THE COARSENING OF LAMELLAE IN Ti–48Al–2Mn–2Nb

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Abstract—The thermal stability of as-cast Ti–48Al–2Mn–2Nb alloys has been investigated as a function of time at temperatures of 1200, 1350 and 1420°C. The resultant structures have been characterised using optical microscopy, electron probe microanalysis and transmission electron microscopy. The as-cast structure consists mainly of lamellae of α and γ. Annealing at 1350 and at 1420°C resulted in the continuous and discontinuous coarsening of the primary lamellae. Discontinuous coarsening, which often originates at the sample surface, results in branched irregular secondary lamellae. The average interlamellar spacing of the secondary lamellae is up to a thousand times larger than the primary interlamellar spacing. The extremum principles of maximum velocity and maximum rate of entropy production, used to predict the secondary interlamellar spacing, are inconsistent with the experimental observations. The theoretical predictions of the velocity of the discontinuous coarsening by Livingston and Cahn are used to estimate the value of grain boundary diffusivity at 1350°C. The temperature dependence of discontinuous coarsening is weak, in contrast to the strong effect of lamellar orientation on the rate of discontinuous coarsening.

INTRODUCTION

γ-Based titanium aluminides have been extensively investigated as candidate materials for a number of high temperature applications [1, 2]. The microstructure of as-cast γ-based titanium aluminides usually consists, at room temperature, of equiaxed γ (L12, ordered f.c.c.) grains and lamellar colonies, consisting of alternate plates of γ and α2 (D019, ordered hexagonal) (see, for example, Fig. 1). Examining the binary Ti–Al phase diagram, (which is used, in the absence of a quaternary phase diagram, as a guide) in the region of interest, it can be seen that at high temperatures [3] (Fig. 2), an order-disorder reaction converts the ordered α2 phase to the hexagonal α phase, which is not ordered. In addition to the order-disorder transformation, the main phase transformations that occur in this system are those between the γ, α and α2 phases. Kim [1] has suggested that a microstructure consisting of lamellar colonies and equiaxed γ grains in the volume fraction ratio of 0.3:1 will give the best combination of ductility, tensile strength and creep resistance. It is important to investigate the stability of the lamellar colonies since coarsening of the lamellae or the dissolution of the γ or α2 phases may result in a degradation of the mechanical properties.

Coarsening of lamellae formed from both eutectic and eutectoid reactions has been investigated in a number of alloy systems. Continuous coarsening (CC), which occurs, for example, in the Al–Al2Cu eutectic [4], takes place by the dissolution of the edges of individual lamellae, followed by reprecipitation of solute on neighbouring lamellae [5].

Discontinuous coarsening (DC) of lamellae [6] can occur through the migration of grain boundaries. Livingston and Cahn assumed that the main driving force for DC is the reduction of interfacial energy through a reduction in the interfacial area and the result is a coarsened lamellar structure with an increased average interlamellar spacing (ILS). DC has been observed in a number of alloy systems including Cu–Ni–Fe [7], Ni–Al–Mo [8], Al–Zn [9], Al–Li [10], Co–Si, Cu–In [6] and binary Ti–Al alloys [11]. Shong and Kim [11] reported that in Ti–43Al (in this manuscript, the composition of oxygen is in weight percent, those of the other elements in atomic percent) DC is observed above 900°C, resulting in a four fold increase in ILS, and a change is observed from the high perfection initial (primary) lamellar structure to coarsened branched (secondary) lamellae. Yamabe et al. [12] studied binary Ti–Al alloys containing between 40 and 47 at.% Al and also observed DC and evidence of branching. Wheeler [13] observed coarsening of lamellae in Ti–48Al–2Nb–2Cr after heat treatment at 1350°C and after creep testing at 815°C of the heat treated samples.

