ/mole copper.
- The apparent activation energies for $\theta'$-phase formation is much smaller after slow cooling than after water-quenching. Three factors can influence this apparent activation energy: mobility of dissolved atoms, interfacial energy and direction of growth (normal or perpendicular to the $\theta'$-phase plate). The relative importance of these factors may depend on temperature and cooling rate.

References

CHAPTER IV

A CALORIMETRIC STUDY OF PRECIPITATION IN AN AL-CU ALLOY WITH SILICON PARTICLES

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Abstract

The precipitation of copper and silicon from the Al-rich matrix in an Al-1.3 at%Cu-19.1 at%Si alloy was investigated by Differential Scanning Calorimetry (DSC). Both as-extruded (AE) and solid-quenched (SQ) specimens were studied. The DSC curves of the SQ specimens showed two exothermic effects, A and B. Effect A corresponded to the simultaneous precipitation of silicon and copper, whereas effect B was caused by the transition from the state with the intermediate copper containing phase, \( \theta' \), to the state with the equilibrium copper containing phase, \( \theta \). The heat contents of effect A and B could quantitatively be described in terms of solid solubilities before and after precipitation and the heats of precipitation of the phases involved. From this description it was derived that for heating rates \( \leq 20 \text{ K/min} \) copper precipitated as the \( \theta' \) phase while for heating rates \( \geq 40 \text{ K/min} \) copper precipitated mainly as the \( \theta \) phase. In SQ specimens GP-zone formation occurred during ageing at room temperature with a rate approximately \( 10^4 \) times slower than in the corresponding binary Al-Cu alloy. For the AE specimens it was found that during extrusion precipitation of copper and silicon proceeded to a large extent. However, from DSC experiments and from hardness measurements as a function of ageing time at 453 K, it was deduced that copper precipitation had not finished during extrusion. The hardness increase as observed during ageing directly after extrusion was interpreted to be due to formation of the semi-coherent intermediate \( \theta' \) phase.
1 Introduction

In quenched binary Al-Si alloys precipitation directly results in the formation of the equilibrium phase (1), whereas in quenched Al-Cu alloys precipitation proceeds via intermediate phases according to a temperature dependent sequence. At sufficiently low temperatures, the following scheme applies (2):

supersaturated solid solution $\rightarrow$ GP I/II $\rightarrow$ $\theta'$ $\rightarrow$ $\theta$ 1

where GP I/II stands for Guinier-Preston zones*, $\theta'$ is a transition phase having a structure which is a tetragonal distortion of the CaF$_2$ structure and which has a composition Al$_2$Cu and $\theta$ is the equilibrium phase having a body centred tetragonal structure with the same chemical composition as $\theta'$ (2).

*Until recent publications, discussion about the nature of GP I/II zones has persisted (3). GP II zones are considered to be a slightly modified (multi-layered) form of (predominantly mono-layered) GP I zones, or to be a different phase (then the indication $\theta''$ phase instead of GP II zones is usually preferred). In this paper the indication GP I/II is used. In any case, GP II is subsequent to GP I.

The equilibrium solid solubility of both alloying elements (Si and Cu) decreases with decreasing temperature and the aluminium-rich corner of the Al-Cu-Si system does not show any intermediate ternary phase (4). Hence, on ageing of a quenched Al-Cu-Si alloy, precipitation of the phases as occurring in the constituting binary systems will take place. To our knowledge, no explicit studies on the precipitation phenomena in quenched Al-Cu-Si alloys have been reported until now.

In view of potential applications, the optimisation of the mechanical properties and heat treatments (if required) of metal matrix composites (MMCs) is important. Several studies were devoted to the heat treatment of MMCs (5-10). It was generally found that the ageing response of MMCs was faster than of the corresponding alloy without reinforcement.

Melt-spinning of Al-Cu-Si alloys with amounts of silicon beyond the maximal solid solubility for silicon yields finely grained ribbons with finely, homogeneously dispersed silicon particles (11). After hot extrusion, the silicon size distribution is comparable to the particle size distribution in MMCs (11). As further the Al-Cu-Si alloy combines the presence of a heat treatable Al-matrix with the presence of silicon particles, this alloy can be considered as a model for studying precipitation phenomena in particle-reinforced MMCs. On temperature changes, the presence of silicon particles embedded in an Al-rich
matrix introduces a large volume misfit between matrix and reinforcing particles (also characteristic for most MMCs) because of the large difference in coefficients of thermal expansion of the Al-rich matrix and silicon (23.5 x 10^{-6}K^{-1} and 3 x 10^{-6}K^{-1} respectively, see ref. 12). From a comparative study on heat effects in an Al-Cu alloy with and without silicon particles it appeared that in the Al-Cu alloy with silicon particles GP-zone formation was effectively hindered, whereas the main precipitation of \theta'/\theta phases was enhanced (13). Corresponding changes in precipitation kinetics were observed in several solid-quenched MMCs (6, 7, 8).

As extruded MMCs may be used after a complete heat treatment (solid solution homogenizing, solid quenching plus ageing) as well as directly after extrusion, knowledge of precipitation both after solid quenching and after extrusion is desirable. Therefore it was decided to study the precipitation in a melt-spun Al-Cu-Si alloy both after homogenization and solid quenching and after extrusion. As both silicon and copper precipitation from an Al-rich matrix are associated with enthalpy changes that are large enough to allow differential scanning calorimetry (1, 14), the precipitation study was performed by this technique. In addition hardness measurements were performed.

2 Experimental procedures

Liquid-quenched Al-1.3 at\%Cu-19.1 at\%Si ribbons were produced by melt spinning from 99.998 wt\% Al, 99.99 wt\% Si and 99.9 wt\% Cu. The melt-spinning process was described earlier (15). Typical dimensions of the ribbons obtained were: thickness 50 \mu m and width 3 mm. The ribbons were chopped into flakes with a length ranging from 1 to 5 mm. The flakes were dried up to 24 hours at a temperature of 380 K to eliminate possibly attached moisture. Subsequently the flakes were precompacted to cylindrical billets with a density of about 65% of the maximal density. Prior to extrusion the billets were preheated at the extrusion temperature of 650 K for 20 minutes. Extrusion took place at a reduction ratio of 20:1. A bar with a diameter of 11 mm, of which a large part showed a density of 100%, was produced. After extrusion the bar was cooled in air. For practical reasons the air cooling was completed after ten minutes by a water quench.

From the part of the bar with a density of 100%, thin (thickness about 1 mm) specimens were cut for investigation. Differential Scanning Calorimetry (DSC) was performed in the as-extruded (=AE) condition and in the as-extruded and subsequently aged (AE+A) condition. Ageing took place at 453\pm 2 K. Beside, specimens were homogenized at 793\pm 2 K and subsequently quenched into
water. DSC experiments were conducted one hour after this solid quenching (SQ specimens) or took place as a function of time of natural ageing, i.e. at room temperature (SQ+NA specimens). In Fig. 1 a schematic representation of temperature as a function of time during the production of an AE and/or SQ specimen is given.

![Temperature-Time Diagram](image)

**Fig. 1**: Schematic representation of temperature as a function of time during the production of AE and/or SQ specimens.

The DSC apparatus used was a DuPont type 910. Calibration runs were carried out with pure indium, zinc, tin and lead. Calibration of both the temperature and heat effect scales was obtained using the known (from ref. 16) melting points and heats of melting of these metals. The heat effect scale was calibrated at all heating rates employed. As a reference pure aluminium (99.99%) with a mass close to that of the specimen was used. Both reference and specimen were enclosed in an aluminium pan sealed with an aluminium cover. A protective gas atmosphere of pure argon was employed. For the SQ specimens the following DSC heating rates were applied: 0.5, 2, 5, 20, 40, 80 K/min, for the other specimens only 20 K/min was applied. Runs were recorded between 300 and 791 K. As beyond 740 K only heat effects corresponding to dissolution were observed in the DSC curves, in this precipitation study only the temperature interval 300-740 K will be considered. After the first run, the specimen was maintained at 791 K for 2 minutes, subsequently it was allowed
to cool freely inside the DSC apparatus for 200 min. The cooling of all specimens after the first run was identical and nearly exponential; the cooling rate on passing the copper solvus at 750 K (4) was 22 K/min and on passing 550 K the cooling rate was 6.5 K/min. At the end of the cooling room temperature was reached. Subsequently, a second run, at the same heating rate as the first run, was performed. The DSC curves presented were generally obtained by subtracting the baseline from the first run. The slight differences in heat capacity between the specimen before and after precipitation were ignored. This is justified in view of the fact that all the measured heat capacities of the specimens investigated correspond to the predictions based on the Kopp and Neumann rule (see Ref. 17).

Micro-hardness of the AE+A specimens was measured on longitudinal sections through the axis of the extruded bar using a Leitz-Durimet Vickers hardness tester. For each hardness value at least 10 indentations evenly distributed over a line from the axis to the edge of the bar were made (hardness did not depend on the radial distance to the centre of the bar).
3 Results

Both after extrusion and after solid quenching a homogeneous dispersion of silicon particles was observed both in transverse and longitudinal sections (cf. Figs. 2 and 3). The average silicon particle size after extrusion was about 0.5 to 1 μm (see Fig. 2). After subsequent homogenizing and quenching the silicon particle size had increased to about 1 to 2 μm (see Fig. 3). Typical examples of a first and a second run DSC curve for an SQ specimen are shown in Fig. 4a. From Fig. 4a follows that during the second run no exothermic heat flow occurs. This is interpreted as such that during cooling after the first run precipitation proceeds completely. Thus, the curve obtained by subtracting the second run from the first run reflects only the difference in heat flow during the two runs as caused by the difference in free enthalpy just before the runs (see also Section 2). The DSC curves to be presented in this study are always such rerun-corrected curves.

At sufficiently low heating rates the sequence 1 (see Section 1) for precipitation in quenched Al-Cu alloys is generally revealed by DSC studies*, confirmed by electron microscopy (18), and corroborated by hardness measurements (14). Thus, such a DSC curve displays exothermic effects: GP-zone formation, θ'/θ precipitation and transformation of a state with θ' phase to a state with θ phase, and endothermic effects: GP-zone dissolution, θ'-phase dissolution and θ-phase dissolution (both given in the order from low to high temperature). For solid-quenched Al-Si alloys, the effects in DSC curves cannot be misinterpreted as only one exothermic and one endothermic effect occurs (1). The observed effects beyond 740 K were interpreted before as due to the last stages of copper dissolution and a continuing silicon dissolution (see Ref. 13). Hence the starting temperatures of these effects are independent of the DSC heating rate, as was observed.

*As precipitation reactions are usually controlled by diffusion, an increase of the DSC heating rate results in an increase of the precipitation temperatures. This has a twofold effect: i) the amount of precipitating atoms decreases due to the increased solid solubilities at the increased precipitation temperatures, and ii) the share of phases stable at high temperatures in the total amount of precipitating phases increases. In the case of Al-Cu alloys it can be expected that at sufficiently high heating rates all copper precipitation involves the stable θ phase (see also Sections 4.1.1 and 4.1.2).
Fig. 2: Transverse section of the AE Al-1.3 at%Cu-19.1 at%Si alloy; optical micrograph.

Fig. 3: Longitudinal section of the SQ Al-1.3 at%Cu-19.1 at%Si alloy; optical micrograph.
A typical example of a rerun-corrected curve for an SQ specimen is given in Fig. 4b, in which two effects, A and B, can be discerned. As the free enthalpy of the specimen just before the first run is higher than before the second run (the matrix of the SQ specimen is supersaturated), the effects to be observed in the rerun-corrected curve will generally be exothermic. Based upon the foregoing (see previous paragraph) the exothermic effects A and B in Fig. 4b are interpreted as follows. Effect A is the simultaneous precipitation of silicon and $\theta$ or $\theta'$ phase. Effect B is the transformation from a state with $\theta'$ phase precipitates to a state with $\theta$ phase precipitates. As the DSC heating rate was increased the effects were observed to shift to higher temperatures, implying an increase of the peak and end temperatures of effect A.

![Graph showing DSC curves](image)

Fig. 4a: DSC curves of the first and the second run of the SQ Al-1.3 at%Cu-19.1 at%Si specimen (heating rate is indicated).

All heat contents presented were determined by measuring the area between the rerun-corrected DSC curve and a straight line obtained by connecting points on the DSC curves at 350 and 740 K. At low heating rates, the effects A and B were observed separately, whereas at heating rates of 40 and 80 K/min, overlap of effects A and B occurred. In these cases the respective heat contents were
obtained by a correction based on an extrapolation of the heat flow of effect A at temperatures where effects A and B co-existed. The effect B did not show a well defined peak temperature as effect A did, at the heating rates of 20 and 40 K/min two maxima could be discerned for effect B. In Table I, the peak and end temperatures of effect A and the heat contents of effect A and B are gathered. It is observed that the heat contents of effect A and B decrease with increasing DSC heating rate.

Fig. 4b: Rerun-corrected DSC curve of the SQ Al-1.3 at%Cu-19.1 at%Si specimen (heating rate is indicated).

The heat contents of the effects A and B as observed for the SQ+NA specimens did not depend on the times of natural ageing applied. However, after natural ageing a small endothermic effect was observed just in advance of effect A (see Fig. 5). This endothermic effect is thought to be caused by the dissolution of GP zones (see Section 4.1.3). The heat content of this effect increases with increasing time of natural ageing (see Fig. 6).

The DSC curves taken after extrusion (AE) and after ageing (AE+A) for 4, 28 and 192 h at 453 K did not show pronounced peaks that could be related to some precipitation reaction, i.e. the first DSC run and the rerun showed a strong
resemblance. Nevertheless, the rerun-corrected DSC curves resulting from the subtraction of the rerun scans from the first run scans indicate (see Fig. 7):

i) The heat flows observed above 675 K for the AE and AE+A specimens are equal within the experimental error, indicating corresponding end states;

ii) For the AE specimen, a small exothermic effect is observed between about 350 and 600 K. No such effect is observed for the AE+A specimens; and

iii) For the AE+A specimens, an endothermic effect is observed between about 500 and 650 K. The magnitude of this effect increases with increasing ageing time.

Fig. 5 : First part of the rerun-corrected DSC curve of the SQ Al-1.3 at%Cu-19.1 at%Si specimen aged for 1032 h at room temperature. Note the scale difference with Fig. 4 (heating rate is indicated).

The AE specimens show a marked response to ageing: Fig. 8 shows the hardness as a function of the time of ageing at 453 K. It is observed that 0.5 hour ageing significantly increases the hardness of the AE specimens. Maximum hardness is reached after about 30 h of ageing, followed by overageing (hardness decrease).
Table I: Peak and end temperatures of effect A and heat content of effect A and B in SQ Al-1.3 at%Cu-19.1 at%Si as a function of DSC heating rate.

<table>
<thead>
<tr>
<th>Heating rate (K/min)</th>
<th>Peak Temperature of Effect A (K) ±3 K</th>
<th>End Temperature of Effect A (K) ±5 K</th>
<th>Heat Content of Effect A (J per mole alloy)</th>
<th>B (J per mole alloy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>488</td>
<td>525</td>
<td>770±40</td>
<td>80±30</td>
</tr>
<tr>
<td>2</td>
<td>514</td>
<td>570</td>
<td>730±30</td>
<td>60±20</td>
</tr>
<tr>
<td>5</td>
<td>538</td>
<td>595</td>
<td>710±30</td>
<td>60±20</td>
</tr>
<tr>
<td>20</td>
<td>567</td>
<td>640</td>
<td>610±30</td>
<td>41±11</td>
</tr>
<tr>
<td>40</td>
<td>600</td>
<td>675</td>
<td>640±20</td>
<td>12±5</td>
</tr>
<tr>
<td>80</td>
<td>617</td>
<td>705</td>
<td>580±30</td>
<td>8±5</td>
</tr>
</tbody>
</table>

Fig. 6: Heat content of the endothermic effect preceding effect A as a function of the time of natural ageing.
Fig. 7: Rerun-corrected DSC curves of the AE and the AE+A Al-1.3 at%Cu-19.1 at%Si specimens. For the AE+A specimens the time of ageing at 453 K is indicated. For reasons of clarity the zero points of the curves were separated.
4 Discussion

4.1 Precipitation phenomena observed for SQ specimens

4.1.1 Effect A

It is thought that the effect A can be understood as a result of the precipitation of the phases as occurring in the constituting binary alloys (see Section 3). The solid solubility of silicon in the precipitated $\theta$ (Al$_2$Cu) phase, as well as the solid solubilities of copper and aluminium in the silicon phase are negligible (19). As can be deduced from the aluminium-rich corner of the Al-Cu-Si phase diagram (4), the solid solubility of either alloying element below the homogenizing temperature applied is not influenced by the presence of the other alloying element in solid solution. In view of the low solid solubilities concerned it can be assumed that the heat effect of precipitation/dissolution of one element also is not influenced by the presence of the other element.

![Graph showing hardness vs. time of ageing](image)

Fig. 8: Hardness of the AE and the AE+A Al-1.3 at\%Cu-19.1 at\%Si specimens as a function of time of ageing at 453 K.
Thus it is reasonable to assume that the total heat of precipitation for the ternary alloy is the sum of the heats of precipitation for the constituting binary aluminium alloys. The theoretical calculation of the total heat content of effect A based on these assumptions is outlined in Appendix 1 and 2. To perform the calculation outlined in Appendix 1, values for the mole fractions of copper and silicon dissolved in the Al-rich matrix before and after precipitation, $x_{Cu}^0$, $x_{Si}^0$, $x_{Cu}^*$, and $x_{Si}^*$, respectively, are necessary (see eqs. A12 and A13). The value for $x_{Si}^*$ (1.05x10^{-2}) was taken equal to the mole fraction of silicon dissolved at the homogenizing temperature (4). The value of $x_{Cu}^0$ (1.6x10^{-2}) was calculated according to equation A2 (see Appendix 1), assuming complete dissolution of copper in the Al-rich matrix after solid quenching. It is noted that the equilibrium solid solubility of copper in the Al-rich matrix of the Al-Cu-Si alloy at the homogenizing temperature is larger than 1.6x10^{-2} (4). To obtain values of $x_{Cu}^*$ and $x_{Si}^*$ the following assumptions need to be made: i.) at the end temperature of effect A no net precipitation is taking place, i.e. the composition of the Al-rich matrix is given by the solid solubilities of copper and silicon, and ii.) the solid solubilities of copper and silicon are independent, i.e. the presence of silicon in solution does not alter the solubility of copper, and vice versa. Then the values of $x_{Cu}^*$ and $x_{Si}^*$ can simply be taken equal to the solid solubilities of copper and silicon in the Al-rich matrix as obtained from the respective binary phase diagrams (2, 20) at the end temperature of effect A (see Table II).

Table II: End temperatures of effect A, binary equilibrium and metastable solid solubilities of copper and solid solubility of silicon as a function of heating rate (2, 20).

<table>
<thead>
<tr>
<th>Heating Rate (K/min)</th>
<th>End Temperature of Effect A (K)</th>
<th>Binary Solid Solubility of Copper (x10^2)</th>
<th>Equilibrium</th>
<th>Metastable</th>
<th>Silicon (x10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>525</td>
<td>0.10</td>
<td>0.10</td>
<td>0.46</td>
<td>0.018</td>
</tr>
<tr>
<td>2</td>
<td>570</td>
<td>0.18</td>
<td>0.18</td>
<td>0.61</td>
<td>0.044</td>
</tr>
<tr>
<td>5</td>
<td>595</td>
<td>0.24</td>
<td>0.24</td>
<td>0.71</td>
<td>0.069</td>
</tr>
<tr>
<td>20</td>
<td>640</td>
<td>0.41</td>
<td>0.41</td>
<td>1.08</td>
<td>0.147</td>
</tr>
<tr>
<td>40</td>
<td>675</td>
<td>0.60</td>
<td>0.60</td>
<td>1.58</td>
<td>0.235</td>
</tr>
<tr>
<td>80</td>
<td>705</td>
<td>0.83</td>
<td>0.83</td>
<td>&gt;2</td>
<td>0.353</td>
</tr>
</tbody>
</table>

As silicon precipitates directly into the equilibrium phase a single value for $x_{Si}^*$ results. Alternatively, two values are possible for copper: a value based on
the equilibrium solid solubility corresponding to the precipitation of the $\theta$ phase and a value based on the metastable solid solubility corresponding to the precipitation of the $\theta'$ phase. Hence, the calculation in Appendix 1 was performed for the two types of copper precipitation indicated. Note that the difference between $x_{\text{Cu}}^0$ and $x_{\text{Cu}}^*$ is larger for the precipitation of the equilibrium $\theta$ phase than for the precipitation of the metastable $\theta'$ phase. In the case of the $\theta'$-phase precipitation, application of equation A11 for heating rates $\geq 40 \text{ K/min}$ results in a zero or negative value of the amount of precipitating copper atoms. Apparently, no precipitation of copper as the $\theta'$ phase can then be expected. The result of the calculations are shown in Fig. 9, where the calculated and the experimentally observed heat content of effect A is plotted as a function of the DSC heating rate. As follows from the binary phase diagrams, the values of $x_{\text{Cu}}^*$ and $x_{\text{Si}}^*$ increase with increasing end temperature, i.e. increasing DSC heating rate. Hence, the amounts of silicon and copper atoms to precipitate decrease (see eqs. A12 and A13) and so the heat content of effect A decreases also (see Eq. A15).

![Graph showing heat content of effect A vs. heating rate](image-url)

**Fig. 9:** The heat content of effect A for the SQ Al-1.3 at%Cu-19.1 at%Si alloy as a function of the DSC heating rate. The calculated values were obtained by applying Eq. A12-A15 and using solid solubility values from Table II.
It is observed from Fig. 9 that the values for the combined silicon/θ-phase precipitation are larger than for the combined silicon/θ'-phase precipitation. This is due to the fact that i.) the heat of precipitation for the θ phase is larger than the heat of precipitation for the θ' phase (see Appendix 2); and ii.) the number of copper atoms involved in θ-phase precipitation is larger than the number of copper atoms involved in θ'-phase precipitation (see Eq. A13).

From Fig. 9 it is observed that the measured values of the heat content of effect A are always situated between the limits calculated for the cases of silicon/θ' and of silicon/θ precipitation. At the low heating rates (≤ 20 K/min), the experimental heat contents correspond very well with the calculated values for the case of the combined silicon/θ'-phase precipitation. At these low heating rates copper apparently precipitates mainly as the metastable θ' phase. For the high DSC heating rates (≥ 40 K/min) the experimental values correspond fairly well to the calculated values for the combined silicon/θ-phase precipitation. Apparently, copper precipitation then proceeds mainly as equilibrium θ-phase precipitation.

4.1.2 Effect B

As silicon precipitates directly into its equilibrium phase, the only possible transformation giving rise to an exothermic heat effect after effect A is the transition from a state with the θ' phase into a state with the θ phase. A similar effect in the same temperature range was described by several authors (8, 14, 21-24). According to the findings of the previous section the amount of θ' phase precipitated decreases with increasing DSC heating rate. Hence, interpreting effect B as due to the transition indicated, it is expected that the heat content of effect B decreases with increasing DSC heating rate. This is indeed observed (see Table I). In the temperature range of effect B, a competition occurs between the transition of the state with copper precipitated as θ' phase to the state with copper precipitated as θ phase, and the redissolution of copper. The two maxima of effect B observed at DSC heating rates 20 and 40 K/min may be related to this competition.

The amount of θ' phase precipitated, u, follows from eqs. A13 and A4 and is given by:

\[ u = \frac{1 - x_{Si}^g}{1 - x_{Si}^g} \frac{x_{Cu}^0 - x_{Cu}'^0}{1 - (x_{Si}^0 + 3x_{Cu}^0)} \]

where \( x_{Si}^g \) is the gross silicon content of the alloy.
The amount of heat produced by the transition from the state with copper precipitated as \( \theta' \) phase to the state with copper precipitated as \( \theta \) phase, \( Q_u \), is now given by:

\[
Q_u = u \cdot \Delta H_{\theta'}^\theta,
\]

where \( \Delta H_{\theta'}^\theta \) represents the difference between the heats of precipitation of the \( \theta' \) phase and the \( \theta \) phase and is taken equal to 10 kJ per mole copper (see Appendix 2).

In Table III the theoretical estimates based on Eq. 3 are compared with the experimental values of the heat content of effect B. As can be seen the theoretical predictions correspond very well to the experimentally observed values. These results also confirm that at low heating rates (\( \leq 20 \, \text{K/min} \)) copper precipitates mainly as \( \theta' \) phase, whereas at high heating rates (\( \geq 40 \, \text{K/min} \)) the \( \theta' \)-phase precipitation is nearly absent. As at the end temperatures related to the heating rates of 40 and 80 K/min, \( x_{Cu}^\theta \) is larger than \( x_{Cu}^{\theta'} \), eqs. 1 and 2 predict a zero value of \( Q_t \) for these heating rates. The non-zero values observed however indicate, that even at these high heating rates small amounts of \( \theta' \) phase were still formed during the evolution of effect A.

<table>
<thead>
<tr>
<th>heating rate (K/min)</th>
<th>calculated amount of ( \theta' )-phase precipitated (Eq. 2) (millimole)</th>
<th>heat content of effect B observed (J per mole alloy)</th>
<th>heat content of effect B calculated (J per mole alloy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>9.4</td>
<td>80±30</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>8.2</td>
<td>60±20</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>7.4</td>
<td>60±20</td>
<td>74</td>
</tr>
<tr>
<td>20</td>
<td>4.3</td>
<td>41±11</td>
<td>43</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>12±5</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>8±5</td>
<td>0</td>
</tr>
</tbody>
</table>

4.1.3 GP-zone formation

Large changes in enthalpy have been determined to be indicative of GP-zone formation in Al-Cu type alloys (25). In the SQ+NA specimens studied, an endothermic effect was observed just in advance of the main precipitation effect (Fig. 5). The temperature range of this endothermic effect coincides with the
temperature ranges for GP-zone dissolution in Al-Cu alloys observed by several authors (24, 25). So this endothermic effect is interpreted as due to GP-zone dissolution. Increasing the time of natural ageing should increase the amount of GP zones formed and the magnitude of this dissolution effect during DSC analysis should, therefore, accordingly increase. This behaviour is indeed observed (Fig. 6).

The heat effect of dissolution of GP zones formed at room temperature equals about 13 kJ per mole copper present as GP zones (25). Using this value, the mole fraction of copper present as GP zones in the SQ+NA specimens can be estimated. As can be deduced from Fig. 6, the heat of dissolution of GP zones after 1000 h of ageing at room temperature is 17 J per mole alloy, which equals 21 J per mole Al-rich matrix (Eq. A4). Then, the fraction of copper atoms transformed into GP zones, \( f_{Cu}^{GP} \), can readily be obtained:

\[
f_{Cu}^{GP} = \frac{21}{13 \times 10^3 x_{Cu}^0} \approx 0.1
\]

Literature data indicate that the formation of GP zones in conventional SQ Al-Cu alloys is finished within 200 hours of ageing at ambient temperature (25, 26, 27). Baur and Gerold (26) found that the fraction of copper atoms transformed into GP zones was 0.1 after 0.1 h ageing at 301 K. Comparing this to the calculated fraction transformed of 0.1 after 1000 hours at room temperature in our alloy (see above) leads to an estimation of the relative formation rate of GP-zone formation: the GP-zone formation in the SQ Al-Cu-Si alloy is about 10^4 times slower than in the conventional SQ Al-Cu alloy. Here the small difference in ageing temperatures is neglected. This is justified since this difference does not significantly influence the outcome of the estimation (activation energy of GP-zone formation in SQ Al-Cu is about 0.6 eV (19)).

