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Thermal stability in the Al-Al_3Ti system

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Directionally solidified samples of an Al-2 wt% Ti alloy were annealed at temperatures between 435° C and 660° C to investigate the thermal stability of phases formed during an incomplete peritectic transformation. The proportion of Al_3Ti present in the as-solidified alloy is less than equilibrium up to about 480° C, and more than equilibrium at higher temperatures. Hence, Al_3Ti particles will be stable up to about 500° C and will tend to dissolve at higher temperatures. Diffusion due to non-equilibrium composition of the α phase continues at all temperatures but is sluggish up to about 600° C. The diffusion coefficient of Ti in Al at 635° C is estimated to be 2×10^{-11} cm^2 sec^{-1}.

1. Introduction

The peritectic reaction provides the opportunity for the development of alloys with reinforcing phases stable at elevated temperatures, since the primary phase forms at temperatures that may be well above the melting point of the matrix phase. However, the departure from equilibrium which is typical of peritectic solidification can result in extensive solute diffusion as equilibrium is attained at lower temperatures and this could reduce the stability of a desired phase distribution. The opportunity was therefore taken, following studies of the Al–Al_3Ti peritectic reaction [1, 2], to observe the thermal stability of the constituent phases. The thermal stability of Al_3Ti is relatively unknown. The only data is supplied by Fink *et al.* [3], who annealed a 0.75% Ti alloy* at 662° C for five hours and produced completely spheroidized Al_3Ti particles. The stability of the Al–Ti alpha solid solution has been studied more extensively [5–10].

In Al–Al_3Ti alloys the high melting point Al_3Ti forms primary plate-like dendrites in a matrix of alpha solid solution [2]. At 665° C (see Fig. 1) an incomplete peritectic reaction produces a thin envelope of alpha of composition 1.15% Ti enclosing each primary particle. Subsequent thickening of the peritectic envelope occurs by a diffusion controlled peritectic transformation as temperature and composition change down the alpha solidus towards 661° C and 0.15% Ti, giving the curve of Fig. 3a. In unidirectional solidification the amount of alpha phase formed in this way was found to be minor, most of the alpha being formed by a simultaneous advance of a separate interface at 661° C at which the liquid freezes directly to alpha containing 0.15% Ti [1]. This forms the matrix alpha seen in Fig. 2a. The Al_3Ti composition (37.5% Ti) is independent of temperature, so there is no appreciable composition variation through the thickness of the primary platelets. Because the peritectic transformation does not occur to any significant extent, the proportion of Al_3Ti in the solidified alloy is found by using the lever rule just above the peritectic temperature rather than below. This means that in the as-solidified alloy of composition 2% Ti, there is approximately 5% Al_3Ti.

2. Experimental procedure

For the thermal stability experiments samples were cut from a rod of 2% Ti alloy which had been unidirectionally solidified at 5 μm sec^{-1}. In this alloy the plate-like Al_3Ti particles were coarse and widely separated (Figs. 2a and 4a), so that composition gradients adjacent to and between particles could be clearly observed. Separate samples were annealed for 24 hours at 435, 535, 635 and 660 ± 5° C. After the anneal each sample was deep-etched in a solution of

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*All compositions and phase proportions are given in wt%.

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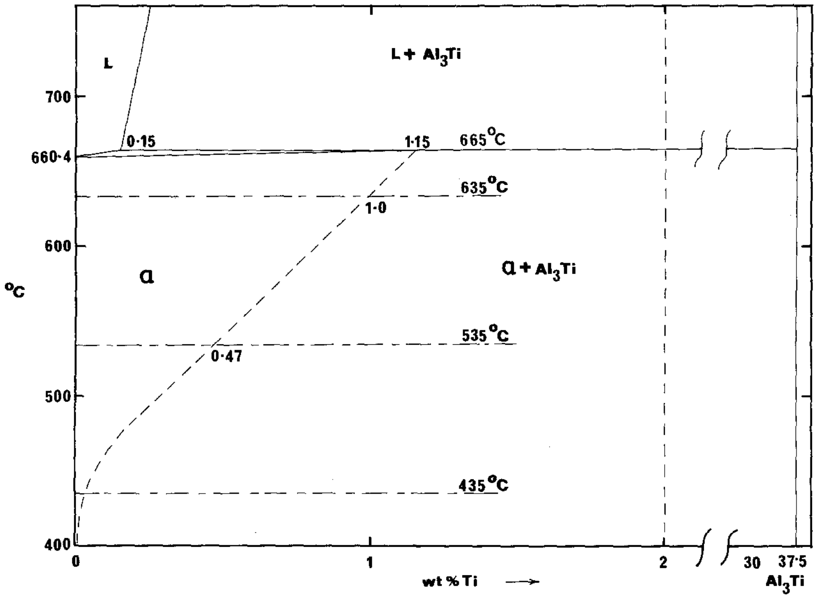

