# High temperature oxidation of β-NIAlCr model coating alloys:

Effect of the reactive elements Y, Zr and Hf on growth and adhesion of the oxide layer

Hans Kranenburg May 2003





Faculty of Applied Sciences Department of Materials, Science and Technology Section Physical and Chemical Materials Science Delft University of Technology

.

# High temperature oxidation of β-NiAICr model coating alloys: Effect of the reactive elements Y, Zr and Hf

on growth and adhesion of the oxide layer

Hans Kranenburg

Graduation report May 2003

Daily supervisor:I.J. BennettSupervisor:W.G. Sloof

Delft University of Technology Faculty of Applied Science Department of Materials Science and Technology Section Physical and Chemical Materials Science

### Preface

In this report I describe the experiments and the calculations performed in my graduation research project. The graduation research project is the last part of the M.Sc. course Materials Science and Technology at Delft University of Technology.

The work is carried out in the section Physical and Chemical Materials Science.

I thank Ian Bennett, my daily supervisor, for his supervision, his encouragement and for everything I learned from him. I thank Wim Sloof for his supervision and for the enthusiastic and thorough reading of the draft-version of this report.

Further I thank Lars Jeurgens, Thijs Nijdam, Kees Kwakernaak, Han Kiersch and Kees Borsboom for their help with various practical things, for the discussions and for giving me the impression that I was of some help to them. Many thanks to Niek van der Pers and Han van Lent for performing the X-ray diffraction measurements.

The thermal cycling experiment was carried out at the Dutch Aerospace Laboratory NLR in Marknesse. I thank Arjen Kloosterman and his colleagues for performing this experiment. I enjoyed the company of Sietske, Abrar, Willem and Merijn. It is good to be in the Bragg Dancing. Many thanks!

### Summary

Thermal barrier coating systems are used on components in aero-engines and industrial turbine engines where the temperature of the gas next to the component is very hot. In combination with internal cooling of the component, the TBC system reduces the metal temperature relative to the hot gas temperature. The thermal barrier coating system consists of

- A thermally isolating ceramic (the actual thermal barrier);
- A thermally grown oxide layer that protects the underlying metal against hot corrosion and oxidation;
- A metallic coating that forms the protective oxide layer.

Adding a reactive element to the metallic coating material modifies the growth of the oxide. Further it enhances the adhesion of the oxide to the metallic coating. In this study the effect of the addition of Y, Zr, and Hf to  $\beta$ -NiAlCr on the growth and adhesion of the formed protective oxide layer is investigated.

These  $\beta$ -NiAlCr materials are a new type of coating material for high temperature applications, and are relatively rich in Al compared to alloys that are currently used for metallic coatings.

Calculations show that, ignoring crystallographic orientation relationships between the alloy and the oxide, the difference in the work of adhesion of the various systems  $Y_2O_3/NiAl$ ,  $ZrO_2/NiAl$ ,  $HfO_2/NiAl$ ,  $YAIO_3/NiAl$ ,  $Y_3Al_5O_{12}/NiAl$  cannot explain the observed reduction in delamination of the oxide from the NiAl.

The reactive elements have a high affinity for oxygen, so it is not expected that they are present as metallic atoms. If, however, the state in which the RE is present at the interface is best modelled as metallic, the presence of RE increases the adhesion for all the RE considered. In this case, the bond between the alumina and the Hf-doped NiAl (or alumina and Zr-doped NiAl) is better than the bond between alumina and Y-doped NiAl.

It is found that addition of Y or Zr to the alloy enhances the  $\theta$ -alumina to  $\alpha$ -alumina transformation and reduces the outward cation transport, resulting in less voids at the oxide/alloy interface).

Voids present at the oxide/alloy interface initiate buckling and should be avoided. The strain in the oxide is for the greater part due to the fact that upon cooling from oxidation temperature the alloy forces the adherent oxide to shrink.

The solubility of the different reactive elements in NiAl is modelled, but the calculation of accurate values for the solubility was found to be too challenging for the model employed.

In an oxygen gas atmosphere, a driving force for segregation of the RE to the NiAl surface (or oxide/NiAl interface) is present. The driving force is largest for Hf, and smallest (but still large) for Y.

ii

Carbon in  $\beta$ -NiAlCr deteriorates both the oxidation and the adhesion behaviour of the alloy. The oxide surface morphology and the void density at the oxide/alloy interface strongly depend on the crystallographic orientation of the underlying alloy grain.

The enhanced oxidation and adhesion properties due to reactive elements can lengthen the servicetime of the component. A longer lifetime of thermal barrier coating systems results in lower operational costs and lower environmental load.

### Table of contents

1	Int	roduction1
	1.1	The thermal barrier coating system1
	1.2	Model coating material and aim of this research2
	1.3	Sustainability and thermal barrier coating systems
	1.4	Outline of this report
2	O	sidation of $\beta$ -NiAl and the reactive element effect
	2.1	Oxidation of β-NiAl5
	2.2	Voids
	2.3	Influence of chromium on the oxidation of $\beta$ -NiAl
	2.4	Mechanisms by which reactive elements influence adhesion
	2.5	Influence of yttrium on oxidation and adhesion14
	2.6	Influence of zirconium on oxidation and adhesion15
	2.7	Influence of hafnium on oxidation and adhesion17
3	Sc	ale failure
	3.1	Strain energy
	3.2	Failure mechanisms20
4	Ef	fect of reactive elements on work of adhesion27
	4.1	Introduction to the macroscopic atom model27
	4.2	Al <sub>2</sub> O <sub>3</sub> / NiAl interface
	4.3	RE-oxide / NiAl interface
	4.4	Al <sub>2</sub> O <sub>3</sub> / RE/ NiAl system
5	So	olubility of RE in NiAl
	5.1	Approach45
	5.2	Calculation of $\Delta H(RE$ -dissolved in NiAl)
	5.3	Calculation of $\Delta H^{f}_{NiAIRE}$
	5.4	Comparison of solubility of Y, Zr and Hf in NiAl52
	5.5	Conclusion
6	Sı	rface segregation
	6.1	Surface segregation under vacuum
	6.2	Segregation to oxide/NiAl interface62

7	Expe	erimental65	
	7.1	Sample preparation	
	7.2	Isothermal oxidation	
	7.3	Thermal cycling experiments	
	7.4	Characterisation	
	7.5	Specimen cross section preparation	
	7.6	Growth-kinetics determination	
8	Resu	ılts69	
	8.1	Colour	
	8.2	Phase identification	
	8.3	Surface morphology	
	8.4	Oxide layer microstructure (cross-section)	
	8.5	Growth kinetics	
	8.6	Adhesion behaviour of isothermally grown oxide layers96	
	8.7	Thermal cycling oxidation behaviour103	
9	Disc	ussion	
	9.1	Possible mechanism for the RE-effect113	
	9.2	Scale failure	
	9.3	Refinements for modelling of the work of adhesion116	
	9.4	Solubility and segregation	
	9.5	Isothermal oxidation118	
	9.6	Thermal cycling	
10	Conc	lusion121	
Re	eference	s125	
Appendix A: Model coating alloy characterisation			
Appendix B: Calculation of $C_{Al}^{s}$ and $C_{Ni}^{s}$			

## List of symbols

$A_A$	Area necessary to store one mole of A	[m <sup>2</sup> /mole]
$C_A$	Fraction of component A	
$C_A^S$	Surface fraction of component A	
$C_0$	Geometrical constant to calculate molar area	
d	Oxide thickness	[m]
d	Distance between crystallographic planes	[m] or [Å]
Ε	Young's modulus	[Pa]
$f_B^A$	Extent to which A is surrounded by B	
$f^{A}_{vacuum}$	Fraction of A-atom surrounded by vacuum	
G	Shear modulus	[Pa]
$\Delta G$	Change in Gibbs free energy	[J] or [J/mole]
$\Delta G_{mix}$	Gibbs free energy due to mixing-'randomness'	[J] or [J/mole]
$\Delta H^{interface}_{\Lambda in P}$	Enthalpy associated with the interface of A atoms	[J/mole A]
Amb	fully surrounded by B atoms	
$\Delta H_A^{ u a p}$	Enthalpy of vaporisation	[J/mole A]
$\Delta H_A^{surf}$	Surface enthalpy	[J/mole A atoms at surface]
$\Delta H^{ ext{ surface segregation}}$	Enthalpy change upon segregation to the surface	[J/mole]
h <sub>oxide</sub>	Oxide thickness	[m]
K	Bulk modulus	[Pa]
k	Oxide growth rate	$[m^2/s]$
$k_p$	Parabolic weight change rate	$[g^2/cm^4s]$
n <sub>ws</sub>	Electron density at boundary of Wigner-Seitz cell	Density units
p	Fraction of atom at interface in contact with atom	
	on other side of interface	
$Q = \frac{4\gamma_o}{f_{wi}\lambda}$	Wedging initiation parameter	[J/m <sup>3</sup> ]
q	Fraction of Gibbs free energy of mixing lost upon	
	segregation to the surface	
R	Gas constant	[J/mole K]
$R_O$	Ionic radius of O	[m]
r	Strain-energy release factor	
$\Delta S$	Entropy	[J/mole K]

Т	Temperature	[K]
$V_A$	Volume occupied by one mole of A	[m <sup>3</sup> ]
$W^{ad}$	Work of adhesion	[J/m <sup>2</sup> ]
x	Atomic fraction RE	
$\Gamma_i^0$	Interface fracture toughness in mode 1	[J/m <sup>2</sup> ]
$\gamma_A$	Surface energy of A	[J/m <sup>2</sup> ]
$\gamma_{A-B}^{interaction}$	Interaction energy between A and B	[J/m <sup>2</sup> ]
$\gamma_F$	Energy necessary for fracture	[J/m <sup>2</sup> ]
ε	Strain	
v	Poisson's ratio	
σ	Stress	[Pa]
$\phi^*_A$	Adjusted work function of metal A	[V]

### List of abbreviations

Al	Aluminium
BSE	Back-scattered electron
BSI	Back-scattered image
Cr	Chromium
EDS	Energy-dispersive (X-ray) spectroscopy
EPMA	Electron probe X-ray microanalysis
Hf	Hafnium
LCA	Life cycle assessment (or: life cycle analysis)
NO <sub>x</sub>	Nitrogen oxides
Ni	Nickel
RE	Reactive element (Y, Zr, Hf,)
SEM	Secondary electron microscope
SEI	Secondary electron image
TBC	Thermal barrier coating
XRD	X-ray diffraction
Y	Yttrium
YSZ	Yttria stabilised zirconia
Zr	Zirconium

viii

#### **1** Introduction

This research is about the effect of the reactive elements Y, Zr and Hf on growth and adhesion of the oxide layer that forms during high temperature oxidation of  $\beta$ -NiAlCr coating alloys. Such coatings are usually part of a thermal barrier coating system. Such thermal barrier coating systems are applied in modern airplane engines and power plants (Figure 1.1).

A thermal barrier coating system is pictured in Figure 1.1. It consists of an insulating oxide and a metallic coating that forms a protective oxide layer in-between the insulating oxide and the metallic coating. Thermal barrier coating systems are applied on the combustor chamber and on the turbine components. At these places the gas is very hot, up to 1900 K.



Figure 1.1: On the turbine components of an aeroplane engine, often a thermal barrier coating system is applied

#### 1.1 The thermal barrier coating system

The thermal barrier coating system consists of a ceramic top layer, a protective oxide layer and a metallic coating. The thermally insulating oxide layer is the actual thermal barrier (Figure 1.1). This layer is usually yttrium-stabilised zirconia. It is about 150  $\mu$ m thick [1]. In combination with internal cooling (cooling channels are visible on the blade in Figure 1.1) this insulation reduces the metal temperature relative to the hot gas temperature by up to 150 K [1,2].

The metallic coating protects the super alloy against oxidation, corrosion and hot salt corrosion by forming the protective oxide layer [3]. This protective oxide layer is usually  $\alpha$ -alumina (Al<sub>2</sub>O<sub>3</sub> in a very dense packed crystal structure). An oxide layer is called protective if it is thermodynamically

stable, is closed (seals off the metal completely), grows slowly, adheres to the substrate, and forms easily and re-forms easily after spallation [4]. This oxide layer also promotes adhesion of the TBC material to the metal [5].

#### 1.2 Model coating material and aim of this research

In this study is focussed on the effect of the reactive elements Y, Zr, and Hf on the growth and microstructure evolution of the thermally grown protective oxide layer. Special emphasis is put on the effect of the reactive elements on the oxide scale adhesion, which is one of the factors determining the performance in practical applications.

A new type of coating material for high temperature applications is  $\beta$ -NiAlCr. These  $\beta$ -NiAlCr materials are relatively rich in Al compared to the  $\gamma'$ -Ni<sub>3</sub>Al or dual phase  $\gamma'$ -Ni<sub>3</sub>Al /  $\beta$ -NiAl based compositions that are currently used for metallic coatings. The high Al-content has as an advantage that it will not deplete in Al easily (Al is used in the formation of the protective oxide layer). Depletion of aluminium results in the formation of less protective oxides than  $\alpha$ -alumina. As  $\beta$ -NiAl depletes not so easily, metallic coatings of only 50-70 µm thick can be used, which is thin compared to the current metallic coating thicknesses of 100-200 µm. Applying thinner metallic coatings results in a weight saving. Weight savings are important in aero-applications, especially on fast-rotating components as turbine blades [5].

A disadvantage compared to  $\gamma'$ -Ni<sub>3</sub>Al or  $\gamma'$ -Ni<sub>3</sub>Al /  $\beta$ -NiAl based coatings is that  $\beta$ -NiAl coatings are more brittle, but as the layer is thin, this problem may be small.

In the current study the metallic coating is modelled with a β-NiAlCr alloy cast as cylindrical rods. To optimise all relevant mechanical properties and all oxidation properties, metallic coatings usually are alloyed with small additions of many elements. To reduce the effects of factors playing a role, only Cr and Y, Zr or Hf additions were present in the model coating alloys. The composition of the model coating materials is approximately 37 at.% Al, 4 at.% Cr, and 0.2 at.% reactive element (either Y, Zr or Hf), balance Ni. Unfortunately, some carbon was also present as a result of the production process of the model coating alloys.

The thermally isolating ceramic top coating is not applied on the materials in the current study.

#### 1.3 Sustainability and thermal barrier coating systems

In an earlier study [5] the relation between sustainable development and improvements in the thermal barrier coating systems was investigated. Sustainable development is described as 'development that meets the needs of the present generation without compromising the ability of future generations to meet their needs'. Sustainability has both environmental (pollution, depletion of resources) and social aspects (fair distribution of wealth).

Improving the thermal barrier coating systems can either prolong the lifetime of the component or make a raise in the operating temperatures of the engine possible. In the last 40 years, use of better materials for turbine blades, turbine vanes and combustor components, allowed a significant raise in operating temperatures (Figure 1.2). Together with many other improvements, this higher operating temperature resulted in an efficiency-improvement of aero-engines of about 30% [5,6].



# Figure 1.2: Improvements in the alloys and in the thermal barrier coating systems allowed significant rise in turbine entry temperature and thus in efficiency [2]

In the case an improvement in the TBC is used to allow a rise in the operating temperature, redesign of the entire engine is required to get optimal benefits and to avoid a large increase in the  $NO_x$  emissions. Because of the certification process and the high costs of ownership, it will take ten years or more from the moment the engine is re-designed before it has replaced the older engines on significant scale.

When the oxide spalls off from the metallic coating, this results in loss of the ceramic top layer also. Placing a thermal barrier coating system on turbine components is a energy-consuming and material-consuming process. Increasing the life-time of the coating system results in a lower load on the environment per flight-hour.

From sustainability point of view, if the life-time can be increased by adding a RE to the metallic coating, this is recommended. The RE that is most effective in increasing the lifetime of the coating system is the preferred addition, as

- for neither Y, Zr or Hf depletion is a problem, as the materials are readily available;
- the score is equal for the three elements, as far as health hazards are concerned;
- the increase in lifetime is the dominant variable.

As far as the environment is concerned, the above-discussed improvements in thermal barrier coating systems are positive. The improvements have only very small impact on the 'social sustainability'.

#### 1.4 Outline of this report

An introduction on the effect of reactive elements on the growth of the oxide scale is given in chapter 2. The mechanisms by which a RE can alter the oxidation process and the properties of the oxide(s) formed during oxidation include:

- Heterogenous nucleation of the oxide;
- Enhancement of α-alumina nucleation
- Reduction of the cation outward transport
- Enhanced scale plasticity
- Graded seal formation

These effects on the oxidation mechanisms and properties of the oxide(s) formed have an indirect effect on the adhesion of the thermally grown oxide. Other mechanisms that determine the adhesion of the oxide are directly related to the oxide / alloy interface. These mechanisms include:

- Oxide pegging
- Vacancy sink provision
- Chemical bonding
- Sulphur scavenging

Poor adhesion of the oxide results in delamination. Two routes of oxide delamination (namely wedging and buckling) are discussed in chapter 3. Calculations on initiation and propagation of wedging and buckling, and on the stress in the oxide layer are included.

The chemical bonding is modelled in chapter 4, using the macroscopic atom model. The macroscopic atom model also provides clues to model the solubility of RE in NiAl and the segregation behaviour of RE to the NiAl surface. These aspects are explored in chapter 5 and 6, respectively.

Experimentally, the phases formed in the oxide layer and in the substrate, the growth rate of the oxide, the form of the oxide/metal interface and the degree of adhesion of the oxide layer are determined. These results and other related observations are discussed in chapter 8. The calculations and observations are discussed in chapter 9. Conclusions are presented in chapter 10.

#### 2 Oxidation of β-NiAl and the reactive element effect

#### 2.1 Oxidation of $\beta$ -NiAl

The oxidation of  $\beta$ -NiAl can be divided in two stages: first transient oxidation and then steady-state oxidation. The transition from the initial oxidation stage to the second coincides with the formation of a protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer. An oxide layer is a protective layer if it

- is thermodynamically stable;
- has a slow growth rate;
- adheres well to the substrate;
- is closed (protects the entire surface).

In contrast to the transient aluminas,  $\alpha$ -alumina is thermodynamically stable. It also has a much slower growth rate. Therefore, unlike the transient oxides,  $\alpha$ -alumina is a protective oxide layer.

#### 2.1.1 Transient oxide scales

In the literature it has been observed that transition  $Al_2O_3$  scales form a platelet structure. This structure is caused by fast outward Al diffusion [7,8]. SIMS-analysis using <sup>18</sup>O<sub>2</sub> has provided conclusive evidence that the transient scales grow by outward Al diffusion rather than by inward oxygen diffusion [7]. The specific platelet morphology is (at least at 1223 K) due to outward Al transport along twinned planes in the platelets, parallel to the platelet surface [8]. As for most outward-growing scales, the transient scales formed on NiAl are crystallographically textured and are subject to the effects of substrate grain orientation.

The main metastable aluminas reported to be formed during the transient stages of oxidation, are  $\gamma$ ,  $\theta$  and  $\delta$ -Al<sub>2</sub>O<sub>3</sub>. The only stable alumina is  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The transformation sequence  $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$  has been proposed, but direct evidence for this transformation path is lacking [8].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has been described as a cubic spinel type structure,  $\delta$ - Al<sub>2</sub>O<sub>3</sub> as a superlattice of the spinel structure, and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> has monoclinic symmetry [8].

At lower temperatures (for instance 1223 K [8]) the platelet structure consists of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (although some authors argue that  $\theta$ -Al<sub>2</sub>O<sub>3</sub> forms instead of  $\gamma$  [9, 24]). The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> platelets are twinned along the (111) planes. At higher temperatures (1373 K) the transient oxide consists only of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> [9].

#### 2.1.2 $\theta$ to $\alpha$ transformation

The location where the  $\theta$  to  $\alpha$  transformation initiates is disputed. Doychak argues that the  $\theta$  to  $\alpha$  transformation initiates at the scale/gas interface and progresses in to the oxide (and then radially over the surface) [7]. Other authors argue that the  $\theta$  to  $\alpha$  transformation nucleates at the

5

metal/oxide interface: Tolpygo and Clarke [10] observed, using (luminescence) stress measurements, on a (Ni,Pt)Al alloy that the compressive stress of the first  $\alpha$ -alumina they found, was quite high. They concluded that the  $\theta$  to  $\alpha$  transformation nucleated not in the stress-free whiskers, but lower in the scale. Also Yang [8,11] observed, with TEM, that the transformation initiated at the substrate/oxide interface (at 1223 K; equiatomic NiAl with 0.01wt%Y and 0.0006wt%S).

#### 2.1.3 Protective $\alpha$ -alumina scales

The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> present after the  $\theta$  to  $\alpha$  transformation has a ridged morphology and is textured, but the crystallographic orientation relationships of the transient scale are not carried through the transformation to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [7].

A protective  $\alpha$ -alumina scale can have different morphologies. On most alumina-forming alloys the columnar morphology develops (Figure 2.1). However on  $\beta$ -NiAl, which forms in the transient stage almost exclusively alumina with few nickel or chromium oxides, a ridged morphology is seen. Only some Ni-containing oxides (such as NiAl<sub>2</sub>O<sub>4</sub>) have been observed during initial oxidation of  $\beta$ -NiAl at temperatures below about 1273 K [7].

The columnar oxide consists of large, randomly oriented  $\alpha$ -alumina grains and forms as a result of nucleation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> beneath a transient oxide with a lot of impurity oxides.





The ridged morphology is more relevant for the alloy considered in this study. It consists of flat  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> radial subgrains, often arranged in a pie-shaped fashion with ridges forming at high-angle grain boundaries where the pie-shaped grains intersect. The ridged morphology forms when transition Al<sub>2</sub>O<sub>3</sub> phases, such as  $\gamma$ -,  $\delta$ - or  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, comprise the majority of the transient oxide scale. Because of the composition of the transient scales (nearly pure Al<sub>2</sub>O<sub>3</sub>), the phase

transformations occur within the scale, eventually resulting in the entire scale transforming to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The specific nature of this transformation results in the ridged morphology.

Two types of ridges exist. 'Intrinsic' ridges are formed at grain boundaries (where the outward diffused Al forms new oxide), when the surface diffusion cannot keep up with the grain boundary diffusion [12].

Other ridges are 'extrinsic', i.e. caused by scale cracking as a result of the  $\theta$  to  $\alpha$  transformation and subsequent new scale growth, or because of impinging  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nuclei.



Figure 2.2: Intrinsic ridges observed at each grain boundary at the gas/oxide interface, fracture cross section of the  $\alpha$ -alumina scale on undoped, cast  $\beta$ -NiAl after 100 hr oxidation at 1473 K[12]; the white arrows indicate voids that will be discussed later



Figure 2.3: The ridge structure at the gas interface coarsens with time as a result of grain growth in the oxide, SEM plan-view image of the oxide on undoped  $\beta$ -NiAl after oxidation at 1673 K for a: 1 hour, or b: 50 hour [12]

Scale growth occurs primarily at the ridges and at cracks within the scales formed as a result of transformation stresses [7].

Transport through the ridges depends on temperature, time, ridge density, and possibly other variables. The first hours, at 1473 K, outward Al diffusion is the most important transport mechanism for the growth of oxide at the ridges [13]. Following this, the ridged structure coarsens: the ridges become taller and wider (and coalesce) and the flat areas between the ridges gradually disappear. After coarsening, the scale growth occurs by both inward oxygen and outward Al diffusion [13] (according to [7] the inward O diffusion becomes even more important than the outward Al diffusion).

As there is less high-angle grain-boundary area to act as fast diffusion paths, ridged  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> generally grows more slowly than columnar-grained scales until the ridge-morphology coarsens [14]. Once the ridges have coarsened, the growth is similar in most respects to growth of columnar-morphology Al<sub>2</sub>O<sub>3</sub> scales.

#### 2.1.4 Parabolic growth

From the moment that diffusion through the protective oxide scale is the rate-limiting step for further oxide growth, and the diffusion constant D has a constant value, the oxidation reaction of scales follows a parabolic rate equation [7]. If the entire oxide thickness is protective oxide, i.e. no layer of non-protective oxide is present above or below the protective oxide [15], this parabolic rate equation reads as

$$d^{2} - d_{0}^{2} = k(t - t_{0}) \quad \text{for } t > t_{0}$$
(2.1)

where d is the scale thickness, t is time and k is the parabolic growth rate constant.  $d_0$  and  $t_0$  signify the thickness of the oxide and the time when the oxide starts to show parabolic behaviour, respectively. At  $t < t_0$ , the protective scale is not yet formed or D is not yet constant, so equation 2.1 is not yet valid.

The growth rate depends on the flux *J* through existing oxide of ions that form new oxide [16]  $k = 2V_{MO}J$  (2.2)

with  $V_{MO}$  the volume of oxide formed per oxygen or aluminium atom combined. The flux *J* depends on the diffusion constant of alumina *D*, and on the oxygen partial pressure concentration difference over the oxide scale. The diffusion depends on factors like the vacancy density and the grain size of the oxide and on the oxygen partial pressure. Also the diffusion constant *D* itself depends on the oxygen partial pressure [p409ref 17].

#### 2.2 Voids

Often, voids form at the scale/substrate interface [7]. The extent and shapes of the voids depend on the crystallographic orientation and composition of the  $\beta$ -NiAl substrate. The extent and shape of the voids affect scale spallation. The presence of the voids does not impede scale growth, since aluminium vapour transport across the voids is sufficiently fast above 1173 K [18].

Brumm and Grabke [18] expect that the voids at the oxide/metal interface form due to Ni and Al diffusion away from the oxide/alloy interface. Al diffuses through the oxide to form new oxide within the oxide or at the gas/oxide interface; to lower the concentration gradient in the NiAl, Ni diffuses into the NiAl. In Al-rich alloys lowering of the concentration gradient also takes place by diffusion of Al from the bulk of the alloy to the oxide/metal interface. Therefore in Al-rich alloys less Ni diffuses into the alloy than in Ni-rich alloys Therefore less voids form in Al-rich than in Ni-rich  $\beta$ -NiAl.

Void formation both in the oxide and at the oxide/metal interface is due to [12] volume reduction of the oxide caused by the  $\theta$  to  $\alpha$  alumina transition, or to plastic deformation combined with grain growth (the 'Kofstad mechanism'). Another void formation mechanism is suggested by Pint [12]: voids within oxide grains are created when the new oxide formed at the grain boundaries seals off empty spaces present at the gas/oxide or oxide/alloy interface (Figure 2.4d). These empty spaces (voids) are inherently present (Figure 2.4a), for instance due to one of the mechanisms presented above. New oxide grows at the oxide boundaries (Figure 2.4b) and seals of the voids (Figure 2.4d).



Figure 2.4: grain boundary ridges form in the oxide scale adjacent to the interface; the ridges can eventually neck and seal of the interfacial void, thus forming an internal void [12]



Figure 2.5: SEM cross-section of the spalled alumina scale, formed after oxidation for 200 hr at 1473 K on HfO<sub>2</sub>-dispersed  $\beta$ -NiAl shows ridges at the metal/oxide interface [12]

In Figure 2.2, voids are observed near the gas/oxide interface within oxide grains. Probably ridges (like the ridges in Figure 2.3) touch each other, and seal off empty space, thus creating the voids [12].

Sulphur segregation increases the surface energy associated with the metal/oxide interface  $\gamma_{int}$  and lowers the surface energy of the free metal surface  $\gamma_m$ . The energy necessary for void growth depends on these two energies, and the result of the sulphur is a decrease of the energy necessary for void growth [12].



#### Figure 2.6: surface energy at the edge of an interfacial void [12]

According to Pint [12] the formation of voids can probably not be avoided but the growth of the voids can be avoided by de-sulphurisation of the alloy [19].

Van Manen [20] observed that at 1173 K, the presence of sulphur has an influence on the oxidation rate of NiAl. The presence of 50 ppm S results in a slightly lower oxidation rate than without S, the presence of 200 ppm S results in a considerable higher oxidation rate. The presence of Y counteracts this higher oxidation rate.

#### 2.3 Influence of chromium on the oxidation of $\beta$ -NiAl

Chromium enhances the protective scale formation on NiAl. Some possible mechanisms are [21]:

- Cr 'getters' oxygen by reacting with oxygen before it can react with Ni or diffuse into the alloy, therefore compositions with lower Al content still can form a protective alumina layer. This effect is especially important for γ'-Ni<sub>3</sub>Al and Al-doped γ-Ni, that will form NiO + internal oxides if no Cr is present. However, β-NiAl forms alumina even if no Cr is present [21];
- 2. Oxides formed by the gettering action block oxygen transport and reduce its flow into the base metal;
- Chromium increases the flux of protective-oxide forming elements such as Al to the oxidemetal interface;
- 4.  $Cr_2O_3$ -nuclei formed in the initial stages of oxidation serve as nucleation sites for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

The first three proposed mechanisms alone cannot explain all observations. Some observations supporting the 4<sup>th</sup> mechanism are:

- A decrease in the parabolic rate constant is seen at lower temperature for the Cr-containing alloy as compared to the alloy without Cr. The parabolic rate constants associated with the α-alumina on the Cr-doped alloy are higher than the parabolic rate constants on chromium-free alloys. This is probably due to the smaller oxide grain size on the Cr-containing alloy [22, 23] as due to the chromium addition there is more α-alumina nucleation (Figure 2.7).
- Klumpes, Marée, Schramm and De Wit [24] observed by XRD-measurements that the presence of chromium in the β-NiAl accelerated the θ to α transformation: the transformation was complete after 1 hour for 11 at.% Cr (1373 K, pure oxygen), compared to 8 hour for 1 at.% Cr.



Figure 2.7: Arrhenius diagrams for (a) pure NiAl, and (b) NiAlCr (symbols) in comparison to pure NiAl (lines) [22]

#### 2.4 Mechanisms by which reactive elements influence adhesion

Many authors observed that doping with reactive element improved the adhesion or reduced the delamination of the oxide. In this paragraph some effects attributed to RE on the oxidation behaviour are listed. The influences described apply to alloys in general, not especially to  $\beta$ -NiAl.

#### 1. Heterogenous nucleation of transient oxide

Dispersed RE-oxide particles in an alloy surface can act as heterogenous nucleation sites for all the first formed oxides, thereby reducing internuclei spacings [25]. Less time will be required for subsequent lateral growth processes to link the nuclei and form a closed layer of oxide. Therefore, at the moment the layer is closed, it will be less thick than for an undoped alloy. In a less thick oxide layer, less elastic strain energy is stored, so the scale will adhere better (the relation between stored elastic strain and adhesion behaviour will be discussed in more detail in chapter 3).

#### 2. Enhancement of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nucleation

The RE may enhance the transition from metastable alumina to  $\alpha$ -alumina. This mechanism is not listed by Moon [25] but should not be forgotten.

#### 3. Reducing cation outward transport

If reactive element is segregated at oxide grain boundaries, it may block cationic transport along these boundaries [25]. Oxide grain boundaries in alumina are fast diffusion paths. If these fast diffusion paths are blocked, three effects can occur:

- 1. The doping with RE results in a less thick scale than on undoped alloys, resulting in less stored energy.
- 2. The change in the relative contributions of cation and anion transport may avoid the formation of new oxide in the scale (due to the RE the formation of oxide shifts to the oxide/metal interface), and thus avoid the build-up of the associated compressive growth stresses.
- 3. Due to the suppression of outward cation diffusion, fewer voids are formed at the oxide/metal interface, and voids that form are easily filled with new oxide.

#### 4. Enhanced scale plasticity

RE might decrease the oxide scale grain size [25]. Smaller grains enhance plasticity. Plastic deformation decreases the stress (or at least the stress concentrations) in the oxide. As stress is the driving force for delamination, a decrease in stress means an enhancement of the adhesion.

#### 5. Graded seal formation

A layer of RE containing mixed oxide phase with a thermal expansion coefficient intermediate between that of the main scale and the substrate is suggested to develop at the oxide/alloy interface

12

[25]. This layer would reduce the sharp mismatch in thermal contraction stress between the oxide and the alloy that might otherwise lead to interfacial decohesion during thermal cycling. However, there is no sound evidence of such a layer in any reported investigation. In addition, the chemical and mechanical properties of RE oxides may not be suitable for this effect: the difference between the thermal expansion coefficients of NiAl and  $Al_2O_3$  is smaller than the difference between the thermal expansion coefficients of NiAl and Y2O3, ZrO2 or HfO2 [26,27]. The RE-oxides do have a lower Young's modulus (bulk values) so the stress at the interface may be reduced and the energy stored in a RE-oxide interlayer may be low [28], especially for yttria.

#### 6. Oxide pegging

Small pegs protruding into a substrate may provide mechanical keying of a scale to an alloy, improving interfacial adhesion [25]. Peg growth is assisted by oxygen short circuit diffusion through RE oxide or along the incoherent boundary between RE oxide and alloy. A fine RE distribution (for instance homogenous dissolution in the alloy matrix) and a low RE content of the alloy results in the small pegs. Large pegs may have the opposite effect: they could promote scale cracking and spallation.

The development of an uneven scale/substrate interface, without discrete peg formation, could improve adhesion through the same effects.

Improvement of adhesion due to RE is also observed on alloys that did not show pegs, so peg formation is not the most important factor for adhesion.

