Analysis of Interface Reactions of TiAl/Al₂O₃ and TiAl/TiO₂ by the Use of Chemical Potential Diagram

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化学ポテンシャル図を用いた TiAl/Al₂O₃ 及び TiAl/TiO₂ の界面反応の解析

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Interface reactions for the diffusion couples of TiAl/Al₂O₃ and TiAl/TiO₂ were investigated and the reaction paths were analyzed by the use of chemical potential diagram. No essential reaction was observed at 1273 K for the diffusion couple of TiAl/Al₂O₃, but Ti₃Al(O) was formed between TiAl(O) and Al₂O₃ phases at 1373 K. In the case of TiAl/TiO₂, Ti₃Al(O) and Al₂O₃ were formed between TiAl(O) and TiO₂ phases. These reaction paths were reasonably elucidated by the use of chemical potential diagram of the Ti-Al-O system, which was constructed using the data of Gibbs energy of formation for the compounds composed of Ti, Al and O. The reaction paths for the diffusion couple of Ti/Al₂O₃ and oxidation of TiAl obtained from the literature data were also reasonably elucidated by the use of the same chemical potential diagram.

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1. Introduction

Since the interface reactions of ceramic-metal combinations have become increasingly important for high temperature applications such as diffusion bonding, surface coating, composite materials, the control of multi-component grain-boundary in ceramics, and oxidation of alloys, the analysis of these reactions is necessary not only in the area of basic solid state chemistry but also in the development of materials.

Intermetallic compounds such as TiAl and FeAl have received much attention as high-temperature structural materials, especially for aerospace applications, because of their lightness and high specific-strength at high temperatures.^{1,2)} These compounds are stable up to their melting points, but are oxidized at oxidizing atmospheres at high temperatures. The oxidation reaction of the intermetallic compounds of Ti-Al system has been studied by many investigators³⁾⁻⁸⁾ and it has been found that the anti-oxidation character is much dependent on the Al content of the intermetallic compounds. Compounds of TiO₂, Al₂O₃ and Ti₃Al were found as oxidation products of TiAl by Shida and Anada,³⁾ but the thermodynamic analysis of the oxidation reaction has not been conducted yet.

The reaction for the diffusion couple of Ti/Al₂O₃ has been investigated by many researchers in the view of diffusion bonding,⁹⁾⁻¹²⁾ composite materials,¹³⁾ surface reactions^{14),15)} and reaction path.^{16),17)} Various layer sequences after the reaction of Ti/Al₂O₃ reported by various investigators were analyzed by Li et al.¹⁶⁾ on the basis of the isothermal section of phase diagram of Ti-Al-O system.

Yokokawa et al.¹⁸⁾⁻²²⁾ have proposed the use of chemical potential diagram to analyze the multi-component interface reactions, since the driving force of the chemical reaction and diffusion is the gradient of chemical potential. They have successfully elucidated the layer sequence of the

phases formed by the interface reactions by the use of the multi-component chemical potential diagrams, assuming a local equilibrium at the interface.

Inaba^{21),22)} has investigated the interface reaction of Cu₂O/Ni and Cu₂O (NiO doped)/Ni and analyzed the reaction path on the chemical potential diagram for the undoped and the doped samples, because the reaction path is changed by doping and has a non-equilibrium character. It has been shown that the reaction and diffusion path being a function of time is represented and reasonably explained on the chemical potential diagram obtained from a thermodynamic treatment.

In this study, the interface reactions of TiAl/Al₂O₃ and TiAl/TiO₂ have been investigated and the reaction paths have been analyzed using the chemical potential diagram of Ti-Al-O system.

