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Precipitation of β particles in a fully lamellar Ti-47Al-2Nb-1Mn-0.5W-0.5Mo-0.2Si (at.%) alloy

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The precipitation of β (B2) particles at intermediate temperatures, between 760°C and 1050°C, is investigated in a fully lamellar TiAl-WMoSi alloy. The β particles, having a thin-plate shape, usually precipitate on the α_2 side of α_2/γ interfaces at low aging temperatures in an uneven two-dimensional growth mode. While those formed at higher aging temperatures, growing extensively within the α_2 plate and into the adjacent γ lamellae, have an ellipsoid shape. The growth of β particles at low aging temperatures yields an activation energy of about 366 kJ/mol. It is suggested that at low aging temperatures the growth of β particles proceeds via an $\alpha_2 \rightarrow \beta$ precipitation process controlled by diffusion of W and Mo along the β/α_2 and β/γ interfaces.

1. Introduction

The B2 structure can be obtained in near γ-TiAl alloys with addition of β stabilizing elements such as Cr [1], Nb [2], W [3, 4] and Mo [5, 6], and this structure can exist with a cuboidal morphology [1, 2] or as fine precipitates [3, 4]. It was believed that cuboidal B2 phase along grain boundaries is detrimental to the creep resistance [7, 8], whereas the β (B2) precipitation was expected to enhance creep resistance [9]. A recent report revealed a positive effect of β precipitation on creep resistance in a Ti-Al-W alloy [10]. A few reports regarding precipitation of β phase at intermediate temperatures in near γ-TiAl alloys were presented [4, 10, 11], but the precipitation process remains unclear, although it was suggested that a ternary $\alpha_2 + \gamma + \beta$ phase region exists in the intermediate temperature range in the Ti-Al-Nb [12], Ti-Al-NbZrSi [13] and Ti-Al-WMoSi [11] systems.

Many chemical reactions are temperature dependent and the rate of these reactions as a function of temperature can be expressed by the Arrhenius equation: Rate of reaction $= Ce^{-Q/RT}$, where Q is the activation energy for the reaction and C is a constant. The isothermal formation of β phase in TiAl alloys may be considered to obey Arrhenius reaction kinetics.

Aaronson and Laird [14, 15] proposed a short 'circuit-type mechanism' of mass transport for the lengthening kinetics of plate-like θ' precipitates in an Al -4at.% Cu alloy. In this proposed mechanism, misfit dislocations distribute on the broad surface of θ' plates (Fig. 1a), and those around the edges of precipitate plates provide suitable conduits for accelerated diffusion, leading to faster lengthening of the θ' plates than allowed by volume diffusion. On the other hand, thickening of the plate-like precipitates would be based on a ledge mechanism (Fig. 1b) in which ledges would spread across the broad faces of θ' plates at volume diffusion-controlled rates. Application of Fick's first law to the short circuit type diffusion controlling lengthening of plate-like precipitates yields the dimension of precipitates as a function of time as [15]:

$$l^2/t \propto D, \qquad (1)$$

where l is the length of plate-like precipitates, and D is the solute diffusivity. If only one thermally activated diffusion process is present, the temperature dependence of diffusivity yields an Arrhenius type equation $D = D_0 e^{-Q/RT}$, with Q being the activation energy of solute diffusion. Therefore, Equation 1 becomes:

$$l^2/t \propto D_0 e^{-Q/RT}. \qquad (2)$$

The aim of this work is to investigate the formation of β phase in the intermediate temperature range, between 760°C and 1050°C, in a fully lamellar investment cast Ti-47Al-2Nb-1Mn-0.5W-0.5Mo-0.2Si alloy.

2. Experimental procedure

An investment cast near γ-TiAl alloy with a nominal composition Ti-47Al-2Nb-1Mn-0.5W-0.5Mo-0.2Si(at.%), namely TiAl-WMoSi alloy, was supplied by Howmet Corporation. The material was HIP'ed at