#### 7. Vacancy sink provision

Apart from the reduction of the outward cation diffusion, the RE can also decrease the (effect of) void formation at the metal/oxide interface by other mechanisms [25].

A RE-particle that is not dissolved in the matrix provides a boundary. This boundary between particle and matrix can be incoherent, enabling this boundary to trap vacancies [25]. If the RE is dissolved in solid solution in the alloy matrix, it may trap vacancies to decrease the internal strain in the metal lattice.

# 8. Chemical bonding and reduction of crystallographic mismatch between the oxide and the alloy

Reactive element additions may improve adhesion by the direct promotion of chemical bonding across the scale/alloy interface. Further it may promote bonding by indirect influences like grain size reduction and change of the orientation of the oxide relative to the alloy [12,25].

#### 9. Sulphur scavenging

Impurities such as S present at levels <100 ppm within alloys may accumulate at the scale/substrate interface during oxidation and weaken the adhesion. The RE can interact with these impurities, reducing the amount of S free to migrate to the interface [25].

#### 2.5 Influence of yttrium on oxidation and adhesion

The presence of yttrium as RE slows the formation of the ridged morphology [13] and reduces, for most conditions, the formation of needles [29]. These factors are probably caused by a reduction in the outward cation diffusion through the oxide grain boundaries.

Oxidation of NiAl+0.1wt%Y at 1473 K (12 hr in  ${}^{16}O_2$ , then 12 hr in  ${}^{18}O_2$ , 1.33 kPa oxygen pressure) shows [13] that Y reduces the formation of new oxide at the gas/oxide interface. The yttrium is mostly present in or on top of the oxide. SIMS-imaging showed that Y is combined with the oxygen fed later during the oxidation. Y slows down the outward diffusion of cations (a decrease in the outward diffusion of Al-cations due to Y is most likely, although some evidence for the opposite exists [25,30]). The outward diffusion is not completely blocked, as needle formation still occurs [29].

The presence of Y inhibits the formation of whiskers [31] (oxidation of  $\beta$ -NiAl at 1373 K). No ridges are observed. Instead, the blade-like grains grow and, subsequently, loose their sharp contours.

Jedlinski [14] observed that Y changes the oxide scale morphology. The oxide scale on Yimplanted  $\beta$ -NiAl after 240 hour oxidation (at 1473 or 1523 K for 240 hr) is equiaxed, with a grain size of about 1  $\mu$ m. The scale formed on unimplanted  $\beta$ -NiAl is columnar (diameter 2  $\mu$ m; height 10  $\mu$ m).

Yttrium reduces the formation of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> and enhances the nucleation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Figure 2.8). It may be that yttrium accelerates the  $\theta$  to  $\alpha$  transformation, but some authors doubt this. Anyhow, when  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nucleates at the metal/oxide interface, it can undergrow the metastable oxides, thereby stopping their growth, and nucleating the  $\theta$  to  $\alpha$  transformation [23].



Figure 2.8: XRD measurements of  $\theta$  and  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> formation at 1223 K and 1273 K [32], Y reduces the  $\theta$ -alumina formation, a: undoped NiAl; b: NiAl + 0.4% Y

The solubility of Y in alumina is very small. In massive alumina, it segregates to the grain boundaries of alumina and induces a decrease in oxide grain size. It also segregates to the surface of the alumina [33,34].

Prüssner [29] observed after oxidation (at lower temperature and oxygen pressure than Prescott) Y at  $\alpha$ -alumina grain boundaries and, to a lesser extent, at the oxide/substrate interface. Prüssner also observed a layer of fine Y-Al-O containing grains (probably YAG) in-between the transition alumina and the  $\alpha$ -alumina.

Oxide protrusions into the Y-doped alloy are seen [29]. This can be attributed to enhanced oxygen diffusion through or along internal Y-rich oxide formed at Y-rich sites at the alloy surface.

Rommerskirchen and Kolarik [32] observed that the mass gain during oxidation at 1273 K and 0.5 Pa oxygen partial pressure for 0.39 wt% Y doped NiAl is similar to the mass gain for undoped NiAl.

#### 2.6 Influence of zirconium on oxidation and adhesion

Studies on the effect of Zr on the oxidation behaviour of chromia- and alumina-formers have not always demonstrated a benefit [35]. Zr appears to provide the same beneficial effects as Y in terms of improving the scale adhesion and slightly reducing the oxidation rate [35].

<sup>18</sup>O tracers have shown that the effect of Zr is analogous to that of Y in changing the growth mechanism of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by reducing the outward transport of Al [13,35]. However, SIMS experiments have shown that some fast outward Al transport still takes place. The newly formed oxide is found at the outer ridge areas, at the grain boundaries in the scale and at the oxide/alloy interface.

Addition of 0.2 wt% Zr slows down the formation of ridges at the gas/oxide interface [13] compared to undoped material.

The defect structure of  $ZrO_2$  allows fast oxygen diffusion [7].



Figure 2.9: SIMS <sup>18</sup>O isotope mapping of alumina scale formed on NiAl + Zr at 1473 K, oxidation in <sup>16</sup>O followed by <sup>18</sup>O, a: plan view after 1+1 hr oxidation; b: taper cross-section after 200+400 hr oxidation [36]

After 200 hrs oxidation at 1473 K the  $ZrO_2$  is dispersed through the oxide [13]. At the oxide/alloy interface the  $ZrO_2$  particles are coarser, at the outer portion of the scale the particles are finer.

Pint [35] performed GAXRD (glancing angle XRD) measurements to compare the oxidation of  $\beta$ -NiAl and  $\beta$ -NiAl+0.23 wt% Zr in flowing oxygen at 1273 K (31.5 wt% Al). After one hour oxidation the oxide layer on the Zr-containing sample consisted of 90%  $\theta$  and 10%  $\alpha$ , compared to 25%  $\theta$  for samples without Zr. The initial promotion of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> formation is also indicated by the higher mass gain during the first 4 hours of oxidation. Thus the Zr addition appears to stabilise the first-forming  $\theta$ -phase.

After 50 hours all oxide had transformed to  $\alpha$ -oxide [35]. Zr-rich particles were not uniformly distributed in the scale. Voids are present throughout the sample, most likely a result of the  $\theta$  to  $\alpha$  transformation, which involves a volume reduction. Some small Ni-rich oxide particles were also observed, presumably formed during the transient stage.

For the oxidation of Zr-doped  $\beta$ -NiAl, Zr is found in the scale as Zr-rich oxides and as ions segregated to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> grain boundaries [35,36] and to the oxide/alloy interface.

Zr additions change the nature of the scale-spalling process during cooling so that the oxide spalls near the oxide/air interface at a relatively low depth within the scale [37]. Without Zr, the predominantly  $\alpha$ -alumina scale tends to spall randomly to bare metal, resulting in relatively high loss rates, particularly at 1423 K or 1473 K. This leads to higher rates of Al consumption for the Zr-free aluminide and much earlier depletion of Al.

Scales formed on 0.1 at.% Zr containing  $\gamma$ ' FeCrAl can support higher strains at T $\geq$ 1273 K than scales formed on Zr free FeCrAl [38].

Pint [35] found that the effect of zirconium depends on temperature. Compared to  $\beta$ -NiAl,  $\beta$ -NiAl+Zr had at 1273 K a higher mass gain due to more  $\theta$ -Al<sub>2</sub>O<sub>3</sub> formation; at 1473 K the spallation during cyclic oxidation was reduced and the isothermal mass gain lower; during isothermal oxidation at 1673 K after about 20 hour on Zr-doped NiAl, break down of the oxide scale occurred. However, for cyclic oxidation the Zr-doping improves adherence during the first 10 cycles of 1 hour. Higher temperature causes the oxidation process and the diffusion of Zr to increase, but the diffusion of Zr increases more than the scale growth rate [35].

A higher oxidation temperature results in more Zr in the  $\alpha$ -  $Al_2O_3$  scale: the volume of Zr-rich oxide particles in the oxide increases. The apparent Zr/Al ratio on the oxide grain boundaries (measured with EDS) also increases with temperature.

#### 2.7 Influence of hafnium on oxidation and adhesion

Hf (like Zr) is believed to inhibit the outward cation transport along the oxide grain boundaries [40], resulting in growth primarily by inward grain boundary diffusion of oxygen. Hf ions were detected as segregants to the oxide grain boundaries and at the oxide/alloy interface [40]. This segregation of Hf ions is the most likely explanation for the reduction of the oxide growth rate compared to undoped NiAl.

Allam [39] observed that on (CoAl  $\beta$ ' and Co-rich  $\alpha$ ) CoCrAl alloys the presence of Hf or HfO<sub>2</sub> dispersions speeds up the formation of a continuous layer of Al<sub>2</sub>O<sub>3</sub>, both at first exposure and after spallation has occurred. The dispersed HfO<sub>2</sub> particles are thought to cause more nucleation, resulting in a quicker achievement of a continuous layer and a finer-grained initial oxide film.

Rommerskirchen [32] observed  $\theta$ -alumina during oxidation of NiAl in air at 1273 K(3.9 wt% Hf, 31.3 wt% Al). The  $\theta$ -phase was present for 7 hours, compared to 5 hours for the undoped material (on the Y-doped material no  $\theta$ -alumina was observed). When the  $\theta$ -alumina has transformed  $\alpha$ -alumina, further growth of the oxide is slowed down.

Allam observed that  $HfO_2$  dispersions decrease the apparent growth rate of the oxide. Pint [40] performed cyclic oxidation experiments at 1373 K (1 hour at temperature in oxygen, cooling for 10 min to room temperature). The scale formed on (0.05 at.%) Hf-doped equiatomic NiAl was less thick than the scale formed on undoped and Pt-doped NiAl (Figure 2.10).



Figure 2.10: Hf addition results in lower growth rates [40]

Pint [40] observed a reduction of void formation due to Hf-doping on NiAl (50 at.% Al, 0.05 at.% Hf). Allam [39] observed reduction of void formation on (CoAl  $\beta$ ' and Co-rich  $\alpha$ ) CoCrAl alloys due to the presence of Hf or HfO<sub>2</sub> dispersions. Internal oxidation (peg-formation) occurs during oxidation at 1373 K and 1473 K. The pegs consist of precipitates of HfO<sub>2</sub>, enveloped by alumina.

Scales formed on 0.15at.% Hf containing  $\gamma$ ' FeCrAl can support higher strains at T $\geq$ 1273 K than scales formed on RE free FeCrAl [38].

Hf reduces the growth rate of the oxide. When 2 or 5 at.% Cr is added, however, this beneficial effect vanishes [40]. At higher cyclic oxidation temperatures (>1450 K), the co-doping with Cr also cancels the beneficial effect of Hf on the spallation resistance, presumably due to the occurrence of small  $\alpha$ -Cr particles at the oxide/alloy interface. Also in the substrate small precipitates occur.

#### 3 Scale failure

#### 3.1 Strain energy

The driving force for spallation is the strain energy stored in the oxide (and in the metal). The strain in the oxide layer is determined by [41,42]:

- 1. The differences in thermal expansion coefficient of the oxide and the alloy (during cooling from oxidation temperature the oxide is forced to contract more than it would contract if it were not attached to the alloy);
- 2. The strain resulting from the oxide growth process;
- 3. The volume contraction (approximately 9%) due to the  $\theta$  or  $\gamma$  to  $\alpha$  phase transformations occurring in the oxide [43];
- 4. Relaxation (creep) in the oxide and (if thin substrates are used) in the substrate.

When the deformation is elastic, the energy (per unit area) stored in a biaxially ( $\varepsilon_1 = \varepsilon_2 = \varepsilon_{ll}$ ) stressed layer of thickness *h* is

$$\int_{z=0}^{z=h} \left(\frac{1}{2}\sigma_{1}\varepsilon_{1} + \frac{1}{2}\sigma_{2}\varepsilon_{2}\right) dz = \int_{z=0}^{z=h} \frac{E}{1-\nu}\varepsilon_{ll}^{2} dz$$
(3.1)

where E is the modulus of elasticity and v is the Poisson's ratio.

Strain energy is stored both in the oxide and in the substrate. If the NiAl is much thicker than the oxide, the strain energy stored in the substrate is much lower than the strain energy stored in the oxide [44].

If the stress and the strain are constant through the oxide thickness h and the strain energy stored in the substrate can be neglected, the total strain energy per unit oxide/alloy interface is

$$\gamma^{strain} = h_{oxide} \left( \frac{E_{oxide}}{1 - \nu} \right) \varepsilon_{ll}^2 = h_{oxide} \varepsilon_{ll} \sigma$$
(3.2)

The strain parallel to the metal-oxide interface due to the difference in thermal expansion (shrink) between NiAl and the oxide is

$$\varepsilon_{\prime\prime,\text{therm mismatch}} = \int_{100K}^{293K} (\alpha_{NiAl} - \alpha_{Al2O3}) dT$$
(3.3)

Lipkin [41] measured the stress in alumina formed on NiAl at 1373 K by a fluorescence technique. After cooling to room temperature, the compressive stress was about 3.5 GPa. He also observed cracks in the oxide. These cracks probably relieve tensile stresses in the oxide resulting from the phase transformations during the early stages of oxidation. Lipkin measured a compressive stress in the oxide after cooling to room temperature of 2.9 GPa for oxidation up to 2 hour. At longer oxidation times, the compressive stresses are higher, due to the fact that cracks originating from the  $\theta$  to  $\alpha$  transition are filled with new oxide, and therefore are less effective in relaxing the stress during cooling. Another cause for the higher stresses at longer oxidation time is that transient oxides with lower Young's modulus or higher coefficient of thermal expansion than  $\alpha$ -alumina disappear. Relaxation of the stresses in  $\alpha$ -alumina by deformation of these oxides with lower Young's modulus is then no longer possible.



Figure 3.1: Mean stress in the oxide scale formed on NiAl during oxidation at 1373 K, determined from the shift of the fluorescence lines [41]

Lipkin expected, using the thermal expansion of  $Al_2O_3$  and NiAl over the full range between 1373 and 293 K, a compressive thermal stress and strain in the oxide due to thermal expansion of 3.3 ±0.2 GPa and 0.61%, respectively [41]. This stress can account for the largest part of the stress states displayed in Figure 3.1. Sarioglu [45] measured that the growth stresses in alumina grown on NiAl are small, so the thermal expansion mismatch is the most important cause for the large compressive stresses observed by Lipkin. Also the results listed by Huntz [46] show that the main cause for the compressive stress is the mismatch in coefficient of thermal expansion. Based on a stress and strain of 3.3 GPa and 0.61% respectively, for an oxide thickness of 1 µm (cf. section 8.5) the strain energy  $\gamma^{strain}$  is 20 J/m<sup>2</sup> (equation 3.2).

#### 3.2 Failure mechanisms

Evans and Lobb describe two failure mechanisms for systems where the stress in the oxide is compressive: either wedging or buckling [47]. In this section for both mechanisms criteria are presented that describe when these failure mechanism can initiate or propagate along a *flat* oxide/alloy interface. Initiation at a wavy interface (non-planar stress distributions in the oxide) may be easier than at a flat interface [44]. In section 3.2.2 based on the criteria for the two mechanisms, a 'spallation maps' are drawn. In section 8.6 is discussed which failure mechanism is most likely to occur in the current study.

#### 3.2.1 Wedging and buckling

*Wedging* occurs in the case of a strong interface and a weak oxide. Wedging (Figure 3.2) is initiated by oxide cracking. Wedging propagates when the oxide 'peels off' to further accommodate the stress. Spallation takes place when delaminated zones meet each other. As the oxide layer has cracked, oxygen can easily reach the exposed metal so new oxide may form rapidly under the delaminated oxide, accelerating the delamination process.



#### <sup>r</sup> Figure 3.2 : Oxide failure by wedging [47]

To allow some simple calculations on wedging initiation a square array of four cracks is modelled. This square array of four cracks of side-length  $\lambda$  forms if the compressive stress [47]

$$\sigma \ge \sqrt{\frac{E}{(1-\nu)} \frac{4\gamma_o}{f_{wi}\lambda}} \tag{3.4}$$

or if a tensile stress, for instance arising from the  $\theta$  to  $\alpha$  transformation, is so high that tensile cracking of the oxide occurs. In equation 3.4, *E* is the Young's modulus of the oxide,  $\gamma_0$  is the energy required to produce unit area of oxide and  $\nu$  is the Poisson's constant. The fraction  $f_{wi}$ relates the stored energy within the oxide volume  $\lambda^2 h$  to the energy that is used during the wedging initiating process [47]. In this study  $f_{wi} = 0.05$  is assumed. If not on four but only on one side of the area a crack is formed, the factor 4 has to be removed from equation 3.4. Wedging propagates when the oxide delaminates from the metal. This delamination occurs if the compressive stress

$$\sigma \ge \sqrt{\frac{E}{(1-\nu)} \frac{\gamma^F}{f_{wp}h}} \tag{3.5}$$

or alternatively, if

$$\gamma^{strain} \geq \frac{\gamma^F}{f_{wp}}$$

(3.6)

The factor  $f_{wp}$  is the fraction of stored energy used in the wedge propagation process (in Figure 3.4, graphs are presented for  $f_{wp} = 0.60$  and 0.80) and *h* is the oxide thickness. If fracture is entirely elastic (i.e. no plastic deformation during fraction occurs), the energy necessary for fracture,  $\gamma^F$ , equals the work of adhesion  $W^{ad}$  [44].  $W^{ad}$  is calculated in chapter 4.

*Buckling* [47] occurs in the case of a weak interface and a strong oxide. Non-adherent oxide buckles (Figure 3.3) to relieve the compressive stresses (initiation). Further stress-relief takes place when the buckle becomes larger (propagation). At some stage, tensile cracking of the oxide occurs at points of maximum curvature in the oxide, resulting in spallation.



#### Figure 3.3: Oxide failure by buckling [47]

Buckling initiates if the compressive stress in the oxide over a non-adherent interface area (radius R) is [44,49]

$$\sigma \ge \frac{1.22E}{(1-\nu^2)} \left(\frac{h}{R}\right)^2 \tag{3.7}$$

The buckle propagates if

$$\sigma \ge 1.85 \sqrt{\frac{E\Gamma_i^0}{(1-\nu)h}} \tag{3.8}$$

or alternatively, if

 $\gamma^{\text{strain}} \ge (1.85)^2 \Gamma_i^0 \tag{3.9}$ 

 $\Gamma_i^0$  is the interface fracture toughness in mode 1. For atomically sharp cracks  $\Gamma_i^0 = W^{ad}$  [48]. If crack tip blunting occurs,  $\Gamma_i^0 > W^{ad}$ . Wang and Evans [49] measured  $\Gamma_i^0 \approx 5 \text{ J/m}^2$  for alumina on Ni<sub>3</sub>Al.

#### 3.2.2 Spallation map

According to H.E. Evans and Taylor [50] spallation nearly always will take place by the wedging mechanism; the buckling mode of failure will occur only for thin oxides where a large area of non-adherent interface is present. However, Wang and A.G. Evans [49] expect buckling to be the dominating mechanism.

Some authors model the cracking behaviour with a critical oxide thickness  $h_c$ . Cracking occurs if  $h > h_c$ . When such modelling describes the observed delamination behaviour well, this indicates that the propagation step is the limiting step in the delamination process.

Indicative spallation maps of Al<sub>2</sub>O<sub>3</sub> on NiAl are shown in Figure 3.4a and b. The criterions for wedge initiation, wedge propagation, buckle initiation and buckle propagation are drawn. Apart from the initiation and propagation steps, the failure mechanisms also include a final spallation step. Spallation takes place for the wedging mechanism when the wedge has propagated so much that a piece of oxide with dimensions  $\lambda^2$  has no longer has contact with the metal. For the buckling mechanism, spallation takes place when tensile cracking of the oxide occurs at the places of maximum curvature of the oxide. Criterions for spallation are not included, as propagation will finally lead to spallation anyway.

For the wedging initiation some less precisely known parameters are grouped in the parameter Q (unit: J/m3):

$$Q = \frac{4\gamma_o}{f_{wl}\lambda} \tag{3.10}$$

The sensitivity of delamination behaviour with respect to Q is demonstrated in Figure 3.4a. Figure 3.4 shows that for oxide layers of about 1  $\mu$ m thick under a compressive stress of 3.5 GPa, buckling will not initiate if no void or impurity (causing poor adherence) or out-of-plane stress is present at the oxide/alloy interface. Voids or impurities with radius *R* larger than 4  $\mu$ m are necessary to initiate buckling.

Parameter	Value and Unit	Source
E A1203	386 GPa	[41,51]
V A1203	0.27	[41,51]
$\Gamma_i^0$ (only relevant for buckling)	5 J/m <sup>2</sup>	
$f_{wp}$ (only relevant for wedging)	0.8	

Table 3.1: parameters used for the spallation maps

As can be easily seen from equation 3.6 and 3.9, for both failure mechanisms, whether or not propagation takes place depends on the magnitude of the (thermal) strain energy relative to an energy term describing the adhesion. When the fracture is brittle and atomically sharp this term is equal to the work of adhesion. Therefore an interface with a high work of adhesion is optimal. As a thicker oxide thickness results in higher strain energy, a low growth rate of the oxide is preferable.



Figure 3.4: Indicative spallation maps for Al<sub>2</sub>O<sub>3</sub> on NiAl, a: if both wedging initiation and wedging propagation occurs (marked area) the oxide layer will delaminate; b: if both buckling initiation and propagation occur (marked area) the oxide layer will delaminate; (the curves representing the criteria will shift in the direction indicated by arrows if the displayed parameter increases)

The strain energy due to difference between the thermal expansion coefficient of NiAl and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (section 3.1) is much higher than the work of adhesion calculated in the chapter 4. If  $f_{wp}$  is not very small, for both failure mechanisms, the propagation criterion is met (equation 3.6 and 3.9). Therefore, if oxide cracking or buckling occurs, propagation will take place.
Brumm and Grabke [52] observed voids at the oxide/metal interface through the oxide. The origin of these voids is discussed in section 2.2. These voids make delamination occur more easily. The buckling mechanism in particular becomes more feasible. According to their calculations [52], voids at the oxide/metal interface do not inhibit further scale growth as vaporisation of Al ensures enough Al-transport (from the metal over the void to the oxide).

# 4 Effect of reactive elements on work of adhesion

In this chapter the adhesion over  $Al_2O_3/NiAl$  interfaces is modelled. A measure for adhesion is the work of adhesion,  $W^{ad}$ . The model used to estimate the value for the work of adhesion is the 'macroscopic atom' model, also referred to as the 'Miedema-model'. At the interface modelled, reactive elements or their oxides are present. The calculations show the influence of their presence on the work of adhesion over the interface.

## 4.1 Introduction to the macroscopic atom model

In the macroscopic atom model an atom A is in its reference state when it is completely surrounded by other A atoms. When an A atom is completely surrounded by B atoms instead, an interface energy effect occurs. This energy is called  $\gamma_{A-B}^{interaction}$ . For (most) combinations of metal A and metal B that form alloys,  $\gamma_{A-B}^{interaction}$  is negative. The magnitude of  $\gamma_{A-B}^{interaction}$  is [53]:

$$\gamma_{A-B}^{0,interaction} = \frac{\Delta H_{AinB}^{0,interface}}{C_0 V_A^{2/3}} = \frac{-P(\Delta \phi^*)^2 + Q(\Delta (n_{WS}^{1/3}))^2}{C_0 \left(n_{WS}^{-1/3}\right)_{A_V}}$$
(4.1)

The superscript 0 denotes the temperature. Only at zero Kelvin is equation 1.1 exactly valid.  $V_A$  is the volume per mol of atoms A;  $C_0$  is a constant that relates the surface area of one mole of atoms to  $V_A^{2/3}$  and depends on the shape of the Wigner-Seitz cell. On average  $C_0$  can be taken as 4.5E08 [53]; *P* and *Q* are constants;  $\Delta \phi^*$  is the difference between the (adjusted) work functions of A and B. Adjusted work functions can be found in reference 53.  $n_{WS}$  is the electron density at the cell boundary of the Wigner-Seitz cell for the pure metals. These are also presented in ref 94.  $(n_{WS}^{-1/3})_{AV}$ is the average of  $n_{Ws}^{-1/3}$  for A and  $n_{Ws}^{-1/3}$  for B.

When an A atom is at the surface of a block of metal A, it is partly surrounded by vacuum (instead of by other A atoms). The extra energy associated with such atoms is the surface energy  $\gamma_A$  [54]:

$$\gamma_A^0 = \frac{\Delta H_A^{vap}}{C_0 V_A^{2/3}} = \frac{\Delta H_A^{surf}}{f_{vacuum}^A C_0 V_A^{2/3}}$$
(4.2)

Where  $\Delta H^{vap}$  and  $\Delta H^{surf}$  are the enthalpy of vaporisation and the surface enthalpy, respectively. The fraction of the cell surface of A in contact with vacuum, denoted by  $f_{vacuum}^{A}$ , is about 0.35 [p 673ref 53].

When a block of metal A is brought into contact with a block of metal B, the surface energy of the two initially free surfaces is released. Further, an interfacial energy according to equation 4.1 is built up between the dissimilar cells at the interface. The total energy changes can be depicted as:



# Figure 4.1: Surface A and surface B (with the energy $\gamma_A$ and $\gamma_B$ ) are replaced by an interface over which chemical interaction takes place (energy $\gamma_{A-B}$ )

In Figure 4.1 the energy effect over the interface is

$$\gamma_{A-B} = \gamma_{A-B}^{interaction} + \gamma_{A-B}^{mismatch} = \frac{\Delta H_{AinB}^{interface}}{C_0 V_A^{2/3}} + \gamma_{A-B}^{mismatch}$$
(4.3)

This  $\gamma_{A-B}$  is often negative, and therefore pointing downwards. In the first term of this interface enthalpy equation 4.1 can be recognised. To calculate the chemical interaction  $\gamma_{A-B}^{interaction}$  over an interface, instead of using  $C_0 V_A^{2/3}$ , often the energy per mole A entirely surrounded by B is multiplied by the number of atoms per unit area at the interface and by the fraction p of that atom in contact with atoms at the other side of the interface. The number of atoms per unit area is the reciprocal of the area  $A_A$  necessary to store one mole of A atoms. In this study  $C_0 V^{2/3}$  will be used, however.

$$\gamma_{A-B}^{interaction} = p \frac{\Delta H_{AinB}^{interface}}{A_A} = \frac{p \Delta H_{AinB}^{interface}}{p C_0 V_A^{2/3}}$$
(4.4)

The second term in equation 4.3 is the mismatch energy. For metals it is about equal to the energy of large-angle grain boundaries, and is therefore estimated as  $0.15(\gamma_A + \gamma_B)$  [p689ref53]. It is not sure whether this estimation is also valid for metal/oxide interfaces. Crystallographic calculations and HREM-observations will provide more insight.

The work of adhesion is the opposite of the energy released when a block of A atoms is joined with the a block of B atoms. At zero Kelvin, its magnitude is [p690ref53,55]:

$$W^{ad} = \gamma_A + \gamma_B - \gamma_{A-B}^{interaction} - \gamma_{A-B}^{mismatch}$$
(4.5)

In this study the crystallographic relationships between the metal and the oxide are neglected. Therefore the misfit energy is not calculated, so the work of adhesion calculated in this study is too high.

# 4.2 Al<sub>2</sub>O<sub>3</sub> / NiAl interface

#### 4.2.1 Interaction energy

The interactions that can occur over a Al<sub>2</sub>O<sub>3</sub> / NiAl interface, are summarised in Table 4.1. Their contribution to the interaction-energy  $\gamma_{Al2O3-NiAl}^{interaction}$  is also indicated. A negative energy-effect refers to a process that is exothermic compared to the reference state. The subscripts 'ox' and 'met' indicate the location of the Al-atom. The alumina is considered to be  $\alpha$ -alumina. It is assumed that the chance that (or the extent to which) an oxide ion meets an Al-atom or a Ni-atom is purely determined by the surface fractions of Ni and Al.

The surface fraction  $C_{Al}^{s}$  is the sum of all surfaces of the Al atoms in the metal, divided by the sum of all surfaces of all metal atoms. The atomic cells of Al shrink and the atomic cells of Ni expand upon NiAl formation, as Ni has a higher work function (is more electronegative) than Al. In appendix B a procedure is described to take this effect into account, resulting in an adjusted  $C_{Al}^{s}$ and  $C_{Ni}^{s}$ . The surface fraction of Al and Ni at the oxide/alloy interface is  $(C_{Al}^{s})_{int}$  and  $(C_{Ni}^{s})_{int}$ , respectively. When segregation occurs,  $(C^{s})_{int}$  differs from  $C^{s}$ .

From the distances between the ions (the O-O and the Al-O distance can be found ref [56] from the Inorganic Crystal Structure Database [57]) the ionic radii  $R_{Al}$  and  $R_0$  are determined. These ionic radii correspond well with the radii tabulated by Shannon [58] and with geometric calculations based on the crystal structure [59] with the anions touching each other. Between the spherical volumes, free space  $V_{free}$  is present. The total volume  $V_{Al2O3}^{total}$  containing 30 mole ions is from [56,59]. Where  $N_{Av}$  is Avogadro's number,

$$V_{o}^{spheres} = N_{Av} \left(\frac{4}{3}\pi R_{o}^{3}\right) \quad \text{and} \quad V_{Al_{ox}}^{spheres} = N_{Av} \left(\frac{4}{3}\pi R_{Al}^{3}\right)$$

$$V_{free} = V_{Al2O3}^{total} - 18V_{o}^{spheres} - 12V_{Al_{ox}}^{spheres}$$

$$(4.6)$$

This free space is divided over the ions according to the volume ratios of the ions present, as proposed by Jeurgens [appendix D in 60]. Then

$$V_{o} = V_{o}^{spheres} + \frac{V_{o}^{spheres}}{V_{Al2O3}^{total} - V_{free}} V_{free} \text{ and } V_{Al_{ox}} = V_{Al_{ox}}^{spheres} + \frac{V_{Al_{ox}}^{spheres}}{V_{Al2O3}^{total} - V_{free}} V_{free}$$
(4.7)

One mole of Al has a surface area of  $C_o V_{Al,ox}^{2/3}$ . To have a neutrally charged surface, on a surface area where one mole Al is present, 1.5 mole O is also present. From this, the total surface needed to store one mole of Al is calculated. Neglecting the strain energy gives the equations shown in Table 4.1. The total interaction energy is the sum of all interactions taking place over the interface. An added benefit of dividing the free volume over the ions present (equation 4.7) is that the calculation becomes numerically less sensitive to errors in the atomic radii.

Table 4.1: The interactions taking place over the interface; the interaction energy	$\gamma_{Al2O3-NiAl}^{interaction}$
is the sum of the contributions in the third column	

	<b>T</b>	
Atom in	Atom in	Energy-contribution to interaction energy
metal	oxide	
Ni	Al	$(C_{Ni}^{S})_{\text{int}} \frac{p_{Al_{ox}} \Delta H_{AlinNi}^{0,interface}}{p_{Al_{ox}} C_{0} V_{Al_{ox}}^{2/3} + \frac{3}{2} p_{O} C_{0} V_{O}^{2/3}} = (C_{Ni}^{S})_{\text{int}} \frac{\Delta H_{AlinNi}^{0,interface}}{C_{0} V_{Al_{ox}}^{2/3} + \frac{3}{2} C_{0} V_{O}^{2/3}}$
	0	$(C_{Ni}^{S})_{\text{int}} \frac{\Delta H_{OinNi}^{\infty}}{C_{0}V_{O}^{2/3} + \frac{2}{3}C_{0}V_{Al_{ox}}^{2/3}}$
Al	Al	$(C_{Al_{met}}^{S})_{int} \frac{\Delta H_{AlimAI}^{0,interface}}{C_{0}V_{Al_{ox}}^{2/3} + \frac{3}{2}C_{0}V_{O}^{2/3}} = 0$
	0	$(C_{Al_{met}}^{S})_{int} \frac{\Delta H_{OinAl}^{\infty}}{C_{0}V_{O}^{2/3} + \frac{2}{3}C_{0}V_{Al_{ox}}^{2/3}}$

As indicated in the first equation in Table 4.1, it is assumed that the fraction in contact with atoms at the other side of the interface, p, is equal for an O-atom and for an Al-atom. This assumption is made in all equations in Table 4.1.

The interaction between Ni and O depends on the enthalpy of mixing at infinite dilution, of 1 mol O (g) atoms in nickel,  $\Delta H^{\infty}$  [60]. In ref [53]  $\Delta H^{\infty}$  is denoted as  $\left(\Delta H_{O \text{ in } Ni}^{interface}\right)^{extrapolated}$ . Its magnitude is obtained from the experimentally measured enthalpies of formation of different Ni-oxides,  $\Delta H_{O \text{ in } Ni}^{f}$ . The most negative enthalpy of formation per mole of oxygen atoms is then  $\left(\Delta H_{O \text{ in } Ni}^{interface}\right)^{extrapolated}$  [p643 ref53]. In the following calculations  $\left(\Delta H_{O \text{ in } Ni}^{interface}\right)^{extrapolated}$  is used. A

slightly different approach can be found in [p17 ref 60]. Values obtained via that procedure differ less than two percent.

The interaction-energy between Al atoms in the metal substrate and Al ions in the oxide is zero, as this surrounding corresponds to the reference state [61]. Therefore  $\Delta H_{Al in Al}^{interface}$  is zero.