We report, for the first time, the results of investigations, using optical microscopy, electron probe microanalysis (EPMA) and transmission electron microscopy (TEM), on the stability of the lamellar structure in Ti–48Al–2Mn–2Nb. We find that substantial, though inhomogeneous, continuous and discontinuous coarsening of the lamellae takes place at
1350°C and at 1420°C resulting in up to a thousand fold increase in ILS. The speed of the DC reaction at 1350°C of the order of 1 μm/s, about a thousand times greater than that at 1000°C. This DC reaction could result in a degradation of the mechanical properties of this alloy.

**EXPERIMENTAL**

A 100 mm cylindrical ingot of length 750 mm and nominal composition Ti-48Al-2Mn-2Nb was prepared by plasma arc melting. The actual composition of the sample used in the present investigation is Ti-50Al-2.0Mn-2.1Nb and the oxygen content is 650 ppm. Details of the macrochemistry and microstructure have been presented elsewhere [14]. Electrical discharge machining was used in the initial stages to section the ingot, followed in the final stages by sectioning using a low speed diamond saw. Transverse sections of the ingot were examined throughout this analysis. Samples for heat treatment were first wrapped in tantalum foil and placed in silica tubes which were then evacuated, backfilled with argon and subsequently sealed. All heat treatments were conducted with a calibrated thermocouple placed next to the samples. Heat treatments were conducted at 1200°C for 48 and 140 h and 1350 and 1420°C for various annealing times up to 4 h followed by water quenching. Thin slices were cut from the heat treated samples using a low speed diamond saw. These slices were mounted in bakelite, ground down with 1200 grit emery paper and polished with colloidal silica. The etchant used is 1% HF and 10% HNO₃ in distilled water. Electron probe microanalysis (EPMA) results were obtained using a JEOL 840A interfaced to a LINK 10000 system. The error in the analysis of the composition of aluminium and titanium is less than one atomic percent [15]. TEM results were obtained using a Philips CM20 and JEOL 4000FX microscopes operated at 200 kV.

**RESULTS**

The transverse section of the as-cast microstructure of Ti-48Al-2Mn-2Nb (Fig. 1) consists mainly of lamellar colonies (average size 600 μm) of α₂ and γ with a small volume fraction of equiaxed γ grains. TEM of the as-cast microstructure (Fig. 3) shows that the lamellae consist of regular plates of α₂ and γ with an average interlamellar spacing of 1 μm. Heat treatment at 1200°C for 48 h results (Fig. 4) in the dissolution of the α₂ plates resulting in a microstructure of equiaxed γ grains (average size 300 μm) and a small volume fraction of α₂ precipitates. Extending
the annealing time to 140 h did not significantly change the microstructure. At 1350°C, both CC and DC were observed in some parts of the sample after only 10 min, the shortest annealing time used in the present investigation [Fig. 5(a)]. At 1420°C, coarsening was observed in some parts of the sample at an annealing time of 2 h [Fig. 5(b)]. In many cases, DC was initiated at the sample surfaces, in agreement with the observations of Livingston and Cahn. Fig. 5(c) shows an example of the highly coarsened structure that develops as a result of DC. The secondary ILS (i.e. the ILS after coarsening) varies strongly with the orientation of the primary lamellae relative to the growth front. The secondary ILS can be as large as 500 μm, and occasionally, secondary ILS of 1 mm are observed. A curious feature of DC is that some lamellar colonies are untransformed and are enveloped by discontinuously coarsened secondary lamellae. The DC growth front also grew around equiaxed γ grains. These grains often contained laths with a composition corresponding to the precipitation of α in the γ matrix. The composition of the laths and the matrix in samples heat treated at 1350°C have been determined by EMPA (Table 1). The composition of γ and α₂ in the discontinuously coarsened regions and the average composition of the untransformed lamellar region were also determined by EMPA (Table 1). EMPA performed on samples annealed at 1420°C for 2 h, in the region undergoing DC, showed that the γ composition is Ti-50.1Al-2.1Mn-1.8Nb while the α₂ composition is Ti-48.6-2.2Mn-1.7Nb. The DC growth front was highly irregular but measurements performed on samples annealed at 1350°C for 10, 30, 60, 120, and 240 min and samples annealed at 1420°C for 2 h showed that the average velocity of the growth front at 1350 and 1420°C was approximately 1.66 μm/s and independent of time. Qualitative assessment of the microstructures showed that much more CC was observed at 1420°C than at 1350°C.