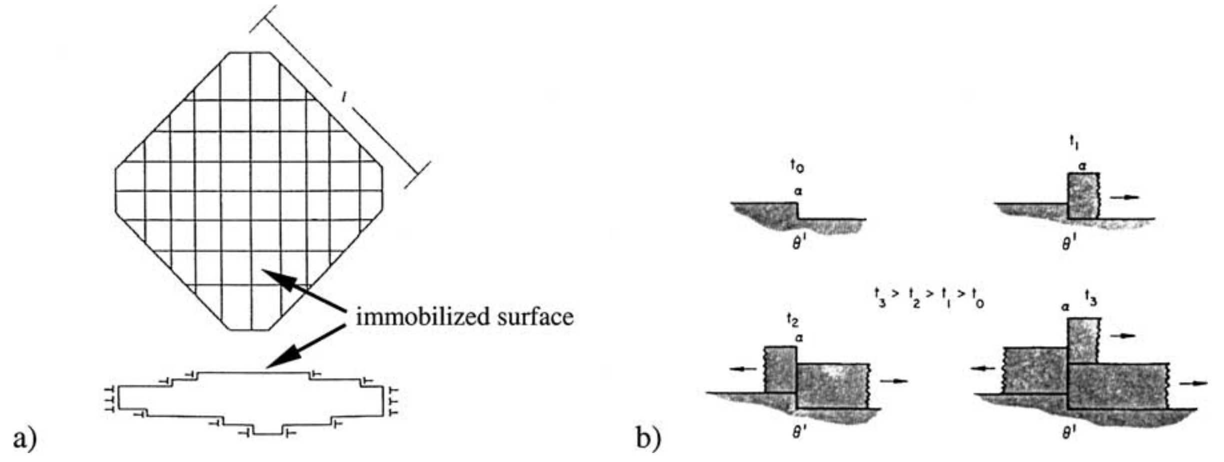

Figure 1 A plate-like precipitate with misfit dislocations on its broad faces (a) and the schematic of the thickening of such a plate via repeatable step mechanism resulting from the displacement of part of an immobilized interface (b) [14, 15].

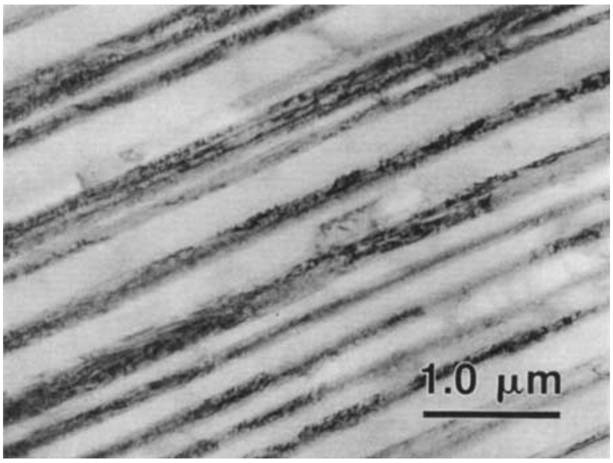

Figure 2 Fully lamellar structure formed after homogenization + solution heat treatment.

1260°C and 172 MPa for 4 hours. To avoid specimen oxidation, all the heat treatments were conducted in a protective atmosphere by encapsulating samples in quartz tubing. The samples were wrapped in tantalum foil to prevent reactions with the tubing. The tubes were evacuated, backfilled with argon and subsequently sealed. The fully lamellar (FL) structure was produced by a homogenization treatment at 1300°C for 20 hours and a subsequent solution treatment at 1380°C for 20 minutes, followed by furnace cooling + air cooling [11]. Aging treatments were conducted at temperatures between 760°C and 1050°C.

Samples for transmission electron microscopic (TEM) analysis were mechanically polished to about 50 micron in thickness, followed by electrolytic jet-polishing at temperatures between −45°C and −50°C, using a solution of 64% methanol +31% butanol +5% perchloric acid. TEM foils were examined using a Philips EM201 transmission electron microscope equipped with a goniometer capable of foil rotation and tilting. For each microstructural condition, multiple foils were examined to determine the precipitate particle size by measuring the maximum projected area of the particles from the TEM micrographs. A Philips CM20 FEG transmission electron microscope capable of generating a fine spot size (as small as 1.2 nm) was used to determine the crystalline structure of precipitates by electron diffraction analysis.

3. Results

3.1. Morphologies of β particles

The starting microstructure following the homogenization and solution heat treatment is a nearly β-free fully lamellar (FL) structure (Fig. 2). Very fine precipitate particles appear within the lamellar structure when aged at 760°C for 24 hours, but the number of precipitates is small (Fig. 3a). As the aging time and temperature increase, both the projected area and density of precipitates increase (Figs 3 and 4). Most of these precipitate particles, preferentially appearing on the α_2 side of α_2/γ interfaces, are thin-plate-like β particles (Fig. 5), and the thickness of these β precipitates increases very slowly during aging at temperatures below 850°C. These β particles have an ordered BCC structure with a = 0.3208 nm (Fig. 6), close to that in a Ti-Al-Cr system [16].

As the aging temperature further increases, the dimension of β particles increases (Fig. 7) and they are farther apart, compared to that after aging at relatively lower temperatures (Figs 3–5). Furthermore, at temperatures above 900°C the β particles formed have a lower aspect ratio than those resulting from lower aging temperatures and are unevenly distributed within the lamellar grains. β particles usually grow extensively within the α_2 lamellae, and they have ellipsoid shape (Fig. 7b and c), when aged at relatively high temperatures. Both thin platelet- and ellipsoid β particles can be observed when the lamellar structure is aged at 900°C (Fig. 7a).