Figure 1 Relevant portion of the Al–Al_3Ti phase diagram (from [6]), showing temperatures at which the as-cast samples were annealed.

HCl (50 ml), HNO_3, (25 ml), $CuCl_2$ (1 gm) and H_2O (150 ml). The etch is very sensitive to Ti content so that the main body of the alpha is most heavily attacked and the peritectic envelope, enriched in titanium relative to the matrix, appears in relief as a layer attached to each Al_3Ti platelet (Fig. 2, a to d). The Al_3Ti is not attacked. Between the primary plates the matrix concentration is approximately uniform except for Ti depletion at the cellular dendrite boundaries, which again is clearly revealed by the etch. Within the peritectic envelope the height above the matrix increases with Ti concentration, to a maximum at the interface with Al_3Ti. This Ti distribution was confirmed by the microprobe analysis profile shown in Fig. 3a. Changes on subsequent annealing are recorded in Figs. 3b, c and d and correlate with Figs. 2b, c and d. The curves were obtained by spot analyses on polished cross-sections at 1 μm intervals, along a line normal to the Al_3Ti-α interface. Each point was obtained from a 100 second count of a spot $\simeq 1\ \mu$m diameter with a JEOL 50A electron probe microanalyser. The measured compositions, after correction, were accurate to within ± 4%, e.g. 0.5 ± 0.02% Ti.

3. Al_3Ti stability

In order to investigate the thermal stability of Al_3Ti it was necessary to look for changes in shape of the Al_3Ti particles during annealing. For this purpose the photographs of Fig. 4 show Al_3Ti platelets almost detached by the deep etch, so that the edge contours are clearly visible. The as-solidified platelet in Fig. 4a shows a flat (0 0 1) surface with faceted edges parallel to (0 1 0) and (1 0 0). This is the typical configuration of large Al_3Ti dendrites [2]. Shape changes may occur on re-heating due to dissolution of the Al_3Ti or a tendency to form spheroids, and should first become visible as a rounding of the edge facets. The facets remain sharp in Figs. 4b and c, annealed at 435° C and 535° C respectively, indicating stability at these temperatures. In Fig. 4d, annealed at 635° C, there is a pronounced rounding of the edge facets. (In this sample the dendritic origin of the plates is also much more apparent). In Fig. 4e, annealed at 660° C, the edge facets have almost completely disappeared, but it is also apparent that the nominal annealing temperature was exceeded, since the Al-rich matrix has melted and re-solidified (see also Fig. 2e).

From this evidence it can be anticipated that small particles of Al_3Ti in Al-rich matrix would be stable up to about 500° C but would start to spheroidize towards 600° C. Application of the lever rule in Fig. 1 indicates that below approximately 480° C there should be no tendency for dissolution of Al_3Ti, since the equilibrium proportion of Al_3Ti within the two-phase region increases with falling temperature. However, in