An Al-content of 40 at.% Al (balance Ni) is chosen, so  $C_{Al} = 0.4$ . This results in  $C_{Al}^{S} = 0.437$  (appendix B). This value is also adopted for  $(C_{Al}^{S})_{int}$ , i.e. it is assumed that no surface segregation in the alloy takes place.

Variable	Value	Unit	Comment
$\Delta H^{interface} Al$ in Ni	-1.39E+05	J/mole Al	table V-4.10 ref [94]
$\Delta H^{interface}O$ in Ni	-2.41E+05	J/mole O	table V-4.27 ref [94]
$\Delta H^{interface} Al$ in $Al$	0	J/mole Al	reference state
$\Delta H^{interface}O$ in Al	-5.58E+05	J/mole O	table V-4.27 ref [94]
R <sub>Al</sub>	0.64	Å	
R <sub>O</sub>	1.27	Å	
$V_{Al} / N_{Av}$	1.7	Å <sup>3</sup>	
$V_O / N_{Av}$	13.0	Å <sup>3</sup>	
$C_o V_O^{2/3} + (2/3) C_o V_{Al}^{2/3}$	2.08E+05	m <sup>2</sup> /mole	0
$C_o V_{Al}^{2/3} + (3/2) C_o V_O^{2/3}$	3.12E+05	m <sup>2</sup> /mole	Al
$C^{S}Al$	0.437		See appendix
C <sup>S</sup> Ni	0.563		See appendix

Table 4.2: Calculation of the interaction energy over the Al<sub>2</sub>O<sub>3</sub> / NiAl interface

This results in  $\gamma_{Al2O3-NiAl}^{interaction} = -2.08 \text{ J/m}^2$ .

The interface enthalpies listed in table 2 apply at zero kelvin, while the work of adhesion at room temperature is needed. Inspection of the changes in enthalpies of formation of oxides [62] and intermetallics [53] due to temperature indicates that interface energies can be 1 or 2 % more negative. This results in an interaction-energy 1 or 2 % lower than the calculated -2.08 J/m<sup>2</sup>. This difference is negligible.

For comparison: an interfacial energy of -3.61 J/m<sup>2</sup> is calculated for  $\alpha$ - Al<sub>2</sub>O<sub>3</sub> on niobium [63], indicating that the calculated interfacial energy is of the right order of magnitude.

#### 4.2.2 Contribution from surface energies

Apart from the interaction energy and the mismatch energy, another contribution to the work of adhesion exists (equation 4.5). This contribution is the energy associated with the surfaces that form when the interface breaks apart. Both the surface energy of the NiAl and the surface energy of the oxide have to be included. Thus:

$$\gamma_{NiAI}^{0} = \frac{\Delta H_{Ni}^{surf}}{f_{vacuum}}^{Ni} \left( C_{0}V_{Ni}^{2/3} + \frac{\left(C_{AI,met}\right)_{int}}{\left(C_{Ni}\right)_{int}} C_{0}V_{AI,met}^{2/3} \right) + \frac{\Delta H_{AI}^{surf}}{f_{vacuum}}^{AI,met} \left( C_{0}V_{AI,met}^{2/3} + \frac{\left(C_{Ni}\right)_{int}}{\left(C_{AI,met}\right)_{int}} C_{0}V_{Ni}^{2/3} \right)$$
(4.8)

$$\gamma^{0}_{Al_{2}O_{3}} = \frac{\Delta H_{O}^{surf}}{f_{vacuum}^{o} \left(C_{0}V_{O}^{2/3} + \frac{2}{3}C_{0}V_{Al_{ox}}^{2/3}\right)} + \frac{\Delta H_{Al}^{surf}}{f_{vacuum}^{Al_{ox}} \left(C_{0}V_{Al_{ox}}^{2/3} + \frac{3}{2}C_{0}V_{O}^{2/3}\right)}$$
(4.9)

 $(C_{Ni})_{int}$  and  $(C_{Al,met})_{int}$  are the atomic fractions of Ni and Al at the surface of the NiAl (before debonding: the interface between Al<sub>2</sub>O<sub>3</sub> and NiAl), respectively.

 $\Delta H^{surf}_{o}$  is estimated to be 50 kJ/mole O (no precise value found),  $\Delta H^{surf}_{Al} = 76$  kJ/mole [94],  $\Delta H^{surf}_{Ni} = 121$  kJ/mole [94]. f = 0.31, as this is in-between 0.35 [p 673 ref 94] and 0.27 [66], and with this value the surface energies for pure Ni and pure Al relate well with  $\Delta H^{surf}_{Al}$  and  $\Delta H^{surf}_{Ni}$ . This results in  $\gamma_{NiAl} = 1.85$  J/m<sup>2</sup> and  $\gamma_{Al2O3} = 1.56$  J/m<sup>2</sup>. The latter is strongly dependent on the uncertain surface enthalpy for oxygen.

Manassidis and Gillan [64] did first-principle calculations and arrived at surface energies for alumina of (depending on the chosen plane) 1.4 to 2.5 J/m<sup>2</sup> for relaxed surfaces, and even higher for unrelaxed surfaces. In [55] first principle surface energies for alumina are tabulated ranging from 1.5 to 4.0 J/m<sup>2</sup> (relaxed surfaces), together with an experimental value extrapolated to zero temperature of about 0.93 J/m<sup>2</sup>. Both calculations [55,64] indicate that the aluminium ions tend to move away from the surface for most orientations. The oxygen-terminated orientations, for instance (10<sup>-10</sup>), have the lowest surface energies [64].

A check on the surface energy of NiAl is the following: with the surface energy calculated above and a chemical interaction energy (both calculated with the macroscopic atom model), a work of adhesion for NiAl / NiAl can be calculated. The work of adhesion is the sum of the surface energy on both sides of a fracture area (=2 x 1.85 J/m<sup>2</sup>) minus the interaction energy over that area (- 0.51 J/m<sup>2</sup>). This results in  $W^{ad}$  = 4.2 J/m<sup>2</sup>. First-principle calculations [65] indicate a comparable work of adhesion of NiAl / NiAl: 5.5 or 6.3 J/m<sup>2</sup>. This gives confidence in the surface energy of NiAl calculated in this section.

Also in the calculations presented in this section, zero temperature values are used. Inspection of the trend of the surface energy with the temperature reveals that at 298 K the surface energies are 2-3% lower [66], thus counteracting the change with temperature in the interaction energy. Therefore, the effect of temperature on the values of the work of adhesion can be neglected.

#### 4.2.3 Work of adhesion

The interaction energy and the surface energies calculated in the preceding sections result in a work of adhesion  $W^{ad}_{NiAl-Al2O3} = 5.48 \text{ J/m}^2$  (equation 4.5, neglecting the mismatch energy). In comparison with literature data this value is high (Table 4.3).

System	$\gamma^{interaction}_{Al2O3-NiAl}$ (J/m <sup>2</sup> )	Work of adhesion (J/m <sup>2</sup> )	Method and source
$NiAl - Al_2O_3$	-2.08	5.48	Current work
$Al - Al_2O_3$	-2.68 (using $C_{Al}^{S} = 1$ )	5.40	
$Ni - Al_2O_3$	$-1.60 \text{ (using C}^{S}_{Ni} = 1)$	5.61	
$Al - Al_2O_3$	+0.89	1.2	Experimental values
$Ni - Al_2O_3$	+2.54	1.13	extrapolated to room
			temperature [67]
Ni – Al <sub>2</sub> O <sub>3</sub>	+2.14	0.65 (at 1273 K in H <sub>2</sub> )	Modified sessile-drop
			method, TEM particle
			profile [68]
Ni (111) –	+2 to 3	0.46	First principle
Al <sub>2</sub> O <sub>3</sub>			calculations (three oxygen
			layers parallel to
			interface) [69]
$Al_2O_3 - Co$ -		3	No method stated, [70]
40Ni			
MgO – Ag		0.45 ±0.1 (work of	UHV-contact angle
		separation)	measurements [71]
MgO – Al		1.1 (work of separation)	First principle
MgO – Ag		1.9 (work of separation)	calculations [72]
MgO – Ag		1.6 (work of separation)	First principle
MgO – Ti		2.2 (work of separation)	calculations [73]

 Table 4.3: Work of adhesion between metal and oxide found in literature

The work of adhesion is too high. The most important cause for this high work of adhesion is that in these calculations the mismatch energy is not taken into account. Taking the mismatch energy into account results in a lower work of adhesion. The mismatch depends on the misfit between planes in the oxide and planes in NiAl, so the mismatch energy depends on the crystallographic orientation.

This mismatch is a possible origin for the differences in the stresses observed [74] in alumina on (001) oriented NiAl and alumina on (111), (1<sup>-</sup>10) and (110) oriented NiAl. The least compressive stress after cooling is observed on (001) NiAl.

The chemical interaction energy depends on the area needed to store one mole of ions of a certain kind. Therefore, the chemical interaction also depends on orientation. In the current calculation, the area necessary to store one mole of ions is an average over all orientations. The effect of the mismatch on the interfacial energy will be larger than the refinement due to a more accurate

calculation of the area needed to store one mole of ions, so refining the calculations by taking into account the crystallographic orientations will lead to a lower work of adhesion.

The interaction energy is made up of two contributions, one arising from matching of the electron densities at the Wigner Seitz-cell boundaries  $n_{WS}$ , and one arising from charge transfer. The charge transfer depends on the difference in the work functions  $\Delta \phi^*$ . In the macroscopic atom model it is assumed that the interaction between an atom and its neighbour on one side, does not affect its interaction with its neighbour at the other side. Especially when ionic bonds are involved, this assumption can cause inaccuracy. If for instance the ionic bond between Al-cations and O-anions results in charge transfer in the oxide, it increases the work functions of Al and decreases the work function of O. As the work function of O is higher than that of Ni, a decrease in the work function of O will lead to smaller difference in the work functions and decrease the energy effect due to the O-Ni interaction. This results in a lower work of adhesion.

Equation 4.1 is built up of two first terms of a series expansion. When  $\Delta \phi^*$  and  $\Delta n_{WS}^{1/3}$  are large, the series expansion is less accurate [pag 75 ref94]. Therefore,  $\Delta H^{interface}$  and thus  $\gamma^{interaction}$  become less accurate.

Al-termination of the metal lattice results in a higher  $(C_{Al}^{S})_{int}$  and a more negative interaction energy. Therefore, it is expected that the metal lattice prefers to end with Al-atoms. A higher  $(C_{Al}^{S})_{int}$  results in a lower energy of the surface formed after fracture, so the changes in the work of adhesion  $W^{ad}$  are small.

# 4.3 RE-oxide / NiAl interface

To investigate the influence of reactive elements on the adhesion, the work of adhesion is calculated for the situation that the oxide above the NiAl is RE-oxide.

Whether or not that oxide actually forms in practice, depends on kinetic and thermodynamic factors. One of these factors is the Gibbs energy of oxide formation per mole oxygen, nearly equal to  $\Delta H_{O in RE}^{interface}$ . However, these calculations are beyond the scope of this work.



Figure 4.2: Schematic representation of an interface consisting partly of a RE-oxide / NiAl interface and partly of a  $Al_2O_3$  / NiAl interface

As over the RE-oxide /  $Al_2O_3$  interface ionic bonding is possible, the weakest interface will be between the oxide and the metal. Christensen and Carter calculate a higher work of adhesion between  $Al_2O_3$  and  $ZrO_2$  than between  $Al_2O_3$  and NiAl [75,83].

If the interface is built up partly of a RE-oxide / NiAl and partly of a  $Al_2O_3$  / interface (Figure 4.2), the work of adhesion is a proportional combination of  $W^{ad}$  of the respective interfaces (if strain effects can be neglected).

The interactions that can occur over the interface between NiAl and the oxide are summarised below for zirconia, which serves also as an example for the other RE-oxides. The contribution of each interaction to the interaction-energy  $\gamma_{ZrO2-NiAl}^{0,interaction}$  is also indicated. The chemical formula of zirconia is ZrO<sub>2</sub>; the index *n* is 2. The atomic radii and the volume of the unit cells are again from [57]. The atomic radii correspond reasonably with [58].

Table 4.4: The interactions occuring over the NiAl /  $Y_2O_3$  interface; the interaction energy  $\gamma^{interaction}_{NiAl-Y2O3}$  is the sum of the contributions listed in the table

Atom in	Atom in	Energy-contribution to interaction energy
metal	oxide	
Ni	Zr	$(C_{Ni}^{S})_{\text{int}} \frac{\Delta H_{Zr \text{ in } Ni}^{0, interface}}{C_0 V_{Zr}^{2/3} + n C_0 V_O^{2/3}}$
	0	$(C_{Ni}^{S})_{\text{int}} \frac{\Delta H_{O}^{\infty} \text{ in Ni}}{C_{0} V_{O}^{2/3} + \frac{1}{n} C_{Zr}^{2/3}}$
Al	Zr	$(C_{Al}^{S})_{\text{int}} \frac{\Delta H_{Zr \text{ in } Al}^{0, \text{interface}}}{C_0 V_{Zr}^{2/3} + n C_0 V_0^{2/3}}$
	0	$(C_{Al}^{S})_{\text{int}} \frac{\Delta H_{O \text{ in } Al}^{\infty}}{C_{0} V_{O}^{2/3} + \frac{1}{n} C_{0} V_{Zr}^{2/3}}$

The surface energy of newly formed surface also contributes to the work of adhesion (Equations 4.5, 4.8, 4.9)

The interaction enthalpies of reactive element with Ni are not corrected for filling of the d-band. This filling of the d-band might result in lower interaction enthalpies. However, as the RE in contact with Ni cannot donate enough electrons to fill the Ni-d band (due to the presence of O anions), a change in the interaction enthalpy is not expected and the correction for filling of the dband is unnecessary.

The resulting surface energy for zirconia is in the range indicated by First-Principles calculations [76]. Depending on the orientation, the unrelaxed surface energy of monoclinic zirconia at zero temperature is 1.6 to  $3.5 \text{ J/m}^2$ , and the relaxed surface energy is 1.2 to 2.5 (on average 1.74)  $\text{J/m}^2$ .

Variable	Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	HfO <sub>2</sub>	Unit
$\Delta H^{interface} O$ in Ni	-2.41E+05	-2.41E+05	-2.41E+05	-2.41E+05	J/mole O
$\Delta H^{interface} RE$ in Ni	-1.39E+05	-1.62E+05	-2.37E+05	-2.04E+05	J/mole cations
$\Delta H^{interface} O in Al$	-5.58E+05	-5.58E+05	-5.58E+05	-5.58E+05	J/mole O
$\Delta H^{interface} RE$ in Al	0	-2.21E+05	-2.40E+05	-2.15E+05	J/mole cations
$V_O / N_{Av}$	13.0	20.9	16.3	15.2	Å <sup>3</sup>
V <sub>cation</sub> / N <sub>Av</sub>	1.7	5.8	2.5	4.2	Å <sup>3</sup>
$C_o V_O^{2/3} + (1/n) C_o V_{Cation}^{2/3}$	2.08E+05	3.13E+05	2.36E+05	2.38E+05	m²/mole
$C_o V_{Cation}^{2/3} + n C_o V_O^{2/3}$	3.12E+05	4.69E+05	4.72E+05	4.77E+05	m <sup>2</sup> /mole
2 <sup>interaction</sup>	-2.08	-1.61	-2.11	-2.03	J/m <sup>2</sup>
$\Delta H^{surf}_{cation}$	7.6E+04	1.16E+05	1.63E+05	1.71E+05	J/mole
Yoxide	1.56	1.31	1.80	1.83	J/m <sup>2</sup>
ŶNiAI	1.85				J/m <sup>2</sup>
Work of adhesion	5.48	4.77	5.76	5.71	J/m <sup>2</sup>

Table 4.5: calculation of the work of adhesion for several RE-oxides on Ni<sub>0.6</sub>Al<sub>0.4</sub>

 $\Delta H^{surf}_{o}$  used for calculating  $\gamma_{oxide}$  is 50 kJ/mole O. As the surface enthalpy of the anions is not precisely known, the calculation in Table 4.5 is repeated in Table 4.6 with  $\Delta H^{surf}_{o} = 100$  kJ/mole O. Although the magnitude of the differences between the various oxide / NiAl systems changes, for reasonable estimates for  $\Delta H^{surf}_{o}$  the trend between the oxide / NiAl systems remains the same.

Table 4.6: Calcula	tion of wor	k of adhesion	with $\Delta H^{sur}$	<sup>r</sup> o = 100 kJ/mole
--------------------	-------------	---------------	-----------------------	------------------------------

Variable	Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	HfO <sub>2</sub>	Unit
Yoxide	2.34	1.83	2.48	2.51	J/m <sup>2</sup>
Work of adhesion	6.26	5.29	6.44	6.39	J/m <sup>2</sup>

The results (Table 4.5) show that if yttria is present at the interface, it does not increase the adhesion. The other reactive element oxides do increase the adhesion a little. With computational

methods, Anderson *et al* [77] also found no difference between the adherence of  $[AIO_6]^{6-}$  or  $[YO_6]^{6-}$  to a Ni<sub>10</sub> cluster.

The result that yttria does not enhance the adhesion is quite surprising. It may be that the way the reactive element is distributed in the oxide is important. Therefore in the next section the work of adhesion for a combined yttrium-aluminium oxide is calculated.

#### 4.3.1 Combined RE-Al oxides

The solubility of monoclinic  $ZrO_2$  in  $Al_2O_3$  appears to be negligible and no combined oxide is observed after sintering  $ZrO_2$  and  $Al_2O_3$  at 1373 K and cooling to room temperature [78]. Apart from  $Zr_5Al_3O_{0.5}$  no RE-Al oxide can be found in the JCPDS or Landolt-Börnstein [79] either. No RE-Al-O compounds are found for the Hf-Al-O system. More feasible candidates for combined oxides to be formed during oxidation exist for the yttrium-containing alloy. These candidates are: yttrium-aluminium garnet (YAG, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>); YAP (perovskite-type, YAlO<sub>3</sub>) and YAM (monoclinic, Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>).

The work of adhesion of YAG and YAP is calculated using the ionic radii and the volume per unit cell from [80] and [81], respectively. They are tabulated in [57]. The calculation is summarised in Table 4.7.

Variable	YAG	YAP	Unit
$C_o V_O^{2/3} + (1/n) C_o V_{Al}^{2/3} +$	2.43E+05	2.36E+05	m <sup>2</sup> / mole
$(1/m) C_o V_Y^{2/3}$			
$n C_o V_O^{2/3} + C_o V_{Al}^{2/3} + (n/m)$	5.82E+05	7.09E+05	m <sup>2</sup> / mole
$C_o V_Y^{2/33}$			
$m C_o V_O^{2/3} + (m/n) C_o V_{Al}^{2/3} +$	9.70E+05	7.09E+05	m <sup>2</sup> / mole
$C_o V_Y^{2/3}$			
vinteraction	-1.89	-1.98	J/m <sup>2</sup>
Yoxide	1.47	1.56	J/m <sup>2</sup>
Yniai	1.85		J/m <sup>2</sup>
Work of adhesion	5.21	5.39	J/m <sup>2</sup>

Table 4.7: Calculation of work of adhesion for YAG (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>) and YAP (YAlO<sub>3</sub>)

This leads to a higher work of adhesion than for yttria, but lower than for alumina. The difference between the work of adhesion of yttria and the combined Y and Al oxides are due to the fact that in YAG and YAP the atoms are more closely packed than in yttria.

For every crystal discussed in section 4.3 further calculations are necessary to calculate the mismatch energy. The best-fit orientation of every oxide crystal on the orientations of NiAl present

may either fit better or worse than the best-fit orientation of alumina. The mechanical properties of the oxides also differ. Therefore the mismatch energy between RE-oxide and NiAl may be lower or higher than for alumina.

Several yttrium-containing oxides are possible. Each of those crystals has a number of crystallographic planes (i.e. orientations). It would not be surprising if for the yttrium-containing oxides in the set of possible planes (a *quite large set* due to the combined Y-Al oxides YAP, YAG, and YAM), a planar orientation is found with lower mismatch energy than the best fitting orientation of alumina.

# 4.4 Al<sub>2</sub>O<sub>3</sub> / RE/ NiAl system

The case that the reactive element is present in metallic state, as a layer between the NiAl and the Al<sub>2</sub>O<sub>3</sub> (Figure 4.3), is investigated in this section. Whether or not the RE can be present in the metallic state depends on kinetic and thermodynamic factors (for instance:  $\Delta H_{O in Y}^{interface}$  is quite high, so yttrium probably prefers to be present as oxide). As the fracture will find the weakest link, both the Al<sub>2</sub>O<sub>3</sub> /RE and the RE / NiAl interface are investigated. However, even if the RE /NiAl interface will probably not be the weakest link, as on that interface, plasticity during cracking increases the energy necessary for fracture. Therefore, the total work necessary for cracking over that interface will be larger than the work of adhesion.



#### Figure 4.3: Al<sub>2</sub>O<sub>3</sub> / RE /NiAl system

For alumina on reactive element ( $C_{RE}^{s}=1$ ) the work of adhesion  $W^{ad}$  is calculated (Table 4.8). For comparison, the interaction energy and the work of adhesion for alumina / sulphur are also calculated. The interface enthalpy of O in sulphur is not tabulated, so the calculation on sulphur has limited accuracy. The interface energies  $\Delta H_{O in RE}^{interface}$  and  $\Delta H_{Al in RE}^{interface}$  and the surface energies of pure metals are from ref [94]. In these calculations, again, the crystallographic relationships between RE-metal and alumina, and its effects on the interaction energy  $\gamma^{interaction}$  are ignored.

	Y	Zr	Hf	S	
$\Delta H^{interface} Al$ in RE	-1.61E+05	-2.08E+05	-1.89E+05	-3.63E+05	J/mole Al
$\Delta H^{interface}O$ in RE	-6.35E+05	-5.49E+05	-5.57E+05	-5.00E+04 *	J/mole O
yinteraction	-3.57	-3.31	-3.28	-1.40	J/m <sup>2</sup>
YAI2O3	1.56				J/m <sup>2</sup>
Ŷre	1.13	2.00	2.15	0.078 [ref 82]	J/m <sup>2</sup>
Work of adhesion	6.25	6.87	6.99	3.04 *	J/m <sup>2</sup>

Table 4.8: Work of adhesion between a thin RE metallic layer and alumina

(\* indicates an uncertain value)

The work of adhesion for  $Al_2O_3$  /RE is higher than the work of adhesion for  $Al_2O_3$  / NiAl. The work of adhesion for S is lower than the work of adhesion for  $Al_2O_3$  /NiAl. The higher adhesion between  $Al_2O_3$  / Y compared to  $Al_2O_3$  /Ni (5.61 J/m<sup>2</sup>) agrees with the calculations by Anderson *et al* [77] that showed that the adhesion between an [AlO6]<sup>6-</sup> and a Ni<sub>10</sub> cluster increases when Ni atoms from the Ni-cluster are replaced by Y-atoms.

Similar calculations as in Table 4.8 indicate that the work of adhesion increases when atoms at the surface of NiAl are replaced by Cr-atoms (the work of adhesion for  $Al_2O_3$  / Cr is 5.95 J/m<sup>2</sup>).

As a chain is as strong as its weakest link, the work of adhesion between the thin layer of RE and the metal is also calculated. As the surface fraction of RE at the RE / NiAl interface is unity, the interaction energy can be calculated as:

$$\gamma^{interaction} = \frac{\Delta H_{Ni \text{ in } RE}^{0, interface}}{C_0 V_{Ni}^{2/3} + \frac{(C_{Al, met})_{\text{int}}}{(C_{Ni})_{\text{int}}} C_0 V_{Al, met}^{2/3} + \frac{\Delta H_{Al \text{ in } RE}^{0, interface}}{C_0 V_{Al, met}^{2/3} + \frac{(C_{Ni})_{\text{int}}}{(C_{Al, met})_{\text{int}}} C_0 V_{Ni}^{2/3}$$
(4.10)

	Y	Zr	Hf	S	
$\Delta H^{interface} Al$ in RE	-1.61E+05	-2.08E+05	-1.89E+05	-3.63E+05	J/mole Al
$\Delta H^{interface} Ni$ in RE	-9.70E+04	-1.65E+05	-1.45E+05	-1.35E+05	J/mole Ni
$C_0 V_{Al}^{2/3} + \frac{0.6}{0.4} C_0 V_{Ni}^{2/3}$	4.5E+05				m <sup>2</sup> / mole Al
$C_0 V_{Ni}^{2/3} + \frac{0.4}{0.6} C_0 V_{Al}^{2/3}$	3.0E+05				m <sup>2</sup> / mole Ni
ynteract	-0.68	-1.01	-0.90	-1.26	J/m <sup>2</sup>
ÝRE	1.13	2.00	2.15	0.078	J/m <sup>2</sup>
				[ref 82]	
YNIAI	1.85				J/m <sup>2</sup>
Work of adhesion	3.65	4.86	4.90	3.18 *	J/m <sup>2</sup>

Table 4.9: calculation of work of adhesion between RE-metallic layer and NiAl

(\* indicates an uncertain value)

For comparison: the work of adhesion  $Al_2O_3$  /  $Al_2O_3$  (through the oxide) calculated with the macroscopic atom model is 6.15 J/m<sup>2</sup> and the work of adhesion NiAl / NiAl (through the metal) is 4.2 J/m<sup>2</sup>.

If the 'Sulphur-layer' is thick enough that cracking through that layer can occur, the work of adhesion will be only twice the surface energy of the sulphur layer. As no ductile behaviour is expected through that 'layer', that layer will be the weakest link.

According to the macroscopic atom-model, the work of adhesion between oxide and RE-metal is larger than between RE-metal and NiAl. The work of adhesion for the  $Al_2O_3$  / RE-metal interface is also higher than for a RE-metal/RE-metal interface, as the latter is only twice the surface energy if the RE-layer is thick enough. However, much more plasticity occurs during fracture over a metal/metal interface or through a metal than for a fracture over a ceramic / metal interface. Further, mismatch energy, for a RE / NiAl interface about 0.15 ( $\gamma_{RE}+\gamma_{NiAl}$ ), may be higher for a ceramic / metal interface. The mismatch energy was neglected in the current calculations, and taking it into account results in a lower work of adhesion. Therefore, most probably the  $Al_2O_3$ / RE interface is the weakest interface, notwithstanding its high work of adhesion.

In conclusion, the alumina adheres slightly better on the hafnium-containing alloy than on the zirconium-containing alloy. Alumina is expected to adhere much better on the hafnium and zirconium alloy than on the RE-free alloy, if the fracture mechanism (and thus the ratio between  $W^{ad}$  and the energy actual necessary for fracture) is the same for all systems. If the oxide/metal is the weakest link, metallic yttrium at the interface increases the adhesion of  $Al_2O_3$ , as the work of adhesion over the  $Al_2O_3$ /Y interface is higher than over the  $Al_2O_3$ /NiAl interface. However, the increase in adhesion is not so large as for zirconium or hafnium doped surfaces.

These results correspond with the results of Jarvis and Carter [83]. They show with density functional calculations that the work of adhesion for the interface between alumina (two atomic layers) on (111) Ni increases if the interface is doped with half a monolayer of Y or Zr, Table 4.10. They also found that dopant - Ni bonding inhibits cleavage between the dopant ½ monolayer and the Ni-substrate. The oxygen-dopant coordination correlates with the adhesion. Calculations on these kind (oxygen-dopant coordination) are beyond the scope of the macroscopic atom model.

Table 4.10: results of Jarvis and Carter [69,83] showing the effect of half a me	onolayer
interface dopant	

Interface dopant	Work of adhesion (J/m <sup>2</sup> )	<b>Dopant-Oxygen coordination</b>
Ni	1.88	1
Al	1.49	1
Y	3.24	~2
Ti	3.69	~2-3
Zr	3.21	3

For various systems it is proved that sulphur decreases the work of separation [84], especially if the sulphur is present as interstitial atoms. The S-O repulsion separates the metal from the oxide. The current calculations show that the work of adhesion for  $Al_2O_3$  / S is low. Fracture due to S will occur at the  $Al_2O_3$  / S interface, or even more probable, through the S-layer. The work of adhesion through the S layer is twice the surface energy, which is expected to be quite low. Another mechanism by which S might play a role is by decreasing the plasticity during fracture, thereby decreasing the energy necessary for crack propagation.

# 5 Solubility of RE in NiAl

The distribution of reactive elements (abbreviated: RE) in the coating material is one of the factors that determine how much effect the RE will have on the oxidation behaviour of  $\beta$ -NiAl. The distribution may also influence the adherence of the resulting oxide layer. The distribution of the RE in the coating material is determined by (among other factors) the solubility: the amount of RE that can be dissolved as solid solution in the  $\beta$ -NiAl phase.

It is thought that when the RE dissolves easy in the  $\beta$ -NiAl phase, it will be uniformly distributed in the material, so the RE-effect acts over all the surface area. This uniformity may provide uniformly good oxidation and adhesion properties. There is one drawback: the segregation of the RE to the surface may be low, so a relatively high RE-doping level is needed to get the RE-effect, especially in the initial stages of oxidation.

A poorly dissolving RE will segregate to grain boundaries (or it may segregate within grains). If the RE segregates to the grain boundaries, it can migrate along the grain boundaries to the surface. This migration can be fast, as the grain boundaries serve as fast diffusion paths. Therefore it can have an effect already in the initial stages of the oxidation, which is thought to be very positive. In this case a fine-grained microstructure is optimal; a microstructure with large  $\beta$ -NiAl grains will result in large surface areas where no RE-effect occurs and other surface areas with too much RE. At these RE-rich regions protrusions into the alloy (cf. Figure 8.12b, Figure 8.22) and localised oxidation spots at the gas/oxide may occur. These macropegs and localised oxidation spots are most probably not improving the oxidation and adhesion-properties. The segregation behaviour of RE is explored further in Chapter 6.

Ternary phase diagrams like Figure 5.1 show the solubility of RE in  $\beta$ -NiAl. At 1073 K, the solubility of Zr, Hf and Y in equiatomic  $\beta$ -NiAl is about 1.4 at.%, 1.1 at.% and 0 at.%, respectively. Zr and Hf dissolve better in  $\beta$ -NiAl than Y.



Figure 5.1: Ternary phase diagrams of a: Ni-Al-Y; b: Ni-Al-Zr and c: Ni-Al-Hf at 1073 K (grit in at.%, axis in wt%) [85]

The macroscopic atom model provides an alternative approach to determine the RE solubility. The macroscopic atom model is especially suitable to give a data trend, in this case: indicating the solubility of one RE relative to another. The macroscopic atom model can be used in further

research to predict the solubility of reactive elements for which no reliable ternary phase diagram is available.

# 5.1 Approach

At temperatures below 1073 K, for the three RE's of interest, a NiAlRE-phase exists. These NiAlRE -phases (NiAlY, NiAlZr, and NiAlHf) have the same crystal structure, denoted as  $\tau_1$  for NiAlZr and NiAlHf and  $\tau_9$  for NiAlY. Between the NiAlRE and the  $\beta$ -NiAl phase regions, a twophase region is present. For compositions in this region in equilibrium situation both  $\beta$ -NiAl grains and NiAlRE -precipitates are present.

For the Ni-Al-Y system, the two-phase region is very narrow. In fact, the NiAl equiatomic line extending from the NiAlY phase to the  $\beta$ -NiAl phase is the two-phase region. For the Ni-Al-Zr and Ni-Al-Hf system, the coloured area in Figure 5.1b and Figure 5.1c indicates the two-phase region. The NiAl equiatomic line is in the two-phase region (for the Ni-Al-Zr system) or nearly in the two-phase region (for the Ni-Al-Hf system), Figure 5.1b and Figure 5.1c.

The most stable situation is the situation with the lowest Gibbs free energy G. The formation of NiAl from pure Ni and Al is an exothermic process. The energy theoretically released during formation is the enthalpy of formation,  $\Delta H^f$ . This enthalpy is related to the Gibbs free energy of formation,  $\Delta G^f$  [86]:

$$\Delta G^{f}(T) = \Delta H^{f}(T) - T\Delta S^{f}(T)$$
(5.1)

The enthalpy of formation, Gibbs free energy and Gibbs free energy of formation of equiatomic NiAl per mole atoms are listed in Table 5.1

Variable	Value	Unit
$\Delta H^{f}$	-59.2	kJ/mole atoms
$\Delta G^{\prime}$	-58.6	kJ/mole atoms
G	-67.3	kJ/mole atoms

Table 5.1: The enthalpy and Gibbs free energies of NiAl [86] at 298 K

A slightly different amount of energy is released when  $\beta$ -NiAl forms in which some RE is incorporated. In other words: the enthalpy of formation of  $\beta$ -NiAl and the Gibbs free energy of formation depend on the amount of RE dissolved in  $\beta$ -NiAl. This is indicated by the ' $\beta$ -NiAl phase curve' in Figure 5.2 (the solid curve at the right hand side). The curve at the left hand side of Figure 5.2 depicts the influence of composition on the enthalpy of formation of NiAlRE. In Figure 5.2, three regions can be seen: a region where the left solid curve is the lowest, a region where the right solid curve is the lowest and in-between a region where a dashed line is the lowest (the grey-shaded region). The dashed line is positioned as low as possible (at as negative *G* as possible). In the grey shaded area, the energy of a combination of  $\beta$ -NiAl and NiAIRE-phase is lower than if all RE were dissolved in  $\beta$ -NiAl (solid curve at the right) or if all material would be in a NiAIRE-crystal structure (solid curve at the left). The dashed line indicates the lowest energy possible for that composition in the grey-shaded area. This state of lowest energy is achieved by a combination of  $\beta$ -NiAl (with a certain amount of RE dissolved in it) and NiAIRE. The aim of the calculations is to determine the solubility-limit. The solubility limit is the maximum RE-content in the  $\beta$ -NiAl where the energy associated with the situation that all RE is dissolved in  $\beta$ -NiAl is not higher than the energy associated with the situation that both NiAl (with some RE dissolved in it) and NiAIRE are present. Graphically, this is the RE-content where the  $\beta$ -NiAl curve and the dashed line touch.