As such, we may conclude that at below 850°C, β particles form predominantly on the α_2 side at the α_2/γ interfaces and grow in an uneven two-dimensional mode, as illustrated in Fig. 8. Almost all of the β particles are within the α_2 plates when aged in the low temperature range and grow into the γ plates only at higher aging temperatures (Fig. 7b).

3.2. Kinetics of β growth

Noticing that the lengthening of plate-like θ' plates in Al −4 at.% Cu alloy proceeds via relatively even

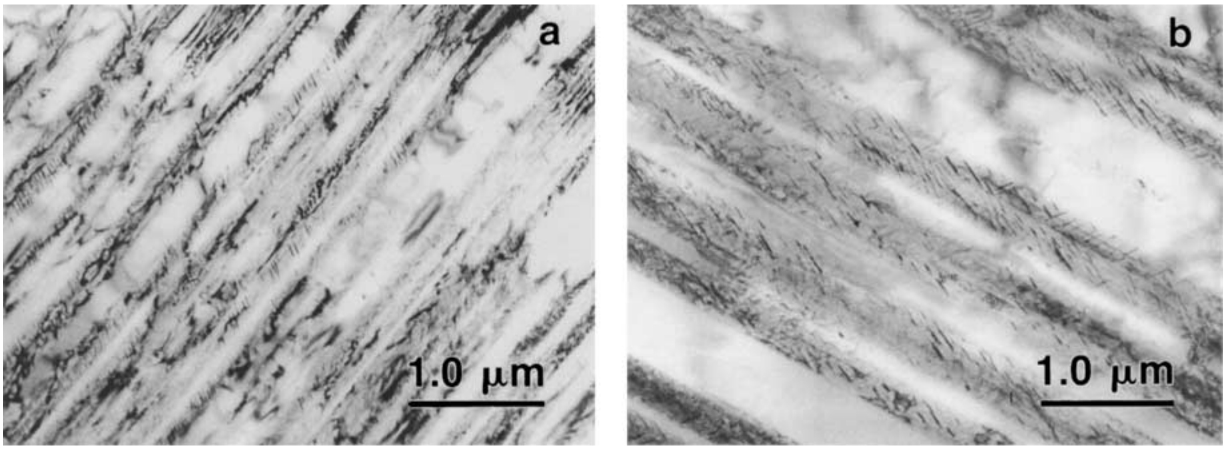

Figure 3 β particles formed at 760°C. (a) 24 hours and (b) 100 hours. TEM bright field images.

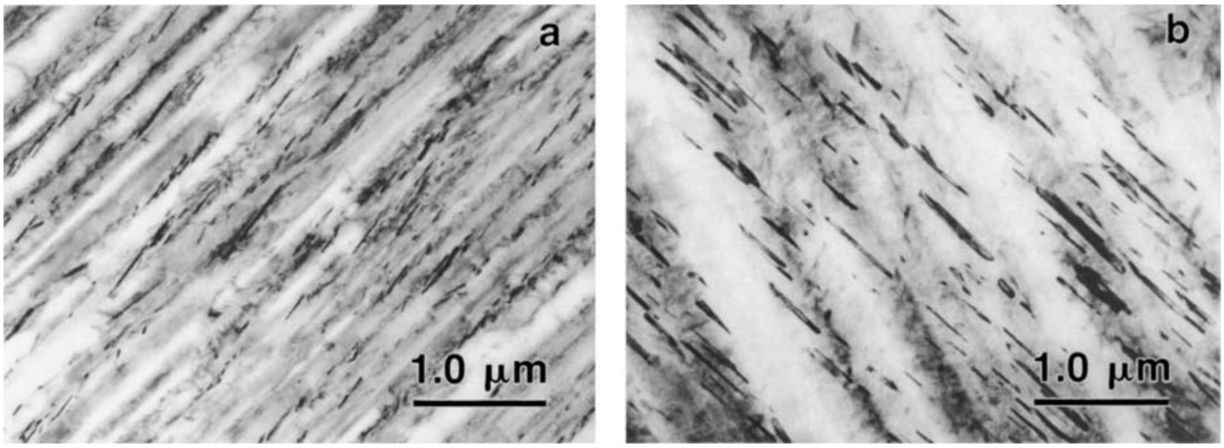

Figure 4 β particles formed at 850°C. (a) 24 hours and (b) 72 hours. TEM bright field images.

