Effect of Nb on the high temperature oxidation of Ti–(0–50 at.%)Al

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Abstract

The oxidation behavior of Ti–Nb, Ti3Al–Nb and TiAl–Nb (Nb: 0–30 at.%) has been investigated at 1173 K in air. When Nb is in solid solution with TiO2, the addition of Nb can improve the oxidation resistance of the alloys by impeding mass transfer in TiO2. However, Nb decreases the oxidation resistance when the amount of Nb is too high and forms TiNb2O7 or AlNbO4 phases in the scale. © 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Effect of Nb; Ti–Al alloys; Oxidation; Kinetics; Morphology

1. Introduction

The two intermetallic compounds α2-Ti3Al and γ-TiAl are the most attractive heat-resisting light materials in the area of astronautics and aeronautics [1–3]. However, their temperature limit for high temperature oxidation is lower than that for high temperature mechanical properties in these two intermetallic compounds, and this has become an important obstacle for the application of these materials [4,5].

It was shown that alloying can effectively improve the oxidation resistance of Ti3Al and TiAl, e.g., by addition of Nb [6–13], Cr [14], W [15], Mo [16], and Si [17]. Among these elements, Nb not only significantly improves the oxidation resistance of the materials, but also their creep resistance and room temperature toughness [18–20]. The effect of Nb on the oxidation behavior can be summarized: (1) Nb ions replace Ti ions, i.e., TiO2 is doped by Nb, leading to a decrease in oxygen vacancies, which slows diffusion of oxygen [7]. (2) Nb increases the thermodynamic activity of Al relative to that of Ti, which favors the formation of a stable alumina scale [8,9]. (3) Nb lowers the solubility of oxygen in the alloy, thus restraining the internal oxidation of the alloy [10]. (4) Nb promotes the formation of TiN at the MO/M interface, which impedes the diffusion of titanium and oxygen ions [11,12].

To appraise the effect of Nb on the oxidation behavior of Ti–Al alloys at elevated temperatures, three series of alloys were selected, i.e., Ti–Nb,
Ti₃Al–Nb (Ti:Al = 3:1) and TiAl–Nb (Ti:Al = 1:1), each of them with additions of Nb from 0 to 30 at.%. The effect of Nb on the oxidation of the Ti–Al system was studied from the dependence of the parabolic oxidation rate constant $K_p$, the oxidation products and the distribution of the elements on the cross-section of the oxidized specimens on the Nb content.

### 2. Experimental methods

High purity Ti, Al and Nb (O < 1540 ppm) powders were used to prepare the specimens. The powders were mixed thoroughly according to predetermined proportions, as shown in Table 1. After consolidation by cold pressing, the specimens were hung in a high frequency induction furnace and soaked at 923 K for 0.5 h in vacuum for alloying by diffusion. Then high purity argon was let into the heating chamber. Finally, the specimens were heated to melting. The melt drops fell freely into a copper container and were rapidly cooled and solidified. The chemical compositions of the resultant alloy were controlled within plus or minus 0.2 at.%

The specimens for oxidation tests were cut into a size of $10 \times 5 \times 1$ mm$^3$. The surfaces of the specimens were ground to 1500# SiC paper, and then degreased in acetone prior to oxidation test.

The oxidation tests were conducted using a thermal gravimetric balance (model MTC-1000S). The specimens were exposed to 1173 K in dry air at a flow rate of 100 ml/min for 24 h. After oxidation tests, the phases formed in the scales were identified by XRD. The morphology of the scale and the distribution of the elements were examined by SEM and EPMA, respectively.