2. Experimental

The raw materials used in this study were 99.9999 mass% aluminum and 99.99 mass% sponge titanium. A button ingot of Ti-50.0 mol% Al was prepared by a tri-arc furnace under a highly purified argon atmosphere. The melting operation was repeated more than four times to increase homogeneity of the ingot. The ingot was sealed in a quartz tube filled with highly purified argon and then homogenized at 1273 K for 167h. Sheets of 1 mm in thickness were cut from the button ingot and then polished to about 1 μm roughness. The impurity of the homogenized ingot was Na : 14, Mg : 3, Si : 20, Ca : 32, Cr : 22, Mn : <1, Fe : 12 and Cu : 10 ppm. The content of Al in TiAl was determined as 50.00 at% within the error of 0.05% by the chemical analysis. For the diffusion couples of TiAl/Al₂O₃ and TiAl/TiO₂, powders of Al₂O₃ and TiO₂ with 99.9% purity were used. TiAl sample of the cylindrical shape with 8 mm in diameter and 1 mm in thickness was packed in Al₂O₃ or TiO₂ powder in a stainless steel cylinder for the diffusion couple of TiAl/Al₂O₃ or TiAl/TiO₂. The sample was pressed using a stainless steel ram at the top of the stainless cylinder, which was similar to the one by Laheij et al.²³⁾ and was automatically sealed by sintering between the ram and the cylinder during

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the heating process of annealing. The cylinders were annealed at 1273 K or 1373 K for 48, 96, 144 and 192h and were cut along the radial direction for the analysis. The profiles of Ti, Al and O atoms after the reaction were analyzed by an electron probe microanalyser (EPMA). The line-analysis of EPMA was carried out with the voltage of 15 kV, beam current of 50 nA, the diameter of the beam of about $1\text{ }\mu\text{m}$ and the scan speed of $50\text{ }\mu\text{m}\cdot\text{min}^{-1}$. The two-dimensional EPMA profiles for Ti, Al and O were also taken and layered reaction products were obtained for the diffusion couple of TiAl/ Al_2O_3 or TiAl/ TiO_2 and therefore the results of the line scan are only shown.

3. Results

The EPMA profiles of Ti, Al and O atoms after the reaction at 1273 K for 144h for the diffusion couple of TiAl/ Al_2O_3 are shown in Fig. 1, where no reaction product can be seen between TiAl and Al_2O_3 phases. When the reaction temperature was raised to 1373 K for the diffusion couple of TiAl/ Al_2O_3 , a new phase was observed between the TiAl and Al_2O_3 phases as shown in Fig. 2. The new phase is considered to be a $\text{Ti}_3\text{Al}(\text{O})$ phase according to the intensity ratio of Ti, Al and O of EPMA in Fig. 2, where (O) in $\text{Ti}_3\text{Al}(\text{O})$ means the dissolved oxygen in the $\text{Ti}_3\text{Al}(\text{O})$ phase. The content of oxygen dissolved in the $\text{Ti}_3\text{Al}(\text{O})$ phase was not determined quantitatively, but it is supposed to be a considerable amount such as 0.11 atomic ratio per metal at 1373 K as reported by Li et al.¹⁶⁾ judging from the intensity level of EPMA in Fig. 2. The appearance of the $\text{Ti}_3\text{Al}(\text{O})$ phase is considered to be due to the temperature effect on the reaction path resulting from the stabilization of $\text{Ti}_3\text{Al}(\text{O})$ at high temperatures. In Fig. 2, the phase TiAl(O) instead of TiAl is shown, since TiAl is considered to dissolve oxygen more or less when it is subjected to an oxygen potential. According to Fig. 2, the content of dissolved oxygen in TiAl(O) is thought to be considerably smaller than that of $\text{Ti}_3\text{Al}(\text{O})$ as Li et al.¹⁶⁾ reported that it was 0.03 atomic ratio per metal at 1373 K. It is noted that the increase of Al content and the decrease of Ti content in TiAl(O) phase were observed near the TiAl(O)/ $\text{Ti}_3\text{Al}(\text{O})$ boundary, which will be discussed in the next section. The EPMA profiles of Ti, Al and O after the reaction at 1273 K for 96h for the diffusion couple of TiAl/ TiO_2 are shown in Fig. 3. In this case, Al_2O_3 and $\text{Ti}_3\text{Al}(\text{O})$ phases were observed between TiAl(O) and TiO_2 phases.

Fig. 1. EPMA profiles of Ti, Al and O after the reaction at 1273 K for 144h for the diffusion couple of TiAl/ Al_2O_3 . No reaction product was observed in this case.

Fig. 2. EPMA profiles of Ti, Al and O after the reaction at 1373 K for 144h for the diffusion couple of TiAl/ Al_2O_3 . The phases shown in the figure are the inferred ones from the EPMA data.