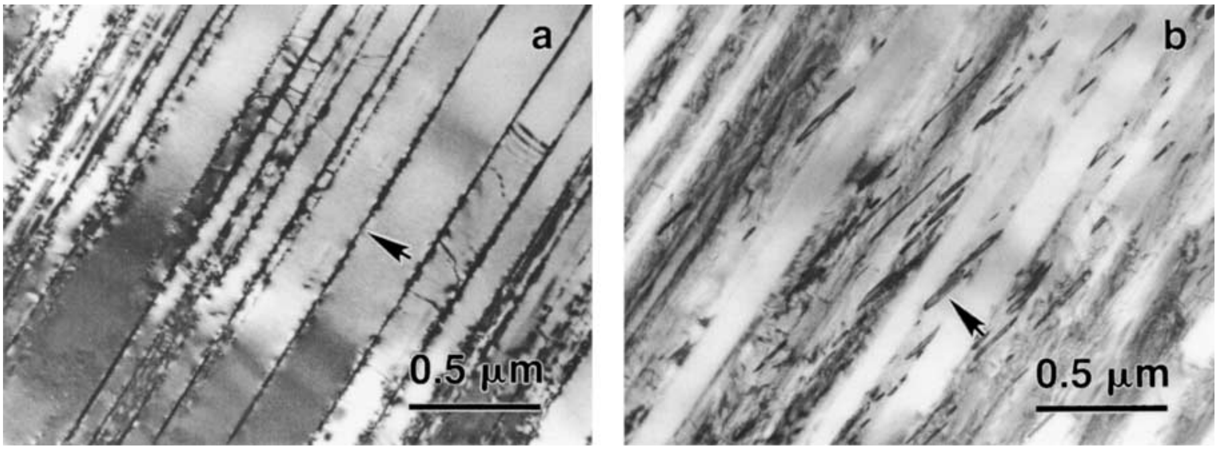

Figure 5 β particles formed after aging at 850°C for 24 hours. (b) is the same area as in (a) but with sample titled. The width of the β particle indicated by arrow in (b) is greater than the thickness of α_2 plate that contains this particle, as indicated by arrow in (a), suggesting that these β particles are of thin-plate shape.

two-dimensional growth [14, 15], and that in the TiAl-WMoSi alloy β particles grow in an uneven two-dimensional mode (Fig. 8), we may modify Equation 2 to

$$A/t \propto D_0 e^{-Q/RT}, \qquad (3)$$

where A is the projected area of β particles (Figs 3–6), if assuming that the growth of both thin platelet- and ellipsoid-shaped β particles proceeds in a manner analogous to 'short-circuit mechanism'. Thus, we may be able to determine the β precipitation kinetics by measuring the maximum projected area of β particles after various aging treatments. During aging between 760°C and 950°C, the projected area (A) of β particles increases linearly as aging time increases (Fig. 9), indicating that after nucleation, β particles grow at a nearly constant speed. As the aging temperature increases, the growth rate of β particles increases up to 850°C, however, an increase in the growth

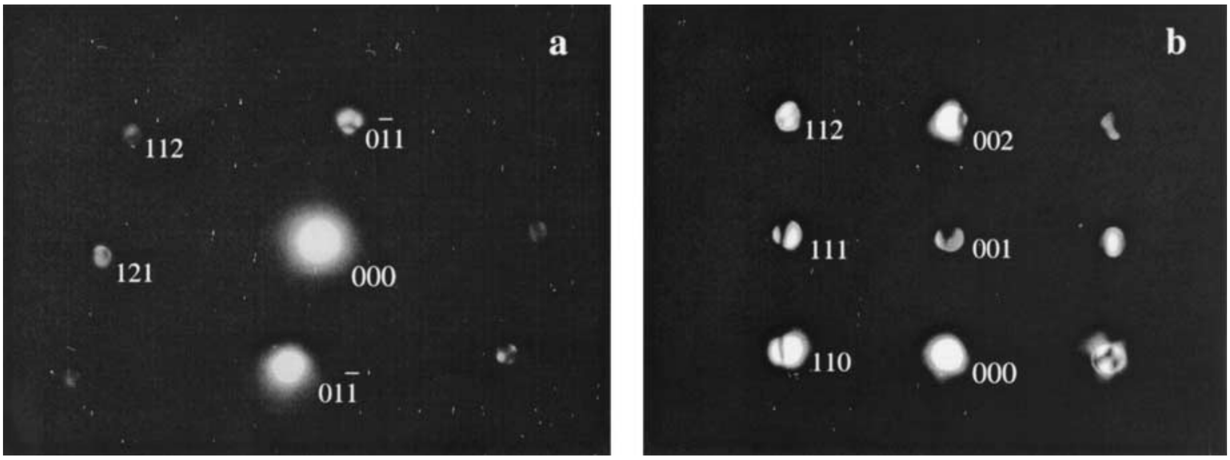

Figure 6 Electron diffraction pattern of β precipitates. (a) $[\bar{3}\,1\,1]_\beta$ and (b) $[\bar{1}\,1\,0]_\beta$. Convergent beams (2 nm).

rate is not observed as aging temperature increases to 950°C.