The slope of the dashed line is by definition dG/dx, where x is the atomic fraction RE. Note that x is 0 at the right of Figure 5.2 and 0.33 at the left, so x increases to the left. The solubility limit is found by varying the place where the dashed line crosses or touches the  $\beta$ -NiAl phase curve (different x), and calculating the slope of the dashed line. The atomic fraction x where the slope dG/dx(x) of the dashed line is maximum is the solubility limit. Here, the dashed line touches the solid  $\beta$ -NiAl curve at a tangent (except if the solubility is zero).



Figure 5.2: Calculation of the solubility limit of RE in  $\beta$ -NiAl: the maximum RE-content in the  $\beta$ -NiAl phase where that phase has not a higher enthalpy of formation than a combination of  $\beta$ -NiAl and NiAlRE phase; if the solubility limit is exceeded (left of the solubility limit, the shaded area), two phases are present

The form of the  $\beta$ -NiAl *G*-curve has a large influence on the calculated maximum solubility, and thus on the precision of the solubility-calculations. For the NiAlRE-curve, the stoichiometric composition (0.33 Ni, 0.33 Al, 0.33 RE) suffices, as dissolving extra Ni and Al in NiAlRE does barely affect the calculated maximum solubility of RE in  $\beta$ -NiAl (further: the solubility of extra Ni and Al in the NiAlRE phase is low, see Figure 5.1)

As G of NiAlRE was not found, for the calculations  $\Delta H^{f}$  is used. If  $S_{NiAlRE} = S_{NiAl}$ ,

$$G_{NiAIRE} - G_{NiAI} = \Delta H_{NiAIRE}^{f} - \Delta H_{NiAI}^{f}$$
(5.2)

Equation 5.2 is valid if the heat capacity  $C_p$  of NiAl and the heat capacity of NiAlRE are such that the integral

$$S = \int_{T=0K}^{T=T_1} \frac{C_p}{T} dT$$
(5.3)

returns the same value for NiAl and NiAlRE. As the entropy contribution to the Gibbs free energy is *-TS*, this condition becomes more stringent at higher temperatures.

Upon adding RE to the NiAl alloy, the distribution of this RE constitutes a configurational degree of freedom. This entropy effect lowers the Gibbs free energy by  $\Delta G_{mix}$ . This term is included (section 5.2.4).

If *G* of NiAlRE were known, a more precise determination of the solubility limit would use the macroscopic atom model only to calculate the change with composition of the  $\beta$ -NiAl curve (solid line at right hand side of Figure 5.2). Setting the crossing point with the axis at the right hand side equal to  $G_{NiAl}$  would provide the 'height' of the curve.

Deviation in the Ni:Al ratio of the  $\beta$ -NiAl results in less negative enthalpy of formation (Figure 5.3). This can also be verified theoretically with the macroscopic atom model, or with a glance at the binary phase diagram of Ni-Al (the highest melting temperature is at stoichiometric composition [87]). Therefore the line from the composition 0.50 Ni 0.50Al to 0.33 Ni, 0.33Al, 0.33 RE in the phase diagram is probably a so-called 'tie-line', a condition necessary for the method explained in Figure 5.2.

47



Figure 5.3: Enthalpy of formation of β-NiAl is lowest at or near stoichiometric composition [88]

## 5.2 Calculation of ∆H(RE-dissolved in NiAl)

The enthalpy of interest is built up of a chemical interaction energy, an elastic energy term and a structure term [p76ref89]. The change in Gibbs free energy due to mixing,  $\Delta G_{mix}$ , is also included. For NiAl with RE dissolved in it, the relevant energy per mole atoms is

$$\Delta H_{RE in NiAl} + \Delta G_{mix} = \left(xf_{Ni}^{RE} \Delta H_{REinNi}^{interface} + xf_{Al}^{RE} \Delta H_{REinAl}^{interface} + \frac{1-x}{2} f_{Ni}^{Al} \Delta H_{AlinNi}^{interface}\right) + x\Delta H_{RE in NiAl}^{elastic} + x\Delta H_{RE in NiAl}^{structure} - T\Delta S_{mix}$$

$$(5.4)$$

where x is the atomic fraction RE in solid solution and  $f_{Ni}^{RE}$  is the extent to which the RE is surrounded by Ni.  $\frac{1-x}{2}$  is the fraction of Ni, and also the fraction of Al, as stoichiometric compositions are investigated.

#### 5.2.1 Chemical interaction energies

Zirconium and yttrium take substitutional (not interstitial) places in the NiAl lattice [88]. The extent to which a Ni-site is surrounded by Al can be calculated as described in Appendix B, where the volume change upon alloying is taken into account.

If the RE is on Ni-sites, upon increasing the atomic fraction RE, x, sites originally part of the Alsublattice are being occupied by Ni-atoms (and to a much lesser extent by RE-atoms).

As here three elements are involved, some extensions to the equations in appendix B are necessary. The sum of the Ni-fraction and the RE-fraction is

$$C_{Ni,RE} = C_{Ni} + C_{RE} = \frac{1-x}{2} + x$$
(5.5)

Using  $C_{Ni,RE}$  the surface fraction  $C_{Ni,RE}^{S}$  is calculated according to appendix B. RE-atoms are forced to behave like Ni-atoms, as they take Ni-places. Of course, RE-atoms do not have the same work functions and volume change upon alloying, but the effect of this error on the calculated degree to which an Al-atom is surrounded by non-Al atoms, and on the calculated degree to which a Ni or RE-atom is surrounded by Al, is negligible. Then the degree to which an Al atom is surrounded by other atoms than Al is

$$f_{Ni,RE}^{Al} = C_{Ni,RE}^{S} \left( 1 + 8(C_{Al}^{S}(C_{Ni,RE}^{S})^{2}) \right)$$
(5.6)

The degree to which an atomic cell of Al is surrounded by Ni,  $f_{Ni}^{Al}$ , is calculated using the fraction of the not-Al atoms that are Ni-atoms, which is

$$\frac{C_{Ni}}{C_{Ni} + C_{RE}} = \frac{1 - x}{1 + x}$$
(5.7)

Then

$$f_{Ni}^{Al} = \frac{1-x}{1+x} f_{Ni,RE}^{Al} = \frac{1-x}{1+x} C_{Ni,RE}^{S} \left( 1 + 8(C_{Al}^{S} C_{Ni,RE}^{S})^{2} \right)$$
(5.8)

The degree to which RE is surrounded by Ni,  $f_{Ni}^{RE}$ , is a large fraction of the degree to which an atomic cell of Ni or RE is surrounded by Ni or RE

$$f_{Ni}^{RE} = \frac{1-x}{1+x} f_{Ni,RE}^{Ni,RE} = \frac{1-x}{1+x} (1 - f_{AI}^{Ni,RE}) = \frac{1-x}{1+x} \left( 1 - C_{AI}^{S} \left( 1 + 8(C_{AI}^{S} C_{Ni,RE}^{S})^{2} \right) \right)$$
(5.9)

The degree to which RE is surrounded by Al is

$$f_{Al}^{RE} = f_{Al}^{Ni,RE} = C_{Al}^{S} \left( 1 + 8(C_{Al}^{S} C_{Ni,RE}^{S})^{2} \right)$$
(5.10)

As an example, the fractions f for one composition are given in Table 5.2

Table 5.2: Calculation of parameters for an atomic fraction RE of 0.01, RE located at a Nisite

$C_{RE} = x$	0.010	$\int_{-\infty}^{Ni,RE} Al$	0.782
$C_{Ni}$	0.495	f <sup>AI</sup> Ni	0.701
$C_{AI}$	0.495	$\int_{Al}^{RE} f^{RE}$	0.782
$C^{S}_{Al}$	0.522	f <sup>RE</sup> <sub>Ni</sub>	0.213
$C^{S}_{Ni,RE}$	0.478	$f^{RE}_{RE}$	0.004
$f^{Al}_{Ni,RE}$	0.716		

Similar calculations can be done for the situation that the RE is at an Al-position. In equations 5.5 to 5.10 then the subscripts Ni and Al have to be interchanged. The superscripts have to be interchanged also.

In the bulk an atom is totally surrounded, i.e.

$$f_{Al}^{RE} + f_{Ni}^{RE} + f_{RE}^{RE} = 1$$
(5.11)

The calculation of the interface energies is now straightforward.

#### 5.2.2 Elastic energy

The elastic energy per mole of solute is [p77ref94]

$$\Delta H_{REinNiAl}^{elastic} = \frac{2K_{RE}G_{NiAl}\left(W_{NiAl} - W_{RE}\right)^2}{3K_{RE}W_{NiAl} + 4G_{NiAl}W_{RE}}$$
(5.12)

where a spherical hole in a NiAl matrix is filled by an RE-atom with volume  $W_{RE}$ . *G* is the shear modulus. As the stress field of the dissolved atom is expected to be large, for the calculation of the elastic energy the same value for *G* is taken, independent of whether the RE-atom is at a Ni-site or at an Al-site.  $G_{NiAl}$  is 71.5 GPa [88].  $K_{RE}$  is the bulk modulus.

$$K_{RE} = \frac{E_{RE}}{3(1 - 2\nu_{RE})}$$
(5.13)

At room temperature K is 41, 71 or 110 GPa for yttrium, zirconium and hafnium, respectively [90].

The volume of the constituent atomic cells changes on alloying, so  $W_{RE}$  differs from  $V_{RE}$  in pure RE. This volume change is calculated with

$$W_{RE}^{2/3} = V_{RE}^{2/3} \left( 1 + 0.07 \left( f_{Ni}^{RE} (\phi_{RE}^* - \phi_{Ni}^*) + f_{Al}^{RE} (\phi_{RE}^* - \phi_{Al}^*) \right) \right)$$
(5.14)

This is the standard equation of the macroscopic atom model for volume change upon alloying, modified by taking into account the degree by which the RE atomic cell is surrounded by Ni or Al, respectively, resulting is the presence of both a term with  $f_{Ni}^{RE}$  and a term with  $f_{Al}^{RE}$ .

The size of the hole in NiAl is estimated by calculating the relative volume change of the atoms next to the RE. The relative volume increase of the surrounding atoms determines the relative volume decrease of the site where the RE is to be located.

If the RE is to be located at a Ni-site with volume  $(V_{Ni})_{NiAl}$ , partial electron transfer from the RE will increase the volume of the neighbouring Al-atoms. These Al-atoms do now not meet a Ni-atom, but a RE-atom instead. The volume of the neighbouring Ni-atoms changes also. Taking into account the degree by which the RE will be surrounded by Ni,  $f_{Ni}^{RE}$ , or by Al,  $f_{Al}^{RE}$ , results in

$$W_{NiAl}^{2/3} = \left(V_{Ni}^{2/3}\right)_{NiAl} + \left(V_{Ni}^{2/3}\right)_{NiAl} \begin{pmatrix} f_{Al}^{RE} \left(0.07 \left(\phi_{Al}^{*} - \phi_{Ni}^{*}\right) - \left(\phi_{Al}^{*} - \phi_{RE}^{*}\right)\right) \\ + f_{Ni}^{RE} \left(0.10 \left(\phi_{Ni}^{*} - \phi_{Ni}^{*}\right) - \left(\phi_{Ni}^{*} - \phi_{RE}^{*}\right)\right) \end{pmatrix}$$
(5.15)

For the situation that the RE-atom is located at an Al-site:

$$W_{NiAl}^{2/3} = \left(V_{Al}^{2/3}\right)_{NiAl} + \left(V_{Al}^{2/3}\right)_{NiAl} \begin{pmatrix} f_{Al}^{RE} \left(0.07 \left(\phi_{Al}^{*} - \phi_{Al}^{*}\right) - \left(\phi_{Al}^{*} - \phi_{RE}^{*}\right)\right) \\ + f_{Ni}^{RE} \left(0.10 \left(\phi_{Ni}^{*} - \phi_{Al}^{*}\right) - \left(\phi_{Ni}^{*} - \phi_{RE}^{*}\right)\right) \end{pmatrix}$$
(5.16)

Now, the elastic energy per mole solute can be calculated with equation 5.12.

#### 5.2.3 Structural energy

The structural energy is estimated with the help of table II-4 [ref 94]. Pure yttrium normally has a hexagonal structure. It is dissolved in BCC-type NiAl. Ni originally has 10 and Al has 3 valence electrons per atom [91]. So equiatomic NiAl has on average 6.5 valence electrons per atom. Yttrium has three valence electrons per atom.  $\Delta H^{structure}$  for a solute with three valence electrons per dissolved atoms and a solvent with 6.5 valence electrons per atom is interpolated from  $\Delta H^{structure}$  for a solvent with 6 valence electrons (-21 kJ/mole solute) and a solvent with 7 valence electrons per atom (70 kJ/mole solute). This results in 24.5 kJ/mole solute for yttrium.

Zirconium and hafnium have 4 valence electrons per atom. Interpolation between -17 and +52 kJ/mole solute results in 17.5 kJ/mole solute.

#### 5.2.4 Change in Gibbs free energy due to mixing

Here it is assumed that the RE-atoms can only be present on one sublattice, which is a good approximation for low RE-content as one of the sublattices is energetically more favourable than the other. If we consider one mole atoms,  $xN_{Av}$  RE-atoms are present, which can divide over in total  $\frac{1}{2}N_{Av}$  sites. Under these circumstances [92], per mole atoms in total

$$\Delta G_{mix} = -T\Delta S = -kT \ln\left(\frac{\left(\left(\frac{1}{2}N_{Av} - xN_{Av}\right) + xN_{Av}\right)!}{\left(\frac{1}{2}N_{Av} - xN_{Av}\right)!(xN_{Av})!}\right)$$
(5.17)

Then, using Stirling's approximation,

$$\Delta G_{mix} = \frac{1}{2} RT \left( (1 - 2x) \ln (1 - 2x) + 2x \ln (2x) \right)$$
(5.18)

# 5.3 Calculation of △H<sup>f</sup><sub>NiAIRE</sub>

For a stoichiometric compound, the chemical interaction energy is the only contribution to the enthalpy of formation. The strain energy and structural energy are only important for non-stoichiometric solid solutions [p644ref94]. For x = 0.333

$$x = C_{RE} = \frac{1}{3} = C_{AI} = C_{Ni}$$

and

$$\Delta H_{NiAIRE} = \frac{1}{3} f_{Ni}^{RE} \Delta H_{REinNi}^{interface} + \frac{1}{3} f_{Al}^{RE} \Delta H_{REinAl}^{interface} + \frac{1}{3} f_{Ni}^{Al} \Delta H_{AlinNi}^{interface}$$
(5.19)

The extent to which RE atoms are surrounded by RE atoms is calculated using an extended version of the equations in appendix B.

$$f_{RE}^{RE} = 1 - \left(C_{Ni}^{S} + C_{AI}^{S}\right) \left(1 + 8(C_{RE}^{S}(C_{Ni}^{S} + C_{AI}^{S}))^{2}\right)$$
(5.20)

$$f_{Ni}^{RE} = \frac{C_{Ni}^{S}}{C_{Ni}^{S} + C_{Al}^{S}} \left(1 - f_{RE}^{RE}\right)$$
(5.21)

In this way all nine *f*-terms are calculated. Then for Re, Ni and Al atoms the volume change upon alloying is calculated. The volume change for the RE is:

$$\left(V_{RE}^{2/3}\right)_{alloy} = V_{RE}^{2/3} \left(1 + 0.07 (f_{Ni}^{RE}(\phi_{RE}^* - \phi_{Ni}^*) + f_{Al}^{RE}(\phi_{RE}^* - \phi_{Al}^*))\right)$$
(5.22)

More precise surface fractions  $C_{RE}^{s}$ ,  $C_{Ni}^{s}$  and  $C_{Al}^{s}$  are calculated by iterating (using equation 5.20 to 5.22 again), resulting in a more precise determination of the *f*-terms needed to calculate  $\Delta H_{NiAIRE}$ .

Variable	Value	Unit
ΔH Y in Ni	-1.62E+05	J/mole Y
ΔH Y in Al	-2.21E+05	J/mole Y
ΔH Ni in Al	-1.18E+05	J/mole Ni
ΔH Al in Ni	-1.39E+05	J/mole Al
$f_{Ni}^{Y}$	0.38	
$f_{Al}^{Y}$	0.46	
$f_{Al}^{Ni}$	0.40	
$f_{Ni}^{Al}$	0.35	
$\Delta H^{f}_{NiAlY}$	-6.96E+04	J/mole atoms

Table 5.3: Calculation of  $\Delta H^{f}_{NiAIRE}$ 

# 5.4 Comparison of solubility of Y, Zr and Hf in NiAl

The enthalpy of formation for the NiAl with Y dissolved in the NiAl and the enthalpy of formation of NiAlY is plotted below as a function of *x*, the atomic fraction RE.

The enthalpy associated with RE dissolved in NiAl is calculated for the case that Y occupies an Alsite in NiAl, and for the case that Y occupies an Ni-site. When Y is on an Ni-site, the positive strain energy is higher (as the Ni-sites are smaller than the Al-sites) but the interaction energy is more negative. According to the macroscopic atom model calculations, Y on a Ni-site has the lowest total energy, so the Y-atoms are expected to be located at Ni-sites.



Figure 5.4:  $\Delta$ H-composition diagram (equiatomic Ni:Al ratio) for the Y-Ni-Al system; the slope of the line connecting the curve with the point at the left is plotted also, the maximum of this slope indicates the solubility limit

The solubility limit occurs where the slope of the line connecting the NiAlRE to the  $\beta$ -NiAl curve has a maximum (is least negative). The slope is

 $\frac{\Delta H_{NiAIRE}^{f} - \left(\Delta H_{RE in NiAI}(x) + \Delta G_{mix}(x)\right)}{0.333 - x}$ 

For Y on a Ni-site, the slope is also plotted in Figure 5.4. The slope has a maximum at about x = 0.011. So 1.1 at. % is the solubility limit of Y in NiAl.

This is higher than expected from the ternary phase diagram [85] and also higher than measured on the model coating alloys used in the current study (appendix A). Possibly, the interaction energy between Y and Al is overestimated or the strain energy is underestimated.

Table 5.4: Chemical interaction, elastic energy and structural energy result in a total enthalpy; using the slope of the line connecting the total energy per mole for Y in NiAl and NiAlY, the maximum solubility is determined

x (atomic	∆H chemical	∆H elast	$\Delta H$ struct	$\Delta G_{mix}$	$\Delta G_{mix} + \Delta H$	Slope of
fraction)	interaction	(J/mole)	(J/mole)		Y in NiAl on	connecting line
	(J/mole)				Ni-site (J/mole)	(J/mole)
0	-48054	0	0	0	-4.81E+04	-64782
0.001	-48288	139	25	-18	-4.81E+04	-64710
0.004	-48983	557	98	-58	-4.84E+04	-64562
0.010	-50332	1394	245	-121	-4.88E+04	-64431
0.012	-50770	1673	294	-140	-4.89E+04	-64431
0.015	-51416	2091	368	-167	-4.91E+04	-64472
0.020	-52462	2789	490	-208	-4.94E+04	-64651
		* ,		•		
0.33					∆H NiAlY	
					-6.96E+04	

The term  $\Delta H^{f}$  at x = 0 is the formation enthalpy of equiatomic NiAl. The value calculated with the macroscopic atom model is about 20% smaller than the literature values (Figure 5.3, Table 5.1).

A similar treatment results for zirconium in NiAl in a solubility limit of 2.5 at.%. Again, the situation that the RE is located at a Ni-site is more energetically favourable than the situation that the RE is located at an Al-site. This contradicts the first-principle calculations of Song [93] (discrete variational cluster calculations based on LDA-density functional theory), who concluded that Zr has some preference for the Al-sublattice. Song also tabulates some other theoretical investigations (BFS-model, LMTO-calculation) and an X-ray diffraction study that show that Zr resides at an Al-site.

54



Figure 5.5:  $\Delta H$  per mole atoms for equiatomic NiAl as a function of x, the atomic fraction Zr or Hf

Table 5.5: Chemical interaction of Zr on a Ni-site in NiAl, elastic energy and structural energy result in a total enthalpy; using the slope of the line connecting 'Zr dissolved in NiAl' with 'NiAlZr', the maximum solubility of Zr in NiAl is determined

x (at frac)	∆H chemical	∆H elast	ΔH struct	$\Delta G_{mix}$	$\Delta G_{mix} + \Delta H$	Slope
	interaction	(J/mole)	(J/mole)		Zr in NiAl on	(J/mole)
	(J/mol)				Ni-site	
					(J/mole)	
0	-48054	0	0	0	-4.81E+04	-117533
0.01	-50641	1042	175	-121	-4.95E+04	-116556
0.02	-53096	2092	350	-208	-5.09E+04	-116074
0.025	-54272	2619	438	-246	-5.15E+04	-116013
0.03	-55414	3149	525	-281	-5.20E+04	-116081
0.05	-59622	5289	875	-403	-5.39E+04	-117780
0.33					∆H NiAlZr	
					-8.72E+04	

In a similar way as for Y and Zr, the solubility of Hf in NiAl is determined (Figure 5.5). The solubility of hafnium is calculated to be 1.1 at.%, slightly lower than the solubility of Y in NiAl. Again, the RE-atoms prefer a Ni-site, in contrast with the tendency found in Song's article [93].

## 5.5 Conclusion

Calculations using the macroscopic atom model are especially fit for comparative use. The calculations presented in this chapter clearly show that the solubility of Zr in NiAl is higher than the solubility of Y.

The model indicates that the solubility increases with temperature, as the Young's modulus and shear modulus and therefore  $\Delta H_{RE in NiAI}^{elastic}$  decrease with temperature.

The model suggests that the solubility of Y in NiAl is slightly higher than the solubility of Hf in NiAl. This indicates that the model should be refined.

Another indication is that according to this model, the RE is located at a Ni-site, while Song [93] suggests that the RE takes an Al-site. If the lattice strain were higher, it would force the RE to reside at an Al-site. The indicated direction for refinement is therefore to improve the modelling of that energy contribution. Further, a refinement in the determination of  $\Delta H^{structure}$  (something better than the interpolation) is advisable.

The treatment in this chapter is rather challenging for the macroscopic atom model: it uses the maximum of a slope of a tangent line; this makes this determination susceptible to errors in parameters and errors due to simplifications inherent to the model. If *G* of NiAlRE were known, the macroscopic atom model can be used to calculate only the *change* in  $G_{NiAl}$  with composition *x*, allowing a more precise determination of the solubility limit. This is especially advisable for higher temperatures, as then the difference between  $G_{NiAIRE} - G_{NiAl}$  and  $\Delta H_{NiAIRE}^f - \Delta H_{NiAl}^f$  may increase [86].

# 6 Surface segregation

The presence of a reactive element (abbreviated: RE) at the surface of the alloy, and the moment when this reactive element is available at the coating material surface, has influence on the extent of the RE-effect. If the RE is present early in the oxidation process (due to fast segregation), it will already have an effect in those initial stages. If the RE segregates extensively to the interface, the direct effects of the RE on adhesion (like enhancement of the chemical bonding or modification of the oxides formed) can be larger than if the RE does not segregates so extensively. In this chapter the segregation behaviour of the reactive elements Y, Zr and Hf is compared.

A modified basic equation relating the atomic composition of the surface layer  $C_{RE}^{sl}$  to the bulk composition  $C_{RE}$  is [p684ref 94]

$$\frac{C_{RE}^{sl}}{C_{RE}} = \exp\left(\frac{-\left(\Delta H^{surface \ segregation} - q\Delta G_{mix}\right)}{RT}\right)$$
(6.1)

 $\Delta H^{surface segregation}$  is the change in enthalpy upon transferring a RE-atom from the bulk NiAl to the surface layer, *R* is the gas constant and *T* is the absolute temperature. When a RE-atom is transferred from the bulk of a NiAl grain to its surface, several enthalpies change, namely:

- the energy associated with the chemical interaction inside that grain,
- the surface energy of the grain, and
- the elastically stored energy.

Although not included in the original equation [94,95], also an increase in the Gibbs free energy can be expected due to a decrease in the 'randomness'. Due to the randomness, before segregation a negative term  $\Delta G_{mix}$  contributes to the Gibbs free energy. This contribution to the Gibbs free energy decreases due to segregation by an amount  $q\Delta G_{mix}$ . The change in total structural energy (an energy contribution due to the difference between the valence of the RE and the valence of the NiAl matrix, see section 5.2.3), is probably small. For sake of simplicity, it is left out of consideration.

#### 6.1 Surface segregation under vacuum

Miedema [95] assumes that when a large atom takes the place of a small atom at the surface, the metal surface atoms will minimise the total metallic area exposed to vacuum. As a consequence, the strain energy that a RE-atom experiences in the bulk is only partly relieved upon transferring to the surface (Figure 6.1). Due to this minimisation of the surface area, the surface layer of atoms is strained.

In line with this assumption, it is also assumed that the fraction of the RE-atom in contact with vacuum is the same as the fraction of a Ni-atom or an Al-atom in contact with vacuum.

AI	Ni	AI	RE	AI	Ni	AI
Ni	AI	Ni	AI	Ni	AI	Ni
AI	Ni	AI	Ni	AI	Ni	AI
Ni	AI	Ni	AI	Ni	AI	Ni

Figure 6.1: A large atom at the interface exerts a force on its neighbours to minimise total surface area, as a consequence, strain energy is present; for sake of simplicity an equal number and size of Ni and Al atoms are drawn

The change in Gibbs free energy per mole surface Ni-atoms changing places with a mole RE-atoms in the bulk is an elaborated form of the equations used in [94, 95]:

$$\Delta H^{surface \, segregation} - q\Delta G_{mix} = \frac{f}{3} \left( -\left( f_{Ni}^{RE} \Delta H_{REinNi}^{interface} + f_{Al}^{RE} \Delta H_{REinAl}^{interface} \right) + f_{Al}^{RE} \Delta H_{NiinAl}^{interface} \right) + \left( -\Delta H_{Ni}^{surface} + \Delta H_{RE}^{surface} \right) - r\Delta H_{REinNil}^{elastic} - q\Delta G_{mix}$$

$$(6.2)$$

If the RE-atom at the Al-sublattice interchanges position with an Al-atom at the interface, the superscripts and subscripts of Ni and Al in equation 6.2 should be interchanged.

The first term in equation 6.2 is the chemical interaction energy. As NiAl is a binary alloy, the extent to which the RE-atoms used to be surrounded by Ni and by Al is taken into account. When the RE-atom is in the bulk, it is surrounded to an extent  $f_{Ni}^{RE}$  by Ni and to an extent  $f_{Al}^{RE}$  by Al. The energy associated with this arrangement is partially lost since the RE-atom is no longer in contact with atoms at all sides. An interaction between Al and Ni is formed instead. An atom at the surface is for  $\frac{f}{3} = 0.24$  surrounded by vacuum (The factor f = 0.71 is due to surface relaxation [95]). In [95] factors explaining the difference between  $\frac{f}{3}$  and 0.31 (used in chapter 4) are discussed. In the calculation it is implied that the ratio between the extent to which a RE-atom is surrounded by Ni and the extent to which it is surrounded by Al, is at the surface the same as in the bulk, namely  $f_{Ni}^{RE} : f_{Al}^{RE}$ .

The second term in equation 6.2 accounts for the change in surface energy.  $\Delta H_{Ni}^{surface}$  is the energy associated with the exposure to vacuum of one mole of Ni-atoms present at the surface. Values are tabulated in ref 94.

When a RE-atom is present in the bulk, it causes a strain energy,  $\Delta H_{RE in NiAl}^{elastic}$ . This energy is partly released when the RE-atom is transferred to the surface. The strain energy is not totally released, as explained in Figure 6.1, so in this study a strain energy release factor *r* is used. Often, *r* is assumed to be about 0.5 but Miedema [95] argues that this estimate is too high. In this study *r* = 0.4 is applied.

When a RE-atom is dissolved in the bulk, many different distributions of the RE-atoms over the available sites are possible. This configurational randomness causes  $\Delta G_{mix}$ . When segregation occurs this  $\Delta G_{mix}$  is partly lost, as expressed by the factor q ( $0 \le q \le 1$ ). The precise value of q depends on the surface and the bulk RE-concentration after segregation (so it depends on the surface to volume ratio of the grain and on the initial RE-concentration; if the very unlikely situation occurs that at the surface the RE occupies exactly all sites it is allowed to occupy, and in the bulk totally no RE is present anymore, then q = 1). In Table 6.1 and Table 6.2,  $\Delta H^{surface segregation}$  is presented for q = 0.2 and for q = 0.4 (a rather high estimate for the loss of  $\Delta G_{mix}$ ).

A composition of 0.1 at.% RE (x = 0.001) and equal Ni and Al content was chosen. According to the calculations in chapter 5 at this composition all RE is dissolved when considering Y, Zr and Hf. The elastic energy and the *f*-terms indicating the surrounding of the RE (Table 6.1) are calculated as described in chapter 5.

RE on	Al-sublattice	Ni-sublattice	
ΔH <sup>surf</sup> Y	1.16E+05	1.16E+05	J/mole Y
ΔH <sup>surf</sup> Al or Ni	7.60E+04	1.21E+05	J/moleNi
ΔH Y in Ni	-1.62E+05		J/mole Y
ΔH Yin Al	-2.21E+05		J/mole Y
ΔH Ni in Al		-1.18E+05	J/mole Ni
ΔH Al in Ni	-1.39E+05		J/mole Al
f <sup>Y</sup> <sub>Ni</sub>	0.69	0.20	
f <sup>Y</sup> <sub>Al</sub>	0.31	0.80	
f <sup>Ni</sup> <sub>Al</sub>	0.80		
f <sup>Al</sup> <sub>Ni</sub>	0.69	0.69	
$f_{Ni}^{RE} \Delta H_{REinNi}^{interface} + f_{Al}^{RE} \Delta H_{REinAl}^{interface}$	-1.80E+05	-2.09E+05	J/mole Y
$f_{Ni}^{RE} \Delta H_{AlinNi}^{interface}$ or $f_{Al}^{RE} \Delta H_{NiinAl}^{interface}$	-9.60E+04	-9.45E+04	J/mole transferred Y
ΔH <sup>elast</sup>	7.23E+04	1.39E+05	J/mole Y
$\Delta G_{mix}$	-1.79E+04	-1.79E+04	J/mole Y
$\Delta H^{ ext{surface segregation}} - 0.2 \Delta G_{ ext{mix}}$	3.48E+04	-2.96E+04	J/mole transferred Y
$\Delta H^{surface segregation} - 0.4 \Delta G_{mix}$	3.84E+04	-2.60E+04	J/mole transferred Y

Table 6.1: Segregation of Y in solid solution to the surface of NiAl

The exchange of an Y-atom at the Al-sublattice in the bulk with an Al-atom at the surface is energetically not favourable (positive change in Gibbs free energy). Surface segregation on this sublattice will not occur.

The exchange of an Y atom at the Ni-sublattice in the bulk with a Ni-atom at the surface is energetically favourable, as  $\Delta H^{\text{surface segregation}} - 0.2\Delta G_{mix}$  is negative.

 $\Delta H^{\text{surface segregation}} - 0.2\Delta G_{mix} = -29.6 \text{ kJ/mole results in (equation 6.1)} C_{RE}^{sl} = 1.6E05 C_{RE} = 160 \square 0.5$ Physically this means that all Ni sublattice-sites at the surface are occupied by Y-atoms ( $C_{RE}^{sl} = 0.5$ ) at room temperature (kinetic factors not taken into account). However, with increasing Y-content of the surface layer, Y-atoms at the surface hinder the release of the elastic energy of adjacent Y-atoms. This will change the factor r in equation 6.2. Surface segregation then becomes less favourable. Therefore it is not sure whether only Y-atoms are present on Ni-sites at the surface.
From the calculated change of enthalpy it is concluded that an extensive driving force for surface segregation is present.

Without the strain energy decrease  $(r\Delta H_{RE in NiAI}^{elastic})$ , the change in Gibbs free energy (equation 6.2) would be positive, so no segregation would occur. The strain energy depends on the mechanical properties of NiAl and RE. As the Young's modulus *E* and shear modulus *G* will decrease with increasing temperature, the change in Gibbs free energy (equation 6.2) will become less negative, possibly become even positive. So the driving force for surface segregation will decrease with temperature.

Apart from this, also equation 6.1 indicates that thermodynamically (apart from kinetical factors) at higher temperature the surface segregation is less.