The secondary lamellae observed after DC are highly irregular and are formed roughly parallel to the local direction of grain boundary migration. As previously observed by Shong and Kim [11] and Yamabe et al. [12], the primary high perfection lamellae are replaced by secondary lamellae which show branching and a more imperfect structure [Fig. 5(d)].

TEM analysis of samples annealed at 1350°C for 1 h in regions undergoing CC showed that primary lamellae are dissolving in the centre of the lamellae. In samples annealed at 1420°C for 2 h, this process can lead to the dissolution of γ plates (Fig. 6). Figure 7 shows that a variety of dissolution processes, mainly at faulted regions containing many dislocations, leads to CC of lamellae. Dissolution of the lamellar edges was also observed by TEM.

DISCUSSION

Our results show that annealing of the as-cast Ti-48Al-2Mn-2Nb at 1350 and 1420°C can lead to considerable continuous and discontinuous coarsening of the primary lamellar structure. Coarsening, which occurs in order to reduce the interfacial energy through a reduction in the interfacial area competes and can occur along with other transformations which are also occurring simultaneously. For example, at 1420°C, the stable phase has been determined to be the γ phase [16], hence, depending on the relative rates of the phase transformations involved, dissolution of the α phase and subsequent growth of α grains can occur in parts of the sample, while in other parts CC and DC can occur. An attempt has been made to take into account these changes in volume fraction as well as the reduction in interfacial area in making an assessment of the driving force for coarsening.

NUCLEATION OF THE COARSENING REACTION

In the case of CC, faulted regions containing dislocations and the termination of lamellae are the

Table 1. EPMA analysis of sample annealed at 1350°C for 60 min

<table>
<thead>
<tr>
<th>Discontinuous region</th>
<th>Untransformed lamellar region</th>
<th>Equiaxed γ grains</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average composition</td>
<td>with lath shaped</td>
</tr>
<tr>
<td></td>
<td>matrix</td>
<td>precipitates</td>
</tr>
<tr>
<td></td>
<td>lath</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>44.9</td>
<td>46.1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>51.7</td>
<td>50.1</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Niobium</td>
<td>2.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

2777
preferred sites for coarsening. Shong and Kim have shown that the initiation of the DC reaction in binary Ti–Al alloys is by the displacement of a grain bound-

ary segment by the growth of the edges of secondary lamellae to form a discontinuously coarsened region on one side of the grain boundary. This can be followed by the sideways growth of the secondary lamellae to form DC regions on both sides of the grain boundary. Funkenbusch [8] and Williams and

Fig. 5. (a) Coarsened lamellar colonies after annealing at 1350°C for 10 min followed by water quenching. Note that the interlamellar spacing after coarsening varies from one lamellar colony to another. (b) Coarsened regions in part of sample annealed at 1420°C for 2 h, followed by water quenching. Note the change in lamellar orientation from one coarsened lamellar colony to another. (c) Highly discontinuously coarsened region surrounding lamellar regions that have not undergone coarsening in a sample annealed at 1350°C for 30 min. (d) Interface between two lamellar colonies that have discontinuously coarsened, showing the branched irregular nature of coarsened regions samples annealed at 1420°C for 2 h.

Fig. 6. Bright field TEM micrograph from a sample annealed at 1420°C for 2 h showing the dissolution of a plate (identified as γ from diffraction analysis). Note the dislocations in the region that is dissolving (indicated by arrows) as well as the faceted nature of dissolving plates. Beam direction is near [101] for the dissolving γ plate.