The Arrhenius plot for the growth rates (A/t) of β particles is shown in Fig. 10. The growth rate of β particles increases as aging temperature increases only up to 850°C, indicating that there may be a change in growth mechanism of β particles from low to high aging temperatures. Bearing this in mind, we can determine an activation energy of about 366 kJ/mol for β growth at temperatures between 760°C and 850°C.

4. Discussion

The precipitation of β phase at temperatures between 760°C and 1050°C suggests that there is a $\alpha_2 + \gamma + \beta$ region within this temperature range for this alloy, consistent with the observations that a $\alpha_2 + \gamma + \beta$ region can exist in γ base alloys containing β stabilizing elements [11–13]. W and Mo are β stabilizing elements, and during aging at high temperatures (>900°C in this alloy) some areas within the lamellar structure enriched in these two elements likely undergo a $\alpha_2 + \gamma \rightarrow \alpha_2 + \gamma + \beta$ transformation. The formation of β precipitates proceeds at the expense of α_2 and then γ phases, as indicated by the β/γ interfaces moving towards the interior of γ plates (Fig. 7b). While at low aging temperatures, a transformation of $\alpha_2 \rightarrow \beta$ seems to be more likely for the formation of β precipitates, since almost all of the β particles precipitate on α_2 side of the α_2/γ interfaces and grow within α_2 lamellae (Fig. 5).

The uneven two-dimensional character of β precipitation suggests that the growth of β particles might have an orientation relationship with α_2 matrix of $\{0001\}_{\alpha 2}//\{110\}_\beta$ and $\langle 11\bar{2}0\rangle_{\alpha 2}//\langle 1\bar{1}1\rangle_\beta$ [1]. Almost all of the β particles, enriched in W and Mo [11], are within the α_2 plates when aged in the low temperature range, and grow into the γ plates only at higher aging temperatures (Fig. 7b). The change from β formation with a strong orientation (Figs 3 and 4) at low aging temperatures to less orientation dependence (Fig. 7) at higher aging temperatures suggests a loss of coherency between β particles and the matrix. This could be explained by the requirement to decrease the surface area to reduce the energy associated with these particles at high aging temperatures.

It has been shown that for self-diffusion of major elements in titanium aluminides, $Q_{\mathrm{Ti}} = 250$–291 kJ/mol, $Q_{\mathrm{Al}} = 360$ kJ/mol in γ-TiAl [17, 18], while $Q_{\mathrm{Ti}} = 288$ kJ/mol, $Q_{\mathrm{Al}} = 395$ kJ/mol in $\mathrm{Ti_3Al}$ [19, 20]. Also, the activation energy for substitutional diffusion of Nb is 339 kJ/mol in $\mathrm{Ti_3Al}$ [20], where Nb is a substitutional element in the alloy. Considering the similar electronic configurations among Nb, W and Mo atoms (group V for Nb, group VI for W and Mo), as well as the atomic mass of each element, we may expect that the diffusivity of Mo is close to that of Nb, and that of W is lower than that of Nb. Therefore, we can expect that activation energies for substitutional diffusion of W and Mo should be higher than that for Nb, that is, $Q_{\mathrm{W}} \geq Q_{\mathrm{Mo}} \geq 339$ kJ/mol, leading to the low diffusivity of W [21, 22]. The activation energy derived for β formation is 366 kJ/mol at temperatures between 760°C and 850°C, which is greater than that for substitutional diffusion of Nb [20]. In addition, β precipitates are enriched in W and Mo. This suggests that the growth of β particles at between 760°C and 850°C could be controlled by the diffusion of W and Mo.

It is difficult to determine quantitatively if the growth of β particles during aging is controlled by substitutional diffusion of W and Mo, since activation energies for substitutional diffusion of W and Mo in γ-TiAl are not available. However, it is likely that the diffusion of W and Mo at β/α_2 and β/γ interfaces accounts for the growth of β particles at temperatures between 760°C and 850°C. This is based on the constrained growth of β particles at the interfaces between α_2 and γ plates and the two-dimensional growth of β platelets (Fig. 8) between 760°C and 850°C. The two-dimensional growth of β platelets suggests that diffusion of W and Mo across the β/γ interfaces and the β/α_2 interfaces that are parallel to those β/γ interfaces is very slow, compared to the interfacial diffusion along the β/α_2 and β/γ interfaces, which is similar to the situation described by the 'short-circuit mechanism' [14, 15]. The limited diffusion of W across β/γ interfaces was recently reported [23]. Diffusion of W and Mo at β/α_2 and β/γ interfaces is likely easier than that within the α_2 and γ phases, due to the misfit dislocations at these semi-coherent interfaces [24].