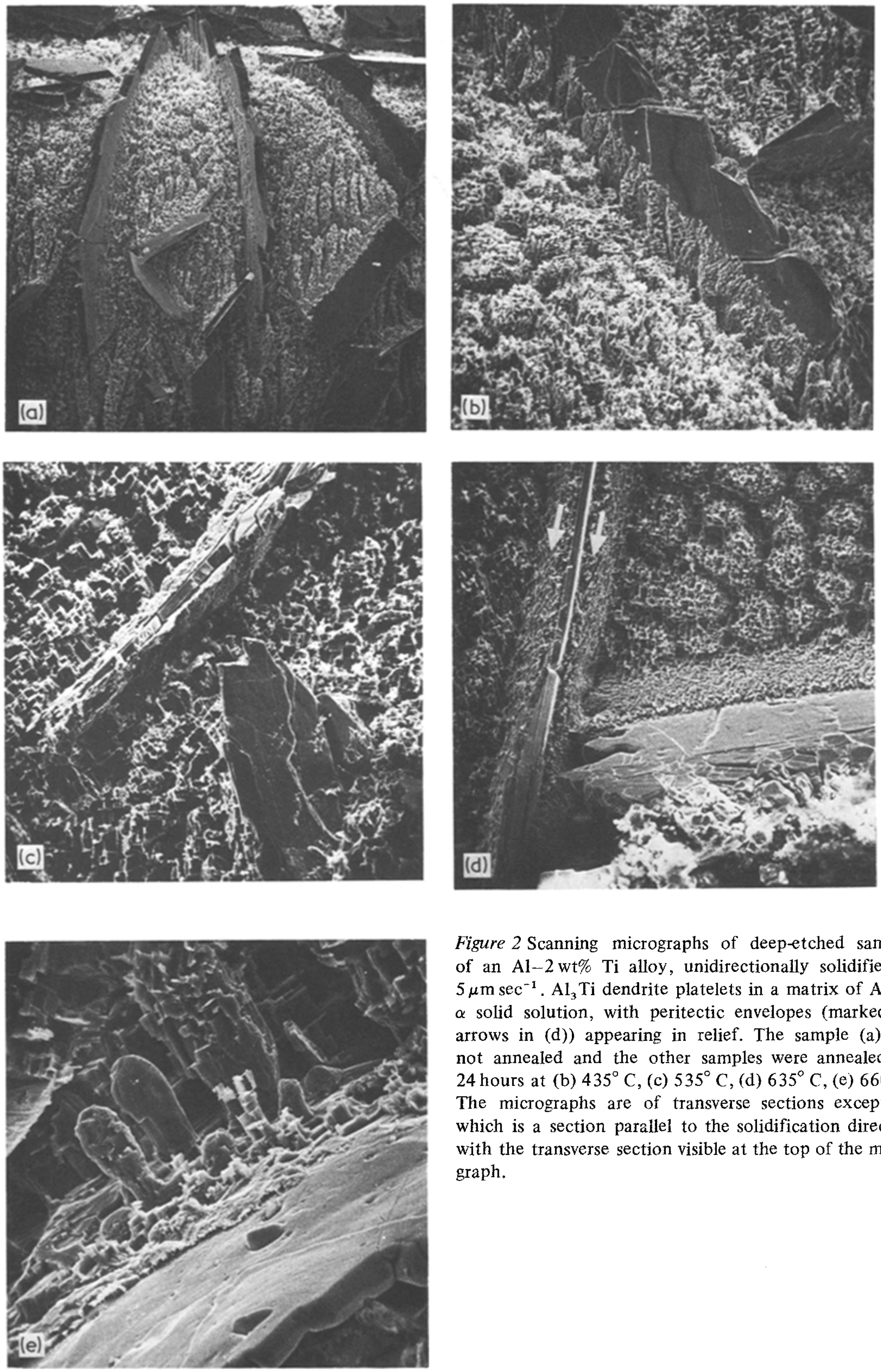

Figure 2 Scanning micrographs of deep-etched samples of an Al–2 wt% Ti alloy, unidirectionally solidified at 5 μm sec^{-1}. Al$_3$Ti dendrite platelets in a matrix of Al–Ti α solid solution, with peritectic envelopes (marked by arrows in (d)) appearing in relief. The sample (a) was not annealed and the other samples were annealed for 24 hours at (b) 435° C, (c) 535° C, (d) 635° C, (e) 660° C. The micrographs are of transverse sections except (a) which is a section parallel to the solidification direction with the transverse section visible at the top of the micrograph.

