STUDY OF Ti-Al-Cr OXIDATION RESISTANT COATINGS FOR $\gamma$-TiAl BASED INTERMETALDIC ALLOYS

BY

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ABSTRACT

Magnetron sputter deposition with single target materials was used to produce amorphous and crystalline Ti-Al-(Cr) alloy coatings on a Ti-50Al substrate. The following coatings were studied: Ti-50Al-10Cr, Ti-53Al-15Cr, Ti-50Al-20Cr and Ti-48Al. The microstructures of the coatings were studied in the as deposited condition and after devitrification and heat treatment. A random distribution of nano-precipitates was formed in amorphous as-deposited coatings. Columnar features were present when the as-received deposit had crystallised during sputter deposition. If crystallisation occurred during deposition, a columnar microstructure formed with the columnar fibres being parallel to the deposition direction. For the Ti-50Al-10Cr and Ti-53Al-15Cr deposits, the crystalline domains consisted of lamellar γ<111> // a<0002>, i.e. the crystalline deposits had a γ<111> // a<0002> texture. The α → α₂ transformation occurred during deposition.

Phase competition in the alloys was studied by combining thermodynamic modelling and transformation kinetics. At 1173K, the Ti-50Al-10Cr alloy transformed to a two-phase microstructure, consisting of the γ and C14 Ti(Al, Cr)₂ phases. The Ti-53Al-15Cr alloy transformed to a three-phase microstructure, consisting of the γ, τ and the C14 Laves phase. The γ and τ phases were mixed finely, with γ<100> // τ<100>. The Ti-50Al-20Cr alloy transformed to a two-phase microstructure, consisting of the γ and the C14 Laves phase. No orientation relationship between the γ and the C14 Laves phase was observed. Phase evolution studies at lower temperatures in the range 773K to 973K indicated that for the amorphous Ti-48Al alloy, the phase transformation path is: the amorphous phase → α → γ + α/α₂. A fine lamellar structure was formed, with γ being the dominant phase. For the Ti-50Al-20Cr alloy, the phase transformation path was: the amorphous phase → γ → γ + Ti(Al, Cr)₂.

The experimental observations and the modelling results have clearly suggested a tendency of amorphous phase stabilisation via Cr addition. Thermodynamic modelling also indicated that the driving force for amorphous alloy formation is not much less than that for the precipitation of disordered solution phases. Kinetically, the amorphous phase formation during sputter deposition is related to the suppression of surface diffusion at low substrate temperatures.

The temperature processing window for ordered phase formation in the Ti-Al(-Cr) alloys during magnetron sputter deposition was evaluated by the effective diffusion distance. Time dependent nucleation calculations showed that in the Ti-48Al amorphous alloy, it would be kinetically easier to precipitate the α phase than the γ phase. In the case of the Ti-50Al-20Cr alloy, the γ phase forms in preference of α, which is consistent with experimental observations.

Diffusion phenomena at the coating/substrate interface and the oxidisation of the coatings were also studied. The experimental Cr diffusion profiles and the simulations for the Ti-Al-Cr coatings and the Ti-50Al substrate indicated that diffusion at 1173K is reasonably slow. The Ti-50Al-10Cr, Ti-53Al-15Cr and the Ti-50Al-20Cr coatings could form protective oxide scales at 1173K. When a columnar structure was present in the crystalline deposit, cracking of the coating was observed when the coating was subject to thermal cycling from elevated temperatures. It is concluded that if cracking of the coatings was to be avoided, amorphous deposits should be preferred.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>BF</td>
<td>Bright field</td>
</tr>
<tr>
<td>BS</td>
<td>Back scattered</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent beam electron diffraction</td>
</tr>
<tr>
<td>DF</td>
<td>Dark field</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray (analysis)</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron probe micro analysis</td>
</tr>
<tr>
<td>HREM</td>
<td>High Resolution Electron Microscopy</td>
</tr>
<tr>
<td>HRI</td>
<td>High resolution image</td>
</tr>
<tr>
<td>MD</td>
<td>Micro-area diffraction</td>
</tr>
<tr>
<td>MDP</td>
<td>Micro-area diffraction pattern</td>
</tr>
<tr>
<td>SAD</td>
<td>Selected area diffraction</td>
</tr>
<tr>
<td>SADP</td>
<td>Selected area diffraction pattern</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SF</td>
<td>Structural fluctuation</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>WDX</td>
<td>Wavelength dispersive X-ray</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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Titanium aluminides (particularly $\alpha_2$-Ti$_3$Al and $\gamma$-TiAl) are candidate structural materials for applications in the aerospace industry, due to an attractive combination of properties such as low density, high specific strength and modulus of elasticity, good corrosion and oxidation resistance. In particular, the $\gamma$-TiAl based alloys are most promising. However, the oxidation resistance of these alloys degrades significantly at elevated temperatures, i.e. above 1023K, since at these temperatures continuous alumina scale cannot form. Efforts to improve their oxidation resistance through modification of alloy chemistry are often accompanied by degradation in mechanical properties and increase in density.

Surface modification techniques and coatings have been employed in order to improve the high temperature performance of the $\gamma$-TiAl based alloys. In recent years the Ti-Al-Cr alloy system has attracted much attention, as alloys containing combinations of certain phase(s) have demonstrated excellent high temperature performance. Furthermore, Ti-Al-Cr alloys often have similar thermal expansion coefficients to the $\gamma$-TiAl based substrates.

The work discussed in this thesis is part of a wider research programme on the development of intermetallic alloys for high temperature applications. The project is a collaborative programme between the University of Surrey and the Institute of Metal Research, Academia Sinica, Shenyang, China. The objectives of the research described in this thesis were to:

1. Produce ternary Ti-Al-Cr deposits on a Ti-50Al substrate using magnetron sputter deposition.
2. Understand the selection of metastable phases during magnetron sputter deposition.

3. Study the relationship between processing parameters and microstructures.

4. Analyse the phase equilibria in ternary Ti-Al-Cr alloys at 1173K to understand the phase competition and selection in TiAl(Cr) alloys produced by non-equilibrium processing.

5. Evaluate the high temperature performance of the Ti-Al-Cr deposits on the Ti-50Al substrate.

The strategies adopted for realising the above objectives include:

1. The design of coating alloys of different compositions.

2. The use of the magnetron sputter deposition technique to achieve different microstructures under different processing conditions.

3. The use of a range of experimental techniques to evaluate the microstructure and high temperature oxidation behaviour of the coatings.

4. The use of thermodynamic data together with the CALPHAD (Calculation of Phase Diagram) method for a thermodynamic analysis of phase competition.

The thesis begins with a brief review of the literature on the titanium alloys and the intermetallics studied in this work, the oxidation behaviour at elevated temperatures of certain Ti-Al and Ti-Al-Cr alloys, as well as a brief background to phase evolution. The experimental procedures are then discussed in Chapter 3. Chapters 4 and 5 are dedicated to the experimental results, the analysis of the microstructures and the phase identifications in the as-received and the heat-treated deposits. Thermodynamic and kinetic analysis of the results is presented in Chapter 6. Chapter 7 describes the results on the Cr diffusion and oxidation behaviour of the ternary deposits. The conclusions of the research discussed in this thesis and suggestions for future work are given in Chapter 8.
2.1 Introduction

This chapter gives a brief review of the literature that is relevant to this thesis. It is divided into four sections. The first section focuses on titanium alloys and intermetallics, with the emphasis being on the structural aspects, mechanical properties and oxidation behaviour of these materials. The next section reviews certain aspects of the theory of phase transformations. Since amorphous coatings have been produced in this study, the third section is devoted to the amorphous metallic materials. Finally, techniques of applying coatings on metallic substrates are briefly discussed at the end of this chapter.

2.2 Titanium Alloys and Intermetallics

2.2.1 Conventional Titanium Alloys

Titanium is a transition metal in group IVb in the periodic table, with an incomplete d-shell which enables it to form solid solutions with most substitutional elements having a size factor within ±20%. At 1155K, Ti undergoes an allotropic transformation from a low temperature, hexagonal close packed (h.c.p) structured $\alpha$ phase ($a = 0.29511\text{nm}$, $c = 0.46843\text{nm}$) to a body centred cubic (b.c.c) $\beta$ phase ($a = 0.3307\text{nm}$ at 1173K) that remains stable up to the melting point (Okamoto, 1993).

Different alloying elements tend to stabilise either the $\alpha$ or $\beta$ phase. This behaviour is related to the number of bonding electrons. Elements that stabilise the $\alpha$ phase are either
transition metal elements with electron to atom ratio (e/a) < 4 or non-transition metal elements. Among these, Al, O, N are the major α-stabilisers. Transition metal elements with e/a > 4 depress the α/β transus and stabilise the β phase. They are called β-stabilisers and include Cu, Cr, Fe, Mn, Ni, Co, Mo, W and V. Elements with e/a of 4 are neutral. Zr and Si are regarded as being this type.

Elements that depress the α/β transus could be further divided into two sub-groups. The first group will form binary systems of the β-isomorphous type; the other will favour the β-eutectoid transformation. However, in practice, the eutectoid reaction is very sluggish in some alloys, e.g. Ti-Mn and Ti-Fe. These alloys often behave as if they have conformed to the β-isomorphous phase diagram (Polmear, 1995). The basic types of phase diagram of titanium alloys containing α/β stabilisers are illustrated in figure 2.1.

Aluminium, an effective α-stabilising element, is the most important alloying addition in the conventional titanium alloys. The aluminium equivalence Al_{eq} is a major empirical parameter that measures the total alloying effect due to α-stabilising elements. If measured by weight, aluminium equivalence is given by (Polmear, 1989):

$$\text{Al}_{eq} = \text{Al} + \frac{\text{Zr}}{6} + \frac{\text{Sn}}{3} + 10 \times (\text{O} + \text{C} + 2\text{N})$$ (2.1)

For conventional α-based Ti alloys, Al_{eq} is practically limited to be < 9wt.% in order to avoid embrittlement of the alloys due to chemical ordering in the α phase to form the α_{2}-Ti_{3}Al phase.

The ordering reaction of the α phase has been widely studied, especially in binary Ti-Al alloys. It is known that ageing at elevated temperatures of alloys with an Al content greater than 5 ~ 6at.% can lead to the formation of a finely dispersed α_{2} phase. This ordered phase is coherent with the of α phase over a wide range of temperature. It has a
general formula of Ti$_3$X and has the DO$_{19}$ crystal structure. Continuing ageing can lead to $\alpha_2$ coarsening. The formation of the $\alpha_2$ phase reduces the ductility of the $\alpha$ phase. In other $\alpha$ alloys such as Ti-Sn, and in more complex compositions, the $\alpha_2$ phase formation becomes more difficult, as the misfit between the $\alpha$ and $\alpha_2$ lattices increases.

The $\beta$ titanium alloys contain enough $\beta$-stabilising elements to retain a fully $\beta$-structure on quenching from above the $\beta$-transus. Alloys that compositionally lie between the critical minimum level of $\beta$-stabiliser content (i.e. where the $M_s$ line intersects the room temperature axis, see figure 2.1) and the similar intersection point of the $\beta$-transus line are often referred to as metastable $\beta$ alloys, since they precipitate a second phase, usually $\alpha$, during ageing. The $\beta$ alloys offer high-strength, good formability and potentially high-hardenability (the latter is achieved by adding a high concentration of solute elements). However, the $\beta$ alloys may form the $\omega$ phase during heat-treatment, which leads to their embrittlement. Elements that stabilise the $\beta$-eutectoid transformation may cause the formation of an intermetallic compound (e.g. TiCr$_2$), which may also cause embrittlement.

### 2.2.2 The Ti-Al System

The titanium aluminides of interest in the aerospace industry are the $\alpha_2$-Ti$_3$Al and $\gamma$-TiAl phases, both of which exist over a range of compositions, together with the stoichiometric compound TiAl$_3$. These titanium aluminides offer advantages, such as:

- Improved levels of specific stiffness combined with lower density, compared with the nickel based superalloys (their densities are approximately half of the nickel based superalloys).
- Higher values of elastic modules than conventional titanium alloys.
- Good oxidation resistance, especially as the Al content is increased.
- Enhanced creep resistance because the strong bonding between the two different atoms in the superlattices of the ordered crystal structures restricts both dislocation motion and atomic diffusion at elevated temperatures (Polmear, 1995).
Chapter 2  Literature Survey

The disadvantage of these aluminides is that they have low values of ambient temperature ductility, due to their limited capacity to undergo slip. Moreover, the $\alpha_2$ phase does not undergo deformation by twinning, unlike most other hexagonal metals and alloys (Polmear, 1995).

The Ti-Al phase diagram is shown in figure 2.2 and the phase data are given in table 2.1. The Ti$_3$Al based alloys are the oldest and most studied titanium aluminides. The Ti$_3$Al undergoes an order/disorder transition within the composition range 22-39at.% Al to form the ordered DO$_{19}$ hexagonal structure, the $\alpha_2$ phase (Blackburn and Williams, 1969). The lattice constant $a$ of $\alpha_2$ is approximately twice that of the $\alpha$ phase. In the Ti-Al alloy system, there is a general agreement concerning the $\alpha/(\alpha + \alpha_2)$ phase boundary up to 1073K. There has been much controversy as to whether $\alpha_2$ forms by peritectic reaction involving $\beta$ and the intermediate compound TiAl, or by phase separation of $\alpha$ at higher temperatures. Research relating to this part of phase equilibria is still going on (Palm et al., 2002).

When alloys are quenched from the $\beta$ phase field, they undergo a martensitic transformation. It has been noted that the addition of $\beta$ stabilising elements such as Nb, Mo and V can promote formation of a ductile ordered b.c.c phase, B2, in which $\omega$ or $\omega$ related phases may form during cooling to room temperature. It has been reported that the basket weave configuration of secondary Widmanstätten plates of $\alpha_2$ together with the B2 phase offers the best overall combination of mechanical properties (Polmear, 1995).

The development of $\gamma$-TiAl based alloys is more recent and has attracted great amount of attention, even though this compound has less room temperature ductility than $\alpha_2$-Ti$_3$Al. Nevertheless, the growing attention to $\gamma$-TiAl based alloys is attributed to lower densities combined with superior values of elastic modulus, oxidation resistance (up to around 973K), thermal stability and the fact that they show plasticity at elevated temperatures.
The γ-TiAl phase has a face centred tetragonal structure with the lattice constants being $a = 0.4005$ nm and $c = 0.4070$ nm and is of the L1₀ structural type. In the γ-TiAl, the Al atoms occupy the corners of the lattice as well as the centre of the top and bottom planes; the Ti atoms occupy the centre of the four planes. Thus, the γ-TiAl phase can be considered as Al and Ti atoms arranged in alternating layers.

The composition of γ-TiAl may extend from 48.5 to 66 at.% Al. The most practical interest, however, lies at the lower end of this range. Most γ-TiAl based alloys studied to date are in the composition ranging from 46 ~ 52 at.% Al. They can be classified as single-phase γ and two-phase (γ + α₂) alloys (Kim, 1989). The γ-TiAl compound remains ordered up to its melting point of about 1733K. Tetragonality (i.e. the c/a ratio) is close to unity, varying from 1.01 to 1.03 for the two extremes of aluminium content. Dislocation mobility is severely restricted. Twinning occurs at elevated temperatures and it is considered to contribute to the increased plasticity of γ.

The microstructure of the γ-TiAl based alloys can be controlled by heat treatment and thermomechanical processing. It has been noted that the microstructures developed from forged two-phase alloys are virtually unlimited in variations depending on such conditions as heating rate, heat treatment temperature and time, cooling rate and heat treatment schedule, ageing temperature and time (McCullough, 1989). The microstructure of γ-TiAl based alloys can be categorised into three major types:

- Lamellar microstructures, which are common, consist of colonies of γ plates or, in two-phase alloys, alternating plates of γ and α₂.
- Equi-axed microstructures consist entirely of γ grains in single-phase alloys; in two-phase alloys, this structure is predominantly γ grains surrounded by α₂ particles at grain boundaries.
- The duplex microstructures consist of mixtures of equi-axed grains and lamellar colonies.
These three types of microstructures exhibit different mechanical properties. A two-phase, lamellar morphology is generally considered to provide the best balance, as long as the grain size is kept fine (Kim, 1991, Kim, 1992).

The compound Al$_3$Ti has also attracted some attention as a potential high temperature structural material because of its relatively high melting point and good oxidation resistance. Compared with the above aluminides, Al$_3$Ti exhibits the highest specific stiffness and oxidation resistance. However, Al$_3$Ti has a low symmetry tetragonal D0$_{22}$ structure and is brittle at lower temperatures. At low temperatures the deformation occurs solely by (111)[112] twinning (Nakayama and Mabuchi, 1993).

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Phases in the Ti-Al equilibrium system (Villars and Calvert, 1985).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pearson symbol</td>
<td>Space group</td>
</tr>
<tr>
<td>$\beta$</td>
<td>cI2</td>
</tr>
</tbody>
</table>
| $\alpha$ | hP2 | P6$_3$/mmc | a = 0.29508  \\
|          |       |             | c = 0.46855 |
| Ti$_3$Al | hP8 | P6$_3$/mmc | a = 0.5782  \\
|          |       |             | c = 0.4629 |
| $\gamma$-TiAl | tP4 | P4/mmm | a = 0.4005  \\
|          |       |             | c = 0.4070 |
| TiAl$_2$ | tf24 | I4/amd | a = 0.3976  \\
|          |       |             | c = 2.4360 |
| $\delta$ | (a) | ... | Not available |
| TiAl$_3$ | tf8 | I4/mmm | a = 0.3848  \\
|          |       |             | c = 0.8596 |
| $\alpha$-TiAl$_3$ | (b) | ... | Not available |

(a) Long-period superlattice structure.
(b) Tetragonal; a superstructure of the D0$_{22}$ lattice.

It is known that replacement of a certain amount of aluminium atoms in Al$_3$Ti with 3-d transition metals such as Zn, Cr, and Ni transforms the structure of Al$_3$Ti to the more
symmetric L1₂ structure (ordered face-centred cube (f.c.c)), which is known as the τ phase (Raman and Schubert, 1965a, 1965b, Seibold, 1981). Even so, the ternary compounds are still brittle and exhibit cleavage fracture.

Less work has been carried out on other phases in the binary Ti-Al system, such as δ, which is known to have a long-period superlattice structure; the TiAl₂, Ti₃Al₅ phases are also known to be very brittle (Klansky et al., 1994). These phases will not be considered further in this review. Crystal lattice data for the above phases in the Ti-Al system are summarised in table 2.1.

2.2.3 The Ti-Al-Cr System
Improvement of the mechanical properties of α₂ and γ have been sought in alloying with β stabilising elements. Niobium, molybdenum and vanadium were used to improve the ductility of the Ti₃Al phase. For two-phase γ-TiAl based alloys, particularly two-phase alloys, 46 ~ 49 at.% of aluminium, 1 ~ 4 at.% of the transition metals such as Cr, V, Mn and Nb were added. A reduced oxidation resistance was observed in the latter alloys. Examples of two-phase alloys are Ti-48Al-2Nb-2Cr (at.%), Ti-48Al-2V and Ti-47Al-2.5Nb-2[Cr+V].

Since the oxidation resistance of γ-TiAl based alloys deteriorates significantly at higher temperatures (973K), work has been carried out to design ternary or quarternary alloys to improve their high temperature performance. The interest in the Ti-Al-Cr alloy system is attributed to the fact that for certain alloy compositions (Cr content greater than 10 at.%), oxidation resistance at high temperatures is enhanced.

Work on the phase equilibria of the Ti-Al-Cr alloy system at elevated temperatures was reported in the early nineties. Hayes (1992) summarised the Ti-Al, Ti-Cr and Al-Cr systems and outlined a very primitive ternary phase diagram. Klansky et al. (1994) studied phase equilibrium with the L1₂ τ phase at 1473K. Jewett and co-workers
studied partial isothermal sections at 1273K and 1073K, mainly at the Al and Cr corner and around the $\tau$ and Ti(Cr,Al)$_2$ phases (Jewett et al., 1996). Using the available data, the Ti-Al-Cr phase equilibria at 1273K and 1073K has been constructed, and are shown in figures 2.3 and 2.4 (Shao and Tsakiropoulos, 1999b, 2000). It can be seen that the phase equilibria are relatively well understood at 1273K, whereas systematic data at other temperatures are still lacking.

The $\alpha$ and $\alpha_2$ phases have relatively limited Cr solubility. The $\gamma$ phase can accommodate up to 7 at.% of Cr. The structure of the $\tau$ phase is closely related to the DO$_{22}$ structure of the Al$_3$Ti phase. The lattice constant is 0.3960nm, as reported by Nakayama and Mabuchi (1993). It has been reported that the $\tau$ phase can be in direct equilibrium with the liquid phase (Shao and Tsakiropoulos, 1998). At 1273K the $\tau$ phase field is centred at $\approx$Cr$_{67}$$\approx$Al$_{67}$ with a deviation of $\approx$1 at.% (Jewett et al., 1996).

Another phase of interest in the Ti-Al-Cr alloy system is the Ti(Cr,Al)$_2$ phase. It is the $\gamma$-TiCr$_2$ phase stabilized in the Ti-Al-Cr ternary system through Al substitutions for Cr to at least 19 at.% Al at 1273K and to at least 24 at.% Al at 1073K (Jewett and Dahms, 1996). The Ti(Cr,Al)$_2$ phase can be in equilibrium with various phases. Thus it could play an important role in alloy design.

The $\gamma$-TiCr$_2$ phase is classified as a Laves phase of the C14 structure. In the Ti-Al-Cr alloy system, Al atoms take a number of the lattice sites of Cr, thus forming the Ti(Cr,Al)$_2$ phase. Compounds of this class have a stoichiometric composition $AB_2$. The Laves phases crystallise in one of the three closely related structures, which are isomorphous with the compounds MgCu$_2$, MgZn$_2$ and MgNi$_2$. The MgCu$_2$ structure is cubic, and the MgZn$_2$ and MgNi$_2$ structures are hexagonal. The $A$ and $B$ components may be chosen from any group of the Periodic Table, but in all cases the $A$ component is larger than the $B$ component. Thus these phases are essentially interpreted as 'size-factor' compounds and the ideal ratio of atomic diameters $d_A : d_B$ is approximately 1.2 : 1, if atomic sizes are calculated on the basis of $AA$ and $BB$ contact (Hume-Rothery et al., 1969). By arranging atoms as such, the closest packing in space is obtained. Within
the three structure types, the C14 Ti(Cr,Al)2 is isomorphic with MgZn2. A unit cell of
\[ \gamma\text{-TiCr}_2 \] is shown in figure 2.5. The solubility range of the Laves phase, a line
compound, can be increased via alloying significantly.

The lattice parameters of the Ti(Cr,Al)2 phase are dependent on the Al content. The Al
atom mainly occupies the Cr lattice site, so that the Ti content of the Ti(Cr,Al)2 phase
is virtually constant. Jewett and Dahms (1996) have measured the effect of Al
substitution for Cr on the lattice parameters of Ti(Cr,Al)2 using X-ray diffraction. Their
results are summarised in figure 2.6. Within limits of error of various measurements,
the c/a ratio for the C14 Ti(Cr,Al)2 phase between 6-33.5 at.% Al remains nearly
constant, close to the ideal ratio of 1.633.

The Ti-Al-Cr alloy system was also noted to be not rapidly equilibrated. In particular,
the Ti(Cr,Al)2 phase is very slow to form. Once formed, it greatly lengthens the
diffusion time due to the very slow diffusion in and through the phase (Jewett and
Dahms, 1995).

2.2.4 Alloys of the Ti-Al(-Cr) System Synthesised via Sputtering Deposition and
Mechanical Alloying

There has been very limited research on sputter deposited Ti-Al alloys and no account
on sputter deposited Ti-Al-Cr alloys. There has been some research on mechanically
alloyed Ti-Al(-Cr) alloys. The latter can also be useful for the study of phase evolution
in the Ti-Al(-Cr) alloys. This research is summarised in this section.

Banerjee and his co-workers are among the earliest researchers, produce
magnetron sputter deposited TiAl films. Banerjee et al. (1996) used the magnetron
sputtering technique and a \( \gamma\)-TiAl target to produce Ti-48Al and Ti-52Al thin films on
an oxidised silicon wafer. Both deposits were 1.6 \( \mu \)m thick. The as-deposited alloy
films consisted of an amorphous matrix with a small fraction of embedded \( \alpha \) particles.
Chapter 2 Literature Survey

No \(\gamma\)-TiAl phase was found. A Ti-48Al-2Nb-2Mn thin film, produced under the same processing scheme, was fully amorphous. Since aluminium and titanium pure metal thin films synthesised in the same way in the same magnetron sputtering chamber were crystalline (Ahuja et al., 1994), Banerjee et al. (1996) then suggested that as the number of elements contained in the alloy increases, so does the tendency for the films to be amorphous, and this could be because of the increased difficulty of forming critical-sized nuclei.

Banerjee et al. (2000) reproduced the Ti-48Al alloy and studied \textit{in-situ} phase evolution during heat-treatment from 573 to 873K in transmission electron microscopy (TEM). They reported that two parallel processes occurred above 753K. One was that existent \(\alpha\) grains continued to grow, resulting in a relatively coarse grained microstructure. The other process was the nucleation of \(\gamma\)-TiAl (as they believed) in the amorphous matrix, which finally led to a much refined microstructure consisting of \(\gamma + \alpha_2\). However, there was lack of sufficient evidence for the latter process, showing that \(\gamma\)-TiAl precipitation was indeed prior to that of \(\alpha_2\). On the other hand, these results should be treated carefully, as they relate to crystallisation in thin films rather than bulk amorphous materials, since in these two cases different diffusion mechanisms (surface diffusion vs. bulk diffusion) would be governing phase transformation kinetics.

Padmaprabu et al. (2000) used a direct current magnetron co-sputtering system to produce several TiAl thin films less than 1 \(\mu\)m thick. Dual targets (aluminium and titanium) were used. It was noted that the Al showed better deposition efficiency than Ti, and that the Al content increased with increasing substrate temperature. They reported that the crystalline TiAl thin films consisted of the \(\gamma\) phase, and had a \(\gamma\langle111\rangle\) texture.

Alloys of the Ti-Al and Ti-Al-Cr systems have been prepared by mechanical alloying, which is another non-equilibrium process. Much attention was given to metastable phase transformation and the amorphisation of the alloys. Guo and his co-workers investigated mechanically alloyed Ti-20, 25, 50 and 60 at.%Al alloys (Guo et al. 1991,
The formation of an f.c.c. phase with a = 0.42 nm in the Ti-20 and 25Al alloys was reported. In the Ti-50Al alloy, the h.c.p \( \alpha \) phase was formed after milling for 5 hours. Guo et al. (1994) investigated the effect of the size of balls used for mechanically alloying a Ti-60Al alloy. They observed that an amorphous phase was formed when the diameter of balls was 5 or 8 mm; a mixture of an amorphous and f.c.c phases formed when 12 mm diameter balls were used. Guo et al. suggested that the f.c.c phase was the disordered form of the face-centred-tetragonal (f.c.t.) \( \gamma \)-TiAl phase.

Suryanarayana et al. (1992) studied phase evolution in the Ti-24 and 50 at.%Al alloys prepared by mechanically alloying pure Ti and Al powders. They reported that the phase evolution sequence for the Ti-24Al alloy was: Ti(Al) solid solution \( \rightarrow \) Ti(Al) + amorphous + f.c.c phases \( \rightarrow \) f.c.c phase; for the Ti-50Al alloy the phase evolution sequence was: Ti(Al) + Al \( \rightarrow \) amorphous phase \( \rightarrow \) f.c.c phase. Suryanarayana suggested that the f.c.c phase formed in mechanically alloyed TiAl alloys could be attributed to contamination and that the contaminant product was TiN (Suryanarayana, 1995).