The foregoing explains why nearly no traces of GP-zone dissolution could be detected during DSC measurements performed directly after solid quenching of the alloy studied: the lapse of time between solid quenching and the start of DSC experiments was far to small to allow the formation of an appreciable amount of GP zones. The suppression of GP-zone formation was also observed in quenched MMCs (6,7,8). Comparing DSC runs of rapidly cooled and subsequently aged specimens of an Al-Cu alloy with reinforcement (20wt% Al2O3/SiO2 fibres) and without reinforcement, Abis and Donzelli (8) observed that the reinforced alloy showed no trace of GP-zone dissolution while the unreinforced alloy did show significant GP-zone dissolution. Papazian (7) also observed reduced GP-zone dissolution enthalpies in a quenched fibre-reinforced Al-Cu alloy (2219) as compared to the corresponding unreinforced alloy. Also in a fibre reinforced Al-Mg-Si alloy (6061) a suppression of GP-zone formation has
been observed (6). The reduced GP-zone formation was explained by the annihilation of excess vacancies by misfit dislocations, which were created in the reinforced alloys on cooling after thermal treatment by virtue of the large difference in thermal expansion coefficients of matrix and reinforcement (7,8). As in the Al-Cu-Si alloy studied, the silicon particles and the Al-rich matrix also have a large difference in thermal expansion coefficients, misfit will occur on cooling or quenching between the matrix and the silicon particles. Analogously to the case of the quenched particle-reinforced MMCs, the suppression of GP-zone formation observed for the SQ Al-Cu-Si alloy can be related to that misfit (for a more detailed discussion see Ref. 13).

4.1.4 Kinetics of precipitation

Consider the state variable $\beta$ defined by:

$$\beta(t) = \int_0^t k \, dt = \int_0^t k_0 \, \exp\left( \frac{-E_A}{k_B T} \right) \, dt$$

where $E_A$ is an effective activation energy describing the overall precipitation process and $t$, $k_0$, $k_B$ and $T$ denote, respectively, time of ageing, a pre-exponential factor, Boltzmann’s constant and the absolute temperature. For non-isothermal annealing with a constant heating rate (i.e. the case of DSC experiments) it can be shown (28), that the following relationship between the temperature for a fixed stage of transformation, $T_f$, and the heating rate, $\Phi$, holds:

$$\ln \frac{T_f^2}{\Phi} = \frac{E_A}{k_B T_f} + \ln \beta_f$$

In deriving Eq. 5, it was assumed that $\beta$ could be considered as a state variable fully determining the extent of the transformation process involved. It can be shown that the maximal transformation rate corresponds to an approximately constant stage of transformation and that for DSC experiments the temperature of maximal transformation rate is given by the peak temperature (28, 29). In the case of the precipitation in an SQ Al-Cu-Si alloy, the heat evolution observed during a DSC experiment results from the simultaneously proceeding silicon and copper precipitation (see § 4.1.1): for the heating rates $\leq 20$ K/min, it appeared that the heat evolution stems solely from the combined silicon/\(\theta'\)-phase precipitation, whereas at 40 and 80 K/min the \(\theta\)-phase precipitation must also be taken into account. Thus it was decided to obtain an effective value for the activation energy only for heating rates $\leq 20$ K/min. From the slope of straight lines through the data points of the plots of
\ln(T_f^2/\Phi) \text{ versus } 1/T_f, \text{ at certain transformation stages, values of effective activation energies were obtained. Four transformation stages were chosen: 1) at the peak temperature, and 2) at 10\%, 3) at 50\%, and 4) at 90\% of the total heat development during effect A. The values obtained for the four different stages of combined precipitation did not differ significantly. The average value of the effective activation energy was calculated to be:}

\[ E_A = 1.00 \pm 0.07 \text{ eV}. \]

This value corresponds fairly well to the value of the activation energy of silicon precipitation in solid-quenched ribbons of an Al-Si alloy (1), where an excess of vacancies could be expected. The values for the activation energy for self diffusion in aluminium and for both silicon and copper diffusion in aluminium (all about 1.3 eV (19)) are larger than the value obtained for \( E_A \). As both silicon and copper atoms are substitutionally dissolved in the Al-matrix and both silicon and copper precipitation can only proceed via a vacancy mechanism, the low activation energy of precipitation in the SQ Al-Cu-Si alloy suggests that the precipitation kinetics are enhanced by excess vacancies. This result may be somewhat surprising in view of the presence of a large amount of finely dispersed silicon particles and specifically, the large amount of interfaces that can act as vacancy sinks. However, silicon occupies a much larger volume when precipitated than when dissolved in the Al-rich matrix (12). The volume misfit between silicon particles just precipitated and the surrounding Al-rich matrix can be accommodated by excess vacancies (30), which may, according to Russell (31), precipitate near the precipitate/matrix interface, thus relieving transformation strains. Thus, the newly formed interfaces can also act as temporary sources of vacancies. Further, on quenching excess vacancies can condense into vacancy loops which on ageing also may act as temporary sources of vacancies (32, 33). Also the suppression of GP-zone formation observed for the SQ Al-Cu-Si alloy (see Section 4.1.3) can contribute, at least partly, to the retaining of excess vacancies (13).

The temperature region of silicon precipitation in SQ Al-Si alloys during heating with a heating rate of 5 K/min is located at about 460 to 560 K (this follows from Ref. 1). This corresponds fairly well to the temperature range of effect A (the combined silicon and copper precipitation) in our alloy. The precipitation of copper in an SQ Al-Cu however, proceeds in a higher temperature range (520 to 630 K at 5 K/min, see Ref. 13). Given also the good correspondence between the effective activation energy for precipitation and the activation energy for silicon precipitation in solid-quenched Al-Si ribbons, these results suggest that the precipitation is lead by a vacancy-enhanced precipitation of silicon atoms dragging the copper atoms.
4.2 Precipitation effects directly after extrusion

The absence of effects A and B in the DSC curves of the AE specimen (Fig. 7) indicates that during preheating for 20 min and subsequent extrusion precipitation had already proceeded to a large extent. However, the hardness increase as observed on ageing of the AE specimen (Fig. 8) can only be interpreted as due to precipitation of a copper containing phase, as silicon precipitation does not cause a significant hardness increase (19).

At the preheating and extrusion temperature the equilibrium and the metastable solid solubilities of copper are 0.5 $10^{-2}$ and 1.3 $10^{-2}$, respectively (2). It is unlikely that during extrusion $\theta'$ phase was formed, since, in that case, the AE specimens should possess an Al-rich matrix with a dissolved copper fraction of at least 1.3 $10^{-2}$ (cooling after extrusion was relatively fast: 10 min in air followed by a water quench). However, DSC analysis shows that no such large supersaturation in AE specimens exists, since no exothermic precipitation effect is observed. Hence it can safely be assumed that preheating and extrusion resulted in precipitation of the equilibrium $\theta$ phase, thus leaving an Al-rich matrix with a copper fraction of about 0.5$x10^{-2}$ after cooling.

Thus, the Al-rich matrix in the SQ specimen possessed a higher copper fraction than the Al-rich matrix in the AE specimens. As GP-zone formation in the SQ specimens was suppressed (see Section 4.1.3), GP-zone formation in the AE specimens can not be expected. This is confirmed: no traces of GP-zone dissolution are observed in the DSC curves for the AE and AE+A specimens (Fig. 7). The only copper precipitate apart from GP zones that can cause the observed hardness increase upon ageing is the semi-coherent $\theta'$-phase precipitate (19). So it is concluded that in the AE specimens precipitation involves the formation of $\theta'$ phase. Increasing the time of ageing at 453 K increases the amount of semi-coherent $\theta'$ phase formed and this causes an initial increase of the hardness as a function of ageing time. Later, beyond 28 h of ageing at 453 K, the hardness decreases (see Fig. 8). This may be related to coarsening of the $\theta'$ phase (see Ref. 14). The endothermic effects observed in Fig. 7 for the AE+A specimens can only be caused by a dissolution effect starting at lower temperatures than the temperatures of the equilibrium-phase dissolution during the rescan (see Section 3). Indeed, the $\theta'$-phase dissolution starts at lower temperatures than the $\theta$-phase dissolution (2). Therefore, the increasing magnitude of the endothermic effect as observed in Fig. 7, is interpreted as caused by the dissolution of increasing amounts of $\theta'$ phase. Apparently, the formation of $\theta'$ phase continues up to 192 h of ageing at 453 K.
5. Conclusions

- The heat content of the combined precipitation peak in the SQ Al-Cu-Si alloy (effect A) can quantitatively be described in terms of the heats of precipitation of both alloying elements and in terms of solid solubilities of the constituting binary alloys.

- The heat content of the exothermic effect due to the replacement of the $\theta'$ phase by the $\theta$ phase, effect B in the SQ Al-Cu-Si alloy, agrees with the difference in heat of precipitation of these phases.

- During non-isothermal annealing with constant heating rate of the SQ Al-Cu-Si alloy, silicon and copper atoms precipitate simultaneously: at low heating rates ($\leq 20$ K/min) as silicon and $\theta'$ phase and at high heating rates ($\geq 40$ K/min) mainly as silicon and $\theta$ phase.

- The temperature range of the combined precipitation in the SQ Al-Cu-Si alloy corresponds to that of the precipitation in the SQ Al-Si alloy but is much lower than that of the precipitation in the SQ Al-Cu alloy.

- The effective activation energy for the combined precipitation in the SQ Al-Cu-Si alloy is much lower than the activation energy for self diffusion and for copper and silicon diffusion in aluminium, denoting a vacancy enhanced precipitation mechanism.

- GP-zone formation in the SQ Al-Cu-Si alloy is approximately $10^4$ times slower than in SQ Al-Cu alloys.

- The matrix of the AE Al-Cu-Si alloy is supersaturated with copper; ageing at 453 K after extrusion yields a hardness increase due to the formation of $\theta'$-phase precipitates.

Appendix 1

Consider one mole of the ternary Al-Cu-Si alloy with gross silicon and copper contents $x^{g}_{Si}$ mole and $x^{g}_{Cu}$ mole, respectively. At the start of precipitation silicon is partly dissolved in the Al-rich matrix and copper is wholly dissolved in the Al-rich matrix. It is assumed that no aluminium is dissolved in silicon. Let the heats of precipitation per mole precipitating silicon or copper be $\Delta H_{Si}$ and $\Delta H_{Cu}$, respectively. Let $\Delta H_{Si}$ and $\Delta H_{Cu}$ for the ternary alloy be equal to the values for the respective binary alloy systems. Denote $Q$ as the heat evolved during precipitation per mole alloy and $Q_{M}$ as the heat evolved during precipitation per mole matrix. The amount of aluminium present is given by:

$$1 - \left( x^{g}_{Si} + x^{g}_{Cu} \right)$$
If the amount of silicon dissolved in the Al-rich matrix is given by $s$ moles, then the mole fraction silicon dissolved in the Al-rich matrix at the start of precipitation, $x_{Si}^o$, is given by (1, 34):

$$
x_{Si}^o = \frac{s}{1 - (x_{Si}^g + x_{Cu}^g) + s + x_{Cu}^g} = \frac{s}{1 - x_{Si}^g + s}
$$

A1

The mole fraction copper of the Al-rich matrix at the start of precipitation, $x_{Cu}^o$, is given by:

$$
x_{Cu}^o = \frac{x_{Cu}^g}{1 - x_{Si}^g + s}
$$

A2

From A1 follows:

$$
s = \frac{1 - x_{Si}^o}{x_{Si}^o} x_{Si}^o
$$

A3

and the amount of Al-rich matrix (number of moles) is:

$$
1 - x_{Si}^g + s = \frac{1 - x_{Si}^o}{x_{Si}^o}
$$

A4

After a certain precipitation time, the mole fractions silicon and copper of the Al-rich matrix are given by $x_{Si}^\prime$ and $x_{Cu}^\prime$, respectively. The precipitation reaction can be represented by:

$$
Al_{[1 - (x_{Si}^o + x_{Cu}^o)]} Si_{x_{Si}^o} Cu_{x_{Cu}^o} \rightarrow r Al_{[1 - (x_{Si}^\prime + x_{Cu}^\prime)]} Si_{x_{Si}^\prime} Cu_{x_{Cu}^\prime} + p Si + q Al_2Cu
$$

A5

where $r$, $p$, and $q$ represent the amounts (number of moles) of Al-rich phase, silicon phase and $Al_2Cu$ phase ($\theta$ or $\theta'$), respectively. It is assumed that the $\theta$ phase and the $\theta'$ phase have the same chemical composition: $Al_2Cu$, and that silicon precipitates as pure silicon.

Conservation of mass requires:

- for aluminium:

$$
1 - (x_{Si}^o + x_{Cu}^o) = r (1 - (x_{Si}^\prime + x_{Cu}^\prime)) + 2 q
$$

A6

- for silicon:

$$
x_{Si}^o = r x_{Si}^\prime + p
$$

A7

- for copper:

$$
x_{Cu}^o = r x_{Cu}^\prime + q
$$

A8

69
From A6 - A8 follows:

\[
p = \frac{x_{Si}^0 - x_{Si}^\prime - 3 \left( x_{Si}^0 x_{Cu}^\prime - x_{Si}^\prime x_{Cu}^0 \right)}{1 - (x_{Si}^\prime + 3x_{Cu}^0)} \tag{A9}
\]

\[
q = \frac{x_{Cu}^0 - x_{Cu}^\prime - (x_{Si}^0 x_{Cu}^0 - x_{Si}^\prime x_{Cu}^\prime)}{1 - (x_{Si}^\prime + 3x_{Cu}^\prime)} \tag{A10}
\]

\[
r = \frac{1 - (x_{Si}^0 + 3x_{Cu}^0)}{1 - (x_{Si}^\prime + 3x_{Cu}^\prime)} \tag{A11}
\]

In view of the maximal values possible for the concentrations occurring in these formulas (see Table II), the product terms in eqs. A9, A10 can generally be neglected; this gives:

\[
p = \frac{x_{Si}^0 - x_{Si}^\prime}{1 - (x_{Si}^\prime + 3x_{Cu}^\prime)} \tag{A12}
\]

\[
q = \frac{x_{Cu}^0 - x_{Cu}^\prime}{1 - (x_{Si}^\prime + 3x_{Cu}^\prime)} \tag{A13}
\]

The value of \(Q_M\) is now given by:

\[
Q_M = p \Delta H_{Si} + q \Delta H_{Cu} \tag{A14}
\]

and the value of \(Q\) by:

\[
Q = Q_M \frac{1 - x_{Si}^g}{1 - x_{Si}^0} \tag{A15}
\]

Appendix 2

The value of \(\Delta H_{Si}\) can be obtained from literature data (1): \(\Delta H_{Si} = 54 \text{ kJ/mole}\). Following the reasoning of Van Rooyen and Mittemeijer (1), values for \(\Delta H_{Cu}\) can be obtained from literature data on the solid solubility of copper in the Al-rich matrix. In the case of the precipitation of copper as the equilibrium \(\theta\) phase, the heat of precipitation \(\Delta H_{Cu}^\theta\) is obtained from the slope of the straight line through the data points of the plot of the logarithm of the equilibrium solid solubility versus the reciprocal temperature. Solid solubility data were taken from Refs. 35-38, also cited by Murray (2). The slope of the resultant line and
thus $\Delta H_{\text{Cu}}^{\theta}$ was determined to be $44\pm1$ kJ/mole. Nakamura et al. (39) obtained a corresponding value based on independently determined solid solubility data. The heat of precipitation of copper as the metastable $\theta'$ phase, $\Delta H_{\text{Cu}}^{\theta'}$, was obtained analogously (data from the metastable solvus were taken from Refs. 23, 38 and 40, as cited by Murray (2)), yielding: $\Delta H_{\text{Cu}}^{\theta'} = 34\pm4$ kJ/mole. This value is intermediate between the values reported for the heat of formation of GP II zones and for the heat of formation of the equilibrium $\theta$ phase (cf. Ref. 39). This is in accordance with thermodynamics which predicts an increasing stability of the precipitates successively formed during the full precipitation sequence. Now, the heat of the transition from the state with copper precipitated as $\theta'$ phase to the state with copper precipitated as $\theta$ phase is given by:

$$\Delta H_{\theta}^{\theta'} = \Delta H_{\text{Cu}}^{\theta} - \Delta H_{\text{Cu}}^{\theta'} = 10\pm5$$ kJ/mole.

References

CHAPTER V

LATTICE PARAMETER VARIATIONS RESULTING FROM PRECIPITATION AND MISFIT ACCOMMODATION IN A QUENCHED AND AGED Al-Cu ALLOY WITH SILICON PARTICLES

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Abstract

Quenched and aged specimens of the Al-1.3at%Cu-19.1at%Si model alloy were studied by X-ray diffraction and hardness measurements. During isothermal ageing of the solid-quenched Al-1.3at%Cu-19.1at%Si alloy the Cu and Si atoms precipitate simultaneously. This causes the Al-rich phase lattice parameter to increase from a value below to a value higher than the equilibrium value of pure aluminium. Since in the corresponding binary alloys Si and Cu precipitation occurs at very different times, the simultaneous precipitation of Si and Cu indicates some linkage between the two precipitation processes. The θ' phase is the main hardening precipitate in the alloy. Due to misfit after quenching from heat treatment temperatures all lattice parameters are influenced by stresses in the specimen. The model describing the stress state around a single misfitting spherical inclusion in an infinite matrix which shows ideal plastic behaviour as given by Lee et al., is extended to describe the stress state in a finite composite. Comparison of the model incorporating elastic accommodation and the model incorporating ideal plastic accommodation with measured stresses show significant discrepancies, especially for the low temperature range (ΔT < 200 K). A possible reason for this is the volume effect of defects (dislocations, vacancies) created in the plastic zone. Elastic stresses in the solid-quenched Al-1.3at%Cu-19.1at%Si alloy at room temperature are reduced by quenching in liquid nitrogen.
Introduction

Rapid solidification of aluminium alloys with a high percentage of silicon (about 20 at%) yields finely grained microstructures with a fine dispersion of silicon particles (1, 2). By consolidation of the rapidly solidified ribbons or powders, aluminium alloys with improved mechanical properties as compared to conventional aluminium alloys can be produced. These improved properties include increased wear resistance and reduced thermal expansion (3), which makes these alloys attractive for applications like parts of combustion engines. Also the yield and the tensile strength are slightly improved as a result of the presence of the fine silicon dispersoids (4). In many aspects, e.g. volume fraction, size and thermal expansion of dispersed particles, the rapidly solidified aluminium alloys with a large silicon content resemble particulate-reinforced metal matrix composites (MMCs). Thus, these alloys are considered as an in-situ composite.

An important mechanism for increasing the room-temperature strength of aluminium alloys is precipitation hardening. The presence of reinforcing particles in an aluminium alloy can result in an alteration of the kinetics of precipitation from the matrix of such an alloy (5, 6, 7, 8, 9). This alteration is usually explained as follows. The difference in shrinkage on cooling, due to the difference in the respective coefficients of thermal expansion (CTE) of the dispersed particles and the surrounding matrix, introduces a thermal misfit between particles and matrix. This thermal misfit is accommodated by elastic and plastic deformation of the matrix (10), the latter by the creation of misfit dislocations. These act as extra nucleation sites (enhancing precipitation) or annihilate excess vacancies (retarding precipitation). Elastic misfit accommodation can also influence precipitation phenomena (11, 12).

The Al-1.3at%Cu-19.1at%Si model alloy produced via melt spinning and subsequent extrusion combines the attractive mechanical properties of aluminium alloys with a large silicon content with the possibility of age-hardening of the matrix. The combination of a heat-treatable Al-matrix with the presence of silicon particles allows the study of important effects in MMCs, such as thermal stresses and precipitation. The non-isothermal precipitation in the solid-quenched Al-1.3at%Cu-19.1at%Si alloy was studied before (13). In the present work the isothermal precipitation in the solid-quenched Al-1.3at%Cu-19.1at%Si alloy is studied by measurement of lattice parameter variations of the Al-rich phase and the Si-rich phase. In addition some hardness measurements were performed.
Experimental procedures

2.1 Preparation of specimens

A high purity Al-1.3at\%Cu-19.1at\%Si alloy was produced by melt spinning and subsequent extrusion. The production route of the alloy was described earlier (13). From the centre of the extruded bars, cylindrical specimens were machined with a diameter of 0.5 mm and length of about 5 mm. The axis of the specimen was parallel to the extrusion direction. These specimens were intended for X-ray diffraction experiments with a Debije-Scherrer camera.

The specimens were solution treated for 5 minutes at 793 K in a vertical tube furnace and subsequently quenched in water at room temperature. A part of the specimens was stored at room temperature before further experiments took place. Another part of the specimens was stored in liquid nitrogen before further experiments. The corresponding indications are SQ/RT and SQ/LN, respectively. The quenched specimens were aged at 423, 453 and 483 K. The quenched and aged specimens will be indicated as SQ+A specimens, followed by the ageing temperature. The ageing treatment was performed in an oil bath with temperature stability ± 1.5 K and was terminated by a direct quench into water at room temperature.

In order to study the effect of specimen size on the Al-rich phase lattice parameter after quenching, a melt-spun ribbon (thickness ~ 50 μm) was aged for 700 h at 423 K and subsequently quenched in water at room temperature. This liquid-quenched and aged specimen will be referred to as the LQ+A423 specimen.

In order to study the effect of dissolved Cu and Si atoms on the Al-rich phase lattice parameter in the absence of Si particles, an Al-1.07at\%Cu-1.01at\%Si alloy was produced from 99.999\% pure Al, 99.99\% pure Si and a 99.95\% pure Al-50\%Cu master alloy (all percentages by weight) by conventional casting. The ingot was homogenized at 798 K for 5 days and subsequently quenched in water at room temperature. Filings were prepared from a slice cut from the ingot. These filings were collected in a quartz tube, homogenized for 2 hours at 798±2 K and subsequently quenched in water at room temperature.

2.2 X-ray diffraction

For measurement of the lattice parameter of the Al-rich phase and the Si-rich phase of the Al-1.3at\%Cu-19.1at\%Si alloy, X-ray diffraction experiments were performed using a Debije-Scherrer (DbS) camera. Unfiltered copper radiation was used. The films in the DbS camera were exposed for 3 hours.
During the exposure the temperature inside the DbS camera, at a point close to the specimen was measured and recorded. Temperatures during the measurements were between 294 and 297 K. Temperature variations during single experiments were typically in the order of 0.5 K. Film type and film development procedures were identical for all experiments.

After development of the DbS film, the line positions were measured. Accuracy of the line position measurements of the two lines corresponding to the highest diffraction angle was improved by taking the average of at least five determinations of the position. The lattice parameters of the Al-rich phase and the Si-rich phase were determined using the Nelson-Riley extrapolation (see Ref. 14) and were corrected for the average temperature during the measurement by adopting the linear expansion coefficient of pure aluminium and pure silicon: 23.5 $10^{-6}$ and 3 $10^{-6}$, respectively (15). All lattice parameters presented in this work are valid at 298 K.

2.3 Hardness measurements

Hardness measurements were performed after ageing at 423 K of two water-quenched specimens. One specimen had been naturally aged for 14 months between quenching and the start of ageing, the other one was naturally aged for 24 hours. Microhardness was measured on polished longitudinal sections through the axis of the extruded bar using a Leitz-Durimet Vickers hardness tester. For each hardness value at least 10 indentations evenly distributed over a line from the axis to the edge of the bar were made (hardness did not depend on the radial distance to the centre of the bar). Indentation force was 0.981 N.
3 Results

3.1 X-ray diffraction

The exposed films always showed lines diffracted from the Al-rich and the Si-rich phases. In some cases also lines from the \( \theta \) and/or \( \theta' \) phases (both Al\(_2\)Cu) were observed. Beside these four phases, no other phases were observed in any of the specimens. For the as-extruded (AE) specimens, the \( \theta \) phase was the only intermetallic phase observed. In SQ specimens no intermetallic phase was observed. On ageing, the lines diffracted by the Al\(_2\)Cu phases appear after certain times. After an Al\(_2\)Cu phase has been detected it remains present at subsequent ageing times studied. In Table I the minimum ageing times for the appearance of the Al\(_2\)Cu phases in SQ+A specimens are given. The lattice parameters of the Al-rich and the Si-rich phases in AE and SQ specimens are gathered in Table II. It is observed that the Si-rich phase lattice parameter after quenching and storage in liquid nitrogen (SQ/LN) is much higher than after quenching and storage at room temperature (SQ/RT). The Al-rich phase lattice parameter after SQ/LN is somewhat lower than after SQ/RT. In the AE specimen the lattice parameter of the Al-rich phase is within the experimental error equal to the value for pure aluminium (0.40496 nm, see Ref. 16).

To obtain a reference value for the lattice parameter of pure, unstrained silicon the lattice parameter of pure silicon (NBS SRM 640 powder) was determined twice. This yielded \( a_{Si} = 0.54308 \pm 0.00001 \) nm. The measured lattice parameters of the Si-rich phase in the Al-1.3at\%Cu-19.1at\%Si alloy are in all cases lower than this value.

| Table I: Minimum ageing times, \( t_m \), required for the appearance of lines diffracted by the Al\(_2\)Cu phases in SQ+A specimens. In specimens aged at 453 K the \( \theta \) phase was not observed up until the maximum ageing time employed, 510 h. |
|---|---|---|
| | SQ+A 423K | SQ+A 453K | SQ+A 483K |
| \( \theta' \) | \( t_m \) (h) | \( t_m \) (h) | \( t_m \) (h) |
| 8 | 3.5 | 2 |
| \( \theta \) | 512 | 128 | 16 |

The lattice parameters of the Al-rich and the Si-rich phases as a function of ageing time are presented in Figs. 1 and 2, respectively. It is observed that during ageing at 483 K the Al-rich phase lattice parameters obtained from specimens stored at room temperature coincide with the ones obtained from
specimens stored in liquid nitrogen. Thus, the difference in storage temperature between quenching and ageing has no significant effect on the kinetics of ageing at 483 K. Also the Si-rich phase lattice parameter during ageing at 483 K is not significantly influenced by the difference in storage temperature. During ageing the Al-rich phase lattice parameter increases from values around 0.4042 nm to about 0.4051 nm. This last value is significantly higher than the lattice parameter of pure Al (0.40496 nm). During ageing, the Si-rich phase lattice parameter remains approximately constant. Only for the ageing temperature of 453 K, the Si-rich phase lattice parameter shows a slight tendency to decrease during ageing. It is observed that the lattice parameter of the Si-rich phase decreases with increasing ageing temperature.

The DbS experiment on the melt-spun ribbon aged at 423 K (LQ+A423) yielded an Al-rich phase lattice parameter of 0.40516±0.00002 nm. Besides Al-rich phase lines only Si-rich phase lines and θ-phase lines were observed.

![Graph showing Al-rich phase lattice parameter vs. ageing time](image)

**Fig. 1:** The Al-rich phase lattice parameters as a function of time of ageing at the indicated temperatures; storage between quenching and ageing was at room temperature (RT) or in liquid nitrogen (LN). The lattice parameter for pure aluminium, $a_{Al}^0$, is indicated.
Fig. 2: The Si-rich phase lattice parameter as a function of time of ageing at the indicated temperatures; storage between quenching and ageing was at room temperature (RT) or in liquid nitrogen (LN). The lattice parameter for pure silicon, $a_{Si}^0$, is indicated.

Table II: Lattice parameters of the Al-rich and Si-rich phases ($a_{Al}$ and $a_{Si}$, respectively) in an AE specimen and four SQ specimens. The SQ specimens were either stored at room temperature after quenching (RT) or in liquid nitrogen (LN).

