Reactions and phase relations in the Ti-Al-O system

Citation for published version (APA):

DOI:
10.1016/0956-7151(92)90478-W

Document status and date:
Published: 01/01/1992

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.
Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain.
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 04. Oct. 2020
REACTIONS AND PHASE RELATIONS IN THE Ti–Al–O SYSTEM

X. L. LI, R. HILLEL, F. TEYSSANDIER, S. K. CHOI and F. J. J. VAN LOO

1Laboratoire de Physicochimie minérale, CNRS-URA 116, Université Claude Bernard, F-69622 Villeurbanne Cedex, France, 2IMP-CNRS, Université de Perpignan, F-66860 Perpignan, France and 3Laboratory of Solid State Chemistry and Material Science, University of Technology, 5600 MB Eindhoven, The Netherlands

(Received 9 December 1991; in revised form 6 February 1992)

Abstract—Reactions between titanium and alumina were studied experimentally for Al₂O₃ substrates with a titanium-based coating and for planar Ti–Al₂O₃ diffusion couples in the temperature range between 800 and 1100°C. Isothermal sections through the phase diagram were determined by using these results as well as by investigating equilibrated alloys. These experimental sections agree with those calculated from thermodynamic data. The morphology and layer thickness of the observed reaction zones have been explained on the basis of these phase relations, making use of diffusion data from the binary systems Ti–O and Ti–Al. The important role of the initial Ti thickness on the type of reaction products has been demonstrated.


1. INTRODUCTION

Because of the increasing importance of ceramic–metal combinations for high temperature applications, like in composites or in the joining and coating technology, a better understanding of their mutual interaction is necessary. It would especially be fruitful if these interactions could be predicted from the more or less easily accessible data on the relevant phase diagrams and on the diffusivities in the binary systems which are involved.

For a number of relatively simple metal–ceramic combinations with Cell-defined stoichiometric compounds such predictions turned out to be possible by using a model developed by Van Loo et al. [1, 2]. The principle is shown in Fig. 1. The key idea is the impossibility for atoms or ions to intrinsically diffuse into a direction where its own chemical activity is increased. It might be worthwhile to stress at this point the word "intrinsically". The equations for the interdiffusional fluxes in a ternary diffusion couple are dependent on the chemical potential gradients of two components. The intrinsic flux of a component, measured in the Kirkendall frame of reference, depends only upon its own potential gradient as shown by Lane and Kirkaldy [3]. Since the relative values of the chemical activities in simple ternary systems can be found from the slopes of the lines, important conclusions can be drawn a priori concerning the sequence of the compounds formed during the reaction in a diffusion couple.

For the case of Fig. 1(b), for example, the layer sequence A|AX|BX is excluded because of the fact, that species X then should diffuse from BX through the phase B towards the phase AX where its chemical activity is higher than in BX. This process is thermo-
Fig. 1. (a,b) Phase relations in the A-B-X system in a rectangular configuration. (c,d) The activity of X as a function of the metal mole ratio. The dots represent the activity of X in a saturated solid solution (A,B). (e,f,g) Basic morphologies for the reaction zone in the displacement reaction A + BX → B + AX (see Refs [1, 4]).

dynamically not allowed. In the case of Fig. 1(a), no sequence is excluded on thermodynamic grounds. The diffusion kinetics determine the morphology of the reaction layer. Using Rapp's criterion [4] one may predict whether two single-phase layers or one two-phase layer is formed.

