Original Research

ω₀ phase precipitation in annealed high Nb containing TiAl alloys

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Abstract

The ordered ω phases in high Nb containing TiAl (Nb-TiAl) alloys have been garnering increasing attention in the recent years. However, the investigations on the Nb dependence on the ω₀ precipitation are scarce. In this study, the effect of Nb content on the ω₀ precipitation in high Nb (6–10 at%) containing TiAl alloys after long-time annealing at 850 °C has been studied. The results show that small ordered ω particles in the retained β₂ phase cannot be discerned under scanning electron microscope (SEM) but can be observed using transmission electron microscopy (TEM). Although the Nb segregation can be eliminated after the homogenization heat treatment, the ω₀ phase precipitated in all the alloys studied after annealing at 850 °C. TEM examination reveals that the orientation relationship between the ω₀ and α₂ phases can be derived as: [0001]ω₀/[1120]α₂; (1120)ω₀//(0001)α₂, which indicates that the ω₀ phase is directly transformed from the parent α₂ phase. Small γ particles are also observed within the ω₀ areas. The α₂→ω₀+γ decomposition process is expected during annealing. It is concluded that ω₀ phase is an equilibrium phase in high Nb-TiAl alloys at 850 °C.

Keywords: TiAl alloys; Phase transformation; Ordered omega phase; TEM; Annealing

1. Introduction

Recently, high Nb-TiAl alloys have drawn increasing attention because of their high temperature strength, improved creep properties and good oxidation resistance compared to conventional TiAl alloys [1–3]. Many investigations have been carried out on the microstructure evolution as well as composition control of the alloys, which are important in optimizing their mechanical properties. However, the β₂ phase, which is induced by Nb segregation, is considered detrimental to the room temperature ductility [4,5]. Moreover, ω₀ phase always precipitates within the parent β₂ phase, which is difficult to be eliminated according to recent studies [6–8]. Commonly, the designation ω is restricted to the disordered ω phase (space group P6/mmm) in alloys. Phases with a similar crystal structure but with two or more differently occupied atom sites in intermetallic alloys are designated as ω-related phases or ordered ω phases. These are the trigonal ω′ and ω″ phases as well as the hexagonal ω₀ with B8₂ structure. Because the diffusion less β₂→ω′ transformation yields a structure with four distinct Wyckoff sites but only two distinct occupancies directly inherits the β₂(B2) chemical order and the ω′ phase is inherently unstable, thus the ω₀ and ω″ phases are commonly observed in the as-cast microstructures [9]. Earlier, Bendersky et al. systematically revealed the ordered ω evolution in Ti-37.5Al-12.5Nb alloy (all the compositions in the present study are given in at%) during cooling [9]. They also found that the ω₀ phase with B8₂ structure is an equilibrium phase after long-time annealing at 700 °C. Bystrzanowski et al. reported that the ω₀ phase was observed after long-time creep tests conducted on Ti-46Al-9Nb sheets [10]. Moreover, Yu et al. also reported the ω₀ phase precipitation within the β₂ phase in Ti-40Al-10Nb alloy during heat treatment below 850 °C [11]. In a word, previous publications generally consider that the ω₀ phase is transformed from the β₂ phase without direct relation with other phases. However, recent works of Huang et al. indicated that the β₂(ω′) phase (a mixture of β₂ phase and ordered ω phases) was found within the α₂+γ...
lamellar colonies due to the $\alpha_2 \rightarrow \beta_o(\omega)$ decomposition [12–15]. Therefore, it is necessary to study the $\omega_o$ phase precipitation at intermediate temperatures for the better understanding of the phase equilibrium at these temperatures. The present paper focuses on the $\omega_o$ phase precipitation in the fully-lamellar microstructures in Ti-45Al-(6–10)Nb alloys during annealing at 850 °C.