<table>
<thead>
<tr>
<th>specimen</th>
<th>$a_{Al}$ (nm)</th>
<th>$a_{Si}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AE</td>
<td>0.40495±0.00002</td>
<td>0.54284±0.00003</td>
</tr>
<tr>
<td>SQ/LN1</td>
<td>0.40417±0.00004</td>
<td>0.54306±0.00003</td>
</tr>
<tr>
<td>SQ/LN2</td>
<td>0.40422±0.00003</td>
<td>0.54293±0.00002</td>
</tr>
<tr>
<td>SQ/RT1</td>
<td>0.40431±0.00003</td>
<td>0.54254±0.00005</td>
</tr>
<tr>
<td>SQ/RT2</td>
<td>0.40426±0.00003</td>
<td>0.54254±0.00003</td>
</tr>
</tbody>
</table>
In the DbS experiment on the conventionally cast, homogenized and solid-quenched Al-1.07at%Cu-1.01at%Si alloy, the Al-rich phase lattice parameter equalled 0.40428±0.00001 nm. Only lines diffracted from the Al-rich phase were observed.

3.2 Hardness measurements

The hardness as a function of time of artificial ageing for two SQ specimens is shown in Fig. 3. One specimen was naturally aged for 24 hours between quenching and the start of artificial ageing, the other specimen was naturally aged for 14 months between quenching and the start of artificial ageing. It is observed that the hardness of the SQ specimen is increased by 14 months natural ageing. During the initial part of artificial ageing at 423 K, this difference in hardness remains. For ageing times beyond 30 hours, the difference disappears. Both specimens reach a peak hardness after about 70 hours of ageing at 423 K.

![Graph showing hardness vs. ageing time](image)

Fig. 3: Hardness of two solid-quenched specimens during ageing at 423 K. The two specimens were naturally aged for 24 hours or for 14 months in between quenching and the start of artificial ageing. For comparison also the Al-rich phase lattice parameter of the SQ+A423 specimen is given (see Fig. 1).
4 Discussion

It has been shown by van Mourik et al. (17) that lattice parameter variations during ageing of solid-quenched binary aluminium alloys with a high percentage of silicon can fairly well be described assuming only elastic accommodation of thermal misfit and a linear dependence of the amount of Si atoms dissolved in the Al-rich phase and the lattice parameter. However, even at temperature drops as low as 100 K, plastic accommodation of thermal misfit can readily occur in Al-based composites (10).

Assuming ideal plastic accommodation, Lee et al. were able to give a full description of the stress state around a misfitting spherical inclusion embedded in an infinite matrix. In Section 4.1 a short description will be given of the stress state in a finite, two-phase alloy. Then, after correction of the lattice parameter shift due to dissolved atoms in Section 4.2, this model will be compared with the measured lattice parameter shifts in Section 4.3.

In Section 4.4 the kinetics of precipitation in the present alloy will be discussed.

4.1 Misfit stresses for the case of a spherical inclusion embedded in a plastically deforming, finite matrix.

For a spherical inclusion B in a continuous matrix phase A the misfit parameter is defined as:

\[ \varepsilon = \frac{r_B^0 - r_A^0}{r_A^0} \]  

(1)

where \( r_B^0 \) and \( r_A^0 \) are the radii of the free undeformed inclusion B and the empty undeformed cavity in the matrix A, respectively. For the case of misfit due to a temperature change, \( \Delta T \), the misfit parameter is given by:

\[ \varepsilon = (\alpha_A - \alpha_B) \Delta T \]  

(2)

where \( \alpha_A \) and \( \alpha_B \) are the coefficients of thermal expansion of matrix and inclusion, respectively. When a misfitting inclusion is placed in the cavity, strains and stresses will develop to accommodate the misfit. In the following we will consider the case of a positive misfit parameter, i.e. \( r_B^0 > r_A^0 \). For the case of a negative misfit parameter similar formulas can be derived. For the case of elastic accommodation of misfit in an infinite elastically isotropical matrix the inclusion (also assumed elastically isotropical) will be in a state of hydrostatic compression. The pressure inside the inclusion for an infinitely small volume fraction of inclusions is given by (see Ref. 17):

\[ p_B = 3K_B (C-1) \varepsilon \]  

(3)
where
\[ C = \frac{3 \alpha B}{3 \alpha B + 4 \mu A} \]  
(4)

where \( \mu \) is the shear modulus and \( \lambda \) is the bulk modulus. (Note that since the inclusion is in a state of compression \( p_B \) is negative.)

In a finite matrix it is required that the surface of the matrix is traction free, i.e. that the stresses normal to the surface are zero. The boundary condition requiring that \( \sigma_r = 0 \) on the surface of the matrix, is equivalent to requiring that on any plane through the finite specimen the compressive stress in the inclusion must be balanced by tensile stresses in the matrix. In a spherical symmetric case this can be obtained from the solution of the stresses in the infinite matrix by adding a uniform hydrostatic stress. This balancing stress is usually termed the image stress, \( p^i \). Assuming that the stress state in the inclusions is not disturbed by interaction of stress fields, the balance of forces requires:
\[ p^i + y_B p_B = 0 \]  
(5)

where \( y_B \) is the volume fraction of inclusions. (Note that \( p^i \) is positive and hence represents a hydrostatic tension.)

Lee et al. (18) have calculated the stress state in the case of a spherical misfitting inclusion in an infinite matrix which deforms plastically around the inclusions. In their model the matrix is assumed to be a perfectly plastic material (non-strain hardening), the flow stress-strain behaviour is assumed to be independent of strain rate and of stress orientation, and both inclusion and matrix are assumed to be isotropic. As a yielding criterion the von Mises yielding criterion is used. This criterion states that yielding occurs when an equivalent stress, \( \sigma_e \), exceeds the yield stress, \( \sigma_y \), where \( \sigma_e \) is given by:
\[ \sigma_e = \frac{1}{\sqrt{2}} \left[ (\sigma_r - \sigma_\theta)^2 + (\sigma_\theta - \sigma_\phi)^2 + (\sigma_\phi - \sigma_r)^2 \right]^{1/2} \]  
(6)

For the case of a spherical symmetrical stress state this equation reduces to:
\[ \sigma_e = |\sigma_r - \sigma_\theta| \]  
(7)

Lee et al. (23) obtained the following expressions for the stress components in the inclusion, plastically deformed matrix and elastically deformed matrix:
\[ \sigma_r = \sigma_\theta = p_B \quad r < a \]  
(8a)
\[ \sigma_r = \sigma_\theta - \sigma_\phi = 2 \sigma_y \ln \left( \frac{r}{a} \right) + p_B; \quad a \leq r \leq r_p \]  
(8b)
\[ \sigma_r = -2 \sigma_\theta = -\frac{2}{3} \sigma_\phi \left( \frac{r_p}{r} \right)^3; \quad r > r_p \]  
(8c)

where \( r_p \) is the radius of the plastically deformed zone and \( a \) is the radius of the inclusion. Thus the inclusion is in a state of uniform hydrostatic compression. Since the stresses at the plastic front must be continuous it follows:
\[ r_p = a \exp \left[ -\frac{p_{B \perp}}{2\sigma_y} - \frac{1}{3} \right] \]  \hspace{1cm} (9)

Continuity conditions of displacements and stresses yield an expression from which \( p_{B \perp} \) can be evaluated:

\[ \frac{6\eta\mu e}{\sigma_y} \left[ 1 + \frac{p_{B \perp}}{3K_B e} - \frac{p_{B \perp}}{3K_A e} \right] = \exp \left[ -\frac{3p_{B \perp}}{2\sigma_y} - 1 \right] \]  \hspace{1cm} (10)

where \( \eta = (1+v)/(1-v) \) (\( v \) is Poisson's ratio of the matrix).

Now consider the case of a spherical inclusion with radius \( a \) in a spherical matrix with radius \( R \). From the spherical symmetry follows that in this finite spherical specimen the radial components of the stresses are obtained by adding the image stress, \( p^i \), to the stresses in the case of the finite matrix:

\[ \sigma_r = p_{B \perp} + p^i \quad r < a \]  \hspace{1cm} (11a)

\[ \sigma_r = 2\sigma_y \ln \left( \frac{r}{a} \right) + p_{B \perp} + p^i ; \quad a \leq r \leq r_p \]  \hspace{1cm} (11b)

\[ \sigma_r = \frac{2}{3} \sigma_y \left( \frac{r_p}{R} \right)^3 + p^i \quad r > r_p \]  \hspace{1cm} (11c)

Since the boundary equation requires that \( \sigma_r = 0 \) on the surface, the image stress can directly be obtained from equations 11b and 11c:

\[ p^i = -p_{B \perp} - 2\sigma_y \ln \left( \frac{r}{a} \right) ; \quad R \leq r_p \]  \hspace{1cm} (12a)

\[ p^i = \frac{2}{3} \sigma_y \left( \frac{r_p}{R} \right)^3 ; \quad R \geq r_p \]  \hspace{1cm} (12b)

Again, as in the case of elastic accommodation of misfit, it is assumed that the stress state in the inclusions is not disturbed by interaction of stress fields and that \( p_{B \perp} \) is not influenced by \( p^i \). Then the volume fraction of precipitates can be substituted for the ratio \( a/R \):

\[ y_B = \left( \frac{a}{R} \right)^3 \]  \hspace{1cm} (13)

and the combination of Eqs. 9, 10, 12 and 13 gives the image stress in a composite with spherical inclusions.

4.2 Influence of misfit stresses and dissolved atoms on lattice parameters

For binary Al-Si alloys, the lattice parameter of the Al-rich phase, \( a_{Al} \), is proportional to the atomic fraction of silicon dissolved in the Al-rich phase, \( x_{Si} \),

\[ \frac{a_{Al} - a_{Al}^0}{a_{Al}^0} = \frac{\Delta a_{Al}}{a_{Al}^0} = p_{Si} x_{Si} \]  \hspace{1cm} (14)

in which \( a_{Al}^0 \) is the equilibrium value of the lattice parameter of pure aluminium. In this formula \( p_{Si} \) is the Vegard constant for Si atoms dissolved in Al. The Vegard constant for Si dissolved in Al is obtained from literature data: \( p_{Si} = -4.30 \times 10^{-2} \) (see Ref. 17).
In the case of our ternary Al-1.3at%Cu-19.1at%Si alloy, the effects of copper on the lattice parameter should also be taken into account. Since in many ternary alloy systems the lattice parameter can be calculated from binary data using additive relationships (19), and since only about 1 at% Si and Cu can be dissolved in the Al-rich phase, it seems reasonable to assume that the effects of both alloying elements are independent and additive. Since also in the case of Al-Cu alloys the lattice parameter depends linearly on the dissolved Cu fraction in the Al-rich phase (see 20), an extra term $p_{Cu} x_{Cu}$ must be added to Eq. 14, i.e.:

$$\frac{\Delta a_{Al}}{a_{Al}} = p_{Si} x_{Si} + p_{Cu} x_{Cu}$$  \hspace{1cm} (15)

From lattice parameter data on homogenized and solid-quenched Al-Cu alloys it follows: $p_{Cu} = -1.18 \times 10^{-1}$ (see 20). Now the assumption of additivity can be checked for the homogenized Al-1.07at%Cu-1.01at%Si alloy. For this alloy it was found that $a_{Al} = 0.40428 \pm 0.00001$ nm. From Eq. 15 combined with the values for $p_{Si}$ and $p_{Cu}$ as stated above one finds $a_{Al} = 0.404273$ nm. From this it is concluded that the effects of Si and Cu dissolved of the Al-rich phase are indeed additive.

At the solution treatment temperature applied to the ternary Al-Cu alloy with silicon particles, the copper atoms can be completely dissolved. The silicon solubility at this temperature is obtained from Ref. 13. As long as no significant precipitation occurs, the composition of the Al-rich phase can be considered to remain equal to the one just after solid quenching.

For the AE alloy, the Al-rich and the Si-rich phases, were shown to be present together with the $\theta$ phase. No $\theta'$ phase was detected. Therefore, the composition of the Al-rich phase is supposed to be equal to that given by the equilibrium solvus of the Al-Cu-Si system at the extrusion temperature.

The beginning of the increase of the Al-rich phase lattice parameter during ageing of the SQ specimens coincides with the detection of $\theta'$ phase by X-ray diffraction (cf. Table I and Fig. 1). This phase remained present during the entire range of ageing times applied. The equilibrium $\theta$ phase was detected at the very end of the ageing, when the Al-rich phase lattice parameter had reached a stable value (cf. Table I and Fig. 1). Therefore it can reasonably be assumed that the copper content of the Al-rich phase at the end of the ageing times applied can be obtained from the $\theta'$-phase solvus. Since the silicon content of the Al-rich phase at these temperatures can be neglected, the $\theta'$-phase solvus in the Al-Cu system is used to obtain the copper content of the Al-rich phase at the end of the ageing times applied (see Ref. 21).

For the LQ+A423 specimen the equilibrium $\theta$ phase was the only intermetallic phase observed. The ageing time used is sufficient to reach a
stable state (see Fig. 1) and hence the copper content of the Al-rich phase can be obtained from the equilibrium θ-phase solvus.

On the basis of the foregoing the lattice parameter shift due to dissolved atoms for the specimens in the states mentioned, \( a^d \), can now be calculated. The results of these calculations are presented in Table III. For the ternary alloys studied, free silicon particles are always present at a volume fraction that can be considered to be nearly constant during ageing. The misfit stresses resulting from the difference in thermal shrinkage on cooling after heat treatment, are expected to exert a significant influence on the Al-rich phase lattice parameter. The magnitude of this effect is equal to:

\[
\Delta a^m = a^e - a^d
\]  

(16)

where \( a^e \) is the experimentally obtained Al-rich phase lattice parameter. The values for \( \Delta a^m \) thus obtained are presented in Table III.

From Table III follows directly that atoms dissolved in the Al-rich phase account for the largest part of the observed Al-rich phase lattice parameter shifts. It is further noted that the misfit effects before and after precipitation at each of the three ageing temperatures applied are equal within the experimental error. This gives a further indication that the calculations of the effects of dissolved atoms on the Al-rich phase lattice parameter are correct and that the effect of misfitting θ/θ'-phase particles on the lattice parameter is negligible (see also next Section).

<table>
<thead>
<tr>
<th>heat treatment</th>
<th>( \Delta T ) (K)</th>
<th>( x_{\text{Cu}} ) (x10^2)</th>
<th>( x_{\text{Si}} ) (x10^2)</th>
<th>( a^d ) (nm)</th>
<th>( a^e ) (nm)</th>
<th>misfit effect (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LQ+A423, t=700h</td>
<td>130</td>
<td>0.01</td>
<td>0</td>
<td>0.40496</td>
<td>0.40516</td>
<td>0.20</td>
</tr>
<tr>
<td>AE</td>
<td>360</td>
<td>0.5</td>
<td>0.2</td>
<td>0.40469</td>
<td>0.40495</td>
<td>0.26</td>
</tr>
<tr>
<td>SQ/RT</td>
<td>500</td>
<td>1.59</td>
<td>1.05</td>
<td>0.40402</td>
<td>0.40424</td>
<td>0.22</td>
</tr>
<tr>
<td>SQ+A423, t&lt;1h</td>
<td>130</td>
<td>1.59</td>
<td>1.05</td>
<td>0.40402</td>
<td>0.40421</td>
<td>0.19</td>
</tr>
<tr>
<td>SQ+A453, t&lt;0.3h</td>
<td>160</td>
<td>1.59</td>
<td>1.05</td>
<td>0.40402</td>
<td>0.40424</td>
<td>0.22</td>
</tr>
<tr>
<td>SQ+A483, t&lt;0.1h</td>
<td>190</td>
<td>1.59</td>
<td>1.05</td>
<td>0.40402</td>
<td>0.40431</td>
<td>0.29</td>
</tr>
<tr>
<td>SQ+A423, t&gt;200h</td>
<td>130</td>
<td>0.11</td>
<td>0</td>
<td>0.40490</td>
<td>0.40510</td>
<td>0.20</td>
</tr>
<tr>
<td>SQ+A453, t&gt;100h</td>
<td>160</td>
<td>0.15</td>
<td>0</td>
<td>0.40489</td>
<td>0.40512</td>
<td>0.23</td>
</tr>
<tr>
<td>SQ+A483, t&gt;10h</td>
<td>190</td>
<td>0.27</td>
<td>0</td>
<td>0.40483</td>
<td>0.40511</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table III: Lattice parameters of the Al-rich phase as measured (\( a^e \)) and as calculated for strain free specimens (\( a^d \)). The difference, \( \Delta a^m \), is ascribed to misfit.
Below the eutectic temperature the solid solubility of Al in the Si-rich phase in binary Al-Si is smaller than $10^{-5}$ \((22)\). The maximum solid solubility of Cu in the Si-rich phase in binary Si-Cu is about $2 \times 10^{-5}$ \((23)\). These amounts of atoms dissolved in the Si-rich phase are too small to cause any measurable change in the lattice parameter. Also in the ternary system the solubilities of Al and Cu in the Si-rich phase can be considered to be negligible \((24)\). Thus, the lattice parameter of the Si-rich phase is not influenced by dissolved atoms.

### 4.3 Comparison of observed misfit strains with model predictions

In our case the image stress is mainly caused by misfitting Si particles, but also misfitting $\theta$ and/or $\theta'$ phase particles might contribute to the image stress. The volume fraction of Si and $\theta/\theta'$-phase precipitates, $y_{Si}$ and $y_{Cu}$, can be calculated from $x_{Si}$ and $x_{Cu}$ using the chemical composition of the alloy and the densities of the phases, 0.100 mole/cm$^3$, 0.083 mole Si/cm$^3$ and 0.037 mole Cu/cm$^3$ for the Al-rich phase, the Si phase and the Al$_2$Cu phases, respectively. (Actually, the density of the $\theta'$ phase, 0.035 mole Cu/cm$^3$, is slightly lower than the density of the $\theta$ phase, 0.037 mole Cu/cm$^3$. This small difference is neglected.) Little is known concerning the effect of misfitting $\theta$ and/or $\theta'$ phase particles on the lattice parameter of the Al-rich phase. Since no data on the elastic constants of these phases or values for the thermal expansion of $\theta'$ phase are known, we will use the following assumptions to be able to estimate this effect:

- the C constant for $\theta$ and $\theta'$ phase particles in the Al-rich matrix is (approximately) equal to the one for Si in Al
- the coefficient of thermal expansion of $\theta'$ phase is equal to that of $\theta$, namely 17.2 $10^{-6}$ K$^{-1}$ \((24)\)

From this follows directly that for the Al-1.3at\%Cu-19.1at\%Si alloy, the effect of misfitting Al$_2$Cu particles on $\rho_i$ is always at least one order of magnitude smaller than the effect of misfitting Si particles. For this reason we will neglect the contribution of these misfitting particles to the image stress.

Finite element analysis of misfit stresses in a two dimensional aluminium-based composite with inclusions of a size similar to the Si particles in our alloy indicate that disturbance of the average macrostress at the surface occurs in a layer of about 7 $\mu$m \((25)\). The penetration depth of X-rays in aluminium is much larger, and the effect of surface relaxation on the stresses determined by X-ray diffraction are about 2% \((25)\). Considering the accuracy of our lattice parameter determinations, surface relaxation effects are negligible (see also Ref. 26).

For the LQ+A423 specimen the penetration depth of the Cu K$_{\alpha}$ X-rays in aluminium (about 75 $\mu$m) is larger than the thickness of the sample (about
50 μm). Hence, the Δa_m calculated for this specimen is an average over the entire specimen. One might be inclined to think that variations of (the hydrostatic component of) the stresses over a range of about 100 to 200 μm below the surface of the SQ+A specimens, for which the diameter (500 μm) is much larger than the penetration depth of the X-rays, can significantly influence the measured lattice parameters. However, the fact that Δa_m calculated for the LQ423 specimen is within experimental error equal to the one calculated for the SQ+A423 specimen (see Table III), indicates that also for SQ+A specimens the long range variations of the stresses (if present) do not significantly influence the lattice parameters.

Thus, the lattice parameter shifts caused by the misfit stresses, Δa_m, can be obtained directly from the image stress and the compressibility modulii. For the elastically deforming part of the matrix it holds:

$$\frac{\Delta a_m}{a_A} = \frac{p_i}{3K_A}$$  \hspace{1cm} (17)

The stress in the inclusion is the sum of the image stress and p_B. Hence it holds:

$$\frac{\Delta a_B}{a_B} = \frac{p_B + p_i}{3K_B}$$  \hspace{1cm} (18)

A problem in the evaluation of the formulas for the misfit stresses is the anisotropy of aluminium and silicon. The theory described in Section 4.1, which is based on non-interacting stress fields and isotropy of inclusions and matrix, predicts that the inclusions are in a state of hydrostatic stress. In that case the strains in the Si particles are determined solely by the S_{11} and S_{12} elastic compliances of the Si inclusion. Interaction of stress fields and anisotropy of the phases in the alloy will cause deviations from the pure hydrostatic stress state in the inclusions. Providing that these disturbances are small it is justified to obtain the elastic constants of the Si inclusions from the S_{11} and S_{12} compliances. The anisotropy of aluminium is relatively small. For this reason the elastic constants of polycrystalline aluminium are used for the calculations. The yield strength of the Al-Si-Cu alloy was estimated to be equal to the yield strength of an Al-1.6at%Cu in the T4 condition (200 MPa, see Ref. 24). The material property values used in this work are gathered in Table IV.

In Fig. 4 the experimental values for Δa_m_{Al}/a_{Al}, as obtained in the previous section, are plotted as a function of the temperature drop ΔT. In this figure the Al-rich phase lattice parameter shift for purely elastic accommodation (obtained from Eqs. 3-5 and 17) is represented by the straight line through the origin. In the case of plastic accommodation (Eqs. 9-13 and 17) the average lattice parameters of the elastically deforming part of the matrix and of the plastically deformed part of the matrix are different. Hence, in Fig. 4 two lattice
parameter shifts are given. One curved line represent $\Delta a_{\text{Al}}^{m}/a_{\text{Al}}$ in the elastically deforming part of the matrix (the part with the largest lattice parameter), while the other one gives the average value of $\Delta a_{\text{Al}}^{m}/a_{\text{Al}}$ as obtained from the average volume change of the entire matrix (plastically and elastically deforming zones). It should be noted that since the microstrains in the plastic zones may be different from those in the elastic zone, this average value of $\Delta a_{\text{p}}/\Delta a_{\text{Al}}$ of the matrix may deviate from the lattice parameter shift obtained from measurement of the diffraction angle corresponding to peak intensities in the diffraction pattern.

Table IV: Elastic constants, yield strength and coefficients of thermal expansion used in this work. The elastic constants of Si are obtained from the $S_{11}$ and $S_{12}$ compliances given by Smithells (15). For the elastic constants of the Al-rich matrix values for polycrystalline pure aluminium were used (see Ref. 15). The yield strength of the Al-Si-Cu alloy was estimated to equal the yield strength of Al-1.7at%Cu in the T4 condition (24).

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$</th>
<th>$K$</th>
<th>$\mu$</th>
<th>$\sigma_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10^{-6} K^{-1}</td>
<td>GPa</td>
<td></td>
<td>MPa</td>
</tr>
<tr>
<td>matrix Al-Cu-Si</td>
<td>23.5</td>
<td>69</td>
<td>27</td>
<td>200</td>
</tr>
<tr>
<td>Si</td>
<td>3.0</td>
<td>99</td>
<td>51</td>
<td>-</td>
</tr>
</tbody>
</table>

It is clear that for $\Delta T < 200$ K, the observed values are much higher than the theoretical predictions for both models. For these low values of $\Delta T$, $\Delta a_{\text{Al}}^{m}/a_{\text{Al}}$ appears to be proportional to $\Delta T$. However, due the relatively small range of $\Delta T$ values studied, and the relatively large uncertainties in the determination of $\Delta a_{\text{Al}}^{m}$, this proportionality can not definitely be established. Alternatively one could suggest that, if the observed deviation from the model predictions is caused by some kind of non-ideal plastic behaviour of the matrix, $\Delta a_{\text{Al}}^{m}/a_{\text{Al}}$ for lower values of $\Delta T$ would correspond to the model prediction for pure elastic accommodation. Then $\Delta a_{\text{Al}}^{m}/a_{\text{Al}}$ would not be proportional to $\Delta T$ for the entire temperature range below 200 K. In order to clarify this point, additional Dbs experiments were performed on a specimen which was aged for 4, 24 and 200 hours at 365 K and subsequently quenched in water. For these experiments the specimen which was previously aged 512 h at 453 K was chosen. The additional ageing at 365 K failed to produce any significant changes in either the Al-rich phase or the Si-rich phase lattice parameter. Apparently the ageing temperature of 365 K is too low to relieve the stress state that was introduced by
quenching from the initial ageing temperature of 453 K, and after subsequent cooling to room temperature this stress state was again restored. In view of this, further experiments in this temperature range were abandoned.

Fig. 4: Measured data and model predictions of the lattice parameter shift of the Al-rich phase due to misfit accommodation. The measured data for underaged and for overaged Al-Cu-Si alloys are obtained from Table III. For the case of elastic/plastic accommodation both the lattice parameter shift of the elastically deforming part of the matrix and the average lattice parameter shift of the matrix (as obtained from the average volume change of the matrix) are given. For $\Delta T < 84$ K no plastic accommodation occurs according to the von Mises criterion.

Table V gathers the values for the misfit effects on the Si-rich phase lattice parameter based on the theory for elastic and for elastic/plastic accommodation (Eqs 9-13 and 18), as well as the experimentally observed values (for the SQ+A specimens the average Si-rich phase lattice parameter shift during ageing is given). It is observed that the elastic model predictions are significantly higher than the observed values. The calculated values for the elastic/plastic model correspond much better to the observed values but also in this case differences remain.
Table V: Comparison of measured Δa_{Si}/a_{Si} values with theoretical predictions for the Al-1.3at\%Cu-19.1at\%Si alloy.

<table>
<thead>
<tr>
<th>ΔT (K)</th>
<th>r_p/a</th>
<th>-Δa_{Si}/a_{Si} elastic 10^{-4}</th>
<th>-Δa_{Si}/a_{Si} elastic/plastic 10^{-4}</th>
<th>-Δa_{Si}/a_{Si} measured 10^{-4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>1.16</td>
<td>5.8</td>
<td>5.1</td>
<td>3.7±0.6</td>
</tr>
<tr>
<td>160</td>
<td>1.24</td>
<td>7.1</td>
<td>5.6</td>
<td>4.8±0.6</td>
</tr>
<tr>
<td>190</td>
<td>1.31</td>
<td>8.5</td>
<td>6.1</td>
<td>6.4±0.6</td>
</tr>
<tr>
<td>360</td>
<td>1.60</td>
<td>15.4</td>
<td>7.2</td>
<td>4.3±0.6</td>
</tr>
<tr>
<td>500</td>
<td>1.78</td>
<td>22.3</td>
<td>7.2</td>
<td>10.0±0.6</td>
</tr>
</tbody>
</table>

The comparisons between theoretical models and measurements made above point at some significant discrepancies. Also for several other Al-based composites the predictions of Esbshley type models for the stress in matrices due to elastic misfit accommodation are lower than the measured stresses (27, 28, 29, 30). In Fig. 5 the lattice parameter shifts for the elastic-plastic model divided by those for the pure elastic model, Δap_{pl}/Δa_{el}, are given as a function of the yield strength of the matrix for ΔT = 153 K. This figure again shows that the lattice parameter of the elastically deforming zone is only marginally lower for the elastic-plastic accommodation model as compared to the elastic accommodation model. This implies that the higher than predicted values measured for the Al-rich phase lattice parameter shifts can not result from an inaccurate estimation of the yield strength of the matrix. Fig. 5 further shows that the lattice parameter shift in the plastic zone is less than in the elastic part of the matrix. This effect becomes larger when σ_y increases. This implies that the higher than predicted values measured for the Al-rich phase lattice parameter shifts can not be the result of the assumption that the lattice parameter of the plastically deforming zone can be neglected. Fig. 5 further demonstrates that the yield strength of the matrix has a profound influence on the lattice parameter shift of the inclusion.