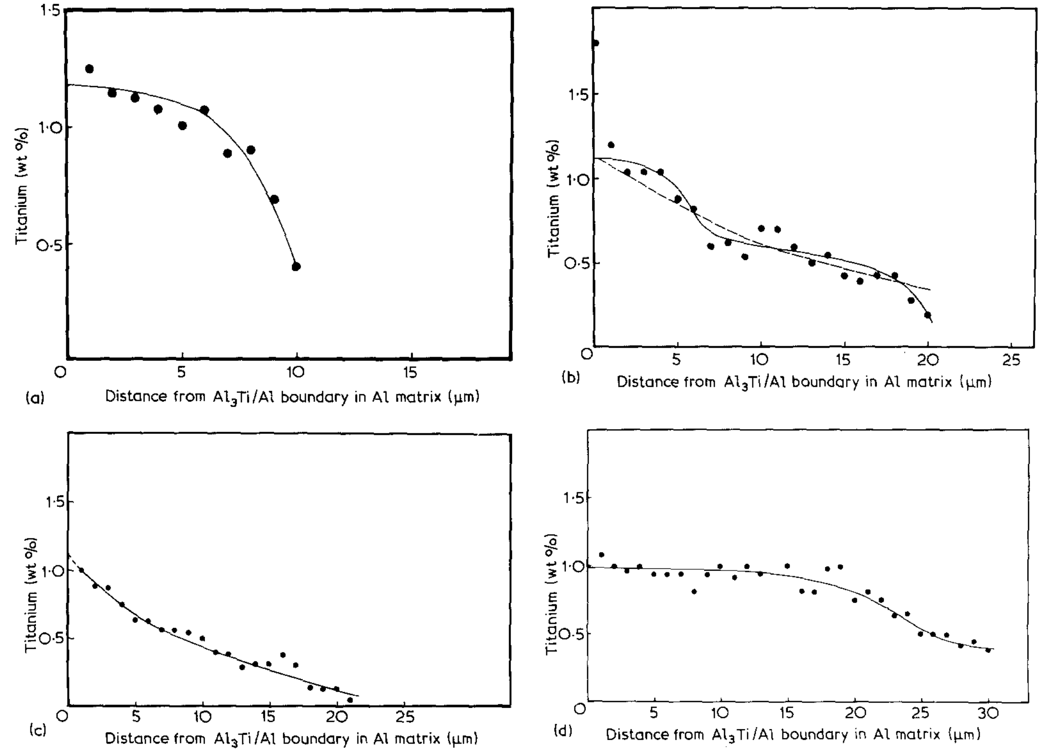

Figure 3 Microprobe analysis profiles take from the Al_3Ti/Al boundary into the Al matrix to show the effects of annealing on the peritectic envelope: (a) no anneal, (b) 435° C, (c) 535° C, (d) 635° C.

the temperature range 480° C to 665° C, the peritectic temperature, the equilibrium amount of Al_3Ti is actually less than the amount formed in the initial solidification, 5% Al_3Ti. The observed rounding of facets in this region is therefore attributed to the dissolution of Al_3Ti combined with a tendency to a reduction of interfacial energy by spheroid formation.

4. Stability of Al–Ti solid solution

The photographs of Fig. 2 were taken to show the cellular-dendritic structure of the Al-rich matrix between the Al_3Ti primary plates, as well as the form of the peritectic envelopes. Cells of about 70 μm diameter evident in the as-cast sample of Fig. 2a persist in Fig. 2d, indicating that homogenization was incomplete after 24 hours annealing at 635° C. However, annealing at each temperature produced substantial changes in the shape of the peritectic envelope which can be understood by reference to Figs. 1 and 3.