2. Experiments

Alloys buttons with nominal compositions of Ti-45Al-(6–10)Nb were prepared by vacuum arc melting under argon atmosphere. The ingots were remelted four times to ensure the homogeneity and buttons in sizes of $\Phi 35 \times 15$-mm were obtained. Samples with dimensions of $\Phi 8 \times 6$-mm were cut from the as-cast ingot and encapsulated in quartz tubes prior to heat treatments. The homogenization treatment was conducted at 1400 °C for 5 h followed by furnace-cooled to 1000 °C and then air-cooled to room temperature. After the homogenization treatment, the samples were heat treated in a pre-heated furnace at 850 °C for 500 h and then water quenched to room temperature. The microstructure examinations were conducted for the as-cast, homogenized and annealed specimens using a Zeiss Supra 55 scanning electron microscope in the back-scattering electron (BSE) mode. Image analysis was conducted using the SEM-BSE images to determine the volume fraction of the $\omega_o$ precipitation in the annealed samples. Specifically, the as-cast and annealed specimens of Ti-45Al-9Nb alloy were examined using a Tecnai G2 F30 field-emission transmission electron microscope operated at 300 kV. TEM thin foils were prepared by standard twin-jet electropolishing in a solution of 30 ml perchloric acid, 175 ml butan-l-ol, and 300 ml methanol at 30 V and −30 °C.

![Fig. 1. SEM-BSE images of the as-cast microstructures of (a) Ti-45Al-6Nb, (b) Ti-45Al-7Nb, (c) Ti-45Al-8Nb, (d) Ti-45Al-9Nb, and (e) Ti-45Al-10Nb.](image-url)
3. Results and discussion

3.1. The as-cast microstructure of Ti-45Al-(6–10)Nb alloys

Fig. 1 shows the SEM-BSE images of the as-cast microstructures of Ti-45Al-(6–10)Nb alloys. Generally, nearly fully-lamellar microstructures were obtained in the as-cast ingots and the extent of Nb micro-segregation increased with the increase of Nb addition. Because of the fast cooling rate of the ingots, the β-segregation is inevitable during the β → α phase transformation process, which distributes both inside and at the boundaries of the colonies [2,4]. The bright contrast with high concentration of Nb elements was once identified as the retained β₀(B2) phase, because the magnified SEM images indicated that no other contrasts could be distinguished in the bright contrast areas [4–6]. However, TEM observation reveals that the bright contrast areas in the as-cast ingots are actually a mixture of ordered ω phases and β₀ matrix, as shown in Fig. 2.

The β₀(ω) phase is observed in a blurry morphology consisting of numerous nanoscale ordered ω particles within a lamellar colony. Considering the small sizes of the button ingots, the cooling rate of the ingot after melting is relatively faster than those in the larger ingots reported in our previous works [6–8]. Since the growth of the ordered ω particles is diffusion controlled [8,16], the sizes of the ordered ω particles are limited to a small scale due to the limited duration at high temperatures. Moreover, it is difficult to identify the exact structures of the ordered ω particles due to its small sizes and overlapping effects. However, the co-existence of α² and α₀ phases in the blurry areas is expected because of the different solvs of the two phases, i.e. the α₀ phase formed at a higher temperature while the α² formed at a lower temperature. At higher temperature range, the growth rate of α₀ is relatively fast and the growth can proceed to a certain extent, forming larger particles in tens of nanometers. As the temperature of the ingot decreases further below the ω/α² solvs, the α² embryos may form in the retained β₀. However, since the diffusion rate is lower, the sizes of the newly formed α² particles are restricted to a much smaller level. As a result, it is difficult to clearly distinguish the ω/α² and α₀ phases, thus forming the blurry β₀(ω) areas observed at room temperature [8,17,18]. Furthermore, some γ grains can be observed in the vicinity of the β₀(ω) phase. The selected area diffraction pattern (SADP) of the circled area indicated in Fig. 2(a) is shown and indexed in Fig. 2(b). It can be deduced that there exists an orientation relationship between the β₀(ω) areas and lamellar structure, which can be derived as:

\[
[111]β₀/\langle0001\rangleω/\langle101\rangleγ/\langle11\overline{2}0\rangleα₂; (1\overline{1}0)β₀/\langle1\overline{1}\overline{2}0\rangleω/\langle1\overline{1}0\rangleγ/\langle0001\rangleα₂
\]

This orientation relationship indicates that both the β₀(ω) and α₂+γ lamellar structure are resulted from a single primary β dendrite. The phase transformation path of this area can be concluded as β → β + α → β + α₂ + γ → β₀(ω) + α₂ + γ, which corresponds to the 10Nb quasi-phase diagram reported in the literature [19], wherein a three phase region β₀ + α₂ + γ can be found at lower temperatures.