The elastic strain energy stored in a composite, E_{com}, is the sum of the elastic energy stored in the inclusion, E_{inc}, the elastic energy stored in the plastic zone, E_{pl}, and the elastic energy stored in the elastic zone, E_{el}, i.e.:

\[ E_{\text{com}} = E_{\text{inc}} + E_{\text{pl}} + E_{\text{el}} \]  \hspace{1cm} (19)
The lattice parameter shifts for the elastic-plastic model divided by those for the pure elastic model as a function of the yield strength of the matrix for $\Delta T = 153$ K. Four lattice parameter shifts are given: the lattice parameter shift of the elastically deforming part of the matrix (only influenced by $p^1$), the average lattice parameter shift of the plastically deforming part of the matrix (as obtained from the average volume change of that part of the matrix), the average lattice parameter shift of the matrix (as obtained from the average volume change of the matrix) and the average lattice parameter shift of the inclusion. The elastic constants used for the calculations are given in Table IV. Due to severe overlap of plastic zones, the model predictions for low values of $\sigma_y$ (dotted lines) are probably inadequate.

Expressions for these elastic energies for the case of one inclusion in an infinite matrix are given by Lee et. al (18). Since the energy density in the infinite matrix decreases rapidly with increasing distance from the inclusion (the energy density is proportional to $r^6$, see Ref. 31), the influence of interactions of strain fields on $E_{\text{com}}^c$ in the case of a real (multi-particle) composite are expected to be negligible. Then these equations can be applied to a real multi-particle composite. For the case of pure elastic accommodation around one particle in an infinite matrix (i.e. $y_B=0$), the elastic strain energy in a composite per unit volume of misfitting inclusion, $E_{\text{el}}^c$, is given by (see Ref. 18):

\[ E_{\text{el}}^c = \ldots \]
\( E_{\text{el}}^{\text{com}}(y_B=0) = \frac{6 \mu_A e^2}{K_B - 1 + \eta^{-1}} K_A \)  \hspace{1cm} (20)

This energy can be considered to be the maximum elastic strain energy that can be stored in a composite in the absence of a hydrostatic stress component in the matrix. For the case of a finite volume fraction of particles the image force adds extra terms to the total energy of the composite:

\[ E_{\text{el}}^{\text{comp}} = E_{\text{el}}^{\text{com}}(y_B=0) + \frac{1}{2} \frac{p^2}{K_A y_B} (1-y_B) + \frac{1}{2} \frac{(p^i+p_B)^2 - p_B^2}{K_B} \]

\[ = E_{\text{el}}^{\text{com}}(y_B=0) + \frac{1}{2} p^2 \left[ \frac{y_B}{K_A} + \frac{1}{K_B} \right] + \frac{p^i p_B}{K_B} \]  \hspace{1cm} (21)

(in Eqs. 20-22 the elastic energies are given per unit volume of misfitting inclusion). Also for the case of partially plastically accommodated inclusions, the image force adds extra terms to the energy of the composite. Approximating the hydrostatic component of the stresses in the plastically deformed zone by \( \frac{1}{2} p_B + \frac{1}{3} \sigma_Y \) (the average of the hydrostatic components at \( r = a \) and at \( r = r_p \)) it follows:

\[ E_{\text{pe}}^{\text{comp}} = E_{\text{pe}}^{\text{com}}(y_B=0) + \frac{1}{2} \frac{p^2}{K_A y_B} (1-\left(\frac{r_p}{a}\right)^3 y_B) + \frac{1}{2} \frac{(p^i+p_B)^2 - p_B^2}{K_B} + \]

\[ + \frac{1}{2} \left( \frac{p^i}{2} + \frac{1}{3} \sigma_Y \right)^2 - \frac{1}{2} \left( \frac{p_B + \frac{1}{3} \sigma_Y}{2} \right)^2 \left( \left(\frac{r_p}{a}\right)^3 - 1 \right) \]

\[ = E_{\text{pe}}^{\text{com}}(y_B=0) + \frac{1}{2} \frac{p^2}{K_A y_B} (1-y_B) + \left( \frac{p^2}{2} + 2 \frac{p_B p^i}{K_B} + \frac{p^i (p_B + \frac{2}{3} \sigma_Y)}{2 K_A} \right) \left( \left(\frac{r_p}{a}\right)^3 - 1 \right) \]

\[ = E_{\text{pe}}^{\text{com}}(y_B=0) + \frac{1}{2} p^2 \left[ \frac{y_B}{K_A} + \frac{1}{K_B} \right] + \frac{p^i}{2} \left( \left(\frac{r_p}{a}\right)^3 - 1 \right) \frac{(p_B + \frac{2}{3} \sigma_Y)}{2 K_A} + \frac{p_B}{K_B} \]  \hspace{1cm} (22)

Now we will apply these equations to consider the energy balance of our composite for the case that \( \Delta T = 130 \text{ K} \). Using the expressions given by Lee et. al (18) it follows:

\[ E_{\text{pe}}^{\text{com}}(y_B=0) / E_{\text{el}}^{\text{com}}(y_B=0) = 0.86 \hspace{1cm} (\Delta T = 130 \text{ K}) \]  \hspace{1cm} (23)

Hence 14% of the elastic energy that is available in the case of pure elastic accommodation will be released as a result of plastic deformation of the matrix around the inclusion. Part of the released energy will be converted to heat and will be lost to the environment. Another part will be used to create defects like dislocations, vacancies and subgrains in the plastically deformed zone (32). These defects in itself will be new sources of misfit. Dislocations and vacancies, which both increase the specific volume of metals (33, 34), will increase the total
misfit associated with inclusion and plastically deformed zone around it, and will consequently increase the image force. From Eqs. 20-23 it follows that if all energy released by plastic deformation would be used to increase $p^i$, the image force would increase with a factor 2.5. This shows that the observed lattice parameter shifts for $\Delta T = 130$ K are consistent with preservation of energy, provided that the energy associated with the microstrains around defects in the plastic zone and the energy lost due to heat production are both significantly lower than the energy related to the image stress. Similar calculations show that also for higher $\Delta T$ values the lattice parameter shifts are consistent with preservation of energy under similar provisions. For instance at $\Delta T = 190$, $p^i$ can be increased by a factor 3.3 if all released elastic energy is used to increase $p^i$.

The calculations presented above show that while the measured lattice parameter shifts do not agree with the lattice parameter shifts predicted by the model based on ideal plastic deformation, these measured values are within the limits given by the requirement of preservation of energy. This indicates that defects created in the plastic zone (i.e. non-ideal plastic deformation) might explain the measured lattice parameter shifts, provided that both the energy associated with the microstrains around defects in the plastic zone and the energy lost due to heat production are lower than the energy related to the image stress. It might on first inspection be odd that the energy associated with the microstrains around defects could be lower than the energy related to the image stress, since for elastically accommodated, spherical inclusions in a finite matrix the energy associated with the microstrains is much larger than energy related to the image stress (this follows from Eqs. 3-5, 20 and 21). Here it should be noted that the driving force for defect creation in a plastic zone is the reduction of the total elastic energy. Thus the various types of defects, which all have different stress fields around them, will be arranged in such a way that the elastic energy is minimized and the energy associated with the microstrains can thus be much lower than for the case of randomly distributed spherical particles.

An indication that the transfer of energy associated with the microstrains to energy associated with the image stress during the creation of defects in the plastically deformed zone, as suggested above, can occur in composites is found in work by Mittemeijer and coworkers (27, 35). They have shown that in binary Al-Si alloys quenched from 447 K to room temperature, the average macrostrains are higher than the model predictions based on pure elastic accommodation, while the microstrain is lower than predictions based on the same model. Further indications for this energy transfer can be obtained from
the work of Ericsson et al. (36), who studied the line broadening and the average stresses in a 6061 alloy reinforced with 20.5 vol% SiC whiskers after quenching with a temperature drop, $\Delta T$, between 180 and 430 K. In that work it is shown that the line broadening, which is related with the microstrain energy, is nearly independent of $\Delta T$, while the average hydrostatic pressure, which is related to macrostrain energy, varies strongly and in a rather complex manner with $\Delta T$.

It is noted that the Si-rich phase lattice parameter after solid quenching depends strongly on the storage temperature (see Table II). In the specimens which were stored at room temperature after solid quenching the lattice parameter shift of the Si-rich phase was largest of all heat treated specimens studied. Storage in liquid nitrogen increases the lattice parameter of the Si-rich phase to values close to the equilibrium value of pure silicon. Since dissolved atoms do not significantly influence the lattice parameter of the Si-rich phase this can only be explained by a decrease in elastic stresses due to the storage in liquid nitrogen. Although the effect is less drastic as in the case of the Si-rich phase also the lattice parameter of the Al-rich phase is influenced by the storage temperature. In this case the lattice parameter is decreased by storage in liquid nitrogen (see Table II). Ericsson et al. (36) have observed that quenching in liquid nitrogen reduces the internal stresses in the aluminium matrix of a 6061 aluminium alloy reinforced with SiC whiskers by about 70% as compared to quenching in water at room temperature. Since also the coefficient of thermal expansion of SiC is much lower than that of Al this relaxation of the stresses is thought to result from the same mechanism.

In attempting to explain the observed effect of storage in liquid nitrogen it is first noted that the theory incorporating plastic accommodation as given in Section 4.1 can in this case not be used since i) large overlap of plastic zones is expected to occur, and ii) the size of the plastic zone is not determined by the misfit at room temperature but by the misfit at the boiling point of liquid nitrogen. From Eqs. 3, 4, 5 and 18 it follows that pure elastic accommodation of misfits introduced by quenching to room temperature would decrease the Si-rich phase lattice parameter by 0.0118 nm. The observed deviation from the unstrained lattice parameter is 0.0053 nm (see Table II), indicating that about 55% of the misfit is relaxed by plastic deformation. By storing solid-quenched specimens in liquid nitrogen (boiling point 77 K), the thermal misfit which has built up during quenching to room temperature is further increased. It is expected that also this additional misfit is for a large part accommodated by plastic deformation. When, after the storage period, the temperature of these specimens is increased to room temperature, the balance of misfit
accommodation mode (initially 55% plastic and 45% elastic deformation) is altered. Now plastic deformation introduced by quenching in liquid nitrogen can diminish the level of elastic accommodation. In fact Si-rich phase lattice parameter after storage in liquid nitrogen indicates that nearly no elastic deformation is present in the Si-particles.

4.4 Precipitation

The results of the previous section indicate that the amount of plastic accommodation in solid-quenched specimens is significantly higher than in solid-quenched and subsequently artificially aged specimens. Since dislocations increase the hardness of the Al-matrix, this explains the observed drop in hardness of SQ specimens after a short time of artificial ageing (see Fig. 3). Fig. 3 further shows that during the precipitation of copper and silicon atoms from the Al-rich phase on ageing at 423 K the hardness of the alloy increases. Precipitation of silicon is generally thought not to cause a hardness increase (24). The increase in hardness coincides with the detection of the semi-coherent θ' phase. This indicates that the formation of θ' precipitates is the main hardening mechanism in the Al-Cu-Si alloy. The hardness of the Al-Cu-Si specimen naturally aged for 14 months after solid quenching is about 10 HV higher than that of the solid-quenched specimen. It has been shown before that on natural ageing for several months after solid quenching, GP zones are formed in this alloy (13). These zones are thought to be the cause of the observed hardness increase on natural ageing. After about 5 hours ageing at 423 K, the difference in hardness between the two specimens is about the same as in the naturally aged conditions. This indicates that the zones do not dissolve during 5 hours ageing (the ageing temperature is below the GP-zone solvus in Al-Cu). On continued ageing the difference in hardness between the two specimens gradually decreases. This might indicate that GP zones gradually dissolve (in DSC experiments on room temperature aged Al-Cu-Si alloy the GP zones start to dissolve from 360 K onwards, see Ref. 13). Further, the gradual decrease in the difference in the hardness of the two specimens might partly be due to the formation of θ' phase, since the contribution of this phase to the hardness is more important than the contribution of GP zones. Both specimens reach essentially the same maximum hardness (135 HV) after about 60 hours of ageing. This indicates that pre-ageing at room temperature does not significantly influence the formation of the θ' phase.

In solid-quenched binary Al-Si and Al-Cu alloys, the precipitation of alloying elements from the Al-rich phase occurs at different ageing times. In SQ Al-Si alloys the precipitation of Si occurs between about 0.01 and 0.2 h at 492 K (17).
On ageing a SQ alloy with about the same percentage of Cu atoms dissolved in the Al-rich phase (Al-1.7at%Cu) at the same temperature, the precipitation of the θ' phase starts after about 0.5 h, and is completed in about 10 h (37).

The increase of the Al-rich phase lattice parameter on ageing of the SQ Al-Si-Cu alloy is due to the precipitation of Cu and Si atoms from the Al-rich phase. A comparison of the times at which θ' and θ phase lines appear during ageing (Table II) with the lattice parameter change during ageing (Fig. 1), shows that nearly the entire variation of the lattice parameter change is caused by θ' and Si formation. The curves representing the variation of the lattice parameter as a function of the ageing time are very smooth and do not show any plateau or multiple inflection points. This corresponds to precipitation experiments performed on the same alloy by differential scanning calorimetry (DSC), which show that the precipitation of copper and silicon gives rise to one single heat evolution peak (13). This indicates that the precipitation of Si phase and the θ' phase strongly overlaps. During ageing at 493 K, precipitation occurs between about 0.1 and 4 h. This is intermediate between the ageing times required for precipitation in the respective binary systems (see above). The above points at some interaction between the precipitation of Si phase and the θ' phase.

A way in which the precipitation of the Si phase and the θ' phase can be linked is through misfit stresses. Since the volume occupied by a silicon atom in the Si-rich phase is larger than the volume occupied by the same atom dissolved in the Al-rich phase (the linear misfit parameter εv is about 6.4%, see Ref. 27), the precipitation of silicon atoms from the Al-rich phase will result in misfit stresses. The formation of θ'-phase precipitates causes misfit stresses in the direction normal to the θ' plate (38). It has been shown by Perovic et al. (39, 40) that, through minimizing the interaction term of the strain fields, the formation of new θ'-phase precipitates is facilitated by the elastic strain fields of existing θ'-phase precipitates. This interaction between the strain fields of existing precipitates and the strain field of a newly forming precipitate leads to the formation of linear arrays of plate shaped θ' precipitates in the first stage of ageing of Al-Cu alloys, as were indeed observed by TEM (40). Also the strain fields around Si particles and those around θ' precipitates can interact to facilitate the formation of either of these phases. This is illustrated in Fig. 6 in which two orientations of a plate-shaped θ' precipitate relative to a spherical Si precipitate are depicted. Since θ' is semicoherent, the misfit of the θ'-phase plate normal to the plate is much larger than the misfit parallel to the plate. Since in the nucleation stage the precipitates are to small to induce plastic accommodation of misfit (see 18), only elastic stresses are considered. Then the 'surface-normal' orientation (Fig. 6a) is energetically favourable in the
case that the sign of the misfit is equal for both precipitates. The 'surface-parallel' orientation (Fig. 6b) is energetically favourable in the case where the misfits are of opposite sign (see also Ref. 12). This shows that the strain fields around Si precipitates can lower nucleation barriers for 0'-phase formation and vice versa. This might explain why the precipitation of Cu and Si from the Al-rich phase in the Al-Cu-Si alloy proceeds synchronous.

![Diagram](image)

Fig. 6: Two possible orientations of a plate shaped particle relative to a spherical particle: a) the surface-normal orientation and b) the surface-parallel orientation.

Due to the strong overlap between the Si and Cu precipitation processes it is not possible to obtain the extent of the two precipitation processes separately. It
is however possible to define the complement of the extent of the combined reaction by:

\[ 1-x(t) = \frac{(a_{A1}(t) - a_{A1}(t=\infty))}{(a_{A1}(t=0) - a_{A1}(t=\infty))} \]  

(24)

in which \(a_{A1}(t)\) is the Al-rich phase lattice parameter during ageing, \(a_{A1}(t=\infty)\) is the Al-rich phase lattice parameter after completion of precipitation and \(a_{A1}(t=0)\) is the Al-rich phase lattice parameter during ageing before the start of precipitation. Arrhenius plots were constructed for \(x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7\) and \(0.8\). The correlation coefficients of the straight lines through these plots are all satisfactory close to unity (all \(R^2\) are between 0.95 and 0.98). The average value of the apparent activation energy for the combined process was 0.95±0.06 eV. No significant variations with the extent of the reaction (i.e. with \(x\)) were observed. This last observation indicates that the interaction between the two precipitation reactions is very strong and that as consequence the activation energies of the two processes are about identical. The activation energy agrees well with the apparent activation energy of the combined Si and \(\theta'\) precipitation as obtained from DSC experiments on the same alloy (1.00 eV, see 13). The apparent effective activation energy for precipitation in Al-Cu-Si is intermediate between the apparent activation energy of Si precipitation in solid-quenched Al-Si alloys (0.89 eV, see Ref. 41) and the apparent activation energy of \(\theta'\) formation in solid-quenched Al-Cu (about 1.1 eV for \(T < 550\) K, see Ref. 36).

5 Conclusions

X-ray diffraction and hardness measurements on a quenched and aged Al-1.3at\%Cu-19.1at\%Si alloy showed:

- Due to dissolved Cu and Si atoms the Al-rich phase lattice parameter after quenching is smaller than its equilibrium value.

- For the homogenized Al-1.07at\%Cu-1.01at\%Si alloy the effects of dissolved Cu and Si atoms on the lattice parameter of the Al-rich phase are independent and additive. It is assumed that additivity also holds for other ternary compositions.

- During ageing after solid quenching the Al-rich phase lattice parameter increases due to precipitation of Si and Cu atoms.

- During isothermal ageing of the solid-quenched Al-1.3at\%Cu-19.1at\%Si alloy the Cu and Si atoms precipitate simultaneously.

- The observed age hardening of the Al-1.3at\%Cu-19.1at\%Si alloy is caused by \(\theta'\) phase precipitation.

- Due to misfit after quenching from heat treatment temperatures all lattice parameters are influenced by stresses in the specimen.
The model describing the stress state around a single misfitting spherical inclusion in an infinite matrix which shows ideal plastic behaviour as given by Lee et al. (18), is extended to describe the stress state in a finite composite. This model predicts an average hydrostatic stress in the matrix which is somewhat lower than in the case of pure elastic accommodation.

Comparison of the model incorporating elastic accommodation and the model incorporating ideal plastic accommodation with measured stresses show significant discrepancies, especially for the low temperature range (ΔT < 200 K).

Elastic stresses in the solid-quenched Al-1.3at%Cu-19.1at%Si alloy at room temperature are reduced by quenching in liquid nitrogen.

References

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Part 2. Precipitation in Al-Si-Cu-Mg alloys reinforced with aluminium oxide particles

Chapter VI Hardness, melting reactions and heat treatment of Al-Si-Cu-Mg alloys reinforced with aluminium oxide particles

Chapter VII Precipitation in a solid-quenched, particle reinforced Al-Si-Cu-Mg alloy: phase identification and kinetics

Chapter VIII Lattice parameter and hardness variations resulting from precipitation and misfit accommodation in a particle reinforced Al-Si-Cu-Mg alloy
CHAPTER VI

HARDNESS, MELTING REACTIONS AND HEAT TREATMENT OF
AL-SI-CU-MG ALLOYS REINFORCED WITH
ALUMINIUMOXIDE PARTICLES

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Abstract

Results of a study mainly by Differential Scanning Calorimetry (DSC) on an
Al-20at%Si-1.5at%C u-1at%Mg (ASCM) alloy with 0, 2.5, 5, and 10 vol% 
aluminiumoxide (Al2O3) particles are reported. The alloys were produced by
gas atomisation, mixing with particles and subsequent extrusion. DSC scans of
the as-extruded alloys showed no precipitation reactions. Between 780 and 800 K
the melting of the Q (Al5Cu2Mg8Si6) and the Al7Cu2Fe (ASCM contains a small
amount of iron) phases was observed. On heating the matrix melts between
about 810 K to 840 K, subsequently silicon dissolves in the melt. The
microstructure of the AE alloys with Al2O3 particles (size about 1 to 6 µm)
showed no clustering of Al2O3 particles. During DSC after solid quenching the
formation of GPB zones was observed. After dissolution of the zones, Q phase
and θ phase precipitate. Hardness measurements show, that both GPB zones
and Q phase precipitates can improve the room-temperature-strength of the
ASCM alloy by about 75%, compared to the as-extruded alloy. Heat treatments
producing GP or GPB zones (ageing at temperatures below about 440 K) do not
contribute to the strength of the alloy at elevated temperature. Q-phase
precipitates improve the hardness after an additional overageing treatment at
473 K by about 60% (as compared to the as-extruded alloy).
1. Introduction

The wear resistance of aluminium alloys can be improved by the introduction of finely dispersed hard particles to the alloy (1, 2). For example, a fine dispersion of silicon particles can be obtained by rapid solidification of a molten aluminium alloy with a high silicon content (3). A dispersion of ceramic particles in aluminium alloys can be obtained via various production routes, e.g. by compocasting or by mixing particles with aluminium alloy powders followed by extrusion. Metals reinforced by dispersed (ceramic) particles are generally referred to as Metal Matrix Composites (MMCs). Their increased wear resistance, low thermal expansion and improved high-temperature strength, make MMCs attractive for applications like parts of combustion engines.

In this contribution, results of a study on the heat treatment of Al-20at%Si-1.5at%Cu-1.1at%Mg (ASCM) alloys reinforced with 0, 2.5, 5, and 10 vol% aluminiumoxide (Al$_2$O$_3$) particles are presented. These alloys combine the presence of two reinforcing components (silicon and Al$_2$O$_3$ particles) with the possibility of age hardening of the Al-rich phase. Hence, an appropriate heat treatment is necessary to optimize the mechanical properties at room and elevated temperatures. The presence of dispersed particles in solid-quenched age-hardenable aluminium alloys generally influences the kinetics and sequences of precipitation processes, as compared to corresponding unreinforced alloys (4). Appropriate heat-treatment procedures for these alloys are, as yet, unknown. This applies for both the solution annealing treatment (temperature) and the age hardening (temperature and time). Therefore, it is necessary to establish appropriate solid-solution temperatures and age-hardening procedures for MMCs. Hence, melting and precipitation phenomena should be investigated. As melting and precipitation involve large enthalpy changes, differential scanning calorimetry (DSC) was used as the main investigation method. Beside, hardness measurements, optical microscopy and X-ray diffraction were applied as well.

2. Experimental Procedures

2.1. Production Route

The alloys under investigation were made available the Japanese firm Showa Denko K.K. The base alloy was rapidly solidified by gas atomisation, yielding fine powder (sizes range from 1 to 100 μm, with a median size of about
The cooling rate during gas atomisation is about $10^4$ to $10^6$ K/s (3). Subsequently, the powder was mixed with ceramic Al$_2$O$_3$ particles, in order to obtain mixtures with 0, 2.5, 5 and 10 volume percent of ceramic particles. Finally, the mixtures were extruded at about 670 K into round bars with a diameter of about 20 mm.

The chemical compositions of the extruded alloys are presented in Table I. The four alloys are indicated by ASCM0, ASCM2.5, ASCM5 and ASCM10, in which the last number refers to the volume percentage Al$_2$O$_3$ particles. The main impurities in the base alloy (as measured by X-ray fluorescence) are: Ni (~0.02 at%), Zn (~0.01 at%), Ti (~0.006 at%) and Cr (~0.005 at%).

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>Al$_2$O$_3$ Vol %</th>
<th>Si Alloy wt%</th>
<th>Si Base at%</th>
<th>Cu Alloy wt%</th>
<th>Cu Base at%</th>
<th>Mg Alloy wt%</th>
<th>Mg Base at%</th>
<th>Fe Alloy wt%</th>
<th>Fe Base at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASCM0</td>
<td>-</td>
<td>20.2</td>
<td>19.9</td>
<td>3.47</td>
<td>1.52</td>
<td>0.96</td>
<td>1.10</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>ASCM2.5</td>
<td>2.5</td>
<td>19.7</td>
<td>20.2</td>
<td>3.44</td>
<td>1.56</td>
<td>0.89</td>
<td>1.05</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>ASCM5</td>
<td>5.2</td>
<td>18.9</td>
<td>20.1</td>
<td>3.32</td>
<td>1.57</td>
<td>0.88</td>
<td>1.09</td>
<td>0.23</td>
<td>0.12</td>
</tr>
<tr>
<td>ASCM10</td>
<td>10.4</td>
<td>16.9</td>
<td>19.6</td>
<td>2.97</td>
<td>1.52</td>
<td>0.77</td>
<td>1.03</td>
<td>0.20</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*) Calculated from measured weight percentages using the densities of the ASCM base alloy, 2.67 g/cm$^3$ and of α-Al$_2$O$_3$, 3.98 g/cm$^3$ (6).

2.2. Differential Scanning Calorimetry

A DuPont 910 differential scanning calorimeter was used. Inside the DSC cell a protective gas atmosphere was maintained by flushing with 99.999% pure argon (flushing started 10 min before the experiment). Both specimen and reference were enclosed in an aluminium pan with an aluminium cover. Heating rates between 0.5 and 40 K/min were used. Per specimen three scans were performed; the second after cooling at about 10 K/min and the third after cooling at 2 K/min. The calibration procedures and baseline corrections were described earlier (7).

2.3. Heat Treatment

Experiments were performed on specimens after various production stages and heat treatments. These are denoted as follows:
- **LQ:** liquid-quenched, gas-atomised powder (stored at room temperature).
- **AE:** as-extruded alloy (stored at room temperature).
- **SQ:** solution-annealed (10 min at 768 K) and quenched (in water at room temperature) AE specimen. The SQ specimens were stored at room temperature for 1 hour after quenching.
- **SQ NA(x h):** an SQ specimen aged at room temperature for x hours.
- **SQ DSC(y K):** an SQ specimen heated to y K inside the DSC cell at a heating rate 2 K/min, and subsequently cooled down to room temperature at about 10 K/min. This cooling rate is sufficiently fast (as compared to the heating rate) to avoid reactions during cooling.
- **SQ AA(z K):** an SQ specimen aged at room temperature for 4 days, and subsequently artificially aged at z K for 24 hours.

To investigate mechanical properties after a long-time application at elevated temperatures, hardness measurements were performed on selected specimens which were aged at 473 K for four days (essentially an additional overageing treatment, see Section 3.3). All artificial ageing treatments were performed in an oil bath with temperature control within 1.5 K.

### 2.4. Optical microscopy and hardness measurements

Vickers hardness (HV) was measured on polished surfaces parallel to the extrusion direction. The apparatus used was a Leitz-Durimet hardness tester with an indentation force of 0.981 N. The values reported are the average of ten determinations; the reported errors equal the standard deviation.

Jena Neophot 30 and Jena Neophot 2 optical microscopes were used to characterize the microstructures and the distribution of Al₂O₃ particles. Polished specimens were etched with a 1:1 mixture of Keller and Wilcox reagent and 5% Nital.