Fig. 3. EPMA profiles of Ti, Al and O after the reaction at 1273 K for 96h for the diffusion couple of TiAl/ TiO_2 . The phases shown in the figure are the inferred ones from the EPMA data.

4. Discussion

4.1 Construction of chemical potential diagram

As has been described by Yokokawa et al.,¹⁸⁾⁻²²⁾ the use of chemical potential diagram is very useful in order to interpret multi-component interface reactions. The chemical potential diagram of Ti-Al-O system has been constructed as follows.¹⁸⁾⁻²²⁾ Consider the compounds of $\text{Ti}_k\text{Al}_l\text{O}_{m_i}$ and calculate the chemical potential of each component, μ_i , when three phases of the compounds coexist. If we consider the following reaction:

where k_i , l_i and m_i are the stoichiometric numbers of the compound, then the chemical potential of the compound can be represented by the sum of each component as:

$$\mu(\text{Ti}_k\text{Al}_l\text{O}_{m_i}) = k_i \mu(\text{Ti}) + l_i \mu(\text{Al}) + m_i \mu(\text{O}). \quad (2)$$

Since the chemical potential of a phase i is equal to the Gibbs energy of formation of the phase i , we obtain

$$\mu(\text{phase}_i) = \Delta_f G^\circ(\text{phase}_i). \quad (3)$$

When we apply Eq. (3) to the chemical potential of coexisting TiAl, TiAl_3 and Al_2O_3 phases as an example, we obtain

Fig. 4. Chemical potential diagram of Ti-Al-O system at 1273 K. The solution effect of oxygen in TiAl and Ti₃Al phases is not considered in this diagram.

$$\mu(\text{Ti}_{\text{TiAl}}) + \mu(\text{Al}_{\text{TiAl}}) = \Delta_f G^\circ(\text{TiAl}) \quad (4)$$

$$\mu(\text{Ti}_{\text{TiAl}_3}) + 3\mu(\text{Al}_{\text{TiAl}_3}) = \Delta_f G^\circ(\text{TiAl}_3) \quad (5)$$

$$2\mu(\text{Al}_{\text{Al}_2\text{O}_3}) + 3\mu(\text{O}_{\text{Al}_2\text{O}_3}) = \Delta_f G^\circ(\text{Al}_2\text{O}_3), \quad (6)$$

where $\mu(M_i)$ means a chemical potential of M in the phase i .

Since these three phases coexist, we have

$$\mu(\text{Ti}_{\text{TiAl}}) = \mu(\text{Ti}_{\text{TiAl}_3}), \quad (7)$$

$$\mu(\text{Al}_{\text{TiAl}}) = \mu(\text{Al}_{\text{TiAl}_3}) = \mu(\text{Al}_{\text{Al}_2\text{O}_3}), \quad (8)$$

$$\mu(\text{O}_{\text{TiAl}}) = \mu(\text{O}_{\text{TiAl}_3}) = \mu(\text{O}_{\text{Al}_2\text{O}_3}). \quad (9)$$

Then Eqs. (4) – (6) can be solved, since we can obtain the values of $\Delta_f G^\circ(\text{phase}_i)$ from the thermodynamic database of MALT2²⁴⁾ and/or some other data sources and we only have the three unknown parameters of $\mu(\text{Ti})$, $\mu(\text{Al})$ and $\mu(\text{O})$. The solution of Eqs. (4)–(6) is obtained as a triple point surrounded by TiAl, TiAl₃ and Al₂O₃ phases in the chemical potential diagram and is shown by A in Fig. 4. Applying Eq. (3) to all possible phases composed of the Ti-Al-O system, we can construct a chemical potential diagram as a group of polygons by connecting the lines of these triple points like A as shown in Fig. 4. Gibbs energy of formation for Ti₂O was obtained based on the thermodynamic data by Kubashewski and Alcock,²⁵⁾ since it is not available in MALT2.

4.2 Analysis of the interface reactions of TiAl/Al₂O₃ and TiAl/TiO₂

The following assumptions^{21),22)} have been made for the analysis of interface reactions by using the chemical potential diagram:

(1) The local equilibrium is attained at the interfaces, although the whole system is under a non-equilibrium condition.