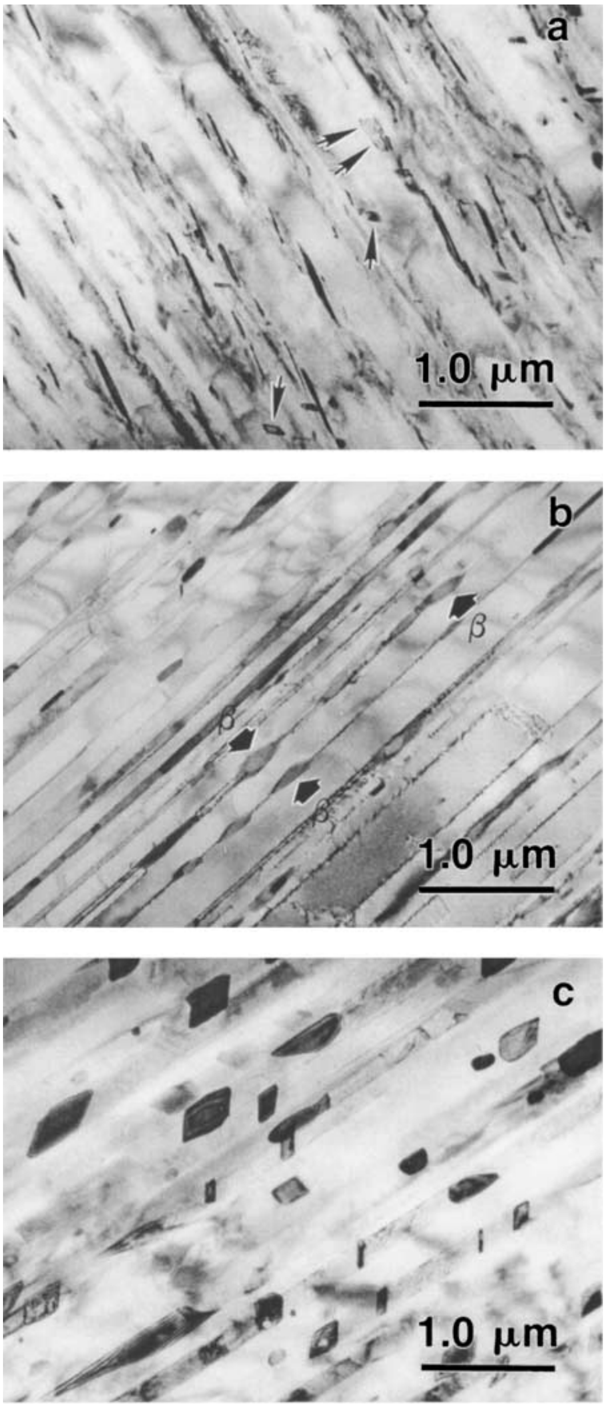

Figure 7 β particles formed at temperatures above 900°C. (a) both thin platelet-shaped and ellipsoid β particles (indicated by arrows) show up after 900°C/24 hr aging, (b) and (c) ellipsoid β particles grow (arrows) extensively within the α_2 plates and into the adjacent γ lamellae after 1050°C/24 hr aging.

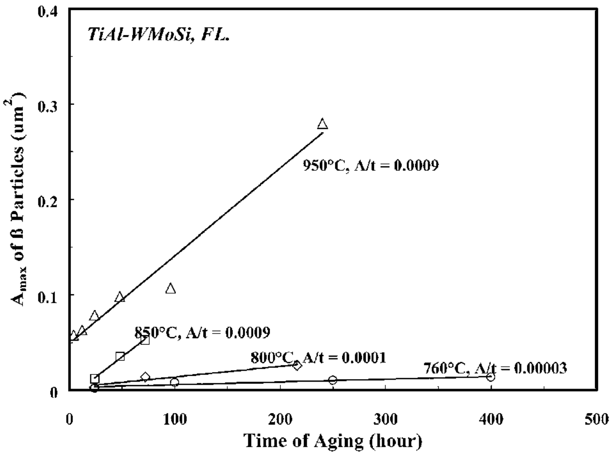

Figure 9 Maximum projected area of β particles as a function of time.

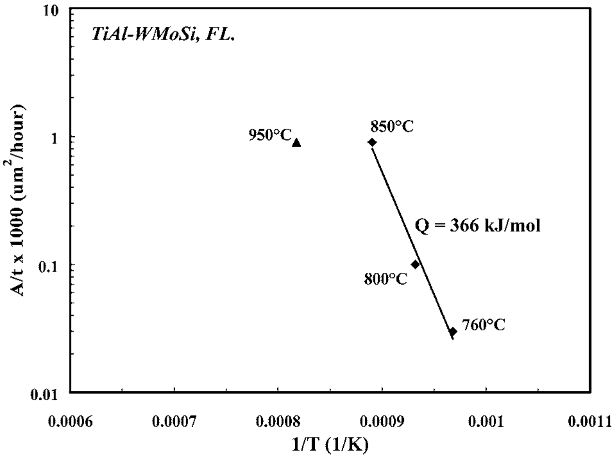

Figure 10 Arrhenius plots of the growth rates (A/t) of β particles at temperatures between 760°C and 950°C.

