Effect of the Third Elements on High Temperature Oxidation Resistance of TiAl₃ Intermetallic Compounds

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The brittleness of TiAl₃ is improved by the addition of third elements such as manganese, silver, chromium and so on. The effects of the third elements on oxidation resistance of TiAl₃ have been investigated in the point of view of the microstructure and products of oxidation layer. The oxidation test was carried out at 1000°C for 25 h or 30 d in air. For the copper-substituted alloy, Ti(Al, Cu)₃, the oxidation layer consisted of TiO₂, whose microstructure was porous. Thus Ti(Al, Cu)₃ showed very low oxidation resistance. While, for the manganese, silver, iron or chromium-substituted alloys, these oxidation layers consisted of only Al₂O₃. These alloys showed the oxidation resistance. It is not expected that the iron- or chromium-substituted alloys show the oxidation resistance of long duration, because oxygen atom was detected by EDS analysis in Al-depleted layer after the oxidation test for 30 d. In the oxidation test at 1000°C, the oxidation layer of the iron- or chromium-substituted alloys was constituted of only α-Al₂O₃ and θ-Al₂O₃. On the other hand, that of the manganese- or silver-substituted alloys was constituted of only α-Al₂O₃ and their oxidation layer is dense. From these results, it was understood that the substitution elements would influence on the temperature of θ → α transformation. That is, Fe and Cr would solute to θ-Al₂O₃, and then θ → α transformation temperature would increase. While, Mn and Ag would scarcely solute to θ-Al₂O₃, and then θ → α transformation temperature would be almost the same as that of pure θ-Al₂O₃. In the oxidation test at 1000°C, the residence of θ-Al₂O₃ decides oxidation resistance of Ti(Al, X)₃ materials. The choice of the substitution element promoting the transformation from θ-Al₂O₃ to α-Al₂O₃ during heating process is important for improving in the oxidation resistance.

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1. Introduction

It is expected to apply TiAl to materials used in high temperatures such as spacecraft parts, because titanium aluminide intermetallic compounds have some dominant properties which are low specific gravity, high strength at high temperatures and so on.¹⁻⁷ However, TiAl has a problem with oxidation resistance above 800°C.¹⁻⁶ On the other hand, TiAl₃ is an attractive material, for that TiAl₃ is more aluminum-rich than TiAl. Aluminum is an important element for the oxidation resistance.¹⁻³,⁵ In the case of the use as high temperature structural materials, however, there is a problem with brittleness of TiAl₃. The improvement in the brittleness of TiAl₃ has been tried by substituting the element X (X=Cr, Mn, Fe etc.) for Al. The crystal structure transforms from D0₂₂ type (I₄/mmm) to L₁₂ type (Pm₃m), and the symmetry of crystal structure becomes high.⁸ However, there are few reports on oxidation resistance of Ti(Al, X)₃.

In this paper, the influence of the third elements X on the oxidation resistance of Ti(Al, X)₃ (X=Mn, Ag, Fe, Cr, Cu) has been investigated in the point of view of the microstructure and products of the oxidation layer. Besides, stability of the oxidation layer has been discussed for the duration of the oxidation test.

2. Experimental Procedure

2.1 Preparation of the specimens Ti(Al, X)₃

Figure 1 shows the experimental procedure employed in this study. Titanium, aluminum and the third element X were melted together in an arc melt furnace to prepare intermetallic compounds Ti(Al, X)₃ (X=Mn, Ag, Fe, Cr, Cu) composed of 25 mol%Ti, 65 mol%Al and 10 mol%X. The substitution element of about 10 mol% leads Ti(Al, X)₃ into L₁₂ type crystal structure.⁹ It has been reported that the element X of about

![Experimental procedure for isothermal oxidation tests.](image-url)
10 mol% were substituted for Al site.\textsuperscript{8,9} \(\text{Ti(Al, X)3}\) single-phase specimens were prepared by annealing at 1000°C for 24 h in Ar gas atmosphere, and identified as single-phase by X-ray diffraction (XRD) using CuK\textalpha radiation at 30 kV and 15 mA.

### 2.2 Vickers hardness test

The Vickers hardness test was carried out to discuss influence of the third element on mechanical properties. The Vickers hardness test was performed with the load of 0.49 N, the load speed of 10 \(\mu\)m/s and holding time of 5 s, and repeated 10 times for one specimen.