### 2.2.5 Oxidation Behaviour of Alloys in the Ti-Al(-Cr) System

It is well known that the oxidation resistance of \( \gamma \)-TiAl based alloys deteriorates above 1073K. A considerable amount of research has attempted to understand the oxidation behaviour of Ti-Al(-Cr) alloys. Such work is informative for the development of oxidation resistant coatings for the \( \gamma \)-TiAl based alloys.

Oxygen solubility in binary and ternary alloys of the Ti-Al and Ti-Al-Cr systems has been studied using atom probe analysis (Menand et al., 1998, Kim et al., 1998, Nerac-Partaix et al., 1995, Nerac-Partaix and Menand, 1996, Huguet and Menand, 1994, Kad and Fraser, 1994). It has been reported that the oxygen atoms were preferentially located in the \( \alpha \) phase in a Ti-48Al alloy with a two phase lamellar microstructure (see table 2.2). This result has been misinterpreted as showing a simple scavenging effect of
the $\alpha_2$ phase. In other words, the oxygen level in the $\gamma$ phase is supposed to decrease when the $\alpha_2$ volume fraction increases. The results of Menand et al. (1998) showed that the oxygen concentration in the $\gamma$ matrix is the same for both single phase alloys and $\alpha_2/\gamma$ two-phase alloys. It is believed that the maximum solubility of oxygen in $\gamma$ is not influenced by the addition of a third element (Cr, Mn, Nb) (Nerac-Parraix and Menand, 1996).

Table 2.2 Oxygen concentration measured in the Ti-48Al alloy using atom probe analysis (Menand et al., 1998).

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$</th>
<th>$\alpha_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (at.%)</td>
<td>45-50</td>
<td>62.8 ± 0.5</td>
</tr>
<tr>
<td>Al (at.%)</td>
<td>50-50</td>
<td>35.7 ± 0.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>450-850 at.ppm*</td>
<td>1.6 ± 0.1 at. %</td>
</tr>
</tbody>
</table>

* atomic part per million

One strategy for designing oxidation resistant materials is to design for $\text{Al}_2\text{O}_3$ formation. The $\text{Al}_2\text{O}_3$ scale, with its extremely slow, parabolic growth, is protective at temperatures over 1473K. Unfortunately, a mixture of titania and alumina forms during the oxidation of the $\gamma$-TiAl based Ti-Al alloys in air. This intermixed scale is generally protective only to about 1023K, because $\text{TiO}_2$ has a much higher growth rate than $\text{Al}_2\text{O}_3$ and the oxygen diffusivity in $\text{TiO}_2$ is also higher (Brady et al., 1996).

Thermodynamic analysis of the oxides of titanium showed that the most stable oxide of titanium, usually TiO (depending on temperatures), is nearly as stable as $\text{Al}_2\text{O}_3$ on most $\gamma$-TiAl based alloys. The activity of Al in the Ti-Al system is believed to exhibit a large negative deviation from ideality (Hoch and Usell, 1971). The phase relationships in the Ti-Al-O system were first studied in the early seventies in order to understand the kinetics of reactions of Ti and Ti alloys with $\text{Al}_2\text{O}_3$. In the early nineties, new versions of the Ti-Al-O phase diagram were established. Figure 2.7a is the isothermal
section of the Ti-Al-O phase diagram at 1373K proposed by Li et al. (1992), and is in agreement with a calculated phase diagram by Lee and Saunders (1997). It shows that Al₂O₃ is stable on the γ and γ + α₂ alloys at 1373K. Thermodynamic calculations at 1073K by Luthra (1991) and Rahmel and his co-workers (Rahmel and Spencer, 1991, Becker et al., 1992), however, indicate that TiO is stable on the binary Ti-Al alloys containing up to 50% Al (figure 2.7b). Li et al. proposed that the discrepancy between the experimental observation and the calculated phase diagrams was due to the oxygen solubility in the metal phases (i.e. the α₂ and γ phases), which was neglected in the thermodynamic calculations of Li et al. (1992).

Significant progress has been made towards understanding the more fundamental aspects of the oxidation behaviour of binary two phase γ+α₂ Ti-Al alloys. Most of the research concentrated on short term oxidation (<1000hr) at high temperatures (1173~1273K) (Zheng et al., 1995a, 1995b, Rakowski et al., 1995, Beye and Gronsky, 1994). It was reported that for a typical two phase α₂ + γ Ti-Al alloy, a thin layer (1 µm) of alumina was formed on the alloy surface after exposure in Ar+20%O₂ at 1173K. Beneath the scale an aluminium depleted layer consisting of one phase was formed. This phase was named as the Z phase by Zheng et al.. With increasing oxidation time, the alumina based scale was destroyed locally and nodules consisting of a mixture of TiO₂ and Al₂O₃ were being formed. Beneath the nodule the depleted layer consisted of two-phases. After longer time, the whole specimen became covered with a mixed titanium/alumina scale that was 20~30 µm thick. The two phases in the depleted layer were arranged in columnar form and protruded into the internal part of the two phase γ + α₂ Ti-Al alloy. Similar behaviour was observed on alloys exposed in air.

Zheng et al. (1995a, 1995b) believed that in the early stage of oxidation, when the oxide was mainly Al₂O₃, the depletion layer consists of only one phase, the Z phase. The continuous consumption of Al on further exposure led to the formation of α₂ in the depleted layer, in addition to the Z phase. Due to the high solubility of oxygen in
α₂, oxidation of titanium occurred, which increased the scale growth rate and destroyed the alumina scale. This Z phase was related to a cubic lattice with \( a = 0.69 \) nm and was considered to be a TiAlO compound. Other Ti₅Al₃O₂ compounds have also been reported (Beye and Gronsky, 1996, Cheng et al., 1996, Dowling and Donlon, 1992, Menand et al., 1998). For example, Menand et al. suggested that a metastable Ti₅Al₃O₂ compound based on f.c.c lattice could be present in a Ti-48Al alloy, which was heat-treated at 1073K. There is still much uncertainty around the identity of the TiAlO compound.

Some researchers have reported that the oxidation behaviour of the γ-TiAl based alloys could be influenced by nitrogen (Rakowski et al., 1995, Meier et al., 1993). It has been proposed that after oxides formed upon initial reaction with air, the local gas composition shifted in the direction of the arrow, as shown in figure 2.8. Continued oxygen depletion caused the gas composition to move into the region where TiN and Al₂O₃ were both stable phases. The presence of the nitrides disrupted the continuity of the alumina and allowed the development of an oxide morphology with continuous paths of TiO₂, through which Ti, Al and O were all transported rapidly. The TiN was oxidised at essentially the same rate as Ti (Ichimura and Kawana, 1993) and the mixed scale was thus formed. This so-called 'nitrogen effect' is still a controversy in the oxidation of Ti-Al alloys.

To improve the oxidation resistance of γ-TiAl based alloys, various attempts have been made to design ternary or quaternary alloys, with alloying elements such as Cr, Y, Nb, etc. The initial interest in the Ti-Al-Cr alloys was raised by Perkins and Meier, as they discovered that the Ti-Al-Cr alloys containing a minimum of 8–10 at.% Cr were continuous Al₂O₃ scale formers (1073K – 1573K in air) (Perkins and Meier, 1989).

Various Ti-Al-Cr alloys have been studied in terms of their oxidation behaviour. Alloys with lower Cr content (less than 5 at.%) had improved ductility, but could exhibit a degradation of oxidation resistance. For example, the 'single phase' γ Ti-Al-Cr
alloy (with composition Ti-52Al-5Cr) was reported to have poor oxidation resistance in air at 1273K (Brady et al., 1997a). After 100 hours exposure in air, the following phases were observed along the direction from the Ti-Al-Cr surface to the bulk of the alloy: titania mixed with discrete alumina particles → mixed alumina and titania subscale → nitride region → Al-enriched region (Ti-65Al-11Cr).

However, the Ti-48Al-5Cr alloy studied by Zheng et al. showed good oxidation resistance in an Ar + 20% O2 atmosphere (Zheng et al., 1995b). The discrepancy between these two experiments might be related to the nitrogen effect. The experiment, however by Zheng et al., was not carried out in air for comparison.

Brady et al. (1997a) studied a diffusion couple consisting of the alloy Ti-35Al-16Cr, containing β (the major phase) + γ, and Al2O3 as diffusion couple at 1273K. The aim of the experiment was to examine the stability of Al2O3 on the alloy. An extensive reaction zone was observed, which indicated a high Al2O3 dissolution into the alloy.

The research done on alloys of the Ti-Al-Cr system suggests that the Ti-Al-Cr alloys belonging in the γ + Laves or τ + Laves phase fields demonstrate good oxidation resistance, as they are the continuous Al2O3 scale formers (Brady et al., 1995, 1997a, 1997b, Berztiss1995).

In order to study the oxidation resistance of the C14 Laves phase Ti(Cr,Al)2, Brady et al. (1997b) studied the Ti-42Al-27Cr and Ti-37Al-29Cr alloys, mainly containing the Laves phase, with a small volume fraction of a second phase, either γ or τ. The results indicated a mixed picture in terms of oxidation resistance for the Ti(Cr,Al)2 based alloy. They suggested that only the alloy with the higher Al content could form a protective alumina scale.
2.2.6 Microhardness of the Ti-Al-Cr Compounds

Although the evaluation of the mechanical properties of coatings is beyond the scope of this work, some survey of those properties can be helpful in coating design. Coatings need to be ductile so that they can resist cracking under stress. Ideally, their thermal-expansion coefficient should be close to that of the substrate, if the coating is expected to experience thermal shocks. In many cases, hardness had been used to assess the ductility of coatings. In general, loads required to cause cracking are inversely proportional to the hardness of coatings. Therefore, those coatings with the lowest hardness value exhibit the greatest resistance to cracking.

Table 2.3 summarised the results obtained by Klansky et al. (1994). The data show that the \( \gamma \) and \( \gamma \) phases exhibit the greatest resistance to cracking, whereas the highest hardness values were found for the Ti(Cr,Al)\(_2\) Laves phase and the AlCr\(_2\) phase.

<table>
<thead>
<tr>
<th>phase</th>
<th>structure</th>
<th>Composition of the Phase (at.%)</th>
<th>Hardness (DPH*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )</td>
<td>L1(_0)</td>
<td>Al-45Ti</td>
<td>220 ± 7</td>
</tr>
<tr>
<td>Al(_2)Ti</td>
<td>Ga(_2)Hf, tI24</td>
<td>Al-35Ti</td>
<td>336 ± 33</td>
</tr>
<tr>
<td>Al(_3)Ti</td>
<td>D0(_2)</td>
<td>Al-25Ti</td>
<td>362 ± 40</td>
</tr>
<tr>
<td>AlCr(_2)</td>
<td>C1(_1)b</td>
<td>Al-68Cr</td>
<td>496 ± 23</td>
</tr>
<tr>
<td>Al(_{17})Cr(_9)</td>
<td>...</td>
<td>Al-40Cr</td>
<td>695 ± 38</td>
</tr>
<tr>
<td>( \tau )</td>
<td>L1(_2)</td>
<td>Al-25Ti-8Cr</td>
<td>151 ± 2</td>
</tr>
<tr>
<td>Ti(Cr,Al)(_2)</td>
<td>C14</td>
<td>Al-32Ti-28Cr</td>
<td>526 ± 46</td>
</tr>
</tbody>
</table>

* Diamond pyramid hardness

Brady and co-workers have also studied the microhardness of several phases of the Ti-Al-Cr alloy system. The study of the microhardness of the Ti(Cr,Al)\(_2\) Laves phase used a load of 100g. After heat treatment at 1073K and 1273K for 100 hours, microcracks
were observed to emanate from the microhardness indentations. The formation of microcracks under such a small load is indicative of extreme brittleness. The \( \tau \) phase was relatively ductile, but decomposition of the \( \tau \) phase to \( \text{Al}_2\text{Ti} \) and \( \text{AlCr}_2 \) after exposure at 1073K resulted in a 160% increase in the Vickers hardness (Brady et al., 1995). In general, the cracking resistance of multiphase Ti-Al-Cr alloys appeared to benefit from the presence of the less hard phases. In addition, in the alloys containing the \( \gamma \) phase, it was observed that the cracking resistance of the alloys deteriorated with decreasing volume fraction of the \( \gamma \) phase (Brady, 1995).

2.3 Phase Transformations

2.3.1 Thermodynamic Aspects in Phase Transformations

A reduction of Gibbs free energy in a system is the driving force of phase transformation. It has long been known that during non-equilibrium solidification, the new-born phase may fall inside a wide composition range, and may even precipitate from the mother phase with little compositional change. There have been many discussions regarding the change of Gibbs free energy during non-equilibrium phase-transformation.

In 1960 Hillert constructed a model describing the possibility of a partitionless phase transformation for the martensite transformation (Hillert, 1960), using a free energy dissipation approach. From the Gibbs free energy aspect, this model can be graphically illustrated by figure 2.9. In this case, his model assumes that there are two independent processes involved. If a \( \alpha \) phase is to form from the \( \gamma \) phase, the first process transforms the lattice from \( \gamma \) to \( \alpha \) and would be itself diffusionless. It may be regarded as a co-operative process by which the grain interface migrates and the energy reduction is necessary for overcoming the friction of the interface. This energy is represented by \( D^\alpha \) or \( \Delta G^m \) in figure 2.9, where \( x_{\gamma/\alpha} \) represents the composition in the \( \gamma \) phase at the interface. Then the other process would allow the diffusion across the
grain interface so that the composition of the $\alpha$ phase would move towards $x_B^\alpha$. Solute atoms will pile up in front of the advancing interface and form a thin spike (Karlyn et al., 1969, Hillert, 1970, 1999). The free energy dissipated in this process is represented by $\Delta G^i$. The total free energy change, $D_{\text{int Chem}} = \Delta G^m + \Delta G^i$, is thus the driving force for the process inside the interface, if no energy is "wasted" on side-reactions. In this model, the composition of the child phase, $\alpha$, may vary from $x_B^\alpha$ to $x_B^{\alpha_{\text{max}}}$, where $x_B^{\alpha_{\text{max}}}$ is obtained from the intersection point of the tangent of the $\gamma$ free energy curve at $x_B^{\gamma_{\alpha}}$ and the free energy curve of the $\alpha$ phase. The situation in which the $\alpha$ composition is greater than $x_B^\alpha$ corresponds to the phenomenon of 'solute trapping'.

On the other hand, there are certain cases where the build-up of a solute spike in front of the advancing interface during the massive phase transformation is not allowed due to lack of diffusion. It has thus been proposed that the point where the two phases have the same free energy should be the natural limit of the massive transformation in the phase diagram (Massalski, 1970, Massalski, 1984, Perepezko, 1984, Menon, 1988).

2.3.2 Kinetic Aspects in Phase Transformations

A large amount of work on the nucleation theory has been aimed at understanding phenomena such as crystallisation of a liquid, condensation of a supersaturated vapour, devitrification of glasses and orientational ordering in molecular crystals. Much experimental and theoretical study led to the formation of the classical nucleation theory, starting with the pioneering work of Volmer and Weber (1926). The steady-state nucleation theory assumes that clusters evolve slowly in size by a series of bimolecular reactions, i.e.

$$E_{n-1} + E_1 \xrightleftharpoons[k_{\alpha}^+]{k_{\alpha}^-} E_n \text{ and } E_n + E_1 \xrightleftharpoons[k_{\alpha}^+]{k_{\alpha}^-} E_{n+1}$$

(2.2)

Here $E_n$ represents a cluster of $n$ molecules, $k_{\alpha}^+$ is the rate of a monomer addition to a cluster of size $n$ and $k_{\alpha}^-$ is the rate of loss. The time-dependent cluster density, $N_n$, is
determined by solving a system of coupled differential equations of the following form (Kelton et al., 1983) 

$$\frac{dN_{n,t}}{dt} = N_{n-1,t}k^+_{n-1} - [N_{n,t}k^-_n + N_{n,t}k^+_{n}] + N_{n+1,t}k^-_{n+1}$$ (2.3)

The time dependent nucleation rate is therefore expressed as

$$I_{n,t} = N_{n,t}k^+_n - N_{n+1,t}k^-_{n+1}$$ (2.4)

Long before the numerical calculation could be practically carried out, plenty of work was devoted to the analytical solution of equation 2.4. Based on the continuum approximation, the analytical treatments of transient nucleation led to equation 2.3 into the partial differential equation, the so-called Zeldovich-Frenkel equation:

$$\frac{\partial N_{n,t}}{\partial t} = \frac{\partial}{\partial n} \left( k^+_n N^*_n \frac{\partial}{\partial n} \frac{N_{n,t}}{N^*_n} \right)$$ (2.5)

Here $N^*_n (= N_A \exp[-\Delta G_n / k_B T])$ is the equilibrium cluster size distribution per mole, and $N_A$ is Avogadro’s number of atoms.

The most thorough treatment of the above equation was done by Kashchiev (1969). This treatment was largely based on mathematical transformations of equation 2.5 and he avoided making assumptions about the physics of the process. He derived the analytical expression for transient nucleation rate, which is:

$$I_{n,t} = I^*[1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp(-\frac{m^2t}{\tau_k})]$$ (2.6)

where $\tau_k$ is the time lag. Analysing the result obtained from this solution, he introduced the term, transition time $t_r$ (often called transient time or incubation time), which is the time required for nucleation rate to reach 99% of its steady state value. It can be expressed as follows:
\[ t_w = -\frac{4kT}{D_k \left[ \beta^2 \Delta G(x) / \alpha x^2 \right]_{x=x_k}} \]  

(2.7)

Here \( D_k \) is the probability per unit time of an atom joining a cluster and \( x_k \) is the size of a critical nucleus. According to Kashchiev, the time lag \( \tau_k \) should be of the same order as the transient time, with the transient time being approximately five times the time lag. The transient time for nucleation provides a useful time scale for comparing interdiffusion and nucleation processes (Thompson, 1992).

There are other treatments, which led to different formulations of the transient nucleation rate, \( \dot{I}_{n,t} \). For example, the well known treatment by Wakeshima (1954) gives

\[ \dot{I}_{n,t} = I^* [1 - \exp(-t/\tau_w)] \]  

(2.8)

Here the time lag is marked with the subscript \( w \) to distinguish it from that in Kashchiev's solution.

Numerical solution for equation 2.5 has shown good agreement with the analytical calculations (Kelton, 1983). The results showed that the population of clusters of a given size would increase with time monotonically until a steady state is reached. The nucleation rate \( \dot{I}_{n,t} \) would also increase with time, and for different cluster sizes it would converge to the steady state. For smaller clusters, the nucleation rate increases with time, then experiences a maximum, before reducing to the value of the steady state.

This monomer nucleation model, which assumes that a cluster grows or shrinks by one atom at a time, was then extended into the binary system, and the atom added or detached can be either of the elements in the alloy (Reiss, 1950, Temkin and Shevelev, 1984, Joseph, 1974). The work on binary and multicomponent systems has concentrated on mathematical modelling.
2.4 The Metallic Amorphous Phases

2.4.1 Obtaining Metallic Amorphous Phases

The amorphous metallic phase is a metastable phase often formed during non-equilibrium processing, e.g. rapid solidification of liquids and vapour deposition. Amorphous metallic material (sometimes called a metallic glass) is the structurally relaxed metastable state of an alloy which exhibits no long-range order (Bormann and Zöltzer, 1992). Research on amorphous alloys has gained much attention in materials science both from a technical point of view as well as in basic research of phase transformation.

One of the earliest attempts of producing a metallic glass was to force a small volume of liquid alloy to impinge very rapidly onto a highly conducting substrate (Duwez et al., 1960). Au-Si alloys (Klement et al., 1960) and Ni alloys (Davies et al., 1973) were among the first metallic glasses studied. A variety of techniques were employed later for the preparation of amorphous metallic materials. These methods include annealing thin layered composites (Schwarz and Johnson, 1983, Johnson, 1986) or a supersaturated solid solution (Schlütter et al., 1988, Blatter and Almén, 1985), mechanical milling of elemental powder mixtures (Koch et al., 1983) or intermetallic compounds (Schwarz and Johnson, 1983), co-sputtering of the elemental components (Bormann et al., 1988) and ion implantation (Grant et al., 1978).

2.4.2 Short-Range Structure in Amorphous Metallic Alloys

The amorphous state of an alloy is not a unique state, but contains a considerable and continuous variation of its microscopic state (Egami, 1983). Such a microscopic state is described by the atomic short range order. This is because a completely random mixture is not attained, so that the chemical composition around the atoms of each alloying component is different from the average. The system then is said to have chemical short-range order. This atomic ordering within an amorphous alloy could thus
lead to a property varying from one run of production to another, or from one portion of the material to another. While many properties depend on chemical short-range order, they also depend on the details of the geometry of the structure itself, or the degree of randomness of the structure. This is a more subtle kind of short range order, called geometrical short-range order (Egami, 1983).

There have been various attempts to model structures of the amorphous alloys. One of the earliest is the hard-sphere model, which assumes that all atoms are close packed following a true random manner (Bernal, 1960). With the understanding of the short-range ordering in amorphous materials, other models were built to simulate the ‘real’ amorphous alloy structures. One main approach is to build a network by joining trigonal prismatic units, which are first built to satisfy the requirement of chemical ordering (Gaskell, 1979). Later experimental results showed that many such units do indeed remain in amorphous alloys (Gellatly, 1982). This model put the emphasis on chemical ordering at the expense of packing constrains. Other methods were developed to include the packing constrains, e.g. by starting from a single-component system, then feeding in the chemical ordering information (Finney, 1983). All these models still have their own problems, mainly in terms of constructing a non-crystalline assembly that is consistent with both local chemical ordering and the overall packing constraints.

2.4.3 Amorphisation and Devitrification

There has been considerable research on amorphisation and the stability of amorphous metallic phases. In accordance with the kinetic view of glass formation, it is likely that amorphous phase formation could always be obtained in alloys, given a sufficiently high cooling rate and cooling to a temperature that is sufficiently low to avoid spontaneous crystallisation. The situation for pure metals and very dilute alloys is less clear.
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The early theories pointed out that the amorphous alloy forming tendency can be roughly considered as being proportional to the heat of vaporisation $H_v$ and inversely proportional to the melting temperature $T_m$ (Cohen and Turnbull, 1961). It was also suggested that the formation tendency and stability of amorphous metallic phases should be considered separately in order to understand their behaviour clearly, i.e. amorphous phase formation is closely related to the processing scheme whereas the stability is strongly determined by thermodynamic properties (Davies et al., 1974, Chen, 1976).

For condensation processes such as vapour deposition and sputtering, the ranges of alloy systems and compositions over which amorphous alloys are formed are wider than for liquid quenching (often of the order to $10^6$ to $10^9$ K/s), as the effective cooling rate is much higher. Indeed, vapour deposition gives an effective quenching rate of the order of $10^{13}$ K/s. In the case of vapour deposition, deposition rate and substrate temperature must also be controlled to avoid crystallisation.

Apart from cooling rate, there are other factors influencing the amorphous alloy formation ability. For instance, it has been reported that the minimum cooling rate required to form an amorphous metallic phase of a given thickness could be sensitive to alloy compositions (Chen and Park, 1973, Lewis and Davies, 1976). Eckler et al. suggested that metastable phases could be formed, if they have lower solid-liquid interface energy (Eckler et al., 1997).

A considerable volume of research has also been attempted to understand the mechanism of devitrification. Common techniques include X-ray diffraction, electron microscopy and thermal analysis such as DSC (Differential Scanning Calorimetry). The devitrification process of an amorphous alloy when heated can be described as consisting of three steps: glass transition, supercooled liquid state and crystallisation (Inoue et al., 1990, Inoue, 1998). This is shown in figure 2.10 (Zhou and Sommer, 1999), where $T_g$ and $T_c$ represent the glass transition and crystallisation temperatures, and the section in between represents the state of supercooled liquid.
A two-stage glass transition has also been observed in some alloys, e.g. in the quaternary Zr_{60-x}Y_xAl_{15}Ni_{25} amorphous alloys. The DSC curves obtained at 0.67 K/s showed two glass transitions and supercooled liquid regions before the completion of crystallisation (Inoue, 1998). In these particular alloys, it is believed that the first-stage reactions of glass transition and crystallisation result from the Y-rich Y-Al-Ni amorphous phase, and the second-stage reactions are due to the Zr-rich Zr-Al-Ni amorphous phase. It was proposed that the mutual insolubility of Zr and Y elements has led to the split of the glass transition and crystallisation reactions into two stages.

### 2.4.4 The Glass Transition Temperature

The glass transition temperature $T_g$ is an important parameter. $T_g/T_m$, where $T_m$ is the melting point, is often used as a relative measure of the thermal stability of glass phases. The $T_g$ may be a function of the quenching rate during formation of the glass and of the heating rate during subsequent calorimetric test (Davies, 1976). The fact that $T_g$ cannot be uniquely determined is because of the problem of deciding where on a given thermal analysis $T_g$ should be defined: either at the onset, or the turning point or the maximum value of the DSC trace (Sinning and Haessner, 1988). Meanwhile, there is a lack of agreement as to which technique should be used. The $T_g$ has been reported to relate to the thermal history of a sample and to the heating rate in thermal analysis, yielding a range of $T_g$ values even for the same material (Owen, 1985, Shi, 1994). Cooling rate was also found to closely influence glass transition temperature: Ramachandrarao (1978) used various quenching rates for a Pd-6.0Cu-16.5Si glass. Increasing the quenching rate from $10^3$ to $10^8$K/s caused $T_g$ to increase by more than 50K. Contamination of samples (by oxygen or hydrogen) may also result in different experimental values for $T_g$ (Jiang and Baram, 1996).

Experimentally, $T_g$ is often determined by DSC analysis, which measures the heat of reaction and transition quantitatively. The convention for determining the glass transition temperature is to extend the straight line portion of the base line and the
linear portion of the endothermic slope, marking their intersection (Speyer, 1994). To obtain good signal-to-noise ratios the sample mass needed for the experiment varies, depending on the sensitivity of the instrument and the nature of the reaction, and can be from less than 1 to 20 mg. For thin-films, a free-standing sample is often required to further enhance the signal-to-noise ratio, so is a reasonably higher heating rate (Michaelsen et al., 1997). Electrical resistivity measurements have also been used as a sensitive probe of crystallisation processes in amorphous metallic alloys (Pekala et al., 1992).

A great amount of research has been done to determine $T_g$ in various glass forming systems to establish empirical relationships between $T_g$ and $T_m$. Boyer proposed a simple linear ("Beaman - Boyer") relationship between the amorphisation and melting temperatures (Boyer, 1976),

$$T_g = k T_m$$

(2.9)

Another proposed formulation for binary alloys is based on the melting points of the two components as follows (Rivlin and Baram, 1994):

$$T_g = F \times [0.25(1 - x)T_m(A) + xT_m(B)]$$

(2.10)

where $F$ is an estimated factor (Cahn, 1992, Tanner, 1979). It has been reported that this method has relatively low accuracy (Jiang and Baram, 1996).

In equation 2.9, the value of $k$ for pure metals is constrained to be around 0.25, while for glass-forming alloys it is often within the range $0.5 < k < 0.8$ (Takayama, 1976, Uhlmann and Yinnon, 1983, Polk and Giessen, 1978, Chen and Jackson, 1978, Hafner, 1983, Battezzati, 1987). Jiang and Baram (1996) collected ninety measurements of $T_g$ for binary, ternary and some quaternary systems, mostly metallic alloys, and generalised the correlation for the amorphisation and melting temperature using the Beaman-Boyer relationship:
\[ T_g = (0.56 \pm 0.05)T_m \]  
for metallic glasses \[ T_g = (0.65 \pm 0.03)T_m \]  
for non-metallic glasses

### 2.4.5 Thermodynamics of Amorphous Alloy Formation

Understanding the thermodynamics of amorphous phase formation is of great importance for the purpose of fabricating promising new materials or for avoiding the formation of unwanted amorphous phases. There have been a few attempts to model the thermodynamics of amorphous phases. For instance Golczewski et al. (1998) modelled the amorphous silicates. They assumed the heat capacity of an amorphous phase to be equal to the heat capacity of the crystalline phase at temperatures lower than \( T_g \), while equal to that of the liquid at temperatures higher than \( T_g \). This is illustrated in figure 2.11. The evaluation of the model parameters of a given system depends on the thermodynamic properties, e.g. the enthalpy change, \( \Delta H_v \), which is given as \( \Delta H_v = H_{\text{amorphous}}(298\text{K}) - H_{\text{crystalline}}(298\text{K}) \). Therefore, being able to experimentally measure these properties, including those of the amorphous phase, is a prerequisite to analysing a given system.