Fig. 3a shows the Ti distribution in the peritectic envelope which appears in relief in Fig. 2a. The adjacent cellular matrix was shown in other measurements [1] to have an average composition of 0.15% Ti, which is the limit of solubility of Ti in Al at the peritectic temperature. After annealing for 24 hours at 435° C (Figs. 2b and 3b) the maximum titanium content in the peritectic envelope remained unchanged at about 1.15% Ti, but the concentration gradient was flattened, in an uneven fashion, by diffusion of Ti into the alpha matrix. This is an approach to homogenization, but at 435° C the solubility of Ti in Al is almost zero (Fig. 1), so that the alpha in both envelope and matrix is supersaturated. Precipitation of Al_3Ti should occur, but was not observed. This is in accord with Asboll and Ryum [5] who annealed supersaturated solutions in this temperature range and did not detect Al_3Ti precipitates by electron microscopy until after 24 hours of anneal. They attributed this sluggishness in decomposition to a difficulty in nucleating the Al_3Ti phase. This may be true, but in the present experiments the supersaturated alpha was in contact with primary Al_3Ti, so that precipitation on these surfaces could have occurred without the necessity for fresh nucleation, assisted by the increase in equilibrium proportion of Al_3Ti from 2.7% at 665° C to 5.3% at 435° C. It is clear that there