The activation energy for bulk diffusion, a kinetic factor, also has its influence on whether surface segregation occurs or not. As at 1373 K diffusion through NiAl is fast, this kinetic factor will only determine the rate at which surface segregation develops. Whether surface segregation occurs or not, is at that temperature determined only by the sign of the Gibbs free energy.

	Zr on Al-	Zr on Ni-	Hf on Al-	Hf on Ni-	
	sublattice	sublattice	sublattice	sublattice	
ΔH surf RE	1.63E+05	1.63E+05	1.71E+05	1.71E+05	J/mole RE
ΔH surf Al or Ni	7.60E+04	1.21E+05	7.60E+04	1.21E+05	J/mole Ni
ΔH RE in Ni	-2.37E+05		-2.04E+05		J/mole RE
ΔH RE in Al	-2.40E+05		-2.15E+05		J/mole RE
$ f_{Ni}^{RE} \Delta H_{REinNi}^{interface} + f_{Al}^{RE} \Delta H_{REinAl}^{interface} $	-2.38E+05	-2.39E+05	-2.07E+05	-2.13E+05	J/mole RE
$f_{Ni}^{RE} \Delta H_{AlinNi}^{interface}$ or $f_{Al}^{RE} \Delta H_{NiinAl}^{interface}$	-9.60E+04	-9.45E+04	-9.60E+04	-9.45E+04	J/mole transferred RE- atoms
$\Delta H^{elast}$	3.63E+04	1.04E+05	3.60E+04	1.23E+05	J/mole RE
$\Delta G_{mix}$	-1.79E+04	-1.79E+04	-1.79E+04	-1.79E+04	
$\Delta H^{ m surface\ segregation} - 0.2 \Delta G_{mix}$	1.10E+05	3.88E+04	1.11E+05	3.29E+04	J/mole RE

 Table 6.2: Segregation of Hf and Zr to the NiAl surface

No segregation of Zr or Hf in solid solution to the vacuum/metal interface is expected, as the 'Gibbs free energy'  $\Delta H^{surface segregation} - 0.2\Delta G_{mix}$  increases (Table 6.2).

If not all RE is dissolved in the NiAl (for instance at higher RE-contents), an important contribution to the driving force for segregation will be the reduction of grain boundary area. A positive energy is associated with grain boundary area, so if small NiAlRE-grains or  $Y_2Ni_7$ -grains disappear due to segregation of the RE to the interface (and dissolution of the Ni and Al in the  $\beta$ -NiAl), this energy disappears.

Strain energy contributes only to the driving force if the NiAlRE-grain or  $Y_2Ni_7$  grain is strained (compressed). Diffusion of the RE to the surface will reduce this strain.

Diffusion along grain boundaries is often faster than bulk diffusion (the relative contribution of both types of diffusion depending on temperature). As small precipitates are often located between grains of the matrix, the diffusion from such small grains to the interface may be faster than the diffusion from the bulk. In principle, due to a kinetic factor like the diffusion rate the actual segregation can be higher even if the driving force is smaller. Of course the change in Gibbs free energy has to be negative, otherwise there is no driving force.

#### 6.2 Segregation to oxide/NiAl interface

Under oxide, the tendency to keep the total metal interface area as low as possible may be absent, as opposed to the tendency to minimise surface area under vacuum [95]. This is due to the fact that  $\Delta H_{Me \text{ in } 0}^{\text{interface}}$  is negative and  $\Delta H^{\text{surface}}$  is positive for most metals. This has two consequences:

- more elastic energy may be released, and
- the assumption that the roughness of the grain surface remains equal upon interchanging a Ni or Al with a RE-atom may no longer be valid.

For segregation to the oxide/NiAl interface equation 6.2 reads (for interchange of a RE on the Nisublattice with an Ni-atom at the surface)

$$\Delta H^{\text{surface segregation}} - q \Delta G_{\text{mix}} = \frac{1}{3} \left( - \left( f_{Ni}^{RE} \Delta H_{REinNi}^{\text{interface}} + f_{Al}^{RE} \Delta H_{REinAl}^{\text{interface}} \right) + f_{Al}^{RE} \Delta H_{NiinAl}^{\text{interface}} \right) + \left( -\frac{1}{3} \Delta H_{NiinO}^{\text{interface}} + \frac{1}{3} \Delta H_{REinO}^{\text{interface}} \right) - r \Delta H_{REinNiAl}^{\text{elastic}} - q \Delta G_{\text{mix}}$$

$$(6.3)$$

Here, the interaction with the cations in the oxide is neglected, as cations are smaller than anions so the the extent to which the atoms at the surface are surrounded by anions is larger than the extent to which the atoms are surrounded by cations.

A small error may be implicit in equation 6.3. As discussed in section 4.2.1,  $\Delta H_{Me \text{ in } O}^{\text{interface}}$  is calculated from experimental heats of formation of the oxide. The extent to which the Me-cation in MeO is surrounded by oxygen will be nearly unity, but slight differences may exist between different oxides (larger cations may touch other cations). As the calculation in equation 6.3 is based on the surface-fraction of the RE in contact with oxygen, and  $\Delta H_{Me \text{ in } O}^{interface}$  is per mole (not per area of Me), a small error is made in equation 6.3.

Another factor affecting the surface fraction of the RE-atoms in contact with O is due to the presence of the very electronegative oxygen. This volume change will counteract the effect of the error presented above (as the larger elements usually have lower work function  $\phi$  than the smaller elements [94,96] ).

	Y on Al-	Y on Ni-	Zr on Al-	Zr on Ni-	Hf on Al-	Hf on Ni-	
	sublattice	sublattice	sublattice	sublattice	sublattice	sublattice	
$\Delta H RE$ in O	-9.53E+05	-9.53E+05	-1.10E+06	-1.10E+06	-1.11E+06	-1.11E+06	J/mole RE
$\Delta H Al$ in O or	-8.38E+05	-2.41E+05	-8.38E+05	-2.41E+05	-8.38E+05	-2.41E+05	J/mole Al,
$\Delta H$ Ni in O							J/mole Ni
$f_{\scriptscriptstyle Ni}^{\scriptscriptstyle RE}\Delta H_{\scriptscriptstyle REinNi}^{\scriptscriptstyle interface}$	-1.80E+05	-2.09E+05	-2.38E+05	-2.39E+05	-2.07E+05	-2.13E+05	J/mole RE
$+ f_{Al}^{RE} \Delta H_{REinAl}^{interface}$							
$f_{Ni}^{RE} \Delta H_{AlinNi}^{interface} or$	-9.60E+04	-9.45E+04	-9.60E+04	-9.45E+04	-9.60E+04	-9.45E+04	J/mole
$f^{\it RE}_{\it Al}\Delta H^{\it interface}_{\it NiinAl}$							
$\Delta H^{elast}$	7.23E+04	1.39E+05	3.63E+04	1.04E+05	3.60E+04	1.23E+05	J/mole RE
$\Delta G_{mix}$	-1.79E+04						J/mole RE
$\Delta H$ surface segregation	-3.56E+04	-2.51E+05	-5.03E+04	-2.75E+05	-6.54E+04	-2.97E+05	J/mole RE
$-0.2\Delta G_{mix}$							

Table 6.3: Segregation of Y, Zr and Hf to the oxide/NiAl interface, for $r = 0.4$ and $q = 0.4$
---

Important observations are:

- For all RE, the driving force for segregation to the oxide/NiAl interface is much larger than the driving force for segregation to the NiAl surface under vacuum (cf. Table 6.1, Table 6.2, Table 6.3).
- The driving force for segregation to the oxide/NiAl interface is largest for Hf, and lowest for Y.
- If the strain energy release factor *r* increases, the tendency to segregate increases, especially for the Y-doped NiAl. If the strain energy is completely released upon transferring of the RE to the interface, the driving forces for segregation of Y and for Zr are equal. The driving force for Hf-segregation to the oxide/NiAl interface is still larger than for Y and Zr.
- The elastic strain energy component decreases with increasing temperature. Even without the elastic strain energy component, a driving force for segregation to the oxide/NiAl interface still exists for all RE. The decrease of the elastic strain energy with temperature does not change the trend that Hf segregates most and Y segregates least.

Smialek and Browning [97] observed with AES and XPS that Y and Zr segregate to the top of  $\gamma'/\beta$ -NiCrAl alloys with a thin oxide layer on top of it. This oxide is formed during very short oxidation (5 minutes) at very low oxygen pressure (1.3E-04 Pa O<sub>2</sub>) at 1023 K. The segregation of Y and Zr into the oxide or to the oxide/NiCrAl interface is in agreement with the calculation that segregation to the oxide/alloy interface should occur (Table 6.3). These AES and XPS measurements on the surface of the oxide/alloy system cannot reveal whether the RE is located at the oxide/NiAl interface or in the oxide.

#### 6.2.1 Segregation under an oxygen atmosphere

Another condition for segregation occurs if the surface of the sample is oxide-free (for instance after sputtering) and then is introduced into a poor vacuum or an oxygen atmosphere (in practical terms: oxygen is present in the 'vacuum' in which the sample is sputtered). It is suggested that in this case, segregation behaviour will probably be in-between the segregation behaviour under vacuum (section 6.1) and the segregation behaviour under an oxide (section 6.2), but more resembling the latter than the first. In the case that bare metal is exposed to oxygen the binding of oxygen ad-atoms or ad-molecules to the NiAl is probably less tight than in the case of an oxide on top of the NiAl. Within very short time the oxygen ad-atoms or ad-molecules will start forming an oxide layer.

Smialek and Browning [97] observed that Y and Zr segregate to the surface of  $\gamma'/\beta$ -NiCrAl alloys during annealing under vacuum (<7E-07 Pa) at 1023 K. They employed AES and XPS. The segregation of Y to the surface is in agreement with the results from Table 6.1. The segregation of Zr to the surface is in disagreement with the positive change in Gibbs free energy (lowest row in Table 6.2). This disagreement is probably due to some oxygen on the surface of the material. An oxygen signal is observed in their Auger measurements, and the presence of oxygen on the surface is still expected (this pressure is higher than the oxygen partial pressure at which oxide decomposes).

More segregation of Zr is observed to the oxidised surface than to the surface annealed under vacuum (<7E-07 Pa) at 1023 K [97]. This is in agreement with the calculations, as the driving force for segregation of Zr to an oxide/NiAl interface (Table 6.3) is more negative than for segregation to a NiAl surface (Table 6.2).

### 7 Experimental

#### 7.1 Sample preparation

As model-coating alloys, four different  $\beta$ -NiAlCr alloys were supplied by Surface Preparation Laboratory, Zaandam, The Netherlands. Three of these alloys were doped with a small amount of Y, Zr and Hf respectively. The purity of the starting materials used to make the alloys was Ni 4N (=99.99 wt% pure), Cr 3N5 (=99.95 wt% pure), Al 5N. The Y and Zr-doped alloys were cast in Cu-crucibles; the undoped and Hf-doped alloys were cast in carbon crucibles. The alloys were delivered as cylindrical rods.

The Y-doped and Zr-doped alloys were annealed separately for 300 hours and the undoped and Hfdoped alloys were annealed separately for 55 hours in a sealed quartz tube filled with argon at 1373 K in order to homogenise the alloy.

Disk-shaped specimens (diameter 10 mm and thickness 2 mm) were cut using spark-erosion. Prior to oxidation, the alloy surface was successively grinded and polished. The polishing steps were 3  $\mu$ m, followed by 1  $\mu$ m, diamond grains. A chemical resistant cloth with 0.04  $\mu$ m silica in distilled water was used for the final polishing step. After each polishing step the specimens were ultrasonically cleaned with isopropanol and blow-dried with pure compressed nitrogen gas. For details about the composition and microstructure of the model-coating alloys see Appendix A.

#### 7.2 Isothermal oxidation

Oxidation experiments were performed in a horizontal alumina tube furnace (Lenton PTF 16/75/610; tube inner diameter 75 mm) at 1373 K. A gas mixture of argon (99.998 vol.% Ar) and 20 vol.% oxygen gas (99.998 vol.%  $O_2$ ) was passed through the furnace at a total pressure of  $1 \times 10^5$  Pa with a controlled flow rate of 750 ml/min. The specimens were placed in an annealed alumina crucible and introduced into the hot-zone of the tube furnace in as short a time as possible. Oxidation times of 30 minutes, 1, 2, 4, 64 and 256 (or 261) hours were used for the alloys. After oxidation, the alloys were allowed to cool in the cold-zone of the furnace for a short time.

#### 7.3 Thermal cycling experiments

The thermal cycling experiments were performed at the Dutch Aerospace Laboratory NLR in Marknesse. The samples were exposed to standard cycles: 8-9 minutes heating to 1373 K and 45 minutes at 1373 K, 8-9 minutes cooling to < 373 K. An electrical furnace was used. Cooling took place by withdrawing the samples from the furnace. The oxidation atmosphere is air. Prior to cyclic oxidation and after certain numbers of cycles each sample was weighted with a microbalance (accuracy about 0.00001 g) at room temperature. The samples were also photographed with a digital camera, at both sides, to give insight in the extent of delamination.

When the weight of a sample had decreased more than 5 mg, that sample was no longer exposed to further thermal cycling.

#### 7.4 Characterisation

*Electron probe X-ray microanalysis* (EPMA) was used to determine the composition of the alloys. A JEOL JXA 8900R WD/ED combined microanalyser, equipped with five wavelength-dispersive spectrometers (WDS) and one energy-dispersive spectrometer (EDS) was used. The EPMA was operated with an electron beam energy of 15 keV and a current of 20 nA.

The composition of the alloy including the precipitates was measured using a defocused beam and averaging many measurements. The electron beam was defocused to  $10 \,\mu$ m.

The composition of the precipitates and the composition of the  $\beta$ -phase were measured with a well-focussed beam.

The crystalline phases present in the oxide layers and in the alloys were identified by *X-ray diffraction* (XRD). A Bruker AXS D5005 diffractometer with Position Sensitive Detection was used for these measurements. A monochromatic Cu K<sub> $\alpha$ 1</sub> incident X-ray beam ( $\lambda = 0.15406$  nm) was used. The sample rotated during the measurement with a speed of 30 rpm. Usually, diffractograms were recorded in a 20 range of 20 to 80° with a step size of 0.0388° and with 36 s per step. Only for the model coating alloys oxidised for 64 and 256 hours XRD was performed with a diffracted beam monochromator and Co K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.17903$  nm), again with a Bruker AXS D5005 diffractometer. The sample rotated during the measurement with a speed of 30 rpm. The diffractograms were recorded in a 20 range of 25 to 95° with a step size of 0.050° and with 18 s per step.

The JCPDS database (JCPDS-International Center for Diffraction Data, Swarthemore, PA) was used for phase identification.

The surface morphology and structure of the oxide layers was studied with *scanning electron microscopy* (SEM) using a JEOL JSM 6500F scanning electron microscope (SEM) equipped with a Schottky-type field emission gun. Also energy-dispersive spectrometry and backscattered electron imaging was used.

*Energy-dispersive spectrometry* (EDS) was employed for semi-quantitative composition analysis. The X-rays were recorded using a Noran Pioneer detector with a 30 mm<sup>2</sup> Si(Li)-crystal and an energy resolution of 138 eV. The spectra acquisition and processing was performed with a Noran Voyager or a ThermoNoran Vantage analysis system.

Backscattered electrons (BSE) were detected with an Autrata-type detector.

#### 7.5 Specimen cross section preparation

Cross-sections of the oxidised samples were prepared as follows:

First a thin copper coating (only a few nanometres thick) was deposited on the oxidised surface of the alloys using an evaporator (OMICRON EFM3). The samples were cut perpendicular to the oxidised surface using an ISOMET 4000 linear precision saw with a diamond blade, Buehler ltd. Later samples were covered with a thin (about 10 nm) gold film using a Balzers sputtering device 07-120, instead of the copper coating.

Subsequently, one of the pieces of the sample was plated with nickel using a Watts bath [98] (the gold or the copper is necessary for the Ni-plating process; the Ni is needed to support the oxide layer during the preparation of cross-sections). The oxide/alloy cross-sections are clamped in a steel holder with Al-foil between the holder and the sample. The subsequent grinding and polishing was similar to the procedure described in section 7.1.

#### 7.6 Growth-kinetics determination

SEM images of the oxide/alloy cross-sections were used to determine the oxide-layer growth kinetics. The gas/oxide and the oxide/metal interface were traced, and the enclosed area was determined. Of this area, the average height was determined. Repeating this procedure on several images per sample made determination of the standard deviation possible.

The parabolic growth constant is determined by fitting with Matlab. A cubic-parabolic growth function was fitted [99,100]:

$$d = a \sqrt[b]{t}$$
 for  $t \le t_0$ 

and

$$d^{2} - d_{0}^{2} = k(t - t_{0})$$
 for  $t \ge t_{0}$ 

The parameters  $d_0$  and  $t_0$  signify the thickness of the oxide and the time when the oxide starts to show parabolic behaviour, respectively. The values for the constants *a* and *b* follow from the constraint that the growth curve is continuously differentiable at  $(t_0, d_0)$ . The parabolic growth constant *k* is to be compared with literature.

. ·

.

### 8 Results

In this section the results of the oxidation experiments for the four model coating alloys are presented. The isothermal oxidation took place at 1373 K in a 750 ml/min gas fow (80% Ar, 20%  $O_2$ , 100 kPa ). Different oxidation times were applied. In this chapter, the phases present in the oxide, the oxide surface morphology, the oxide microstructure and the growth kinetics are presented. Also the delamination during the isothermal oxidation experiments is addressed. Finally, the results of the cyclic oxidation test are presented (8-9 minutes heating in air to 1373 K, 45 minutes oxidation in air at 1373 K, 8-9 minutes cooling to < 373 K). The results of the cycling experiments include both the weight gain and photographic images.

#### 8.1 Colour

The colour of the samples after cooling following long oxidation times is presented in Table 8.1. Colour-differences and speckles are caused by oxide thickness, the degree of delamination and surface roughness.

	After 64 hours oxidation	After 261 hours oxidation	Duplicate sample: 256 hours oxidation
Undoped	Grey, spallation visible	Grey, spallation visible	Grey-white
Y-doped	Brown-grey	Grey	Silver-grey
Zr-doped	Brown	Brown	Brown-black
Hf-doped	Blue-grey, speckled due to spallation	Blue-grey, speckled	No duplicate

Table 8.1: Colour of the oxidised samples oxidised for long oxidation time

On the Y-doped samples, a pattern of shade-differences is seen that corresponds to the grain structure of the alloy. On the Zr-doped alloys, the colour is very uniform.

#### 8.2 Phase identification

To determine which phases are present in the oxide layer formed during the oxidation experiments, X-ray diffraction is employed (section 7.4). The most interesting features of the diffractograms after oxidation are found by comparison with a diffractogram recorded prior to oxidation, therefore in Figure 8.1 to Figure 8.5, a diffractogram prior to oxidation is included.

#### 8.2.1 Undoped model coating alloy

- Prior to oxidation, in the undoped model coating alloy β-NiAl and Cr<sub>3</sub>C<sub>2</sub> are present (Figure 8.1). In the lower plot in Figure 8.1, the sharp small peaks are Cr<sub>3</sub>C<sub>2</sub>, and the large peaks (and the peak at d=1.28 Å) are β-NiAl reflections.
- The α-Al<sub>2</sub>O<sub>3</sub> peaks (JCPDS 46-1212) increase in intensity with oxidation time (Figure 8.1).
   They are stronger than the θ-peaks. Especially at longer oxidation times (between 2 and 4 hours) the increase in α-alumina is greater than the increase in θ-alumina.
- After up to 2 hours of oxidation, and maybe even up to 4 hours, θ-Al<sub>2</sub>O<sub>3</sub> (JCPDS 35-0121) is present. The θ-Al<sub>2</sub>O<sub>3</sub> peaks (pink vertical lines in Figure 8.1) are strongest after 1 or 2 hours of oxidation. The prominent peak (at d=2.74 Å) is located on top of a chromium carbide peak, however a clear increase in intensity is observed so it is concluded that θ-Al<sub>2</sub>O<sub>3</sub> has developed. Uran [101] no longer observed θ-alumina after one hour of oxidation at 1100°C on stoichiometric β-NiAl, on most surfaces. Only on the (001) oriented NiAl surfaces was some θ-alumina still seen, together with some α-alumina. In the current study after 2 hour of oxidation, the high intensity at d=2.74Å indicates that θ-Al<sub>2</sub>O<sub>3</sub> is still present.
- Little Cr<sub>2</sub>O<sub>3</sub> is present (pale blue vertical lines, best visible at d=3.61Å and 1.30Å). After longer oxidation times no Cr<sub>2</sub>O<sub>3</sub> could be identified, as the peak at 1.30Å disappears and the peak at 3.61Å is overlapped by a γ'-Ni<sub>3</sub>Al peak.
- NiAl<sub>2</sub>O<sub>4</sub>-spinel forms during 64 and 261 hours of oxidation (JCPDS 10-0339); a little NiO (JCPDS 04-0835) forms during 64 hours oxidation. More NiO, but still only a little, is present after 261 hours of oxidation (Figure 8.2).
- Some γ'-Ni<sub>3</sub>Al was formed already after 1 hour of oxidation (pale green pattern, JCPDS 09-0097): at least at some places so much Al from the alloy is used in the oxidation process that β-NiAl transforms into γ'-Ni<sub>3</sub>Al. After 4 hours of oxidation, more γ'-Ni<sub>3</sub>Al is present.
- After 64 hours of oxidation, the amount of Ni<sub>3</sub>Al has increased, compared to after 4 hours.
   After 261 hours of oxidation, so much Ni<sub>3</sub>Al has formed that the β-NiAl phase is no longer visible (Figure 8.2), cf. section 8.4.1. Apart from the cubic Ni<sub>3</sub>Al, tetragonal Ni<sub>3</sub>Al (JCPDS 21-0008) also forms.
- On a 1-hour oxidised sample cooled very slowly (about 5 K/minute) in the furnace in Aratmosphere, less (but still some) Ni<sub>3</sub>Al was observed than on the sample withdrawn from the furnace and cooled more quickly in air. Al diffusion from the bulk of the alloy to the surface, or Ni-diffusion from the surface to the bulk results in Ni<sub>3</sub>Al transforming into NiAl.
- On the duplicate sample, oxidised for 256 hours, no Ni<sub>3</sub>Al formation was observed. After disintegration of the oxide layer (during ultrasonic cleaning), its diffractogram was nearly



identical to the diffractogram of the unoxidised sample, the difference being very small  $\alpha$ -

Figure 8.1: Diffractogram of undoped alloy prior to oxidation (bottom) and after  $\frac{1}{2}$  and 4 hrs of oxidation (top) showing formation of  $\alpha$ -alumina (labelled ' $\alpha$ '),  $\theta$ -alumina (labelled ' $\theta$ ') and Ni<sub>3</sub>Al



Figure 8.2: Diffractogram of undoped alloy prior to oxidation (bottom) and after 4, 64 and 261 hrs of oxidation (top) showing formation of α-alumina (labelled 'α'), NiO (NiO), NiAl<sub>2</sub>O<sub>4</sub>-spinel (Sp) and Ni<sub>3</sub>Al; the β-NiAl disappears

#### 8.2.2 Yttrium-doped model coating alloy

- Prior to oxidation, NiAl, Y<sub>2</sub>Ni<sub>7</sub>, some chromiumcarbide and some YC<sub>0.4</sub> are present (lowest scan in Figure 8.3).
- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (red vertical lines) is the major phase present in the oxide layer. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase develops with time. The increase in intensity of the  $\alpha$  Al<sub>2</sub>O<sub>3</sub> between 0.5 and 4 hours is smaller than on the undoped alloy.
- The θ-Al<sub>2</sub>O<sub>3</sub> peak at d=2.74 Å is observed after 0.5 hours of oxidation and after 2 hours of oxidation, but not after 1 hour of oxidation (top scan in Figure 8.3).
- Other formed phases include Y<sub>2</sub>O<sub>3</sub> (JCPDS 43-0661), Cr<sub>2</sub>O<sub>3</sub> (JCPDS 38-1479), Al<sub>5</sub>Y<sub>3</sub>O<sub>12</sub> (JCPDS 33-0040) and AlYO<sub>3</sub> (JCPDS 33-0041).
- Only very little Ni<sub>3</sub>Al is observed after 4 hours of oxidation, so the Al-depletion is more homogeneous than on the undoped alloy.



Figure 8.3: Diffractogram of Y-doped model alloys prior to oxidation (bottom) and after  $\frac{1}{2}$  hr and 1 hr oxidation (top); during oxidation  $\alpha$ -alumina (" $\alpha$ "),  $\theta$ -alumina (" $\theta$ "),  $Y_2O_3$ ,  $Cr_2O_3$ ,  $Y_3Al_5O_{12}$  and YAIO<sub>3</sub> form

#### 8.2.3 Zirconium-doped model coating alloy

- Prior to oxidation, β-NiAl, ZrC and Cr<sub>7</sub>C<sub>3</sub> are present (lower plot in Figure 8.4). The 220-reflection of ZrC at d=1.66Å is sometimes very strong.
- During oxidation, α-Al<sub>2</sub>O<sub>3</sub> (red vertical lines) forms. The intensity of the α-alumina peaks increases (Figure 8.4).
- The large peak at d=2.74Å, only visible after 0.5 hour oxidation, is probably caused by θ-Al<sub>2</sub>O<sub>3</sub>. An alternative explanation for this peak is Ni<sub>3</sub>Al or Cr<sub>3</sub>C<sub>2</sub> but then most other reflections are missing.
- Some baddeleyite, ZrO<sub>2</sub>, (pink vertical lines, JCPDS 37-1484) is formed. The amount of baddeleyite increases during oxidation. The peak is wide compared to α-alumina, indicating a small grain size or micro stresses. Another zirconium oxide (JCPDS 17-0923) is also present.
- No Cr<sub>2</sub>O<sub>3</sub> is identified, as ZrO<sub>2</sub> masks all possible Cr<sub>2</sub>O<sub>3</sub> peaks. Some Cr<sub>2</sub>O<sub>3</sub> might be present.
- Ni<sub>3</sub>Al is present after 0.5, 2 and 4 hrs of oxidation. After 2 and 4 hours oxidation, the intensity of the peaks is low. Virtually no Ni<sub>3</sub>Al is observed after the longer oxidation times.

After oxidation times longer than 2 hours, a large peak is visible at d=2.43Å, indicating most probably Al<sub>2</sub>Zr<sub>3</sub> formation (JCPDS 16-0415). After 2 and 4 hours of oxidation, this peak is large compared to α-alumina, so it is probably not caused by NiAl<sub>2</sub>O<sub>4</sub> (JCPDS 10-0339).



Figure 8.4: diffractogram of Zr-doped model coating alloy prior to oxidation (bottom) and after  $\frac{1}{2}$  hr, 4 hrs and 261 hrs oxidation (top); during oxidation  $\alpha$ -alumina (" $\alpha$ ") and zirconium oxide ("ZrO2") form;  $\theta$ -alumina (" $\theta$ ") is present only after 0.5 hr of oxidation; virtually no Ni<sub>3</sub>Al forms; probably some Al<sub>2</sub>Zr<sub>3</sub> forms after 2 hrs of oxidation

#### 8.2.4 Hafnium-doped model coating alloy

- Prior to oxidation, NiAl, HfC and Cr<sub>7</sub>C<sub>3</sub> are present (lower scan in Figure 8.5).
- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (red vertical lines) forms during oxidation. The intensity increases during oxidation, with the largest increase between 1 and 2 hours oxidation.
- θ-Al<sub>2</sub>O<sub>3</sub> (pink vertical lines in Figure 8.5) is identified after 0.5 and 1 hour of oxidation. The peaks at 2.73 and 2.45 are well visible.
- The (-1 1 1) reflection of HfO<sub>2</sub> (pale-green vertical lines, JCPDS 06-0318) is observed for the oxidised samples at d=3.15Å. This is one of the strongest reflections of HfO<sub>2</sub>. The other HfO<sub>2</sub> reflections are not distinguishable, so the HfO<sub>2</sub> may be textured. The HfO<sub>2</sub> reflection becomes only slightly stronger after longer oxidation times.
- No Ni-oxides or Cr-oxides could be identified.
- Some Ni<sub>3</sub>Al forms, especially after 0.5 hours of oxidation (d=2.07).



Figure 8.5: diffractogram of Hf-doped model coating alloy prior to oxidation (bottom) and after  $\frac{1}{2}$  hr, 1 hr and 4 hrs oxidation (top); during oxidation  $\alpha$ -alumina (" $\alpha$ ") and hafnium oxide ("HfO2") form; probably  $\theta$ -alumina (" $\theta$ ") is present only after up to 0.5 hr of oxidation; some Ni<sub>3</sub>Al forms

### 8.3 Surface morphology

In Table 8.2 the surface morphology of the oxidised model coating alloys is summarised.

Table 8.2: Summary of the main features of the surface r	morphology
--	------------

Model coating	Short oxidation times	Long oxidation times
alloy		
Undoped	Needles; after 4 hrs still present	64 hrs: flat + some needles
		261 hrs: bands of ridges + small
		needles
		Duplicate (256 hrs): ridges everywhere
Y-doped	Needles are less sharp than for	Small grains, shell-like ridges
	undoped, Zr-doped and Hf-doped	
	alloys, amount of needles decreases	
	during first 4 hrs	
Zr-doped	Needles/platelets, amount of	Ridges, shell-like ridges, needles
	needles/platelets decreases during first	
	4 hrs	
Hf-doped	Needles or platelets, amount of	64 hrs: Flat with some ridges and
	needles/platelets decreases during first	blunted needles
	4 hrs	

The most important conclusions drawn from the results presented in section 8.3.1 to 8.3.4 are:

- The most pronounced effect of a reactive element on the morphology is observed for the yttrium-doped alloy: the needles on the Y-doped alloy are smaller and less sharp than on the other alloys;
- The development of a ridged oxide surface morphology on the Zr-doped alloy indicates that some outward cation transport still takes place;
- The substrate grain orientation has a large influence on the surface morphology;
- Duplicate experiments show differences in surface morphology, especially for the undoped alloy.

#### 8.3.1 Undoped model coating alloy

After 30 minutes of oxidation, SEM images of the surface of this alloy show the development of fine needle-like crystals, Figure 8.6a. The needles are approximately 1 µm long. Two distinct substructures can be identified: areas where the needles grow on a flat surface and areas where the needles grow on an undulating surface (left and right in Figure 8.6a, respectively). Regions of these two structures form a radial pattern with it origin at the centre of the sample. This is similar to the grain structures of the starting materials. No difference is found in the composition of these two

areas when measured with EDS. Both are alumina with about 2.5 wt% Cr and 2-7 wt% Ni. The high Ni-contents (7 wt%) were measured in the samples oxidised for 1 hour, where part of the EDX-signal originates from the substrate (a rather high accelerating voltage was used), so the actual Ni-content is lower.

At oxidation times up to 4 hours, the needle-like crystals are retained, with little change in their dimensions.



Figure 8.6: SEI of undoped model coating alloy oxidised for a: 0.5 hour, both flat and undulating substructure visible; b: 2 hours, undulating substructure; c: 4 hours, flat substructure; d: 4 hours, undulating substructure

Other surface features include several small cavities, that are either round with a diameter of a few micrometers (like in Figure 8.6b) or elongated with a width of a few micrometers and a length up to  $10 \,\mu\text{m}$ . EDS of these cavities shows high chrome levels. The oxide directly next to these features has no needles.

After 64 and 261 hours of oxidation, large parts of the oxide had delaminated (Figure 8.27), and on other areas the oxide is irregular and porous (Figure 8.9). The regular oxide after 64 hours of oxidation is quite flat (Figure 8.7). Some small needles can be seen. These needles have about the

same size as after 4 hrs. The density of the needles after 64 hours oxidation is less than after 4 hours. Large parts of the surface area do not show needles.



Figure 8.7: SEI of undoped model coating alloy oxidised for 64 hrs, a: mostly flat oxide, a small agglomerate of ridges at the lower left corner, small needles; b: close-up of the small needles

After 261 hours of oxidation, large parts of the oxide are ridged and other parts have many small needles (Figure 8.8). There is less flat oxide visible.



Figure 8.8: SEI of undoped model coating alloy oxidised for 261 hours, a: many ridges, many small needles present; b: some flat areas present

After 64 hours of oxidation, the grains at the gas/oxide interface are small, about 0.4  $\mu$ m (measured on an area without ridges or needles). After 261 hours oxidation, on ridged parts and near holes formed by Cr-oxide evaporation, the alumina contains up to 13 wt% Ni (5 at.%), but very low Ni-contents were also measured. The Ni-signal is not attributable to the underlying substrate, as the oxide is thick and the accelerating voltage is only 10 kV. In addition several agglomerates of NiO-crystals were seen (facetted crystals in the lower-left corner of Figure 8.10a).

# Table 8.3: Cr and Ni content (wt%) of the alumina on the undoped model coating alloy after various oxidation times

	0.5 hrs	64 hrs	261 hrs	Porous oxide
Remark	Both on flat and undulating substructure	Dense oxide	Dense oxide	
Accelerating voltage	15 kV	10 kV, 15 kV	10 kV	10kV, 15kV
Cr	2.5	3-4	0.5-4 (or higher near cavities where Cr-oxide evaporated)	1-3
Ni	1.5-4	0.6-6	0-13	2-4

The porous oxide has crevices (Figure 8.9).