Fig. 7. Bright field TEM micrograph from a sample annealed at 1420°C for 2 h showing several plates that are dissolving at faulted regions (indicated by arrows).
Edington [10] have previously noted that there is a strong dependence of the nucleation and growth of DC reaction on the relative orientation of the grain boundaries. In the present investigation, DC is well advanced after annealing for only 10 min at 1350°C, hence no direct observations of the nucleation process are possible. However, the frequent occurrence of DC initiated at cut sample surfaces, also noted by Livingston and Cahn, indicates that surface recrystallisation, induced by damage introduced during cutting, and surface stresses could result in the formation of new highly mobile grain boundaries which can initiate DC.

VELOCITY OF DC

The velocity of the DC growth front has been theoretically modelled by Livingston and Cahn. It is assumed that the driving force is the reduction in interfacial area by the large increase in ILS in the secondary lamellae relative to the primary lamellae. Funkenbusch proposed a change in the driving force term (P) to account for changes in the phase chemistry and volume fraction accompanying DC. This change in P has been incorporated in the present analysis with the remaining terms retaining their meaning. It is assumed that the grain boundary energy is isotropic and that the normal surface-tension forces at the grain boundary are converted into concentration differences which drive lateral diffusion (Gibbs–Thompson effect) at the tips of the lamellae. The steady state velocity (v) is given by [6]:

\[ v = \frac{4C_bD_b\delta_bmP}{[f_1^2f_2^2(c_e - c_s) \pi^2RT]} \]  

(1)

where \(D_b\) and \(c_b\) are the grain boundary diffusivity and the equilibrium grain boundary concentration in the absence of curvature, respectively, \(\delta_b\) is the grain boundary thickness, \(m\) is the molar volume, \(P\) is the driving force for the reaction, \(f_1\) and \(f_2\) are the volume fractions before coarsening of the \(\alpha\) and \(\gamma\) phases, respectively. \(c_e\) and \(c_s\) are the concentrations before coarsening of the rate controlling species in the \(\alpha\) and \(\gamma\) phases, respectively, \(\pi_2\) is the interlamellar spacing after coarsening (secondary ILS), \(R\) is the gas constant and \(T\) the temperature. The above equation can be used to estimate the grain boundary diffusivity needed to account for the high migration velocities observed in the present investigation.

Calculation of the driving force \(P\)

The driving force arising from the changes in the relative volume fraction of the \(\alpha\) and \(\gamma\) phases, \(P\), can be calculated using the solution thermodynamics results of Murray [18]. It is assumed that the chemistry of the two phases is unchanged as a result of coarsening and that the system can be modelled as a binary Ti–Al system with the aluminium concentrations given in Table 1. The free energy of the \(\alpha\) and \(\gamma\) phases are given by \(G_\alpha\) and \(G_\gamma\):

\[ G_\alpha = aG_{Al(hcp)} + (1 - a)G_{Ti(hcp)} + RT[\ln a + (1 - a)\ln(1 - a) + a(1 - a)(B + C(1 - 2a))] \]  

(2)

\[ G_\gamma = gG_{Al(fcc)} + (1 - g)G_{Ti(fcc)} + RT[g\ln g + (1 - g)\ln(1 - g) + g(1 - g)(D + E(1 - 2g))] \]  

(3)

where \(a\) and \(g\) are the mole fractions of the aluminium in the \(\alpha\) and \(\gamma\) phases, \(B, C, D\) and \(E\) are solution constants, \(G_{Al(hcp)}\) is the standard free energy of aluminium in the h.c.p. crystal structure (measured relative to the liquid state) with a corresponding meaning for the other standard state terms. From Murray, we note that (in units of J/mol and J/mol K as appropriate):

\[ G_{Al(hcp)} = -5230 + 9.707T \]  