It seemed interesting to us to verify, whether such a simple model also can be applied to systems in which the phase diagram is more complicated, especially in systems where large regions of solid solutions are formed instead of stoichiometric line-compounds. We chose a study into the Ti-Al-O system, reported here, and the Ti-Si-O system on which we will report separately. Both systems are interesting from a technological point of view, especially in composite materials [5, 6] and in metal-ceramic joining [7, 8]. A literature search into the reaction between Ti and Al₂O₃ and into the Ti-Al-O phase diagram revealed a number of often conflicting results [9–17]. For instance, using infinite or finite diffusion couples, various sequences of layers were proposed:

\[
\begin{align*}
\text{Ti/} & \alpha\text{-Ti(O)/Ti₃Al/Al₂O₃} [11]; \\
\text{Ti/} & Ti₃Al/TiO/Al₂O₃ [12]; \\
& \alpha\text{-Ti(O,Al)/TiAl(O)/Al₂O₃} [13]; \\
& Ti/Ti₃Al(O)/TiAl(O)/Al₂O₃ [14]; \\
& \alpha\text{-Ti(O)/Ti₃Al(O)/Al₂O₃} [17].
\end{align*}
\]

It is shown in this paper that these differences partly originate from the different thicknesses of the titanium end member (thin coatings or thick slices) and that the actual phenomena can readily be explained (and predicted) from the isothermal section through the ternary phase diagram.
2. EXPERIMENTAL

2.1. Diffusion couple preparation

Ti–Al$_2$O$_3$ diffusion couples were prepared in two ways, viz. by applying titanium-based coatings on sintered alumina or single-crystalline sapphire by gaseous cementation and by hot-pressing polished slices of titanium and alumina in a vacuum furnace.

In the first method, plane alumina substrates [sintered alumina 99.7 wt% or (102) cleaved sapphire crystals, dimensions 10:10:1 mm] were treated by reactive CVD in closed silica capsules, filled with thin titanium foils and HCl. The HCl concentration was equal to $1.07 \times 10^{-5}$ mol·cm$^{-3}$ and the quantity of titanium corresponded to an atomic ratio Ti/Cl = 100. The capsules were sealed and annealed in the range of 600–800°C during 0.25–200 h. We have shown [6] that at these temperatures the gaseous phase consisted of a mixture of TiCl$_4$, TiCl$_3$ and H$_2$. In this way titanium was transported to the alumina substrate and reacted to a coating with two distinct layers, arranged as $\alpha$-Ti(O,A1)/Ti$_3$AI(O)/Al$_2$O$_3$. The thickness and exact composition of these layers depended on the experimental conditions [5, 6].

For the hot pressed diffusion couples, 10 mm diameter discs of sintered alumina (99.9 wt%) and titanium (99.8 wt%) were pressed together using a uniaxial pressure of 4 MPa in the centre of a hot chamber which was evacuated to 10$^{-3}$ Pa. They were heated during $\frac{1}{2}$ h at 900°C, and then wrapped in Ta-foil, annealed in an evacuated silica capsule in a tube furnace at 1100°C and quenched after 72 or 140 h. Parallel with these methods, a direct joint was made in a vacuum furnace (10$^{-4}$ Pa vacuum, uniaxial pressure 0.2 MPa) at 100°C for 50 and 100 h. The standards were pure titanium and aluminium and Fe$_2$O$_3$ for oxygen. Using the PROZA and the thin-film programs of Bastin [18, 19] we were able to measure the actual bulk composition of the alloys and in the diffusion couple cross sections as well as the thickness and composition of the surface films. In the composition range of interest, the Ti/Al molar ratio was not affected by the presence of the oxide film.

We made use of this fact by developing a combined X-ray diffraction and SEM equipped with energy dispersive spectroscopy (EDS) analysis to determine the composition of especially, the $\alpha$-Ti(O,A1) and Ti$_3$AI(O) solid solutions. Using literature data [20, 21] and our own X-ray measurements on binary Ti-O and Ti-Al alloys [6], we constructed a set of calibration curves for the volume of the lattice cell vs the amount of oxygen or aluminium, assuming that the interstitially dissolved oxygen and the substitutionally dissolved Al do not influence their individual effect on the cell volume (Fig. 2).

To check this procedure, ternary alloys made by the powder method were analysed in this way. The weighed-in and estimated composition are in good agreement for the aluminium-poor alloys (Table 1).