Recently, a model was proposed by Shao to estimate the thermodynamic properties of amorphous metallic phases (Shao, 2000a). The model was inspired by the long noticed phenomenon that changes in extensive thermodynamic properties (e.g., volume \( V \), entropy \( S \), enthalpy \( H \) and Gibbs energy \( G \)) are continuous during the glass transition (\( \text{Liquid} \rightarrow \text{Amorphous} \)), while quantities such as heat capacity and thermal expansion coefficient change abruptly at the glass transition temperature \( T_g \) (Elliott, 1990). Such thermodynamic behaviour is typical of a second order phase transformation (Elliott, 1990, Saunders and Miodownik, 1998).

In Shao’s approach, the modelling of the high temperature liquid phase is based on the Redlich-Kister-Muggianu model, which is a popular formalism in the CALPHAD
method for modelling solution phases (Saunders and Miodownik, 1998, Muggianu et al., 1975). For a multi-component solution phase, the Gibbs energy is presented as:

\[ G = \sum x_i G_i + RT \sum x_i \ln x_i + G^\alpha \]  

(2.12)

where \( x_i \) is the molar fraction of element \( i \), \( G_i \) is the Gibbs energy of element \( i \), \( R \) is the gas constant and \( T \) is temperature. The extra energy of mixing \( G^\alpha \) is described via the interaction parameter \( L_{ij} \) as:

\[ G^\alpha = \sum x_i x_j \sum L_{ij} (x_i - x_j)^2 \]  

(2.13)

In order to model the glass transition \((L \rightarrow Am)\) as a second order transformation, the Gibbs energy of the amorphous solid needs to be formalised in such a way that the change in entropy \( (\Delta S^{L\rightarrow Am}) \) and free energy \( (\Delta G^{L\rightarrow Am}) \) become zero above the glass transition temperature \( T_g \). Below \( T_g \), \( \Delta S^{L\rightarrow Am} \) approaches the maximum entropy change and \( \Delta G^{L\rightarrow Am} \) approaches \( \Delta H_{max} \) at \( T = 0 \). There is still lack of fundamental understanding for the thermodynamic behaviour of the amorphous structure at a temperature near \( T_g \) and an accurate formalism for the Gibbs energy of the amorphous phase around \( T_g \) is impossible at the moment. Fortunately, for most practical problems with material processing, the accuracy around \( T_g \) is not important, as it is the region far below \( T_g \) that is relevant to the maximum stability of the amorphous phase.

To model the glass transition as a second order phase transformation, a formalism (Shao, 2000a, Liu, 2001), based on the phenomenological model for magnetism (Hillert and Jarl, 1978), is used, as shown in equation 2.14. It enables the Gibbs energy of the amorphous solid to be derived using data for the high temperature liquid phase and the ground state stable phase.
\[ \Delta G^{L\rightarrow Am} = -RT \ln(1 + \alpha) f(\tau) \] (2.14)

where \( f(\tau) \) is a series expansion of \( \tau = T/T_g \), expressed as:

\[
\begin{align*}
  f(\tau) &= 1 - 9.916728 \times 10^{-1} \tau^{-1} - 1.11737779 \times 10^{-4} \tau^3 - 4.9612349 \times 10^{-7} \tau^9 \\
  &\quad - 1.11737779 \times 10^{-3} \tau^{15} \\
  &\text{for } \tau \leq 1 \\
  f(\tau) &= -1.05443689 \times 10^{-1} \tau^{-5} - 3.34741816 \times 10^{-3} \tau^{-15} - 7.02957924 \times 10^{-4} \tau^{25} \\
  &\text{for } \tau > 1.
\end{align*}
\]

For a binary \( i-j \) alloy,

\[ T_{g}^{ij} = x_i T_g^i + x_j T_g^j + x_i x_j \left[ \Omega_{0}^{ij} + \Omega_{1}^{ij} (x_i - x_j) + \Omega_{2}^{ij} (x_i - x_j)^2 \right], \] (2.16)

where \( \Omega_{n}^{ij} \) are the temperature interaction parameters.

The constant \( \alpha \) is a factor due to the amorphization stabilization of the liquid phase via glass transition. For a binary \( i-j \) alloy it is expressed as

\[ \alpha = x_i \alpha^i + x_j \alpha^j + x_i x_j \left[ \Lambda_{0}^{ij} + \Lambda_{1}^{ij} (x_i - x_j) + \Lambda_{2}^{ij} (x_i - x_j)^2 \right] \] (2.17)

where \( \Lambda_{n}^{ij} \) are the stabilization interaction parameters.

The maximum change in entropy and free energy due to amorphous phase formation are therefore

\[ \Delta S_{max} = -R \ln(1 + \alpha) \] (2.18)

\[ \Delta H_{max} = -RT_g \ln(1 + \alpha) \] (2.19)

The maximum entropy due to glass transition approaches the entropy of fusion of the ground state crystalline phase \( \Delta S^{L\rightarrow C} \) (Hillert and Jarl, 1978, Borman and Zöltzer,

... (2.15)
The glass transition temperature is often taken as $T_g = 0.25T_m$ ($T_m$ is the melting temperature) for pure metals (Turbull, 1950, Shao and Tsakiropoulos, 1994, Thompson and Spaepen, 1983, Jiang and Baram, 1996). For the glass forming metallic alloys, experimental observation has led to the following approximation: $T_g = kT_m$, $0.5 < k < 0.8$ (Jiang and Baram, 1996, Lu et al. 2000), see also section 2.4.2.

In Shao's amorphous transition model, it is assumed that the entropy of the amorphous phase approaches that of the ground state crystalline structure as the temperature decreases below $T_g$ and the lowest entropy of the amorphous phases cannot be lower than that of the ground state crystalline phase (Shao, 2000a). With this model, once the equilibrium phases in an alloy system have been assessed, the thermodynamic background for glass formation is therefore predictable. This model would be very useful during thermodynamic assessment when there is lack of experimental data for the amorphous phase. Shao used pure Zr as the starting point (see figure 2.12), and extended to binary systems such as Ni-Zr, Cu-Zr, Pd-Si, Co-Si and Fe-B. He has showed very good agreement between such estimations and experimental data. In this thesis, Shao's method was applied to the binary Ti-Al and the ternary Ti-Al-Cr system for phase stability studies.

### 2.5 Surface Coatings for High-temperature Alloys

#### 2.5.1 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is achieved by exposing the heated substrate to a source of vapour species capable of interaction with the substrate surface to achieve the desired composition change. The gaseous species are carried over the surface by the flow of an inert carrier gas, usually argon. If the substrate is not reactive, the component gases are mixed at a relatively low temperature, and then brought via manifolds to the hot substrate suspended in the gas phase, where a number of different reactions may occur, such as displacement reaction with the substrate, hydrogen
reduction, or thermal decomposition. Chromizing and aluminizing steels are two typical CVD processes (Mattox, 1998).

One significant advantage that CVD processes have is that the interior of hollow parts, e.g., turbine blades and cooling holes, can also be coated. The deposition processes may not require expensive and cumbersome vacuum equipment. However, CVD processes are generally batch processes which are considered to be somewhat limited in their ability to effect a variety of compositional changes. Meanwhile, the control of waste gases can be troublesome and present expensive environmental problems.

2.5.2 Physical Vapour Deposition

Physical vapour deposition (PVD) processes are atomistic deposition processes in which material is vaporised from a solid or liquid source in the form of atoms or molecules, transported in the form of a vapour through a vacuum or low pressure plasma to the substrate where it condenses (Mattox, 1998). PVD processes can be used to deposit films of elements and alloys as well as compounds using reactive deposition processes.

PVD mainly encompasses three principal vacuum techniques for the deposition of atoms/ions: evaporation, sputtering and ion plating. Vacuum evaporation is a PVD process in which materials from a thermal vaporisation source reach the substrate with little collision with gas molecules. The thermal vaporisation rate can be very high compared to other vaporisation methods. Ion plating uses bombardment of the atomic-sized energetic particles to modify the properties of the depositing films (Mattox, 1998). The depositing material may be vaporised either by evaporation, sputtering or decomposition of a chemical vapour precursor. Ions of inert or reactive gas are usually used for bombardment.
Sputter deposition is the process which uses the physical sputtering process to vaporise a target material and deposit the vaporised particles on a substrate. The physical sputtering is a non-thermal vaporisation process where surface atoms are physically ejected from a solid surface by an atomic-sized energetic bombarding particle, which is usually a gaseous ion accelerated from a plasma (Mattox, 1998).

The sputtering methods are often categorised into planar diode, triode and magnetron sputtering. Magnetron sputtering is perhaps the most widely investigated amongst sputter deposition methods since the application of refractory and high temperature wear resistant materials deposition found increasing industrial use. In each sputtering method, an anode (filament) is needed to produce electrons which ionise the working gas, e.g. Ar. A sputtering process, in general, is a momentum transfer process in which a fast particle, e.g. Ar⁺, ejects an atom from a cathodic surface. 75% of the transferred energy causes target (cathode) heating and the rest of that energy is transferred into the dynamic energy of atoms ejected from the target material. The substrate is placed near the cathode so that the sputtered atoms will coat it. In magnetron sputtering, electric and magnetic fields cause the filament’s electrons to follow long non-linear paths giving many more which ionise more Ar.

Compared with evaporation, sputtering is slower, but is justified if a substrate will not tolerate much heating. Generally, sputtered films have a compressive stress whereas evaporative deposited films have a tensile stress (Hocking, 1989). The inert gas discharging magnetron sputtering process is similar to the system used in ion plating, but in the latter the substrate is the cathode. The major advantage of PVD processes is that they allow extreme versatility in composition of the deposit (virtually any metal, alloy, refractory or intermetallic compound, some polymeric type materials, and their mixtures can be easily deposited), compared to competitive processes such as electrodeposition, CVD and plasma spray. Other advantages are the possibility to vary the substrate temperature within very wide limits, from sub-zero to high temperatures,
high purity of the deposits and excellent surface finish, which can be equal to that of the substrate.

2.5.3 Thermal Spray Processing
In these deposition processes, molten or solid particles are ejected from high-energy guns to impact on the substrate. Depending on the source of energy supplied to the guns, the processes are classified as plasma spraying, flame spraying and detonation spraying. The microstructure, properties and adherence of the resulting coating are dependent on solidification or sintering of the particles. The spraying particles are obtained by melting the powders of the desired composition in the spray cone. They are driven to the substrate by the flowing gas stream, usually argon. The substrate can be preheated to improve the coating bond and to minimise the thermal shock upon cooling.

Being a line-of-sight process, thermal spraying is limited to the coatings of simple shapes. In the absence of ideal control of processing parameters, thermal spray processes can suffer from porosity and unmelted particle inclusions.
Figure 2.1  Basic types of phase diagrams for titanium alloys: (a) $\alpha$-stabilising, (b) $\beta$-isomorphous type and (c) $\beta$-eutectic type. The dotted phase boundaries in (a) refer specifically to the Ti-Al system. The dotted lines in (b) and (c) are the martensite start ($M_s$) temperatures (Polmear, 1995).

Figure 2.2  The Ti-Al phase diagram (Massalski, 1990).
Figure 2.3  Isothermal section of the Ti-Al-Cr system at 1273K (Shao and Tsakiropoulos, 1999b); the broken lines are tentative.

Figure 2.4  Isothermal section of the Ti-Al-Cr system at 1073K (Shao and Tsakiropoulos, 2000c); the broken lines are tentative.
Chapter 2 Literature Survey

Figure 2.5 A unit cell of the $\gamma$-TiCr$_2$ phase. The bright spheres are the Ti atoms and the dark spheres are Cr atoms.

Figure 2.6 Lattice parameters versus Al composition for the Ti(Cr,Al)$_2$. The results were obtained from the Ti-Al-Cr samples annealed at 1273K and quenched (Jewett and Dahms, 1996).
Figure 2.7  (a) Isothermal section of the Ti-Al-O phase diagram experimentally determined at 1373K (Li et al., 1992); (b) a schematic partial Ti-Al-O phase diagram obtained from thermodynamic calculations (Rahmel and Spencer, 1991).

Figure 2.8  Superposed isothermal stability diagrams for the Ti-N-O and Al-N-O systems at 1173K (Meier et al., 1993).
Figure 2.9 Molar Gibbs energy diagram for the $\gamma$ (parent) $\rightarrow$ $\alpha$ (child) transformation in a binary with a substitutional alloy element (Hillert, 1999).

Figure 2.10 DSC curve for the amorphous $\text{Al}_{25}\text{Cu}_{10}\text{La}_{55}\text{Ni}_{10}$ alloy at a heating rate of 0.67 K/s. $T_g$ and $T_c$ represent the glass transition and crystallisation temperatures respectively (Zhou and Sommer, 1999).
Figure 2.11 Schematic plot of the change of enthalpy of crystalline, liquid and amorphous silicates (Golczewski, 1998).

Figure 2.12 The changes of (a) Gibbs free energy and (b) entropy for competing phases in pure Zr. Those of the amorphous phase were obtained using the model by Shao (Shao, 2000a).
Chapter 3
Experimental Work

3.1 Introduction

This chapter gives the experimental procedure for the work described in this thesis. First, alloy selection is outlined. Then details about the sputter deposition process, the heat treatment procedures and the techniques used to study the morphology and microstructural evolution in the deposits are given.

3.2 Alloy Selection

Three ternary Ti-Al-Cr alloys were chosen as coatings in this research, namely Ti-50Al-10Cr, Ti-53Al-15Cr and Ti-50Al-20Cr (at.%). The key to the selection of these alloys was the Laves phase Ti(Cr,Al)\textsubscript{2}. As discussed in the previous chapter, the Cr to the Ti-Al alloys could lead to the formation of a protective oxide scale at elevated temperatures (Perkins and Meier, 1989, Brady et al., 1995, 1997a, 1997b). Studies of the oxidation behaviour of Ti-Al-Cr alloys indicated that alloys containing the Laves phase exhibit good oxidation resistance at elevated temperatures. Multiphase alloys containing the Laves phase exhibit reasonable ductility, which includes alloys containing the $\gamma$ and $\tau$ phases (see section 2.2.5).

Therefore, this research has concentrated on alloys where the Laves phase co-exists with the $\gamma$ or $\tau$ phases. Based on the proposed isothermal phase diagram of the Ti-Al-Cr system at 1273K (see figure 2.3), the three alloys mentioned above were chosen. The phases present in the microstructures of these alloys at equilibrium are summarised below:
Chapter 3. Experimental Work

A. Ti-50Al-10Cr --- γ + Laves [Ti(Cr,Al)$_2$]
B. Ti-53Al-15Cr --- γ + τ + Laves [Ti(Cr,Al)$_2$]
C. Ti-50Al-20Cr --- τ + Laves [Ti(Cr,Al)$_2$]

The binary Ti-Al alloy with Al content of 48at.% has also been studied in this thesis. It was decided to study the Ti-Al alloy without Cr addition once it was discovered that amorphous Ti-Al-Cr coatings could be produced. This study of the Ti-Al coatings aimed to understand the devitrification behaviour and the microstructural evolution. This study also formed the foundation for understanding the interplay between thermodynamics and kinetics in the devitrification of both the Ti-Al and Ti-Al-Cr systems. Devitrification was studied using X-ray diffraction and electron microscopy.

3.3 Magnetron Sputter Deposition Processing

Magnetron sputter deposition is the most widely investigated method amongst the sputter deposition methods, due to its increasing use for the deposition of refractory and high temperature wear resistant materials. During the sputtering process, a filament (anode) is needed to produce electrons, which ionise the working gas (Hocking, 1989). In this work, Ar was chosen as the carrier gas. The electric and magnetic fields cause the filament’s electrons to follow long non-linear paths giving many more collisions and ionising more Ar. Figure 3.1 shows the motion of electrons in a static magnetic and electric field. The Ar$^+$ ions are also accelerated in the electric and magnetic field rapidly, and can eject atoms from the cathode – the target material(s) by momentum transfer. Usually 75% of the transferred energy causes heating of the target. The rest of the energy is transferred into the dynamic energy of the ejected atoms. The substrate is placed near the cathode, so that the sputtered atoms can coat it. The cathode can be multiple targets, each made of a single element, to perform co-deposition. It can also be a single target alloy of the desired composition.

In this study the chosen coating alloys were produced by magnetron sputter deposition using single target materials, which were cast from pure metals into ingots of the same
nominal composition as given in section 3.2. The sputter deposition was done in the State Key Laboratory for Corrosion and Protection, Institute of Corrosion and Protection of Metals, Academia Sinica, Shenyang, China.

The Ti-50Al substrate was also cast using pure metals. The TiAl ingot was then cut into $20 \times 10 \times 3 \text{ mm}^3$ blocks, ground down using 600# SiC paper, peened and ultrasonically cleaned in ethanol prior to deposition. Peening was done to improve the adhesion of the deposit on the TiAl substrate. All blocks were pierced in order to hang them in the chamber. They were rotated during the deposition process continuously to achieve a deposit of uniform thickness.

Table 3.1 lists the sputtering process parameters used in this work. The substrate temperature during deposition was estimated to be between 523K ~ 623K soon after the deposition process started. The temperature rise is attributed to the absorption of the kinetic energies of the depositing atoms.

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Magnetron sputter deposition processing parameters used in this work.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background vacuum</td>
<td>0.001 Pa</td>
</tr>
<tr>
<td>Argon pressure</td>
<td>0.2 ~ 0.3 Pa</td>
</tr>
<tr>
<td>Power</td>
<td>2.3 kW</td>
</tr>
<tr>
<td>Substrate temperature before deposition</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Target dimension</td>
<td>$380 \times 126 \times 8 \text{ mm}^3$</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>$10^9 \text{ m/s}$</td>
</tr>
<tr>
<td>Processing period</td>
<td>8 hours</td>
</tr>
</tbody>
</table>

A microstructural study of the deposits produced in the early runs found that crystallisation had occurred in some of the deposits. This was related to the temperature rise of the substrate during deposition. These deposits are referred to as deposits produced by the continuous route. In order to eliminate the temperature rise and resultant crystallisation, a discontinuous route was adopted. In this processing route deposition was done in stages, each stage consisting of deposition for 10 minutes
followed by an interval of 10 minutes duration. The Ti-50Al-10Cr deposit was reproduced using the discontinuous route. The Ti-48Al deposit was also made using this route. The deposits produced and the corresponding processing route are summarised in table 3.2.

Table 3.2 The deposits produced in this work and the processing route used.

<table>
<thead>
<tr>
<th>Nominal compositions of alloys produced</th>
<th>Processing route</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Continuous</td>
</tr>
<tr>
<td>Ti50Al10Cr</td>
<td>✓</td>
</tr>
<tr>
<td>Ti53Al15Cr</td>
<td>✓</td>
</tr>
<tr>
<td>Ti50Al20Cr</td>
<td>✓</td>
</tr>
<tr>
<td>Ti48Al</td>
<td></td>
</tr>
</tbody>
</table>

3.4 Heat treatments

3.4.1 High Temperature Phase Equilibria in the Ti-Al-Cr System
The ternary Ti-Al-Cr alloys of interest to this work are candidate coating materials for application at temperatures in the range of 973K to 1173K or even higher. As already discussed in the previous chapter, Ti-Al-Cr phase equilibria have been explored at 1273K (see figure 2.3). There has been also some work done at 1073K, but there is still great amount of uncertainty (see dash-lines in figure 2.4). Thus, in this work it was decided to study the phase equilibria at 1173K.

For the heat treatment, the samples were placed on an alumina boat and positioned in the centre of the heating zone of a Carbolite tube furnace. In order to minimise oxidation, the heat treatment was carried out under a low partial pressure of oxygen by maintaining a continuous flow of high purity argon (>99.998% purity, BOC Pureshield grade). The samples were heat-treated at 1173K for at least 10 hours before
TEM specimens were made to study phase equilibria. All samples were furnace cooled.

3.4.2 Devitrification at Intermediate Temperatures

The survey of the literature done as part of this thesis did not find any work on the devitrification of amorphous amorphous Ti-Al-Cr alloys. There have been limited reports on devitrification at intermediate temperatures for Ti-Al thin films (Banerjee et al., 1996, 2000, Padmaprabu et al., 2000). Thus, in this work phase evolution in Ti-Al and Ti-Al-Cr deposits was studied at temperatures in the range of 773K to 973K.

Ideally, in any study of phase equilibria, samples of an alloy of a reactive element such as Ti should undergo heat treatment within a protective atmosphere to avoid oxidation. Thus, the heat treatment scheme described in the previous section was chosen for studies of phase equilibria. However, if the heat treatment time is not long enough (say less than < 5 hr), the heating up and cooling down periods should not be ignored, when compared with the whole heat treatment duration. For instance, temperature – time data recorded for the Carbolite tube furnace used in this work showed that the heating rate was about 20K/min (see figure 3.2). The cooling rate was non-linear against time, being around 8K/min when the temperature reduced from 773K to 573K and slowing down as the temperature decreased. For studies of phase equilibria, or for heat treatment over 10 hours, this presents little problem. For studies of devitrification, in which heat treatment could be as short as 3 minutes, the heating up and cooling down processes cannot be ignored. On the other hand, our preliminary tests showed that the oxidation of the heat-treated samples was slow. Thus, to study the devitrification of the deposits, heat treatments (T ≤ 973K) were not performed in the tube furnace, because in some cases heat treatment must be short enough (e.g. a few minutes) to capture the early stage of transition. Instead, a box-furnace was used, which allowed the samples to be inserted or removed from the furnace swiftly.
3.5 X-ray Diffraction

X-ray diffraction (XRD) analysis using a Philips diffractometer with monochromatic CuKα radiation (46kV, 35 mA and a step size of 0.05°) and a Ni filter was used to help phase identification in the as-deposited and heat-treated samples. General scans were acquired with the 2θ angle ranging between 20° to 80°. The surfaces of all samples were cleaned by acetone and dried in hot airflow prior to inspection.

For diffraction peak identification, information was taken from the Inorganic Substance Powder Diffraction database. X-ray diffraction simulation was also performed using the PowderCell software written by the Federal Institute for Materials Research and Testing in Germany. The simulation in the software is based on crystallographic information such as lattice constants, space group, element (atomic number) and atomic positions in a unit cell. The detailed XRD data for the experiments are given in Appendix A. The presentation of the XRD results in Chapters 4 and 5 is done in the form of spectra, with most of the peaks identified.

Texture analysis of the deposits was carried out at the Centre de Métallurgie Structurale, Laboratoire de Métallurgie et Matériaux Polycrystallins Université de Metz, France. The texture experiments were conducted using Fe Kα radiation. Pole figures and axial pole figures were obtained.

3.6 SEM and EPMA Studies

3.6.1 Sample Preparation

All cross sectional specimens were cut from the coated buttons using a Struers metal-bonded diamond wheel in a Struers accutom. Most of them were mounted in a conducting bakelite using Struers Prontopress, which heated the samples at 423K for 5 min before cooling for a further 3 min. There were also a few samples mounted in epoxy resin. The problem with epoxy resin, however, was that it was much softer than the titanium alloys. During the grinding process, the sample edges, where the deposits
stood, were more liable to damaged. Therefore, this mounting material was avoided in further work. All samples were ground on the SiC paper from 500# to 2400# with running water, then polished down to a finish of 1 μm using the Struers diamond spray and cloth. The samples embedded in non-conducting materials were carbon coated prior to imaging and analysis.

3.6.2 Imaging Using Secondary and Backscattered Electrons
A HITACHI S-3200N and an electron microprobe (JEOL JXA 8600 Superprobe) were used in the current work for imaging and microanalysis. Imaging was mainly carried out in backscattered (BS) mode on cross sectional specimens to study phase distribution. Secondary electron (SE) mode was used only for surface morphology inspection (the specimens were tilted to around 15° to 45° for better 3-D representation). In order to avoid charging, silver tags were placed on the bakelite or resin mounted samples, before inserting them in the microscope.

The HITACHI S-3200N microscope was operated at an accelerated voltage between 15 and 20 kV and a working distance of 15 – 16 mm. Secondary and backscattered electron imaging were used to study the morphology and microstructures of the deposits. These observations were combined with EDX spectra collected from the phases in order to get qualitative estimations about their identity. EDX elemental mapping and line scanning were also employed in some cases to facilitate the distinction and identification of phases.

The backscattered electrons are known to be able to diffuse to a considerable distance from the impact point to the escaping position (Murata et al., 1971). This beam-specimen interaction can be a limiting factor for the image effect. Consequently, although the chemical compositions of two adjacent phases change abruptly, the backscattered coefficient changes gradually over a distance. At high magnifications, the phase boundary will therefore be poorly defined and appears “fuzzy”. This limitation was encountered in this work repeatedly due to the fine structures in some samples.
3.6.3 X-ray Microanalysis

The chemical compositions were measured using electron probe microanalysis (EPMA) on a JEOL JXA 8600 superprobe. Energy dispersive X-ray (EDX) analysis was the main technique used for this purpose. One of the advantages of EDX analysis is that X-rays can be collected very efficiently. Elements with atomic number $Z \geq 11$ can thus be identified in a few minutes easily (Lifshin and Ciccarelli, 1973). In order to have statistically significant peaks and obtain adequate counts in the spectrum, a high count rate would be required. However, as the count rate increases, the EDX becomes more liable to introducing artefacts. For the SEM used in this work, dead time was kept around 20% to 30%. Calibration of the analyser (an Oxford Link ISIS) using a pure Co standard was performed prior to collection of spectra from each phase present in the sample under examination. This was repeated every hour in order to cancel out any possible errors arising from drift in the electron beam current.

The spatial resolution of EPMA during spot analysis is associated with the electron beam voltage, the composition and the density of the phase being analysed. An optimum spatial resolution of 1–2 $\mu$m would be achieved with the smallest voltage used — 15kV. Taking this into consideration, accurate analysis is only achievable on particles over 4–5 $\mu$m. In many cases for our alloys, the precipitates were much smaller than this limit, thus the EPMA composition analysis could only be taken qualitatively.

Other parameters, such as probe current stability, condition of the specimens and standards etc. would also affect the accuracy of the analysis. Special care was taken to minimise the possible errors, e.g. sufficient time was given prior to any analysis to ensure that the probe current had stabilised. The probe current was checked frequently to ensure its stability.

The energy resolution of EDX is relatively poor. Two closely spaced peaks are difficult to resolve. In WDX, the X-ray radiation is filtered so that only X-rays of a chosen wavelength can reach the detector, therefore, the energy resolution is much higher. WDX was used especially when study of oxide scale was involved, due to its
excellent energy resolution, ability to detect X-rays from light elements and the high counting rate, which allows data collection from a single element in a very short counting time.

3.7 Transmission Electron Microscopy

3.7.1 Thin Film Specimen Preparation
Transmission electron microscopy studies were carried out on thin-film specimens using a Philips 400 and a computer aided Philips CM200 transmission electron microscope.

Thin-film specimens were prepared using a Gatan and a PIPS ion beam miller. Both cross section and planar specimens were made. For cross section specimens, a face-to-face technique was used. This was done by cutting cross sectional slices, which were then glued in pairs, bringing two of the deposited sides together. They were ground down to a smooth surface, glued to copper rings, then carefully ground from the other side till about 100 μm thick. In the ion beam miller, double Ar beams were used shooting from both sides of the rotating specimens. For planar specimens, slices were first cut off from the buttons, attached to copper rings from the deposit side, then ground down from the other side to about 100 μm thick. Single Ar beam was used during ion beam thinning on the substrate side until a small penetration was obtained. The deposit side (the side not being polished by the Ar beam) had to be covered in order to avoid re-deposition. The procedure would be finished by a final thinning from both sides, giving a planar view close to the top of the deposits. Liquid nitrogen was used in the Gatan miller to prevent temperature rise of as-deposited materials in the chamber.