### 2.5. X-ray diffraction

For identification of phases, X-ray diffraction was performed using a Guinier camera. Diffraction patterns of the AE ASCM0 alloy at room temperature and of SQ ASCM0 during heating at a constant rate (0.5 K/min) from 293 to 773 K were recorded.
3. Results

3.1. Gas-atomised powders

DSC scans of the gas-atomised ASCM powder are presented in Fig. 1. During the first scan the heat flow is exothermic over almost the entire temperature range, except for a small endothermic effect in the temperature range 360 to 420 K. After this endothermic effect a clearly defined exothermic effect is observed, with peak temperature 480 K. Since this effect seems to overlap with an exothermic effect located around 570 K, the end temperature of the effect around 480 K is not clearly identifiable. The heat content of the effect around 480 K, $\Delta Q_{MP}$, is estimated by integration of the heat flow from 420 to 535 K. The value thus found is 607 J/mole ASCM powder. Beyond 590 K the heat flow continues to be exothermic. The heat flow in this temperature range does not show a clearly defined peak. In the second and the third runs no exothermic effects are observed. Instead, both runs show an endothermic effect beyond 550 K.

![DSC scans between 293 and 773 K on gas-atomized ASCM powder.](image)

Fig. 1: DSC scans between 293 and 773 K on gas-atomized ASCM powder.
After completion of the three runs the mass of the powder specimen was higher than at the start of the experiment. The increase amounted to 39±5 μg, which corresponds to 0.17% of the original mass of the specimen.

3.2. As-extruded alloys

Isothermal X-ray diffraction (at 298 K) reveals the presence of the following phases in the AE ASCM0 alloy: the Al-rich phase, the Si phase (diamond structure), the θ phase (Al2Cu), the Q phase (Al5Cu2Mg8Si6) and the Al7Cu2Fe phase.

In Figs. 2a and b optical micrographs of AE ASCM and ASCM10 are presented. The following observations are made:

i. Although bands along the extrusion direction seem to be enriched with Al2O3 particles (black colour), no clustering of Al2O3 particles is observed.

ii. The sizes of the irregular shaped Al2O3 particles range from about 1 to 6 μm, with an average of about 2 μm.

iii. Elongated Al2O3 particles are aligned along the extrusion direction.

iv. The Si-phase particles (dark grey), which are homogeneously dispersed in the Al-rich phase (light grey), have a grain size between about 1 and 10 μm, with an average of about 4 μm.

v. Also a third type of precipitate (grey) can locally be discerned. Considering the phase identification by X-ray diffraction, these are probably Q or Al7Cu2Fe-phase precipitates.

By increasing the etching time to about 1 min, the grain boundaries of the Al-rich phase become visible (pictures not presented here). The grain size of the Al-rich phase is about 5 μm.

In Fig. 3, taken from an AE ASCM0 specimen heated twice to 890 K, severe coarsening of silicon particles and clustering of the Al2O3 particles is observed.

DSC experiments were performed on AE ASCM0 and AE ASCM10. These experiments were aimed at determining a suitable temperature for solution annealing before solid quenching. During solution annealing, melting should be avoided and hence the temperature at which melting starts has to be known. Fig. 4 shows the first and the second DSC runs on AE ASCM0. For a temperature range of 750 to 860 K, Fig. 5 shows the second and the third DSC runs on AE ASCM10, which were performed after a first DSC run until 773 K. Note that in Fig. 5 only endothermic effects are observed, and that the effects are much larger than the ones shown in Fig. 4.
Fig. 2a and b: Optical micrographs of longitudinal sections of AE ASCM0 and ASCM10. Extrusion direction is horizontal. Etching time: 10 sec.
The effects shown in Fig. 5 are caused by melting reactions, while those in Fig. 4 are caused by dissolution reactions (see Section 4.2). The following observations are made:

i. No substantial exothermic effect is observed in the DSC scan of the AE alloys.

ii. Both the first and the second run of AE ASCM0 (Fig. 4) are dominated by an endothermic effect, which starts at 610 K. This endothermic effect seems to be divided into at least two subeffects: one effect continues up to about 750 K, while the other effect continues beyond 785 K.

iii. The melting of the SQ ASCM10 alloy is subdivided into several separate stages. Four melting reactions are indicated by A, B, C, and D (see Fig. 5). Effect C is by far the largest. Effect D seems to continue beyond the temperature range studied in this experiment.

Comparison of the DSC runs presented in Figs. 4 and 5 with DSC runs of AE ASCM10 performed at heating rate 20 K/min (not presented here) additionally shows:

iv. The end temperature of the first endothermic subeffect in Fig. 4 is largely uninfluenced by heating rate or Al₂O₃-particle content.

v. The peak temperatures of the melting reactions are independent of reactions heating rate or Al₂O₃-particle content.

For the temperature of solution annealing before solid quenching, a temperature below the start of melting should be selected. In order to have a
safety margin of about 10 K to the start of melting 768 K is selected as solution annealing temperature (see Section 4.2).

![Graph showing DSC scans](image)

Fig. 4: DSC scans of AE ASCM0 in the temperature range below 790 K.

3.3. **Solid-quenched and heat-treated alloys**

DSC scans of SQ ASCM0 and ASCM10 alloys are presented in Fig. 6. In line with literature data and on the basis of X-ray diffraction, the effects occurring in the DSC of scans these alloys are attributed to the following reactions (see Section 4.3 and (7)):

i. the formation of GPB (Al-Cu-Mg) zones,
ii. the dissolution of GPB zones,
iii. precipitation of the Q phase (Al₅Cu₂Mg₈Si₆),
iv. precipitation of the θ' and θ phases (both Al₂Cu),
v. the dissolution of the Q and θ phases.

Only effect i can be considered as a separated effect, the other effects show overlap. The influence of the presence of Al₂O₃ particles on the DSC curves of the SQ alloys is rather small. For a discussion of the influence of Al₂O₃ particles on the precipitation kinetics in SQ ASCM alloys, see Ref. 7.
Fig. 5: DSC scans of the AE ASCM10 alloy in the temperature range beyond 760 K. The second and the third run are presented; the end temperature of the first run was 773 K. All heat effects are endothermic. Note the large difference in heat flow scale as compared to Figs. 4 and 6.

The room-temperature hardness of SQ ASCM0 was measured after various heat treatments (see Section 2.3). The results are gathered in Figs. 7 and 8. In Fig. 7 the room-temperature hardness of SQ DSC specimens are plotted as a function of DSC end temperature, together with the room-temperature hardness of the same specimens after an additional overageing treatment (4 days at 473 K). In Fig. 8 the room-temperature hardness of SQ ASCM0 after various heat treatments is compared with the room-temperature hardness of the same specimens after the additional overageing treatment. The following observations are made.

i. The maximum hardness, both after initial heat treatment and after the additional overageing treatment, is obtained for the SQ DSC(487 K) specimen. This DSC end temperature corresponds to the end temperature of effect iii observed during the DSC scan.

ii. Natural ageing of SQ ASCM0 results in a remarkable increase of hardness.
iii. Artificial ageing of SQ ASCM0 for 24 hours at 393 K and at 433 K also yields a remarkable hardness increase.

iv. The additional overageing treatment considerably reduces the hardness of the the specimens (with the exception of the SQ DSC(575 K) specimen), but even then, the hardness of the heat treated specimens remains higher than that of the AE ASCM0 specimen.

v. After the additional overageing treatment the hardness of nearly all solid-quenched and subsequently aged specimens has dropped to about 120 HV. The only exceptions are SQ DSC(487 K) and SQ DSC (507 K) which retain a hardness of about 140 HV after additional overageing.

**Fig. 6:** DSC scans of SQ ASCM0 and SQ ASCM10.
4. Discussion

4.1. Gas-atomised powders

The liquidus of the Al-Si-Cu-Mg system (8) shows that during slow cooling of a molten Al-20at%Si-1.5at%Cu-1.1at%Mg alloy (the small amount of Fe present in the ASCM alloys will be neglected in this part of the discussion) the solidification starts with the following reactions:

\[ \text{liq} \rightarrow \text{Si} \quad (1) \]
\[ \text{liq} \rightarrow \text{Si} + \text{Mg}_2\text{Si} \quad (2) \]

During the completion of the solidification, the initially formed Mg$_2$Si will disappear again (Mg$_2$Si is not stable below about 790 K (8)), and the Q phase will form. This proceeds via the reaction (8):

\[ \text{liq} + \text{Mg}_2\text{Si} + \text{Si} \rightarrow \text{Q} + \text{Al} \quad (3) \]

Fig. 7: Room-temperature hardness of SQ DSC ASCM0 specimens as a function of the DSC end temperature (curve I). Also the hardness of these specimens after an additional overageing treatment (4 days at 473 K) is given as a function of the DSC end temperature (curve II).
Fig. 8: Room-temperature hardness of various heat treated specimens (black bars). For some of the specimens also the hardness after an additional overageing treatment (4 days at 473 K) is given (grey bars).

This peritectic reaction occurs at 802 K (8). Since above this temperature no copper containing phases are formed, it is assumed that above 802 K the solidification process can be described on the basis of the Al-Mg-Si phase diagram. From this diagram (8) follows that during cooling the Al-rich phase will start to form at 828 K with the following reaction:

\[ \text{liq -> Al+Si+Mg}_2\text{Si} \] (4)

During gas atomisation, the solidification rate is very fast: about $10^5$ K/sec (3). For the peritectic reaction 3, solid state diffusion is necessary. Since this process is relatively slow, it is expected that during rapid solidification the peritectic reaction 3 is suppressed, leading to the presence of metastable Mg$_2$Si in the rapidly solidified powder. This phase has indeed been observed in gas atomised ASCM powders (3).

Rapid quenching from the melt directly to room temperature, e.g. gas atomisation, can generally result in a supersaturated Al-rich phase. The amount of Si dissolved in the Al-rich phase of rapidly solidified hyper eutectic Al-Si alloys can be as high as 3.3 at%, which is much larger than the
maximum equilibrium solid solubility (9). Hence, a high atomic fraction of Si dissolved in the Al-rich phase of the in the gas-atomised ASCM alloys is expected.

For most hypoeutectic, binary Al-rich alloys, including Al-Cu alloys, it is impossible to dissolve all the alloying elements in the Al-rich phase by liquid quenching (9, 10). It can thus be expected that in the gas-atomised powder only a limited fraction of the copper is dissolved in the Al-rich phase. This is supported by the presence of the phase in gas-atomised ASCM powder (3), whereas this phase is absent in SQ ASCM (7).

The above suggests that the Al-rich phase of gas-atomised powder contains a higher fraction of silicon and a lower fraction of copper and magnesium as compared to the Al-rich phase of the SQ ASCM alloys. The increased silicon fraction is expected to result in precipitation of the Si phase during DSC heating. The main exothermic effect in the gas-atomised ASCM powder is observed between 430 and 510 K. This temperature range corresponds closely to the temperature ranges observed for silicon precipitation in hypereutectic rapidly solidified Al-Si alloys (9). From this it is assumed that this exothermic effect is mainly caused by silicon precipitation. Using the enthalpy of silicon precipitation from the Al-rich phase, $\Delta H_{Si}$ (54 kJ/mole Si, see (9)), it is now possible to estimate the atomic silicon fraction in the Al-rich phase after gas atomisation from:

$$x_{Si} = \Delta Q_{MP}/(x_{\alpha} \cdot \Delta H_{Si})$$

in which $x_{\alpha}$ is the fraction of Al-rich phase ($\alpha$) in the gas-atomised powder (approximately equal to the fraction of Al atoms in the alloy, 0.78). Using this expression, a value of 0.014 is found for $x_{Si}$. This is indeed much larger than the maximal equilibrium solid solubility of Si in the Al-rich phase in ASCM alloys which equals about 0.004 (8).

The DSC scan of the gas-atomised ASCM powder shows a small endothermic effect just in advance of the main exothermic effect. Endothermic effects in this temperature range are indicative for GP-zone dissolution (see Section 3.3 and (7)). The GP-zone dissolution effect in the gas-atomised powder is much smaller than the GP-zone dissolution effect in SQ ASCM alloys (in the SQ ASCM alloys GP-zone formation mainly involves the formation of Al-Cu-Mg type GPB zones). This corroborates the above assumption that the atomic fractions of Mg and Cu atoms in the Al-rich phase of the ASCM powders are lower than in the Al-rich phase of the SQ ASCM0 alloy.

From about 590 K to the end temperature of the DSC scan, 773 K, the first DSC scan of the gas-atomised powder is dominated by a broad exothermic effect. As the Mg$_2$Si phase is unstable in the solid ASCM alloys (see first
paragraph of this section), this phase must eventually transform into Q phase. As this is a thermally activated reaction from a metastable to a stable state, this transformation involves an exothermic reaction with a clearly defined peak temperature. Since no clear peak is observed in the first run on LQ ASCM0 beyond 590 K, the exothermic heat flow beyond 590 K is thought to be largely unaffected by this transformation. The temperature range of the broad exothermic effect in the DSC scan of gas-atomised powder is much broader, and located at much higher temperatures, than the ones usually encountered in the case of precipitation reactions. Indeed, no such effect is observed in DSC scans of SQ ASCM (see Section 3.3). The second and the third scans of the gas-atomised powder do not show this exothermic effect. Instead they show only endothermic effects, which, over a large temperature range, resemble the corresponding parts of the first and second run of the AE ASCM0 alloy. These endothermic effects are caused by the dissolution of the Q, Si and θ phases (see Section 4.2). Close to the end temperature of the DSC scan, also the second and the third DSC scans deviate from the scans of the AE ASCM0 specimen: beyond 750 K the endothermic heat flow seems to decrease in the powders. These effects, and the broad exothermic effect in the first run, are thought to be caused by oxide formation on the surface of the powders. This will be substantiated below.

During heating of gas-atomised Al-based alloys a series of reactions occur on the surface of the powders. These reactions involve the evolution of gases, and include (11):

\[
\begin{align*}
\text{Al(OH)}_3 & \rightarrow \text{AlOOH} + \text{H}_2\text{O} \quad (5) \\
2 \text{AlOOH} & \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \quad (6) \\
\frac{2}{3} \text{Al} + \text{H}_2\text{O} & \rightarrow \frac{1}{3} \text{Al}_2\text{O}_3 + \text{H}_2 \quad (7)
\end{align*}
\]

The water consumed during reaction 7 can either be provided by reactions 5 and/or 6, or H$_2$O molecules adsorbed by the oxide layer can be used. If sufficient oxygen is present also the direct oxidation reaction can occur:

\[
\frac{4}{3} \text{Al} + \text{O}_2 \rightarrow \frac{2}{3} \text{Al}_2\text{O}_3 \quad (8)
\]

From these four reactions reaction 8 results in the largest enthalpy change (1.68 MJ per mole Al$_2$O$_3$ at 700 K, see Appendix). Because of their high specific surface area (0.17 m$^2$/g), surface reactions can cause a significant heat evolution during DSC experiments on the gas-atomised ASCM powder (see Appendix). Since oxide layers on aluminium are always in the order of 10 to 100 nm, and since the gas-atomised powder already possesses a 40 nm thick oxide layer (3) it is assumed that the thickness of the oxide layer formed during the DSC run is of the order of 10 nm. The formation of a 10 nm thick oxide layer by reaction 8 produces about 3.1 kJ per mole powder. The formation an identical
oxide layer by reaction 7 produces about 1.7 kJ per mole powder. The heats produced by reactions 5 and 6 are about one order of magnitude smaller. The actual heat production during heating of the powder inside the DSC is estimated from the area between the first and the third run in the temperature range where the effect occurs (590 to 773 K). This gives the value 1.6 kJ per mole powder, which agrees fairly well with the above presented estimates for the formation of a 10 nm oxide layer. It is however not possible to distinguish between the two oxide-formation modes (reactions 7 and 8). The mass of the gas-atomised powder increases by 0.17% during the three DSC runs. Since only the direct oxidation (reaction 8) results in a mass increase, this indicates that the oxide formation during the DSC scan is, at least partly, caused by this reaction. Assuming that the mass increase is caused by direct oxidation, a 0.17% mass increase corresponds to a released heat of 1.7 kJ per mole ASCM powder. Thus, the released heat measured can entirely be ascribed to the direct oxidation.

Apparently a significant amount of O₂ is either adsorbed by the oxide layer or trapped between the powder particles forming the DSC specimen. This O₂ is apparently not completely removed by flushing with argon before the start of the DSC experiment.

4.2 Melting and dissolution reactions in AE ASCM

The peak temperatures of the exothermic and the endothermic effects appeared to be insensitive to variations of the heating rate. Therefore these endothermic effects are thought to be related to processes that are, to a large extent, equilibrium processes. As Al₂O₃ particles are supposed to be inert, this implies that these effects are insensitive to addition of Al₂O₃ particles, as has been observed.

From phase diagrams of the Al-Cu-Mg-Si system (8,12), it can be deduced that in the ASCM alloy no melting reaction occurs below 780 K. It is well established in literature that endothermic effects occurring between about 350 K and the melting of Al-Cu-Mg, Al-Cu-Si and Al-Cu-Mg-Si type alloys, are caused by the dissolution of alloying elements in the Al-rich phase (see for instance (7)). Accordingly, the endothermic effects in Fig. 4 are ascribed to dissolution of Cu, Mg and Si atoms in the Al-rich phase (since the maximum solid solubility of Fe in the Al phase is lower than 0.01 at% (8), the dissolution of Fe is neglected). From phase diagrams of the Al-Cu-Mg-Si system (8,12), it can be deduced that for the ASCM alloy the dissolution of the θ phase will be completed between 733 and 775 K. This is confirmed by high-temperature X-ray diffraction (see (7)), during which θ-phase lines disappear at 745±10 K. Thus it is
concluded that the endothermic effect between 610 and 740 K mainly concerns θ-phase dissolution. As the Si phase and the Q phase are present on the whole temperature range of the high-temperature X-ray diffraction experiment, the remaining part of the dissolution effect is caused by continuing dissolution of the Q and Si phases.

An AE ASCM10 specimen heated twice to 870 K shows severe clustering of Al₂O₃ particles (see Fig. 3), which indicates that a large part of the alloy (including the Al-rich phase) had been melted. The endothermic effects in Fig. 5 are much larger than those in Fig. 4. Since melting reactions generally involve much larger enthalpy changes as solid state reactions do, and since in Al-rich Al-Cu-Mg-Si alloys the first stage of melting can occur starting from about 780 K (8), the endothermic effects occurring in Fig. 5 are ascribed to melting reactions. From Fig. 5 it is concluded that the melting of the base alloy of ASCM10 is divided into four stages A, B, C and D (the melting point of Al₂O₃ particles, about 2300 K, lies far beyond the DSC temperature range). Considering the solidification reactions denoted by the liquidus surface of the Al-Cu-Mg-Si system (see Section 4.1), reaction D is clearly related to the melting of Si phase and Mg₂Si phase. Since effect C represents by far the largest endothermic heat content, this effect must be related to the melting of the (majority) Al-rich phase by the inverse of reaction 4. From the above it is is clear that the remaining reactions (reactions A and B) must be linked to the melting of the Q and Al₇Cu₂Fe phases. From literature (8) it is known that in Al-Cu-Mg-Si alloys various reactions involving the melting of the Q phase can occur in the temperature range 780 to 802 K. It is also known (from (8)) that in Al-Cu-Fe-Mg and in Al-Cu-Fe-Si alloys eutectic melting of the Al₇Cu₂Fe phase occurs at 778 and 793 K, respectively (data on the Al-Cu-Fe-Mg-Si system are unknown until now). So, the known temperature ranges of the Q and Al₇Cu₂Fe-phase melting reactions, while confirming that these two reactions are linked with the observed reactions A and B, give no clear indication which of the two phases melts first. However, in Fig. 5, reaction B is absent during the third run. This is interpreted as follows. During the second run, at the end of which the specimen is almost entirely melted, the melt reacts with the aluminium pan. This decreases the concentrations of Cu, Mg, Fe, and Si atoms in the alloy. From the Al-Cu-Mg-Si phase diagram at 775 K (8) follows that a decrease of the percentage of Mg in these alloys can result in dissolution of the Q phase in the Al-rich phase below 775 K. Then, melting of the Q phase will not occur. So, from the absence of the effect B in the third run of Fig. 5, it is concluded that effect B is most likely caused by the melting of the Q phase. Then, effect A has to be caused by melting of the Al₇Cu₂Fe phase.

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4.3. Precipitation in SQ ASCM

The hardness of an alloy is closely related to its microstructure. From Fig. 6 follows, that the presence of Al₂O₃ particles has a limited influence on the precipitation processes in SQ ASCM (see also (7)). Hence, the optimal heat treatment found for an SQ ASCM0 alloy can be applied for SQ ASCM alloys with Al₂O₃ particles.

For a number of MMCs it has been observed that introduction of ceramic particles alters the kinetics of precipitation (4). This is generally ascribed to the misfit between Al-rich phase and ceramic particles after solid quenching, by virtue of the difference in thermal expansion (4). In the Al-rich phases of ASCM alloys, a large volume fraction of misfitting silicon particles (about 22 vol%) is present after solid quenching. This may explain why Al₂O₃ particles, in this case, have little influence on the kinetics of precipitation. For a discussion of the influence of Al₂O₃ particles on the precipitation in ASCM alloys, see Ref. 7.

From hardness of the SQNA specimens (Fig. 8) it is concluded that solid-quenched ASCM0 can be hardened by natural ageing. This hardening effect is caused by the formation of GPB (Al-Cu-Mg) zones (13). From a comparison of Fig. 6 with Fig. 7, it becomes apparent that the maximum hardness for SQ ASCM0 is reached just after completion of the Q-phase precipitation (see Section 3.3). The additional overageing treatment generally lowers the hardness of the SQDSC specimens (see curve I and II in Fig. 7). The initial difference between curves I and II below 473 K can be explained as follows. SQ ASCM0 is kept at room temperature at least one hour before start of the DSC run. During room-temperature storage and during heating up to low DSC end temperatures (lower than 400 K) GPB zones are formed, which contribute to the hardness. During DSC runs on the SQ ASCM alloys the GPB zones start to dissolve from about 400 K, but dissolution is not completed before 473 K (see Fig. 6). The additional overageing treatment is sufficient to allow the dissolution of the GPB zones, leading to a marked drop in hardness. Beside the dissolution of GPB zones, also the annealing out of dislocations (formed during quenching, see (7)) can cause softening of the quenched specimens.

From the foregoing discussion it becomes apparent that two reactions contribute to the hardening of SQDSC ASCM0: i. GPB-zone formation and ii. Q-phase precipitation. Also the hardness changes of the specimens presented in Fig. 8 are interpreted in terms of these two hardening mechanisms.

Natural ageing results in GPB-zone formation. Thus increasing the time of natural ageing results in an increasing hardness (see Fig. 8). The slight decrease in hardness after long-time natural ageing may be related to
relaxation of elastic tensions originally present after solid quenching (14). As Q-phase formation occurs at temperatures around 480 K, the hardness increase observed on artificial ageing at 393 and 433 K is probably also due to GPB-zone formation. In the SQAA(433 K) specimen also θ' and Al-Cu type GP-zones might contribute to the hardness (13,15). Since both GP zones and θ' are unstable, this explains why after additional overageing the hardness of the SQAA specimens is reduced to about the same value as is observed for the SQNA specimen and the SQDSC specimens with DSC end temperatures lower than 473 K after the additional overageing treatment.

5. Conclusions

- The Q and Al₇Cu₂Fe phases, which are not (completely) dissolvable in the Al-rich phase, start melting from 780 K. Hence, the optimal solution treatment temperature is just below 780 K. The Al-rich phase of the ASCM alloys melts between 810 and 840 K.
- The hardness of the extruded ASCM alloy can be increased by about 75% by heat treatments which produce either GPB zones or Q-phase precipitates (ageing temperatures 433 to 500 K).
- For high-temperature applications (> 470 K), only ageing treatments at temperatures around 480 K, giving rise to the formation of the Q phase, are useful. These ageing treatments can increase the room-temperature hardness of the ASCM0 alloy by about 60% (as compared to the as extruded alloy).
- The presence of Al₂O₃ particles in the ASCM alloy has little influence on the precipitation after solid quenching.

Appendix

The exothermic heat effect produced by the growth of aluminium oxide layers of average thickness, d, on powders, is given by:

$$\Delta Q_{ox} = A_S \cdot d \cdot \Delta H \cdot \rho_{ox} \cdot \frac{M_{ASCM}}{M_{Al_2O_3}}$$

in which $A_S$ is the specific surface area of the powders, $\Delta H$ is the change in enthalpy of the reacting substances due to the oxide forming reaction, per mole oxide, $\rho_{ox}$ is the average density of the oxide layer, and $M_{ASCM}$ and $M_{Al_2O_3}$ are the atomic masses of the ASCM powder (27.7 g/mole) and Al₂O₃ (102 g/mole), respectively. The specific surface area of the gas-atomised ASCM powders equals 0.17 m²/g (3). For the enthalpy change of the oxide forming reactions,
ΔH, the value of ΔH at 700 K is used (the small variations of ΔH with temperature, about 1% per 100K at 700K (16), are neglected). Then ΔH is given by 0.95 and 1.68 kJ per mole Al₂O₃ for reactions 7 and 8, respectively (16). The ΔH of reaction 6 is about one order of magnitude smaller (11). The density of fully dense α-Al₂O₃ (corundum) equals 3.98 g/cm³. This value will be used as an estimate for ρox.

References

CHAPTER VII

PRECIPITATION IN A SOLID-QUENCHED, PARTICLE-REINFORCED AL-SI-CU-MG ALLOY: PHASE IDENTIFICATION AND KINETICS

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Abstract

Precipitation studies on solid-quenched specimens of the Al-20at%Si-1.5at%Cu-1at%Mg (ASCM) alloys with 0, 2.5, 5, and 10 vol% Al₂O₃ particles were performed by differential scanning calorimetry (DSC). For all Al₂O₃-particle volume fractions, similar DSC recordings were obtained. The DSC effects were attributed to the following reactions: GPB-zone formation, GPB-zone dissolution, the main precipitation reaction containing Q and θ precipitation, and dissolution of Q and θ phases. Kissinger analysis yielded activation energies of 0.66±0.05 eV for GPB-zone formation and 1.25±0.07 eV for Q-phase precipitation. The total heat evolution during the main precipitation effect decreased with increasing heating rate for the alloy without Al₂O₃ particles, but increased with increasing heating rate for the alloy with 10 vol% Al₂O₃ particles. This is explained by the increased misfit-dislocation density due to the presence of Al₂O₃ particles.
1. **Introduction**

Matrix age hardening can be important for the optimisation of the mechanical properties of aluminium-based metal matrix composites (MMCs), e.g. for the application at elevated temperatures. Precipitation studies in quenched MMCs are important because of the role of misfitting particles and interfaces in precipitation kinetics or sequences (1). The difference in shrinkage on cooling, due to the difference in the respective coefficients of thermal expansion (CTE) of the dispersed particles and the surrounding matrix, introduces a misfit between particles and matrix. This thermal misfit is accommodated by elastic and plastic deformation of the matrix (2), the latter by the creation of misfit dislocations. These act as extra nucleation sites (enhancing precipitation) or annihilate excess vacancies (retarding precipitation). Elastic misfit accommodation can also influence precipitation phenomena (3).

An aluminium alloy with a high content of small silicon particles can be considered as a model for an MMC, since these silicon particles have similar characteristics (size, shape, CTE) as the particles normally applied in Al-based MMCs (for instance SiC or Al₂O₃). Studies of solid-quenched Al-Si-Cu-Mg alloys with and without reinforcing Al₂O₃ particles, enables the investigation of the effects of these dispersed particles on precipitation.

In this paper, results are presented of a study on precipitation in extruded and subsequently solid-quenched (SQ) Al-20at%Si-1.5at%Cu-1at%Mg (ASCM) alloys with various volume fractions of aluminium oxide (Al₂O₃) particles. As precipitation involves large enthalpy changes, this study has been performed by differential scanning calorimetry (DSC). Non-isothermal X-ray diffraction at a constant heating rate was applied to facilitate phase identification.