3. RESULTS

The isothermal sections determined at 1000 and 1100°C were in quite close agreement. They show, as the one determined at 1100°C (Fig. 3), tie-lines radiating from Al$_2$O$_3$ to all other phases present in the diagram, except for the $\beta$-Ti solid solution which is in equilibrium with $\alpha$-Ti(O,A1).

The diffusion paths (average composition measured in a diffusion couple from one end member to the other) shown in Fig. 3 for couples with thin
Li et al.: Phase Relations in the Ti–Al–O System

3152

0.037 ~ 0.036 ~ 0.0355 ~ 0.0350 ~ 0.0345 ~ 0.0340 ~ 0.0335 ~ 0.0330

Fig. 2. Calculated volumes of the hexagonal cell of $\alpha$-Ti(O, Al) and Ti$_3$Al(O) as a function of the composition. The bold line is the estimated boundary of $\alpha$-Ti(O, Al).

4. DISCUSSION

The isothermal sections found by us differ from the diagrams published by Tressler [12] (Fig. 6), especially in the phase equilibria between TiAl, Ti$_3$Al, $\alpha$-Ti(O, Al), TiO and Al$_2$O$_3$. In order to verify whether our results were consistent with the published thermodynamic properties of the Ti–O and Ti–Al alloys we determined the phase relations at 1373 K by Gibbs free energy minimisation of the total system. Calculations were performed with the Solgasmix program taking into account the line compounds given in Table 2 and the solid solution $\alpha$-Ti(O). Due to the low solubility of oxygen in $\beta$-Ti, the $\beta$-Ti(O) solid solution was not considered for the calculation.

Table 1. Comparison between the prepared and estimated composition of the $\alpha$-Ti(O, Al) phase

<table>
<thead>
<tr>
<th>Weighted-in composition</th>
<th>Measured volume of the cell (nm$^3$)</th>
<th>Estimated composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.13}$</td>
<td>0.03515 ± 0.00002</td>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.12}$</td>
</tr>
<tr>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.14}$</td>
<td>0.03550 ± 0.00009</td>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.14}$</td>
</tr>
<tr>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.15}$</td>
<td>0.03549 ± 0.00009</td>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.15}$</td>
</tr>
<tr>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.16}$</td>
<td>0.03559 ± 0.0001</td>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.16}$</td>
</tr>
<tr>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.22}$</td>
<td>0.03628 ± 0.00004</td>
<td>Ti$<em>{0.5}$O$</em>{0.5}$Al$_{0.22}$</td>
</tr>
</tbody>
</table>

4.1. Ti–O binary phase diagram

The Gibbs free energies of formation of the Ti–O stoichiometric compounds came from Chase et al. [22] and are consistent with JANAF [23] and Pankratz [24]. The variation of the Gibbs free energies of the solid solution $\alpha$-Ti(O) as a function of the composition at 1373 K was obtained in the following way. The information we have about the $\alpha$-Ti(O) phase is

--- According to the assessed Ti–O Murray [20] phase diagram, the upper and lower phase boundary compositions of $\alpha$-Ti(O) are Ti$_{0.667}$O$_{0.333}$ and Ti$_{0.915}$O$_{0.085}$.
--- The corresponding free energy of formation based on the data given by Kubaschewski and Alcock [29] on the Ti–O system is $\Delta G^{1373}$ Ti$_{0.915}$O$_{0.085} = -44,272$ J/mol
--- $\Delta G^{1373}$ Ti$_{0.667}$O$_{0.333} = -152,000$ J/mol.

As a result of this boundary composition we know that the tangent to the $\Delta G$ $\alpha$-Ti(O) curve for the composition $X_0 = 0.33$ includes the point corresponding to $\Delta G$ $\beta$Ti$_{0.5}$O$_{0.5}$.