The growth rate of β particles at 950°C does not agree with the derived Arrhenius relationship for aging between 760°C and 850°C, suggesting that the growth process of β particles at temperatures above 850°C changes. Consistent with this result, a change in the morphology of β particles (from thin platelets to ellipsoid) occurs at about 900°C (Fig. 7a), which may also imply that the mechanism for β growth changes from low to higher aging temperatures. It is also noticeable that the distribution of β particles formed at low aging temperatures, below 850°C, is relative uniform (Figs 3 and 4), compared to that at high aging temperatures (Fig. 7). The change from β formation with a strong orientation (Figs 3 and 4) at low aging

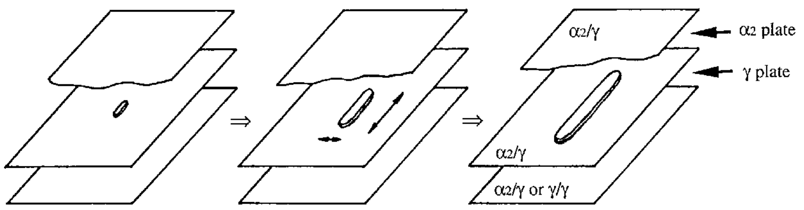

Figure 8 Speculated growth of thin plate-like β particle at an α_2/γ interface at temperatures below 850°C.

temperatures to less orientation dependence (Fig. 7) at higher aging temperatures suggests a loss of coherency between β particles and the matrix, which could be explained by the requirement to decrease the surface area to reduce energy at high aging temperatures. Such growth has to be accompanied by further diffusion of the major elements existing in the particles, i.e. W and Mo in this alloy, along the β/α_2 and β/γ interfaces. However, the low growth rate at 950°C does not agree with this mechanism that requires W and Mo interfacial diffusion. Also, the more inhomogeneous distribution of β particles formed at relatively higher temperatures (Fig. 7) suggests that the formation of β particles above 900°C is likely associated with the non-uniform distribution of W and Mo in the fully lamellar structure [11].

It can be expected that during aging, β particles nucleate and grow via $\alpha_2 \rightarrow \beta$ transformation, as a result of diffusion of W and Mo, due to the existence of the $\alpha_2 + \gamma + \beta$ phase region [11–13]. Segregation of W and Mo can be expected after casting [21, 25], and complete homogenization of W is very difficult [21]. At low aging temperatures, the driving force for $\alpha_2 \rightarrow \beta$ transformation may be quite small and at the same time, the diffusivity of W and Mo is low. Consequently extensive interfacial diffusion of W and Mo occurs within α_2 lamellae, forming relatively homogeneously distributed β precipitates mostly inside the α_2 lamellae. The misfit dislocations along the β/α_2 and β/γ interfaces may serve as diffusion short circuits [15] increasing the diffusivity of W and Mo.

However, at high aging temperatures, the driving force for $\alpha_2 \rightarrow \beta$ transformation may be quite large and the diffusivity of W and Mo is higher. Therefore, during the early stage of aging, areas rich in W and Mo transform to β particles rapidly due to the heterogeneous nucleation and short-range diffusion of W and Mo within these areas, before extensive diffusion of these two elements can occur. As aging further proceeds, diffusion of W and Mo from surrounding areas to β particles becomes important after the initial $\alpha_2 \rightarrow \beta$ transformation in the W- and Mo-rich regions, leading to a reduced growth rate during extended thermal exposure at high aging temperatures (Fig. 10). Thus, the initial rapid increase in projected area in Fig. 10 at 950°C is probably due to the heterogeneously nucleated $\alpha_2 \rightarrow \beta$ transformation controlled by short-range diffusion of W and Mo within the W- and Mo-rich areas, while the growth rate during subsequent aging is controlled by W and Mo diffusion from the surroundings.

5. Summary

The precipitation of β particles in a fully lamellar structure of Ti-47Al-2Nb-1Mn-0.5W-0.5Mo-0.2Si(at.%) alloy was studied. β particles formed at temperatures below 850°C exist predominantly in the form of thin platelets, while those formed at higher temperatures appear with an ellipsoid morphology.