### 2.3 High temperature oxidation tests

The specimens, whose size were 2 mm \(\times\) 2 mm \(\times\) 2 mm for the oxidation test of short duration and 10 mm \(\times\) 10 mm \(\times\) 2 mm for the oxidation test of long duration, were cut from an annealed ingot and their surfaces were polished by buffing after polishing with emery papers. The oxidation test of short duration was performed with a differential thermal analysis (TG-DTA) apparatus equipped with thermal gravimetry at 1000°C for 25 h with heating rate of 15°C·min\textsuperscript{-1}. The oxidation test of long duration was performed by using a siliconit electric furnace at 1000°C for 30 d. The weight of each specimen was measured by using an electric balance before and after oxidation test. The oxidation products were identified by XRD. The microstructure of the oxidation layer was observed with scanning electron microscopy (SEM). The element distribution in the oxidation layer was measured by energy-dispersive X-ray (EDS) analysis.

### 3. Results and Discussion

#### 3.1 Preparation of the samples

Figure 2 shows XRD patterns of Ti(Al, Fe)\textsubscript{3} before and after annealing. The sample without annealing includes the segregated phase such as Al\textsubscript{2}Fe. By annealing at 1000°C for 24 h in Ar gas atmosphere, the amount of segregated phase was decreased, and then it changed into L1\textsubscript{2} type Ti(Al, Fe)\textsubscript{3}. Similarly, other L1\textsubscript{2} type intermetallic compounds, Ti(Al, X)\textsubscript{3} were obtained by annealing at the condition. The chemical composition of the samples determined by EDS analysis is shown in Table 1. It was confirmed that the chemical compositions of the obtained samples were almost similar to the prepared compositions of Ti, Al and third element X.

#### 3.2 Vickers hardness test

The Vickers hardness of each sample is shown in Table 2. The L1\textsubscript{2} type intermetallic compounds have smaller Vickers hardness than TiAl\textsubscript{3} (Hv = 515). This result implies that the addition of the third elements leads to the improvement in brittleness. Mabuchi also has reported similar results.\textsuperscript{8} From these results, it is expected that substituting elements X for Al act effectively on the improvement in brittleness. Ti(Al, Mn)\textsubscript{3} especially shows smaller Vickers hardness by about 200 than TiAl\textsubscript{3}, and then Mn is particularly an excellent element for the improvement in brittleness.

#### 3.3 High temperature oxidation tests

##### 3.3.1 Oxidation test for short duration

The mass changes of each sample during heating are shown in Fig. 3. Axes of ordinate and abscissa show square of mass change per unit area and oxidation time including heating time, respectively. The oxidation rate constant \(K_p\) (kg\textsuperscript{2}·m\textsuperscript{-4}·s\textsuperscript{-2}) at 1000°C was determined from formula (1) owing to the behavior of isothermal oxidation follows parabolic law.

\[
\Delta M^2 = K_p \cdot t,
\]

Table 1 The composition of the samples. (at%)

<table>
<thead>
<tr>
<th>Ti</th>
<th>Al</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(Al, Mn)\textsubscript{3}</td>
<td>25.6</td>
<td>64.8</td>
</tr>
<tr>
<td>Ti(Al, Ag)\textsubscript{3}</td>
<td>23.9</td>
<td>67.6</td>
</tr>
<tr>
<td>Ti(Al, Fe)\textsubscript{3}</td>
<td>26.0</td>
<td>63.3</td>
</tr>
<tr>
<td>Ti(Al, Cr)\textsubscript{3}</td>
<td>25.4</td>
<td>65.4</td>
</tr>
<tr>
<td>Ti(Al, Cu)\textsubscript{3}</td>
<td>25.4</td>
<td>64.0</td>
</tr>
<tr>
<td>TiAl\textsubscript{3}</td>
<td>26.7</td>
<td>73.3</td>
</tr>
</tbody>
</table>

\*X shows the substitution elements (Mn, Ag, Fe, Cr, Cu)

Table 2 The Vickers hardness of the samples.

<table>
<thead>
<tr>
<th>Ti(Al, Mn)\textsubscript{3}</th>
<th>Ti(Al, Ag)\textsubscript{3}</th>
<th>Ti(Al, Fe)\textsubscript{3}</th>
<th>Ti(Al, Cr)\textsubscript{3}</th>
<th>Ti(Al, Cu)\textsubscript{3}</th>
<th>TiAl\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>319</td>
<td>339</td>
<td>324</td>
<td>327</td>
<td>450</td>
<td>515</td>
</tr>
</tbody>
</table>

Fig. 2 XRD patterns for Ti(Al, Fe)\textsubscript{3} (a) before and (b) after annealing at 1000°C for 24 h in Ar.

Fig. 3 Relationship between square of mass change per unit area and oxidation time at 1000°C.
where $\Delta M$ (kg·m$^{-2}$) is mass gain per unit area, $t$ (s) is oxidation time at 1000°C. The oxidation rate constant is shown in Fig. 4. In this figure, three lines represent Arrhenius plots for formation of $\alpha$, $\theta$, and $\gamma$-alumina in oxidation of NiAl.$^{10}$

A sample with smaller $K_P$ has more excellent oxidation resistance than that with larger $K_P$, that is, Ti(Al, Mn)$_3$ is superior to other materials in oxidation resistance, while Ti(Al, Cu)$_3$ is inferior to other materials. The oxidation rate constants of Ti(Al, Mn)$_3$ and Ti(Al, Ag)$_3$ are similar to that of formation of $\alpha$-Al$_2$O$_3$ in oxidation of NiAl.