Fig. 3. Isothermal section of the Ti–Al–O phase diagram experimentally determined at 1100°C.
Five conditions are then obtained which allow the determination of five parameters: the two coefficients of the tangent, the lattice stability of oxygen between the h.c.p. and gas state (which is not given in the literature) and two parameters ($A$ and $B$) for the equation of $\Delta G_{\alpha\text{-Ti}(O)}$

$$\Delta G_{\text{Ti}(1-x)O_x} \text{(ref. Ti h.c.p., O h.c.p.)} = x(1-x)(AX + B).$$

Taking into account the lattice stability of titanium determined by Kaufman [26] ($G_{\text{Ti(1-x)Ti(1-x)}} - G_{\text{Ti h.c.p.}} = -4351 + 3.766 \cdot T$ J/mol), the calculation gives $A = -848,533$, $B = -678,039$, $G_{1/202 \text{hcp} - G_{1/202 \text{gas}}} = 201,456$ J/mol. The corresponding Gibbs diagram is presented in Fig. 7.

### 4.2. Ti–Al binary phase diagram

The Ti–Al system was first investigated by Kaufman [26] who determined the Gibbs free energy of formation of Ti$_3$Al, TiAl and TiAl$_3$, described as line compounds. The $\alpha$- and $\beta$-Ti(Al) solid solutions were modelized as regular solutions. More recently, Murray [27] did the same calculation but included the homogeneity range of Ti$_3$Al and TiAl as well as order parameters, with a model which combines the sub-lattice description and the Bragg-Williams approximation. The Ti–Al system has also been studied by Gros et al. [28] but the calculation involves only the Ti-rich corner which includes liquid, b.c.c., h.c.p. and Ti$_3$Al phases.

The calculation of Murray is one of the most recent and complete but does not take into account TiAl$_2$, whose existence seems now to be well established. We have thus undertaken a new calculation based on the data of Murray [27] for TiAl$_3$ and the $\alpha$– and $\beta$-Ti(Al) solid solutions and including TiAl$_2$. We were not able to use the Gibbs free energy of TiAl$_3$ established by Kaufman [26] which is too high according to the data of Murray. Our own estimation of this value at 1373 K is: $\Delta G^{1373} \text{ Ti}_{0.33}\text{Al}_{0.67} = -26,000$ J/mol.
Table 2. Gibbs free energy of formation of the line compounds, taken into account in our calculations

<table>
<thead>
<tr>
<th>Line compounds</th>
<th>AG (J/mol) 1373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 TiO</td>
<td>-205,907</td>
</tr>
<tr>
<td>1/5 Ti₃O₅</td>
<td>-229,223</td>
</tr>
<tr>
<td>1/4 Ti₄O₇</td>
<td>-232,032</td>
</tr>
<tr>
<td>1/3 + 1/2 Ti₃O₅</td>
<td>-231,664</td>
</tr>
<tr>
<td>1/3 TiO₂ rutile</td>
<td>-231,994</td>
</tr>
<tr>
<td>1/2 Ti₃Al</td>
<td>-18,377</td>
</tr>
<tr>
<td>1/3 Ti₃Al₂</td>
<td>-26,165</td>
</tr>
<tr>
<td>1/4 Ti₃Al₃</td>
<td>-26,000</td>
</tr>
<tr>
<td>1/4 Ti₃Al₄</td>
<td>-23,000</td>
</tr>
</tbody>
</table>

We used a polynomial expansion for the excess Gibbs free energy of Ti₃Al and Ti₃Al in their homogeneity range

Ti₃Al (ref. Ti h.c.p., Al h.c.p.)

$$\Delta G = X_\text{Al} \cdot (1 - X_\text{Al}) \cdot (C \cdot X_\text{Al} + D)$$

Ti₃Al (ref. Ti f.c.c., Al f.c.c.)

$$\Delta G = X_\text{Al} \cdot (1 - X_\text{Al}) \cdot (L \cdot X_\text{Al}^2 + M \cdot X_\text{Al} + N)$$