(2) There is no kinetic barrier such as the chemical reaction at the interface and nucleation.

(3) The interface reaction goes through the path so as to maintain materials balance.

(4) The driving force of reaction and diffusion is the gradient of chemical potentials and the reaction and diffusion path follows the diffusion equation at each phase.

The mechanism of the interface reactions of TiAl/Al₂O₃ and TiAl/TiO₂ can be analyzed using the chemical potential diagram of Ti-Al-O system and these assumptions.

The EPMA profiles after the reaction at 1273 K for 144h for the diffusion couple of TiAl/Al₂O₃ shown in Fig. 1 indicate that no essential reaction occurs between TiAl and Al₂O₃ at this temperature. This is compatible with the chemical potential diagram of Ti-Al-O system at 1273 K shown in Fig. 4, where TiAl and Al₂O₃ phases are adjoined each other. When temperature was raised to 1373 K, the new

Ti₃Al(O) phase was formed between TiAl and Al₂O₃ phases as shown in Fig. 2, which cannot be explained by Fig. 4. This is due to the ignorance of the dissolving effect of oxygen in the TiAl and Ti₃Al phases on the construction of the chemical potential diagram of Ti-Al-O system. Li et al.¹⁶⁾ constructed the isothermal section of phase diagram of Ti-Al-O system at 1373 K including the TiAl(O) and Ti₃Al(O) phases in order to analyze the reaction products of Ti/Al₂O₃. According to their estimation, the TiAl(O) phase dissolves oxygen in the formula Ti_{0.485}Al_{0.485}O_{0.03} at 1373 K with a Gibbs energy of formation: $-39837 \text{ J} \cdot \text{mol}^{-1}$, which includes the stabilization energy due to dissolution of oxygen in Ti_{0.5}Al_{0.5}: $-13672 \text{ J} \cdot \text{mol}^{-1}$. Similarly, the Ti₃Al(O) phase dissolves oxygen in the formula Ti_{0.668}Al_{0.222}O_{0.11} at 1373 K with a Gibbs energy of formation: $-68282 \text{ J} \cdot \text{mol}^{-1}$ and the stabilization energy due to dissolution of oxygen in Ti_{0.75}Al_{0.25}: $-49895 \text{ J} \cdot \text{mol}^{-1}$. Using the thermodynamic data and the oxygen contents for TiAl(O) and Ti₃Al(O) at 1373 K obtained by Li et al.,¹⁶⁾ the chemical potential diagram at 1373 K is constructed and shown in Fig. 5. It is noted in Fig. 5 that TiAl and TiAl(O), and Ti₃Al and Ti₃Al(O) should be essentially the same phases and the transition from one composition to the other should be continuous without a boundary line or sharp change in angle. We just take into consideration the terminal compositions in such solution phases for the sake of convenience.

At 1373 K, the reaction path was changed to pass the Ti₃Al(O) phase between the TiAl(O) and Al₂O₃ phases as seen in Fig. 2. The formation of the Ti₃Al(O) phase at this temperature may be due to the larger solubility of oxygen with the larger stabilization energy¹⁶⁾ in the solution of oxygen. The estimated reaction path for the diffusion couple of TiAl/Al₂O₃ at 1373 K is shown by (3) in Fig. 5, which reasonably explains the layer sequence shown in Fig. 2. It should be noted that the increase of Al content and the decrease of Ti content in the TiAl(O) phase was observed near the TiAl(O)/Ti₃Al(O) boundary in Fig. 2. This fact is considered to be caused by the conservation of materials (assumption 3 for the analysis of interface reaction). During the reaction, Al and O in the Ti₃Al(O) phase come from Al₂O₃ phase and Ti in the Ti₃Al(O) phase should come from the TiAl(O) phase. Since the content of Ti in the Ti₃Al(O) phase is larger than in the TiAl(O) phase, Ti

Fig. 5. Chemical potential diagram of Ti-Al-O system taking into consideration of the TiAl(O) and Ti₃Al(O) phases at 1373 K. The estimated diffusion paths for the diffusion couples of Ti/Al₂O₃ with the thick and thin Ti samples investigated by Choi et al.¹⁷⁾ are shown by (1) and (2), respectively. The estimated diffusion path for the diffusion couple of TiAl/Al₂O₃ at 1373 K is shown by (3).