Figure 5 shows XRD patterns of Ti(Al, Mn)$_3$ before and after isothermal oxidation test at 1000°C (a) un-oxidation, (b) for 25 h and (c) for 30 d.

For Ti(Al, Cr)$_3$, in addition to $\alpha$-Al$_2$O$_3$, $\theta$-Al$_2$O$_3$ was identified by XRD (Fig. 7(b)). $\theta$-Al$_2$O$_3$ was observed as needle-like crystals$^{11}$ in SEM observation (Fig. 6(b)). Similarly, the needle-like crystals were observed on the oxidation surfaces of Ti(Al, Fe)$_3$ and TiAl$_3$. In the case of coexistence $\alpha$-Al$_2$O$_3$ and $\theta$-Al$_2$O$_3$ in the oxidation layer, the oxidation resistance is not enough because $\theta$-Al$_2$O$_3$ would not contribute to oxidation resistance. Therefore Ti(Al, Cr)$_3$ and Ti(Al, Fe)$_3$ showed larger mass gain than Ti(Al, Mn)$_3$ and Ti(Al, Ag)$_3$.

In Ti(Al, Cu)$_3$ showing the highest oxidation rate constant, in addition to $\alpha$-Al$_2$O$_3$, TiO$_2$ (rutile) and CuO were identified by XRD (Fig. 8(b)). The oxidation layer containing TiO$_2$ and CuO did not act fully as a protected film, because the oxidation layer is porous due to the columnar crystals (TiO$_2$) (Fig. 6(c)). Consequently, the mass change is notable increment. Besides, the magnitude of diffusion coefficient of oxygen in TiO$_2$ would be assigned as the reason for remarkable mass gain. That is, the diffusion coefficient of oxygen in TiO$_2$ is $1 \times 10^{-13}$ cm$^2$·s$^{-1}$ at 1000°C, while that of $\alpha$-Al$_2$O$_3$ is $1 \times 10^{-17}$ cm$^2$·s$^{-1}$ at 1000°C.$^{12}$ From above results, the oxygen atom would be fed through TiO$_2$ into Ti(Al, Cu)$_3$, and then Ti(Al, Cu)$_3$ exhibits low oxidation resistance.

### 3.3.2 Oxidation test for long duration

The mass change for samples oxidized for 30 days at 1000°C is shown in Table 3. The order of mass gain in this test is the same as that of the short duration, and Ti(Al, Mn)$_3$ and Ti(Al, Ag)$_3$ are superior to other materials, while Ti(Al, Cu)$_3$ is inferior to other materials in oxidation resistance.

After the oxidation of Ti(Al, Mn)$_3$, only $\alpha$-Al$_2$O$_3$ is confirmed from XRD (Fig. 5(c)). Besides, the microstructure of oxidation layer is dense and similar to that formed on Ti(Al, Mn)$_3$ after the oxidation test for short duration (Fig. 9(a)). Similarly, $\alpha$-Al$_2$O$_3$ was formed and the dense microstructure was observed in the oxidation layer after the oxidation for long duration for Ti(Al, Ag)$_3$. These results indicate that $\alpha$-Al$_2$O$_3$ is a stable protecting film for a long time.

For Ti(Al, Cr)$_3$, it was found from XRD and SEM that a metastable phase, $\theta$-Al$_2$O$_3$, remained after oxidation test for 30 d (Figs. 7(c), 9(b)). Similarly, $\theta$-Al$_2$O$_3$ remained after oxidation test for long duration for Ti(Al, Fe)$_3$ and TiAl$_3$. Oxygen was detected in Al-depleted layer between the oxidation layer and the matrix by means of EDS analysis of the cross section of these samples (Fig. 10). In Ti(Al, Mn)$_3$ and Ti(Al, Ag)$_3$ with high oxidation resistance, this Al-depleted layer was also observed. However, no oxygen is in the Al-depleted layer in these two compounds (Table 4). These results indicate that oxygen atoms pass through the oxidation films formed on Ti(Al, Cr)$_3$, Ti(Al, Fe)$_3$, and TiAl$_3$ because of the formation of $\theta$-Al$_2$O$_3$. Therefore Ti(Al, Cr)$_3$, Ti(Al, Fe)$_3$
and TiAl₃ is unsuitable for using for long period due to the character of these oxidation films.

The mass change of Ti(Al, Cu)₃ after oxidation for 30 d is forty times as much as that of Ti(Al, Mn)₃. It is clear that oxidation resistance of Ti(Al, Cu)₃ is very low.