3.7.2 TEM Imaging
Direct microstructure observation can be obtained from TEM imaging. A bright field (BF) image is obtained if the direct transmitted electron beam is used. Contrast may arise by mass-thickness, diffraction or phase mechanisms. If the crystal has been tilted
to certain positions and a diffraction pattern is obtained, one of the strong diffracted beam can be selected to form a dark field (DF) image. The BF and DF image pair can be useful to reveal fine microstructures.

Ideally, when the incident beam interacts with one diffracted beam, one will obtain groups of lattice fringes, with each dark line corresponding to a lattice plane (Goodhew and Humphreys, 1988). In high resolution electron microscopy (HREM) imaging, where more diffracted beams are allowed, a “structure image” is achieved. In this work, HREM imaging was done to examine the microstructure of the crystalline as-received deposit. A low indexed zone-axis orientation was obtained first in order to achieve the diffracted beams. Certain amount of defocus was also necessary.

3.7.3 Diffraction and Phase Identification
TEM diffraction patterns obtained from systematic tilting were combined with XRD data to identify constituent phases in the alloys. There are two methods used to define the area of the specimen from which the diffraction pattern originates. One of these uses a defocussed electron beam so that a large area of the specimen is illuminated with electrons and hence this large area contributes to the diffraction beams. An aperture is inserted in the first image plane so that only the area confined by the aperture will be able to contribute to the diffraction pattern. The focused diffraction pattern, giving bright sharp spots on the screen, is the selected area diffraction pattern (SADP). The other technique, micro-area diffraction (MD), involves condensing the electron beam on to the area of interest, so that the illuminated area uniquely defines from where the diffracted beam originated.

The MD technique allows the crystallographic information to be obtained from very fine precipitates, which are too small to obtain by SADP. The drawback of MD, however, is that contamination is easily incurred when an area is under the condensed electron beam. Hence, in this work, MD was only performed when the SADP technique did not give satisfying diffraction on very fine precipitates. Liquid nitrogen was employed to eliminate contamination of specimens.
No matter what technique is used, diffraction occurs when the Ewald sphere touches a reciprocal lattice point (a relrod) and a diffraction pattern may be formed. The geometry of the real crystals gives rise to the shape effect on the reciprocal lattice. The principle of relating the shape factor of the real space and the reciprocal space can be summarised as “small becomes large” and vice versa (Williams and Carter, 1996). It tells that if a particle is very small in a certain direction, the size of relrod in this direction becomes large, as shown in figure 3.3. This phenomenon was observed in some of our samples, and it could help us to further understand the microstructure of our crystals.

In this work, the electron diffraction patterns were indexed using the versatile on-line software EMS (developed by Centre Interdepartmental De Microscopie Electronique), and the results were constantly checked using d-spacing and interplanar angles. Calculation of interplanar spacings (d-spacing) was using a variety of programs such as EMS or PowderCell, or computed using programs written by the author.
Chapter 3. Experimental Work

Figure 3.1 Electron motion in static magnetic and electric fields (Hockings, 1989).

Figure 3.2 The temperature — time curve recorded for the tube furnace (with Ar flow) used in this work, showing the heat treatment history of a specimen with a nominal heat treatment duration of 30 min at 773K.
Figure 3.3   Schematic illustration of the relation between the shape of the grain and the relrods.
Chapter 4
As-deposited Alloys

4.1 Introduction

In this chapter, the results of microstructural studies of the as-deposited alloys are presented. Overall structural features of various deposits were observed using SEM are given in section 4.2. Detailed microstructural characterisations are discussed in sections 4.3 and 4.4. In section 4.5 results on texture analysis are presented. A brief summary of the structural features of all the deposits is given in section 4.6.

4.2 Overall SEM Observations

As described in Chapter 3, two different processing routes have been employed in this study. In the continuous route the deposition would last for eight hours. The discontinuous route was designed to reduce the temperature rise in the substrate. In the discontinuous route the deposition was carried out in stages, each stage consisting of deposition for 10 minutes followed by an interval of 10 minutes duration.

Five deposits were produced in total, namely Ti-50Al-10Cr, Ti-53Al-15Cr and Ti-50Al-20Cr were produced using the continuous route. The Ti-50Al-10Cr was reproduced using the discontinuous route. The discontinuous processing route was also chosen to obtain the Ti-48Al deposit. Compositions of these deposits were determined by EPMA from the cross-sectional specimens and the results are listed in table 4.1.
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All alloys had a silvery finish and a matt appearance under visual inspection. An undulating feature was revealed under SEM for all the deposits. Figure 4.1 shows the surface morphology of the continuous route products, i.e. for the Ti-50Al-10Cr, Ti-53Al-15Cr and Ti-50Al-20Cr deposits; those of the discontinuous route products, i.e. for the Ti-50Al-10Cr and Ti-48Al deposits are given in figure 4.2. Certain samples were slightly tilted in the SEM so as to obtain a better 3-D view of the undulating feature. The surfaces were found to be like overlapping hillocks, which suggested that the deposit growth would be by island growth mechanism (Padmaprabu et al., 2000).

Table 4.1  Compositions, status and corresponding processing routes of the Ti-Al(-Cr) deposits described in this thesis. The equilibrium phases of the alloys at 1273K are given for comparison with the deposits heat-treated at 1173K.

<table>
<thead>
<tr>
<th>Nominal alloy compositions</th>
<th>Phase equilibria at 1273K</th>
<th>Composition determined by EPMA (at.%)</th>
<th>Processing route</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-50Al-10Cr</td>
<td>γ + Laves</td>
<td>40.2Ti-50.5Al-9.3Cr</td>
<td>✓</td>
</tr>
<tr>
<td>Ti-53Al-15Cr</td>
<td>γ + τ + Laves</td>
<td>33.3Ti-51.8Al-14.9Cr</td>
<td>✓</td>
</tr>
<tr>
<td>Ti-50Al-20Cr</td>
<td>τ + Laves</td>
<td>32.6Ti-48.3Al-19.1Cr</td>
<td>✓</td>
</tr>
<tr>
<td>Ti-50Al-10Cr</td>
<td>γ + Laves</td>
<td>40.0Ti-48.9Al-11.1Cr</td>
<td>✓</td>
</tr>
<tr>
<td>Ti-48Al</td>
<td>*</td>
<td>51.9Ti-48.1Al</td>
<td>✓</td>
</tr>
</tbody>
</table>

* At 1400K this alloy is close to the γ / γ+α2 phase boundary.

The deposits produced by the continuous route were about 30 μm thick. The discontinuous route products were slightly thinner, being about 20–25 μm thick. Although a network of micro-grooves was observed on the surfaces in planar view (see figures 4.1 and 4.2), cross sectional study did not show these grooves extending into the bulk deposits. Therefore, these micro-grooves existed only on the top of the deposits and were estimated to be less than 1 μm deep, according to the observation of cross sections in the SEM. Similar surface morphology was also reported by Padmaprabu et al. (2000) on their sputter deposited Ti-48Al thin films. They produced TiAl thin films of less than 5 μm thickness with a roughness in the range of 60-100 Å.
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The films were crack-free, while a similar network of micro-grooves was present on the top of the deposits.

No contrast due to phase separation could be observed using SEM for any polished cross-sectional samples in the BS mode, even though the Ti-50Al-10Cr and Ti-53Al-15Cr alloys were crystalline (as confirmed by the XRD analysis, see section 4.3). This is due to the very small size of the crystalline precipitates. EDX line scans and mapping showed uniform elemental distributions in all deposits. Figure 4.3 gives the typical BS cross-sectional images and elemental mapping for the Ti-50Al-10Cr (crystalline) and Ti-50Al-20Cr (amorphous) deposits obtained by the continuous processing scheme. No evidence of elemental segregation could be observed.

4.3 Deposits Produced by the Continuous Route

4.3.1 The Ti-50Al-10Cr Deposit

Phase characterisation of the as-deposited alloys was carried out using XRD and TEM analysis, as described in chapter 3. Figure 4.4 shows the XRD • • • of the as-deposited Ti-50Al-10Cr obtained from the continuous route. The diffraction peaks clearly indicated the presence of crystalline phase(s). The high intensity of the two major crystalline diffraction peaks suggested strong orientation preferences. Due to the limited number of diffraction peaks, it was difficult to index the X-ray diffractogram. Combined with the TEM analysis, it was concluded that each major peak (e.g. the peak at $2\theta \approx 40^\circ$) was the result of superimposition of the diffraction of $\alpha$, $\alpha_2$ and $\gamma$ phases. Simulations of the XRD diffraction of the three phases are also given in figure 4.4 for comparison. For detailed XRD data, see table 1 in Appendix A.

Since no phase separation could be observed using SEM, a cross-sectional TEM specimen was prepared. Figure 4.5 is a typical TEM BF image showing a cross section of the Ti-50Al-10Cr deposit. Close to the deposit-substrate interface was a thin amorphous layer. The crystalline grains were formed on top of this amorphous deposit.
They exhibited a columnar leafy structure, with the "roots" embedded in the amorphous matrix. It can be observed that each domain of the columnar structure contained very fine structures and a lamella feature was evident inside domains. Figure 4.6 is a typical TEM DF image of a few grains in the crystalline deposit, also revealing a leafy structure.

The SADPs taken from the amorphous area showed typical diffuse rings (see figure 4.7). Careful observation did not find any evidence of crystalline embryos. The amorphous part of the deposit layer was determined to be around 1–3 μm thick.

Figure 4.8 shows a typical SADP taken from an area containing both crystalline and amorphous material. The broken diffraction ring of the crystalline phases superimposed on the diffuse ring indicated a texture structure.

Figure 4.9 shows a SADP taken from one of the crystalline domains. The strong streaking effect was due to the shape effect of the crystallites. The diffraction "archs" indicated that there was a slight orientation change between the crystallites. This pattern was found to be the overlapped $\alpha <2\overline{1}0>$ and $\gamma <101>$ patterns, with very weak reflections attributed to the superlattice reflections of the $\alpha_2$ phase (see figure 4.10 for indexing key).

In order to identify the crystalline phases, micro-area diffraction (MD) was employed. In the MD mode, it was noted that the diffraction pattern rotated slightly when the electron beam was moved across the same domain. Figure 4.10a shows a MD pattern corresponding to the same orientation as shown in figure 4.9. This pattern was the result of superimposition of $\gamma <101>$ (figure 4.10c) and $\alpha <2\overline{1}0>$ (figure 4.10b) together with $\alpha_2$ superlattice spots (figure 4.10d).

The sample was then carefully tilted to the $\gamma <112>$ and $\alpha <01\overline{1}0>$ orientation, and the superlattice spots of the $\gamma$ phase were also present (see figure 4.11). The diffraction simulations are shown along with the MD patterns for comparison and indexing results.
are marked in the simulated patterns. Table 4.2 gives some d-spacing of these three phases, showing the closeness of d-spacings for certain crystal planes.

Streaking was observed in the $\alpha <2\overline{1}0> / \gamma <101>$ patterns (see figures 4.9 and 4.10), indicating that the crystallites were plate-like (see figure 4.9 for diffraction pattern and figure 3.3 for illustration of shape effect). As streaking was only observed along the $\alpha <0001> // \gamma <111>$ direction, it indicated that the phases were plate-like with the normal to the plates being $\alpha <0001> // \gamma <111>$.

| Table 4-2. Comparison of some d-spacings of the $\alpha$, $\alpha_2$ and $\gamma$ phases. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | $\alpha(0002)$ | $\alpha_2(0002)$ | $\gamma(111)$  | $\alpha(<\overline{1}11>)$ | $\alpha_2(0221)$ | $\gamma(020)$  |
| d-spacing / nm  | 0.233           | 0.233           | 0.233           | 0.226           | 0.220           | 0.200           |

In the course of the diffraction study of various crystalline domains, it was noted that the positions of the zone axis (e.g. $\alpha <0001> // \gamma <101>$) of many of these domains were very close. This also suggested that the growth of the $\gamma/\alpha$ grains had certain orientation preferences.

In order to examine the shape and phase boundaries of these crystallites directly, high-resolution imaging was performed. Figure 4.12 presents the typical HREM images near the zone axis of $\alpha <2\overline{1}0> // \gamma <101>$ showing lattice fringes. It clearly shows that the crystalline domain was highly faulted and all crystallites were plate-like. Each crystalline plate was only a few nanometers thick. As indicated by the streaking feature, the normal to the plates corresponds to $\alpha <0001> // \gamma <111>$. 
4.3.2 The Ti-53Al-15Cr Deposit

The XRD spectrum of this deposit and the diffraction simulations of α, α2 and γ are shown in figure 4.13 (see also table 2 in Appendix A). The deposit consisted of a small amount of amorphous material, apart from the crystalline α and γ phases, as shown in the TEM BF image (see figure 4.14). As for the Ti-50Al-10Cr deposit, the Ti-53Al-15Cr deposit was amorphous in the early stages of deposition and leafy crystalline domains were formed on top of the amorphous layer, with their “roots” embedded in the amorphous matrix. From the BF images, the laminar structure was discernible. Analysis of the TEM diffraction patterns gave the same results as for the Ti-50Al-10Cr deposit. Figure 4.15 shows the MDPs of α <0110> // γ <112> and α <2110> // γ <101>. The streaking effect indicated that the crystallites in this deposit were also plate-like, with the normal to the crystalline plate being α <0001> and γ <111>.

4.3.3 The Ti-50Al-20Cr Deposit

Although the Ti-50Al-20Cr deposit was produced under the same conditions as the previous two deposits, it was found to be completely amorphous. The XRD spectrum of this alloy is given in figure 4.16, which shows two amorphous hillocks. Since a small amount of crystallites might not be detected from the XRD analysis, cross sectional TEM specimens were studied. No evidence of any crystallites was found. Figure 4.17 shows a TEM BF image of the amorphous Ti-50Al-20Cr. The SADP shows diffuse rings, indicating the presence of the amorphous material.

4.4 Deposits Produced by the Discontinuous Route

The discontinuous route was employed to avoid significant temperature rise during sputter deposition. The Ti-50Al-10Cr deposit, which was found to have crystalline phases when produced using the continuous deposition route, was re-produced using the discontinuous route. The Ti-48Al was also deposited using this route.
XRD diffractograms showed the typical amorphous hillocks for both deposits, as seen in figure 4.18. However, a sharp crystalline diffraction peak was observed around $2\theta \approx 29.9^\circ$. Indexing of the XRD peak led to the $\alpha_2$ phase (1120), which was present in the substrate.

TEM study was then carried out on the planar specimens. A general TEM study of the Ti-50Al-10Cr deposit revealed an amorphous feature, as shown in the BF image in figure 4.19. Careful inspection revealed that there existed a small amount of nanocrystallites in some areas (see figure 4.20), with most of the deposit being amorphous. In the Ti-48Al deposit no crystallites were found (see figure 4.21).

### 4.5 Texture Study

The XRD diffractograms of the Ti-50Al-10Cr and Ti-53Al-15Cr deposits produced by the continuous route indicated strong orientation preference. TEM showed that the crystalline domains formed in the Ti-50Al-10Cr deposit had a columnar structure and many of these columns were almost perpendicular to the substrate surface. The columns contained large amounts of alternating $\alpha$ (0001) // $\gamma$ (111) plates. However, TEM analysis provided very localised information. Texture analysis using X-ray (Fe K\textsubscript{\alpha} radiation) with a texture goniometer was thus carried out for further confirmation.

The texture of the intermetallic $\gamma$ phase was characterised by measurements of the $\gamma$ (111) // $\alpha$ (0001) peak. When present, the texture in the deposits was always of a fiber type. The deposits texture will be represented in this work either by pole figures or by axial pole figures. For this second representation, the intensities of the given peaks are followed as a function of the tilted angle. This is possible because intensities are independent of the azimuthal angle for fibre textures. This method was particularly interesting here when characterising the samples that have been slightly oxidised and
for which additional diffraction peaks, some of them nearly overlapping the γ-TiAl peaks, were obtained in the XRD spectra.

The spectrum for the Ti-50Al-10Cr deposit produced by the continuous route obtained using the Fe Kα radiation is given in figure 4.22. One single sharp diffraction peak is observed at 2θ = 49.8°. At this angle, this peak can correspond to the diffraction of the (111) planes of the γ phase and (0001) of the α. This was verified by the pole figure measurements, as illustrated in figures 4.23 and 4.24.

Figure 4.23 is the normalised γ (111)//α (0001) pole figure. It shows a sharp peak in its centre and a ring that are characteristic of a γ <111> // α <0001> fiber with axis perpendicular to the substrate surface. Figure 4.24 shows the γ(111) // α(0001) axial pole figure. In this diagram the high intensity at the peak compared with a random situation indicated the sharpness of this texture.

The reason for such a texture formation could be explained by the crystallography of the two phases. The γ phase has a f.c.t structure, which is very close to a f.c.c structure (due to its specific lattice parameters; see chapter 2). Its most densely packed crystal plane is (111). For the h.c.p α phase, the most densely packed plane is (0001). By forming γ <111> and α <0002> fibres, the surface energy of the crystalline deposit can be reduced.

### 4.6 Summary

In this study, the Ti-50Al-10Cr and Ti-53Al-15Cr deposits produced by the continuous route of magnetron sputter deposition were partially crystalline, with a thin amorphous layer formed in the early stage of deposition. The Ti-50Al-20Cr deposit obtained using the same processing scheme was totally amorphous. The Ti-50Al-10Cr and Ti-48Al deposits, obtained by the discontinuous route were also amorphous. A number of nano-
crystallites were found in the Ti-50Al-10Cr deposit produced by the discontinuous route.

The crystalline material in the two deposits produced by the continuous route exhibited a columnar structure. Phase characterisation clarified that these crystallites mainly consisted of the \(\gamma\) and \(\alpha\) phases. The \(\alpha\) phase was partially ordered. The crystalline fibres mainly consisted of laminar \(\alpha\) and \(\gamma\) phases, with each lamina being only a few nanometers thick. The \(\alpha/\gamma\) lamina were \(\gamma <111> \parallel \alpha <0001>\) oriented, with the normal being parallel to the growth direction of the deposits. Texture analysis confirmed the deposits had \(\gamma <111> \parallel \alpha <0001>\) texture.
Figure 4.1  SEM SE images showing the undulating surface morphology of (a) the crystalline Ti-50Al-10Cr (b) the crystalline Ti-53Al-15Cr and (c) the amorphous Ti-50Al-20Cr deposits; these deposits were produced by the continuous route. All samples were tilted to 15° to obtain a better 3-D effect.
Figure 4.2 SEM SE images showing the undulating feature of (a) the amorphous Ti-50Al-10Cr (b) the amorphous Ti-48Al deposits; these deposits were produced by the discontinuous route. The samples were tilted 45° to obtain a 3-D effect.
Figure 4.3 (a) SEM bright field (BF) cross-sectional image and corresponding elemental maps of the as-deposited Ti-50Al-10Cr (crystalline) deposit produced by the continuous route, showing uniform elemental distributions.
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Figure 4.3 (b) SEM BF cross-sectional image and corresponding elemental maps of the as-deposited Ti-50Al-20Cr (amorphous) deposits produced by the continuous route, showing uniform elemental distributions.
Figure 4.4 XRD diffractograms of the as-deposited Ti-50Al-10Cr, compared with the simulated spectra of the γ-TiAl, α-Ti and α2- Ti3Al phases.
Figure 4.5 A typical TEM BF image showing a cross-section of the as-deposited Ti-50Al-10Cr alloy produced by the continuous route. The leafy crystalline domains could be seen to grow from the amorphous matrix.
Figure 4.6  A TEM DF image showing a cross-section of the crystalline area in the as-deposited Ti-50Al-10Cr alloy produced by the continuous route, revealing a leafy structure.

Figure 4.7  A TEM BF image of the amorphous area in the as-received Ti-50Al-10Cr deposit produced by the continuous route. The insert shows a SADP taken from this area showing typical amorphous diffuse rings.
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Figure 4.8 A SADP taken from an area of the Ti-50Al-10Cr deposit containing both crystalline and amorphous material. The broken diffraction ring superimposed on the diffuse ring indicated a texture structure.

Figure 4.9 A SADP taken from a crystalline domain in the as-deposited Ti-50Al-10Cr thin-film specimen, showing strong streaking in the [111]$_\gamma$ // [0001]$_\alpha$ direction. The SADP contains $\alpha$ <2$\bar{1}$0>, $\alpha_2$ <2$\bar{1}$0> and $\gamma$ <101>.
Figure 4.10  (a) MDP of the mixed pattern of $\alpha <2\bar{1}10>$ and $\gamma <10\bar{1}>$ with $\alpha_2$ superlattice spots for the Ti-50Al-10Cr deposit produced by the continuous route; (b) simulated $\alpha <2\bar{1}10>$ SADP; (c) simulated $\gamma <10\bar{1}>$ SADP and (d) simulated $\alpha_2 <2\bar{1}10>$ SADP.
Figure 4.11  (a) MDP of the mixed pattern of $\alpha <01\overline{1}0>$ and $\gamma <112>$ for the Ti-50Al-10Cr deposit produced by the continuous route; (b) simulated $\alpha <01\overline{1}0>$ SADP; (c) simulated $\gamma <112>$ SADP and (d) simulated $\alpha_2 <01\overline{1}0>$ SADP.
Figure 4.12  HREM images taken for the Ti-50Al-10Cr deposit produced by the continuous route: (a) HREM image taken at the α <2110> and γ <101> zone axis. The lattice fringes show a general view of the lamellar structure of crystallites; (b) HREM image at higher magnification, revealing that the crystallites are of nano-scale and each layer contains only a few atomic planes.
Figure 4.13 XRD diffractograms of the as-deposited Ti-53Al-15Cr alloy and the simulated XRD spectra of the $\gamma$-TiAl, $\alpha$-Ti and $\alpha_2$-Ti$_3$Al phases.
Figure 4.14 TEM BF images showing the cross-section of the as-deposited Ti-53Al-15Cr alloy; (a) leafy crystalline domains were seen growing from the amorphous matrix; (b) the fine laminar structure of the crystalline areas is discernible.
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Figure 4.15  MDPs taken from the crystalline domain of the Ti-53Al-15Cr deposit: (a) $\alpha <0\overline{1}10>$ and $\gamma <112>$ pattern and (b) $\alpha <2\overline{1}0>$ and $\gamma <101>$ pattern. See figure 4.10 for SADP simulations.

Figure 4.16  XRD diffractogram of the as-deposited Ti-50Al-20Cr, showing the typical amorphous hillocks.
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Figure 4.17  TEM BF image of the cross-section of the as-deposited Ti-50Al-20Cr produced by the continuous route. The diffuse rings in the diffraction patterns indicate an amorphous structure.

Figure 4.18  XRD images of the as-deposited Ti-50Al-10Cr and the Ti-48Al produced by the discontinuous route, showing typical amorphous hillocks. The peaks at $2\theta = 29.9^\circ$ are attributed to the $\alpha_2$ phase in the substrate.
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Figure 4.19  TEM BF image of the as-deposited Ti-50Al-10Cr produced by the discontinuous route.

Figure 4.20  TEM BF image of the as-deposited Ti-50Al-10Cr produced by the discontinuous route, showing nano-crystallites embedded in the amorphous matrix. Analysis of the diffraction rings as shown in the insert indicated that they were α crystallites.
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Figure 4.21  TEM BF image of the as-deposited Ti-48Al produced by the discontinuous route; the diffuse rings in the insert indicate that the deposit was amorphous.

Figure 4.22  XRD$\chi$ of the as-deposited Ti-50Al-10Cr produced by the continuous route. The radiation used was Fe K\textalpha. 
Figure 4.23  (111) pole figure of the $\gamma <111>$ fiber for the as-deposited Ti-50Al-10Cr produced using the continuous route.

Figure 4.24  (111) $\gamma$ axial pole figures of the as-deposited Ti-50Al-10Cr produced by the continuous route and the discontinuous route. The fibre texture is actually $<0002>_{\alpha//}<111>_{\gamma}$. 
Chapter 5
Heat-treated Deposits

5.1 Introduction

Heat treatment of the deposits led to the decomposition of the metastable phase(s) and precipitation of new phases. Isothermal heat treatment of the sputtered ternary alloy deposits was carried out at 1173K to understand the phase constitution at equilibrium\(^1\) at this temperature. Heat treatments at lower temperatures were done to study the crystallisation of amorphous Ti-Al(-Cr) alloys.

5.2 Isothermal Heat Treatment at 1173K

5.2.1 The Ti-50Al-10Cr Deposit

Two deposits of this composition were produced, the crystalline Ti-50Al-10Cr (continuous route) and the amorphous Ti-50Al-10Cr (discontinuous route). Both deposits were heat-treated at 1173K in order to study the phase equilibria at this temperature. There was continuous flow of Ar into the tube furnace during heat treatment in order to avoid oxidation of the deposits. The heat-treated samples were studied using XRD, SEM and TEM.

XRD analyses

Figure 5.1a shows the XRD diffractogram of the crystalline Ti-50Al-10Cr heat-treated at 1173K for 100 hours and figure 5.1b shows that of the amorphous Ti-50Al-10Cr heat-treated at 1173K for 10 hours. The XRD results showed that the heat-treated deposits consisted of \(\gamma\)-TiAl and the Laves phase Ti(Al,Cr)\(_2\) (see table 3 and 4 in

\(^1\) The Ti-48Al was excluded from the heat treatments at 1173K because the equilibrium phase diagram for the Ti-Al alloy system has been established.
Appendix A). Diffraction peaks corresponding to alumina were also found (which was in agreement with SEM observations). Peak identification showed that the oxide consisted mainly of alumina. In the XRD spectrum for the heat-treated amorphous Ti-50Al-10Cr, there were two peaks close to the $\alpha_2$ diffraction peaks. This could be attributed to the $\alpha_2$ being present in the substrate.

Comparing the two XRD diffractograms, it was noted that the ratio of $\gamma(111)$ over other $\gamma$ peaks was much greater in the deposit produced by the continuous route than in the discontinuous route. Since it was known that the Ti-50Al-10Cr produced by the continuous route contained a great amount of $\gamma<111>$ fibres (see chapter 4), the XRD results indicated that the textured structure was retained to a certain extent in the heat-treated Ti-50Al-10Cr deposit produced by the continuous route.

**SEM studies**

Figures 5.2a and 5.2b show the cross-sectional morphology of the crystalline Ti-50Al-10Cr heat-treated in Ar at 1173K for 10 hours and 100 hours respectively. The Laves phase (bright precipitates in figure 5.2) is seen in the $\gamma$ matrix. A columnar structure was observed in the cross-sections, which was consistent with the morphology of the as-deposited deposit. The columnar structure was particularly distinct in the sample heat-treated for 10 hours, with the Laves phase precipitates aligned in the direction normal to the substrate/deposit interface. It was less obvious in the sample heat treated for 100 hours, where precipitate coarsening was observed.

In the heat-treated Ti-50Al-10Cr deposit, which was amorphous in the as-deposited condition, no columnar structure was observed. Figure 5.3 shows a cross-sectional SEM BS image of the amorphous Ti-50Al-10Cr deposit heat-treated for 10 hours, showing a random distribution of precipitates.

Oxide scale had formed on the deposit, even though the heat treatment was done under continuous Ar flow, including the cooling period. The oxide is more evident in the BS image, as shown in figure 5.4. These results indicated that even at very...
low oxygen partial pressure, the Ti-50Al-10Cr alloy could still react with oxygen easily. The oxide scales in all three samples (heat-treated for 10 / 100 hours in Ar flow and heat-treated for 10 hours without Ar flow) were about 1 μm thick. This would suggest that the oxide scale was formed rapidly in the early stage of heat treatment, then the growth rate was reduced significantly. Thus, this behaviour would indicate that the Ti-50Al-10Cr alloy could be considered as oxidation resistant coating at high temperatures. EDX analyses showed that these scales were Al rich.