The results of the calculation have to be in accordance with the phase boundaries of the assessed binary Ti-Al phase diagram at 1373 K. Eight conditions can then be determined which allow the determination of the five parameters of the excess Gibbs free energy of Ti₃Al and Ti₃Al, as well as the equations of the common tangents to α-Ti(Al) and Ti₃Al, and Ti₃Al and Ti₃Al₂. The following lattice stability of titanium and aluminium established by Kaufman [26] was used

$$G_{\text{Ti h.c.p.}} - G_{\text{Ti f.c.c.}} = -4351 + 3.766 \cdot T \text{ J/mol}$$

$$G_{\text{Al h.c.p.}} - G_{\text{Al f.c.c.}} = -1004 + 3.766 \cdot T \text{ J/mol}$$

$$G_{\text{TiO₂ rutile}} - G_{\text{Ti₃Al₂}} = -5230 + 9.707 \cdot T \text{ J/mol}$$

$$G_{\text{Ti₃Al₂}} - G_{\text{Al₃O₅}} = -10,740 + 11.506 \cdot T \text{ J/mol.}$$

The results of the polynomial expansion for the excess Gibbs free energy of Ti₃Al and Ti₃Al expressed in J/mol are

$$C = -31,162, D = -70,059$$

$$L = 77,644, M = -157,365, N = -32,187.$$ 

The resulting free energy diagram at 1373 K is given in Fig. 8.

When using these data for the calculation of the isothermal section of the ternary Ti-Al-O phase diagram, tie lines between Ti₃Al and the saturated α-Ti(O) solid solution or β-TiO are obtained instead of the tie line between Al₂O₃ and Ti₃Al as experimentally observed. Two remarks should be made concerning these differences. Firstly, the accuracy of the used free energy values for the compounds is not very high. This is important especially because the free energy values of a reaction in this system are dominated by the much larger values for the oxides compared with the aluminides (see Table 2). Secondly, the solubility of oxygen in Ti₃Al and Ti₃Al, which is suspected to involve a large variation of the free energy value, is neglected.

In order to cope with this difficulty we undertook a new calculation including the solubility of oxygen in Ti₃Al and Ti₃Al. A sublattice model would be suitable for taking into account both the solubility of oxygen and the homogeneity range of the intermetallic compounds. However, due to the lack of information at temperatures other than 1373 K, we focused on the influence of oxygen on Ti₃Al and Ti₃Al considered as line compounds using a simpler model. The Gibbs free energy of Ti₃Al and Ti₃Al were obtained from our previous model

$$\Delta G \text{ Ti₃AlO₅} = -18,377 \text{ J/mol}$$

$$\Delta G \text{ Ti₃AlO₆} = -26,165 \text{ J/mol.}$$

The solubility of oxygen is described by a quasi-binary approximation between Ti₃Al or Ti₃Al and O

$$G_{\text{h.c.p.}} = (1 - X_O)G_{\text{Ti₃AlO₅}} + X_O G_O + RT[X_O \ln X_O + (1 - X_O) \ln (1 - X_O)] + \lambda X_O G_{\text{h.c.p.}}$$

where

$$\lambda X_O G_{\text{h.c.p.}} = \lambda X_O (1 - X_O)$$

λ is the excess parameter of the solid solution described with a regular model. The lattice stability of
LI et al.: PHASE RELATIONS IN THE Ti-Al-O SYSTEM

1/2 \( \text{TiO}_2 \) ~ \( \text{Ti}_2\text{O}_3 \) /~

Fig. 9. Isothermal section of the Ti-Al-O phase diagram calculated at 1373 K.