### 3.3.3 Oxidation resistance and microstructure of oxidation layer

From above results, the third elements can be classified into three groups; (1) Mn, Ag with high oxidation resistance, (2) Cr, Fe with inexpectant oxidation resistance for long periods and (3) Cu without oxidation resistance. Schematic illustration of microstructure of oxidation layer for each group is shown in Fig. 11.

For group (1), the oxidation product was only α-Al₂O₃. On
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Fig. 10 SEM micrograph (a) and EDS analysis (b) of cross section of Ti(Al, Cr)₃ heated at 1000°C for 30 d.

Fig. 11 Schematic illustration of microstructure of the oxidation layer.

Fig. 12 Schematic illustration for crystal structure of θ-Al₂O₃.

Fig. 13 SEM micrographs of surface of (a) Ti(Al, Mn)₃ and (b) Ti(Al, Cr)₃ heated at 800°C for 5 h.

the other hand, for group (2), the oxidation products were α-Al₂O₃ and θ-Al₂O₃. From this fact, it is thought that θ-Al₂O₃ affect the oxidation resistance. The diffusion of oxygen in θ-Al₂O₃ would be easily than that of α-Al₂O₃, because there is continuous space along b-axis in θ-Al₂O₃ crystal (Fig. 12). Therefore the formation of θ-Al₂O₃ degrade the oxidation resistance. For group (3), TiO₂ and CuO constitute the oxidation layer. Oxygen atom is permeable to this oxidation layer due to its porosity. As mentioned above, it is clear that the microstructure of oxidation layer is affected by the kind of substituted element.

Next, behavior of formation of Al₂O₃ in heating process is discussed. Ti(Al, Mn)₃ in group (1) and Ti(Al, Cr)₃ in group (2) were heated at 800°C for 5 h to confirm products. For both samples, needle-like crystal, which is automorphic of θ-Al₂O₃, was observed (Fig. 13), and then θ-Al₂O₃ would form in the heating process. From the results described above and in term 3.3.1, it is understood that for Ti(Al, Mn)₃ the transformation from θ-phase to α-phase was completed until 1000°C. On the other hand, for Ti(Al, Cr)₃ the transformation from the θ-phase to the α-phase is not completed (Fig. 7(b)). This difference would be related to the solubility of third element to θ-Al₂O₃. Namely, Mn is not soluble into θ-Al₂O₃, and then θ- to α-Al₂O₃ phase transformation is not restrained until 1000°C. Since the transformation temperature from the θ-phase to the α-phase increases due to the solution of Cr into θ-Al₂O₃, the transformation is restrained until 1000°C in the case of Ti(Al, Cr)₃. Yoldas[14] has reported that γ- to α-Al₂O₃ phase transformation temperature increased due to soluble silica. Rossignol et al.[15] have reported that θ to α phase transformation of θ-Al₂O₃ doped with Ce, Ba and so on shifted to high temperature. Considering these reports, it is thought
that the solution of Cr to $\theta$-$\text{Al}_2\text{O}_3$ give rise to increment of temperature for $\theta$- to $\alpha$-phase transformation.

From above results, the solution of the element to $\theta$-$\text{Al}_2\text{O}_3$ formed in heating process would affect the formation of $\alpha$-$\text{Al}_2\text{O}_3$, which is most important in oxidation resistance. When a third-element is chosen for improvement in brittleness, it must be attended to the solubility of the chosen element to $\theta$-$\text{Al}_2\text{O}_3$.

4. Conclusions

The effect of the third elements X (Mn, Ag, Fe, Cr, Cu) on oxidation resistance was discussed in the point of view of microstructure of oxidation layer. The results are summarized as follow:

1. Ti(Al, Cu)$_3$ showed remarkable mass gain during the oxidation test at 1000°C for 25 h. Its oxidation resistance was very low due to production of TiO$_2$ (rutile), which has high oxygen permeability.

2. In the oxidation test at 1000°C for 30 days, Ti(Al, Mn)$_3$ and Ti(Al, Ag)$_3$ showed excellent oxidation resistance. On the other hand, Ti(Al, Fe)$_3$ and Ti(Al, Cr)$_3$ did not show enough oxidation resistance due to the presence of oxygen in Al-depleted layer between oxidation layer and matrix. This result indicates that the use of these materials is unsuitable for long period.

3. The solubility of the third elements to $\theta$-$\text{Al}_2\text{O}_3$, which formed in heating process and decreased oxidation resistance, would inhibit from $\theta$- to $\alpha$-phase transformation. When a third element is chosen for improvement in brittleness, it must be attended to the solubility of the chosen element to $\theta$-$\text{Al}_2\text{O}_3$.

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REFERENCES