should be selectively supplied from the TiAl(O) phase and therefore Ti in the TiAl(O) phase is depleted near the TiAl(O)/Ti₃Al(O) boundary. The reaction path due to this phenomenon is shown as an upward curve near the TiAl(O)/Ti₃Al(O) boundary in the TiAl(O) phase rather than a straight line on the chemical potential diagram as shown by (3) in Fig. 5. This reaction path needs a sufficiently large area of the Ti₃Al(O) phase on the chemical potential diagram in order to pass the Ti₃Al(O)/Al₂O₃ boundary, which is realized by the large stabilization energy of the Ti₃Al(O) phase at 1373 K.

Since there are no available data on the Gibbs energy of formation of the TiAl(O) and Ti₃Al(O) phases at 1273 K, we tentatively assume that the difference in Gibbs energy of formation between 1373 K and 1273 K in the TiAl and Ti₃Al phase is the same as that in the TiAl(O) and

Ti₃Al(O) phases, respectively, and then the Gibbs energy of formation of the TiAl(O) and Ti₃Al(O) phases at 1273 K is estimated. The chemical potential diagram at 1273 K is thus constructed and shown in Figs. 6 and 7. The fact that no essential reaction occurred at 1273 K is compatible with the reaction path shown by (1) in Fig. 6.

In the case of the diffusion couple of TiAl/TiO₂, the phases of Al₂O₃ and Ti₃Al(O) were observed between the TiAl and TiO₂ phases as seen in Fig. 3. The reaction path for this diffusion couple is shown by (3) in Fig. 7, which reasonably explains the experimental reaction sequence.

4.3 Interpretation of reference data on the diffusion couple of Ti/Al₂O₃

Many studies have been performed on the diffusion couple of Ti/Al₂O₃, but the reaction products were reported to be strongly dependent on the investigators, the thickness of sample and the reaction temperature. For example, various sequences of layers were reported:

(1) Ti/Ti₃Al(O)/TiAl(O)/Al₂O₃ at 1373 K for a thick sample by Choi et al.¹⁷⁾

(2) Ti₂O/Ti₃Al(O)/Al₂O₃ at 1373 K for a thin sample by Choi et al.¹⁷⁾

(3) Ti/Ti₃Al/TiAl/Al₂O₃ at 1273 K by Hatakeyama et al.¹⁰⁾

(4) Ti/Ti₃Al/TiO/Al₂O₃ at 1254 K by Tressler et al.¹²⁾ These sequences of layers can be reasonably interpreted by using the chemical potential diagram of Ti-Al-O system as follows.

The layer sequence (1) Ti/Ti₃Al(O)/TiAl(O)/Al₂O₃ at 1373 K for a thick sample obtained by Choi et al.¹⁷⁾ is reasonably represented on the chemical potential diagram as shown by (1) in Fig. 5. When they used the thin Ti sample of 0.025 mm for the annealing period of 100h, Ti was consumed and Ti₂O was formed to give the layer sequence (2) Ti₂O/Ti₃Al(O)/Al₂O₃. It is noted, however, that even when we use a thick Ti sample, the layer sequence would become as (2), if the reaction period were sufficiently longer. Thus the transition of the reaction path from the sequence (1) to (2) would occur depending on the reaction period and the sample thickness, as far as we use a finite thickness of sample. The reaction paths corresponding to sequences (1) and (2) are shown on the chemical potential diagram as marked by (1) and (2) in Fig. 5. As the reaction time increases, the chemical potential of Al and O in the Ti phase increases due to the diffusion of Al and O, because the chemical potential of Al and O of alumina side is higher, the line marked by (1) shifts to the right and upper side and approaches the line marked by (2), as shown by an arrow in Fig. 5. Thus the transition of reaction path, which is time dependent and has a non-equilibrium character, can be reasonably interpreted using the chemical potential diagram, which has been derived from the thermodynamic calculation.

The sequence (3) is considered to be essentially identical with the sequence (1), because Hatakeyama et al.¹⁰⁾ probably neglected oxygen solubility in the Ti₃Al and TiAl phases. The reaction path by Hatakeyama et al.¹⁰⁾ can be represented by (2) in Fig. 6.