(4)

\[ G_{Ti(hcp)} = -20585 + 12.134T \]  

(5)

\[ G_{Al(fcc)} = -10740 + 11.506T \]  

(6)

\[ G_{Ti(fcc)} = -17238 + 12.134T \]  

(7)

\[ B = -118239 \]  

(8a)

\[ C = -61415 \]  

(8b)

\[ D = -121496 \]  

(8c)

\[ E = -56715. \]  

(8d)

From Table 1, \(a = 0.486\) and \(g = 0.517\) at a temperature of 1350°C (\(T = 1623\) K). These values of \(a, g, T\), the values of standard free energy at 1623 K from equations (4)–(7) and the solution constants from equations (8a)–(8d) are substituted into equations (2) and (3) to give \(G_\alpha = -34657\) J/mol and \(G_\gamma = -33915\) J/mol. Since the relative volume fractions \(\alpha\) and \(\gamma\) in the primary lamellae have been measured to be 1:1, the initial free energy can be calculated as equal to \(-34286\) J/mol. After DC, the relative volume fractions of \(\alpha\) and \(\gamma\) is 4:1 and so the final free energy is \(-34509\) J/mol. The difference between the final and initial free energy (equal to \(-223\) J/mol) is the driving force per mole, \(P\). However, an error analysis shows that the experimental error of 1 at.% in the aluminium and titanium levels results in values of \(P\), ranging from \(-600\) to \(+125\) J/mol. Thus the error in the measurement of \(P\), is greater than the value of \(-223\) J/mol obtained from the aluminium and titanium levels reported in Table 1. Therefore, no quantitative estimate of \(P\), is possible. To make an estimate of the value of \(D_b\) we assume that \(P\) is approximately equal to \(P_1\).
If the rate controlling species is Al, then from equation (1), the measured values of \( v = 1.66 \mu \text{m/s} \), 
\( f_s = 0.5, \ f_r = 0.5, \ c_r = 0.517, \ c_\text{Al} = 0.486, \ \alpha_1 = 1 \times 10^{-6} \text{m} \) and 
\( \alpha_2 = 1 \times 10^{-4} \text{m} \) and find that 
\( D_\alpha = 1 \times 10^{-10} \text{m}^2/\text{s} \). We assume that \( \delta_\alpha = 5 \times 10^{-16} \text{m} \) 
[19], that \( c_r \) and \( c_\text{Al} \) are unchanged and that the grain boundary concentration is the same as the bulk alloy concentration, namely, \( c_r = 0.5 \). No experimental values of \( D_\varphi \) are available to provide further confirmation of our results. However, the lattice diffusivity (\( D_\varphi \)) can be calculated from the data of Ouchi et al. [20] using the relation 
\( D_\varphi = D_\alpha \exp (-Q/RT) \), with 
\( D_\alpha = 1.5 \times 10^{-4} \text{m}^2/\text{s} \) and the activation energy for lattice diffusion \( Q = 1.8 \times 10^5 \text{J/mol} \). At 1350°C, we find that 
\( D_\varphi = 2.4 \times 10^{-12} \text{m}^2/\text{s} \). Thus the ratio of grain boundary to lattice diffusivity \( (D_\varphi/D_\varphi) \) is 
\( 4 \times 10^8 \). Cottrell [19] has estimated the ratio to be \( 10^9 \) at a temperature of 0.6 times the melting point. Experiments [21] on polycrystalline zinc yields ratios of \( 10^6 \) while theoretical analysis shows that this ratio is larger than \( 5 \times 10^4 \). Thus, the grain boundary diffusivity (\( D_\varphi \)), obtained using the Livingston and Cahn analysis is much higher than that of the average grain boundary diffusivity and perhaps only special grain boundaries with high \( D_\varphi \) play a major role in the DC process. When titanium is assumed to be the rate controlling species a value of \( D_\varphi = 9 \times 10^{-4} \text{m}^2/\text{s} \) is obtained. No value of \( D_\varphi \) for titanium at 1350°C is available to compare with \( D_\varphi \). If niobium and manganese are assumed to be the rate controlling species, the experimental value of \( (c_r - c_\text{Mn}) \), required in equation (1) and tabulated in Table 1, are indistinguishable from zero because of experimental scatter. Hence no value of \( D_\varphi \) can be calculated for Mn and Nb. It may be mentioned here that if the rate controlling species is Al it occupies antisite positions in the Ti-Al lattice, Mn occupies the Al sublattice and Nb occupies the Ti sublattice [22].