The lattice stability of oxygen between the f.c.c. and the gas state as well as the regular parameters were adjusted to represent satisfactorily the experimentally determined limit of solubility

\[ \begin{align*}
\text{Ti}_3\text{Al}-\text{O} & : \ \text{limit } X_0 = 0.11 \quad \Delta G = -720,000 \text{ J/mol} \\
\text{TiAl}-\text{O} & : \ \text{limit } X_0 = 0.03 \quad \Delta G = -630,000 \text{ J/mol} \\
\end{align*} \]

The calculated isothermal ternary section at 1373 K is given in Fig. 9. If we exclude the Ti rich corner where the \( \alpha \)- or \( \beta \)-Ti\((\text{O,Al})\) solid solutions were not taken into account, this diagram agrees very well with the experimental one. These results emphasize the fact that a strong variation of the free energy is induced by the solubility of oxygen

\[ \begin{align*}
\text{Ti}_{0.75}\text{Al}_{0.25} & : \ \Delta G = -18,377 \text{ J/mol} \\
\text{Ti}_{0.662}\text{Al}_{0.222}\text{O}_{0.05} & : \ \Delta G = -68,272 \text{ J/mol} \\
\text{Ti}_{0.50}\text{Al}_{0.50} & : \ \Delta G = -26,165 \text{ J/mol} \\
\text{Ti}_{0.485}\text{Al}_{0.485}\text{O}_{0.03} & : \ \Delta G = -39,837 \text{ J/mol} \\
\end{align*} \]

In the case of TiAl-O this variation represents an increase of more than 50% of \( \Delta G \) for only 3% oxygen dissolved. For \( \text{Ti}_3\text{Al}(\text{O}) \) the free energy value at 11% oxygen is more than three times the initial value.

If we accept the experimentally determined isothermal section to be correct, we can construct from them the rectangular sections shown in Fig. 10(a) and (b), and we can estimate the corresponding plots of \( \ln a_0 \) and \( \ln a_{\text{Al}} \) shown in Fig. 10(c).

These estimates are based on the thermodynamic data in Table 2, on the data given by Kubaschewski [29] on the Ti-O system which takes into consideration the solid solubility range of TiO and on the data of the above mentioned thermodynamic calculation. We now use Fig. 10 (c) and (d) as a starting point for our prediction of the diffusion path in a semi-infinite Ti-Al\(_2\)O\(_3\) couple.

Figure 10(d), for instance, forbids a layer sequence \( \text{Al}_2\text{O}_3/\text{TiO}/\text{Ti}_3\text{Al}/\alpha/\beta\)-Ti, suggested by Tressler [12], since then Al has to diffuse from \( \text{Al}_2\text{O}_3 \) through a minimum activity in TiO to a higher activity in Ti\(_3\)Al, which is thermodynamically impossible.

Figure 10(c) forbids a diffusion path of the type \( \text{Al}_2\text{O}_3/\text{TiAl}_{0.5}/\text{TiAl}_{0.5}/\text{Ti}_3\text{Al}/\alpha/\beta\)-Ti. The reason is that since the activity of oxygen has to decrease going from the \( \text{Al}_2\text{O}_3/\text{TiAl}_{0.5} \) boundary (in \( a_0 \approx -75 \)) towards the \( \alpha \)-solid solution. Such a low activity of oxygen in \( \alpha \) means a negligible concentration of oxygen and that is in conflict with the mass balance, since the oxygen amount which diffuses away from \( \text{Al}_2\text{O}_3 \) must be 3/2 times the amount of aluminium atoms. The sequence \( \text{Al}_2\text{O}_3/\alpha/\text{TiAl}_{0.5}/\alpha/\beta\)-Ti is, from Fig. 10(c) and (d) not necessarily forbidden, but very unlikely since between very small limits in the activities of oxygen and aluminium the path would then enter, leave and re-enter the \( \alpha \)-phase. No problem is offered with a sequence of the type

\[ \begin{align*}
\text{Al}_2\text{O}_3/\text{TiAl}/\text{Ti}_3\text{Al}/\alpha/\beta\)-Ti \\
\end{align*} \]