3.2. α₀ precipitation in the annealed samples

After the homogenization heat treatment, the fully-lamellar microstructures were obtained in all the samples and the Nb micro-segregation was completely eliminated, i.e. no β₀(ω) phase was found in the homogenized samples. Typically, the SEM image of Ti-45Al-10Nb alloy is shown in Fig. 3, whose micro-segregation was the most severe in the as-cast state. The bright contrast Nb-segregation areas in the as-cast ingot are eliminated after the heat treatment. However, after long-time annealing at 850 °C for 500 h, the α₀ precipitation can be observed in all the alloys studied. Fig. 4 shows the SEM images of Ti-45Al-(6, 8, 10)Nb alloys after the annealing treatment. Although the major constitute in these alloys are still the lamellar colonies made up of α₂ and γ laths, a considerable amount of Nb-rich areas in a bright banded contrast emerged both inside and around lamellar colonies.
These phases are proved to be large $\omega_o$ grains under TEM observation. Fig. 5(a and b) show the TEM images of the $\omega_o$ grains in Ti-45Al-9Nb alloy after annealing. According to the symmetry of the B8$_2$ structure, the odd (000$l$) inflections should be absent in the SADP of the $\omega_o$ grains (under [1120] $\omega_o$ zone axis) [9,15]. As shown in the insert of Fig. 5(a), the odd (000$l$) inflections diminished in the SADP of ordered $\omega$ grains, suggesting the definite identification of the $\omega_o$ phase. Large $\omega_o$ grains are in connection with the lamellar colonies at the lamellar boundaries, and the size of the $\omega_o$ grain observed in Fig. 5(a) is more than 5 $\mu$m, which is rarely reported in the previous studies [11,20,21]. It seems that the whole white contrast area observed in the SEM images can be a single $\omega_o$ grain. Thus the phases in Nb-segregation areas in these microstructures should be treated as single $\omega_o$ phase. Some $\omega_o$ grains can also be observed within the $\alpha_2$ phase. Fig. 5(b) shows one example of this kind of $\omega_o$ precipitation. Three $\omega_o$ grains, in the same orientation relationship with the $\alpha_2$ phase, precipitated at different locations; therefore it seems that the $\omega_o$ grains grow up by consuming the $\alpha_2$ matrix. This can be verified by the SADP, as shown in the insert of Fig. 5(b), which can be deduced as:

$$[0001]_{\omega_0} // [11\overline{2}0]_{\alpha_2}, (11\overline{2}0)_{\omega_0} // (0001)_{\alpha_2}$$

Similar orientation relationship between disordered $\alpha$ and $\omega$ phases is frequently reported in the previous studies in titanium alloys [22–24]. In the present study, three $\omega_o$ variants may precipitate within a single $\alpha_2$ grain with their $c$ axes parallel with one of the three [1120] $\alpha_2$ directions. Moreover, the lattice parameters of these two phases are also closely related to the orientation relationship mentioned above, i.e. the values of the interatomic spacing in the [1120] $\alpha_2$ and [0001] $\omega_o$, directions are 0.289 nm and 0.278 nm, and the values of the interplanar spacing of (0002) $\alpha_2$ and (1120) $\omega_o$ are 0.230 nm and 0.229 nm.

That is a 4.0% misfit in the interatomic spacing and a 0.4% mismatch in the interplanar spacing. According to the atomic matching theory proposed by Zhang et al., these are effectively small misfit values so the observed orientation relationship can be probably of low energy [25,26]. Bystrzanowski et al. found that under certain conditions, the direct $\alpha_2 \rightarrow \omega_o$ phase transformation was expected. They claimed that the phase transformation path $\alpha_2 \rightarrow \beta_o \rightarrow \omega_o$ is unlikely from the thermodynamic point of view, since the free energy curve for the $\alpha_2$ phase lies below that of the $\beta_o$ phase [10]. Thus, the $\alpha_2 \rightarrow \beta_o$
transformation would lead to an increase in free energy of the system. In the light of these results, the direct $\alpha_2 \rightarrow \omega_0$ transformation is favored for the interpretation of the obtained experimental observations. Therefore, the orientation relationship between $\omega_0$ and $\alpha_2$ phases observed is reasonable. It should be noted that during the $\beta_0 \rightarrow \omega_0$ phase transformation, four variants of $\omega_0$ phase with different orientations can be produced; thus it is inferred that the different variants of $\omega_0$ phase in the $\alpha_2 \rightarrow \omega_0$ phase transformation can form simultaneously according to their orientation relationship [22–24], which needs to be further confirmed.