The Al-content of the exposed substrate is about 15 wt% ( $\approx 26 \pm 2$  at.%, as some oxygen signal was also measured). This is in the  $\gamma$ '-Ni<sub>3</sub>Al region of the phase diagram. The morphology visible on the exposed substrate is discussed in section 8.6.1



# Figure 8.9: Crevices are present on the porous oxide formed after a: 64 (at the left hand side, the substrate is visible); and b: 256 hours oxidation of undoped alloy

The surface morphology of the duplicate sample oxidised for 256 hrs differs from the surface morphology of the earlier (261 hours oxidation) sample. On the earlier sample, small needles protrude from the surface and some narrow bands with ridges are present. Flat areas are also present. On the duplicate sample the entire surface is ridged. Between the ridges, similar needles are found as on the earlier sample. In EDS-spectra measured on the duplicate, Si was observed. NiO-crystals were not seen on the duplicate sample.



Figure 8.10: Reproducibility after long oxidation time is poor, a: original sample (261 hrs), showing some ridges, delamination and facetted NiO-crystals; b: duplicate (256 hrs), showing more ridges

#### 8.3.2 Y-doped model coating alloy

The surface of the yttrium alloy shows far less needles after 30 minutes of oxidation (Figure 8.11a) than for the undoped alloy. The surface appears roughened when compared to the polished starting material. According to Figure 8.11b this roughening is also present in the metal beneath the oxide (a delaminated area is pictured to show the roughening of the substrate, only little area had spalled). Some areas are partially covered with small needles with an average length less than 1  $\mu$ m. Some regions show more needles than others. After 1 hour of oxidation, the needles still only cover approximately half of the oxidised surface and have the same dimension as after 30 minutes of oxidation. A larger number of needles are seen after 2 hours of oxidation, although there are still many areas where only a few needles can be found. The size of the needles varies from less than 1  $\mu$ m up to approximately 1.5  $\mu$ m in length. Where fewer needles are seen, they are also more rounded. After four hours of oxidation a smaller part of the surface is covered with needles, and the needles are less pronounced (Figure 8.11c). The oxide surface is made up of small round grains with a diameter of less than 0.3  $\mu$ m.



Figure 8.11: SEI showing oxide morphology on Y-doped alloy oxidised for a: 0.5 hour; b: 1 hour, the metal is roughened due to the oxidation; c: 4 hours, more flat areas are present; d: 64 hrs, shell-like ridges and wavy small-grained oxide

After 64 hours of oxidation the oxide surface is wavy (Figure 8.11d). No needles or platelets are observed on the oxide surface. The oxide grains are small. Grain boundaries open up. These open grain boundaries look like pores at the gas / oxide interface, but cross-section images reveal that they are only open grain boundaries.

No needles are protruding from the grains. For the majority of the oxide area, the grains have raised intergranular boundaries that can be described as mini-ridges (left hand side of Figure 8.11d). However, these ridges are not as numerous or as large as on the surface of the Zr-doped alloy, section 8.3.3. Also larger ridged spots, about  $1.5 \,\mu$ m in diameter, are present on the oxide surface.

A number of cavities and localised oxides with a different morphology are seen on the oxide surface for all oxidation times. The cavities show high chrome levels, similar to those observed on the undoped alloy. The localised oxides, which appear as (conglomerates of) pseudo-hexagonal crystals (centre of Figure 8.11a) up to a few micrometers in diameter, show high levels of yttrium when measured with EDS.

On delaminated areas after 64 hours of oxidation the composition is 71 wt% Ni, 21 wt% Al and 3.5 wt% O (measured with EDS) indicating that Al depletion is small (the alloy composition prior to oxidation is 73.4 wt% Ni and 21.8 wt% Al).

#### 8.3.3 Zr-doped model coating alloy

After 30 minutes of oxidation, the oxidised surface of the zirconium alloy is completely covered with needles with a length of 1  $\mu$ m (Figure 8.12a). A few areas are seen where the needles have grown laterally and are less sharp. After 1 hour of oxidation, fewer needles are found and they are less sharp (Figure 8.12b). Further flattening is seen after 2 hours of oxidation (Figure 8.12c). Large areas are found where the needles have disappeared leaving small grains of less than 0.5  $\mu$ m. Less needles are left after 4 hours of oxidation. Most of the surface is composed of small grains with the remnants of the needles protruding from these grains.

After 64 hours of oxidation, ridged areas and areas with shell-like 'ridges' are present (Figure 8.12d and e). Also some areas with needles are present. The distance between ridges is about 1  $\mu$ m; this is a larger distance than between the ridges in the ridged spots found on yttrium-containing alloy. In the areas with shell-like ridges, the surface looks wavier and the ridges are less pronounced. The composition of the wavy surface is about equal to the composition of the ridged area, only the Cr-content shows more scatter, Table 8.4.

Possibly, the shell-like oxide develops into area with less pronounced ridges shown in Figure 8.12f (261 hour of oxidation). Compared to 64 hours of oxidation, after 261 hours the structure is more ridged. Blunted needles protrude from many grains (the blunted needles are located between the ridges at the left-hand side of Figure 8.12f).





Figure 8.12: SEI showing oxide morphology on Zr-doped alloy a: 0.5 hour oxidation, needles on the surface; b: 1 hour, fewer and less sharp needles; c: 2 hrs, blunting continues, flat areas visible; d: 64 hrs, boundary between shell-like oxide on wavy substrate and ridged oxide (apart from these morphologies also areas with needles present); e: 64 hrs, wavy shell-like oxide; f: 261 hrs, ridged oxide (left) and shell-like oxide (right)

······	64 hrs	64 hrs	261 hrs	261 hrs
Place			Ridged area	Lower ridges
Accelerating voltage	15 kV	10 kV	10 kV	10 kV
Zr	0.7-1.9	0-1.8	(1 or) no Zr at all	(0.8 or) no Zr at all
Cr	2.4-3.6	2.3	4-6	2-8
Ni	1.5-2.5	0.4-0.8	0-0.5	0-0.7

Table 8.4: Zr, Cr and Ni content (wt%) of the alumina on the Zr-doped model coating alloy after various oxidation times

Both cavities and localised areas of oxidation with a different morphology are seen on the oxide surface for all oxidation times. A high level of chromium is found at the cavities as for the other

alloys. Up to 63 wt% (30 at.%) zirconium is measured at the localised oxidation spots using EDS, the remainder being alumina. The localised oxidation points are sometimes round, but often have irregular forms (more elongated than the round or pseudo-hexagonal crystals on the Y-doped model coating alloy). Around the localised areas of oxidation, cracks are observed for the oxidation periods longer than one hour. Also holes where Zr or Cr-rich oxide has broken out or evaporated are observed (Figure 8.13).



Figure 8.13: localised oxidation spots: strange forms of Zr-rich oxide particles, cracks, some localised oxidation particles appear to be missing (2 hours oxidation on Zr-doped model coating alloy)

Immediately next to the localised oxidation spots or the cavities the oxide is flat with no needles present. At longer oxidation times the flat area around such spots is larger, see Figure 8.14. Some circular areas without needles are found after 2 hours of oxidation and even more after 64 and 261 hours of oxidation.



Figure 8.14: small round flat areas of about 20  $\mu m,$  a: 261 hrs; b: close-up (2 hrs)

Some scatter is observed in the morphology of oxide formed on Zr-doped model coating alloy. A duplicate sample was oxidised for 256 hours. On this duplicate sample the oxide is flakier and has platelets instead of ridges (cf Figure 8.12f and Figure 8.15). The composition of the oxide on the duplicate is similar to the first sample, except for the chromium content. The Cr content of the duplicate is much lower, only 0.6 wt%. Some silicon was also detected on the duplicate.



Figure 8.15: SEI of duplicate Zr-doped model coating alloy, showing platelets and flakes instead of ridges

#### 8.3.4 Hafnium-containing model coating alloy

After 30 minutes of oxidation most of the surface is covered with platelets (Figure 8.16a). The size of the platelets varies, probably depending on the crystallographic orientation of the underlying grain of the alloy. Typical size for the platelets in the region where the platelets are coarse is about 1  $\mu$ m width (see Figure 8.16a and b). After 1 hour of oxidation the platelets have an increased width and height. After 2 hours (Figure 8.16c) and the area becomes flatter. The flatter areas appear to have a lower Ni-content (Table 8.5). Typical grain size on the flat area surface is 0.5  $\mu$ m (both after 2, 4 and 64 hours of oxidation). After 4 or 64 hours of oxidation, the oxide is flat with some ridges present. Small areas with blunted needles are present, also (Figure 8.16d,e,f).

Table 8.5: Hf, Cr and Ni content (wt%) of the a	lumina on the Hf-doped model coating alloy
after various oxidation times	

	Oxidation times up to	Oxidation times up to	64 hrs
	4 hrs	4 hrs	
Remark	Area with platelets	Flat area	
Accelerating voltage	15 kV	15 kV	10 kV
Hf	0-1.2	0-1.2	0
Cr	2.5-4.5	2.5-4.5	5
Ni	2-6*	1-2*	0.2-1

\* = some Ni-signal from alloy, so real Ni-content is lower

Apart from the flat oxide shown in Figure 8.16f, a lot of irregular, porous oxide was present after 64 and 261 hours of oxidation. Areas where the alloy material was visible were present also. Compared to the undoped model coating alloy, more porous oxide and less substrate was visible on the Hf-doped material. After 64 hours of oxidation, at least on some places the model coating alloy at the surface still has a  $\beta$ -NiAl composition (20.4 wt% Al).



Figure 8.16: SEI of Hf doped alloy oxidised for a: 0.5 hour; b: 1 hour, a porous oxidation spot present in the right corner; c: 2 hrs, flat areas and areas with blunted needles; d: 4 hrs, flat areas with some ridges; e: 4hrs, blunted needles and some ridges present in the flat areas; f: 64 hrs, similar to structure after 4 hrs

On the surface, localised hafnium-rich oxidation spots are visible, containing up to 37 wt% Hf, which corresponds to 5.8 at.%. The diameter of the localised oxidation spots is about 2  $\mu$ m. For short oxidation times, the spots are slightly smaller. Some localised oxidation spots are hexagonal,

others are round. It seems that the spots are richer in Hf (maybe because of the size increase) at longer oxidation times. In the porous oxide, Hf-rich spots were present also.

Another surface feature is elongated and porous. EDX indicates chromium enrichment (7 wt% Cr, compared to 4 wt% in the platelet structure). This surface feature can be seen in the left corner of Figure 8.16b. When all chromium-oxide evaporates, these elongated porous features develop into cavities in the surface (Figure 8.16c,f).

#### 8.4 Oxide layer microstructure (cross-section)

#### 8.4.1 Undoped model coating alloy

For oxidation times up to 4 hours, the majority of the oxide layer on the undoped model coating alloy is seen to consist of a single-phase material. This is demonstrated by the even shade of the oxide in backscattered electron images (BSI). Isolated regions with high chromium content are found at the upper surface of the oxide (appearing lighter than alumina in BSI). The interface between the oxide and the alloy is very sharp and flat.

A large number of voids are seen at the interface between the oxide and the substrate for all oxidation times (Figure 8.17).



Figure 8.17: SEI of cross-sectioned undoped alloy oxidised for 4 hrs, showing a void at the oxide/alloy interface

For oxidation times up to 4 hours, there is usually no internal oxidation. In the cross section of the samples oxidised for longer time (64 and 261 hours), large oxide intrusions into the substrate are seen. The oxide protrudes up to 200  $\mu$ m into the alloy after 64 hours and up to 450  $\mu$ m after 261 hours of oxidation (Figure 8.18).

BSE showed grey and white regions in the oxide for long oxidation times. The white regions are very rich in Ni, up to 66 wt% (40 at.%), the oxygen fraction being too low to be totally just oxide. Other, even whiter spots are totally metallic. Many grey regions are rich in Cr (12 wt%  $\approx$  9 at.% Cr).

In the alloy adjacent to the oxide intrusions, lighter shaded areas are seen with optical microscopy. SEM-EDS revealed that near the oxide intrusions, the substrate is often depleted in aluminium. This composition is located in the  $\gamma$ '-Ni<sub>3</sub>Al phase-region of the phase diagram. Ni<sub>3</sub>Al was observed with XRD (section 8.2.1). XRD revealed that the amount of Ni<sub>3</sub>Al was large after 261 hours of oxidation. Virtually no  $\beta$ -NiAl was observed anymore, indicating that no  $\beta$ -NiAl is present in the top part (first 50-100  $\mu$ m or so) of the alloy.

The width of these lighter shaded (Al-depleted) areas depends on the size of the nearby oxide intrusions. For some areas near large oxide intrusions, no  $\beta$ -NiAl is seen in the first 150  $\mu$ m from the surface (Figure 8.18a). At other places the lighter area is smaller (Figure 8.18b).



# Figure 8.18: Large oxide intrusions into the alloy and a depletion zone in the alloy, optical micrographs, 261 hours of oxidation

In the duplicate sample oxidised for 256 hours, such oxide intrusions are not present. In this sample, the presence of  $Ni_3AI$  is not observed with XRD (section 8.2.1).

#### 8.4.2 Y-doped model coating alloy

At short oxidation times the gas/oxide and the oxide/alloy interfaces are wavy. This was already expected from Figure 8.11a and b, that showed roughening of the oxide surface and of the alloy. Probably the waviness accommodates oxide/alloy planar orientations with low interface energy (another cause for the waviness can be a difference in growth rate for the different oxide orientations). The waviness and the absence of voids indicate inward oxygen transport.



# Figure 8.19: oxide on Y-doped model coating alloy oxidised for 2 hours, showing a wavy oxide/alloy interface and a peg; the gas/oxide and the oxide/alloy interface are indicated

At the oxide-alloy interface, several pegs are observed growing into the alloy (Figure 8.19). The pegs are approximately round or slightly elongated into the alloy and reach a depth of several micrometers. EDS shows that the pegs contain a large amount of Y and O, with some Cr and Al. Also a long and thin, darker phase composed of unoxidised Y with some Cr is present. It reaches tens of micrometers into the alloy. This phase is often observed as a tail to the pegs at the oxide/alloy interface.

The number of pegs increases with oxidation time. Such pegs are not seen for the undoped alloy.

In Figure 8.19 the gas/oxide interface and the oxide/alloy interface are indicated. The darker and brighter bands in the oxide are experimental artefacts, due to charging of the insulating oxide by the electron beam. Whether or not these bands occur depends on the working distance, accelerating voltage and probe current. On a Zr-doped sample, the same brighter and darker bands were observed, but BSI showed the oxide to have about constant composition over the entire thickness. Also SEI at other settings of the microscope showed oxide with a homogenous contrast.

#### 8.4.3 Zr-doped model coating alloy

The oxide/alloy interface has the shape of sharp waves. After short oxidation times (up to 4 hours), the 'waviness' (fluctuation) of the interface is comparable to the waviness on the Y-doped model coating alloy.



# Figure 8.20: cross-section of oxide layer on Zr-doped model coating alloy after 0.5 hr of oxidation

After 64 and 261 hours of oxidation, the 'period' of the waves at the oxide/alloy interface is a bit longer than after short oxidation times (cf. Figure 8.20, Figure 8.22). This is due to the larger size of oxide grains near the oxide/alloy interface after longer oxidation times. The grain size is nearly 1  $\mu$ m (Figure 8.21). After long oxidation times, the grains are columnar (elongated in the oxide layer growth direction). No voids like in Figure 8.17 are present at the oxide/alloy interface.

After longer oxidation times, several Zr-rich oxide particles are found in the oxide layer. The most often observed shape and size is round and very small (Figure 8.22), but also some larger, angular and elongated particles are present (Figure 8.21). Based on EDS, BSI and literature (no mixed Zr-Al oxide is found in literature [102,103]) elongated oxide grains like in Figure 8.21 are concluded to be  $ZrO_2$ .



### Figure 8.21: Cross section of oxide on Zr-doped alloy after 261 hrs oxidation, showing a Zrrich oxide grain near the oxide/alloy interface, a: SEI; b: BSI

Round or elongated pegs into the alloy are found. They reach up several microns into the alloy. The pegs consist of zirconium-rich oxide (light spots in Figure 8.22a) enveloped by alumina (dark band in Figure 8.22a). The number of pegs and their size increases with longer oxidation times.

Very few long, thin dark phases containing zirconium, as found for yttrium in the yttrium alloy, were observed.



Figure 8.22: a: peg on Zr-doped model coating alloy, BSI after 64 hours of oxidation; b: oxide layer after 261 hrs of oxidation with some small round Zr-rich oxide grains (the Zr-rich oxide particles appear white)

After 0.5 hrs the Al content of the alloy just below the oxide (33 or 34 at.% = 20 wt%) is slightly lower than prior to oxidation (38.5 at.% = 23wt%). After 64 and 261 hours, the Al-content is  $22\pm1$ wt%, indicating that Al has diffused from the alloy bulk to the alloy near the oxide to decrease the concentration gradient. This diffusion is consistent with the observation (with XRD, section 8.2.3) that on the Zr-doped model coating alloy no Ni<sub>3</sub>Al is present after long oxidation times while it was observed after short oxidation times.

#### 8.4.4 Hf-doped model coating alloy

On the Hf-doped model coating alloy, the oxide/alloy interface is less wavy than on the Y and Zrdoped model coating alloys. The oxide/alloy interface on the Hf-doped alloy is wavier than the interface on the undoped model coating alloy. Several voids are seen at the oxide/alloy interface.

After 0.5 hour Hf is only rarely found in the scale (EDS on cross-sectioned oxidised samples). Most often no Hf is measured. After 4 hours oxidation some very small Hf-rich particles were found in the oxide scale. Measured away from these Hf-rich particles, the Hf-content of the oxide was negligible. Apart from these Hf-rich particles, the composition of the oxide is mostly homogeneous, as indicated by the uniform colour in the backscattered electrons-image. The chromium and nickel content of the oxide is in agreement with the composition of the oxide measured at during surface characterisation.

Some chromium-rich parts are seen in the oxide, appearing lighter in the in the backscattered electron images.

Chromium-rich and hafnium-rich oxide intrusions into the substrate are seen. After 4 hours of oxidation they are about 10  $\mu$ m long. The peg in Figure 8.23 is probably located at a grain boundary in the alloy. Next to the peg, aluminium-depletion is observed. In the peg both Ni-rich and Hf-rich domains are observed (both appear lighter in the backscattered electron image). Probably, the Ni-rich domain in the oxide intrusion is (partly) metallic, for instance Ni<sub>3</sub>Al.



Figure 8.23: BSI of peg growing into the alloy with small depletion zone near the peg, Hfdoped alloy oxidised for 4 hrs

#### 8.5 Growth kinetics

To investigate the growth kinetics for the oxide growing on the alloy substrate, the thickness of the oxide was measured for a range of oxidation times with SEM.

The thickness of the oxide on the undoped alloy after 30 minutes oxidation was approximately 0.6  $\mu$ m. The oxide layer thickness increases to approximately 1  $\mu$ m after 4 hours of oxidation. For the short oxidation times, the oxide on the zirconium-doped alloy seems to be much thicker than the oxide on the other model coating alloys. However, this trend does not continue at longer oxidation times (64 and 261 hrs). For the oxidation times up to 4 hours, the thickness of the oxide on the other doped alloys is comparable to the thickness on the undoped alloy.

The growth kinetics of all model coating alloys show:

- a considerable oxide thickness after only 30 minutes of oxidation;
- a small increase in thickness during the next 3<sup>1</sup>/<sub>2</sub> hours of oxidation;
- except for the Hf-doped material (which increases monotonically), the other curves show a dip in the curve; this dip is often smaller than the error bars.



b

# Figure 8.24: thickness after oxidation at 1100°C, 20vol.% O2, measured with SEM; a: undoped and Zr-doped alloy; b: Y-doped and Hf-doped alloy

The decrease in oxide growth rate compared to the growth during the first 30 minutes indicates that the initial oxide hinders further oxide growth already after only 30 minutes. XRD shows that on several alloys after 1 hour oxidation  $\theta$ -alumina is still present, so it should not be concluded that further growth should obey a parabolic rate law (transient oxides also hinder further oxide growth but not as effectively as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, cf. ref [104]).

The scatter in the thickness of oxide on the Zr-doped alloy after 2 hours of oxidation is due the limited number of thickness measurements (caused by some preparation difficulties). Possibly (part of) the decrease in the oxide thickness on the Zr-doped coating material between 0.5 and 1 hour is caused by the volume change associated with the  $\theta$  to  $\alpha$  transformation. This corresponds with the diffractograms of the oxidised Zr-doped alloys, if the large peak at d=2.74Å is interpreted as a  $\theta$ -alumina reflection (section 8.2.3).

The thickness of the oxide on the undoped model-coating after 261 hrs was about 7.5  $\mu$ m, measured some distance away from the intrusions. The large oxide intrusions result in Al-depletion in the model coating alloy. Near the oxide/alloy interface much NiAl had transformed to  $\gamma'$ -Ni<sub>3</sub>Al (section 8.4.1). No parabolic growth constant is determined for the undoped model coating alloy. A comparison of the growth rate of the oxide on the Zr-doped  $\beta$ -NiAl alloy to the growth rate of the oxide on the undoped (no longer totally  $\beta$ -NiAl) alloy is not justified.





The thickness of the oxide on the Zr-doped alloy after was 261 hrs  $3.0\pm0.4 \mu m$ . The parameters of the fitted cubic-parabolic growth curve shown in Figure 8.25 are presented in Table 8.6.

### Table 8.6: Parameters of the growth curve fitted to the experimental oxide thickness on the Zr-doped alloy

Parameter	Value
k	7.12E-6 µm <sup>2</sup> /s
$t_0$	17 hr
$d_0$	1.572 μm

The parabolic growth constant for the Zr-doped alloy is 7.1E-06 (± 1.0E-06)  $\mu$ m<sup>2</sup>/s. The parabolic rate constant determined from the thickness, can be related to a parabolic weight change rate constant,  $k_p$  [105]:

$$k_p = \left(\frac{3M_o}{3M_o + 2M_{Al}}\rho_{Al2O3}\right)^2 k$$

with  $M_O$  and  $M_{Al}$  the atomic mass of O and Al, respectively, and  $\rho_{Al2O3}$  the density of alumina. A parabolic growth constant k of 7.1E-06 (± 1.0E-06)  $\mu$ m<sup>2</sup>/s is equivalent to  $k_p$ = 2.5E-13 (± 0.3E-13) g<sup>2</sup>/cm<sup>4</sup>s.

$kp (g^2/cm^4s)$	Experimental	Material	Source
	conditions		
1.0E-12	weight changes,	Undoped β-NiAl	Van Manen
	1373 K in flowing		[p89ref106]
2.1E-14	oxygen	$\beta$ -NiAl with 0.5 wt% Y	Van Manen
			[p89ref106]
8.64E-12	1473 K in static air	undoped NiAl	Barrett [107]
7.43E-12		doped NiAl (48.3 at.%Al	Barrett [107]
		and 0.1 at.%Zr)	
4.31E-12	1423 K in static air	undoped NiAl	Barrett [107]
3.92E-12		doped NiAl (48.3 at.%Al	Barrett [107]
		and 0.1 at.%Zr)	
4.55E-13	1373 K, 20 hr	undoped NiAl with 42 at.%	[108]
	oxidation	Al	
7.5 E-13	1373 K, 200 hr	undoped NiAl with 41.8	[109]
	oxidation	at.% Al	

Table 8.7:	parabolic	growth	constants	from	literature
------------	-----------	--------	-----------	------	------------

The  $k_p$  determined in this study is lower than the values for undoped materials presented above, as can be expected because RE usually lowers the oxide growth rate [110]. Also the presence of Cr may lower the growth rate.

In the determination of the parabolic constant with SEM, the pegs were not taken into account. Therefore with SEM a slightly lower parabolic rate constant should be found than with gravimetric determinations like in Table 8.7.

### 8.6 Adhesion behaviour of isothermally grown oxide layers

A schematic overview of the adhesion of the oxide on the various model coating alloys after cooling, is shown in Table 8.8. The presented percentages are not very precise, but they do give a rough indication.

	Model coating alloy	0.5 hr	1 hr	2 hr	4 hr	64 hrs	261 hrs
	Undoped	Little	Some	Some	Some (7%)	++ (20%)	++ (25%)
	Y-doped	Little	Little	Little	Little	Little (2%)	Large
-	Zr-doped	Little	Little	Little	Little	Little (<2%)	Little
	Hf-doped	Little	Little	Some	Some	++ (18%)	++ (15%)

 Table 8.8: delamination of isothermally grown oxide layers

### 8.6.1 Undoped model coating alloy

Delamination is seen on the undoped model coating alloy after withdrawal from the furnace. Delamination is greatest for the flat substructure, but is also seen on the undulating surface (Figure 8.17, the flat substructure appears white on the SEM-image). The degree of delamination after withdrawal from the furnace increases for longer oxidation time.



# Figure 8.26: SEI of undoped alloy after 4 hours of oxidation at 1373 K, a: overview of flat substructure (white) and undulating substructure (grey); b: close-up of delamination in flat substructure

Especially after longer oxidation times, 64 and 256 hrs, large areas are delaminated. Islands are present where the oxide is still intact (grey in Figure 8.27). Between the islands, the substrate is visible (black or dark grey in Figure 8.27). The white flakes in Figure 8.27 between the oxide
islands are areas with porous oxide. The boundary between the dense oxide and the porous oxide, and between dense oxide and the bare substrate, appears as a series of steps.



Figure 8.27: Delamination behaviour of oxide layer on undoped alloy after 64 hours of oxidation, a: dense oxide, porous oxide and substrate visible; b: close-up of an edge of a dense-oxide island

Where the bare metal is visible, imprints can be seen. These imprints are pseudo-hexagonal, with typical sizes of the hexagons or polygons of  $0.8 \mu m$ . Some chromium carbide filaments are seen, pointing out of the alloy, see Figure 8.28a.



Figure 8.28a: delaminated area with chromium carbide filament (left-hand side) and pseudohexagonal imprints, 64 hrs of oxidation; b: area with imprints of oxide grains on the exposed alloy surface, and facetted, less rough area with fringes, 64 hrs of oxidation

Comparison of the structure observed in the delaminations (Figure 8.28b) with observations by Smialek [109] (Figure 8.29) indicates that the area with oxide imprints lies higher than the large smooth area. The smooth area has to be attributed to void formation at the oxide / alloy interface (section 2.2 and 8.6.4).

Smialek observed that after very short oxidation the smooth areas are not yet facetted. The facets become more pronounced after about 1 hour oxidation. He attributed the polyhedral nature of the

voids (the smooth areas) to the formation of voids along the low-energy  $\{110\}$  planes in  $\beta$ -NiAl. After very short oxidation times, also higher-energy planes are present.

Smialek [109] attributes the spiral steps in Figure 8.29 (probably equivalent to the 'fringes' in Figure 8.28b) to layer-by-layer material removal from the exposed end of dislocations. This step formation suggest that the voids were growing by vapour transport of aluminium from the void surface to the oxide, as discussed in section 2.2.



Figure 8.29: 70° tilted SEI from Smialek [109] showing that facetted smooth surface is located lower than the area with oxide imprints, delaminated area after 100 hr isothermal oxidation at 1373 K, 42 at.% Al

The oxide layer delamination behaviour of the duplicate undoped alloy oxidised for 256 hours was totally different from the delamination behaviour of the oxide on the sample oxidised for 261 hours. Initially the oxide remained attached to the prepared surface of the sample. On ultrasonic cleaning, nearly all the oxide disintegrated into very small oxide particles. The oxide on the (unpolished) backside of the duplicate sample delaminated as very large pieces during cooling. Neither side showed the island-like behaviour of the original sample.

## 8.6.2 Yttrium-doped model coating alloy

Some delamination is observed on the yttrium-doped model coating alloy after short oxidation times. After 64 hours of oxidation (Figure 8.30) an oxide layer is present with some spalled areas, these spalled areas are larger than for the Zr-doped alloy. The delaminated area is about 2% of the total surface area.



Figure 8.30: Optical micrograph of surface of Y-doped alloy after 64 hours of oxidation showing delamination (brilliant spots) and delaminated oxide on top of the regular oxide (grey)

After 261 hours of oxidation, oxide of considerable thickness was only seen on a small area in the middle of the disk and on dispersed small islands (Figure 8.31). At higher magnification of the dark area, Figure 8.31b, pseudo-hexagonal imprints (size:  $1.5 \mu m$ ) are observed between smoother surfaces. As in the middle of this disk small pores were present prior to oxidation, the area with thick oxide (left in Figure 8.31) is not representative. A duplicate sample also showed little oxide of considerable thickness. This lack of thick oxide is either characteristic oxidation behaviour, or it is caused by extreme spallation due to experimental factors. Further research should point out which of both alternatives holds true.



Figure 8.31a: SEI of surface of Y-doped model coating alloy after 261 hours of oxidation showing little oxide; b: close-up of the dark area

## 8.6.3 Zirconium-doped model coating alloy

On the zirconium-doped model coating alloy, some delamination occurred, comparable to the amount of spallation on the yttrium-doped model coating alloy. Also after long oxidation times (64

and 261 hours) there are only a few delaminated areas. A delaminated area is shown at the lefthand side of Figure 8.32a and b. Delamination debris is also visible.



Figure 8.32: oxide on Zr-doped alloy after 64 hours oxidation showing only little delamination and some delamination-debris, a: optical micrograph; b: polarised optical micrograph of the same area, providing more contrast

Some features in Figure 8.32 not related to delamination but to surface morphology, section 8.3.3:

- The small lighter spots in the background are areas where the oxide is flat (SEM-images of these regions are shown in Figure 8.14).
- The grain structure of the sample is reflected in the contrast in the oxide (cf. Appendix A figure 1).

## 8.6.4 Hafnium-doped model coating alloy

On the hafnium-doped model coating alloy, at the shortest oxidation time (30 minutes) only a small amount of spallation is observed. After 1 hour some small areas are observed where spallation has occurred. After 2 hours more spallation is observed. The spalled areas either have sharp edges, and facets on the alloy surface (Figure 8.33a); or (more often) a white 'glassy' surface and less straight edges (Figure 8.33b). Spallation is less severe on the Hf-doped than on the undoped model coating alloy, but more severe than on the Y and Zr-doped alloys.



Figure 8.33: The oxide failure plane is about perpendicular and sometimes very sharp, a: delamination on Hf-doped NiAl oxidised for 1 hour at 1373 K; b: whiter, 'glassy' delamination on Hf-doped alloy oxidised for 2 hours at 1373 K

The Hf-doped samples oxidised for short oxidation times were investigated with optical microscopy (Figure 8.34). Under the undelaminated surface in Figure 8.34, a pattern of darker and lighter areas is visible. Voids formed by the mechanism proposed by Brumm and Grabke (section 2.2) are the most probable explanation for this pattern. The lighter areas are thought to be associated with a non-adherent oxide/alloy interface. The boundary between the different shades has angular edges.

In the delaminated zones, the same pattern of regions with angular boundary is seen. The ratio of non-adherent to 'adherent' regions in the delaminated areas should be higher than under the undelaminated surface, as non-adherent oxide delaminates more easily than adherent oxide. On the right-hand side of Figure 8.34a, the overall colour is in-between the colour of the delaminated zone and the colour of the adherent zone. This suggests that the oxide is still present, but that a large void is developing between the oxide and the alloy. As no cracks are observed around this area, it is thought that the oxide has buckled (not wedged, see section 3.2.1). Small bands are present where the alloy and the oxide still adhere.



Figure 8.34: optical micrograph of oxide surface after 4 hrs oxidation; a: Hf-doped alloy with some delaminated areas and some nearly-delaminated areas; b: schematic overview of the same region





The angular boundaries in the delaminated areas separate regions with different surface roughness (Figure 8.35). The presence of oxide grain imprints in the rougher areas in Figure 8.28 (undoped, 64 hours oxidation) and their absence in Figure 8.35 (Hf-doped, 1 hour oxidation) is due to oxide grain growth. Imprints are possibly present in the rough area in Figure 8.35 also, but at short oxidation times the oxide grains are much smaller, so their imprints are smaller and less deep. Smialek [109] observed imprints only after some oxidation time (not earlier than after 9 cycles of 1-hour oxidation at 1373 K).

Apart from the voids under the oxide, which ease buckling initiation, the morphology of the fracture edges also provides some indications of the type of failure. According to Evans [111] an inclined oxide failure plane indicates that fracture occurred via the wedging mechanism. In the current study the oxide failure plane was usually quite sharp (Figure 8.33 a and b). Often the failure plane was perpendicular to the oxide surface rather than inclined (Figure 8.33).

Wang [112] observed cracks in the longitudinal direction of the buckle (like in the right top corner of Figure 8.33a). The bending of the oxide during buckling causes tensile stress in the oxide, resulting in these cracks.

Oxide next to delaminated areas was sometimes seen that no longer adhered to the alloy. It was possible to look 'under' the oxide. Such raised edges of the oxide are expected for buckling, but not for wedging [figure 24 in ref 111], cf. Figure 2 and 3 in section 3.2.1.