It was interesting to notice that, close to the substrate/deposit interface, the volume fraction of the Laves phase decreased. This could be attributed to Cr diffusing into the substrate, leading to the local equilibrium shifting towards the γ side in the Ti(Al,Cr)_2 + γ area of the phase diagram, see figure 2.3. The Cr diffusion profiles will be discussed in Chapter 6.

**TEM studies**

TEM study was done to identify the phases present in the heat-treated deposit. The Ti-50Al-10Cr deposit produced by the continuous route (crystalline in the as-deposited condition) and heat-treated for 100 hours was studied. As the columnar structure had been observed on a cross-section, planar-view TEM specimens were made. TEM observation showed that precipitates appeared to be equiaxed and distributed randomly, as shown in figure 5.5a. The size of the different phases varied from tens of nanometers to up to 1 μm in diameter.

Careful inspection showed that the Laves phase precipitates appeared in two forms: large Laves phase particles were formed at the γ grain boundaries. Their sizes were about 500 nm to 1 μm in diameter; there were also some spherical Laves phase precipitates embedded within the γ grains, their size being in the range from a few tens of nanometers to a few hundred nanometers (see figure 5.5b).

EDX analyses showed that the chemical composition of the γ and Laves phases were 44Ti-52.5Al-3.5Cr and 33.5Ti-38.5Al-28Cr (at.%) respectively. EDX
analyses carried out on the smaller Laves phase particles embedded in γ grains yielded compositions around 34.5Ti-39.3Al-25.2Cr. The latter data, however, should be considered to be only a qualitative result, since the Laves phase particles were so small that simultaneous analysis of the γ phase information was likely. Even so, the remarkable compositional differences between the γ and the Laves phases made phase identification easier by EDX analyses.

Diffraction patterns were obtained for further phase identification. Figure 5.6 shows the <100>, <101> and <111> patterns taken from a γ-TiAl grain. The SADPs of <0001>, <1012>, <2110> and <3031> taken from the Laves phase are shown in figure 5.7. In these two figures, the SADP simulations are shown together with the indexing keys.

Figure 5.8 shows typical elemental maps acquired from the planar thin-foil specimen, showing the compositional difference between the γ and Laves phases. Figure 5.9 shows elemental maps acquired from a Ti(Cr,Al)2 particle embedded in the γ grain, which was about 100 nm in diameter. The maps show that the particle was Cr rich and slightly poorer in Al than the surrounding γ matrix. In order to confirm the particle identity, MDPs were taken and the C14 Laves <4156> and <3031> patterns are shown in figure 5.10.

No unique orientation relationship was observed between the Laves and γ phases. However, there were some favourable crystallographic relationships between them (Shao, 1995).

Twinning of the γ phase was found to be quite common. For instance, figure 5.11 shows a TEM DF image taken at γ<110> zone axis, showing two γ grains to be 180° twins. Figure 5.12a shows the SADP taken from the area where the two grains meet. Figure 5.12b gives the SADP of γ<110> from one of the γ grains. The indexing key to figure 5.12a is given in figure 5.12c.
5.2.2 The Ti-53Al-15Cr Deposit

The Ti-53Al-15Cr deposit was produced using the continuous route and the as-deposited morphology was very much like that of the Ti-50Al-10Cr deposit produced by the same processing route. On the basis of the result for the heat treatment of the Ti-50Al-10Cr deposit, which showed that Ar flow would not prevent oxidation, the isothermal heat treatment of the Ti-53Al-15Cr deposit was performed without Ar protection.

**XRD analyses**

Figure 5.13 shows the XRD diffractograms of the Ti-53Al-15Cr alloy heat-treated in air for 10 and 100 hours (see also table 5 in Appendix A). From the isothermal section of the phase diagrams at 1273K and 1073K (see figures 2.3 and 2.4), it can be seen that at 1173K this alloy could be in the $\gamma + \text{Laves}$ two phase region, or the $\gamma + \tau + \text{Laves}$ three phase region. From the XRD results, the Laves phase was identified. Since the f.c.c $\tau$ phase and the f.c.t. $\gamma$ phase have very close lattice parameters, their diffraction spectra exhibit great similarity, and XRD on its own could not provide conclusive evidence about their existence. By analysing the TEM diffraction patterns, it was found that both $\gamma$ and $\tau$ phases were present (see below).

**SEM studies**

Figure 5.14 gives a typical SEM BS image showing a cross-section of the Ti-53Al-15Cr deposit heat-treated at 1173K for 10 hours. The Laves phase (the bright precipitates) is seen in the $\gamma$ matrix. The heat-treated microstructure shows evidence of columnar structure, which is less distinct, compared with the crystalline Ti-50Al-10Cr deposit heat-treated for the same duration (figure 5.2a). Similar to the Ti-50Al-10Cr deposit, the oxide scale formed on the Ti-53Al-15Cr deposit was about 1 $\mu$m thick.

**TEM studies**

TEM studies showed that at 1173K the microstructure of the Ti-53Al-15Cr deposit contained three phases. Figure 5.15 is a planar view of this deposit, showing a few large Laves particles about 300 nm in diameter. The typical composition of the
Laves phase, determined by EDX, was about 35.0Ti-36.5Al-29.5Cr (at.%). Figure 5.16 shows the \(<2\overline{1}13>\) and \(<2\overline{1}10>\) patterns of the Laves phase in the heat-treated Ti-53Al-15Cr deposit.

Systematic tilting was performed to clarify whether the \(\tau\) phase was present. The fine structure of mixed \(\tau/\gamma\) domains could only be revealed when it was oriented at a low-index zone axis. Figure 5.17 shows a typical pair of TEM BF and DF images of one such domain inter-mixed with \(\gamma\) and \(\tau\), which was taken at a low-index zone axis (\(\gamma/\tau<100>\)).

Analyses of SADPs showed that the \(\gamma\) and \(\tau\) phases were coherent with each other. Figure 5.18a shows a SADP taken from the above domain, revealing a superimposed \(\gamma<100>\) and \(\tau<100>\) pattern. When using the MD mode, the \(\gamma<100>\) and \(\tau<100>\) patterns could be distinguished, as shown in figure 5.18c and 5.18d. The indexing key is given in figure 5.18b.

Figure 5.19a shows the super-imposed SADP, which could be identified as \(\gamma<112>\) easily. When using the MD mode the super-imposition of \(\gamma<112>\) and \(\tau<112>\) was found, as shown in figures 5.19c and 5.19d. The indexing key is shown in figure 5.19b.

The orientation between the \(\gamma\) and \(\tau\) phases is illustrated in figure 5.20, with \(\gamma/\tau(010)\) being the habit plane. This orientation relationship is reasonable because \(\gamma\) and \(\tau\) have very similar structure and lattice parameters. While being f.c.t structured with \(a = 0.4005\) nm and \(c = 0.407\) nm, the \(\gamma\) cell is very close to a face centred cube (for the f.c.c \(\tau\), \(a = 0.404\) nm).

TEM EDX elemental maps for the Ti-53Al-15Cr deposit heat-treated at 1173K for 10 hours are shown in figure 5.21. The Laves phase is evidently rich in Cr compared with the other phases. The Cr was observed to be unevenly distributed
through the γ/τ domains. This could be attributed to the different γ/τ volume ratio among domains.

5.2.3 The Ti-50Al-20Cr Deposit

Ti-50Al-20Cr deposit was produced using the continuous route. Unlike the other two Ti-Al-Cr deposits using the same processing route, the as-deposited deposit was completely amorphous. Isothermal heat treatment for the Ti-50Al-20Cr was carried out without Ar protection.

XRD analyses
diffractograms

Figure 5.22 shows the XRD of the Ti-50Al-20Cr heat treated at 1173K for 3, 10 and 100 hours respectively. The peak broadening effect was evident for the sample heat-treated for 3 hours, which would suggest that the crystalline grains were still very small. Indexing of the peaks led to the identification of the Laves phase. TEM was used to clarify whether the γ and τ phases were present. The complete XRD data are given in table 6 in Appendix A.

SEM studies

Figure 5.23 gives typical SEM BS images of the Ti-50Al-20Cr deposit heat-treated at 1173K for 10 hours and 100 hours. Coarsening of the microstructure is evident. Since the deposit was amorphous prior to heat treatment, randomly distributed precipitates were observed. In this deposit, the Laves phase, rather than γ, was the dominant constituent. It is noted that, in the deposit heat-treated for 10 hours, the scale of the microstructure near the deposit/substrate interface was significantly finer than in the bulk of the deposit. This feature is attributed to higher nucleation rate near the deposit/substrate interface, presumably due to stresses at the interface.

TEM studies

For further phase identification, cross-sectional TEM studies were conducted on the Ti-50Al-20Cr deposit heat-treated at 1173K for 100 hours. The C14 Laves and γ phases were both identified, and the τ phase was not found. Figure 5.24 shows a
Chapter 5  Heat-treated Deposits

TEM BF image and a DF image of the specimen. It is seen that all the precipitates were equiaxed. Figure 5.25 shows the \(<\underline{21\overline{1}0}>\), \(<\underline{30\overline{3}1}>\), \(<\underline{51\overline{4}6}>\) and \(<\underline{\overline{101}2}>\) SADPs taken from the Laves phase. The \(\gamma\) \(<101\gamma>, <110\gamma>\) and \(<111\gamma>\) SADPs are given in figure 5.26.

Figure 5.27 is a \(<110\gamma>\) SADP taken from a \(\gamma\) phase, and it was found to contain also the Laves \(<10\overline{1}0>\) pattern. However, this seemingly obvious orientation relationship should be a coincidence, since it was not observed repeatedly. This is in agreement with the result for the Ti-50Al-10Cr alloy, where no orientation relationship was found between the \(\gamma\) and Laves phases. EDX analyses showed that the compositions of the Laves and \(\gamma\) phases were around 32.8Ti-37.8Al-29.4Cr and 44.1Ti-51.1Al-4.8Cr (at.%) respectively.

5.3 Early Stage of Phase Transformation in the Amorphous Alloys

5.3.1 The Ti-48Al Deposit

The Ti-48Al deposit was studied in order to understand the devitrification of amorphous deposits. Work on this alloy formed the foundations for further work on the ternary alloys. At equilibrium, the Ti-48Al alloy is very close to the \((\alpha+\gamma) / \gamma\) phase-field boundary when the temperature is lower than 1400K, (see figure 2.2). Rapid solidification of high temperature liquid of this composition usually leads to the precipitation of the \(\alpha\) phase, which then decomposes into a lamellar microstructure of \(\gamma\) and \(\alpha_2\) via the transformation path Liquid → \(\alpha\) → \(\gamma + \alpha_2\).

Figure 5.28 shows the lamellar microstructure of our Ti-50Al substrate, which was cast from pure Ti and Al materials. The same alloy was also used as the target material to produce our Ti-48Al deposit.

Heat treatments were carried out at 773, 873 and 973K in air in order to study the devitrification of the Ti-48Al amorphous deposit. To determine the commencement
of transition and catch the early stages of the phase transformation, samples were isothermally heat-treated for different length of time, and an XRD diffraction spectrum was acquired for each sample. The transition commencement was estimated when crystalline diffraction peaks emerged from the amorphous hillocks\(^1\).

**XRD analyses of the samples heat-treated at 773, 873 and 973K**

First, the Ti-48Al deposit was heat-treated at 773K for various periods. Figure 5.29 gives the XRD\(^2\) of the Ti-48Al isothermally heat-treated for 5, 10, 15 and 20 hours respectively, showing the phase evolution in the deposit. The sharp diffraction peaks were found in the samples heat-treated for 15 hours or longer. Only amorphous hillocks were observed in the samples heat-treated for shorter time.

Due to the similarity between the XRD of the \(\alpha\), \(\alpha_2\) and \(\gamma\) phases, phase identification was not possible with only a few peaks appearing in spectra. TEM work confirmed the presence of all three phases at a later stage. Therefore, the XRD peaks could actually be the superimposition of multi-phase diffraction. Table 7 in Appendix A lists the possible indices for the diffraction peaks found in the Ti-48Al heat-treated at 773K for 15 hours.

Figure 5.30 gives the XRD\(^2\) of the Ti-48Al heat-treated at 873K for 10, 60 and 120 minutes. It shows that devitrification has started within 10 minutes of heat-

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\(^1\) DSC is often employed to study the crystallisation of amorphous materials and to obtain thermodynamic data. Free-standing samples are often required for this purpose (see section 2.4.4). However, numerous attempts to prepare suitable specimens were not successful in this work. The major obstacle was the difficulty of acquiring free-standing samples, or sufficient amount of deposited materials. In this work, in order to obtain samples for DSC studies, first a thin layer of material was cut off from the coated button. The slice contained both the deposit and some substrate material. Then the slice was ground down from the substrate side to around 150 ~ 200 \(\mu\)m thick. Even so, the deposit would always have much more substrate material attached than the deposit itself (the deposits were about 20 ~ 30 \(\mu\)m thick). This led to weak heat exchange peaks upon devitrification. Although in certain cases heat exchange curves were indeed observed, the peaks were so weak that they could not serve as a strong evidence. Therefore, the DSC technique could not be used to study the devitrification of amorphous deposit in this work.
treatment. Figure 5.31 shows that devitrification occurred within 3 minutes at 973K. The indexing of XRD results at 873K and 973K is given respectively in table 8 and 9 in Appendix A. For simplicity, only one spectrum is given at each temperature in the appendix.

TEM studies
The TEM study was concentrated on samples heat-treated at 773K for 15 hours and 973K for 3 minutes.

For the amorphous Ti-48Al deposit heat-treated at 773K for 15 hours, there were two types of morphology in the deposit, apart from the amorphous phase:

i. isolated spherical α crystallites embedded in the amorphous matrix, as shown in figure 5.32;

ii. the leafy domains containing the γ and α lamellar structure in the amorphous matrix, as shown in figure 5.33a; or nearly equiaxed domains containing the γ and α phases, as shown in figure 5.33b. The α phase was also partially ordered (i.e. the α₂ phase was formed) in these domains.

Figure 5.34 shows the α <2110>, <1123> and <2423> MDPs taken from one of the α particles shown in figure 5.32. Figure 5.35a is a SADP taken from a γ/α mixed domain (as shown in figure 5.33), containing superimposed patterns of γ<101>, α<2110>. α₂ superlattice spots are also present, indicating the α phase was partially ordered. Figure 5.35b is a MDP of the same region. It resembles the pattern obtained in the as-deposited Ti-50Al-10Cr deposit by the continuous route (see figure 4.10). These two patterns show strong streaking in the α[111] // γ[0001] direction. For the indexing key see figure 4.10. Figure 5.35c shows the α<2110> MDP taken from such a domain. The γ <101> and <111> MDPs are given in figure 5.36. These results indicated that the metastable phase α was formed first and that further heat treatment led to the precipitation of γ and α₂.
The Ti-48Al deposit heat-treated at 973K for 3 minutes was also studied using TEM. In this sample the devitrification was complete. No amorphous phase was found. Figure 5.37 gives a typical TEM BF image, showing the intermixed $\gamma/\alpha$ domains (the $\alpha$ phase is partially ordered). The lamellar $\gamma/\alpha$ structure is more clearly seen in figure 5.38. The selected-area ring pattern was taken from a relatively large area. The intensity of the diffraction rings appeared to be uniform, indicating that the orientation distribution of those domains was random.

Diffraction patterns confirmed the formation of the $\alpha$ and $\gamma$ phases in the Ti-48Al deposit heat-treated at 973K for 3 minutes. Figure 5.39 shows the $\alpha<2\bar{1}\bar{1}0>/\gamma<10\bar{1}>$ MDP with $\alpha_2$ superlattice spots, which was taken from a $\gamma/\alpha$ domain. The $\alpha_2$ diffraction indicates that the $\alpha$ phase was partially ordered. Figure 5.40 shows the MDP of $\alpha<0\bar{1}\bar{1}0>/\gamma<112>$. It was superimposed on the $\alpha<2\bar{1}\bar{1}0>/\gamma<10\bar{1}>$ pattern.

5.3.2 The Ti-50Al-20Cr Deposit

The same heat treatment strategy was used for the Ti-50Al-20Cr deposit, except that the heat treatments started from 873K in order to shorten the devitrification starting time.

XRD analyses of the samples heat-treated at 873, 923 and 973K

Figure 5.41 shows the XRD diffractograms of the Ti-50Al-20Cr deposit heat-treated at 873K. Sharp diffraction peaks emerged from the diffraction halo for the samples heat-treated for 3 hours. From previous experience, one or more of the $\alpha$, $\gamma$ and the Laves phases were expected in the deposit (since the Laves phase is a line compound, it is unlikely that it would precipitate before the solution phases). Phase characterisation was not possible due to the limited number of peaks present.

The XRD of the Ti-50Al-20Cr heat-treated at 923K are given in figure 5.42. They revealed that devitrification has started within 15 minutes of heat treatment. Within 30 minutes, the Laves phase was also formed. Figure 5.43 shows
that at 973K, devitrification occurred between 3 and 5 minutes. After 5 minutes at 973K, the Laves phase was also formed.

**TEM studies**

TEM study was carried out on the sample heat-treated at 923K for 15 minutes. Figure 5.44a is a TEM BF image showing the distribution of precipitate in the Ti-50Al-20Cr. The nano-scaled precipitates had a cubic configuration. Figure 5.44b shows a few faulted γ precipitates. Figure 5.45 is a typical EDX elemental map acquired for the Ti-50Al-20Cr deposit heat-treated at 923K for 15 min. It shows that the γ precipitates were poorer in Cr than the surrounding amorphous matrix.

SADP indexing led to the identification of γ phase. The Laves phase was not found. Figure 5.46 shows the γ <112> MDP. The γ precipitates also showed evidence of γ twinning, as shown in figure 5.44b. For example, figure 5.47 shows a MDP, which mainly consists of γ <110>, while superimposed with the γ <101> pattern.

**5.4 Texture Study on the Ti-50Al-10Cr Deposit**

As discussed earlier, the as-deposited Ti-50Al-10Cr deposits produced by the continuous route had a columnar structure, which mainly consisted of γ<111>//α<0002> fibres. This columnar structure remained during crystallisation at elevated temperatures.

Texture analysis was performed on the Ti-50Al-10Cr deposit heat-treated in Ar at 1173K for 10 hours. Figure 5.48 is the γ (111) axial pole figure for this deposit. It clearly shows that there was still a strong γ (111) diffraction near θ_{hinging} = 0°, i.e. γ <111> of a large percent of γ precipitates parallel or nearly parallel to the deposit surface normal. Due to crystallisation, the intensity of γ (111) of the heat-treated sample decreased, compared with the as-deposited deposit. For the amorphous Ti-50Al-10Cr deposit, produced by the discontinuous route, the γ (111) orientation
was totally random after heat treatment, as indicated by the almost flat line in the diagram.

The \( \gamma \) (002) and (200) orientation preference was also noted, as shown in figure 5.49. These orientation preferences were much less significant than the \( \gamma \) (111). The intensity peak of \( \gamma \) (002)/(200) appeared at around \( 55^\circ \), which approximates the interplanar angle between \( \gamma \) (111) and (002)/(200) (\( \theta_{(111)-(002)} = 55.2^\circ \), \( \theta_{(111)-(200)} = 54.5^\circ \)). Hence this observed orientation preference could be the result of the \( \gamma \) (111) texture.

### 5.5 Summary

The phase equilibria status of the Ti-Al-Cr deposits at 1173K is summarised as follows:

i. Ti-50Al-10Cr: \( \gamma \) + Laves. The \( \gamma \) precipitates are equiaxed. The Laves phase may form within the \( \gamma \) matrix.

ii. Ti-53Al-15Cr: \( \gamma \) + \( \tau \) + Laves. The Laves grains are equiaxed. The \( \gamma \) and \( \tau \) phases precipitate in a finely intermixed manner, with \( \gamma <001> // \tau <001> \).

iii. Ti-50Al-20Cr: \( \gamma \) + Laves. Crystalline precipitates of both phases are equiaxed.

The morphology of the deposits after heat treatment depends on the as-deposited microstructure. The texture (\( \gamma <111> \)) in the crystalline as-deposited deposits was maintained, while in the amorphous deposits a random distribution of the Laves phase precipitates was observed. No orientation relationship was observed between the \( \gamma \) and Laves phases.

Devitrification of the amorphous Ti-48Al at 773K and 973K led to the phase transformation sequence: amorphous phase \( \rightarrow \alpha \rightarrow \alpha_2 + \gamma \). The \( \alpha/\gamma \) phases precipitated exhibited an intermixed lamellar structure. The crystallisation in the
amorphous Ti-48Al deposit started within 15 hours, 10 minutes and 3 minutes during heat treatments at 773K, 873K and 973K respectively.

In the early stages of devitrification of the amorphous Ti-50Al-20Cr deposit, the γ phase was formed in the amorphous matrix. The γ precipitates tended to have a cubic configuration. Twinning was observed within the γ grains. The crystallisation in the amorphous Ti-50Al-20Cr deposit started within 3 hours, 15 minutes and 5 minutes during heat treatments at 873K, 923K and 973K respectively.
Figure 5.1 XRD diffractograms of (a) Ti-50Al-10Cr deposit (crystalline when as-deposited) heat treated in Ar at 1173K for 100 hours. (b) Ti-50Al-10Cr deposit (amorphous when as-deposited) heat treated in air at 1173K for 10 hours. Diffraction indexing is illustrated in (b).
Figure 5.2 (a) SEM SE image of the crystalline Ti-50Al-10Cr deposit heat-treated at 1173K with Ar flow for 10 hours. (b) SEM BS image of the crystalline Ti-50Al-10Cr heat-treated at 1173K with Ar flow for 100 hours, both images showing the columnar structure. The bright precipitates are the Laves phase; the dark phase is the $\gamma$-TiAl.
Figure 5.3  SEM BS image of the Ti-50Al-10Cr deposit after a heat treatment of 10 hours showing a random distribution of precipitates. This deposit was amorphous in the as-received condition.

Figure 5.4  SEM BS image of the Ti-50Al-10Cr deposit heat-treated at 1173K with continuous Ar flow for 100 hours showing that a thin layer of oxide scale was formed. This deposit was produced by the continuous route.
Figure 5.5  (a) TEM BF image of the Ti-50Al-10Cr deposit heat-treated at 1173K with continuous Ar flow for 100 hours, showing equiaxed precipitates of the γ and Laves phases. (b) TEM BF image showing a few spherical Laves phase precipitates in a γ grain. This deposit was produced by the continuous route and had a columnar structure.
Figure 5.6  TEM SADPs taken from the $\gamma$ phase in the Ti-50Al-10Cr deposit heat-treated at 1173K for 100 hours, showing (a) $<100>$, (c) $<101>$ and (e) $<111>$ patterns; the indexing keys are shown on the right hand side of each pattern. This deposit was produced by the continuous route and had a columnar structure.
Figure 5.7  TEM SADPs taken from the C14 Laves phase in the Ti-50Al-10Cr deposit heat-treated at 1173K for 100 hours, showing the (a) <0001>, (c) <10\bar{1}2> patterns. The indexing keys are shown on the right hand side of each pattern (continued in the next page).
Figure 5.7  (Continued) SADPs taken from the Laves phases in the Ti-50Al-10Cr deposit heat-treated at 1173K for 100 hours, (e) $<\overline{2}\overline{1}0>$ and (g) $<30\overline{3}1>$ patterns. The indexing keys are shown on the right hand side of the patterns. This deposit was produced by the continuous route and had a columnar structure.
Figure 5.8  Typical TEM EDX maps for the Ti-50Al-10Cr deposit heat-treated with Ar flow at 1173K for 100 hours, showing the compositional difference between the $\gamma$ and Laves phases. The deposit was produced by the continuous route and had a columnar structure.
Figure 5.9  TEM EDX elemental maps acquired for a Laves phase particle embedded in a γ grain, showing that it was richer in Cr and slightly poorer in Al than the surrounding γ phase. The particle is about 100 nm in diameter.

Figure 5.10  MDPs taken from the Laves phase embedded in a γ grain, showing (a) \(<41\overline{56}>\) and (b) \(<30\overline{3}1>\) patterns. (c) and (d) give the corresponding indexing keys.
Figure 5.11 A TEM DF image taken from the Ti-50Al-10Cr deposit heat-treated at 1173K for 100 hours, showing two twinned $\gamma$ grains. This deposit was produced by the continuous route and had a columnar structure.

Figure 5.12 (a) Two $\gamma$ <110> SADPs related to the twinning. (b) The $\gamma$ <110> of one of the grains. (c) The indexing key to the SADP in (a).
Figure 5.13 XRD diffractograms of the Ti-53Al-15Cr deposit heat-treated in air for (a) 10 hours, (b) 100 hours; the diffraction indexing is given in (a). This deposit was produced by the continuous route.
Figure 5.14 A typical cross-sectional SEM BS image of the Ti-53Al-15Cr deposit heat-treated in air at 1173K for 10 hours.

Figure 5.15 A typical TEM BF image showing the Laves Ti(Cr,Al)$_2$ phase and the $\gamma/\tau$ intermixed domains formed in the Ti-53Al-15Cr deposit, which was heat-treated at 1173K for 10 hours. This deposit was produced by the continuous route.
Figure 5.16 SADPs taken from the Laves phase in the Ti-53Al-15Cr deposit heat-treated at 1173K for 10 hours, (a) \(<2\bar{1}13>\) and (b) \(<2\bar{1}10>\) SADP. The indexing keys are given in (c) and (d) respectively.
Figure 5.17  (a) TEM BF image and (b) the corresponding DF image showing a domain containing inter-mixed $\gamma$ and $\tau$ phases in the Ti-53Al-15Cr deposit heat-treated at 1173K for 10 hours. The two images were taken at the $\gamma/\tau <100>$ zone axis.
Figure 5.18  (a) SADP taken from the $\gamma/\tau$ inter-mixed domain, shown in figure 5.17, which gives the superimposed $\gamma<100>$ and $\gamma<100>$ pattern; the indexing key is given in (b). The diffraction of $\gamma$ and $\tau$ was distinguished by MDPs: (c) shows the $\gamma<100>$ diffraction and (d) shows the $\tau<100>$ diffraction.
Figure 5.19  (a) SADP taken from a γ/τ inter-mixed domain, showing γ <112> and τ <112> patterns; the indexing key is shown in (b) where squares represent the τ diffraction and solid dots are the overlapped γ and τ diffraction. The diffraction of γ and τ were distinguished by MDPs; (c) gives the γ <112> diffraction and (d) shows the τ <112> diffraction.
Figure 5.20  Schematic illustration of the orientation relationship between the \( \tau \) phase (left) and the \( \gamma \) phase (right).

Figure 5.21  TEM EDX elemental maps acquired from the Ti-53Al-15Cr deposit heat-treated at 1173K for 10 hours, showing the compositional difference between the Laves phase and the \( \gamma/\tau \) domains.
Figure 5.22 XRD diffractograms of the Ti-50Al-20Cr deposit heat-treated in air (a) at 1173K for 3 hours; (b) at 1173K for 10 hours, (c) at 1173K for 100 hours. The broadened peaks in (a) indicate small sizes of the crystal grains in the deposit. The identification of diffraction peaks is given in (c). This deposit was produced by the continuous route.
Figure 5.23  Cross sectional SEM BS images of the Ti-50Al-20Cr deposit heat-treated at 1173K for (a) 10 hours and (b) 100 hours. This deposit was produced by the continuous route.
Figure 5.24  (a) TEM BF and (b) DF images, showing a cross section of the Ti-50Al-20Cr deposit heat-treated at 1173K for 100 hours.
Figure 5.25  SADPs taken from the Laves phase in Ti-50Al-20Cr heat-treated at 1173K for 100 hours, showing the (a) <2\bar{2}0> (b) <30\bar{3}1> (c) <5\bar{1}4\bar{6}> and (d) <10\bar{1}2> patterns. The indexing keys to (c) and (d) are given in (e) and (f). For indexing keys to (a) and (b), see figure 5.7f and 5.7h respectively.
Figure 5.26  SADPs taken from the $\gamma$ phase in the Ti-50Al-20Cr heat-treated at 1173K for 100 hours, showing the (a) $<101>$ (b) $<110>$ and (c) $<111>$ patterns. The indexing key to (b) is given in (d); for indexing keys to (a) and (c), see figures 5.6d and 5.6f respectively.
Figure 5.27  (a) A SADP taken from the Ti-50Al-20Cr deposit heat-treated in air at 1173K for 100 hours, showing the superimposed $\gamma <10\bar{1}>$ and Laves $<10\bar{1}0>$ patterns. The indexing key is given in (b).