**Velocity of CC**

In the present case, CC was observed in the central regions of the lamellar colonies. We can estimate, using a simple diffusion analysis, that the average distance that an aluminium atom can move, at 1350°C is the square root of twice the product of \( D_\varphi \) and time. This distance, for an annealing time of 600 s, is \( 53 \mu \text{m} \). Thus, considerable CC can also occur, in addition to DC, since this average distance is large compared to the primary interlamellar spacing (1 \( \mu \text{m} \)).

**SECTIONING EFFECTS**

The effect of sectioning on the measurement of the interlamellar spacing reported in this manuscript has been shown by Underwood [23] to be governed by the relation that the mean true spacing (m.t.s) is equal to twice the mean random spacing (m.r.s.). By a measurement of several spacings using a test line randomly applied to the microstructure the m.r.s can be determined and m.t.s calculated. This procedure was used in the present analysis.

**EXTREME PRINCIPLES FOR COARSENING RATIO**

The coarsening ratio \( r \) equal to \( \pi_2/\pi_1 \) at both 1350 and 1420°C varies from an average of 100 to as much as 1000. The maximum velocity criterion proposed by Zener [24] predicts that the ratio \( r \) is 2 for lattice diffusion and 1.5 for grain boundary diffusion. The maximum rate of entropy production criterion [25], proposed by Puls and Kirkaldy, predicts that \( r \) is equal to 3 for lattice diffusion and equal to 2 for grain boundary diffusion. Our results and those of Livingston and Cahn show that \( r \) is much larger than the maximum predicted value of three from either the maximum velocity or maximum entropy criterion. Studies on discontinuous precipitation, discussed by Doherty [26], also show that the experimental value of \( r \) is larger than that which is theoretically predicted. It is possible that, as in dendritic growth, a new stability criterion must be invoked in order to explain the experimental results. From Livingston and Cahn these include the results that \( r \) is independent of temperature, can vary strongly from system to system, and can vary with \( \pi_1 \).

**CONCLUSIONS**

The thermal stability of the lamellar structure of as-cast Ti-48Al-2Mn-2Nb has been investigated and it is found that:

1. Annealing at 1200°C results in the dissolution of the \( \alpha \) phase, the final microstructure consisting of equiaxed \( \gamma \) grains with a small volume fraction of \( \alpha_2 \) phase.
2. Annealing at 1350°C even for times as short as 10 min resulted in continuous and discontinuous coarsening of the lamellae. As a result of discontinuous coarsening (which often originated at the sample surfaces), the initial (primary) lamellar structure was converted to an irregular, branched (secondary) lamellar structure with an average interlamellar spacing a hundred times larger than the primary interlamellar spacing. The secondary lamellae are formed approximately normal to the local growth front.
3. TEM analysis of the microstructures developed from continuous coarsening shows that it occurs at the termination of lamellae and in areas in the central regions of the lamellae that are faulted.
4. The two commonly used extremum criteria of maximum velocity and maximum rate of entropy production predict that the ratio of secondary to primary interlamellar spacing after DC should not be greater than three, in sharp disagreement with the present experimental observations.
5. There is a marked effect of lamellar orientation on DC with some lamellar colonies completely un-
affected while surrounding areas are highly coarsened.

6. The difference between the velocity of DC at 1350 and 1420°C is small.

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