2. **Experimental Procedures**

2.1. **Production Route.**

The investigated alloys were made available by Showa Denko, Japan. The base alloy was rapidly solidified by gas atomisation (cooling rate about 10⁴ to 10⁶ K/s, see Ref. 4), yielding fine powder (sizes range from 1 to 100 μm, with a median size of 25 μm, (5)). The powder was mixed with Al₂O₃ particles, in order to obtain mixtures with 0, 2.5, 5 and 10 vol% Al₂O₃ particles. These mixtures were extruded at about 670 K, yielding round bars of about 20 mm diameter. In the extruded alloys, the sizes of the Al₂O₃ particles ranged from 1
to 6 μm (average ≃ 2μm), the sizes of the silicon particles ranged from 2 to 10 μm (average ≃ 4 μm) (6).

In Table I, the chemical compositions of the alloys are presented. The composition of the base alloy was essentially the same for all the alloys. Main impurities (as measured by X-ray fluorescence) were: Ni (~0.02 at%), Zn (~0.01 at%), Ti (~0.006 at%), and Cr (~0.005 at%).

<table>
<thead>
<tr>
<th>alloy name</th>
<th>Al2O3</th>
<th>Si</th>
<th>Cu</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
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<tr>
<td></td>
<td>vol % *)</td>
<td>wt%</td>
<td>at%</td>
<td>wt%</td>
<td>at%</td>
</tr>
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<td>ASCM0</td>
<td>-</td>
<td>20.2</td>
<td>19.9</td>
<td>3.47</td>
<td>1.52</td>
</tr>
<tr>
<td>ASCM2.5</td>
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<td>20.2</td>
<td>3.44</td>
<td>1.56</td>
</tr>
<tr>
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<td>18.9</td>
<td>20.1</td>
<td>3.32</td>
<td>1.57</td>
</tr>
<tr>
<td>ASCM10</td>
<td>10.4</td>
<td>16.9</td>
<td>19.6</td>
<td>2.97</td>
<td>1.52</td>
</tr>
</tbody>
</table>

*) Calculated from measured weight percentages using the densities of the ASCM base alloy, 2.67 g/cm³ and of α-Al2O3 (corundum) 3.98 g/cm³ (7).

2.2. Specimen preparation.

From the centre of the extruded bars, cylindrical specimens (height about 0.5 mm and diameter 6 mm) were cut. All specimens were of nearly identical mass (37±4 mg). They were homogenized for 10 minutes at 768±2 K. The specimens were quenched by dropping from the vertical tube furnace into water at room temperature. Before the DSC experiment, the specimens were stored at room temperature for one hour. The matrix grain size after solid quenching was about 5 μm, no coarsening of the Si particles was observed (6).

2.3. Differential Scanning Calorimetry.

A DuPont 910 differential scanning calorimeter was used with a protective gas atmosphere of pure argon. The temperature and heat flow scales were calibrated (for all heating rates) using the known melting point and heat of fusion of indium (8). Both specimen and reference were enclosed in an aluminium pan with an aluminium cover. DSC runs of SQ ASCM0 and ASCM10 specimens were performed at heating rates of 0.5, 2, 5, 10, 20 and 40 K/min. For SQ ASCM2.5 and ASCM5 specimens, DSC runs were taken at heating rates of 10, 20 and 40 K/min. All DSC scans presented are corrected for
the non-ideal baseline (not straight or varying between experiments) of the DSC apparatus. This was achieved by performing a separate run with inert aluminium pans before each experiment, and subtracting the heat flow during this run from the heat flow during the actual experiment. The scans presented are also corrected for the contribution of differences in heat capacity between specimen and reference to the heat flow (for a description of the heat capacity correction, see Ref. 3).

2.4. X-ray diffraction.

For phase identification, X-ray diffraction was performed using a high-temperature Guinier camera. The analysis was performed on SQ ASCM0 and SQ ASCM10 specimens. The diffraction patterns of Cu Kα1 radiation transmitted through thin (~70 μm) specimens were recorded on a water-cooled photo film during heating the specimen from 293 to 773K with 0.5 K/min.

3. Results

3.1. Non-isothermal X-ray diffraction.

The X-ray diffraction pattern of SQ ASCM0 reveals 43 diffracted lines, of which 41 lines are easily identifiable as lines from the Al-rich phase, the Si phase, the Q phase (Al₅Cu₂Mg₈Si₆), the Al₇Cu₂Fe phase and the θ phase (Al₂Cu). The θ-phase lines were only present between 470 and 740 K (accuracy of these temperature determinations is within 15 K). The intensities of these lines reach maxima at about 620 K. The two remaining diffracted lines (corresponding to interplanar spacings 0.3348 and 0.1738 nm), which are broader than the other lines, are observed only from 550 to 580 K. The values for the interplanar spacing, d, of these two lines correspond closely to the d₁₀₁ and d₂₁₁ of the θ' phase (the intermediate Al₂Cu phase).

The X-ray diffraction pattern of SQ ASCM0 reveals the presence of the Al-rich phase, the Si phase, the Q phase, the Al₇Cu₂Fe phase and the α-Al₂O₃ (corundum) phase over the whole of the temperature range. The θ-phase lines were present between 460 and 750K. The two broad lines detected for the ASCM0 specimen were not detected for the ASCM10 specimen.

3.2. Differential scanning calorimetry.

Fig. 1 shows typical DSC curves of the SQ ASCM0 and ASCM10 specimens. The DSC curves of SQ ASCM2.5 and ASCM5 are very similar to the ones in Fig.
1. So, the differences between the DSC curves of the different SQ ASCM alloys are very small. In line with literature data and on the basis of non-isothermal X-ray diffraction (see Section 4.1), the effects during DSC heating of SQ ASCM alloys are attributed to the following reactions:
   i. the formation of GPB (Al-Cu-Mg) zones
   ii. the dissolution of GPB zones
   iii. precipitation of the Q phase (Al$_6$Cu$_2$Mg$_8$Si$_6$)
   iv. precipitation of the $\theta$ phase
   
   Apart from the GPB-zone formation, most reactions overlap with neighbouring reactions (Fig. 1).

![DSC curves of SQ ASCM with 0 and 10 vol% Al$_2$O$_3$ particles.](image)

Fig. 1: DSC curves of SQ ASCM with 0 and 10 vol% Al$_2$O$_3$ particles.

   The peak temperatures of effects i and iii are gathered in Table II. The addition of Al$_2$O$_3$ particles to the ASCM alloy decreased the peak temperature of the GPB-zone formation (effect i) by about 2 to 6 K. The peak temperatures of effect iii are not significantly changed by addition of Al$_2$O$_3$ particles.

   The heat content per mole base alloy of effect i (GPB-zone formation), $\Delta Q_{GPB}$, depends on heating rate and on the Al$_2$O$_3$-particle content (see Fig. 2). The value of $\Delta Q_{GPB}$ decreases with increasing heating rate (Fig. 2). Due to the varying resolution of the DSC apparatus with heating rate, the inaccuracy in
Table II. Peak temperatures of effects i and iii ($T^i_p$ and $T^{iii}_p$, respectively) for SQ ASCM alloys as a function of DSC heating rate.

<table>
<thead>
<tr>
<th>Heating Rate(K/min)</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>alloy name</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASCM0</td>
<td>344</td>
<td>356</td>
<td>373</td>
<td>498</td>
<td>511</td>
<td>529</td>
</tr>
<tr>
<td>ASCM2.5</td>
<td>342</td>
<td>353</td>
<td>368</td>
<td>498</td>
<td>510</td>
<td>529</td>
</tr>
<tr>
<td>ASCM5</td>
<td>341</td>
<td>354</td>
<td>368</td>
<td>497</td>
<td>510</td>
<td>526</td>
</tr>
<tr>
<td>ASCM10</td>
<td>342</td>
<td>354</td>
<td>366</td>
<td>497</td>
<td>511</td>
<td>526</td>
</tr>
</tbody>
</table>

Fig. 2: Heat content per mole base alloy of GPB-zone formation (effect i), $\Delta Q_{GPB}$, for four SQ ASCM alloys, as a function of the DSC heating rate.

The value of $\Delta Q_{GPB}$ varies with heating rate too: from 50 J/mole base alloy at 0.5 K/min to 5 J/mole base alloy at 40 K/min. The introduction of $\text{Al}_2\text{O}_3$ particles generally lowers the value of $\Delta Q_{GPB}$.

In Fig. 3, the total heat content per mole base alloy during the main precipitation effect (effects iii and iv), $\Delta Q_{iii+iv}$, is plotted as a function of the...
DSC heating rate for SQ ASCM0 and ASCM10. In this case the inaccuracy in the value of $\Delta Q_{\text{iii}+\text{iv}}$ varies with heating rate from 60 J/mole base alloy at 0.5 K/min to 10 J/mole base alloy at 40 K/min. The value of $\Delta Q_{\text{iii}+\text{iv}}$ decreases with increasing heating rate for SQ ASCM0, whereas it increases for SQ ASCM10.

![Graph showing the relationship between $\Delta Q_{\text{iii}+\text{iv}}$ and Heating Rate (K/min).]

Fig. 3 : The total heat content per mole base alloy of the main precipitation effect (effect iii and iv), $\Delta Q_{\text{iii}+\text{iv}}$, for two SQ ASCM alloys, as a function of the DSC heating rate.

4. Discussion

4.1. Identification of DSC effects.

Hardness measurements on SQ ASCM0 specimens have shown that SQ ASCM0 can be hardened by natural ageing (6). This indicates the formation of GP zones. In Al-Cu-Mg and Al-Cu-Mg-Si alloys with atomic Cu:Mg ratios higher than 0.6, only two types of GP zones were observed: the Al-Cu type GP zones and the Al-Cu-Mg type GPB zones (1, 9, 10). The formation rate of GP zones in an Al-Cu alloy is severely reduced by the addition of 20at% Si to the alloy (6). In fact, DSC curves of SQ Al-Cu-Si show no GP-zone formation effect at all. Since the ASCM alloy also contains 20at% Si, it can be expected that also in the SQ ASCM alloys the formation rate of Al-Cu type GP zones is very low.
Bonfield and Datta (9) reported that GPB-zone formation is the first stage of precipitation between ambient temperatures and 400K in an Al-1.7at%Cu-0.9at%Mg-0.8at%Si alloy. After solid quenching, the compositions of the Al-rich phase of this alloy and the Al-rich phases of the ASCM alloys are very similar (see phase diagrams of Al-Cu-Mg-Si (11)). Thus, effect i during the DSC scan (see Fig. 1) is ascribed to GPB-zone formation. According to Papazian (1) and Gupta et. al (10), GPB (Al-Cu-Mg) zones dissolve between about 410 and 510 K. As the quoted temperature range corresponds very well with the one of effect ii, effect ii is ascribed to the dissolution of GPB zones.

The precipitates formed during effect iii increase the hardness of SQ ASCM0 considerably (3). An effect similar to effect iii (same shape and temperature range) occurred in DSC runs of solid-quenched Al-0.65at%Cu-0.84at%Mg-xSi alloys with x between 0.47 and 1.00at%, at lower Si contents such an effect was not observed (10). This indicates that effect iii is caused by the precipitation of a silicon-containing phase. During non-isothermal X-ray diffraction analysis of SQ ASCM0, only two silicon-containing phases are observed (see Section 3.1): the Si phase and the Q (Al5Cu2Mg3Si5) phase (as both phases are present directly after solid quenching, the appearance of new Si or Q precipitates cannot be detected during this experiment). Since Q-phase precipitation yields a hardness increase of SQ aluminium alloys, while Si-phase precipitation does not (11), it is thought that the effect iii is caused by Q-phase precipitation. An additional indication for the formation of Q-phase precipitates rather than Si-phase precipitates can be derived from the work of Gupta et. al. (10) on the SQ Al-0.65at%Cu-0.84at%Mg-xSi alloys. They found that the formation of S' and S phases (both Al2CuMg), otherwise observed around 670K in DSC scans of SQ alloys with x ≤ 0.22 at%, is suppressed in SQ alloys with x between 0.47 and 1.00 at%. The suppression of S' and S phase precipitation coincided with the appearance of the peak at 500 K, which corresponds to effect iii in the SQ ASCM alloys (see above). This suggests that beside Si also Cu and/or Mg are incorporated in the precipitates formed during effect iii.

During heating the SQ ASCM0 and the SQ ASCM10 specimens at 0.5 K/min, the θ phase appears from about 470K (see Section 3.1). The intensities of the diffracted lines of this phase reach maxima (denoting completion of the precipitation reaction) at about 620K. For the SQ ASCM0 specimen, two diffracted lines were observed between 550 and 580 K. This very narrow temperature range is situated around the end temperature of effect iv on the DSC scan for the same heating rate. Thus it is expected that the phase observed here does not contribute significantly to effect iv in SQ ASCM0, and thus effect iv is identified with the precipitation of the θ phase. The two broad lines in SQ
ASCM0 might be due to the metastable S' (Al$_2$CuMg) phase or to $\theta'$ phase, but due to the limited number of lines observed an unambiguous phase identification is impossible. On continued heating, the phases formed during the main precipitation effect eventually dissolve. Thus, effect v is related with the dissolution of the Q and $\theta$ phases (and possibly S' or $\theta'$ phase).

4.2. Precipitation kinetics.

Activation energies for thermally activated processes resulting in clearly defined single-process DSC peaks, can be obtained by applying the Kissinger analysis (see Ref. 12). Hence, such an analysis is only applicable to effects i and iii. The activation energy for GPB-zone formation (effect i) appeared to be:

$$E_{\text{GPB}} = 0.66 \pm 0.05 \text{ eV}.$$  

This activation energy equals the value obtained for GPB-zone formation in the Al-1.9at\%Cu-1.6at\%Mg alloy (13). The activation energy for Q-phase formation (effect iii) was found to be:

$$E_Q = 1.25 \pm 0.07 \text{ eV}.$$  

Although the peak temperature of effect i was influenced by the presence of Al$_2$O$_3$ particles, the activation energy values obtained from the peak temperatures was, within experimental accuracy, independent of the Al$_2$O$_3$ particle content. The peak temperature of effect iii was not influenced by the presence of the Al$_2$O$_3$ particles, and, as a consequence also the activation energy of Q-phase precipitation was independent of Al$_2$O$_3$-particle content. These findings are discussed in Section 4.3.

The low value of $E_{\text{GPB}}$ corresponds to the activation energy of migration of (mono) vacancies in pure aluminium (about 0.64 eV (14)). As the formation of GPB zones can only proceed via vacancy diffusion (the alloying atoms involved are substitutionally dissolved in the Al-rich phase), the low value of $E_{\text{GPB}}$ hints at the presence of a large amount of vacancies. The value of the activation energy for Q-phase precipitation is rather low compared to the activation energies for diffusion of the alloying elements involved in the Q-phase formation (about 1.4 eV for Mg, Cu and Si diffusion in Al (11)). As also Q-phase formation can only proceed via the vacancy diffusion mechanism, the rather low value of $E_Q$ indicates that even after formation and dissolution of GPB zones, excess vacancies are not completely annihilated.

The main precipitation effect (iii and iv) is further characterized by an overlap in time of the precipitation of the Q and $\theta$ phases. Therefore, the Kissinger analysis cannot be applied to the precipitation kinetics of the $\theta$ phase.
4.3. Effects of misfitting particles on precipitation.

Via the plastically and elastically accommodated thermal misfit, the reinforcing particles in an MMC influence the kinetics of precipitation from the supersaturated Al-rich phase (see Section 1). Elastic accommodation of thermal misfit introduces hydrostatic tensions in the Al-rich phase in case the CTE of the inclusion is smaller than the CTE of the Al-rich phase. The CTEs of the three main phases in the ASCM alloys are: silicon 3 \(10^{-6}\), Al\(_2\)O\(_3\) particles 7.1 \(10^{-6}\) and Al-rich phase 23.5 \(10^{-6}\) (see for instance 15).

The influence of plastically accommodated thermal misfit, i.e. by the creation of misfit dislocations, can be twofold (see Section 1): i. excess vacancy annihilation by misfit dislocations, and ii. additional nucleation sites provided by misfit dislocations. Vacancy annihilation generally retards precipitation, whereas additional nucleation sites enhance precipitation.

In the case the misfit of an inclusion is determined by a difference in CTE between inclusion and the surrounding Al-rich phase, the misfit parameter, \(\varepsilon\), can be defined as follows:

\[
\varepsilon = \Delta \alpha \cdot \Delta T,
\]

where \(\Delta \alpha\) is the difference of the CTE of the inclusion and the CTE of the Al-rich phase, and \(\Delta T\) is the temperature drop. The misfit volume, \(\Delta V_M\), of such an inclusion equals:

\[
\Delta V_M = 3 \cdot \Delta \alpha \cdot \Delta T \cdot v_i,
\]

where \(v_i\) is the volume of the inclusion. Thus, the total misfit volume, \(\Delta V_M\), relative to the total volume of the alloy, \(V\), introduced by the misfit of different types of inclusions, inclusion type \(i\) present with volume fraction \(y_i\), and having a CTE difference with the matrix \(\Delta \alpha_i\), can be written as:

\[
\frac{\Delta V_M}{V} = 3 \sum_i \Delta \alpha_i \Delta T y_i
\]

The largest part of the misfit volume in our alloys is caused by misfitting silicon particles which occupy 22 vol% of the base alloy. The addition of up to 10 vol% Al\(_2\)O\(_3\) particles increase the total misfit volume by about 24%. Thus, the misfit volume of the Al\(_2\)O\(_3\) particles is much less important as compared to the misfit volume of silicon particles. Hence, the introduction of Al\(_2\)O\(_3\) particles will only have a limited influence on precipitation. Indeed, the differences in precipitation effects observed between the DSC curves of SQ ASCM0 and SQ ASCM10 are generally small (Fig. 1). Nevertheless, two remarkable effects caused by the addition of Al\(_2\)O\(_3\) particles occur.

The Al\(_2\)O\(_3\)-particle content does not influence the peak temperature of the Q-phase precipitation (see Table II), but it does influence the end temperature of effect iv (see Fig. 1). The heat content of the main precipitation effect
decreases with heating rate for SQ ASCM0, but increases with heating rate for SQ ASCM10 (see Fig. 3). In case of retrograde solid solubilities of the alloying elements in the Al-rich phase, a decrease of the heat of precipitation with increasing heating rate is normally observed (3).

Based on the independence of the peak temperature of effect iii with the Al₂O₃-particle content and on the low solubilities of the alloying elements in the Al-rich phase at the precipitation temperatures, it is assumed that the amount of Q phase precipitated per mole base alloy is constant and not influenced by the Al₂O₃-particle content. From this it follows that the variations in the total heat of precipitation of effect iii and iv, ΔQ_{iii+iv}, are not related with the Q-phase precipitation and must thus be related with the θ-phase precipitation.

A way in which the heating rate and the Al₂O₃ content can influence the θ-phase precipitation is through misfit stresses and dislocation generation resulting from thermal misfit. The addition of Al₂O₃ particles will increase the dislocation density in ASCM alloys for two reasons. Firstly, more dislocations have to be created to accommodate extra misfitting volume, and secondly, due to their irregular shapes and their lower average size the Al₂O₃ particles are more effective in the creation of misfit dislocations than the approximately spherical Si particles (17). Additional misfit dislocations can influence the precipitation kinetics in two ways. Firstly, the dislocations can act as nucleation sites for precipitation and thus enhance precipitation, and secondly they can annihilate vacancies and thus reduce formation rates of precipitates. When the temperature is increased the dislocations and excess vacancies will eventually disappear. These processes are thermally activated and will thus depend on heating rate.

From the above it becomes clear that the accommodation of misfitting Al₂O₃ particles can result in various heating rate-dependent variations of precipitation kinetics. The observed differences in ΔQ_{iii+iv} might be caused by an initially low vacancy concentration in the ASCM10 alloy due to vacancy annihilation by dislocations, reducing the rate of θ-phase formation. As the heating rate is increased, the temperature for precipitation increases, and due to the annealing of dislocations and vacancies, the difference between SQ ASCM10 and ASCM0 gradually disappears. An alternative explanation might be that the availability of extra nucleation sites in the ASCM10 alloy causes the precipitates to be finer as compared to those in the ASCM0 alloy. Since fine precipitates dissolve faster, i.e. at a lower temperature (18), this would reduce ΔQ_{iii+iv}. Again, as the heating rate is increased, the difference between ASCM0 and ASCM10 would gradually disappear due to the annealing of dislocations.
As a consequence, the study of the effects due to the introduction of misfitting (ceramic) particles on precipitation can not be restricted to DSC scans for just one heating rate (or in the case of isothermal studies, one ageing temperature), since at different heating rates these particles can influence the precipitation kinetics in a different way. In the SQ ASCM alloys the presence of 10vol% Al₂O₃ particles decreases the total heat content of the main precipitation effect for low DSC heating rates (≤ 2 K/min) and increases this heat content for high DSC heating rates (≥ 20 K/min).

The total heat content per mole base alloy of the GPB-zone formation effect is slightly lowered by the introduction of Al₂O₃ particles (see Fig. 2 and Table II). This is thought to be due to an increase of the volume of plastically deformed matrix caused by the introduction of these particles. In the plastically deformed zones the rate of GPB-zone formation is reduced due to the annihilation of vacancies by dislocations. In accordance with this Prangnell and Stobbs observed that for a quenched and aged (4 h at 408 K) Al-1.7at%Cu alloy reinforced with 8 vol% SiC particles the density of GP zones in the plastically deformed zone around the misfitting SiC inclusions is lower than further away in the matrix (19).

Conclusions

- During heating the solid-quenched ASCM alloys at constant heating rate, the following reactions occur: GPB-zone formation, GPB-zone dissolution, the main precipitation reaction containing Q and θ precipitation and Q and θ dissolution.
- The kinetics of GPB-zone formation and Q-phase precipitation are largely uninfluenced by the presence of Al₂O₃ particles.
- The total heat evolution during the main precipitation effect decreased with increasing heating rate for the alloy without Al₂O₃ particles, but increased with increasing heating rate for the alloy with 10 vol% Al₂O₃ particles. This is explained by increased misfit-dislocation density due to the presence of Al₂O₃ particles.
References

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CHAPTER VIII

LATTICE PARAMETER AND HARDNESS VARIATIONS RESULTING FROM PRECIPITATION AND MISFIT ACCOMMODATION IN A PARTICLE REINFORCED AL-SI-CU-MG ALLOY

M.J. Starink, V.M.F. Abeels and P. van Mourik

Abstract

Precipitation processes occurring on ageing Al-20at%Si-1.5at%Cu-1.1at%Mg (ASCM) alloys with and without Al₂O₃ particle reinforcement were studied by X-ray diffraction and by hardness measurements. During ageing at 453 K after solid quenching the Q (Al₅Cu₂Mg₈Si₆) phase precipitates first, followed by the θ (Al₂Cu) phase. An optimized T6 heat treatment for the ASCM alloys consists of a short solution treatment at 779 K, followed by water-quenching and ageing for 4 hours at 453 K. After the peak in hardness has been reached, continued ageing causes the hardness to decrease. This overageing results from coarsening of the Q phase. The activation energy for overageing (about 1.6 eV) indicates that the rate of overageing is governed by the product of solid solubility and diffusion rate (classical LSW coarsening theory). After heat treatment, the lattice parameters were influenced by the misfit effects caused by the difference in coefficients of thermal expansion (CTEs) between Al-rich phase, Si-rich phase and Al₂O₃ particles if present. These misfits still existed at room temperature after completed precipitation. A model assuming ideal plastic behaviour of the matrix describes the cooling-induced changes of the Si-rich phase lattice parameter fairly well. For the cooling-induced changes of the Al-rich phase phase lattice parameter significant discrepancies between model predictions and measurements remain.
1 Introduction

The wear resistance of aluminium alloys can be improved by the introduction of finely dispersed hard particles into the alloy (1, 2). A fine dispersion of silicon particles can be obtained by rapid solidification of a molten aluminium alloy with a high silicon content (3). A dispersion of ceramic particles in aluminium alloys can be obtained via various production routes, e.g. by compocasting or by mixing particles with aluminium alloy powders followed by extrusion. Metals reinforced by dispersed (ceramic) particles are generally referred to as metal matrix composites (MMCs). Their increased wear resistance, low thermal expansion and improved high-temperature strength, make MMCs attractive for applications like parts of combustion engines.

In this contribution, results of a study on ageing after solid quenching of Al-20at%Si-1.5at%Cu-1.1at%Mg (ASCM) alloys with and without 10 vol% aluminium oxide (Al₂O₃) particles are presented. These alloys combine the presence of two reinforcing components (silicon and Al₂O₃ particles) with the possibility of age hardening of the Al-rich matrix phase. Hence, an appropriate heat treatment is necessary to optimize the mechanical properties at room and elevated temperatures. The presence of dispersed particles in solid-quinched age-hardenable aluminium alloys generally influences the kinetics and sequences of precipitation processes, as compared to corresponding unreinforced alloys (4, 5, 6). Appropriate heat-treatment procedures for the ASCM alloys are, as yet, unknown.

The non-isothermal precipitation in solid-quinched ASCM alloys was studied before (7, 8). In the present work the isothermal precipitation in solid-quinched ASCM alloys is studied by measurement of lattice parameter variations of the Al-rich phase and the Si-rich phase. Lattice parameter measurements also give information about stresses in the inclusions and in the matrix. Residual stresses in MMCs are important, since they have a significant impact on properties such as elastic modulus, yield strength and fracture behaviour (9). In addition some hardness measurements were performed.
Experimental procedures

2.1 Preparation of specimens

The alloys under investigation were made available by the Japanese firm Showa Denko K.K. The base alloy was rapidly solidified by gas atomisation, yielding fine powder (sizes range from 1 to 100 µm, with a median size of about 24 µm (10)). The cooling rate during gas atomisation is generally about $10^4$ to $10^6$ K/s (3). Subsequently, the powder was mixed with ceramic Al$_2$O$_3$ particles, in order to obtain a mixture with 10 volume percent of ceramic particles. Finally, the mixtures and the base alloy powders were extruded at about 670 K into round bars with a diameter of about 20 mm. The composite shows a fairly homogeneous distribution of Al$_2$O$_3$ particles. The sizes of the Al$_2$O$_3$ particles range from 1 to 6 µm, with an average aspect ratio of about 2. The sizes of the free silicon particles range from about 2 to 10 µm.

The chemical compositions of the extruded alloys are presented in Table I. The four alloys are indicated by ASCM0 and ASCM10, in which the last number refers to the volume percentage Al$_2$O$_3$ particles. The main impurities in the base alloy (as measured by X-ray fluorescence) are: Ni (~0.02 at%), Zn (~0.01 at%), Ti (~0.006 at%) and Cr (~0.005 at%).

<table>
<thead>
<tr>
<th>alloy name</th>
<th>Al$_2$O$_3$ vol % *)</th>
<th>Si wt%</th>
<th>Si at%</th>
<th>Cu wt%</th>
<th>Cu at%</th>
<th>Mg wt%</th>
<th>Mg at%</th>
<th>Fe wt%</th>
<th>Fe at%</th>
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<tbody>
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<td>-</td>
<td>20.2</td>
<td>19.9</td>
<td>3.47</td>
<td>1.52</td>
<td>0.96</td>
<td>1.10</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>ASCM10</td>
<td>10.4</td>
<td>16.9</td>
<td>19.6</td>
<td>2.97</td>
<td>1.52</td>
<td>0.77</td>
<td>1.03</td>
<td>0.20</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*) Calculated from measured weight percentages using the densities of the ASCM base alloy, 2.67 g/cm$^3$ and of α-Al$_2$O$_3$, 3.98 g/cm$^3$ [11].