Preliminary results on the kinetics of β growth give an activation energy of about 366 kJ/mol at temperatures below 850°C, implying that at low aging temperatures the growth of β particles undergoes an $\alpha_2 \rightarrow \beta$ precipitation process controlled by diffusion of W and Mo along the β/α_2 and β/γ interface areas. While at temperatures above 900°C, areas rich in W and Mo likely transform to β phase rapidly via $\alpha_2 \rightarrow \beta$ transformation controlled by short-range diffusion within these areas, during the early stage of aging. Subsequently the nucleated β particles expand at a much lower growth rate (than would be predicted using the determined 366 kJ/mol activation energy) due to the low diffusivity of W and Mo from the surroundings.

Acknowledgements

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References

1. Y. ZHENG, L. ZHAO and K. TANGRI, *Scripta Metallurgica et Materialia* **26** (1992) 219.
2. M. TAKEYAMA, Y. KATO and M. KIKUCHI, “Titanium ’95: Science and Technology,” edited by P. A. Blenkinsop, W. J. Evans and H. M. Flower (The Institute of Materials, Birmingham, UK, 1995) 294.
3. J. BEDDOES, L. ZHAO, J. TRIANTAFILLOU, P. AU and W. WALLACE, “Gamma Titanium Aluminides,” edited by Y-W. Kim, R. Wagner and M. Yamaguchi (The Minerals, Metals and Materials Society, Las Vegas, NV, 1995) p. 959.
4. W. M. YIN, V. LUPINC and L. BATTEZZATI, *Materials Science and Engineering* **A239–250** (1997) 713.
5. T. MAEDA, M. OKADA and Y. SHIDA, “Mechanical Behaviour of Materials - VI,” Vol. 3, edited by M. Jono and T. Inoue (The Society of Materials Science of Japan, Kyoto, Japan, 1992) p. 199.
6. M. A. MORRIS and Y. G. LI, *Materials Science and Engineering* **A197** (1995) 133.
7. P. R. BHOWAL, H. F. MERRICK and D. E. LARSEN, JR., *ibid.* **A192/193** (1995) 685.
8. T. J. KELLY, M. C. JUHAS and S. C. HUANG, *Scripta Metallurgica et Materialia* **29** (1993) 1409.
9. J. BEDDOES, W. WALLACE and L. ZHAO, *International Materials Reviews* **40**(5) (1995) 197.
10. J. BEDDOES, L. ZHAO, W. R. CHEN and X. DU, “High Temperature Ordered Intermetallics VIII,” edited by E. P. George, M. J. Mills and M. Yamaguchi, MRS 552 (Boston, MA, 1999) kk1.1.1.
11. W. R. CHEN, L. ZHAO and J. BEDDOES, “Gamma Titanium Aluminides 1999,” edited by Y-W. Kim, D. M. Dimiduk and M. H. Loretto (TMS, San Diego, CA, 1999) 323.
12. G. CHEN, W. J. ZHANG, Z. C. LIU, S. J. LI and Y-W. KIM, “Gamma Titanium Aluminides 1999,” edited by Y-W. Kim, D. M. Dimiduk and M. H. Loretto (TMS, San Diego, CA, 1999) 371.
13. T. T. CHENG, M. R. WILLIS and I. P. JONES, *Intermetallics* **7** (1999) 89.
14. C. LAIRD and H. I. AARONSON, *Transactions of the Metallurgical Society of AIME* **252**(7) (1968) 1393.
15. H. I. AARONSON and C. LAIRD, *ibid.* **252**(7) (1968) 1437.
16. B. ZHANG, J. WANG, X. WAN and W. R. CHEN, *Scripta Metallurgica et Materialia* **30** (1994) 399.
17. S. KROLL, H. MEHRER, N. STOLWIJK, C. HERZIG, R. ROSENKRANZ and G. FROMMEYER, *Z. Metallkd.* **83** (1992) 591.
18. CHR. HERZIG, T. PRZEORSKI and Y. MISHIN, *Intermetallics* **7** (1999) 389.
19. J. RÜSING and CHR. HERZIG, *ibid.* **4** (1996) 647.
20. J. BREUER, T. WILGER, M. FRISESL and CHR. HERZIG, *ibid.* **7** (1999) 381.

21. G. E. FUCHS, *Materials Science and Engineering* **A192/193** (1995) 707.
22. P. L. MARTIN, H. A. LIPSITT, N. T. NUHFER and J. C. WILLIAMS, "Titanium'80: Science and Technology," edited by H. Kimura and O. Izumi (Kyoto, Japan, 1980) 1255.
23. D. Y. SEO, J. BEDDOES, L. ZHAO and G. A. BOTTON, *Materials Science and Engineering*, in press.
24. B. J. INKSON, H. CLEMENS and J. MARIEN, *Scripta Materialia* **38**(9) (1998) 1377.
25. P. R. BHOWAL, H. F. MERRICK and D. E. LARSEN, JR., *Materials Science and Engineering* **A192/193** (1995) 685.

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