indicated in Fig. 3. Which of these paths will be followed depends, in fact, on the relative ratio of the diffusivities in the TiAl, Ti3Al and \( \alpha \)-Ti(O,Al) phases. The diffusion of oxygen in \( \alpha \)-Ti is fast [30], that of Al in \( \text{Ti}_3\text{Al} \) or \( \alpha \)-Ti is low [31]. In order to let oxygen diffuse freely into \( \alpha \)-Ti and to cope with the mass balance, the formation of TiAl has to be expected and is indeed found. If, on the other hand, the initial Ti thickness is small, then the amount of oxygen which enters Ti is small and the titanium becomes rapidly saturated in oxygen, consequently leading to a change in diffusion path. This path no longer starts at the pure titanium, but at a more or less saturated solid solution \( \alpha \)-Ti(O). During this process, TiAl formed in the beginning of the process, will react with the unsaturated \( \alpha \)-Ti(O) solution of e.g. composition Ti\(_{0.50}\) according to a reaction scheme of the type

\[ \begin{align*}
12 \text{ Ti} + 3 \text{Al}_2\text{O}_3 & \rightarrow 3 \text{Ti}_3\text{O} + 3 \text{Ti}_3\text{Al}(\text{O}) + 3 \text{TiAl}(\text{O}) \\
3 \text{Ti}_3\text{O} + \text{TiAl}(\text{O}) & \rightarrow 3 \text{Ti}_2\text{O} + 3 \text{Ti}_3\text{Al}(\text{O}) \\
12 \text{ Ti} + 2 \text{Al}_2\text{O}_3 & \rightarrow 2 \text{Ti}_3\text{Al}(\text{O}) + 3 \text{Ti}_2\text{O} \\
\end{align*} \]

The limited thickness of the TiAl layer permits its formation from a diffusion point of view. If the reaction given above is represented according to the actual measured average compositions for the thin-foiled Ti–Al\(_2\)O\(_3\) couple, one gets

\[ \begin{align*}
10.2 \text{ Ti} + \text{Al}_2\text{O}_3 & \rightarrow 7.9 \text{ Ti}_{0.662}\text{Al}_{0.228}\text{O}_{0.082} + 7.29 \text{ Ti}_{0.662}\text{Al}_{0.016}\text{O}_{0.322}. \ (4)
\end{align*} \]
The cell volumes (per atom) of the Ti₃Al(O) and α-Ti(O) phases are calculated from Fig. 2 as shown in Table 3. That means, that according to reaction (4) the thickness ratio of the two layers has to be

$$\text{Ti}_3\text{Al(O)} : \alpha - \text{Ti(O)} = \frac{0.0156 \times 7.9}{0.0124 \times 7.29} \approx 1.36:1$$

which is in excellent agreement with the value of 1.39 ± 0.12, experimentally found as shown in Fig. 4. This, in fact, is also an independent confirmation of the composition measurements by EPMA.

5. CONCLUSION

By different experimental techniques a consistent isothermal section of the Ti-Al-O phase diagram has been established in the range 1000-1100°C. From this section, together with estimated thermodynamic data, it is possible to explain in detail the layer sequence and morphology in diffusion couples Al₂O₃-Ti. The same method can, therefore, fruitfully be used to predict the diffusion processes and layer morphologies in this type of system. This will be shown in a future paper dealing with the interaction between SiO₂ and Ti.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Unit cell volume (nm³) (Fig. 2)</th>
<th>Number of at./cell</th>
<th>Volume per atom nm³/at.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₆Al₆O₁₈O₅₄₂</td>
<td>0.0341</td>
<td>2.179</td>
<td>0.0341/2.179 = 0.0156</td>
</tr>
<tr>
<td>Ti₆Al₆O₁₄O₅₄₂</td>
<td>0.0366</td>
<td>2.949</td>
<td>0.0366/2.949 = 0.0124</td>
</tr>
</tbody>
</table>

Fig. 10. Activities data plotted as a function of composition.
REFERENCES