Figure 5.28  TEM BF image showing the lamellar $\gamma/\alpha_2$ microstructure of the Ti-50Al substrate.
Figure 5.29 XRD diffractograms of the Ti-48Al deposit heat-treated at 773K for 5, 10, 15 and 20 hours, showing that crystallisation occurred within 15 hours.
Figure 5.30 XRD diffractograms of the Ti-48Al deposit heat-treated at 873K, showing that crystallisation occurred within 10 min. Diffraction peaks are identified for the deposit heat-treated for 120 minutes.
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Figure 5.33  (a) TEM BF image showing some leafy $\gamma/\alpha$ domains formed in the Ti-48Al deposit, which was heat-treated at 773K for 15 hours; the lamellar structure is discernible in the crystalline domains. (b) TEM BF image of the same specimen, showing a distribution of almost equiaxed $\gamma/\alpha$ domains. The network of gaps indicates that the viewing area in (b) was close to the deposition surface.
Figure 5.34  (a) $\alpha<2\overline{1}0>$ MDP taken from an $\alpha$ precipitate shown in figure 5.32; (b) $\alpha<1\overline{1}23>$ MDP taken from the same $\alpha$ particle and (c) its indexing key; (d) $\alpha<24\overline{2}3>$ MDP taken from the same $\alpha$ particle and (e) its indexing key.
Figure 5.35  (a) A SADP taken from an $\gamma/\alpha$ domain in the Ti-48Al deposit (heat-treated at 773K for 15 min) and (b) the MDP taken from the same domain, showing $\alpha <2\overline{1}0>$ and $\gamma <101>$ and superlattice spots of $\alpha_2$. Both patterns show strong streaking in the $[111]_\gamma // [0001]_\alpha$ direction. See figure 4.10 for the indexing keys. (c) $\alpha<2\overline{1}0>$ MDP.
Figure 5.36  MDPs taken from the $\gamma/\alpha$ domain in the Ti-48Al deposit (heat-treated at 773K for 15 min), showing (a) $\gamma <101>$ and (b) $\gamma <111>$ MDPs. See figure 4.10 and 5.6 for the indexing keys.

Figure 5.37  TEM BF image of the Ti-48Al deposit heat-treated at 973K for 3 min, showing equiaxed $\gamma/\alpha$ domains. These domains are about 100 nm in diameter.
Figure 5.38 A TEM BF image of the Ti-48Al deposit heat-treated at 973K for 3 min, showing lamella structured γ/α domains. The SADP was taken using a large aperture. The continuous rings indicated that the orientation distribution of those domains was random.

Figure 5.39 A MDP taken from the γ/α domain in the Ti-48Al deposit (heat-treated at 973K for 3 min), showing α <2110> and γ <101> and superlattice spots of α2. Both patterns showed strong streaking in the [111]γ // [0001]α direction. See figure 4.10 for the indexing keys.
Figure 5.40  (a) $\alpha<01\bar{1}0> // \gamma<112>$ MDP superimposed on the MDP as shown in figure 5.35b. (b) Illustration showing the two sets of patterns. See figures 4.10 and 4.11 for the indexing keys.
Crystalline diffraction peaks emerged from the amorphous halo in the sample heat-treated for 3 hours. The sharp spikes resulted from noise.
Figure 5.42 XRD diffractograms of the Ti-50Al-20Cr deposit heat-treated at 923K. The crystalline diffraction peaks emerged from the amorphous halo in the sample heat-treated for 15 min, indicating that crystallisation started within 15 min.
Figure 5.43 XRD diffractograms of the Ti-50Al-20Cr deposit heat-treated at 973K. The crystalline diffraction peaks emerged from the amorphous halo in the sample heat-treated for 5 min, indicating that crystallisation started between 3 ~ 5 min.
Figure 5.44  TEM BF images taken from the Ti-50Al-20Cr deposit heat-treated at 923K for 15 min. (a) An overall view of $\gamma$ precipitates embedded in the amorphous matrix. Many of them appeared to be cubic. The precipitates were about 100 nm in diameter. (b) A higher magnification BF image, showing a few $\gamma$ precipitates containing twinned domains.
Chapter 5  Heat-treated Deposits

Figure 5.45  TEM EDX elemental map acquired for the Ti-50Al-20Cr deposit heat-treated at 923K for 15 min, showing that the γ precipitates were poorer in Cr than the surrounding amorphous matrix.

Figure 5.46  γ <112> MDP taken from the Ti-50Al-20Cr deposit heat-treated at 923K for 15 min (see figure 4.11 for the indexing key).
Figure 5.47  (a) A MDP of $\gamma <110> \parallel \gamma <101>$ taken from the Ti-50Al-20Cr deposit heat-treated at 923K for 15 min. The indexing key is given in (b).

Figure 5.48  $\gamma(111)$ axial pole figures for the Ti-50Al-10Cr deposits. $X$ — discontinuous route; $Y$ — continuous route.
Figure 5.49 $\gamma$(200) and $\gamma$(002) axial pole figures for the Ti-50Al-10Cr deposits. X — discontinuous route; Y — continuous route.
Chapter 6

Thermodynamic and Kinetic Aspects of Phase Evolution in the Ti-Al(-Cr) Deposits

6.1 Introduction

The Ti-Al-Cr deposits produced by magnetron sputter deposition had different microstructures, namely amorphous or crystalline, depending on processing conditions and target compositions. When heat-treated, the devitrification of the amorphous Ti-Al(-Cr) led to the formation of stable and/or metastable crystalline phases. In this chapter the phase competition during deposition and heat treatment is discussed using thermodynamic modelling and nucleation theory.

6.2 Amorphous Phase Formation in the Ti-Al-Cr System

6.2.1 The Ti-48Al Deposit

As discussed in chapter 4, under the discontinuous route, the magnetron sputter deposition produced the amorphous Ti-48Al alloy. Under this depositing scheme the substrate temperature was estimated to be less than 473K.

Thermodynamic analysis in this work used the equilibrium thermodynamic data of the Ti-Al and Ti-Al-Cr systems, which is based on the database of titanium alloys developed at the University of Surrey. The database has been used to model the phase equilibria in Ti-Al-Cr alloys successfully, showing good agreement with experimental results (Shao, 1999b). Due to the absence of data for the thermodynamic parameters of the amorphous Ti-Al(-Cr) alloys, this data was estimated using the existing database and Shao’s model (Shao, 2000a).
According to this model, the Gibbs energy of the amorphous phase can be related to the high temperature liquid phase and the ground-state stable phases based on the following two fundamental assumptions (Shao, 2000a):

i. The maximum entropy change due to glass transition would not exceed the entropy change due to crystallisation of the ground-state crystalline phase. This constraint is in agreement with the third law of thermodynamics.

ii. The maximum value of the glass transition temperature would not exceed $0.75\times T_m$ ($T_m$ is the melting point of the alloy). This empirical rule is in agreement with numerous experimental observations (Shao, 2000a).

On this basis, the thermodynamic parameters for amorphous stabilization in the Ti-Al(-Cr) system are related to alloy compositions and temperature. The detailed formulation of these parameters was given in section 2.4.5.

Figure 6.1 shows the estimated maximum glass transition temperature for the Ti-48Al alloy, assuming $T_g \leq 0.75T_m$ ($T_g$ is the glass transition temperature). Figure 6.2 shows the entropy as a function of temperature for the amorphous phase, which was derived using Shao’s model. In comparison, the entropy curves of the h.c.p $\alpha$-Ti, f.c.c Al, $\gamma$-TiAl and $\alpha_2$-$Ti_3Al$ phases in the Ti-48Al alloy are also given. These phases are possible candidates to form when the Ti-48Al liquid or vapour rapidly consolidates. Figure 6.2 shows that as the temperature increases, the entropy of the amorphous phase approaches that of the liquid phase. As the temperature decreases, the entropy of the amorphous phase should approach that of the most thermodynamically stable crystalline phase in the system, in this case the $\gamma$-TiAl.

Figure 6.3 shows the Gibbs free energy of the amorphous phase plotted as a function of temperature. The liquid phase was used as the reference state in this diagram. The continuous change of the free energy of the amorphous phase into the liquid is characteristic of a second order phase transformation. For comparison, the free energies of the $\alpha$-Ti (h.c.p), $\alpha_2$-$Ti_3Al$, f.c.c-Al and $\gamma$-TiAl phases are also shown in the diagram. Since $G = H - T\cdot S$, the slope of the free
energy curve corresponds to the value of entropy. The diagram shows that as the temperature decreases, the free energy curve of the amorphous phase becomes parallel to the $\gamma$-TiAl, the ground-state phase in the Ti-48Al alloy.

Figure 6.4 gives the Gibbs free energy curves of the competing phases in the Ti-Al alloy system as a function of Al concentration. The short vertical line marks the position of the Ti-48Al alloy in the Ti-Al system. The grey line indicates the common tangent between the h.c.p $\alpha$ phase and the $\gamma$-TiAl phase. It shows that the Ti-48Al alloy is on the edge of equilibrium with the $\alpha$ phase. Thus, the equilibrium Ti-48Al microstructure must be $\gamma$ based. However, $\gamma$-TiAl is an intermetallic compound. Due to kinetic limitations, the formation of $\gamma$ could be less favourable under non-equilibrium conditions than the disordered phases, in particular, the h.c.p $\alpha$ phase in this case.

As indicated by the thermodynamic assessment of the amorphous phase in this study, the free energy of the amorphous phase is not very much higher than the disordered solution phases, e.g. the h.c.p $\alpha$ phase, as shown in figures 6.3 and 6.4. In particular, in the case of rapid quenching of the Ti-48Al vapour to a low temperature, the free energy of the vapour phase would be high above any of the condensed phases. Thus, the driving force for the formation of one solid phase would not be too much different from that of another, including the amorphous phase. Therefore, kinetics would be expected to play an important role in phase selection.

6.2.2 The Ti-Al-Cr Deposits

A brief summary of the as-received status of the ternary alloy deposits is given here: three deposits were produced by the continuous route, Ti-50Al-10Cr, Ti-53Al-15Cr and Ti-50Al-20Cr. The Ti-50Al-20Cr deposit was completely amorphous. The Ti-50Al-10Cr and Ti-53Al-15Cr deposits were almost crystalline, with a thin layer of the deposit near the deposit/substrate interface being
amorphous. The amorphous Ti-50Al-10Cr deposit with a small amount of crystalline embryos was produced by the discontinuous route. For the continuous route, the substrate temperature was estimated to be about 623K.

Figures 6.5 to 6.7 give the entropy curves as a function of temperature for various Ti-Al-Cr alloys. The Gibbs free energy curves as a function of temperature are given in figures 6.8 to 6.10 for the Ti-50Al-10Cr, Ti-53Al-15Cr and Ti-50Al-20Cr alloys respectively, where the liquid phase was used as the reference state. The solution phases, h.c.p \( \alpha \), f.c.c Al and the intermetallic \( \gamma \) phase are shown for comparison with the amorphous phase. Other intermetallic phases such as the \( \tau \) phase and the C14 Laves phases were not included in the calculation, because it would be very difficult for these line compounds to form during rapid quenching from the vapour phase, even though they have low free energy values. Here the \( \gamma \) phase is considered for phase competition, because it is relatively thermodynamically stable with a large alloying solubility range, both of which render its formation easy as a combined result of thermodynamic and kinetic factors. The b.c.c-B2 Cr phase can also be ignored for phase competition, since all the Ti-Al-Cr alloys studied in this thesis were far from the Cr corner on the ternary phase diagram.

According to the free energy diagrams in figures 6.8 to 6.10, the solution phases are less stable than the intermetallic phase, i.e. the \( \gamma \) phase. At intermediate temperatures (e.g. around 700K) or lower, the free energy of the amorphous phase is not very different from the solution phases. The free energy of the amorphous phase continues to approach the solution phases (f.c.c and h.c.p), as the temperature decreases further. If the temperature is low enough, the amorphous phase would be equally or even more stable than the solution phases. In Ti-50Al-10Cr, the amorphous phase and the h.c.p \( \alpha \) phase become equally stable at around 300K. In Ti-53Al-15Cr this temperature is about 400K. In the Ti-50Al-20Cr deposit the amorphous and h.c.p \( \alpha \) phases become equally stable within the range 400K to 500K. Therefore, if the precipitation of the ordered intermetallic phase(s) were
suppressed during deposition, the solution phase, i.e. the \( \alpha \) phase, would not be much more thermodynamically favoured than the amorphous phase. This actually allows the amorphous phase to compete with the solution phases during non-equilibrium processing not only from a kinetic point of view but also from a thermodynamic aspect. This is consistent with the microstructures in the as-received deposits, which showed that the discontinuous route produced an amorphous Ti-50Al-10Cr alloy. Furthermore, the microstructures formed in the early stage of deposition of the Ti-50Al-10Cr and Ti-53Al-15Cr deposits obtained from the continuous route were also amorphous.

Figures 6.8 to 6.10 would suggest that with increasing Cr addition, the free energy of the amorphous phase becomes closer to that of the solution phases. Figures 6.11 to 6.13 show the free energy curves plotted against Cr concentration for the Ti-50Al-xCr alloys at various temperatures. The pure elements were used as the reference state. These diagrams clearly suggest an increased stability of the amorphous phase as the Cr concentration increases. At these temperatures, the free energy curves of the amorphous phase and the h.c.p solution phase are very close around the composition Ti-50Al-20Cr. At 500K, the free energy of the two phases is almost equal at this composition. This is in good agreement with the microstructure of the as-received deposits produced by the continuous route, which showed that crystallisation occurred in the Ti-50Al-10Cr and Ti-53Al-15Cr alloys, while the Ti-50Al-20Cr alloy was amorphous.

### 6.2.3 Surface Diffusivity and Amorphous Phase Formation

Amorphous phase formation in co-deposited materials has been attributed to the suppression of crystallisation owing to limited surface diffusion (Cantor and Cahn, 1976, Saunders and Miodownik, 1985, 1987). The kinetic limit due to surface diffusion can be characterised by an effective diffusion distance \( \bar{x} \), which is given as (Saunders and Miodownik, 1985, 1987):
\[ x = \sqrt{\frac{D_s \cdot a}{R}} \]  

(6.1)

where \( a \) is the atomic spacing, \( R \) is the deposition rate and \( D_s \) is the surface diffusion coefficient. According to the studies of the phase transformation kinetics (Saunders and Miodownik, 1985, 1987, Shao and Tsakiropoulos, 2000b):

i. ordering in alloys would be prohibited and a single disordered solution phase could form, if \( x \ll a \).

ii. for \( x \geq 5 \) nm, the stable phase(s) would form, including the ordered phase.

Shao and Tsakiropoulos (2000b) also suggested that \( x < 0.1 \) nm is a reasonable criterion for the suppression of ordered phases in metallic alloys.

The surface diffusivity of metallic systems can be approximated as (Shao and Tsakiropoulos, 2000b):

\[ D_s \approx 10^7 \exp(-10 \cdot \frac{T_m}{T}) \]  

(6.2)

The solidus temperature of Ti-48Al is about 1733K. In our case the deposition rate is \( R = 10^{-9} \) m/s. Given \( a = 0.4 \) nm, one can obtain the values of \( x \) at different substrate temperatures, which are given in table 6.1. According to this calculation, if the substrate temperature is higher than 623K, \( x \) is greater than 0.1 nm, the formation of the ordered phase, \( \gamma \), in the Ti-48Al deposit would be possible. If the substrate temperature is less than 573K, \( x \) is less than the atomic spacing, thus \( \gamma \) formation would be suppressed. As the substrate is kept to even lower temperatures (e.g. 473K, which is the estimated substrate temperature for the Ti-48Al deposit produced in this work), \( x \) would be far less than the atomic spacing and even the formation of the disordered solution phase (h.c.p \( \alpha \)) would be difficult.
Data about phase competition between amorphous phases and disordered solution phases in Ti-Al deposits are also available in the literature. Both amorphous and crystalline Ti-Al deposits produced by sputter deposition have been reported (Abe et al., 1994, Padmarabu et al., 2000, Banerjee et al., 1996). Banerjee et al. (1996) found a small amount of α-Ti(Al) crystals embedded in an amorphous Ti-48Al deposit. The Ti-52Al deposit studied by Abe et al. (1994) was completely amorphous. Unfortunately, the deposition temperature was not reported in either case.

Padmaprabu et al. used pure Ti and Al dual targets in co-deposition and produced amorphous Ti-xAl thin films on silicon substrate (Padmarabu et al., 2000). The substrate temperature \( T_{\text{sub}} \) was controlled and Al concentration \( x \) was found to increase with \( T_{\text{sub}} \). When \( T_{\text{sub}} \) was below 573K, amorphous Ti-xAl deposits were obtained. The Al concentration in the deposit was estimated to be within the range 35 to 55 at.%. At higher \( T_{\text{sub}} \), crystalline deposits consisting of \( \gamma \)-TiAl were produced. The Al content was also found to be higher than those obtained below 573K, \( \alpha \) increased from 55.8% to 62.15%.

<table>
<thead>
<tr>
<th>( T_{\text{sub}} ) (K)</th>
<th>Al (at%)</th>
<th>( D_x ) (m²/s)</th>
<th>( \overline{x} ) (nm)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assessment of the Ti-48Al produced in this work</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_a = 1733K )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>48</td>
<td>( 1.22 \times 10^{-23} )</td>
<td>( 2.2 \times 10^{-3} )</td>
<td>Ordered phase</td>
</tr>
<tr>
<td>523</td>
<td>48</td>
<td>( 4.07 \times 10^{-22} )</td>
<td>( 1.3 \times 10^{-2} )</td>
<td>formation suppressed</td>
</tr>
<tr>
<td>573</td>
<td>48</td>
<td>( 7.33 \times 10^{-21} )</td>
<td>( 5.4 \times 10^{-2} )</td>
<td></td>
</tr>
<tr>
<td>623</td>
<td>48</td>
<td>( 8.30 \times 10^{-20} )</td>
<td>( 1.8 \times 10^{-1} )</td>
<td>Ordered phase</td>
</tr>
<tr>
<td>673</td>
<td>48</td>
<td>( 6.56 \times 10^{-19} )</td>
<td>( 5.1 \times 10^{-1} )</td>
<td>formation possible</td>
</tr>
<tr>
<td>For deposits produced by Padmaprabu et al. (2000)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>573</td>
<td>55.8</td>
<td>( 1.55 \times 10^{-20} )</td>
<td>0.249</td>
<td>Ordered phase</td>
</tr>
<tr>
<td>673</td>
<td>58.0</td>
<td>( 1.48 \times 10^{-18} )</td>
<td>2.43</td>
<td>formation possible</td>
</tr>
<tr>
<td>773</td>
<td>60.9</td>
<td>( 5.03 \times 10^{-17} )</td>
<td>14.18</td>
<td>Ordered phase</td>
</tr>
<tr>
<td>873</td>
<td>62.2</td>
<td>( 6.78 \times 10^{-16} )</td>
<td>52.08</td>
<td>formation allowed</td>
</tr>
</tbody>
</table>
The results of Padmaprabu et al. (2000) were evaluated in this thesis using the effective diffusion distance at different substrate temperatures with their reported deposition rate of $1 \times 10^{-10}$ m/s. These results are detailed in table 6.1. They show that $\bar{x}$ values of the alloys produced at 573K and 673K are greater than 0.1 nm and less than 5 nm. This suggests that it is possible to form the ordered phase (in this case, the $\gamma$ phase) during deposition. For alloys produced at a substrate temperature of 773K and above, $\bar{x}$ becomes greater than 5 nm. Thus ordered phase formation becomes inevitable.

### Table 6.2 Effective mean diffusion distance in Ti-Al-Cr deposits.

<table>
<thead>
<tr>
<th>$T_{sub}$ (K)</th>
<th>$D_s$ (m$^2$/s)</th>
<th>$\bar{x}$ (nm)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-50Al-10Cr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_m = 1662 K$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>$5.5 \times 10^{-23}$</td>
<td>$4.7 \times 10^{-3}$</td>
<td>Phase separation</td>
</tr>
<tr>
<td>523</td>
<td>$1.6 \times 10^{-21}$</td>
<td>$2.5 \times 10^{-2}$</td>
<td>Suppressed</td>
</tr>
<tr>
<td>573</td>
<td>$2.5 \times 10^{-20}$</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>623</td>
<td>$2.6 \times 10^{-19}$</td>
<td>0.32</td>
<td>Phase separation</td>
</tr>
<tr>
<td>673</td>
<td>$1.9 \times 10^{-18}$</td>
<td>0.87</td>
<td>Possible</td>
</tr>
<tr>
<td>Ti-53Al-15Cr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_m = 1688 K$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>$3.17 \times 10^{-23}$</td>
<td>$3.6 \times 10^{-3}$</td>
<td>Phase separation</td>
</tr>
<tr>
<td>523</td>
<td>$9.6 \times 10^{-22}$</td>
<td>$2.0 \times 10^{-2}$</td>
<td>Suppressed</td>
</tr>
<tr>
<td>573</td>
<td>$1.6 \times 10^{-20}$</td>
<td>$8.0 \times 10^{-2}$</td>
<td></td>
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<tr>
<td>623</td>
<td>$1.7 \times 10^{-19}$</td>
<td>0.26</td>
<td>Phase separation</td>
</tr>
<tr>
<td>673</td>
<td>$1.3 \times 10^{-18}$</td>
<td>0.72</td>
<td>Possible</td>
</tr>
<tr>
<td>Ti-50Al-20Cr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_m = 1715$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>$1.79 \times 10^{-22}$</td>
<td>$2.7 \times 10^{-3}$</td>
<td>Phase separation</td>
</tr>
<tr>
<td>523</td>
<td>$5.7 \times 10^{-22}$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>Suppressed</td>
</tr>
<tr>
<td>573</td>
<td>$1.0 \times 10^{-20}$</td>
<td>$6.3 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>623</td>
<td>$1.1 \times 10^{-19}$</td>
<td>0.21</td>
<td>Phase separation</td>
</tr>
<tr>
<td>673</td>
<td>$8.6 \times 10^{-19}$</td>
<td>0.59</td>
<td>Possible</td>
</tr>
</tbody>
</table>
Calculations of effective diffusion distance were done in the same way for ternary alloys produced in this thesis and are shown in table 6.2. For all the three alloys, the \( x \) values are greater than 0.1 nm and less than 5 nm at temperatures higher than 623K. This suggests that the ordered phase may be able to form (the substrate temperature was about 623K during the continuous deposition). At temperatures less than 573K, \( x \) becomes less than the atomic spacing \( \alpha \). Thus, only disordered phase is allowed to form. At 473K (the substrate temperature was about 473K during the discontinuous deposition), \( x \) becomes smaller than \( \alpha \) by about two orders of magnitude. This could suppress even the disordered solution phase formation and lead to the formation of the amorphous phase. It is also seen that at the same substrate temperature, \( x \) decreases as the Cr content increases. This is in agreement with the experiments in this work, since under the same processing conditions, Ti-50Al-20Cr was amorphous, while the other two ternary alloys, with less Cr content, were crystalline.

6.3 Phase Competition in the Amorphous Alloys during Heat-Treatment

6.3.1 The Ti-48Al Deposit

From 573K to 1273K, the h.c.p solution phase \( \alpha \), and the intermetallic phases \( \alpha_2 \)-Ti\(_3\)Al and \( \gamma \)-TiAl are all more stable then the amorphous phase at the composition around 50at.% Al (see figures 6.3, 6.4 and 6.14). The equilibrium phase in Ti-Al alloys with 47 to 57at% Al is the \( \gamma \)-TiAl.

The heat-treatments on the Ti-48Al deposits at intermediate temperatures, i.e. at 773, 873 and 973K, suggested that devitrification of the amorphous phase led to the formation of the h.c.p \( \alpha \) phase. The \( \gamma \) phase was then precipitated, coherent with the \( \alpha \) phase, resulting in the lamellar microstructure of the partially ordered \( \alpha \) phase and the \( \gamma \)-TiAl. This precipitation sequence can be expressed as:
Abe et al. observed the precipitation of the DO$_{19}$ $\alpha_2$ phase during the early stages of crystallisation in their Ti-52Al thin-film heat-treated at 800K. This was followed by a transformation to the equilibrium $\gamma$-TiAl phase (Abe et al., 1994). Banerjee et al. observed coexistence of both $\gamma$ and $\alpha_2$ with a small amount of retained $\alpha$-Ti(Al) phase in their Ti-48Al deposits during heat treatment (Banerjee, 1996). Heat treatment at higher temperature led to rapid precipitation of the $\gamma$-TiAl phase (Banerjee et al., 1996). It is noted that the crystallisation time during heat treatment at 773K, of our deposit was much longer than that reported by Abe et al. We observed a time lag of about 13 hours for the nucleation of the disordered $\alpha$-Ti(Al) phase, while Abe et al. observed that the ordered $\alpha_2$ phase was formed after 2.5 minutes in their Ti-52Al thin-film. This discrepancy could be attributed to the fact that their Ti-52Al film was thinner (less than 2 $\mu$m thick), where surface diffusivity would be dominant during nucleation.

According to the classical time-dependent nucleation theory, there is a time lag before the nucleation rate reaches steady state. Experimentally, it is always difficult to track the time-dependent nucleation rate. However, time lag, i.e. the transient time, can be estimated from experimental observations. In this work, the estimated time lag was compared with the theoretical evaluation using the analytical solution of the transient nucleation formulation.

The devitrification of an amorphous metallic material can be described by the Fokker-Plank equation (Volmer and Weber, 1926, Beker et al., 1935). The time-dependent nucleation rate can be approximated as (Wakeshima, 1954):

$$I_{n^*,t} = I^* \left[1 - \exp(-t/\tau)\right]$$  \hspace{1cm} (6.3)

where $I^*$ is the steady state nucleation rate, $n^*$ is the critical nucleus size, and $\tau$ is the transient time. Nucleation reaches steady state only when $t > \tau$. Thus, one can
study the low temperature nucleation behaviour of the amorphous alloys using time
dependent nucleation. For heterogeneous nucleation of a crystalline phase, the
transient time is (Shao and Tsakiropoulos, 2000b):

$$
\tau = \frac{16Rf(\theta)}{1-cos(\theta)} \alpha^4 \frac{\sigma_m^2 T}{d_a^2 \chi_{eff} D \Delta G_m^2}
$$

(6.4)

$$
\sigma_m \approx 0.44 \times |H_m| + 500 \text{ (J/mol)}
$$

(6.5)

where $R$ is the gas constant, $\alpha$ is the average atomic jump distance, $V_a = d_a^3$, $d_a$ is
the average atomic diameter) is the average atomic volume, $\sigma_m$ is the molar
interface free energy, $H_m$ is the molar latent heat of fusion, $\Delta G_m$ is the molar
volume Gibbs free energy of nucleation, $D$ is the solid state interdiffusion
coefficient in this case (or the surface diffusivity in the case of thin-films). On the
basis of published experimental data, Cottrel was able to conclude that the $D$ can be
approximated by

$$
D = D_0 \exp\left(-\frac{A}{T}\right)
$$

(6.6)

where $A = Q/R \approx 20T_m$, $Q$ is the activation energy, $R$ is the gas constant, $T_m$ is the
melting temperature and $T$ is temperature in degrees Kelvin (Cottrel, 1975).
Considering that the diffusion coefficients of solid metals at $T_m$ are usually $\sim 10^{-13}$
m$^2$/s (Cottrell, 1975), one can have $D_0 \approx 5 \times 10^{-3}$ m$^2$/s (Shao and Tsakiropoulos,
2000b).