The volume fractions of the $\omega_0$ phase increase with the increase of Nb addition, which are summarized in Table 1. Particularly, in the Ti-45Al-10Nb alloy, the mean size and volume fraction of the $\omega_0$ areas increases up to nearly 10 $\mu$m and as large as 8.5%, respectively. The magnified images of the $\omega_0$ phase in each sample are shown in the inserts of Fig. 4. Furthermore, some particles in dark contrast can be observed embedded in the $\omega_0$ phases in all the five alloys. According to the results from Schloffer et al., these particles are newly formed $\gamma$ grains during annealing [21]. These $\gamma$ grains should be results of the $\alpha_2 \rightarrow \omega_0$ transformation. Due to the enrichment of Nb in the $\omega_0$ phase, the surrounding $\alpha_2$ phase can be depleted in Nb and rich in Al. As the $\alpha_2 \rightarrow \omega_0$ transformation proceeds, the composition of the area between the $\omega_0$ particles can be more close to that of $\gamma$ phase, leading to the formation of small $\gamma$ grains between the $\omega_0$ particles, thus forming the particles in dark contrast within the $\omega_0$ phase areas. The TEM image of the precipitated $\gamma$ grains is shown in Fig. 5(c). The SADP of the circled area is shown in the insert. The orientation relationship between $\omega_0$ and $\gamma$ phases can be indexed as: [0001]$_{\omega_0}$// [101]$_{\gamma}$; (112)$_{\omega_0}$//(111)$_{\gamma}$. Thus, the $\alpha_2 \rightarrow \omega_0 + \gamma$ decomposition process can be concluded during annealing. It is inferred that although a homogenization treatment was conducted before the annealing treatment, the $\omega_0$ phase precipitates during annealing, and thus it is an equilibrium phase at
Table 1
The volume fraction of \( \omega \) phase in Ti-45Al-(6–10)Nb alloys after annealed at 850 °C for 500 h.

<table>
<thead>
<tr>
<th>Nb contents</th>
<th>6Nb</th>
<th>7Nb</th>
<th>8Nb</th>
<th>9Nb</th>
<th>10Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume fraction (%)</td>
<td>1.0 ± 0.1</td>
<td>3.6 ± 0.2</td>
<td>6.9 ± 0.5</td>
<td>7.0 ± 0.5</td>
<td>8.4 ± 0.6</td>
</tr>
</tbody>
</table>

this temperature. The nucleation sites of the \( \omega \) phase can be at the \( \alpha_2/h \) interfaces, as observed in Fig. 5(b). The higher Nb content lowers the composition barrier of \( \omega \) phase precipitation, leading to the increase of volume fraction of \( \omega \) phase in alloys with higher Nb addition.

4. Conclusion
In this study, the \( \omega \) precipitation and the related phase transformation mechanisms in annealed Ti-45Al-(6–10)Nb alloys are studied. The main conclusions can be drawn as follows:

1. The retained \( \beta \) areas in cast high Nb-TiAl alloys contain numerous \( \omega \)-related particles. The \( \beta \langle \omega \rangle \) phase follows an orientation relationship with the surrounding lamellar structure:

\[
[11\overline{2}]\beta_0/\langle 0001\rangle_{\omega}/[101]\gamma/\langle 11\overline{2}\overline{0}\rangle_{\alpha_2}; (1\overline{1}0)\beta_0/\langle 11\overline{2}\overline{0}\rangle_{\omega}/\langle 11\overline{1}\rangle_{\gamma}/\langle 0001\rangle_{\alpha_2}.
\]

After a homogenization treatment, the \( \beta \langle \omega \rangle \) phase can be eliminated completely.

2. After annealing at 850 °C for 500 h, \( \omega \) phase precipitates within the samples. With the increase of Nb addition, the volume fraction and average size of \( \omega \) phase increase accordingly. TEM experiments show that the size of the \( \alpha_2 \) phase can be as large as 10\( \mu \)m.

3. TEM observation reveals that in the annealed samples, there is an orientation relationship between the \( \omega \) and \( \alpha_2 \) phases:

\[
[0001]_{\omega}/\langle 11\overline{2}\overline{0}\rangle_{\alpha_2}, (1\overline{1}2\overline{0})_{\omega}/\langle 0001\rangle_{\alpha_2}, \]

which indicates that the \( \omega \) phase can directly precipitated within the parent \( \alpha_2 \) phase. Moreover, small \( \gamma \) grains are transformed from the \( \alpha_2 \) phase and the decomposition process of \( \alpha_2 \) phase can be concluded as \( \alpha_2 \rightarrow \omega + \gamma \). The \( \omega \) phase is an equilibrium phase in high Nb-TiAl alloys at 850 °C.

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