From the centre of the extruded bars, cylindrical specimens were machined with a diameter of 0.5 mm and length of about 5 mm. The axis of the specimen was parallel to the extrusion direction. These specimens were intended for X-ray diffraction experiments with a Debije-Scherrer camera.

The specimens were solution treated for 10 minutes at 779±2 K in a vertical tube furnace and subsequently quenched in water at room temperature. This solution treatment temperature is just below the start of melting of the ASCM alloy (7), and equals the solution treatment temperature for the conventional,
monolithic 2014 aluminium alloy, which has a composition comparable to the matrix of the ASCM alloy. The quenched specimens were aged at 453 K. The quenched and aged specimens will be indicated as SQ+A specimens. The ageing treatment was performed in an oil bath with temperature stability within ±1.5 K and was interrupted after certain intervals by a direct quench into water at room temperature.

2.2 X-ray diffraction

For measurement of the lattice parameter of the Al-rich phase and the Si-rich phase of the ASCM alloys, X-ray diffraction experiments were performed using a Debye-Scherrer (DbS) camera. Copper radiation filtered by Nickel was used. The films in the DbS camera were exposed for 6 hours. During the exposure, the temperature inside the DbS camera, at a point close to the specimen, was measured and recorded. Temperatures during the measurements were between 294 and 297 K. Temperature variations during single experiments were typically in the order of 0.5 K. Film type and film development procedures were identical for all experiments.

After development of the DbS film, the line positions were measured. Accuracy of the line position measurements of the three lines corresponding to the highest diffraction angle was improved by taking the average of at least five determinations of the position. The lattice parameters of the Al-rich phase and the Si-rich phase were determined by using the so-called Nelson-Riley extrapolation (see Ref. 12). They were corrected for the average temperature during the measurement by adopting the coefficient of thermal expansion of pure aluminium and pure silicon: 23.5 $10^{-6}$ and 3 $10^{-6}$, respectively (13). All lattice parameters presented in this work are valid at 298 K.

2.3 Hardness measurements

Hardness measurements were performed on ASCM0 and ASCM10 specimens. Micro-hardness was measured on polished longitudinal sections using a Leitz-Durimet Vickers hardness tester. Indentation force was 0.981 N. For each hardness value at least 10 indentations evenly distributed over the polished surface were made. The indentation (diameter about 30 μm) always covered several Si and Al₂O₃ particles. Irregularly shaped indentations were discarded. The presented values reflect the average of the regularly shaped indentations, the error represents the standard variation.
3 Results

3.1 X-ray diffraction

In all X-ray diffraction experiments on the ASCM0 and ASCM10 alloys lines diffracted from the Al-rich phase, the Si-rich phase, the Q (Al$_5$Cu$_2$Mg$_8$Si$_6$) phase and the Al$_7$Cu$_2$Fe phase were detected. These four phases are equilibrium phases in the ASCM alloy (see 8, 14). In the experiments on the ASCM10 alloy the α-Al$_2$O$_3$ (corundum) phase was detected. For both the ASCM0 and ASCM10 alloys lines diffracted by the θ phase appeared after 4 hours of ageing after solid quenching. Except for these six phases, no other phases were detected during isothermal ageing of the SQ ASCM0 and ASCM10 alloys.

Fig. 1: The Al-rich phase lattice parameters of the ASCM0 and ASCM10 alloys as a function of time of ageing at 453 K. The lattice parameter for pure aluminium, $a_{Al}^0$, is indicated.
Directly after solid-quenching the Al-rich phase lattice parameters of the ASCM0 and ASCM10 alloys are 0.40463±0.00004 nm and 0.40473±0.00003 nm, respectively. The Al-rich phase lattice parameters of the ASCM0 and ASCM10 alloys during ageing at 453 K after solid-quenching are given in Fig. 1. In the initial stage of ageing the Al-rich phase lattice parameters of both the ASCM0 and the ASCM10 alloys remain approximately constant. Between 2 and 32 hours of ageing the lattice parameters of both alloys increase to reach a value which remains approximately constant on prolonged ageing. This stable value is higher than the lattice parameter of pure unstrained aluminium (0.40496 nm, see Ref. 15). In Fig. 2 the difference between the Al-rich phase lattice parameters of the ASCM0 and the ASCM10 alloys is given.

It is observed that the lattice parameter of the ASCM10 alloy is on average 3.1×10⁻⁵ nm higher than the Al-rich phase lattice parameter of the ASCM0 alloy.

![Graph](image)

**Fig. 2:** The difference between the Al-rich phase lattice parameters of ASCM10 and ASCM0 as a function of time of ageing at 453 K.
In obtaining this average, the two lattice parameters values during the middle stages of ageing (4 and 8 h ageing), which deviate significantly from the mean difference, are not considered.

Directly after solid quenching the Si-rich phase lattice parameters of the ASCM0 and ASCM10 alloys are 0.54295±0.00008 nm and 0.54283±0.00004 nm, respectively. In Fig. 3 the Si-rich phase lattice parameters of the ASCM0 and the ASCM10 alloys during ageing at 435 K are presented. The Si-rich phase lattice parameters of both alloys are significantly lower than the lattice parameter of pure unstrained silicon (0.54308 nm, see Ref. 16). The Si-rich phase lattice parameters of the two alloys are nearly identical and remain approximately constant during ageing.

![Graph showing Si-rich phase lattice parameter vs. time of ageing for ASCM0 and ASCM10 alloys.](image)

**Fig. 3:** The Si-rich phase lattice parameter of the ASCM0 and ASCM10 alloys as a function of time of ageing at 453 K. The lattice parameter for pure silicon, $a_{Si}$, is indicated.
### Hardness measurements

The hardness of the ASCM0 and the ASCM10 alloys as a function of time of artificial ageing at 453 K is shown in Fig. 4. The standard deviations of the hardness values in the 10 separate indentations per ageing time are on average 5 HV for the ASCM0 specimen and 10 HV for the ASCM10 specimen. The higher standard deviation for the ASCM10 specimen is probably due to small variations in the local density of Al$_2$O$_3$ particles. It is observed that the hardness of the ASCM10 alloy is always significantly higher than the hardness of the ASCM0 alloy. During artificial ageing the difference is on average 28 HV and remains approximately constant during ageing. After quenching from the solution treatment temperature the difference is 42 HV.

![Graph showing hardness measurements over time](image)

**Fig. 4**: Vickers microhardness, HV, of the ASCM0 and ASCM10 alloys during ageing at 453 K after solid quenching.

For both alloys the time to reach peak hardness is 4 hours, which is slightly shorter than for the conventional 2014 aluminium alloy (ageing time for peak
hardness at 453 K: 3 h). For the ASCM0 alloy the peak hardness is 187 HV. This equals the peak hardness obtained during non-isothermal ageing at a heating rate of 2 K/min for a solid-quenched ASCM0 alloy. It is noted that all hardness values measured during ageing after solid quenching are appreciably higher than the hardness of the as-extruded ASCM0 (107 HV, see Ref. 7).

4 Lattice parameter changes due to dissolved atoms and misfitting inclusions

In an aluminium-based composite material in which alloying elements can dissolve in the Al-rich phase, the deviation of the Al-rich phase lattice parameter from the lattice parameter of pure aluminium is determined by two types of effects: i. the lattice parameter shift due to dissolved atoms and ii. the lattice parameter shift due to misfitting inclusions. Theoretical expressions for these two effects will be obtained in the next two sections.

4.1 Lattice parameter changes due to dissolved atoms

In binary Al-Cu and Al-Si alloys atoms of the alloying element dissolved in the Al-rich phase decrease the lattice parameter of the Al-rich phase. In both alloys the lattice parameter shift is proportional to the amount of dissolved atoms. In Al-Mg alloys dissolved Mg atoms increase the Al-rich phase lattice parameter. For high Mg contents of the Al-rich phase (> 2 at% Mg) the effect increases linearly with the Mg content of the Al-rich phase. For low magnesium contents a non-linear dependence of the Al-rich phase lattice parameter on the magnesium content is observed (see Fig. 5).

In many ternary alloy systems, the lattice parameter change of the Al-rich phase due to two different elements dissolved is in good approximation equal to the sum of two independent contributions (17). In these ternary alloys interaction between the two types of solute atoms can be neglected and lattice parameter shifts can be obtained from the lattice parameter shifts in the binary alloy systems. In the Al-Cu-Si alloy the interaction is negligible (15). In Al-Mg-Si alloys with 0.72 to 1.42 at% of alloying elements dissolved in the Al-rich phase, significant contractions of the Al-rich phase due to solute-solute interactions were observed (18). The lattice parameter shift due to solute-solute interactions reaches its maximum on the quasi-binary composition, associated with the Mg$_2$Si phase. Hill and Axon (18) suggested that the interaction term, $\Delta a^i$, can be approximated by:
where \([\text{Mg}_2\text{Si}]\) is the virtual concentration of Mg\textsubscript{2}Si in the Al-rich phase: \([\text{Mg}_2\text{Si}] = \frac{1}{2} [\text{Mg}]\) when \([\text{Mg}] < 2[\text{Si}]\) or \([\text{Mg}_2\text{Si}] = [\text{Si}]\) when \([\text{Mg}] \geq 2[\text{Si}]\). Also in Al-Cu-Mg alloys contractions due to solute-solute interactions occur (19). The data are too scarce and the uncertainties in the individual points too large to obtain the dependence on the Cu and Mg fractions of the Al-rich phase. The interactions are however very small (maximum shift about 0.00006 nm for Al-(1-x)at\%Cu-2x at\%Mg alloys, where x is in the order of 0.25 to 0.5 (19)). We will take account of the Mg-Cu interactions by using the same type of relation as was found for Mg-Si interactions. In the case of Cu-Mg interactions we will assume that the interactions are proportional to the virtual concentration of S (Al\textsubscript{2}CuMg) phase. Thus it is found:

\[
\Delta a^i_{\text{Cu-Mg}} = - 0.009 \text{ nm } [\text{Al}_2\text{CuMg}]
\]  

(2)

Fig. 5: Al-rich phase lattice parameters of Al-Mg alloys. Data from Refs. 19 (■), 20 (□), 21 (+) and 22 (○). The curved line represents the Al-rich phase lattice parameter as a function of its Mg-content as used in the present work.

To our knowledge no data on the lattice parameters of the Al-rich phase in the quaternary Al-Cu-Mg-Si are available. However, if interactions between Cu,
Mg and Si are negligible, lattice parameter changes of the Al-rich phase in the ASCM alloy due to dissolved atoms, $\Delta a_{Al}^d$, can be obtained from:

$$
\frac{\Delta a_{Al}^d}{a_{Al}^d} = p_{Si}x_{Si} + p_{Cu}x_{Cu} + p_{Mg}(x_{Mg}) + \frac{\Delta a_{Cu-Mg}^i + \Delta a_{Mg-Si}^i}{a_{Al}^d}
$$

(3)

where $x_{Cu}$ and $x_{Si}$ are the concentrations of Cu and Si atoms in the Al-rich phase, $p_{Si}$ and $p_{Cu}$ are the Vegard constants describing the effect of dissolved Si and Cu atoms on the Al-rich phase lattice parameter in the binary alloys (-4.30 10^{-2} and -1.18 10^{-1}, respectively (16)), and $p_{Mg}(x_{Mg})$ is the non-linear function which describes the effect of dissolved Mg atoms on the Al-rich phase lattice parameter.

### 4.2 Lattice parameter changes due to misfit accommodation

When a multi-phase alloy is subjected to temperature changes, misfit stresses will be introduced due to difference in coefficients of thermal expansion of the phases. These misfit stresses include a hydrostatic component which changes the lattice parameters of both the matrix and the misfitting inclusions. A model for the lattice parameter changes due to misfit accommodation in a matrix alloy alloy with spherical misfitting particles was presented in a previous paper (16). In this model the matrix is assumed to be a perfectly plastic material (non-strain hardening), the flow stress-strain behaviour is assumed to be independent of strain rate and of stress orientation, and both inclusion and matrix are assumed to be isotropic. These assumptions lead to the following expressions for the hydrostatic component, $p^i$, of the stresses in the elastically deforming zone of a spherical matrix A (radius R) with a spherical inclusion in its centre:

$$
p^i = -p_B - 2 \sigma_y \ln \left( \frac{R}{a} \right) ; \quad R \leq r_p
$$

(4a)

$$
p^i = \frac{2}{3} \sigma_y \left( \frac{r_p}{R} \right)^3 ; \quad R > r_p
$$

(4b)

where $\sigma_y$ is the yield strength of the matrix, $r_p$ is the radius of the plastic zone, $p_B$ is the internal pressure (the difference between the pressure in the inclusion and $p^i$) and $a$ is the radius of the inclusion. The volume fraction of inclusions, $y_i$, is given by:

$$
y_i = \left( \frac{a}{R} \right)^3
$$

(5)

$r_p$ and $p_B$ can be obtained from:

$$
r_p = a \exp \left[ -\frac{p_B}{2 \sigma_y} - \frac{1}{3} \right]
$$

(6)

$$
\frac{6\eta \mu c}{\sigma_y} \left[ 1 + \frac{p_B}{3K_B \varepsilon} - \frac{2p_B}{3K_A \varepsilon} \right] = \exp \left[ -\frac{3p_B}{2\sigma_y} - 1 \right]
$$

(7)

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where $\mu$ is the shear modulus, $K$ is the bulk modulus, $\eta = (1+\nu)/3(1-\nu)$, and $\varepsilon$ is the linear misfit parameter. For misfit introduced by thermal expansion mismatch it holds:

$$\varepsilon_T = \Delta \alpha \Delta T$$  \hspace{1cm} (8)

where $\Delta \alpha$ is the difference in CTE between matrix and reinforcement and $\Delta T$ is the temperature drop, the difference between annealing temperature and quenching temperature. For the case that the compressibility modulus of the inclusions deviates from the compressibility modulus of the matrix also the image stress contributes to the misfit. This contribution is given by:

$$\varepsilon_{pi} = p^i (K_B^{-1} - K_A^{-1})/3$$ \hspace{1cm} (9)

(Note that for Si and Al$_2$O$_3$ inclusions in an Al matrix $K_B > K_A$ and $\Delta \alpha > 0$. Hence $\varepsilon_T$ and $\varepsilon_{pi}$ are of opposite sign.) This effect is limited for the case of Si particles in an Al-rich matrix, since the compressibility modulii of the two phases are of the same order of magnitude. Due to the high compressibility modulus of the Al$_2$O$_3$ particles this effect can be important for Al$_2$O$_3$ particles in an Al-rich matrix.

The model presented above was derived for one single type of misfitting inclusions. In the ASCM10 alloy both Si particles and Al$_2$O$_3$ particles are present. In order to obtain the image stress for this case we will use an iteration method similar to the one suggested by Hamann et. al (23) for elastic accommodation in a composite containing various types of misfitting inclusions. This iteration method consists of the following steps:

- **Zeroth order**: calculate $(p^i)^{j,0}$ (= the image stress due inclusions of type j in the zeroth order) for each type of inclusion separately, assuming $\varepsilon = \varepsilon_T$.

  Then take:

  $$p^{i,0} = \sum_j (p^i)^{j,0}$$

- **$k$th order**: calculate $(p^i)^{j,k}$ for each type of inclusion separately, assuming $\varepsilon = \varepsilon_T + \varepsilon_{pi}$ with $p^i$ approximated by $p^{i,k-1}$. Then take:

  $$p^{i,k} = \sum_j (p^i)^{j,k}$$

For the case of Si particles and Al$_2$O$_3$ particles in an Al-rich matrix this method converges rapidly (second order corrections are smaller than 1%).

The lattice parameter change of the matrix due to misfit stresses, $\Delta a^m_A$, is now given by:

$$\frac{\Delta a^m_A}{a_A} = \frac{p^i}{3K_A}$$ \hspace{1cm} (10)

Here we have neglected the contribution of the lattice parameter of the plastically deformed zone to the average lattice parameter of the matrix phase. For the inclusion it holds:
\[
\Delta a^B_B = \frac{p_B + p^i}{3K_B}
\]  

(11)

The contribution of misfitting \( \theta \) and \( \theta' \)-phase particles to the total lattice parameter change is about one order of magnitude lower than the contribution of misfitting Si-particles to the lattice parameter change (16). For this reason we will neglect the misfit around \( \theta \) and \( \theta' \)-phase particles. The CTE of the Q phase is not known, however since in the ASCM alloys the amount of Q phase formed is much lower than the amount of Si phase (see Appendix), also the effect of misfitting Q-phase particles on misfit stresses is much smaller than the effect of misfitting Si-phase particles. For this reason we will neglect the contribution of misfitting Q-phase particles to \( p^i \). Now two types of particles causing significant misfit strains are left: Si particles and \( \text{Al}_2\text{O}_3 \) particles.

A problem in the evaluation of the formulas for the misfit stresses is the anisotropy of aluminium, silicon and aluminium oxide. The theory described above, which is based on non-interacting stress fields and isotropy of inclusions and matrix, predicts that the inclusions are in a state of uniform hydrostatic stress. In that case the strains in the Si particles are determined solely by the \( S_{11} \) and \( S_{12} \) elastic compliances. Interaction of stress fields and anisotropy of the phases in the ASCM alloys will cause deviations from the pure hydrostatic stress state in the inclusions. Providing that these disturbances are small it is however still justified to obtain the elastic constants of the Si inclusions from the \( S_{11} \) and \( S_{12} \) compliances. Due to its hexagonal structure the stress state in the \( \alpha-\text{Al}_2\text{O}_3 \) (corundum) particles is very complex (a crystal with hexagonal structure has 5 independent elastic constants). However, since misfitting \( \alpha-\text{Al}_2\text{O}_3 \) particles in an Al matrix are nearly incompressible (the bulk modulus is 350 GPa, which is about 3 times that of silicon) the exact values of the elastic constants are in this case not very important, and in this work Young’s modulus is estimated by the value for polycrystalline alumina as given by Crandall et al. (24), while \( v \) is estimated to equal \(-S_{12}/S_{11}\) as given by Tefft (25). The anisotropy of aluminium is relatively small. For this reason the elastic constants of polycrystalline aluminium are used for the calculations. The yield strength of the matrix around the Si and \( \text{Al}_2\text{O}_3 \) particles in the initial part of ageing (up until about 0.5 h) is estimated to equal the yield strength of the 2014 aluminium alloy (approximate composition Al-2at\%Cu-1.5at\%Mg-1at\%Si), aged for a few minutes at 450 K subsequent to homogenizing and quenching (250 MPa, see Ref. 26). Since the hardness of the overaged ASCM alloy approximately equals the hardness of the alloy in the initial state of ageing (see Section 3.2), the yield strength of the matrix in the overaged state is also estimated as 250 MPa. The material constants used in this work are gathered in Table II.
Table II: Elastic constants, yield strength and coefficients of thermal expansion used in this work. The elastic constants of Si are obtained from the S11 and S12 compliances given by Smithells (13). The elastic constants of Al2O3 were estimated from data by Tefft (25) and by Crandall et al. (24). For the elastic constants of the Al-rich matrix values for polycrystalline pure aluminium were used (see Ref. 13). The yield strength of the Al-Si-Cu alloy was estimated to equal the yield strength of an 2014 aged for a few minutes at 450 K (26).

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$ (10$^{-6}$ K$^{-1}$)</th>
<th>K (GPa)</th>
<th>$\mu$</th>
<th>$\sigma_y$ (MPa)</th>
</tr>
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<td>69</td>
<td>27</td>
<td>250</td>
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<tr>
<td>Si</td>
<td>3.0</td>
<td>99</td>
<td>51</td>
<td>-</td>
</tr>
<tr>
<td>Al2O3</td>
<td>7.1</td>
<td>350</td>
<td>156</td>
<td>-</td>
</tr>
</tbody>
</table>

5 Discussion

5.1 Lattice parameter changes of the ASCM alloys during ageing

In order to apply the formulas in Section 4.1 to the solid-quenched alloys, we need to know the composition of the Al-rich phase at that stage. The calculation of the composition of the Al-rich phase after solid quenching, using the quaternary Al-Cu-Mg-Si phase diagram, is outlined in the appendix. It follows that after solid quenching the fraction of Al-rich phase in the base alloy equals 0.78. The composition of the Al-rich phase in the solid-quenched ASCM alloys is estimated as Al-1.5at%Cu-0.7at%Mg-0.5at%Si.

From Eq. 3 follows that for the case of Q-phase formation in its stoichiometric composition, the effects of Cu, Mg and Si depletion of the matrix approximately balance. So Q-phase formation does not change the Al-rich phase lattice parameter. It is also apparent that $\theta$-phase formation, which involves the precipitation of copper from the Al-rich phase, will increase the Al-rich phase lattice parameter. The formation of these two phases can fully account for the lattice parameter changes during ageing. As was also observed during non-isothermal ageing of solid-quenched ASCM alloys, Q-phase precipitates are the first phase to form. During Q-phase formation the lattice parameter remains approximately constant, while the hardness increases (see Figs. 1 and 4). The increase in hardness during Q-phase formation was also observed during non-isothermal ageing of the same alloy (7). The next phase to precipitate is the $\theta$.
phase, causing an increase of the lattice parameter. The increase of the lattice parameter starts between 2 and 4 hours of ageing (see Fig. 1). This corresponds well with the appearance of \( \theta \)-phase lines after 4 hours ageing. The precipitation of \( \theta \) phase does not increase the hardness (14), which is indeed observed (see Fig. 4). On prolonged ageing (\( > 4 \) h) \( Q \)-phase precipitates will coarsen and overageing occurs (see next Section).

Except for dissolved atoms also misfit accommodation is expected to influence the lattice parameter of the Al-rich phase. Computation of misfit stresses in a two-dimensional aluminium-based composite by the finite-element method indicates that disturbance of the average macrostress at the surface occurs in a layer of about 7 \( \mu \)m (27). The penetration depth of X-rays in aluminium is much larger, and the effect of surface relaxation on the stresses determined by X-ray diffraction is about 2 \% (27). Considering the accuracy of our measurements, the surface relaxation of stresses is negligible. Clear indications for the influence of misfit accommodation can be obtained from the Si-rich phase lattice parameters and from the observed difference in Al-rich phase lattice parameters during ageing of ASCM0 and ASCM10 alloys. In Table III the hydrostatic pressures on misfitting \( \text{Al}_2\text{O}_3 \) and Si particles in an infinite matrix, \( p_B \), and the image stresses as obtained from Eqs. 4-9 are given for the temperature drops \( \Delta T \) studied in this work. From this table follows that after quenching from the ageing temperature 453 K (implying a \( \Delta T \) of 160 K) the difference in hydrostatic stress of the Al-rich phase is 16 MPa, which corresponds to an Al-rich phase lattice parameter shift of 3.1 \( 10^{-5} \) nm. This corresponds very well with the average difference in Al-rich phase lattice parameters for the ASCM0 and ASCM10 alloys quenched from the ageing temperature 453 K (3.1 \( 10^{-5} \) nm, see Section 3.1). After solid quenching, the Al-rich phase lattice parameter of the ASCM10 alloy is (10\( \pm 5 \)) \( 10^{-5} \) nm higher than the Al-rich phase lattice parameter of the ASCM0 alloy. This corresponds within experimental error to the model predictions which predict a difference of 8 \( 10^{-5} \) nm. The Si-rich phase lattice parameters of the ASCM0 and ASCM10 alloys during ageing are on average 2.2 \( 10^{-4} \) nm (= 4.2 \( 10^{-4} \) \( a_{Si}^0 \)) lower than the lattice parameter of pure unstrained Si (see Fig. 3). The Si-rich phase lattice parameter shifts predicted by the model (-6 \( 10^{-4} \) \( a_{Si}^0 \) for ASCM0 and -5.4 \( 10^{-4} \) \( a_{Si}^0 \) for ASCM10, see Table III) are somewhat higher than this average, but are within the range of observed lattice parameter shifts. Models considering only elastic accommodation predict even higher values for the Si-rich phase lattice parameter shift (about 7 \( 10^{-4} \) \( a_{Si}^0 \)).

Directly after solid quenching and in the first part of ageing, the effects of dissolved atoms on the Al-rich phase lattice parameter are much larger than
the effect of the image stress. Because of the large uncertainties involved in the
determination of the effect of dissolved atoms on the Al-rich phase lattice
parameter it is not possible to compare the Al-rich phase lattice parameters at
this stage of ageing with model predictions. Towards the end of the
precipitation the lattice parameter of the ASCMO0 alloy reaches a stable value
which is 3.9 $10^{-4}$ times higher than the lattice parameter of pure unstrained Al.
This is for the largest part caused by the misfit stresses. However, even at this
stage, the effect of dissolved atoms is not negligible. The equilibrium solid
solubilities at this temperature (see Appendix) cause a relative lattice
parameter shift of about -0.3 $10^{-4}$. Thus the relative shift of the Al-rich phase
lattice parameter due to misfit stresses is at least 4.2 $10^{-4}$. The model predicts a
matrix misfit stress of 55 MPa, which would cause a relative lattice parameter
shift of 2.7 $10^{-4}$. Thus a significant discrepancy between misfit stress
predictions by the model and measured misfit stresses exists. Since the misfit
stresses predicted by the model are relatively insensitive to variations in yield
stress and in elastic constants, it is highly unlikely that inaccurate values for
these parameters can explain the discrepancy. If we for instance consider the
extreme case of pure elastic accommodation of incompressible Si particles (i.e.
$\sigma_y=\infty$ and $K_B=\infty$) the relative lattice parameter shift due to misfit would be 3.5
$10^{-4}$ (see for instance Ref. 28), which is still short of the observed shift.

<table>
<thead>
<tr>
<th>$\Delta T$</th>
<th>$p_B$(Si)</th>
<th>$p^i$</th>
<th>$\Delta a_S/a_S$</th>
<th>$p_B$(Al$_2$O$_3$)</th>
<th>$p_B$(Si)</th>
<th>$p^i$</th>
<th>$\Delta a_S/a_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(x $10^{-4}$)</td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(x $10^{-4}$)</td>
</tr>
<tr>
<td>160</td>
<td>-233</td>
<td>55</td>
<td>-6.0</td>
<td>-214</td>
<td>-232</td>
<td>71</td>
<td>-5.4</td>
</tr>
<tr>
<td>486</td>
<td>-412</td>
<td>160</td>
<td>-8.4</td>
<td>-382</td>
<td>-411</td>
<td>203</td>
<td>-7.0</td>
</tr>
</tbody>
</table>

In many different cases the predictions of Eshelby type models for the stress
in matrices of various types of Al-based composites due to elastic misfit
accommodation are found to be lower than the measured stresses (16, 27, 29,
30). This indicates that although the elastic-plastic model described in Section
4.2 provides a more realistic description of misfit accommodation in a
composite than pure elastic models, significant differences with observed thermal misfit strains remain. Another significant discrepancy is that in the ASCM0 specimens the measured stress in the inclusion \( (= p_B + p^i) \) and the image stress, \( p^i \), do not comply with the rule for the equilibrium of forces:

\[
p_B + p^i = p^i
\]  \hspace{1cm} (12)

The discrepancy between models and experimental data as noticed above will be subject of future research. One possible explanation might be an increase of the volume of the plastic zone due to the creation of various types of defects like dislocations and vacancies (see Ref. 16).