For heterogeneous nucleation,

$$
f(\theta) = (2 - 3\cos \theta + \cos^3 \theta)/4
$$

(6.7)
where $\theta$ is the wetting angle. For non-wetting conditions, $\theta = 180^\circ$ and $f(\theta) = 1$.

Equation 6.5 is from Turnbull (Turnbull, 1950) and considers a non-zero interfacial energy between phases of different structures. The term $x_{\text{eff}}$ takes into account the composition of the nucleating phase in alloys (Shao and Tsakiropoulos, 1994).

When the phase formed is of composition different from that of the melt, $x_{\text{eff}} = x_r / x_i$ is often used to adjust the composition effect. The $x_r$ is the nucleus composition in terms of the rich component. At equilibrium, $x_r$ can be determined by applying the common tangent to the Gibbs energy curves of the mother and child phases. In metastable conditions, phase transformation is largely dependent on the thermodynamics at the grain boundary. The composition of a new-born phase can fall inside the two-phase field with its mother phase. This was discussed in the literature review, section 2.3.1. The composition of the new-born phase could be within the two intersecting points on the common tangent of the mother phase and child phase.

In this work, a probability term and a structural term were introduced to account for both compositional and structural effects by defining $x_{\text{eff}} = P \times S$, where $P$ is an effective probability and $S$ is a structure factor.

The term $P$ shows that the nucleation of a solution phase is easy when its composition is close to the composition of the alloy. The term $P$ is defined as follows: assume an infinitely large quantity of an A-B alloy. The formation of clusters will not alter the bulk alloy composition. The probability of forming a cluster of $m$ atoms with $k$ of them being A atoms is

$$P = P\{X = k \mid m\} = C_m^k p^k (1 - p)^{m-k} \quad (6.8)$$
where \( p = x_A \) is the concentration of A in the alloy and \( C_m^k = \frac{m!}{k!(m-k)!} \). This function is illustrated in the example in figure 6.15. This figure shows the probability distribution of forming a cluster containing \( k \) solute atoms in an alloy with the solute concentration being 33at.\%.

If the clusters can form within a composition range \((x_1, x_2)\), the probability of having a cluster falling in this range is given by

\[
P\{k_1 \leq k \leq k_2\} = \sum_{k=k_1}^{k_2} C_m^k p^k (1-p)^{m-k}
\]

where \( k_1 = mx_1, k_2 = mx_2 \). In figure 6.15, equation 6.9 is represented by the grey area, if the solute atoms are limited to be within the range of 25 to 35at.\%.

We define an effective probability \( P \) for \( x_{\text{max}} \leq x_{\text{sys}} \) by

\[
P = \frac{P\{k_1 \leq k \leq k_{\text{max}}\}}{P\{k_1 \leq k \leq k_{\text{sys}}\}} = \frac{P\{x_1 \leq x \leq x_{\text{max}}\}}{P\{x_1 \leq x \leq x_{\text{sys}}\}}
\]

where \( k_i = mx_i, x_i \) is the composition of the equilibrium \( \beta \) phase, \( x_{\text{max}} \) is the thermodynamically allowed maximum composition of \( \beta \), and \( x_{\text{sys}} \) is the average alloy composition, see figure 6.16. When \( x_{\text{sys}} \leq x_{\text{max}} \), \( P = 1 \).

This formulation also suggests that the nucleation of a line compound would be much more difficult when the composition of the alloy deviates from the composition of the compound. The complexity of unit cells of ordered structures is described by \( S \), which is the inverse of the number of effective lattice sites. For example, the \( \text{L1}_0 \) \( \gamma \)-TiAl phase has a face-centred tetragonal structure, with Al and Ti occupying alternating layers in the [001] direction, giving \( S = 1/2 \). For a
disordered solution phase $S = 1$. Thus, a line compound would be the least favoured during phase competition during rapid solidification.

Nucleation kinetics in the Ti-48Al deposit was evaluated according to equation 6.10. The diffusivity was approximated as described by equation 6.6. Data of Gibbs free energy and enthalpy was derived from the thermodynamic database for titanium alloys. For precipitation of $\gamma$-TiAl from the amorphous phase, $P = 1$ and $x_{\text{eff}} = P \cdot S = 1 \div 2$. For the h.c.p $\alpha$-Ti(Al), which is a disordered solution phase, $P = 1$, $S = 1$ and $x_{\text{eff}} = 1$. The results of the calculations are compared with the experimental results in figure 6.17. The calculations showed that in the Ti-48Al the h.c.p $\alpha$ phase would be most favourable to nucleate. The f.c.c Al phase is even more sluggish to nucleate than the intermetallic $\gamma$ phase. The calculation shows a good agreement with the experimental time lag data.

The fact that the disordered $\alpha$-Ti(Al) phase preceded the equilibrium $\gamma$ phase could also be explained qualitatively on the basis of the low interface energy between the $\alpha$ and amorphous phases. Once the $\alpha$ phase is formed, it would transform to the ordered $\alpha_2$ phase due to the structural similarity between the $\alpha$ and $\alpha_2$ phases. The equilibrium $\gamma$ phase would be formed after prolonged heat treatment.

In this work, this method was also applied to evaluate the transient time for the formation of the $\gamma$-TiAl and h.c.p $\alpha$ phase in the case of sputter deposition. In equation 6.4, the surface diffusivity was used instead of solid state diffusivity. The temperatures at which the calculated transient time of the $\alpha$ phase becomes shorter than $\gamma$ showed good agreement with the temperatures at which the ordered phases formation is suppressed in the evaluation of effective diffusion distance. As the effective distance is much easier to obtain and sufficient to provide evaluations for phase formation in the sputter deposition of the Ti-Al(-Cr) alloys, it should be the preferred method in predicting amorphous phase formation.
6.3.2 The Ti-50Al-20Cr Deposit

The evaluation of transient time for the h.c.p $\alpha$ phase formation in the Ti-48Al alloy showed good agreement with experimental observations. Thus, the evaluation was extended into the ternary system. The transient times of the $\alpha$ and $\gamma$ phases in the Ti-50Al-20Cr alloys were evaluated using the above method. The effective probability can also be extended into the ternary system. Assuming that in an infinitely large quantity of an A-B-C alloy, the formation of clusters will not alter the alloy composition, the probability of forming a cluster of $m$ atoms with $k$ of them being A atoms and, $h$ being B atoms can be expressed as:

$$P = C_a^k C_b^h P^k (1 - P)^{m-k} (1 - q)^{m-k-h}$$

where $p$ is the overall concentration of A in the alloy and $q$ is the concentration of B. If a cluster can form within a range, say $k$ within $[k_1, k_2]$, $h$ within $[h_1, h_2]$, the probability of its formation is given by

$$P\{k_1 \leq k \leq k_2, h_1 \leq h \leq h_2, 0 \leq (h + k) \leq m\}$$

$$= \sum_{k=k_1}^{k_2} \sum_{h=h_1}^{h_2} C_a^k C_b^h P^k (1 - P)^{m-k} (1 - q)^{m-k-h}$$

Graphically, if we use the number of A and B atoms as the $x$ and $y$ axis respectively, and $P$ as $z$ axis, the above function can be considered as the volume under the probability convexity, defined by the boundary of $k_1 \leq k \leq k_2, h_1 \leq h \leq h_2, h + k \leq m$.

For the Ti-50Al-20Cr alloy, nucleation of the h.c.p $\alpha$ or of the $\gamma$ phase around the alloy composition is thermodynamically allowed from 500K to 800K. Therefore, $P \approx 1$. As described in the previous section, the value of $S$ for the $\gamma$ and $\alpha$ phases are $1/2$ and 1 respectively. Hence, the term $x_{eff}$ for the h.c.p and $\gamma$ phases can be taken as 1 and $1/2$ respectively.
Figure 6.18 shows the calculation results for the h.c.p $\alpha$ and $\gamma$ phase in the Ti-50Al-20Cr alloy. It is seen that the significant difference in the driving force of phase formation (see figure 6.10) makes the $\alpha$ phase more difficult to nucleate than the $\gamma$ phase. This is in good agreement with the experimental observations.

### 6.4 Summary

During the condensation of the Ti-Al(-Cr) vapour discussed in this thesis, the driving force for the formation of the crystalline phases, especially the disordered solution phases, would not be significantly greater than that of the amorphous phase. Under certain conditions, i.e. increased Cr addition and at low substrate temperatures, the amorphous phase could be even more thermodynamically stable than the disordered solution phase. Thus, kinetic factors could play a relatively more important role in phase competition during the rapid quenching process of the Ti-Al(-Cr) vapour phase. Kinetically, the amorphous alloy formation in co-deposited materials is attributed to the limited surface diffusion, which is characterised by the effective diffusion distance in this work.

The early-stages of phase competition in the amorphous Ti-48Al and Ti-50Al-20Cr alloy during heat-treatment were studied using classical nucleation theory. This work focused on the h.c.p $\alpha$ phase and the $\gamma$ phase. The calculated transient times showed that in the amorphous Ti-48Al alloy, it would be kinetically easier for the $\alpha$ phase to precipitate than $\gamma$. In the amorphous Ti-50Al-20Cr alloy, this sequence would be reversed, due to the decreased thermodynamic stability of the $\alpha$ phase. The calculations were in agreement with the experimental results.
Figure 6.1 Calculated maximum glass transition temperature (broken line) superimposed on the Ti-Al phase diagram, assuming $T_g = 0.75T_m$.

Figure 6.2 Molar entropy of phases in the Ti-48Al alloy plotted as functions of temperature, using h.c.p Ti and f.c.c Al as the reference state. It shows that the entropy of the amorphous phase (Am) approaches the liquid phase (Liq) as the temperature increases, and approaches the $\gamma$-TiAl as the temperature decreases ($\gamma$-TiAl being the most stable phase, i.e. the ground-state in Ti-48Al at low temperatures).
Figure 6.3 Molar Gibbs free energy of various phases (kJ/mol) plotted as a function of temperature for the Ti-48Al alloy, using the liquid phase as the reference state. The energy curve of the amorphous phase is parallel to that of the γ-TiAl below $T_g$, indicating that the entropy values of the two phases are approaching each other.

Figure 6.4 Molar Gibbs free energies (kJ/mol) of the competing phases in the Ti-Al system at 500K plotted as a function of Al composition.
Figure 6.5  Molar entropies of phases in the Ti-50Al-10Cr alloy plotted as a function of temperature, using h.c.p Ti, f.c.c Al and b.c.c Cr (B2) as the reference state.

Figure 6.6  Molar entropies in the Ti-53Al-15Cr alloy plotted as functions of temperature; using h.c.p Ti, f.c.c Al and b.c.c Cr as the reference state.
Figure 6.7  Molar entropies in the Ti-50Al-20Cr alloy plotted as a function of temperature, using h.c.p Ti, f.c.c Al and b.c.c Cr as the reference state.

Figure 6.8  Molar Gibbs free energies (kJ/mol) of phases in the Ti-50Al-10Cr alloy plotted as a function of temperature. The liquid phase was used as the reference state.
Figure 6.9  Molar Gibbs free energy (kJ/mol) of phases in the Ti-53Al-15Cr alloy plotted as a function of temperature. The liquid phase was used as the reference state.

Figure 6.10  Molar Gibbs free energies (kJ/mol) of phases in the Ti-50Al-20Cr alloy plotted as a function of temperature. The liquid phase was used as the reference state.
Figure 6.11  Molar Gibbs free energies (kJ/mol) of phases in the Ti50AlxCr alloys at 500K plotted against Cr concentration, using f.c.c. Al, h.c.p Ti, and b.c.c. Cr as the reference states.

Figure 6.12  Molar Gibbs free energies (kJ/mol) of phases in the Ti50AlxCr alloys at 600K plotted against the Cr concentration, using f.c.c. Al, h.c.p Ti, and b.c.c. Cr as the reference states.
Figure 6.13  Molar Gibbs free energies (kJ/mol) of phases in the Ti50AlxCr alloys at 700K plotted against the Cr concentration, using f.c.c. Al, h.c.p Ti, and b.c.c. Cr as the reference states.

Figure 6.14  Molar Gibbs free energies (kJ/mol) of phases in Ti-52Al plotted against the temperature, using the liquid phase as the reference state.
Figure 6.15 Binomial probability distribution of a cluster containing 60 atoms in an alloy system. The solute concentration in the alloy is 33%. $k$ is the number of atoms of the solute. The shaded area is the probability of the cluster forming within 25 to 35 at% ($P\{0.25 \leq x \leq 0.35\}$).

Figure 6.16 Schematic Gibbs energy versus composition diagram with free energy curves for the mother phase $M$ and the product phase $\beta$, showing the definition of the effective probability term. The area $A$ under the probability distribution curve represents $P = \{k_1 \leq k \leq k_{\text{max}}\}$, and the area $A+B$ represents $P = \{k_1 \leq k \leq k_{\text{sys}}\}$.
Figure 6.17  Temperature versus calculated transient times for the $\alpha$, $\gamma$ and f.c.c Al phases in the Ti-48Al alloy, □ corresponds to experimental observed time lag.

Figure 6.18  Temperature versus calculated transient times for the h.c.p $\alpha$ and $\gamma$-TiAl phases in the Ti-50Al-20Cr alloy.
Figure 6.19  Temperature versus calculated transient times for the h.c.p $\alpha$ and $\gamma$-TiAl phases in the Ti-50Al-10Cr alloy.
Chapter 7

Diffusion and Oxidation

7.1 Introduction

The long term performance of oxidation resistant coatings depends on the stability of the coatings. The latter is affected by diffusion phenomena at the coating/substrate interface. In this chapter, elemental profiles for the Ti-Al-Cr deposits produced by the continuous route on the Ti-50Al substrate are presented in section 7.2. Analysis of diffusion phenomena is employed to assess the diffusion of Cr across the coating/substrate interface. A preliminary study of the oxidation behaviour on the Ti-Al-Cr coatings is discussed in section 7.3 briefly.

7.2 The Diffusion of Chromium

7.2.1 Elemental Profiles

As discussed in previous chapters, the Ti-Al-Cr alloys studied in this thesis are potential candidate oxidation resistant coatings for γ-based Ti-Al substrates. They are to be used in structural applications where the material would be subjected to high temperature exposure and thermal shocks. One of the major concerns is whether there would be substantial Cr diffusion into the substrate at elevated temperatures. The Cr profiles in the deposits and substrates were studied at elevated temperature. The typical profiles obtained are shown in figures 7.1 to 7.4.

Quantitative profiles were measured by EPMA on the heat-treated samples. In the substrate side of the coating/substrate interface, the compositions were measured using
spot analysis. In the deposit side, area analysis was used. Each area “window” was 1 μm wide and over 5 μm long, so that the average composition could be obtained (see figure 7.5). For each sample, at least three sets of profiles, measured at different positions, were acquired, and then were averaged into a single profile. For better accuracy, attention was given to the micro-probe current at all times. Only the profiles, during the acquisition of which the probe current remained steady, were considered. These profiles for the Ti-50Al-10Cr and Ti-50Al-20Cr deposits are shown in figures 7.6 and 7.7.

The profiles for the Ti-50Al-10Cr and Ti-50Al-20Cr coatings show that the Cr diffusion was not very fast. After 10 hours heat-treatment at 1173K, the Cr concentration had approached zero at a depth of 10 μm into the substrate from the interface. After 100 hours, this distance had increased to 40 μm. After 820 hours, the Cr concentration in the substrate approached zero at around 100 μm from the interface.

It was expected that near the coating/substrate interface, due to the higher concentration gradient, one would find a much higher Cr concentration in the Ti-50Al substrate with the Ti-50Al-20Cr coating than in the substrate with the Ti-50Al-10Cr coating. However, the difference in Cr concentration was found not to be significant. For instance, at the interface in the substrate side, the Cr concentration was about 2.85at.% for the Ti-50Al-10Cr coating heat-treated for 100 hours, and about 4.55at.% for the Ti-50Al-20Cr coating, a difference of less than 2at.%. This is attributed to the fact that the Ti-50Al substrate consisted of the γ phase mainly (see figure 5.28), for which the Cr solubility is no more than 5at.% at around 1173K. The solubility limit determined that the maximum Cr concentration in the substrate should be 5at.%. As shown in figures 5.2 and 5.23, in the crystalline Ti-50Al-10Cr deposit, the major constituent was the γ phase, while in the case of the Ti-50Al-20Cr deposit, γ was surrounded by the Laves phase. Thus, during heat-treatment, the substrate (mainly γ-TiAl) would be in direct contact with the ternary γ phase in the Ti-50Al-10Cr deposit.
In the case of the Ti-50Al-20Cr deposit, the substrate would be in direct contact with the ternary Laves phase. Therefore, if given enough time, the γ phase near the interface would be in local equilibrium with the Laves phase. This would allow a higher Cr concentration in the γ phase at the interface, up to the maximum solubility. This would explain the 1.7 at.% difference in Cr near the interface in the substrates coated with the Ti-50Al-10Cr and Ti-50Al-20Cr.

7.2.2 Fitting of Elemental Profiles

The mathematic formulation of the diffusion theory is based on the hypothesis that in isotropic substances the transfer rate of the substance through unit area of a section is proportional to the concentration gradient measured normal to the section, i.e.

\[ F = -D \frac{\partial C}{\partial x} \]  \hspace{1cm} (7.1)

where \( F \) is the transfer rate per unit area of section, \( C \) the concentration of the diffusing substance, \( x \) the space co-ordinate measured normal to this interface, and \( D \) is the diffusion coefficient. Equation 7.2 can therefore be established, as both sides of the equal sign represent the rate at which the amount of diffusing substance increases in a unit volume.

\[ \frac{\partial C}{\partial t} = \text{div}(D \cdot \text{grad}C) \]  \hspace{1cm} (7.2)

If \( D \) is a constant and diffusion is one-dimensional, equation 7.2 becomes

\[ \frac{\partial C}{\partial t} = D \cdot \text{div}(\text{grad}C) = D \frac{\partial^2 C}{\partial x^2} \]  \hspace{1cm} (7.3)
General analytical solutions of the diffusion equation 7.3 can be obtained for a variety of initial and boundary conditions provided that the diffusion coefficient is constant. Most solutions give treatments for diffusion systems where no more than one diffusivity is involved, and the concentration at the interface is continuous. Crank has derived a solution for a more complex situation, namely for the infinite composite medium (Crank, 1956, 1975). The latter solution considers the system where two media with different diffusivities are present, and the concentration at the interface between the two media does not have to be continuous (as expressed in equation 7.4 below). This is different from most other one-dimensional solutions derived by Crank. In this case of infinite composite media, the diffusing substance initially resides evenly in one of the medium, then diffuses to the other medium. It assumes that the lengths of the two media are infinite. It can be used for a finite system for which within the time span of interest, the diffusion process would not have much influence on the composition at the surface of the finite medium.

For the system of infinite composite medium, if $x = 0$ defines the position of the coating/substrate interface, $c_1$ is the concentration in $x > 0$ (in this case the Ti-Al-Cr deposit) and $c_2$ is the concentration in $x < 0$ (the Ti-50Al substrate, which contains no Cr initially). Then the boundary conditions at $x = 0$ may be written as

\begin{align}
\frac{c_2}{c_1} &= k, \quad x = 0, \quad (7.4) \\
\frac{D_1 \partial c_1}{\partial x} &= \frac{D_2 \partial c_2}{\partial x}, \quad x = 0 \quad (7.5)
\end{align}

where $k$ is the ratio of the concentrations in the regions $x < 0$ (the substrate) and $x > 0$ (the deposit). Note that one constrain in this case is that $k$ should never be greater than 1 (Crank, 1956, 1975). $D_1$ and $D_2$ are the average Cr diffusivities in the regions $x > 0$ (the deposit) and $x < 0$ (the substrate) respectively.

The initial condition of this system is
Chapter 7  Diffusion and Oxidation

\[ c_1 = c_0, \quad x > 0, \quad t = 0 \]  
\[ c_2 = 0, \quad x < 0, \quad t = 0 \]  
(7.6)
(7.7)

where \( t \) is time and \( c_0 \) is the Cr concentration in the as-received deposit. The analytical solution to this problem involves the error function and its complementary function, as shown below:

\[ c_1 = \frac{c_0}{1 + k \sqrt{D_2 / D_1}} \left\{ 1 + k \sqrt{D_2 / D_1} \operatorname{erf} \frac{x}{2 \sqrt{D_1 t}} \right\} \]  
(7.8)

\[ c_2 = \frac{kc_0}{1 + k \sqrt{D_2 / D_1}} \operatorname{erfc} \frac{|x|}{2 \sqrt{D_2 t}} \]  
(7.9)

The error function and its complementary function are expressed as:

\[ \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-x^2) \, dx \]  
(7.10)

\[ \operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty \exp(-x^2) \, dx = 1 - \operatorname{erf}(z) \]  
(7.11)

A typical concentration distribution for the infinite composite medium, where \( D_2 = 4 D_1 \) and \( k = \frac{1}{2} \), is shown in figure 7.8.

In this work the Cr profiles were fitted to the above solution (see equations 7.8 and 7.9). The parameters \( D_1 \), \( D_2 \) and \( k \) were optimised using the experimental data (as shown in the Cr elemental profiles in figures 7.6 and 7.7). The least square method was used for optimisation (see appendix B), which produces the best fitting by finding the minimum of the difference between experimental data and predicted values. In order to avoid a local minimum rather than the global one, various starting values were given.
The fitting results are shown in figures 7.9 to 7.11. The fitted parameters are summarised in table 7.1.

From the fitting results, it is seen that the Cr diffusivity in the Ti-50Al substrate \( (D_2) \) did not change significantly with time, which would be expected, since diffusivity is a physical property of the medium and the same substrate was used in this work.

**Table 7.1**  Fitted diffusion parameters (at 1173K) for the Ti-50Al-10Cr and the Ti-50Al-20Cr deposits on the Ti-50Al substrate.

<table>
<thead>
<tr>
<th>Deposit</th>
<th>( D_1/\mu m^2\cdot s^{-1} )</th>
<th>( D_2/\mu m^2\cdot s^{-1} )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-50Al-10Cr, 10 hours</td>
<td>1.33\times 10^{-3}</td>
<td>6.15\times 10^{-4}</td>
<td>0.37</td>
</tr>
<tr>
<td>Ti-50Al-10Cr, 100 hours</td>
<td>7.28\times 10^{-5}</td>
<td>2.37\times 10^{-4}</td>
<td>0.90</td>
</tr>
<tr>
<td>Ti-50Al-10Cr, 820 hours</td>
<td>5.68\times 10^{-5}</td>
<td>4.35\times 10^{-4}</td>
<td>1.00</td>
</tr>
<tr>
<td>Ti-50Al-20Cr, 10 hours</td>
<td>6.37\times 10^{-2}</td>
<td>7.90\times 10^{-4}</td>
<td>0.20</td>
</tr>
<tr>
<td>Ti-50Al-20Cr, 100 hours</td>
<td>1.65\times 10^{-3}</td>
<td>4.09\times 10^{-4}</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The trend of change of Cr diffusivity in the Ti-Al-Cr coatings \( (D_1) \) does not seem clear and care should be taken when comparing \( D_1 \) values. This is because to use this diffusion solution, it has been assumed that the coating is sufficiently thick so that diffusion would not affect the coating surface composition. This assumption would not be true after prolonged heat-treatment. For instance, in the case of the Ti-50Al-10Cr deposit, the Cr concentration at the deposit surface was not reduced much after 100 hours heat-treatment, while decreased by about 1 at.% after 820 hours heat-treatment (see figure 7.6). Meanwhile, during heat-treatment, the deposits experienced changes such as phase transformations and growth of new precipitates. Phase transformations include the metastable phase dissipation (the amorphous phase and the \( \alpha \) phase) and the new phase formation. These changes may affect the value of \( D_2 \).
Figures 7.9 to 7.11 show that the Cr profile in the substrate can be fitted with relatively good precision. With diffusivity and $k$ value estimated from the fitting, the Cr profiles can be roughly predicted. For instance, in the case of Ti-50Al-10Cr, if we take $D_1 = 5.0 \times 10^{-5} \text{ } \mu \text{m}^2 \cdot \text{s}^{-1}$ (extrapolated from the case of 820 hours heat-treatment, see table 7.1), $D_2 = 4.3 \times 10^{-4} \text{ } \mu \text{m}^2 \cdot \text{s}^{-1}$, $k = 1$ when $t = 1000$ hours, one will obtain a diffusion profile as shown in figure 7.12a. For Ti-50Al-20Cr, if we take $D_1 = 0.8 \times 10^{-3} \text{ } \mu \text{m}^2 \cdot \text{s}^{-1}$, $D_2 = 4.0 \times 10^{-4} \text{ } \mu \text{m}^2 \cdot \text{s}^{-1}$, $k = 0.35$ when $t = 1000$ hours, one will obtain a diffusion profile as shown in figure 7.12b. Similarly, the diffusion profiles at 1500 hours of heat-treatment can be obtained, as shown in figure 7.13.

<table>
<thead>
<tr>
<th>Deposits</th>
<th>10 hours</th>
<th>100 hours</th>
<th>820 hours</th>
<th>1000 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-50Al-10Cr</td>
<td>3.28%</td>
<td>11.27%</td>
<td>33.01%</td>
<td>36.45%</td>
</tr>
<tr>
<td>Ti-50Al-20Cr</td>
<td>3.06%</td>
<td>12.57%</td>
<td>38.72%</td>
<td>42.83%</td>
</tr>
</tbody>
</table>

On the other hand, as the Cr profile in the substrate can be fitted with relatively good precision, the percentage of Cr diffused at a given time can be readily estimated. The total amount of Cr in the system, $C_{\text{total}}$, is the initial average Cr concentration in the deposit times the thickness of the coating, as indicated by the rectangular area under the dotted line in figure 7.14. At a given time, as the Cr profile changes to the dark solid curve, the amount of Cr lost via diffusion, $C_t$, is illustrated by the shaded area in figure 7.14. By dividing the two values, the percentage of Cr lost in the coating via diffusion can be obtained. Since the Cr profile at a given time can be simulated using the fitting results, $C_t$ can be obtained by numerical integration of the Cr concentration profile in the substrate. Table 7.2 shows the calculations of the Cr consumption for the experiments carried out in this work. Estimation of Cr consumption was also made for
prolonged heat-treatments. The diffusivity and $k$ values used are the same as detailed in the previous paragraph. These results are shown in italics in table 7.2. A plot of Cr consumption against time shows that the diffusion rate of Cr would gradually level off along with the heat-treatment duration (see figure 7.15).

7.3 Preliminary Study of Oxidation Behaviour

7.3.1 Oxidation During Isothermal Heat-treatment

It has been noticed in chapter 3 and 4 that the Ti-Al-Cr deposits were oxidised during heat treatment even under an Ar atmosphere. For example, figure 5.4 shows a layer of oxide formed on the Ti-50Al-10Cr deposit heat-treated at 1173K in Ar flow for 100 hours. The scales formed were around 1~2 μm thick. In isothermal heat-treatments, no cracking of the deposit or significant oxide nodules were observed.

EDX line-scans of the scales indicated they were Al rich, as can be seen in figures 7.3 to 7.4, and that they might consist of alumina primarily. Quantitative analysis was not possible because of the limited thickness of the scale. Elemental mapping by WDX was carried out on the Ti-50Al-10Cr deposit produced by the discontinuous route, see figure 7.16. The Ti and Cr concentrations were observed to have reduced in the oxide scale, whereas the Al concentration was slightly increased. The relatively high oxygen concentration at the substrate/deposit interface, see figure 7.16e, could be attributed to extraneous materials trapped during sample preparation.

7.3.2 Cyclic Oxidation

Cyclic oxidation tests were carried out on the Ti-50Al-10Cr, Ti-53Al-15Cr and Ti-50Al-20Cr coatings produced by the continuous route. In each cycle of oxidation, the samples, which were placed in a clean crucible, were inserted into a box furnace pre-heated to 1173K, then quickly taken out after 1 hour of heat-treatment and cooled in
The samples were weighted after every twenty such cycles, i.e. every 20 hours of heat-treatment. Table 7.3 shows the weight changes for the three coatings.