Based on the observations on the voids under the oxide and on the observations on the oxide failure planes, buckling is concluded to be the dominant mechanism for the Hf-doped alloy used in the current study, at short oxidation times. According to the calculations and spallation maps (section 3.2.1 and 3.2.2), at an oxide thickness on the Hf-doped model coating alloy of about 0.75  $\mu$ m (section 8.5) a non-adherent oxide/alloy interface with a larger radius *R* than 9  $\mu$ m is necessary. The diameter of the (larger) voids observed is about 8  $\mu$ m so probably some out-of-plane component of the stress is assisting the buckling process (for instance a height difference in the adherent oxide can cause such an out of plane stress component).

The delaminated areas often have an elongated form. The density and the shape of the voids probably cause this elongated form.

At longer oxidation times the surface on the Hf-doped alloy looks similar to the oxide on the undoped model coating alloy: regions with dense oxide, regions with porous oxide, and regions with exposed alloy. The area of bare alloy makes up a smaller fraction of the total area than for the undoped alloy. The porous oxide makes up a larger part than for the undoped alloy.

## 8.7 Thermal cycling oxidation behaviour

### 8.7.1 Weight gain during cyclic oxidation

In order to assess the long term oxidation behaviour of the four model coating alloys under conditions met in practical applications, thermal cycling experiments have been carried out as described in section 7.3.

If during the cycling experiment the weight increases monotonically and slowly, the degree of delamination is low and oxidation is not severe. A large weight increase followed by a weight decrease indicates severe oxidation followed by delamination. The lifetime is considered to be terminated when the weight of a sample decreases to below its original weight.

In principle, a smooth weight gain curve can be caused by re-oxidation and delamination cancelling each other's weight change effect. In practice, the situation that severe re-oxidation and delamination cancel each other out will not last long and will not produce a smooth weight gain curve. On the undoped model coating alloy during the first 60 cycles, severe oxidation takes place (Figure 8.36). After 80 cycles, the weight starts to decrease, indicating that delamination results in a larger weight loss than the weight gain due to re-oxidation. Probably the oxidation is still severe, but delamination is even more severe. After 220 cycles, the weight of the sample drops below its original weight.

The weight of the Y-doped model coating alloy increases monotonically. No onset of weight loss was observed during this experiment (Figure 8.36), indicating that the extent of delamination is small.

The weight of the Zr-doped model coating alloy also increases monotonically. The rate of the weight increase is slightly higher on the Zr-doped model coating alloy than on the Y-doped model coating alloy (Figure 8.36). The extent of delamination on the Zr-doped model coating alloy is also small.

On the Hf-doped model coating alloy during the first 100 cycles, severe oxidation takes place, resulting in a large weight gain. After 100 cycles, the weight decrease due to delamination starts to be larger than the weight increase due to oxidation, resulting in a net weight decrease (Figure 8.36). The net weight decrease is lower than on the undoped model coating alloy. The adhesion on the Hf-doped model coating alloy is better than on the undoped alloy. The weight loss during subsequent cycles is moderate, so the weight does not decrease to below the original weight during this experiment: a certain amount of oxide is retained during the remainder of the thermal cycling experiment, i.e. for 1000 cycles after the onset of weight loss.



number of cycles

Figure 8.36: Weight gain during cyclic oxidation (8-9 minutes heating in air to 1373 K, 45 minutes at 1373 K in air, 8-9 minutes cooling to < 373 K) showing severe oxidation and delamination on the undoped alloy, slow oxidation without severe delamination on the Y-doped and Zr-doped alloy and severe oxidation and moderate delamination on the Hf-doped alloy

Based on the weight gain (Figure 8.36) the sequence from poor to good cyclic oxidation performance is: Undoped, Hf-doped, Zr-doped, Y-doped alloy.

The thermal cycling experiments were performed on two samples per model coating alloy. For each model coating alloy the sample with the best performance is displayed in Figure 8.36. The weight gain of the duplicate samples is very reproducible. Differences in weight gain between duplicates are related to porosity. On several samples, pores (due to the casting process) are located at the centre of the samples. The weight gain of the Zr-doped sample with a large pore in the middle of the sample surrounded by a region with smaller pores was much larger than for the other Zr-doped sample with no large pores. The weight gain of the latter is displayed in Figure 8.36. Also on the Hf-doped sample with the highest initial weight gain and the largest weight loss, large pores and a region with small pores were present, while fewer and smaller pores were present on the displayed Hf-doped sample.

Both Y-doped samples (that both had a small pores in the middle of the sample) have a lower weight gain rate than the best of the Zr-doped samples.

The initial oxidation kinetics during thermal cycling of the Zr-doped and Y-doped model coating alloys is very different from the oxidation kinetics of the Hf-doped and undoped alloys. On the Hfdoped and undoped model coating alloys more oxidation occurs either due to cracks that form in the protective oxide layer during cooling and heating between two cycles, or due to quick ionic transport through or along the (remains of) carbides. Quick ionic transport causes more oxidation. Formation of cracks may be linked with the presence of many carbides in the undoped and Hfdoped model coating alloys causing stress concentration in the oxide, or weak spots in the oxide above the carbides. Cracks cause more oxidation in the next cycle, as they allow oxygen ingress. During isothermal oxidation, the initial growth rate of the alloys did not differ much (Figure 8.24); during thermal cycling, however, the weight gain of the Hf-doped and undoped alloys is much higher than the weight gain of the Zr-doped and Y-doped alloys. The isothermal growth rate is determined with SEM, away from the carbides, so extra oxide formation near the carbides, though observed with SEM, is not taken into account for the thickness determination. The crackingmechanism involves enhanced oxidation after the cracking has occurred, so that is not relevant for isothermal oxidation. So this difference between isothermal and cyclic oxidation experiments for the Hf-doped and undoped alloys is explained.

An alternative cause for the high initial weight gain can be that the Cr is less 'active' as it is bonded by carbon. The Cr alters the oxidation process and may possibly improve adhesion. However, the weight gain of the undoped sample during the first cycles is not only higher than the weight gain of the Zr-doped and Y-doped alloys, but also higher than expected from literature for NiAl without Cr (Table 8.9). Therefore the more plausible explanation is enhanced oxidation near the carbides or cracking of the oxide due to the presence of carbides.

## 8.7.2 Comparison with literature

Compared to literature, the cyclic oxidation behaviour of the undoped model coating alloy is rather poor (Table 8.9): the delamination starts quickly and the initial weight gain is very high.

	Current experiment	Literature				
Onset of weight loss after	80 cycles (45 minutes at	180 cycles (one hour at 1373 K				
	1373 K per cycle)	per cycle, 50 at.% Al) [106]				
		200 or 250 cycles (cycles of one				
		hour, 46.6 at% Al) [107]				
Weight gain after 40 hour at	4.5	0.5 [106]				
1373 K (mg/cm <sup>2</sup> )						
$k_p (g^2/cm^4s)$	1.5E-10 (determined from	7.5E-13 (41.8 at.% Al, [109])				
	the weight gain after 5 to 40	2.5E-13 (46.6 at.% Al, [107])				
	cycles)	3.9E-13 (46.6 at.% Al, [107])				

Table 8.9: Performance during cyclic testing at 1373 K of the undoped model coating alloy

The performance during thermal cycling of the Y-doped model coating alloy is much better than the performance of the undoped and Hf-doped alloy. The weight increases monotonically at a slow rate. The growth rate constant  $k_p$  is about equal to the  $k_p$  for undoped Al-rich NiAl tabulated in Table 8.9. The weight gain is even lower than found in literature (Table 8.10).

	Current experiment	Literature				
Onset of weight loss after	>1090 cycles (monotonically	>1000 cycles of one hour at 1373				
	increasing, onset of weight loss	K, 49.9 at.% Al 0.2 at.%Y) [106]				
	not observed during	(monotonically increasing; onset				
	experiment)	of weight loss not observed during				
	· ·	experiment)				
Weight gain after 200 hour	0.7 (after 267 cycles)	1.0 (after 200 cycles) [106]				
$(mg/cm^2)$		•				
Weight gain after 800 hour	1.0 (after 1067 cycles)	1.7 (after 800 cycles) [106]				
$(mg/cm^2)$						
$k_p$ (g <sup>2</sup> /cm <sup>4</sup> s)	2.0E-13 (best sample)					
	4.4E-13 (sample with porosity)	· ·				

Fable 8.10: Performance during cyclic testing of the Y-doped model coating alloy at	1373	5]	K
---	------	----	---

The cyclic growth rate found for the Zr-doped model coating alloy is in the range of growth rates found for comparable growth rates found in literature (Table 8.11). The weight increases monotonically at a slow rate (slightly higher rate than for the Y-doped alloy).

# Table 8.11: Performance during cyclic testing of the Zr-doped model coating alloy (sample without large porosity) at 1373 K

	Current experiment	Literature				
Onset of weight loss after	>1090 cycles	>3000 cycles (monotonically				
	(monotonically increasing)	increasing),				
		cycles of one hour at 1373 K, both				
		48.3at.% Al, 0.1at.% Zr and				
		38.1at.% Al, 0.1at.% Zr [107]				
Weight gain after 800 hour	1.7 (after 1067 cycles)	1.1 (48.3 Al, 0.1 Zr)				
at 1373 K (mg/ cm <sup>2</sup> )	(38 Al, 3.9 Cr, 0.3 at% Zr)	1.8 (38.1 Al, 0.1 Zr)				
		(after 800 cycles) [107]				
$k_p (g^2/cm^4s)$	9.8E-13	5.6E-13 (48.3 Al, 0.1 Zr)				
		1.4E-12 (38.1 Al, 0.1 Zr)				
		(taken from first 100 cycles) [107]				

The isothermal rate constant  $k_p$  determined in this study by SEM thickness-measurement is 2.5E-13 g<sup>2</sup>/cm<sup>4</sup>s. This is lower than the cyclic rate constant of 9.8E-13 g<sup>2</sup>/cm<sup>4</sup>s. This difference is due to the way the thickness is determined and possibly to pores: the pegs were ignored during SEM-thickness determination, and due to pores the oxidising area (causing weight gain) is higher than the nominal area. The thickness of the oxide formed during thermal cycling will be measured during future research [113]. This will ease comparison.

Due to the carbide formation the Hf-doped model coating alloy has a poor performance. An improved Hf-doped model coating alloy will be tested in future work. Comparison with literature data will be included in that work, therefore no literature data on the cyclic parabolic growth constant of the oxide on Hf-doped NiAl are presented here.

## 8.7.3 Photographic images

On the undoped samples, after the first oxidation cycles photographic images show grey areas. Between these grey areas, areas with yellow and brown speckles are present (Figure 8.37a). The yellow and brown speckled regions show a radial pattern resembling the grain structure of the underlying alloy. In the yellow and the brown regions, either the oxide thickness or surface roughness differs from the grey area or the oxide has delaminated.

After 40 cycles, the oxide roughens. After 100 cycles, between large oxide areas, channels are present where the oxide is thinner or absent (Figure 8.37b). Some channels have the yellow-brown structure. The large areas of oxide shrink and sometimes completely disappear (due to delamination) during further cycling. The area exposed after delamination re-oxidises.





The oxide on the Y-doped model coating alloy is at first uniformly coloured, with a very pronounced radial pattern due to the substrate grain orientations, similar to the Zr-doped alloy (Figure 8.39a). After about 50 cycles, yellow-brown speckled areas develop on some grains. The brown areas of these yellow-brown speckled areas grow (Figure 8.38a). Finally, after about 420 cycles, the entire surface is brown. The substrate grain orientation is no longer visible. On the brown oxide, some yellow spots are present. These spots are no longer present at the same place in the following image. Instead, yellow spots are seen at other points. The size of the light spots increases with increasing number of cycles. These spots are possibly due to delamination. If this is the case, then the actual oxidation rate is slightly higher than the oxidation rate determined from the weight gain, as the weight gain depends on the net effect resulting from oxidation and delamination. Alternative causes for the light spots are differences in surface roughness, or delamination debris (from the sample itself or from other samples).



Figure 8.38: Surface of Y-doped alloy after a: 80 cycles, brown specied spots grow; b: 1090 cycles

The oxide on the Zr-doped alloy is uniformly coloured, with some radial pattern due to the substrate grain orientation (Figure 8.39a). Small yellow spots are present, like on the Y-doped alloy. Also some larger, bright grey spots are seen. The size of the yellow spots increases during oxidation, but even after 1090 cycles the total area fraction of the yellow spots is still quite low (Figure 8.39b). The spots are smaller than on the Y-doped sample. Above 1000 cycles, the surface roughens (Figure 8.39b). This roughness is due either to more rapid oxidation or to a different oxide surface roughness above one grain in the alloy relative to another.



Figure 8.39: Surface of Zr-doped sample after a: 140 and b: 1090 cycles

For the Hf-doped model coating alloy after the first cycles, grey and brown radial areas are seen. There are more brown areas than on the undoped alloy (Figure 8.37a). In the brown areas, less yellow spots are present than in the undoped alloy.

A crumbly oxide structure is seen after 140 cycles (Figure 8.40a). This structure is related to delamination of moderately large pieces of oxide. After 600 cycles, the oxide surface on the Hf-doped model coating alloy is rough (Figure 8.40b). The oxide develops into many small islands that are smaller than those on the undoped alloy (cf. Figure 8.40b and Figure 8.37b).



Figure 8.40: Surface of Hf-doped alloy after a: 140 cycles; b: 600 cycles

# 9 Discussion

In this chapter the effect of the reactive elements on growth and adhesion of the oxide layer is discussed. The mechanisms by which the RE can affect the oxidation and the adhesion presented in section 2.4 are reviewed in the light of the observations and calculations of this study. The calculations and observations not directly linked to one of the nine mechanisms are discussed in the subsequent sections.

## 9.1 Possible mechanism for the RE-effect

#### Heterogeneous nucleation of the oxide

The thickness observed after short oxidation times on the alloys studied do not differ much. Differences in the oxide thickness would be expected if this mechanism is an important effect of the RE-addition. As  $\beta$ -NiAl is rich in Al, (transient) alumina-nucleation is a very fast process. The oxide layer is closed already after 30 minutes of oxidation at 1373 K in 20 vol-% O.

#### Enhancement of α-Al<sub>2</sub>O<sub>3</sub> nucleation

Enhancing the  $\theta$  to  $\alpha$  transformation by providing more nucleation sites should result in smaller  $\alpha$ alumina grains. In future research the oxide grain size may be studied.

 $\theta$ -alumina is present after up to 4 hrs oxidation on the undoped alloy, after 0.5 and 2 hours on the Y-doped alloy, after 0.5 hour on the Zr-doped alloy (very strong peak) and after 0.5 and 1 hour on the Hf-doped alloy, respectively. It appears that the Zr promotes the formation of  $\theta$ -alumina, but also promotes the transformation of  $\theta$ -alumina to  $\alpha$ -alumina. Y and Hf also promote this transition. TEM-imaging will be done anyway, to locate the exact position of the RE-ions in the oxide. This TEM-imaging will also provide supporting evidence on the kinetics of the  $\theta$  to  $\alpha$  transformation.

#### **Reducing cation outward transport**

Grain boundary diffusion is the dominant mechanism for scale growth [114]. If Zr lowers the cation and/or anion transport along the grain boundaries, it is expected to be located at the oxide grain boundaries. Pint (section 2.6) observed Zr located at the oxide grain boundaries. In the current study, apart from the localised oxidation spots and the large Zr-rich oxide grains, also some small Zr-rich oxide grains were observed in the oxide (section 8.4.3). Zr-enrichment of the oxide grain boundaries was not investigated.

Oxygen-anions can easily diffuse through  $ZrO_2$  [115], which is in agreement with the observation that the oxide layer is thicker (the oxide/alloy interface is deflected into the alloy) near Zr-rich oxide grains (Figure 8.21 and Figure 8.22a).

After oxidation for longer than 4 hours on the Zr-doped alloy ridges develop. As these ridges were not present on the sample oxidised for 4 hours, some outward cation transport still occurs.

On the Y-doped sample, a larger effect of the RE on the surface morphology was observed than on the other alloys: the needles were much smaller than on the undoped, Zr-doped and Hf-doped model coating alloy. This proves that Y reduces cation outward transport. This reduction of cation outward transport may be linked with an enhancement of the  $\theta$  to  $\alpha$  transformation. The changes in surface morphology with oxidation time prove that some outward cation transport through the oxide scale still takes place on the Y-doped alloy.

Due to the reduction of outward transport, fewer voids are present at the oxide/alloy interface (section 8.4), the oxide/alloy interface is less flat (observed on the Y-doped and Zr-doped alloy) and the growth rate of the oxide is lower.

The isothermal oxide growth rate on the Zr-doped alloy is determined to be 7.1E-06  $\pm$  1.0E-06  $\mu$ m<sup>2</sup>/s (SEM thickness measurement). This corresponds with a parabolic weight change rate  $k_p$  of 2.5E-13  $\pm$  0.3E-13 g<sup>2</sup>/cm<sup>4</sup>s. It is in the range expected from literature data. This growth rate is lower than the growth rate of oxide usually reported in literature for undoped material. During thermal cycling, the growth rate of the oxide on the Y-doped alloy (2.0E-13 g<sup>2</sup>/cm<sup>4</sup>s) is lower than the growth rate of the oxide on the Zr-doped alloy (9.8E-13 g<sup>2</sup>/cm<sup>4</sup>s), indicating that transport through the oxide scale on the Y-doped alloy is slowest.

#### **Enhanced scale plasticity**

Enhanced scale plasticity depends among other things on the oxide grain size. The oxide grains at the gas/oxide interface on the yttrium-doped sample seem to be smaller than on the undoped alloy (after 64 hours of oxidation 0.3  $\mu$ m compared to 0.4  $\mu$ m). A smaller grain size promotes oxide scale plasticity, and thereby the adhesion of the oxide. The grain size determination at the surface is not yet enough evidence to conclude that the average grain size is smaller, as it is not certain that the trend in the bulk grain size is the same as the trend at the surface. Grain size determinations on cross-sectioned oxide layers (TEM or back-scattered electron imaging) may provide conclusive evidence.

#### **Graded seal formation**

This research does not provide definite conclusions on the proposed 'graded seal formation'. The RE-oxide, which in this mechanism is supposed to be present at the oxide/alloy interface, is not observed in cross sections. If present at all, this layer is thin ( $<0.02 \mu m$ ).

#### **Oxide pegging**

As far as oxide pegging is concerned, large pegs are not expected to improve the adherence, as stress concentration will result in cracking through the oxide near the pegs. Small pegs (up to a micron) may enhance the adhesion.

#### Vacancy sink provision

Voids were observed, indicating that sinks did not annihilate all vacancies. Fewer voids were observed on the Y-doped and Zr-doped alloy (section 8.4). The dominant factor causing this difference in void density is probably not vacancy sink provision due to the RE, but a change in the growth direction of the oxide (reduction of the outward cation transport).

#### Chemical bonding and crystallographic orientation energy effects

The macroscopic atom model calculations (chapter 3) on the work of adhesion indicate that adhesion ( $W^{ad}$ ) between a RE-oxide and the metal is strongest for ZrO<sub>2</sub> on NiAl and lowest for Y<sub>2</sub>O<sub>3</sub> on NiAl (Figure 9.1).

An important observation is that the work of adhesion for  $Al_2O_3$  on NiAl is not much lower than the work of adhesion for  $ZrO_2$  / NiAl or much higher than the work of adhesion for  $Y_2O_3$  / NiAl. Therefore, it is concluded that if the RE is present as oxide, the reactive element effect (enhanced adhesion) is not primarily attributable to an enhancement of the chemical binding across the oxide/metal interface. One or more of the other mechanisms are more important.



# Figure 9.1: The work of adhesion $(W^{ad})$ for different oxides on NiAl, increasing from left to right

The reactive elements have a high affinity for oxygen, so it is not expected that they are present as metallic atoms. If, however, the state in which the RE is present at the interface is best modelled as metallic, the presence of RE increases the adhesion for all the RE considered. In this case, if the enhancement of chemical bonding is the dominant mechanism, the bonding between the metal and the oxide on Hf-doped and Zr-doped NiAl is better ( $W^{ad} \approx 6.9 \text{ J/m}^2$ ) than the bonding on Y-doped NiAl ( $W^{ad} = 6.25 \text{ J/m}^2$ , Table 3.8).

#### Sulphur scavenging

Evidence supporting the 'sulphur scavenging' mechanism is found, as with the macroscopic atom model it is proven that the work of adhesion of a  $Al_2O_3$  / S interface is very low (table 3.8). To make the experimental work more decisive on the 'sulphur scavenging' mechanism, annealing in a mixture of hydrogen and argon (instead of just argon, section 7.1) may be advisable. This annealing may lower the amount of sulphur in the model coating alloy, thereby excluding the 'sulphur scavenging' mechanism, allowing more precise conclusions about the other RE effects on adhesion.

## 9.2 Scale failure

By far the largest driving force for the scale failure is the strain caused by the difference in thermal expansion (shrink) between NiAl and  $Al_2O_3$  upon cooling from the oxidation temperature. The expected stress and strain due to thermal expansion mismatch are large enough to meet the propagation criterion. The most important factor determining whether buckling initiation can occur is the radius of a non-adherent part of the oxide/alloy interface. Such non-adherent regions can be due to voids. Based on the observations on the voids under the oxide and on the observations on the oxide failure planes, buckling is concluded to be the dominant failure mechanism for the oxide layer on the Hf-doped alloy used in the current study, at short oxidation times. On the Hf-doped alloys, many voids were present at the oxide/alloy interface. Buckling initiation occurs at these voids, probably assisted by some out of plane component of the stress.

Buckling indicates that the oxide/alloy interface is the weakest. Therefore it is hoped that further research will lead to stronger interfaces where wedging will become the dominant failure mechanism (the wedging initiation stress depends on inherent properties of the alumina). On the alloys to be used in the continuation of this research, fewer voids were observed after oxidation [116]. This is thought to be due to the absence of carbon, so more Cr and RE is available to enhance the oxidation properties.

It is observed that the void density depends on the grain orientation: some grains show more voids than others, as can be expected from the mechanism causing these voids presented by Brumm and Grabke (section 2.2).

## 9.3 Refinements for modelling of the work of adhesion

The calculations in chapter 4 involved averaging over all crystallographic orientations in the oxide and in the NiAl. A next step is to refine the model by taking the crystallographic orientations into account. Then the strain energy resulting from crystallographic mismatch between planes in the oxide and planes in the NiAl can be taken into account. This will lower the calculated works of adhesion, bringing them more in the range of the works of adhesion calculated with first principle calculations and the range measured with sessile-drop and contact angle measurements (table 4.3). Further, taking into account the crystallographic orientations will slightly change the calculated chemical interaction energy.

If the strain energy resulting from crystallographic mismatch is of the same magnitude for the various oxides (Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, YAG, YAP, ZrO<sub>2</sub>, HfO<sub>2</sub>), it will not change the order presented in Figure 9.1.

In chapter 4 from  $\Delta H_{O \text{ in } Ni}^{\text{interface}}$ ,  $\Delta H_{O \text{ in } Al}^{\text{interface}}$ ,  $\Delta H_{RE \text{ in } Ni}^{\text{interface}}$  and  $\Delta H_{RE \text{ in } Al}^{\text{interface}}$  the chemical interaction energy per unit area is calculated using the area needed to store one mole of anions and the area needed to store one mole of RE-cations (table 4.1). The calculation 'looks from the oxide to the metal'. In principle, a calculation 'looking from the metal to the oxide' using  $\Delta H_{Ni \text{ in } O}^{\text{interface}}$ ,  $\Delta H_{Al \text{ in } O}^{\text{interface}}$ ,  $\Delta H_{Ni \text{ in } RE}^{\text{interface}}$ ,  $\Delta H_{Al \text{ in } RE}^{\text{interface}}$ ,  $\Lambda H_{Al \text{ in } RE}^{\text{interface}}$ ,  $\Lambda H_{Al \text{ in } RE}^{2/3}$  should result in the same interaction energy per unit area.

For instance the interaction energy between Ni in the alloy and O in the oxide is

$$(C_{Ni}^{S})_{\text{int}} \frac{\Delta H_{OinNi}^{\infty}}{C_{0}V_{O}^{2/3} + \frac{2}{3}C_{0}V_{Al_{ox}}^{2/3}} \equiv (C_{O}^{S})_{ox} \frac{\Delta H_{Ni}^{\text{interface}}}{C_{0}V_{Ni}^{2/3} + \frac{C_{AI}}{C_{Ni}}C_{0}V_{Al_{met}}^{2/3}}$$

In practice however, the left-hand and right-hand sides are not equal. Therefore a refinement of the model is advisable.

In the calculation 'looking from the oxide to the metal' used in this study, the effect of a less closely packed oxide crystal structure is most probably best taken into account: if less cations and anions are present at the oxide/metal interface, the chemical interaction energy per unit area is lower.

A model 'looking from the metal to the oxide' is insensitive to a change in the packing density of the oxide. It is only sensitive to a change in the respective surface fractions of the ions present in the oxide. So a change in the packing density of the oxide causes divergence of the values found with the respective approaches. It would be nice if the refinement would overcome this divergence.

## 9.4 Solubility and segregation

The solubility of Zr in NiAl (1.4 at.% at 1073 K) is slightly higher than the solubility of Hf (1.1 at.%) and much higher than the solubility of Y (nearly insoluble in NiAl). This ranking of the solubility of the three RE used in this study is from [117], as the solubility calculations based on the macroscopic atom model (though very interesting) did not have the appropriate precision, see section 5.5.

Due to these differences in solubility, there is a large chance that Y is present as  $Ni_xAl_yY_z$ precipitates at the grain boundaries. As diffusion through grain boundaries is faster than through bulk material, segregation of Y may be faster than segregation of Hf and Zr. A large alloy grain size results in a poor distribution of insoluble RE, therefore in the case of an insoluble RE a small alloy grain size is preferred.

For a RE with a higher solubility the kinetics of the diffusion process may decrease the surface segregation rate, especially at lower temperature. For a RE with a higher solubility a small grain size of the alloy is also preferable, but in this case this parameter is less critical.

Using the macroscopic atom model, it is shown (chapter 6) that at room temperature a large driving force for segregation of RE to an oxide/NiAl interface is present for the three RE's considered. The driving force is largest for Hf. The driving force for exchange of RE atoms on the Ni-sublattice is larger than the driving force for exchange on the Al-sublattice.

If the strain energy associated with RE (especially Y) on the Ni-sublattice in NiAl is underestimated (section 5.5), the driving force for segregation on the Ni-sublattice is underestimated also.

A driving force exists for an Y-atom dissolved in NiAl (at a Ni-site) to change place with a Niatom at the NiAl surface in contact with vacuum (segregation to the surface). A large contribution to this driving force is due to the release of elastic strain energy (a RE atom is larger than the atom it replaces in the NiAl lattice). As the bulk modulus of the RE and the shear modulus decrease with temperature, at 1373 K this driving force will be small or even absent. For Zr and Hf in NiAl, and for Y on the Al-sublattice, no driving force for surface segregation under vacuum is present. When Y is present as Y-rich particles  $Ni_xAl_yY_z$  at the  $\beta$ -NiAl grain boundaries, the diffusion to the surface can be very fast as such particles are mostly located at grain boundaries. When such Y-rich particles are under severe compression, or have a large circumferential surface compared to their volume, segregation of Y from these particles to the surface is very likely.

#### 9.5 Isothermal oxidation

The carbon present especially in the Hf-doped and undoped alloy causes poor performance. Some results are more difficult to interpret and to compare with literature, due to the carbon.

During oxidation for up to several hours some Ni<sub>3</sub>Al forms, especially on the undoped, and to a lesser extent on the Hf-doped alloy. On the Y and Zr-doped alloys some Ni<sub>3</sub>Al also forms during the initial oxidation. When the oxide growth rate decreases, which happens during further growth, the Ni<sub>3</sub>Al can transform to NiAl again due to diffusion in the alloy.

The RE oxidises. On the Y-doped, Zr-doped and Hf-doped sample  $Y_2O_3$ , ZrO<sub>2</sub> and HfO<sub>2</sub> are formed, respectively. On the Y-doped sample also YAl-oxides are formed. No mixed ZrAl-oxide or HfAl-oxide are formed.

The surface morphology is strongly dependent on the orientation of the underlying grain.

Two theories exist to explain the platelet and needle morphology. One argues that the large number of oxide nuclei and the mismatch between the metal and the oxide (not the thermal mismatch, but the lattice mismatch) results in the platelet and needle structure. Another explanation is that within the needle a fast cation outward diffusion path is present. In section 2.1.1 observations of a twinned plane within transient alumina needles are discussed. A combination of both proposed mechanisms can also be responsible for the morphology.

After some time, the needles disappear for all alloys. This is either due to some outward diffusion still taking place, or due to surface diffusion from the top of the needles to the lower 'valleys'. If surface diffusion is the cause, an explanation is necessary for the fact that on undoped alloy the needles still exist after 4 hrs, while on the Hf-doped alloy after 4 hrs much flattening has occurred. If some outward diffusion is the cause for the flattening of the platelets, the flattening of the oxide should be due to filling of all the free space between the platelets, resulting in a thickness increase that is expected to be larger than measured. For instance the thickness on the Hf-doped alloy does not increase much between 0.5 and 2 hours of oxidation.

After long oxidation times, on the undoped model coating alloy huge oxide intrusions into the substrate are observed.  $\gamma$ '-Ni<sub>3</sub>Al formation is also seen. The intrusions have to be caused by inward transport through the oxide. For undoped NiAl, usually outward transport through the oxide is more important than inward transport. Probable causes for the large contribution of inward transport are:

- More carbides were present on the undoped alloy compared to the Y- and Zr-doped alloy, and the carbides present were richer in carbon. The boundary between the chromium carbides and the NiAl, or the remains of partly oxidised or evaporated chromiumcarbides, provides a fast diffusion path for oxygen inward transport.
- The inward oxygen transport is probably assisted by porosities in the  $\beta$ -NiAl due to the casting process.
- Oxide intrusion formation causes  $\beta$ -NiAl to  $\gamma'$ -Ni<sub>3</sub>Al transformation, which has a volume effect that assists further inward growth: the volume of 3 mole equiatomic NiAl (3 mole Ni and 3 mole Al in total) is about 43.6 cm<sup>3</sup> [118], one mole of  $\gamma'$ -Ni<sub>3</sub>Al has a volume of 27.5 cm<sup>3</sup> [119]. As 3 NiAl + 1.5 O<sub>2</sub>  $\rightarrow$  1 Ni<sub>3</sub>Al + 1 Al<sub>2</sub>O<sub>3</sub>, withdrawal of one mole Al from the alloy results in a volume decrease of about 16 cm<sup>3</sup> if the alloy transforms from  $\beta$ -NiAl to  $\gamma'$ -Ni<sub>3</sub>Al.

The volume of one mole  $Al_2O_3$  is about 25.6 cm<sup>3</sup> [120]. The newly formed oxide does not fit in the 16 cm<sup>3</sup> discussed above, so outward transport of cations or deformation of the alloy is necessary for further oxide intrusion growth. If the calculations are based on non-stoichiometric NiAl and Ni<sub>3</sub>Al, the newly formed oxide still does not fit in the 16 cm<sup>3</sup> (3 mole of Ni<sub>1.2</sub>Al<sub>0.8</sub> has a volume of 43.1 cm<sup>3</sup> [121], if it transforms to Ni3Al the volume reduction is 10 cm<sup>3</sup>, the 0.6 mole  $Al_2O_3$  formed has a volume of 15 cm<sup>3</sup>).

The oxide intrusions result in an inhomogeneous stress-distribution that causes the island-like pattern of dense oxide, surrounded by delaminated areas and porous oxide (Figure 8.27).

On the duplicate sample oxidised for 256 hours, no oxide intrusions and no  $Ni_3Al$  formed. It is thought that variations in porosity, composition (some Si detected, section 8.3.1) and microstructure over the length of the cast cilindrical rods are the cause for the poor reproducibility: on the duplicate sample probably less carbides and pores were present. Variations in carbon content over the length of the rod are probable, as the presence of the carbon originates from the crucibles used during the casting process.

No oxide intrusions were formed on the Y-doped and Zr-doped samples, as on the Y-doped and Zrdoped samples fewer carbides were present (appendix A), and the carbides present were poorer in carbon. An extra reason may be that the Y-doped and Zr-doped samples were less porous.

## 9.6 Thermal cycling

Based on the weight gain (Figure 8.36) the sequence from poor to good cyclic oxidation properties (which indicates the performance in practical applications) is: Undoped, Hf-doped, Zr-doped, Y-doped alloy.

The oxidation rate of the Hf-doped and undoped model coating alloy during cyclic oxidation is very high, higher than expected from literature (section 8.7.1). This is most probably due to cracking of the oxide due to the carbides present, or enhanced oxidation near the carbides. On the Hf-doped alloy, the oxide adheres much better to the alloy. The delamination behaviour is totally different from the delamination behaviour on the undoped alloy (cf. Figure 8.37, Figure 8.40).

The cyclic oxidation performance of the Y-doped and Zr-doped alloy is very good as no onset of weight loss occurred and the parabolic growth rates are low. The growth rate of the oxide on the Y-doped alloy is lower than the growth rate of the oxide on the Zr-doped alloy.