### 5.2 The effect of heat treatment on the hardness

The average dislocation density of a heat treated MMC increases with the volume fraction of reinforcement (31, 32), while the subgrain size generally decreases with increasing volume fraction of reinforcement (33, 34). Both of these effects increase the yield strength of the composite with increasing volume fraction. The increase in yield strength, \( \Delta \sigma_Y \), due to an increase in dislocation density, \( \rho \), can be estimated from (see Ref. 35):

\[
\Delta \sigma_Y = A \mu b \rho^{1/2}
\]  \hspace{1cm} (13)

where \( b \) is the Burgers vector in Al (0.286 nm) and \( A \) is a constant usually taken as 1.25 (see 35). The average dislocation density around a spherical misfitting inclusion has been estimated by various workers. The general expression is (see Refs. 36, 37, 38):

\[
\rho = B \frac{y_B \varepsilon}{y_B (1 - y_B)}
\]  \hspace{1cm} (14)

where \( d \) is the smallest dimension of the particle and \( B \) is a numerical constant which depends on the shape of the misfitting inclusion. Different methods for evaluation of \( B \) have been proposed by various workers. According to Arsenault and Shi (36), who considered the minimal amount of dislocations necessary to accommodate a rectangular particle, \( B \) varies between 4 for particles elongated in one direction and 12 for equiaxed particles (36). We will here use the value obtained by Dunand and Mortensen for incompressible spherical particles: \( B = 12 \sqrt{2} \). The yield strength of an Al alloy is usually proportional to its hardness (39). From comparison of hardness measurements with tensile tests performed previously on the ASCM alloys (7, 40) the following proportionality appears to hold:

\[
\sigma_Y \text{ (MPa)} = 2.1 \text{ HV}
\]  \hspace{1cm} (15)

Using Eqs. 13-15 we can now calculate the increase in hardness caused by dislocations introduced by thermal misfit. For the ASCM0 and ASCM10 alloys
this yields a hardness difference of 14 HV after ageing at 453 K and 24 HV after quenching from the solution treatment temperature.

The subgrain structure in our ASCM alloys, which can also have a significant influence on the hardness (33), was not studied. Arsenault et al. (34) measured subgrain sizes and dislocation densities in 1100 and 6061 Al alloys reinforced with SiC particles produced by powder metallurgy routes. They showed that for a volume fraction of inclusions around 20 vol% with sizes in the order of 1 μm the strengthening effect due to subgrains roughly equals the strengthening due to dislocation generation. So it is expected that the increase in hardness, due to dislocation and subgrain strengthening, for the ASCM10 alloy as compared to the ASCM0 alloy equals 28 and 48 HV after artificial ageing and after quenching from solution treatment treatment temperature, respectively. These values agree fairly well with the observed hardness differences after these respective heat treatments (28 and 42 HV, respectively, see Section 3.2).

For application of the ASCM alloy it is interesting to note that an optimised T6 heat treatment consists of solution treatment at 779 K (just below the start of melting, see Ref. 7), quenching and ageing for 4 hours at 453 K (see the hardness measurements presented in Section 3.2). The solution treatment time depends on work piece size and furnace capacity, but should preferably be as short as possible to limit coarsening of the Si particles and the development of pores due to gas evolution (see Ref. 41). Indications exist that a solution treatment of 30 min is sufficient (42). This T6 treatment increases the room temperature hardness of the alloy from 107 HV to about 187 HV (an increase of about 75%).

On continued ageing after the peak hardness has been reached, the hardness decreases. This hardness decrease is expected to be caused by coarsening of Q-phase precipitates. According to Shercliff and Ashby (43), the mean particle radius r at time t_e is related to that, r_0, at time t_0 according to:

$$r^3 - r_0^3 = A_1 \int_{t_0}^{t_e} \frac{E_A}{kT} \exp \left[ \frac{-E_A}{kT} \right] dt$$  \hspace{1cm} (16)

where k is Boltzmann's constant, t is the time, E_A is the activation energy for coarsening, and A_1 is a constant. For reasons of convenience we will define \( \beta \), the temperature corrected time defining the state of the coarsening process, by:

$$\beta = \int_{t_0}^{t_e} \frac{E_A}{kT} \exp \left[ \frac{-E_A}{kT} \right] dt$$  \hspace{1cm} (17)
It is expected that the activation energy for volume diffusion, $E_D$, of the alloying elements determines $E_A$ to a large extend. The activation energies for volume diffusion of Cu, Mg and Si in the Al-rich phase in binary alloys are all between about 1.3 and 1.4 eV (see Ref. 14). According to the classical LSW-coarsening theory, due to Lifshitz and Slyozov (44) and Wagner (45), the rate of coarsening in a binary system is proportional to the product of solubility and diffusion rate. Extensions and modifications of the classical LSW coarsening theory which take finite volume fraction of coarsening particles into account (the original LSW coarsening theory assumed the volume fraction of coarsening particles to be zero) recapture the proportionality of the rate of coarsening with the product of solubility and diffusion rate (46, 47, 48). Thus it is expected that in the quaternary system of interest here, the rate of coarsening is proportional to the solubility of the atoms which determine the coarsening rate, $x_{ae}(T)$, and their diffusivity, $D(T)$. The solubility of alloying atoms in aluminium, $x_{ae}(T)$, is in many cases an exponential function of the temperature:

$$x_{ae}(T) = x_0 \exp\left(-\frac{\Delta H_{sol}}{kT}\right)$$

(18)

where $\Delta H_{sol}$ is the heat of solution of the alloying element and $x_0$ is a constant. The $\Delta H_{sol}$ values for Al-rich Al-Cu, Al-Mg and Al-Si binary solid solutions equal 0.42, 0.19 and 0.52 eV, respectively (see Refs. 49 and 50 for $\Delta H_{sol}$ values of Al-Cu and Al-Si, the $\Delta H_{sol}$ value of Al-Mg was obtained from solid solubility data in Ref. 51). Since both $D(T)$ and $x_{ae}(T)$ have a similar exponential time-dependency, the activation energy for the overall coarsening process will be the sum of the activation energy for diffusion and the heat of solution of the alloying element, i.e.:

$$E_A = E_D + \Delta H_{sol}.$$  

(19)

Since no solid solubility data nor diffusivity data on the quaternary Al-Cu-Mg-Si system at the low temperature range of interest here ($T < 550$ K) are available, it is not clear which alloying element governs the time and temperature dependency of the coarsening. (Based on data from binary systems (14) it is expected that Si is the alloying element with the lowest product of solubility and diffusivity at temperatures below about 600 K.) Another complicating factor is that in the quaternary system $\Delta H_{sol}$ values obtained from the binary systems might not be valid. Further, the apparent activation energy for diffusion might be lowered due to the presence of vacancies. The activation energy for Q-phase precipitation of 1.25 eV, as obtained by differential scanning calorimetry (8), does indeed hint at vacancy-enhanced diffusion. Eventually, on the basis of the available data, the activation energy for coarsening is expected to be between about 1.4 and 1.8 eV. For this reason we will use $E_A = 1.6$ eV.

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In Fig. 6 five sets of data on the drop in hardness during overageing of ASCM alloys are given as a function of ln $\beta$. Two data sets are from isothermal overageing at 453 K of the ASCM0 and ASCM10 alloys (see Fig. 4). The third set of data is from non-isothermal overageing of an ASCM0 alloy at heating rate 2 K/min in the temperature range 507-574 K (see Ref. 7), while the fourth set of data is from the specimens of the third data set, additionally aged for 100 h at 473 K (see Ref. 7). It was observed before that 4 specimens which were initially aged at temperatures below 433 K, the hardness after an additional exposure of 100 h at 473 K drops to 120 HV. These data points are presented as data set #5. (To obtain $\Delta$HV it is assumed that also for these specimens the maximum hardness is 187 HV.) So the five data sets combine data on isothermal overageing, overageing at a constant heating rate and more complex non-isothermal overageing treatments. The data points cover overageing in the temperature range from 453 to 574 K. It is observed that all data points, except for two, fit well to a single curve.

Fig. 6: The hardness drop due to overageing, $\Delta$HV, as a function of the logarithm of the temperature corrected time for coarsening, $\ln \beta$ ($\beta$ in hours). The activation energy for coarsening was chosen as 1.6 eV.
This indicates that, at least in the temperature range and hardness range considered, coarsening is the main effect determining the drop in hardness during overageing (other contributions to the hardness like dislocation strengthening and solid solution hardening, which are expected to increase with increasing final ageing temperature, are apparently not important) and that the activation energy of 1.6 eV chosen above is indeed a good estimate. It should however be noted that similar results can be obtained for activation energies in the range 1.4 to 1.8 eV, and that the current estimate of $E_A$ can not be considered to be an accurate activation energy determination.

The two points which show a significant higher hardness as compared to the hardness given by the curve in Fig. 6 concern hardness values measured after the duplex overageing treatment of heating at 2 K/min to 487 and 507 K, respectively, followed by 100 hours ageing at 473 K. A possible explanation for the observed deviation may be that in these specimens some precipitation continues during the isothermal ageing stage.

Extrapolation of the curve in Fig. 6 predicts that the hardness of a T6 treated ASCM0 specimen is reduced to its original as-extruded hardness (i.e. when $\Delta HV = -80$) when $\beta = -29$. This corresponds for instance with a 100 h isothermal exposure at 500 K or a 1000 h isothermal exposure at 470 K. (Since exposure at elevated temperature also decreases the hardness of as-extruded specimens, the hardness of the T6 treated specimen exposed for 100 h at 500 K will still be higher than the extruded specimen after the same exposure.)

Conclusions

Precipitation in solid-quenched and subsequently aged specimens of Al - 20 w% Si - 3.5 w% Cu - 1 w% Mg (ASCM) alloys reinforced with 0, 2.5, 5 and 10 vol% $\text{Al}_2\text{O}_3$ particles was studied by X-ray diffraction and by hardness measurements. The following conclusions can be drawn:

- During artificial ageing at 453 K, Q phase precipitates first. During Q phase precipitation the Al-rich phase lattice parameter remains approximately constant, while the hardness increases.
- After about 4 hours ageing at 453 K, $\theta$-phase precipitation starts. During $\theta$-phase precipitation the Al-rich phase lattice parameter increases, while the hardness does not increase.
- The presence of $\text{Al}_2\text{O}_3$ particles has little influence on the precipitation kinetics.
- The presence of $\text{Al}_2\text{O}_3$ particles increases the hardness of the ASCM alloy. The increase corresponds well with model predictions based on enhanced
dislocation generation and reduced subgrain size due to the presence of Al₂O₃ particles.

- An optimized T6 heat treatment for the ASCM alloys consists of a short solution treatment at 779 K, followed by water-quenching and ageing for 4 hours at 453 K.

- After the peak in hardness has been reached, continued ageing causes the hardness to decrease. This overageing results from coarsening of the Q phase. The observed hardness drop as a function of temperature and time corresponds to the classical LSW coarsening theory.

- A model assuming ideal plastic behaviour of the matrix describes the cooling-induced changes of the Si-rich phase lattice parameter fairly well. For the cooling-induced changes of the Al-rich phase phase lattice parameter significant discrepancies between model predictions and measurements remain.

**Appendix**

To obtain the composition of the Al-rich phase after homogenizing at 779 K, we will use the Al-Cu-Mg-Si phase diagram at 775 K as given by Mondolfo (14). The small deviations caused by the small temperature difference will be neglected. The phase diagram shows that in the quaternary system all copper can be dissolved. Some of the copper, however, is incorporated in the Al₇Cu₂Fe phase which is observed in all specimens by X-ray diffraction. Since Fe solubility in the Al-Cu-Fe system is negligible, the entire phase is insoluble. Thus for one mole of base alloy the number of atoms in the Al₇Cu₂Fe phase is 10x Fe = 0.012 moles (x Fe is the gross Fe content of the alloy). The magnesium solubility in the Al-rich phase at 775 K is about 0.65 at%. Thus for one mole base alloy the number of atoms in the Q (Al₅Cu₂Mg₈Si₆) phase, x_Q, is (x_Mg - 0.8x 0.0065 - 21/8 = 0.015 moles (for the time being the amount of Al-rich phase, y_A, is estimated at 0.8). The silicon solubility in the Al-rich phase at 775 K is about 0.45 at%. Thus for one mole of base alloy the amount of Si phase is approximately x_Si - 0.8x 0.0045 - 6/21 x_Q = 0.191. The number of copper atoms dissolved in the Al-rich phase is x_Cu - 2x_Fe - 2/21 x_Q = 0.0117 moles. Now we can obtain the number of atoms in the Al-rich phase per mole base alloy by subtracting the number of atoms in the (partially) insoluble phases from the total amount. This gives y_A = 1 - 0.191 - 0.015 - 0.012 = 0.781 moles. From this follows the estimated composition of the Al-rich phase after solid quenching:

Al-1.5at%Cu-0.7at%Mg-0.5wt%Si.

Towards the end of the precipitation times investigated the Al-rich phase lattice parameter reaches a stable value. This indicates that precipitation is
completed and that the composition of the Al-rich phase equals its equilibrium composition at the ageing temperature. The solubilities at the ageing temperature in the quaternary system are not known. However all three relevant solid solubilities are expected to be very low, and a rough estimate will be sufficient for our purpose. The solid solubility of silicon in the Al-rich phase is not much influenced by Cu and Mg additions. Hence the solid solubility can be estimated from (extrapolation in) the binary Al-Si phase diagram. This solid solubility is negligibly low (about 7 $10^{-5}$, see 47), and thus the Cu and Mg solid solubilities can be estimated from the ternary Al-Cu-Mg system. In the ternary Al-Cu-Mg system at 453 K the solid solubilities obey the following rule: $x_{Cu} x_{Mg} = 1 \times 10^{-7}$. In the Al-Cu-Mg system the sum of the two solubilities is maximum for $x_{Cu} = x_{Mg}$. Thus we obtain the following result: $x_{Cu} = x_{Mg} = 3 \times 10^{-4}$.

References

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SUMMARY

This thesis involves a number of publications concerning the heat treatment of metal matrix composites (MMCs) produced via rapid solidification processing (RSP) techniques. Two types of RSP MMCs were studied. The Al-1.3at%Cu-19at%Si alloy was produced via melt spinning, while the Al-20at%Si-1.5at%Cu-1at%Mg (ASCM) alloys reinforced with varying contents of Al₂O₃ particles were produced via gas atomisation and subsequent mixing with Al₂O₃. Both alloys were finally compacted by hot extrusion. In all alloys a high percentage (about 20 vol%) of silicon particles are present. Due to RSP, these particles are spherically shaped and finely dispersed in the matrix, with an average size of 4 μm. In addition to these Si particles, the reinforced ASCM alloys contained up to 10 vol% of irregularly shaped Al₂O₃ particles with sizes ranging from 1 to 6 μm and an average aspect ratio of 2. The alloys were studied by X-ray diffraction, differential scanning calorimetry (DSC), hardness measurements and optical microscopy.

In the final stages of isothermal ageing of the water-quenched (WQ) ASCM and Al-Cu-Si alloys the Al-rich phase lattice parameter, which is initially lower than the lattice parameter of pure aluminium, reaches a stable value which is higher than the lattice parameter of pure aluminium. This difference is due to the hydrostatic component of the misfit stresses (the so-called image stress) caused by misfitting Si and Al₂O₃ particles in the matrix. This misfit after quenching from the ageing temperature results from a difference in thermal expansion between matrix and reinforcement. The lattice parameters of the inclusions are decreased by the thermal misfit stresses. In Chapter V a model is presented which calculates the misfit stresses for the case of misfitting spherical particulates in a matrix which deforms both elastically and (ideally) plastically. Although the present model takes the effect of plastic accommodation into account, significant differences between the measured hydrostatic stresses in the Al-rich phase and model predictions remain. The model predicts the lattice parameter changes in the inclusion fairly well.

In Part I the precipitation in the Al-Cu-Si alloy is studied and compared with a conventionally cast, unreinforced Al-1.6at%Cu alloy. In the water-quenched (WQ) Al-Cu alloy GP-zone formation was nearly completed within one hour of ageing at room temperature. It appeared that in WQ Al-Cu-Si the rate of GP-zone formation is about 10⁴ times lower as in the Al-Cu alloy. This large difference in formation rate is thought to be mainly due to the presence of misfitting Si particles which cause stresses and dislocations in the matrix. The θ' (Al₂Cu) phase precipitation, which is the main hardening mechanism for
both alloys, occurs much faster in the WQ Al-Cu-Si alloy as compared to the WQ Al-Cu alloy. Both during heating at a constant rate and during isothermal ageing of the WQ Al-Cu-Si alloy, the Si and the $\theta'$ phases precipitate simultaneously. Since in the respective binary alloys the temperature ranges for Si and the $\theta'$ phase precipitation differ significantly, this indicates a strong interaction between the two precipitation processes. This interaction is thought to be the result of the interaction of stress fields around the two types of precipitate. The activation energy of the combined precipitation process is 0.97 eV.

The heat contents of the precipitation heat effects occurring in the DSC experiments on Al-Cu and Al-Cu-Si were compared with predictions of a model based on the heat of formation of the phases concerned, $\Delta H_{sol}$, and the amount precipitated, as obtained from the (metastable-) solid solubility at the end temperature of the precipitation effect. For GP-zone formation also the energy related with strain fields around the zones contribute significantly to the total energy of formation. This was taken into account by adopting an effective $\Delta H_{sol}$ value appropriate for GP zones formed at room temperature, which resulted in a good correspondence between the measured heat contents of GP-zone formation and the model predictions. In the Al-Cu alloy the heat content of the combined $\theta'/\theta$ precipitation effect was for all heating rates intermediate between the model predictions for $\theta'$-phase formation and those for $\theta$-phase formation, while the average precipitation energy (36 kJ per mole Cu) was independent of DSC heating rate and quenching rate. For low heating rates ($\leq 20$ K/min) the heat content of the precipitation effect in DSC experiments on the WQ Al-Cu-Si alloy corresponded well with model predictions for the combined $\theta'$ and Si formation. For high heating rates ($\geq 40$ K/min) these heat contents corresponded with the heat contents for the combined $\theta$ and Si formation. Apparently the Cu precipitation shifts from $\theta'$-phase formation to $\theta$-phase formation when the heating rate is increased beyond 20 K/min. In accordance with this an exothermic heat effect due to the transition from $\theta'$ phase to $\theta$ phase was detected beyond the main precipitation peak for heating rates $\leq 20$ K/min.

In Part 2, the precipitation in ASCM alloys with 0, 2.5, 5, and 10 vol% of $\mathrm{Al}_2\mathrm{O}_3$ particles is investigated. During isothermal ageing (at 453 K) and during non-isothermal ageing (at heating rate 0.5 K/min) of the WQ ASCM alloys the following intermetallic phases are detected by X-ray diffraction: Q phase ($\mathrm{Al}_{15}\mathrm{Cu}_2\mathrm{Mg}_8\mathrm{Si}_6$) and $\theta$ phase. The hardness increase during ageing at temperatures above the GP-zone solvus is almost entirely caused by the phase which precipitates first: the Q phase. The addition of $\mathrm{Al}_2\mathrm{O}_3$ particles to the
ASCM alloy has only very limited influence on the kinetic of precipitation, and an optimised artificial ageing treatment (4 h at 453 K) is applicable to ASCM alloys with and without Al₂O₃ particles. This insensitivity to Al₂O₃ additions is thought to be caused by the presence of Si particles which are the main cause for dislocation generation and the creation of misfit stress. The room temperature hardness of the extruded alloy can almost be doubled by solid quenching and subsequent application of the optimised ageing treatment. The only Al-Cu precipitate detected is the equilibrium θ phase, which does not increase the hardness.

After reaching the peak hardness, the ASCM alloys overage and the hardness decreases. This overageing results from coarsening of the Q phase. The activation energy for overageing (about 1.6 eV) indicates that the temperature dependency of the rate of overageing is governed by the product of solid solubility and diffusion rate (as the classical LSW coarsening theory predicts).
SAMENVATTING

 Dit proefschrift bevat verscheidene artikelen over de warmtebehandeling van met snelle stollingsprocessen (SSP) geproduceerde metaal-matrix-composieten (MMC's). Twee typen SSP MMC's werden bestudeerd. De Al-1,3at%Cu-19at%Si legering werd geproduceerd via spingieten; de Al-20at%Si-1,5at%Cu-1at%Mg (ASCM) legeringen versterkt met Al₂O₃-deeltjes werden geproduceerd via gasatomisatie en mengen met Al₂O₃-deeltjes. Beide legeringen werden uiteindelijk gecompacteerd via warme extrusie. In alle legeringen is een hoog percentage (ongeveer 20 vol%) siliconium deeltjes aanwezig. Door de toegepaste snelle stollingsprocessen zijn deze deeltjes bij benadering bolvormig en fijn gedispergeerd in de matrix (de gemiddelde diameter van de deeltjes is ongeveer 4 µm). De ASCM legeringen bevatten behalve deze Si deeltjes tot 10 vol% onregelmatig gevormde Al₂O₃-deeltjes met groottes van 1 tot 6 µm en een aspectverhouding van 2. De legeringen werden bestudeerd met röntgendiffractie, differentieel calorimetrische analyse (engels: differential scanning calorimetry, DSC), hardheidsmetingen en optische microscopie.

In het laatste stadium van isotherm verouderen van in water afgeschrikte ASCM en Al-Cu-Si legeringen bereikt de roosterparameter van de Al-rijke fase een stabiele waarde die hoger is dan de roosterparameter van zuiver aluminium. Dit verschil wordt veroorzaakt door de hydrostatische component van de spanningen die worden veroorzaakt door mispassende Si- en Al₂O₃-deeltjes. Deze mispassing na afschrikken van de verouderingstemperatuur wordt veroorzaakt door een verschil in thermische expansie tussen matrix en versterkende deeltjes. De roosterparameter van de Si-deeltjes wordt verlaagd door de mispassingsspanningen. In hoofdstuk V wordt een model gepresenteerd dat spanningen berekent die veroorzaakt worden door bolvormige, mispassende deeltjes in een ideaal plastisch vervormende matrix. Hoewel in dit model plastische accommodatie in beschouwing wordt genomen, blijven er significante discrepanties tussen de gemeten spanningen en de berekende spanningen. Het model voorspelt de spanningen in de Si-deeltjes echter vrij goed.

In deel 1 wordt de precipitatie in de Al-Cu-Si legering bestudeerd en vergeleken met een conventioneel gegoten Al-1,6at%Cu legering. In de in water afgeschrikte (WQ) Al-Cu legering is de vorming van GP-zones bijna voltooid binnen één uur verouderen op kamertemperatuur. In de WQ Al-Cu-Si legering bleek de snelheid van GP-zone vorming een factor 10⁴ lager te zijn dan in de Al-Cu legering. De mispassende Si-deeltjes die spanningen en dislocaties veroorzaken in de matrix van de Al-Cu-Si legering zijn mogelijk de oorzaak van
dit grote verschil. De precipitatie van de θ' (Al₂Cu)-fase, die voor beide legeringen het belangrijkste hardingsproces is, verloopt het snelst in de WQ Al-Cu-Si legering. In de WQ Al-Cu-Si legering precipiteren zowel gedurende isotherm verouderen als gedurende verouderen met een constante opwarm-snelheid de Si- en de θ'-fase tegelijkertijd. Daar de temperaturen voor de Si- en θ'-fase precipitatie in de respectieve binaire legeringen aanmerkelijk verschillen, duidt dit op een sterke interactie tussen de twee precipitatie-processen. Deze interactie wordt mogelijk veroorzaakt door de interactie van de spanningsvelden rond de twee soorten van precipitatien. De activeringsenergie voor het gecombineerde precipitatieproces is 0,97 eV.

De warmteinhoud van de precipitatie effecten die optreden tijdens de DSC experimenten aan Al-Cu en Al-Cu-Si worden vergeleken met een model dat gebaseerd is op de vormingsenthalpie van de betreffende fasen, \( \Delta H_{\text{sol}} \), en de geprecipiteerde hoeveelheid, zoals verkregen uit de (metastabiele-) oplosbaarheid bij de eindtemperatuur van het precipitatie-effect. In geval van GP-zonevorming geeft ook de energie van de spanningsvelden rond de zones een significante bijdrage tot de totale vormingsenergie. Hiermee wordt rekening gehouden door een effectieve \( \Delta H_{\text{sol}} \)-waarde voor GP-zones gevormd op kamer-temperatuur te gebruiken. Dit leverde uiteindelijk een goede overeenstemming tussen experiment en model op. De warmteinhoud van het gecombineerde θ/θ'-precipitatie-effect in de Al-Cu legering ligt voor alle opwarmsselheden tussen die uit de modellberekeningen voor θ'-fasevorming en die voor θ-fasevorming.

De gemiddelde precipitatiwarme (36 kJ per mol Cu) is onafhankelijk van opwarmsselheid en afschrikzak. Bij lage opwarmsselheden (≤ 20 K/min) komen de warmteinheden van het precipitatie-effect in DSC experimenten aan de WQ Al-Cu-Si legering goed overeen met die uit de modellberekening voor gecombineerde θ'- en Si-precipitatie. Bij hoge opwarmsselheden (≥ 40 K/min) komen deze warmteinheden goed overeen met die uit modellberekening voor gecombineerde θ- en Si-precipitatie. Blijkbaar is er een overgang van θ'-vorming naar θ-vorming als de opwarmsselheid de 20 K/min overschrijdt. In overeenstemming hiermee wordt voor opwarmsselheden ≤ 20 K/min na de hoofdprecipitatiepiek een exotherm warmteëffect als gevolg van de omzetting van θ'-fase in θ-fase gemeten.

In deel 2 wordt de precipitatie in ASCM legeringen met 0, 2,5, 5 en 10 vol% Al₂O₃ bestudeerd. Zowel gedurende isotherm verouderen (op 453 K) als gedurende non-isotherm verouderen (met een opwarmsselheid van 0,5 K/min) van WQ ASCM legeringen worden de volgende intermetallische fasen gedetecteerd met röntgendiffractie: Q-fase (Al₅Cu₂Mg₈Si₆) en θ-fase. De hardheidsstijging tijdens verouderen wordt nagenoeg geheel veroorzaakt door
de eerst precipiterende fase, de Q-fase. De tovoeging van Al₂O₃-deeltjes aan de legering heeft weinig invloed op de kinetiek van precipitatie en één geoptimaliseerde verouderingsbehandeling (4 h bij 453 K) is toepasbaar voor zowel legeringen met als zonder Al₂O₃-deeltjes. Deze ongevoeligheid voor Al₂O₃-tovoegingen wordt verklaard door de aanwezigheid van Si-deeltjes in de ASCM legering, die de belangrijkste oorzaak zijn van dislocatiegeneratie en mispassingsspanningen. De kamertemperatuurhardheid van de geëxtrudeerde ASCM legering kan bijna verdubbeld worden door oplosgloeien en de daarop volgende geoptimaliseerde verouderingsbehandeling. De θ-fase is de enige gedetecteerde Al-Cu fase. Deze fase geeft geen bijdrage tot de hardheid.

Nadat de maximale hardheid is bereikt oververouderen de ASCM legeringen en de hardheid daalt. Dit oververouderen is het gevolg van vergroving van de Q-fase. De activeringsenergie voor oververouderen (ongeveer 1,6 eV) indiceert dat de temperatuursafhankelijkheid van het process wordt bepaald door het product van oplosbaarheid en diffusiesnelheid (zoals de klassieke LSW vergrovingstheorie voorspelt).
NAWOORD

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Marco Starink, april 1992
CURRICULUM VITAE


Vanaf april 1988 tot april 1992 is hij onderzoeker in opleiding in dienst van de stichting voor Fundamenteel Onderzoek der Materie (FOM). In deze tijd wordt onder leiding van Prof. B. M. Korevaar en dr. P. van Mourik in het laboratorium voor materiaalkunde van de Technische Universiteit Delft aan een promotie onderzoek in het kader van het project 'Vervaardiging van aluminium matrix composieten met behulp van snelle stollingsprocessen' gewerkt. Vanaf april 1992 is hij als toegevoegd onderzoeker in dienst van het FOM verbonden aan dit project.