<table>
<thead>
<tr>
<th>Base alloy</th>
<th>Nb (at.%)</th>
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<tbody>
<tr>
<td>Ti</td>
<td>0 5 10 15 20</td>
</tr>
<tr>
<td>Ti₃Al</td>
<td>0 5 10 15 20 30</td>
</tr>
<tr>
<td>(Ti:Al = 3:1)</td>
<td></td>
</tr>
<tr>
<td>TiAl</td>
<td>0 5 10 15 20 30</td>
</tr>
<tr>
<td>(Ti:Al = 1:1)</td>
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</tbody>
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### 3. Results

Fig. 1 shows the variations of parabolic oxidation rate constant ($K_p$) with Nb content ($C_{Nb}$) in the three series of alloys. Since the instantaneous oxidation rate constants of the Nb-containing alloys showed a minor decrease with oxidation time, $K_p$ values used in Fig. 1 are average values. The $K_p$ values of all the three series of alloys first decrease with the increase of $C_{Nb}$ up to a minimum value which is connected by a dotted line in Fig. 1. Beyond the minimum value, $K_p$ values increase with the increase of $C_{Nb}$, resulting in a concave upward characteristic curve. The minimum $K_p$ for the Ti–Nb alloys occurs at about 10 at.% (when $C_{Nb} > 20$ at.%, the oxidation kinetics become linear and are not shown in Fig. 1), and for the Ti₃Al–Nb and TiAl–Nb alloys at around 15 and 20 at.%, respectively.

Fig. 2 shows the relationship between $K_p$ and the Al content ($C_{Al}$) in the three series of alloys for Nb contents $\leq 15$ at.%. It can be seen that $K_p$ decreases with an increase in Al content for all the alloys. The variations of log $K_p$ with $C_{Al}$ in the Ti–Al–Nb ternary alloys seem similar to that in the Ti–Al binary alloys from Fig. 2, but the slope of the curves for the ternary alloys is smaller than that for the binary alloys.

The XRD patterns obtained from the high temperature oxidized specimen surfaces are given in Fig. 3. It demonstrates that in the Ti–Nb alloys, when $C_{Nb} \leq 10$ at.%, the oxide phase is TiO₂. Its
morphology is shown in Fig. 4(a). When $C_{Nb} \geq 15$ at.%, the scale is composed of TiO$_2$ and TiNb$_2$O$_7$. As shown in Fig. 4(d), the dark gray phase is TiO$_2$ and the white bright constituent is TiNb$_2$O$_7$. In the Ti$_3$Al–Nb alloys, when $C_{Nb} \leq 15$ at.%, the products of oxidation are TiO$_2$ and Al$_2$O$_3$, the structural feature of which is shown in Fig. 4(b); and when $C_{Nb} \geq 20$ at.%, the oxides are TiO$_2$ and Al$_2$O$_3$ and AlNbO$_4$, the microstructure of which is shown in Fig. 4(e). For the TiAl–Nb alloys, when $C_{Nb} \leq 20$ at.%, the scale consists of TiO$_2$ and Al$_2$O$_3$; and when $C_{Nb} = 30$ at.%, the oxides formed are TiO$_2$ and Al$_2$O$_3$ and AlNbO$_4$. The morphologies of oxides in TiAl–Nb with $C_{Nb} = 20$ at.% and $C_{Nb} = 30$ at.% are shown in Fig. 4(c) and (f), respectively.

When $C_{Nb}$ are smaller than the Nb content at minimum $K_p$ in Fig. 3, a typical distribution of the elements along the cross-section of the scale in the Ti$_3$Al–10Nb alloy is given in Fig. 5. There are two peaks of Al which are in the outer layer of the scale and in the substrate near the scale/substrate interface, respectively. A peak of Nb exists in the substrate near scale/substrate interface, too.