During cyclic oxidation, on the Zr-doped model-coating alloy no severe delamination is observed. The oxide surface shows roughening. The roughening is in the same form of reflects the grain structure of the alloy. This roughness is due either to more rapid oxidation or to a different oxide surface roughness above one grain in the alloy relative to another.

The Y-doped alloy did not show this roughening, but did show the development and disappearance of a pattern of speckles. Most probably the variation between the oxide thickness and roughness on different alloy grains after about 1000 cycles is less on the Y-doped alloy than on the Zr-doped sample. If anything interesting is found on SEM-images of the cross-section of the samples this will be published later [122].

# **10 Conclusion**

The discussion (chapter 9) of the preceding chapters leads to the following conclusion on the mechanisms by which the reactive element has effect on growth and adhesion of the oxide layer:

- The reactive element enhances the  $\theta$  to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> transformation. The  $\theta$ -alumina transforms faster into  $\alpha$ -alumina on the RE-doped samples.
- The reactive element Zr and especially Y reduce cation outward transport as can be seen from the low growth rates. The growth rate of the oxide on the Zr-doped alloy during isothermal oxidation is  $7.1E-06 \pm 1.0E-06 \ \mu m^2/s$ , which corresponds with a parabolic growth rate constant  $k_p$  of  $2.5E-13 \pm 0.3E-13 \ g^2/cm^4s$ . This is lower than the growth rate usually reported in literature for undoped material.

The growth rate on the Y-doped alloy is lower than the growth rate on the Zr-doped alloy (thermal cycling: on the Y-doped alloy  $k_p = 2.0\text{E}-13 \text{ g}^2/\text{cm}^4\text{s}$ ; on the Zr-doped alloy  $k_p = 9.8\text{E}-13 \text{ g}^2/\text{cm}^4\text{s}$ ), indicating that transport through the oxide scale on the Y-doped alloy is slowest. Also the difference between the oxide surface morphology on the Y-doped and the undoped alloy is larger than the difference between the oxide surface morphology on the Zr-doped and the undoped and the undoped alloy. This indicates that Y probably has a larger influence on outward transport than Zr.

Some outward transport still occurs as can be seen from the changes in surface morphology during oxidation.

Oxygen transport through  $ZrO_2$  particles is fast as indicated by the deflection of the oxide/alloy interface into the alloy near Zr-rich oxide grains (the oxide is thicker).

- Fewer voids are present at the oxide/alloy interface for the doped alloys due to the reduction of outward transport. The change of growth direction also causes the oxide/alloy interface to be less flat on the Y-doped and Zr-doped alloy.
- Voids were observed, indicating that sinks did not annihilate all vacancies ('vacancy sink provision'-mechanism). Fewer voids were observed on the Y-doped and Zr-doped alloy (section 8.4). This difference in void density is probably for the greater part not due to vacancy sink provision, but due to a change in the growth direction of the oxide (reduction of the outward cation transport).
- Calculations indicate that the work of adhesion W<sup>ad</sup> between a RE-oxide and the alloy is strongest for ZrO<sub>2</sub> on NiAl and lowest for Y<sub>2</sub>O<sub>3</sub> on NiAl.
   The work of adhesion for Al<sub>2</sub>O<sub>3</sub> on NiAl is not much lower than the work of adhesion for ZrO<sub>2</sub> / NiAl or much higher than the work of adhesion for Y<sub>2</sub>O<sub>3</sub> / NiAl. Therefore, if the RE is

present as oxide, the enhanced adhesion is not primarily attributable to an enhancement of the chemical binding across the oxide/metal interface. One or more of the other mechanisms are more important!

The reactive elements have a high affinity for oxygen, so it is not expected that they are present as metallic atoms. If, however, the state in which the RE is present at the interface is best modelled as metallic, the presence of RE increases the adhesion for all the RE considered. In this case, and if the enhancement of chemical bonding is the dominant mechanism, the bonding on Hf-doped NiAl will be better than the bonding on Y-doped NiAl.

It is proven that the work of adhesion of a  $Al_2O_3$  / S interface is very low. If sulphur is present in the alloy, the 'sulphur scavenging' mechanism influences the adhesion.

By far the largest driving force for the scale failure is the strain caused by the difference in thermal expansion (shrink) between NiAl and  $Al_2O_3$  upon cooling from the oxidation temperature. The expected stress and strain due to thermal expansion mismatch are large enough to meet the propagation criterion for scale failure. The most important factor determining whether buckling initiation can occur is the radius of a non-adherent part of the oxide/alloy interface. Such non-adherent regions can be due to voids.

Buckling is concluded to be the dominant mechanism for the Hf-doped alloy at short oxidation times, indicating that the oxide/alloy interface is weak. It is shown that on the Hf-doped alloys, many voids were present. Buckling initiation occurs at these voids, probably assisted by some out of plane component of the stress.

The void density at the oxide/alloy interface and the oxide surface morphology are strongly dependent on the orientation of the underlying grain.

At room temperature a large driving force for segregation of RE to an oxide/NiAl interface is present for the three RE's considered. The driving force is largest for Hf. The driving force for exchange of RE atoms on the Ni-sublattice is larger than the driving force for exchange on the Al-sublattice.

A driving force exists for an Y-atom dissolved in NiAl (at a Ni-site) to change place with a Niatom at the NiAl surface in contact with vacuum (segregation to the surface). A large contribution to this driving force is due to the release of elastic strain energy (a RE atom is larger than the atom it replaces in the NiAl lattice). As the bulk modulus of the RE and the shear modulus decrease with increasing temperature, at 1373 K this driving force will be small or even absent. For Zr and Hf in

NiAl, and for Y on the Al-sublattice, no driving force for surface segregation under vacuum is present.

When Y is present as Y-rich particles  $Ni_xAl_yY_z$  at the  $\beta$ -NiAl grain boundaries, the diffusion to the surface may be very fast as such particles are mostly located at grain boundaries.

Carbon present in NiAlCr causes poor performance. Both the oxidation and the adhesion behaviour are deteriorated. The carbon is also an important cause for the large oxide intrusions found on some undoped alloys after longer oxidation times.

Ni<sub>3</sub>Al forms and may react back to form NiAl again. During fast initial oxidation, the diffusion of Al (from the bulk of the alloy to the surface) or Ni (from the surface to the bulk) in NiAl cannot keep up with the rate by which Al is consumed in the oxidation process. When the oxide growth rate decreases, which happens during further growth, the Ni<sub>3</sub>Al can transform to NiAl again due to diffusion in the alloy.

11

The RE oxidises. On the Y-doped, Zr-doped and Hf-doped sample  $Y_2O_3$ ,  $ZrO_2$  and  $HfO_2$  are formed, respectively. On the Y-doped sample also YAl-oxides are formed. No mixed ZrAl-oxide or HfAl-oxide are formed.

The performance in practical applications for the alloys studied is (from poor to good): Undoped, Hf-doped, Zr-doped, Y-doped alloy. The cyclic oxidation performance of the Y-doped and Zr-doped alloy is very good as no onset of weight loss occurred and the parabolic growth rates are low. The growth rate of the oxide on the Y-doped alloy is lower than the growth rate of the oxide on the Zr-doped alloy.

## References

## 1 Introduction

- D.D. Hass, Directed Vapor Deposition of Thermal Barrier Coatings, Ph.D. Dissertation,
   University of Virginia 2000, www.ipm.virginia.edu/research/PVD/Pubs/thesis6/home.html
- [2] M. Peters, C. Leyens, U. Schultz, W.A. Kaysser, Adv Eng Mat 3 (2001) <u>4</u> 193-204
- [3] S.R.J. Saunders, J.R. Nicholls in R.W. Cahn, P. Haasen, *Physical Metallurgy*, Vol 2, 4<sup>th</sup> edition, Elsevier Science, Amsterdam 1996
- [4] J. Doychak Oxidation Behavior of High-Temperature Intermetallics, in J.H. Westbrook,
   R.L. Fleisher, Intermetallic compounds, vol 1, John Wiley & Sons 1994
- [5] H. Kranenburg *Thermal barrier coating systems in turbine engines, impact on sustainability* Delft 2002
- [6] J.E. Penner, D.H. Lister, D.J. Griggs, D.J. Dokken. M. McFarland (IPCC), Aviation and the Global Atmosphere, Cambridge University Press, 1999, <u>http://www.grida.no/climate/ipcc/aviation/index.htm</u>

## 2 Oxidation of $\beta$ -NiAl and the reactive element effect

- J. Doychak Oxidation Behavior of High-Temperature Intermetallics, in J.H. Westbrook,
   R.L. Fleisher, Intermetallic compounds, vol 1, John Wiley & Sons 1994
- [8] J.C. Yang, E. Schumann, I. Levin, M. Rühle, Acta Mater 46 (1998) 6 2195-2201
- [9] J.Doychak, J.L. Smialek, T.E. Mitchell, *Metall Trans* A 20A, (1989) 499-518
- [10] V.K. Tolpygo, D.R. Clarke Microscopy of oxidation 4 (1999), 59-70
- [11] E. Schumann, J.C. Yang, M.J.Graham, M.Rühle, in Grabke, Schütze, Oxidation of Intermetallics, Wiley VCH 1998 (Ch 8)
- [12] B.A. Pint, Oxid of Met 48 (1997) <u>3/4</u> 303-328
- [13] R. Prescott, D.F. Mitchell, M.J. Graham, Symp Microscopy of Oxidation 2 (1993), 455-462
- [14] J. Jedlinski, in *The role of active elements in the oxidation behaviour of high temperature* metals and alloys (ed: E. Lang), Elsevier applied Science, London-New York 1989, p 131
- [15] B. Pieraggi, Oxid of Met 27 (1987) <u>3/4</u> 177-185
- [16] J.R. Kirkaldy, D.J. Young, Diffusion in the condensed state, London 1987
- [17] P. Kofstad *High Temperature Corrosion*, Elsevier London 1988
- [18] M.W. Brumm, H.J. Grabke, Corros Sci 34 (1993) 547
- [19] J.L. Smialek, R. Browning, *Proc symp on high temp mat chem III* (ed: Z.A. Munir, D. Cubicciotti)
- [20] P. Van Manen, *The Mechanism of the Oxidation of Nickel Aluminium Coating Alloys*, 's-Gravenhage 1991 (Ph.D. Dissertation)
- [21] T. Nijdam, Aluminium Depletion from MCrAlY coatings upon High Temperature Oxidation, Delft 2000
- [22] H.J. Grabke, M.W. Brumm, B. Wagemann, in Grabke, Schütze, Oxidation of Intermetallics, Wiley VCH 1998 (Ch 4)

- [23] H.J. Grabke Intermetallics 7 (1999) 1153-1158
- [24] R. Klumpes, C.H.M. Marée, E. Schramm, J.H.W. de Wit, in Grabke, Schütze, Oxidation of Intermetallics, Wiley VCH 1998 (Ch 6)
- [25] D.P. Moon, Mat Sci and Tech 5 (1989) 754-764
- [26] Y.S.Touloukian, R.K. Kirby, R.E. Taylor, T.Y.R. Lee, *Thermal Expansion Nonmetallic solids*, Plenum New York 1977
- [27] Y.S.Touloukian, R.K. Kirby, R.E. Taylor, T.Y.R. Lee, *Thermal Expansion Metallic elements and alloys*, Plenum New York 1975
- [28] http://www.ceramics.nist.gov/srd/summary/Al2O3.htm, ZrO2m.htm, Y2O3.htm, HfO2.htm
- [29] K. Prüssner, J. Bruley, U.Salzberger, H.Zweygart, E. Schumann, M.Rühle, *symp Microscopy of Oxidation 2* (1993), 435-444
- [30] M.H. Lagrange, A.M. Huntz, J.H. Davidson, Corr Sci 24 (1984) 7 613-627
- [31] S.S. Mrowec, A.Gil, A. Jedlinski, Werkstoffe und Korrosion 38 (1987) 563
- [32] I. Rommerskirchen, V. Kolarik, Mat and corr 47 (1996) 625-630
- [33] A.M. Huntz, The role of active elements in the oxidation behaviour of high temperature metals and alloys (ed: E. Lang), Elsevier applied Science, London-New York 1989 p81
- [34] M.K. Loudjani, A.M. Huntz, R. Cortes, J Mat Sci 28 (1993) 6466-6473
- [35] B.A. Pint, A.J. Garratt-Reed, L.W. Hobbs symp Microscopy of Oxidation 2 (1993) 463-475
- [36] J.L. Smialek, Surf Interf Anal 31 (2001) 582-592
- [37] C.A. Barrett, Oxid of met 30 (1998) 5/6 361
- [38] D.Renush, M. Grimsditch, I. Koshelev, B.W. Veal, P.Y. Hou, Oxid Met 48 (1997) 5/6 471
- [39] I.M. Allam, D.P. Whittle, J.Stringer, Oxid of Met 13 (1979) <u>4</u> 381-401
- [40] B.A. Pint, J.A. Haynes, K.L. More, I.G. Wright, C. Leyens, *Superalloys 2000* (ed: T.M. Pollock e.a.), TMS, 2000

#### **3** Scale failure

- [41] D.M. Lipkin, D.R. Clarke, M. Hollatz, M. Bobeth, W. Pompe, Corr Sci 39 (1997) 2 231
- [42] D.M.Lipkin, D.R. Clarke, Oxid of met 45 (1996) 3/4 267-281
- [43] A.M. Butt On the Reactive Element Effect Delft 2003
- [44] H.E. Evans Int Mat Rev 40 (1995) <u>1</u> 1-40
- [45] C. Sarioglu, M.J. Stiger, J.R. Balchere, R. Janakirman, E. Schumann, A. Ashary,
   F.S. Pettit, G.H. Meier, *Mat and Corr* 51 (2000) 358-372
- [46] A.M. Huntz *Mat Sci and Eng* A 201 (1995) 211-228
- [47] H.E. Evans, R.C. Lobb, Corr Sci 24 (1984) <u>3</u> 209-222
- [48] A.G. Evans, J.W. Hutchinson, Y. Wei, Acta Mater 47 (1999) 15 4093-4113
- [49] J.S. Wang, A.G. Evans, Acta Mater 47 (1999) <u>2</u> 699-710
- [50] H.E. Evans, M.P. Taylor, Surf and coat techn 94-95 (1997) 27-33
- [51] http://www.ceramics.nist.gov/srd/summary/Al2O3.htm
- [52] M.W. Brumm, H.J. Grabke, Corros Sci 34 (1993) <u>4</u> 547

#### 4 Effect of reactive element on work of adhesion

- [53] F.R. De Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, *Cohesion in Metals, transition metal alloys*, North-Holland, Amsterdam 1988
- [54] R. Benedictus, A. Böttger, E.J. Mittemeijer, *Phys Rev B*, 54 (1996) <u>13</u> 9109-9125
- [55] E.A.A. Jarvis, A. Christensen, E.A. Carter, Surf Sci 487 (2001) 55-76
- [56] P. Thompson, D.E. Cox, J.B. Hastings, Journ of Appl Crystall 20 (1987) 79
- [57] ICSD, Fachinformationszentrum Karlsruhe, Germany, <u>http://www.cmbi.kun.nl/</u>, http://www.fiz-karlsruhe.de/fiz/products/icsd/
- [58] R.D. Shannon, Acta Cryst A 32 (1976) 751
- [59] International Center for Diffraction Data (ICDD), Powder Diffraction Files JCPDS 46-1212
- [60] L.P. H. Jeurgens, On the Initial Oxidation of Aluminium in Oxygen Gas, Ph-D thesis, Delft 2001
- [61] L.P.H. Jeurgens, W.G. Sloof, F.D. Tichelaar, E.J. Mittemeijer, Phys Rev B 62 (2000) 7 4707-4719
- [62] M.W. Chase, NIST-JANAF Thermochemical Tables 4th ed. Part I, Al-Co (American Institute of Metals, New York, 1998) p 156-159
- [63] D.M. Duffy, J.H. Harding, A.M. Stoneham, Acta Mater 44 (1996) 3293
- [64] I. Manassidis, M.J. Gillan, J Am Ceram Soc 77 (1994) <u>2</u> 335-338
- [65] J.E. Raynolds, J.R. Smith, G.-L. Zhao, D.J. Srolovitz, Phys Rev B 53 (1996) 20 13883-13890
- [66] A.R. Miedema, Z. Metallkd 69 (1978) 287
- [67] D.M. Lipkin, J.N. Israelachvili, D.R. Clarke Phil Mag A 76 (1997) <u>4</u>715-728
- [68] R.M. Pilliar, J. Nutting, *Phil Mag* 16 (1967) 181
- [69] E.A. Jarvis, E.A. Carter, Comput Sci Eng 4 (2002) <u>2</u> 33-41
- [70] M. Ohring, Materials Science of Thin Films, 2nd edition, Academic press, San Diego 2002
- [71] A. Trampert, F. Ernst, C.P. Flynn, H.F. Fischmeister, M. Rühle, *Acta Metall Mater* (1992) <u>40</u> 227, cited by Finnis
- [72] T. Hong, J.R. Smith, D.J. Srolovitz, J Adhesion Sci Technol 8 (1994) 837, cited by Finnis
- [73] U. Schönberger, O.K. Andersen, M. Methfessel, Acta Metall. Mater 40 (1992) 1, cited by Finnis
- [74] S. Uran, M. Grimsditch, B.W. Veal, A.P. Paulikas, Ox of Met, 56 (2001) 5/6 551
- [75] A. Christensen, E.A. Carter, *Phys Rev B* 62 (2000) <u>24</u> 968-983
- [76] A. Christensen, E.A. Carter, *Phys Rev B* 58 (1998) <u>12</u> 8050-8064
- [77] A.B. Anderson, S.P. Mehandru, J.L. Smialek, J Electrochem Soc 132 (1985) 2 1695
- [78] S. Popovic, G. Stefanic, S. Music, *Mater Lett* 31 (1997) <u>1/2</u> 19-22
- [79] K.-H. Hellwege, A.M. Hellwege (Editors), W. Pies, A. Weiss (Authors) Landolt-Börnstein series, Volume III/7: Crystal Structure Data of Inorganic Compounds, 1975
- [80] A. Nakatsuka, A. Yoshiasa, T. Yamanaka, Acta Crystallographica B 55 (1999) 266-272
- [81] N.L. Ross, Phase Transition 58 (1996) 27-41
- [82] J.L. Smialek, R.Browning, Proc of the sump on high temp mat chem. III, eds: Z.A. Munir,
   D. Cubicciotti (1986) 258-272
- [83] E.A.A. Jarvis, E.A. Carter, J Phys Chem B (2002) 106 7995-8004
- [84] M.W. Finnis J Phys Condens Matter 8 (1996) 5811-5836

#### 5 Solubility of RE in NiAl

- [85] G. Petzow *Ternary Alloys* Weinheim VCH 1992
- [86] I. Barin, Thermochemical Data of Pure Substances, 3rd edition, Weinheim VCH 1995
- [87] Th. B. Massalski, H. Okamoto, PR. Subramanian, L. Kacprzak *Binary Alloy Phase Diagrams*, 2<sup>nd</sup> edition ASM International, 1990
- [88] R.D. Noebe, R.R. Bowman, M.V. Nathal, Int Mat Rev 38 (1993) <u>4</u> 193-232
- [89] F.R. De Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, *Cohesion in metals, transition metal alloys*, North-Holland, Amsterdam 1988
- [90] www.webelements.com
- [91] L.C. Feldman, J.W. Mayer, Fundamentals of Surface and Thin Film Analysis, Prentice-Hall, New Yersey 1986 (Appendix 4)
- [92] D.A. Porter, K.E. Easterling, *Phase Transformations in Metals and Alloys*, 2<sup>nd</sup> edition Chapman&Hall, London 1992
- [93] Y.Song, Z.X. Guo, R. Yang, D. Li, Acta Mater 49 (2001) 1647-1654

### 6 Surface segregation

- [94] F.R. De Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, *Cohesion in metals, transition metal alloys*, North-Holland 1988, Amsterdam
- [95] A.R. Miedema, Z. Metallkd 69 (1978) 455
- [96] R.D. Shannon, Acta Cryst A 32 (1976) 751
- [97] J.L. Smialek, R. Browning *Proc of the symp on high temp mat chemistry III* (eds: Z.A. Munir, D. Cubicciotti) (1986) 258-273

#### 7 Experimental

- [98] W. Dettner, Dr. Elze, Handbuch der Galvanotechnik, II, Carl Hanser Verlag, München 1964
- [99] P. Kofstad High Temperature Corrosion, Elsevier London 1988
- [100] B. Pieraggi, Oxid of Met 27 (1987) <u>3/4</u> 177-185

#### 8 Results

- [101] S. Uran, M. Grimsditch, B.W. Veal, A.P. Paulikas, Ox of Met, 56 (2001) 5/6 p551
- [102] S. Popovic, G. Stefanic, S. Music, *Mater Lett* 31 (1997) <u>1/2</u> 19-22
- [103] K.-H. Hellwege, A.M. Hellwege (Editors), W. Pies, A. Weiss (Authors)
   Landolt-Börnstein series, Volume III/7: Crystal Structure Data of Inorganic Compounds, 1975
- [104] P. Kofstad High Temperature Corrosion, Elsevier London 1988
- [105] T. Nijdam, High-temperature oxidation of NiCrAl coating materials, Delft, 2001
- [106] P.E. van Manen, *The mechanism of the oxidation of nickel aluminium coating alloy* (Ph.D. Thesis) 's Gravenhage 1991
- [107] Ch.A. Barrett, Ox of Met 30 (1988) 5/6 361-390
- [108] F.S. Pettit, Trans AIME 239 (1967) 1296
- [109] J.L. Smialek, Metall Trans A 9A (1978) 309

- [110] I. Rommerskirchen, V. Kolarik, Mat and Corr 47 (1996) 625-630
- [111] H.E. Evans Int Mat Rev 40 (1995) <u>1</u> 1-40
- [112] J.S. Wang, A.G. Evans, Acta Mater 47 (1999) <u>2</u> 699-710
- [113] I.J. Bennett, J. Kiersch, to be published

## 9 Discussion

- [114] D.Prot, M.Miloch, C. Monty Mat Sci forum 126-128 (1993) 403-406
- [115] W.W. Smeltzer, Mat Sci Forum 29 (1988) 151-172
- [116] A.M. Butt, I.J. Bennett, W.G. Sloof to be published
- [117] G. Petzow Ternary Alloys Weinheim VCH 1992
- [118] JCPDS 44-1188
- [119] JCPDS 09-0097
- [120] JCPDS 46-1212
- [121] R.D. Noebe, R.R. Bowman, M.V. Nathal Int Mat Rev 38 (1993) 4 193-232
- [122] I.J. Bennett, J. Kiersch, W.G. Sloof to be published

# Appendix A: Model coating alloy characterisation

After annealing the casting-microstructure is still visible in the alloy. The grains are long (>500 $\mu$ m) in the radial direction, and about 100  $\mu$ m in tangential direction, as shown in Figure 1a. Chromium carbide and RE-rich precipitates are visible in the grains, giving a dendrite-like appearance (Figure 1b). Figure 2 and Figure 3 show a close-up of the precipitates.



Figure 1: Hf-doped alloy annealed for 55 hrs, prior to oxidation; a: grain structure observed by polarised light microscopy; (b) precipitates in the alloy, circumference of a grain is indicated, optical micrograph

These small precipitates are undesired (the nominal composition was chosen such that a single phase would form, with only for the Y-doped alloy some Y-rich precipitates). Image analysis of optical microscopy images revealed that the area fractions of the precipitates is about 3.4% for the undoped and 3.2% for the Hf-doped alloy (accuracy about 0.4%). For the other two alloys the area fraction is much lower, only 1 or 2%.



Figure 2: Optical micrographs showing small precipitates; a: Undoped, and b: Hf-doped alloy

Backscatter electron imaging and EDS showed that RE-rich precipitates and the Cr-rich precipitates can be neighbours. However, they are distinct precipitates (Figure 3).



Figure 3: BSI showing Y-rich precipitates (lighter than matrix) and Cr-rich precipitates (darker than matrix) on the Y-doped alloy after extra long annealing; plane perpendicular to oxidised surface

Auger Electron Spectroscopy and X-ray diffraction (Table 1) provided conclusive evidence that the precipitates are carbides. Chromium carbide is present in all alloys. In the undoped and Hf-doped alloy the chromium-carbides are richer in carbon than in the Y-doped model-coating alloy. Auger Electron Spectroscopy proved that in the hafnium-doped alloy, hafnium carbide is present. Apart from the chromium-carbides, also RE-rich phases were identified (Table 1).

	JCPDS-nr	Undoped alloy	Y-doped alloy	Zr-doped alloy	Hf-doped alloy	
β-NiAl	44-1188	++	++	++	++	
Y2Ni7	22-0756		+			
ZrC	35-0784			+		
HfC	09-0368				+	
Cr23C6	35-0783		+			
Cr7C3	36-1482			+	+	
					(stronger than on	
					Zr-doped alloy)	
Cr3C2	35-0804	+				
Y2O2S	24-1424		little			
or	or					
YC0.4	73-0501					

 Table 1: Phases in the model coating alloys as identified with XRD

The overall composition of the alloys was determined with EPMA (section 7.4) employing a defocused electron beam. The average of 100 measurements is presented in Table 2.

The Y-doped and Zr-doped alloys were made at an earlier date than the Hf-doped and undoped alloy. The fact that they are from an earlier batch is most probably the reason for their higher S-content (Table 2).

Alloy	Annealing	Ni with $\sigma_{d}$		Al with $\sigma_{_d}$		Cr with $\sigma_{d}$		RE with $\sigma_{d}$		S with $\sigma_{d}$	
description	time (hr)	(at.%)		(at.%)		(at.%	)	(at.%	)	(at.%)	
Undoped	55	58.48	1.98	37.24	1.43	4.25	3.39	0.00		0.028	0.009
Y-doped	300	58.18	1.97	37.64	1.89	3.89	3.61	0.24	0.43(Y)	0.049	0.009
Zr-doped	300	57.32	1.41	38.46	1.17	3.86	2.34	0.32	0.82(Zr)	0.044	0.010
Hf-doped	55	57.69	2.16	37.39	1.72	4.79	3.78	0.10	0.30(Hf)	0.027	0.010

Table 2: Average composition and standard deviation  $\sigma_d$  measured with EPMA using a defocused electron beam (diameter of electron beam 10  $\mu$ m)

The actual composition of the  $\beta$ -phase is determined using focused EPMA. A large subset of the EPMA-compositions had a nearly constant Ni and Al content, of about 58 at.% Ni and 39 at.% Al (the plateau in Figure 4). This is the expected composition of the  $\beta$ -NiAl phase. The Cr and RE content is determined from this subset and presented in Table 3 and Table 4.



# Figure 4: From datapoint 55 to 172 the Ni and Al content is constant; from the same points the average Cr and Y content is determined

In Figure 4 a high Y-content correlates with a high Ni-content. This is in agreement with the  $Y_2Ni_7$ -phase identified with XRD (Table 1).
	# of	Ni-content	(at.%)	Al-content (at.%)		Cr-content (at.%)			
	measure								
Alloy	ments								
		Average	o <sup>d</sup>	Average	$\sigma_{_{d}}$	Average	Min	Max	$\sigma_{_{d}}$
Undoped	134	59.38	0.61	39.61	0.62	1.01	0.81	1.40	0.12
Y-doped	118	58.10	0.09	39.47	0.11	2.42	2.26	2.77	0.09
Zr-doped	151	57.85	0.15	39.26	0.15	2.86	2.63	3.67	0.11
Hf-doped	151	59.46	0.11	39.48	0.12	1.05	0.85	1.48	0.12

Table 3: Ni, Al and Cr-content of β-phase determined with EPMA with focussed beam

The Hf-doped and undoped alloy also have the lowest Cr-content in the  $\beta$ -phase, about 1.5-2 at.% lower than the Cr-content of the  $\beta$ -NiAl for the Y-doped and Zr-doped alloys (Table 3). This corresponds with the observation that the Hf-doped and undoped alloys have more precipitates, many of them being Cr-carbides (discussed above). The difference in precipitate area fractions (about 1.5-2 %) is in the order of magnitude expected from the difference in Cr-content in the  $\beta$ -NiAl phase (estimation is easy as the total Cr-content is known for all alloys and the Cr-content is much larger than the RE-content).

The precipitates do not form during cooling but are present throughout the annealing, as after oxidation at 1373 K and quick redraw (cooling to room temperature within a minute, 'freezing' the microstructure present at 1373 K), precipitates are still present.

Annealing for 55 hrs at 1373 K should be enough to dissolve all Cr, as diffusion in  $\beta$ -NiAl is fast and the equilibrium situation for the current Ni, Al and Cr content is that all Cr is dissolved [1]. Even after 300 hours and an extra annealing of 450 hrs, the chromium is not dissolved. It is concluded that the bonding by carbon hinders the dissolution of Cr in the  $\beta$ -NiAl.

In the undoped alloy, a carbon-rich chromium carbide was identified and the area fraction of the precipitates is high. On the Hf-doped alloy, the carbide-reflections are stronger, and the area fraction of the precipitates is higher than on the Zr-doped alloy. Therefore it is concluded that the carbon content of the undoped and Hf-doped alloys is higher than the carbon content of the Y-doped alloy. Especially in the undoped and Hf-doped alloys, the carbon hinders dissolution of Cr in the  $\beta$ -NiAl.

Alloy	Average	Median	Min	Max	σ <sub>d</sub>	RE Detection	
	(at.%)	(at.%)	(at.%)	(at.%)	(at.%)	Limits (at.%)	
Y-doped	0.01	0.000	0.00	0.44	0.05	0.02	
Zr-doped	0.03	0.007	0.00	0.49	0.05	0.07	
Hf-doped	0.02	0.009	0.00	0.31	0.03	0.06	

**Table 4: RE-content of β-phase determined with EPMA** 

Due to the size of the spherical volume where the X-rays are generated (about 1  $\mu$ m in diameter), part of the X-rays can originate from a nearby RE-rich precipitate. Therefore, the measured RE-content of the  $\beta$ -phase (Table 4) will be upper estimates for the real RE-content. Therefore, apart from the average, also the median is presented in Table 4. The median indicates that no Y was dissolved in the  $\beta$ -NiAl, and only very little (if any, as it is lower than the detection limit) Zr and Hf.

The solubility of Y in NiAl is neglible [1], so the low Y content of  $\beta$ -NiAl is not surprising. But according to the phase diagram all Hf and nearly all Zr should be dissolved. Probably, again the bonding with the carbon hinders dissolution.

It can be concluded that especially the undoped and the Hf-doped alloys contain much carbon. This carbon forms carbides with chromium and hafnium. A result of this carbide formation is that even after 300 hr annealing the chromium and hafnium are still not fully dissolved in the  $\beta$ -NiAl. In chapter 5, the solubility of REs in NiAl is calculated using the macroscopic atom model.

## Appendix B: Calculation of C<sup>S</sup><sub>Al</sub> and C<sup>S</sup><sub>Ni</sub> [2]

 $V_{AI}^{23}$ ,  $V_{NI}^{23}$ ,  $\phi_{AI}^{*}$ ,  $\phi_{NI}^{*}$ , are the principal model parameters of the macroscopic atom model. These parameters are tabulated for almost all elements in ref [2] (table V – 1.3). V is the molar volume. The surface fraction  $C_{AI}^{s}$  is the sum of all surfaces of the Al atoms in the metal, divided by the sum of all surfaces of all metal atoms. The atomic fraction  $C_{AI}^{s}$  has to be chosen.

$$C_{Al}^{S} = \frac{C_{Al} V_{Al}^{2/3}}{C_{Al} V_{Al}^{2/3} + C_{Ni} V_{Ni}^{2/3}}$$

and

$$C_{Ni}^{S} + C_{Al}^{S} = 1$$

The degree to which an atomic cell of Al is in contact with Ni-atomic cells is for ordered alloys  $f_{Ni}^{Al} = C_{Ni}^{S} \left( 1 + 8(C_{Al}^{S} C_{Ni}^{S})^{2} \right)$ 

likewise, the degree to which an atomic cell of Ni is in contact with Al is

$$f_{Al}^{Ni} = C_{Al}^{S} \left( 1 + 8(C_{Al}^{S} C_{Ni}^{S})^{2} \right) = \frac{C_{Al}^{S}}{C_{Ni}^{S}} f_{Ni}^{Al}$$

The volume of the constituent atomic cells changes upon alloying. The volume parameter  $V^{2/3}$  after alloying is:

$$\begin{split} & \left( V_{Al}^{2/3} \right)_{alloy} = V_{Al}^{2/3} \left( 1 + 0.07 f_{Ni}^{Al} \left( \phi_{Al}^* - \phi_{Ni}^* \right) \right) \\ & \left( V_{Ni}^{2/3} \right)_{alloy} = V_{Ni}^{2/3} \left( 1 + 0.10 f_{Al}^{Ni} \left( \phi_{Ni}^* - \phi_{Al}^* \right) \right) \end{split}$$

From these corrected volumes, the surface fractions are calculated again. The resulting  $C_{Al}^{s}$  and  $C_{Nl}^{s}$  are used in the calculations.

[2] F.R. De Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, *Cohesion in Metals, transition metal alloys,* North-Holland, Amsterdam 1988

<sup>[1]</sup> G. Petzow *Ternary Alloys* Weinheim VCH 1992