The weight gain for all three deposits was very small (usually around ±0.001g, which is the accuracy of the balance used). Thus comparison of weight gains between the deposits was not possible. The weight gain of all alloys plotted against cyclic oxidation duration is shown in figure 7.17 together with that of the unprotected Ti-50Al alloy. It shows that the weight gains of the Ti-50Al substrate coated with Ti-Al-Cr deposits were much lower. Such small weight changes are good news for the deposits, since they indicate slow oxidation rates at 1173K for the Ti-Al-Cr coatings.

Although the above results indicated good cyclic oxidation resistance of the coatings at 1173K, careful inspection revealed that the Ti-50Al-10Cr deposit had suffered from cracking under thermal cycling. In the SEM, lumps of oxidation product were found to emerge from the middle of the cracks, as shown in figure 7.18. Figure 7.19a gives a closer view, showing one nodule emerging from a crack, which is approached by another crack. In some cases, the large oxide nodules were broken into two halves along the crack (figure 7.19b). Cracks appeared after about 40 hours of heat-treatment. Such cracks and oxide nodules, however, were not observed on the Ti-50Al-20Cr and the Ti-53Al-15Cr deposit.

For comparison, figure 7.20a shows the protective oxide scale formed on the Ti-50Al-20Cr deposit after 100 hours isothermal oxidation in air at 1173K. The same oxide morphology was observed on the Ti-50Al-10Cr and Ti-53Al-15Cr coatings where the oxide scales were also found to be continuous. Figure 7.20b shows the morphology of the oxide scale formed on the Ti-50Al-10Cr deposit isothermally heat-treated at 1173K for 820 hours. Cracking, as seen in figure 7.19, was not observed.

EDX elemental maps were acquired for the oxide nodules and a typical map is shown in figure 7.21. Compared to the continuous oxide scale formed on top of the deposit,
the oxide formed within cracks was richer in Ti and leaner in Al than the surrounding oxide.

### Table 7.3

Weight changes of the Ti-50Al-10Cr, Ti-53Al-15Cr and Ti-50Al-20Cr during cyclic oxidation at 1173K.

<table>
<thead>
<tr>
<th>Ti-50Al-10Cr</th>
<th>t/hour</th>
<th>Sample weight/g</th>
<th>Weight change/g</th>
<th>Weight Gain per unit area/g-mm²</th>
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<td>-1.802x10⁻⁶</td>
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<tr>
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<td>1.802x10⁻⁶</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ti-53Al-15Cr</th>
<th>t/hour</th>
<th>Weight/g</th>
<th>Gain/g</th>
<th>Weight Gain/g-mm²</th>
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</thead>
<tbody>
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<td>0</td>
<td>1.8554</td>
<td>0</td>
<td>0</td>
<td>3.189x10⁻⁶</td>
</tr>
<tr>
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<td>1.857</td>
<td>0.0016</td>
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<tr>
<td>40</td>
<td>1.857</td>
<td>0.0016</td>
<td>1.138x10⁻⁶</td>
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</tr>
<tr>
<td>60</td>
<td>1.8563</td>
<td>0.0009</td>
<td>7.587x10⁻⁶</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Ti-50Al-20Cr</th>
<th>t/hour</th>
<th>Weight/g</th>
<th>Gain/g</th>
<th>Weight Gain/g-mm²</th>
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</thead>
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<td>0</td>
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<tr>
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<td>1.611</td>
<td>-0.001</td>
<td>-3.793x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.612</td>
<td>0</td>
<td>1.138x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.6131</td>
<td>0.0011</td>
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<tr>
<td>60</td>
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<td>1.6126</td>
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<td>7.587x10⁻⁶</td>
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</table>
The fact that those cracks were not found on the isothermally heat-treated Ti-50Al-10Cr coatings suggested that thermal shock was the major cause of crack formation. Once cracks were formed, the Ti-50Al substrate could be in direct contact with air. The non-protective oxide was thus rapidly formed on the exposed Ti-50Al alloy, as the Ti-50Al alloy is a γ-TiAl based alloy, the oxidation resistance of which deteriorates significantly at temperatures higher than 1023K (see section 2.2.5).

The fact that cracks appeared on the Ti-50Al-10Cr coating during cyclic oxidation, and not on the other coatings, could be attributed to the different microstructures of the deposits. As shown in figure 5.2, the heat-treated Ti-50Al-10Cr deposit had a very distinct columnar structure, while a random distribution of precipitates was found in the Ti-50Al-20Cr deposit (see figure 5.23). The columnar feature of the heat-treated Ti-53Al-15Cr deposit was much less strong than the Ti-50Al-10Cr deposit. The columnar structure in Ti-50Al-10Cr could render the deposit more liable to cracking under thermal shocks. The oxide formed in the cracks strains the cracks further and tears the coating. Thus, for applications where the coatings would experience thermal cycling, amorphous coatings when as-deposited should be preferred, so that columnar features could be avoided in their microstructures.

7.4 Summary

Elemental profiling and the mathematical fitting showed that the Cr diffusion process was not very fast. The Cr concentration gradient at the coating/substrate interface would be constrained by the solubility of the γ phase, which is the main phase constituent in the Ti-50Al substrate. The experimental data were fitted into a solution of the diffusion problem for infinite composite medium. The Cr profiles in the substrate were fitted with relatively good precision.
Evidence from both isothermal and cyclic oxidation tests indicated that the oxidation of the Ti-Al-Cr coatings discussed in this thesis was slow at 1173K. The continuous oxide scale formed was Al rich, indicating that it mainly consisted of alumina.

Cyclic oxidation tests showed that the Ti-50Al substrate coated with the Ti-Al-Cr coatings discussed in this thesis had much slower oxidation rates than the bare Ti-50Al alloy. However, columnar structure in the coating could lead to coating cracking when thermally shocked. The substrate would then be exposed and the oxide formed on the substrate at elevated temperature would tear the coating further. Thus, amorphous coatings when as-deposited should be preferred.
Figure 7.1  Line-scan analysis of the Ti-50Al-10Cr deposit heat-treated at 1173K for 10 hours. The arrow indicates the coating/substrate interface.

Figure 7.2  Line-scan analysis of the Ti-50Al-10Cr deposit heat-treated at 1173K for 100 hours. The arrow indicates the coating/substrate interface.
Figure 7.3  Line-scan analysis of the Ti-50Al-20Cr deposit heat-treated at 1173K for 10 hours. The arrow indicates the coating/substrate interface.

Figure 7.4  Line-scan analysis of the Ti-50Al-20Cr deposit heat-treated at 1173K for 100 hours. The arrow indicates the coating/substrate interface.
Figure 7.5 Illustration of the measurement scheme used to obtain a quantitative composition profile from the deposit to the substrate.

Figure 7.6 The Cr concentration profiles of the Ti-50Al-10Cr deposit heat-treated at 1173K for (a) 10 hours, (b) 100 hours and (c) 820 hours.
Figure 7.7  The Cr concentration profiles of the Ti-50Al-20Cr deposit heat-treated at 1173K for (a) 10 hours, (b) 100 hours.

Figure 7.8  A typical concentration distribution in a composite medium, where $D_2 = 4D_1$ and $k = \frac{1}{2}$ (Crank, 1956).
Figure 7.9  Fitted diffusion profiles for the Ti-50Al-10Cr deposit heat-treated at 1173K for (a) 10 hours (b) 100 hours.
Figure 7.10  Fitted diffusion profile for the Ti-50Al-10Cr deposit heat-treated at 1173K for 820 hours.

Figure 7.11  Fitted diffusion profiles for the Ti-50Al-20Cr deposit heat-treated at 1173K for (a) 10 hours, (b) 100 hours.
Figure 7.12  Predicted diffusion profiles for (a) the Ti-50Al-10Cr deposit on the Ti-
50Al substrate, (b) the Ti-50Al-20Cr deposit on the Ti-50Al, heat-treated at 1173K for
1000 hours.

Figure 7.13  Predicted diffusion profiles for (a) the Ti-50Al-10Cr deposit on the Ti-
50Al substrate, (b) the Ti-50Al-20Cr deposit on the Ti-50Al, heat-treated at 1173K for
1500 hours.
Figure 7.14  Schematic diagram showing Cr diffusion profile in the substrate and coating.

Figure 7.15  Percentage of Cr diffused into the Ti-50Al substrate from the Ti-50Al-10Cr and Ti-50Al-20Cr deposits plotted against time.
Figure 7.16 A typical WDX map acquired for the Ti-50Al-10Cr deposit isothermally heat-treated at 1173K for 100 hours, showing (a) the SE image of the cross-section, (b) the Al map, (c) the Ti map, (d) the Cr map and (e) the O map.
Figure 7.17  Weight gain plotted against cyclic oxidation duration.

Figure 7.18  SEM SE image of the Ti-50Al-10Cr deposit after cyclic oxidation test in air at 1173K for 100 hours. Massive oxidation products are seen to emerge from cracks.
Figure 7.19  SEM SE images of the Ti-50Al-10Cr deposit after cyclic oxidation test in air at 1173K for 100 hours, showing (a) a close view of an oxide nodule; (b) a large oxide nodule split into two halves along the crack.
Figure 7.20  SEM SE images showing (a) the protective oxide formed on the Ti-50Al-20Cr deposit isothermally heat-treated in air at 1173K for 100 hours; (b) the oxide formed on the Ti-50Al-10Cr deposit isothermally heat-treated in air for 820 hours.
Figure 7.21  EDX elemental maps acquired for the Ti-50Al-10Cr coating after cyclic oxidation in air at 1173K for 100 hours.
Chapter 8
Conclusions and Future Work

8.1 Conclusions

1. Amorphous Ti-Al and Ti-Al-Cr deposits can be produced using the magnetron sputter deposition technique. When crystallisation occurs during deposition, a columnar microstructure would be formed with the columnar fibres parallel to the deposition direction. For the Ti-50Al-10Cr and Ti-53Al-15Cr deposit, the crystalline domains consisted of lamellar $\gamma<111> // \alpha<0002>$, i.e. the crystalline deposits had a $\gamma<111> // \alpha<0002>$ texture. The $\alpha$ phase was also ordered partially, i.e. the transformation $\alpha \rightarrow \alpha_2$ occurred during deposition.

2. The microstructure of the as-received deposit strongly affects the microstructure development during heat-treatment. A random distribution of precipitates was formed, when the as-received deposit was amorphous. Columnar features were present when the as-received deposit had crystallised during sputter deposition. In the latter case, texture was maintained in the $\gamma$ phase.

3. At 1173K, the Ti-50Al-10Cr alloy transformed to a two-phase microstructure, consisting of the $\gamma$ and C14 Ti(Al, Cr)$_2$ phases. The Ti-53Al-15Cr alloy transformed to a three-phase microstructure, consisting of the $\gamma$, $\tau$ and the C14 Laves phase. The $\gamma$ and $\tau$ phases were mixed finely, with $\gamma<100> // \tau<100>$. The Ti-50Al-20Cr alloy transformed to a two-phase microstructure, consisting of the $\gamma$ and the C14 Laves phase. No orientation relationship between the $\gamma$ and the C14 Laves phase was observed.
4. Phase evolution studies at lower temperatures in the range 773K to 973K indicated that for the amorphous Ti-48Al alloy, the phase transformation path is: the amorphous phase \(\rightarrow\) \(\alpha\) \(\rightarrow\) \(\gamma + \alpha/\alpha_2\). A fine lamellar structure was formed, with \(\gamma\) being the dominant phase. For the Ti-50Al-20Cr alloy, the phase transformation path was: the amorphous phase \(\rightarrow\) \(\gamma\) \(\rightarrow\) \(\gamma + Ti(Al, Cr)_2\).

5. The amorphous phase in the Ti-Al and Ti-Al-Cr alloys has been thermodynamically modelled using the CALPHAD method. The experimental observations and the modelling results have clearly suggested a tendency of amorphous phase stabilisation via Cr addition. Thermodynamic modelling also indicated that the driving force for amorphous alloy formation is not much less than that for the precipitation of disordered solution phases. Kinetically, the amorphous phase formation during sputter deposition is related to the suppression of surface diffusion at low substrate temperatures. The temperature processing window for ordered phase formation in the Ti-Al(-Cr) alloys during magnetron sputter deposition can be evaluated by the effective diffusion distance.

6. Phase competition in the amorphous Ti-Al(-Cr) alloys was evaluated using nucleation theory. Transient time calculations showed that in the Ti-48Al amorphous alloy, it would be kinetically easier for the \(\alpha\) phase to precipitate than \(\gamma\). In the case of the Ti-50Al-20Cr alloy, the \(\gamma\) phase forms in preference to \(\alpha\), being consistent with experimental observations.

7. The experimental Cr diffusion profiles and the simulations for the Ti-Al-Cr coatings and the Ti-50Al substrate indicated that diffusion at 1173K is reasonably slow.

8. The Ti-50Al-10Cr, Ti-53Al-15Cr and the Ti-50Al-20Cr coatings could form protective oxide scales at 1173K. When a severe columnar structure was present in the crystalline deposit, cracking of the coating was observed when the coating was
subject to thermal-shocks at elevated temperatures. This exposed the Ti-50Al substrate to air and titanium rich oxide formed, which impaired the coating further.

9. If cracking of the coatings is to be avoided, amorphous deposits are preferred, as columnar structure formation would be prevented.

### 8.2 Suggestions for Future Work

1. Understanding amorphous alloy formation and devitrification is important for alloy design as well as fundamental research in materials science. In this thesis, modelling of amorphous phase in Ti-Al(-Cr) alloys, based on the liquid and ground-state crystalline phase, has enabled the comparison of the thermodynamic properties of the competing phases. It would be essential to test the experimentally determined thermodynamic data against data for devitrification and glass transition temperatures. This should be done by DSC/DTA using free-standing samples.

2. Since the Ti-Al-Cr alloys are candidates as high temperature coating materials, it would be worthwhile to do a thorough study of the oxidation behaviour of these alloys.

3. At 1173K, the Ti-50Al-20Cr alloy was found to contain the $\gamma$ and the Laves phase after equilibration at 1173K, even though this alloy was designed to contain the $\tau$ and the Laves phase instead. This is due to the fact that the effective composition of the alloy was shifted to $32.58\text{Ti-48.28Al-19.14Cr}$. There has been limited work on phase equilibria in Cr-rich Ti-Al-Cr alloys, such as those consisting of the $\tau$ and Laves phases. A detailed study of phase equilibria in such alloys would be very useful for the development of Cr-rich Ti-Al-Cr alloys.
Appendix A XRD Data

Table 1 XRD data of the as-deposited Ti-50Al-10Cr (produced by the continuous route).

<table>
<thead>
<tr>
<th>$d$ (Å) measured</th>
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<th>$d$ (Å) reference</th>
<th>hkl</th>
<th>Phase</th>
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<tr>
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<td>222</td>
<td>$\gamma$</td>
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</table>

Table 2 XRD data of the as-deposited Ti-53Al-15Cr (produced by the continuous route).

<table>
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<td>$\gamma$</td>
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Table 3  XRD data of the crystalline Ti-50Al-10Cr (produced by the continuous route) heat-treated in Ar at 1173K for 100 hours.

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<td>202/2133</td>
<td>γ/ Ti(Cr,Al)₂</td>
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<tr>
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Table 4  XRD data of the amorphous Ti-50Al-10Cr (produced by the discontinuous route) heat-treated at 1173K for 10 hours.

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### Table 5a
XRD data of the crystalline Ti-53Al-15Cr heat-treated in air at 1173K for 10 hours.

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<th>$d$ (Å) reference</th>
<th>$hkl$</th>
<th>Phase</th>
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<td>111/1013/111</td>
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### Table 5b
XRD data of the crystalline Ti-53Al-15Cr heat-treated in air at 1173K for 100 hours.

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<td>113/1012</td>
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<td>2.32/2.33</td>
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Table 6a XRD data of the crystalline Ti-50Al-20Cr (produced by the continuous route) heat-treated in air at 1173K for 3 hours.

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Table 6b  XRD data of the crystalline Ti-50Al-20Cr (produced by the continuous route) heat-treated in air at 1173K for 10 hours.

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Table 6c  XRD data of the crystalline Ti-50Al-20Cr (produced by the continuous route) heat-treated in air at 1173K for 100 hours.

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</tr>
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<td>1.71</td>
<td>2023</td>
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</tr>
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<td>231</td>
<td>TiO₂</td>
</tr>
<tr>
<td>1.454</td>
<td>4</td>
<td>1.45</td>
<td>023</td>
<td>TiO₂</td>
</tr>
<tr>
<td>1.428</td>
<td>6</td>
<td>1.43</td>
<td>202</td>
<td>γ</td>
</tr>
<tr>
<td>1.413</td>
<td>21</td>
<td>1.42</td>
<td>2133</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.398</td>
<td>6</td>
<td>1.416</td>
<td>220</td>
<td>γ</td>
</tr>
<tr>
<td>1.371</td>
<td>16</td>
<td>1.38/1.375</td>
<td>3032/300</td>
<td>Ti(Cr,Al)₂/Al₂O₃</td>
</tr>
<tr>
<td>1.315</td>
<td>13</td>
<td>1.32</td>
<td>2025</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.287</td>
<td>4</td>
<td>1.29</td>
<td>2134</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.26</td>
<td>10</td>
<td>1.26</td>
<td>2240</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.218</td>
<td>6</td>
<td>1.22</td>
<td>113</td>
<td>γ</td>
</tr>
</tbody>
</table>
Table 7  XRD data of the amorphous Ti-48Al (produced by the discontinuous route) heat-treated in air at 773K for 15 hours.

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>I/I₀</th>
<th>d (Å)</th>
<th>hkl</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>measured</td>
<td></td>
<td>reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.299</td>
<td>100</td>
<td>2.325/2.342</td>
<td>111/0002</td>
<td>γ/α</td>
</tr>
<tr>
<td>2.179</td>
<td>60</td>
<td>2.22/2.20</td>
<td>1011/2021</td>
<td>α/α₂</td>
</tr>
<tr>
<td>1.422</td>
<td>29</td>
<td>1.43/1.446</td>
<td>202/2240</td>
<td>γ</td>
</tr>
</tbody>
</table>

Table 8  XRD data of the amorphous Ti-48Al (produced by the discontinuous route) heat-treated in air at 873K for 120 minutes.

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>I/I₀</th>
<th>d (Å)</th>
<th>hkl</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
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<td>measured</td>
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<td>reference</td>
<td></td>
<td></td>
</tr>
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<td>2.825</td>
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<td>2.83</td>
<td>110</td>
<td>γ</td>
</tr>
<tr>
<td>2.463</td>
<td>16</td>
<td>2.53/2.50</td>
<td>1010/2020</td>
<td>α/α₂</td>
</tr>
<tr>
<td>2.313</td>
<td>100</td>
<td>2.33</td>
<td>111</td>
<td>γ</td>
</tr>
<tr>
<td>2.189</td>
<td>17</td>
<td>2.22/2.20</td>
<td>1011/2021</td>
<td>α/α₂</td>
</tr>
<tr>
<td>2.011</td>
<td>18</td>
<td>2.035</td>
<td>002</td>
<td>γ</td>
</tr>
<tr>
<td>1.424</td>
<td>29</td>
<td>1.427</td>
<td>202</td>
<td>γ</td>
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<td>1.211</td>
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<td>1.21</td>
<td>311</td>
<td>γ</td>
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</table>

Table 9  XRD data of the amorphous Ti-48Al (produced by the discontinuous route) heat-treated in air at 973K for 30 minutes.

<table>
<thead>
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<th>d (Å)</th>
<th>I/I₀</th>
<th>d (Å)</th>
<th>hkl</th>
<th>Phase</th>
</tr>
</thead>
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<td></td>
<td>reference</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>24</td>
<td>2.50</td>
<td>2020</td>
<td>α₂</td>
</tr>
<tr>
<td>2.326</td>
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<td>2.32</td>
<td>111</td>
<td>γ</td>
</tr>
<tr>
<td>2.294</td>
<td>100</td>
<td>2.31</td>
<td>0002</td>
<td>α₂</td>
</tr>
<tr>
<td>2.152</td>
<td>58</td>
<td>2.20</td>
<td>2011</td>
<td>α₂</td>
</tr>
<tr>
<td>2.111</td>
<td>61</td>
<td>2.10</td>
<td>1012</td>
<td>α₂</td>
</tr>
<tr>
<td>2.079</td>
<td>26</td>
<td>1.96</td>
<td>113</td>
<td>Al₂O₃</td>
</tr>
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<td>1.982</td>
<td>18</td>
<td>2.00</td>
<td>200</td>
<td>γ</td>
</tr>
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<td>1.416</td>
<td>19</td>
<td>1.43</td>
<td>202</td>
<td>γ</td>
</tr>
<tr>
<td>1.403</td>
<td>16</td>
<td>1.41</td>
<td>220</td>
<td>γ</td>
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<td>1.39</td>
<td>3140</td>
<td>α₂</td>
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<td>2023</td>
<td>α₂</td>
</tr>
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<td>4040</td>
<td>α₂</td>
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**Table 10**  XRD data of the amorphous Ti-50Al-20Cr (produced by the discontinuous route) heat-treated in air at 873K for 3 hours.

<table>
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<th>d (Å) measured</th>
<th>I/I₀</th>
<th>d (Å) reference</th>
<th>hkl</th>
<th>Phase</th>
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<tr>
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<td>100</td>
<td>2.325</td>
<td>111</td>
<td>γ</td>
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<td>220</td>
<td>γ</td>
</tr>
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**Table 11**  XRD data of the amorphous Ti-50Al-20Cr (produced by the discontinuous route) heat-treated in air at 923K for 15 min.

<table>
<thead>
<tr>
<th>d (Å) measured</th>
<th>I/I₀</th>
<th>d (Å) reference</th>
<th>hkl</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.006</td>
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<td>1120</td>
<td>α₂</td>
</tr>
<tr>
<td>2.119</td>
<td>95</td>
<td>2.325</td>
<td>111</td>
<td>γ</td>
</tr>
</tbody>
</table>

**Table 12**  XRD data of the amorphous Ti-50Al-20Cr (produced by the discontinuous route) heat-treated in air at 923K for 30 min.

<table>
<thead>
<tr>
<th>d (Å) measured</th>
<th>I/I₀</th>
<th>d (Å) reference</th>
<th>hkl</th>
<th>Phase</th>
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<tbody>
<tr>
<td>2.52</td>
<td>28</td>
<td>2.530</td>
<td>1120</td>
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</tr>
<tr>
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<td>2.325</td>
<td>111</td>
<td>γ</td>
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<td>2.284</td>
<td>99</td>
<td>2.323</td>
<td>10 13</td>
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</tr>
<tr>
<td>2.174</td>
<td>54</td>
<td>2.191</td>
<td>20 20</td>
<td>Ti(Cr,Al)₂</td>
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<tr>
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<td>100</td>
<td>2.155</td>
<td>1122</td>
<td>Ti(Cr,Al)₂</td>
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<tr>
<td>2.11</td>
<td>58</td>
<td>2.117</td>
<td>20 21</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>2.055</td>
<td>28</td>
<td>2.055</td>
<td>0004</td>
<td>Ti(Cr,Al)₂</td>
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<tr>
<td>1.98</td>
<td>38</td>
<td>2.003</td>
<td>200</td>
<td>γ</td>
</tr>
<tr>
<td>1.416</td>
<td>18</td>
<td>1.427</td>
<td>202</td>
<td>γ</td>
</tr>
<tr>
<td>1.402</td>
<td>26</td>
<td>1.417/1.416</td>
<td>2133/220</td>
<td>Ti(Cr,Al)₂/γ</td>
</tr>
<tr>
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</tr>
<tr>
<td>1.317</td>
<td>20</td>
<td>1.315</td>
<td>20 25</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.263</td>
<td>16</td>
<td>1.265</td>
<td>22 40</td>
<td>Ti(Cr,Al)₂</td>
</tr>
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</table>
Table 13  XRD data of the amorphous Ti-50Al-20Cr (produced by the discontinuous route) heat-treated in air at 973K for 5 min.

<table>
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<tr>
<th>d (Å) measured</th>
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<th>hkl</th>
<th>Phase</th>
</tr>
</thead>
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<td>25</td>
<td>2.53</td>
<td>11 20</td>
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<tr>
<td>2.325</td>
<td>47</td>
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<td>111</td>
<td>γ</td>
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<td>88</td>
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<td>10 13</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>2.177</td>
<td>70</td>
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<td>20 20</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>2.154</td>
<td>100</td>
<td>2.155</td>
<td>11 22</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>2.111</td>
<td>49</td>
<td>2.117</td>
<td>20 21</td>
<td>Ti(Cr,Al)₂</td>
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<tr>
<td>1.984</td>
<td>34</td>
<td>2.003</td>
<td>200</td>
<td>γ</td>
</tr>
<tr>
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<td>1.861</td>
<td>20 22</td>
<td>Ti(Cr,Al)₂</td>
</tr>
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<td>14</td>
<td>1.539</td>
<td>10 15</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.417</td>
<td>17</td>
<td>1.427</td>
<td>202</td>
<td>γ</td>
</tr>
<tr>
<td>1.401</td>
<td>25</td>
<td>1.417/1.416</td>
<td>21 33/220</td>
<td>Ti(Cr,Al)₂/γ</td>
</tr>
<tr>
<td>1.377</td>
<td>16</td>
<td>1.376</td>
<td>30 32</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.319</td>
<td>15</td>
<td>1.315</td>
<td>20 25</td>
<td>Ti(Cr,Al)₂</td>
</tr>
<tr>
<td>1.263</td>
<td>16</td>
<td>1.269</td>
<td>301</td>
<td>γ</td>
</tr>
<tr>
<td>1.255</td>
<td>15</td>
<td>1.265</td>
<td>22 40</td>
<td>Ti(Cr,Al)₂</td>
</tr>
</tbody>
</table>
Appendix B
Determining Coefficients
Using Least-Squares Regression

Least-squares regression is widely used in curve-fitting, which is often used in trend analysis and hypothesis testing. In the latter case, an existing mathematical model is compared with measured data. If model coefficients are unknown, the values of these coefficients can be determined by finding the best fitting to the observed data using least-squares regression. The least-squares regression used in this work is summarised as followed.

Consider a function having one variable $x$ as indicated in equation 1:

$$y = g(a,b)f(x)$$

where $a$ and $b$ are the two unknown coefficients. There would exist an error, or residual, $e$, which is the discrepancy between the true value of $y$ and the modelled value. This residual can be expressed as:

$$e = y_{\text{meas}} - y_{\text{model}}$$

where $y_{\text{meas}}$ is the measured value, and $y_{\text{model}}$ the estimated value. Supposing that there are $n$ measured data, the strategy of finding the best fit of the unknown coefficients is to find the parameters that make the sum of the squares of the residuals a minimum. This sum of squares of residuals is expressed as:

$$S = \sum_{i=1}^{n} e_i^2 = \sum_{i=1}^{n} (y_{i,\text{meas}} - y_{i,\text{model}})^2 = \sum_{i=1}^{n} (y_{i,\text{meas}} - g(a,b)f(x_i))^2$$

Mathematically, in order to determine values for $a$ and $b$, equation 3 is differentiated with respect to each coefficient. Setting these derivatives equal to zero will result in a minimum $S$: 
The optimised values of $a$ and $b$ are thus obtained by solving equation 4.

In cases where analytical derivatives as shown in equation 4 are difficult to obtain, the minimum of $S$ can be evaluated numerically, i.e. the problem is transformed into finding the minimum of equation 3, in which $a$ and $b$ have become the two variables.

There are many algorithms and computing libraries available in terms of numerically searching the function minimum. In the work discussed in this thesis, the minimisation was performed using MATLAB (Version 5.2.0, by The MathWorks Inc.) build-in function \textit{fmins}. This function uses the Nelder-Mead simplex search method (Nelder and Mead, 1965, Chapra and Canale, 1998), which is the most commonly used step method. In this case, the two diffusion coefficients are $a$ and $b$ in equation 3. In order to find the global minimum, different starting points were used.
Appendix C
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