Li et al.¹⁶⁾ discussed the reaction path on the various layered sequences of Ti/Al₂O₃ diffusion couple obtained from various investigators and they concluded that the sequence (4) presented by Tressler et al.¹²⁾ was thermodynamically impossible based on the activity of Al versus O/Ti composition diagram of Ti-Al-O system. They described from the diagram that Al had to diffuse from Al₂O₃ through a minimum in TiO to a higher activity in Ti₃Al, which was thermodynamically impossible. The hypothetical reaction path (4) by Tressler et al.¹²⁾ cannot be explained by Fig. 6 either, which means that this reac-

Fig. 6. Chemical potential diagram of Ti-Al-O system at 1273 K. The solution effect of oxygen in the TiAl and Ti₃Al phases are included in this diagram. The estimated reaction path for the diffusion couple of TiAl/Al₂O₃ at 1273 K is shown by a solid line.

Fig. 7. Chemical potential diagram of Ti-Al-O system taking into consideration of the TiAl(O) and Ti₃Al(O) phases at 1273 K. The estimated diffusion paths for the oxidation reactions using Ti-42 at% Al sample by Hatakeyama et al.¹⁰⁾ at 1273 K and using Ti-36.3 at% Al sample at 1173 K by Shida and Anada³⁾ are shown by (1) and (2), respectively. The estimated diffusion paths for the diffusion couples of TiAl/TiO₂ is shown by (3).

tion path is thermodynamically impossible. The reason why such a reaction path was experimentally observed is not clear at present. One possibility to explain this fact is an impurity effect; some impurities would change the activity of Al or Ti very much. Another possibility is the ignorance the solution effect of Al for the Ti₂O and TiO phases in the thermodynamic calculation both in the present study and that by Li et al.¹⁶⁾

4.4 Interpretation of reference data on the oxidation of TiAl

Many studies have been performed on the oxidation of TiAl, but only a few studies clearly have described the reaction path due to the oxidation. Various sequences of layers for the oxidation of TiAl were reported:

(1) TiAl/Al₂O₃/Al₂O₃ + TiO₂/TiO₂ at 1273 K using Ti-42 at%Al by Hatakeyama et al.,¹⁰⁾ and at 1373 K using Ti-50 at%Al by Kahveci et al.⁸⁾

(2) TiAl/Ti₃Al(O)/Al₂O₃ + TiO₂/Al₂O₃/TiO₂ at 1173 K using Ti-36.3 at%Al by Shida and Anada.³⁾

The reaction sequences (1) and (2) are shown on the chemical potential diagram as marked by (1) and (2), respectively in Fig. 7. The reason for the different reaction sequences between (1) and (2) is ascribed to be the difference in the chemical potential; ($\mu_{\text{Ti}} - \mu_{\text{Al}}$) of Ti-36.3 at%Al sample is higher than that of Ti-42 at%Al. It is noted that the oxidation reaction path (2) is essentially the same as that of the interface reaction of TiAl/TiO₂, which is shown by (3) in Fig. 7.

4.5 On the interpretation of the reaction path

The diffusion equation in terms of chemical potential is described using the irreversible thermodynamics according to Kirkaldy and Young²⁶⁾ as follows. The flux J_i of the component i in the phase k is expressed as:

$$J_i^k = \sum_{j=1}^n L_{ij}^k (-\text{grad } \mu_j). \quad (10)$$

where μ_j is the chemical potential of component j and L_{ij} is the mobility coefficient of component i due to the chemical potential gradient of component j .

Here we apply Eq. (10) to the reaction between TiAl and Al₂O₃ as an example, and then the fluxes of Ti, Al and O atoms in TiAl(O) phase are written as:

$$J_{\text{Ti}}^{\text{TiAl(O)}} = -L_{\text{TiTi}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{Ti}}}{\partial x} - L_{\text{TiAl}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{Al}}}{\partial x} - L_{\text{TiO}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{O}}}{\partial x} \quad (11)$$

$$J_{\text{Al}}^{\text{TiAl(O)}} = -L_{\text{AlTi}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{Ti}}}{\partial x} - L_{\text{AlAl}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{Al}}}{\partial x} - L_{\text{AlO}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{O}}}{\partial x} \quad (12)$$

$$J_{\text{O}}^{\text{TiAl(O)}} = -L_{\text{OTi}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{Ti}}}{\partial x} - L_{\text{OAl}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{Al}}}{\partial x} - L_{\text{OO}}^{\text{TiAl(O)}} \frac{\partial \mu_{\text{O}}}{\partial x} \quad (13)$$