4. Discussion

The concave upward characteristic of the log $K_p$ vs $C_{Nb}$ curves shown in Fig. 1 is probably related to the effect of the existing form of Nb in the scale. When Nb is in solid solution with TiO$_2$, it lowers $K_p$. However, when it forms an additional oxide phase, Nb increases $K_p$. Furthermore, different

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Fig. 3. XRD patterns obtained from the surface of the three series of alloys after oxidizing in air at 1173 K for 24 h: (a) Ti–Nb alloys, (b) Ti$_3$Al–Nb alloys and (c) TiAl–Nb alloys.
concentrations of Nb in the solid solution also affects the extent of its effect, i.e., with the increase of \( C_{\text{Nb}} \), its effect weakens. When the Nb content in TiO\(_2\) saturates, the minimum \( K_p \) appears in the log \( K_p \) vs \( C_{\text{Nb}} \) curve.

In the Ti–Al binary alloys, the effect of Al on oxidation is manifested by Al\(_2\)O\(_3\) as blocks to mass transfer in the scale [21]. The log \( L_p \) decreases with the increase of \( C_{\text{Al}} \), and the slope of log \( K_p \) vs \( C_{\text{Al}} \) curve is controlled by the structure of the scales [5]. From Fig. 2, in the Ti–Al–Nb alloys with different Nb contents, the characteristic of log \( K_p \) vs \( C_{\text{Al}} \) curve seems to be similar to that in the Ti–Al binary alloys. However, the slope of the curves in the ternary alloys is smaller than that in the binary alloys (Fig. 2). This means there is interaction of Al content with Nb addition. The addition of Nb seems decreasing the effect of Al on oxidation rate constant.

Comparing the slope of log \( K_p \) vs \( C_{\text{Nb}} \) curve in the Ti–Nb alloys (Fig. 1) with that of log \( K_p \) vs \( C_{\text{Al}} \) curve in the Ti–Al binary alloys (Fig. 2), it can be seen that the effect of Nb on the oxidation of Ti–Nb alloys is greater than that of Al in the Ti–Al alloys with a same at.%. This implies that the impeding effect of Nb on the mass transfer in the scale is greater than that of the blocking effect of Al\(_2\)O\(_3\).

In the Ti–Al–Nb ternary alloys, \( K_p \) is influenced by the blocking effect of Al\(_2\)O\(_3\) and the impeding...
effect of Nb on the mass transfer simultaneously. The effect of Nb in the Ti–Nb binary alloys is greater than in the Ti–Al–Nb ternary alloys (see the different slopes in Fig. 1), as the effect of Al in the Ti–Al binary alloys is greater than in the Ti–Al–Nb ternary alloys. This indicates that when Nb and Al coexist, each of them can reduce the effect of the other on oxidation.

Generally, in the Ti–Al binary alloys, the ratio Ti/Al in the scale is very close to that in the substrate alloy, and no enrichment of Al could be detected on the substrate side near the scale/substrate interface [21]. On the contrary, impoverishment of Al has been observed [4,22]. In the examination on the cross-section of the oxidized specimens, enrichment of Nb was not found in the Ti–Nb alloys, but in the Ti–Al–Nb alloys, enrichment of both Nb and Al on the substrate side near the scale/substrate interface were observed (Fig. 5). This phenomenon may be related to the interaction of Nb and Al in the scale. Nb in solid solution with TiO₂ not only inhibits the diffusion of Ti and oxygen ions, but also that of Al ions. Similarly, Al₂O₃ in the scale impedes the diffusion of Ti and oxygen ions as well as Nb ions. This mechanism is proposed to explain the phenomena that the Nb content at minimum \( K_p \) increases with the Al content, and that Al and Nb have a mutual reducing effect on the oxidation kinetics.

5. Conclusions

By examination of uninterrupted oxidation of three series of alloys Ti–Nb, Ti₃Al–Nb and TiAl–Nb with Nb up to 30 at.\% at 1173 K in dry air for 24 h, it is concluded that:

1. Nb in solid solution in the scale can improve the oxidation resistance of the alloys; but if it forms an additional oxide phase (TiNb₂O₇ or AlNbO₄), it decreases the oxidation resistance.
2. The effect of Nb on the oxidation of the Ti–Al alloys is mainly manifested by impeding mass transfer in TiO₂.

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