Similar equations can be also obtained for TiAl, Ti₃Al(O) and Al₂O₃ phases. If these L_{ij} values were known for these phases and proper initial and boundary conditions were given, these equations could be solved and the diffusion path for a particular interface reaction might be determined on the chemical potential diagram. However, it is not possible so far to know these constants and to determine the initial condition on the chemical potential diagram. Solubility of Ti and its distribution in Al₂O₃ and the chemical potentials and their gradients of Ti and Al in Al₂O₃, for example, are not possible to be determined quantitatively. Therefore, we try to examine these constants and to understand the diffusion path qualitatively. Generally, off diagonal terms are small as compared with diagonal terms, so that we neglect the off diagonal terms as an approximation. The

slope of the diffusion path of each phase on the chemical potential diagram shown in Fig. 5 is represented as:

$$\frac{\frac{\partial \mu_{\text{Al}}}{\partial x} - \frac{\partial \mu_{\text{Ti}}}{\partial x}}{\frac{\partial \mu_{\text{O}}}{\partial x}} = \frac{\frac{J_{\text{Al}}}{L_{\text{AlAl}}} - \frac{J_{\text{Ti}}}{L_{\text{TiTi}}}}{\frac{J_{\text{O}}}{L_{\text{OO}}}} \quad (14)$$

Generally speaking, the system is not in a steady state, so that the fluxes J_{Al} , J_{Ti} and J_{O} are considered to be dependent on the reaction period and the position of the phase. The slope of the diffusion path of each phase on the chemical potential diagram is, therefore, dependent on the reaction period and the position of the phase and the diffusion path would not be expressed by a line in general. In the present case, since the profiles of Al, Ti and O atoms shown in Figs. 1–3 were similar even when annealing periods are varied between 48 and 192 h, the reaction and diffusions can be regarded as in a steady state as an approximation. Thus the slope represented by Eq. (14) is regarded as a constant and the reaction and diffusion path is represented by the lines connected at the interface as an approximation. The curved reaction path as shown by (3) in Fig. 5 is due to the material balance in the interface reaction as discussed in the previous section.

5. Summary

Interface reactions for TiAl/Al₂O₃ and TiAl/TiO₂ have been investigated by the present study and the reaction for Ti/Al₂O₃ and the oxidation reaction of TiAl obtained from the literatures have been analyzed by the use of chemical potential diagram of Ti–Al–O system. The layer sequences for these interface reactions are summarized as follows.

(1) TiAl/Al₂O₃ at 1273 K: No essential reaction occurred.

(2) TiAl/Al₂O₃ at 1373 K; TiAl(O)/Ti₃Al(O)/Al₂O₃

(3) Ti/Al₂O₃ at 1373 K for a thick sample by Choi et al.¹⁷⁾ Ti/Ti₃Al(O)/TiAl(O)/Al₂O₃

(4) Ti/Al₂O₃ at 1373 K for a thin sample by Choi et al.¹⁷⁾ Ti₂O/Ti₃Al(O)/Al₂O₃

(5) Ti/Al₂O₃ at 1273 K by Hatakeyama et al.¹⁰⁾ Ti/Ti₃Al(O)/TiAl(O)/Al₂O₃

(6) Oxidation of Ti-42 at%Al at 1273 K by Hatakeyama et al.¹⁰⁾ TiAl/Al₂O₃/Al₂O₃ + TiO₂/TiO₂

(7) Oxidation of Ti-36.3 at%Al at 1173 K by Shida and Anada.³⁾ TiAl/Ti₃Al(O)/Al₂O₃ + TiO₂/Al₂O₃/TiO₂

These reaction paths have been reasonably elucidated by the use of chemical potential diagram of Ti–Al–O system, which was constructed using the data of Gibbs energy of formation of the compounds composed of Ti, Al and O.

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