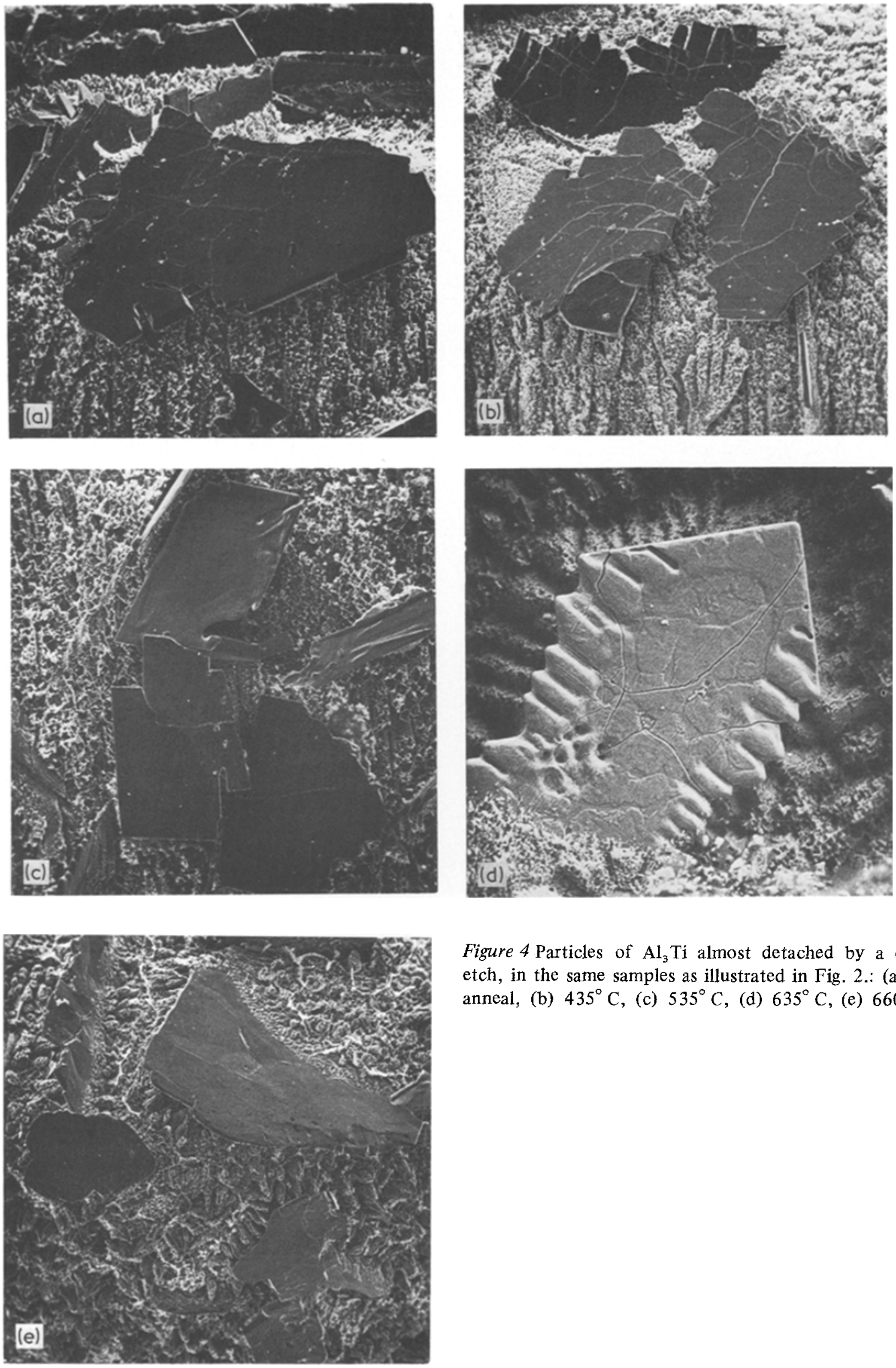

Figure 4 Particles of Al_3Ti almost detached by a deep etch, in the same samples as illustrated in Fig. 2.: (a) no anneal, (b) 435° C, (c) 535° C, (d) 635° C, (e) 660° C.

was no such precipitation, since the facets on the primary particles remained sharp and the Ti concentration in the alpha at the Al_3Ti interface remained close to 1.15%, the peritectic composition. The formation of additional Al_3Ti would first require a local change in alpha composition from 1.15% to 37.5% Ti, so that deposition onto the primary Al_3Ti surface would severely deplete the adjacent alpha in Ti. It would appear that the barrier to Al_3Ti precipitation is this necessity for a very large change in local composition, combined with the slow diffusion rate of Ti in Al. The fluctuations evident in the diffusion curve of Fig. 3b are probably due to clustering of Ti atoms prior to precipitation. Fig. 2c also indicates clustering of Ti atoms as the Ti-rich envelope of Al–Ti α solid solution is no longer smooth or of uniform width along the Al_3Ti platelet edges, as in Figs. 2a, b and d, but appears lumpy and irregular. It is known [6] that Al_3Ti precipitation will occur on long holding in this temperature range and the alpha solid solution must be regarded as metastable, although its mechanical properties may not vary significantly. Asboll and Ryum [5] observed no variation in hardness during precipitation.

When the as-cast sample was annealed at 535° C a much smoother diffusion curve resulted (Fig. 3c). At this temperature the saturated alpha solid solution contains 0.47% Ti, so that there is a driving force for diffusion from the Ti-rich envelope to increase the Ti content of the matrix above 0.15%. The Ti content at the Al_3Ti interface was only slightly reduced, consistent with sluggish diffusion. Any tendency to Al_3Ti precipitation should be confined to the Ti-rich envelope, but no precipitation was observed. It can be anticipated that the diffusion flow would continue on long holding at this temperature and that Al_3Ti dissolution would eventually occur to reduce the Al_3Ti phase towards its equilibrium proportion of 4.2%.

Annealing at 635° C produced a quite different solute distribution (Fig. 3d). The Ti-rich envelope is extended to about twice the original thickness, as is also evident in Fig. 2d, and the Ti level within the envelope is reduced to the equilibrium concentration of approximately 1% (Fig. 1). It is apparent that the diffusion rate at this temperature is sufficient for a relatively stable condition to be reached during the 24 hour anneal. The increase in thickness of the envelope implies that the extra Ti is coming from the Al_3Ti which is dissolving at the Al_3Ti/α interface. The equilibrium proportion of Al_3Ti is about 2.7%, or roughly half the proportion present at the start of the anneal. The rounding of facets evident in Fig. 4d is further clear evidence of dissolution of the Al_3Ti. More extensive rounding is observed in Fig. 4e where the temperature exceeded 660° C and the Al_3Ti was in contact with liquid metal during the anneal. The actual temperature of the anneal must have been above 660° C because the Al–Ti solid solution melted, and on cooling resolidified onto the Al_3Ti platelets as shown in Fig. 2e. At the anneal temperature there should be no appreciable tendency for any change in the proportion of Al_3Ti and the rounding is attributed to surface area reduction. In this sample microprobe profiles through the alpha phase were not relevant, since the alpha had remelted. As might be expected from Fig. 2e the profiles observed were different for each position taken.

An approximate evaluation of the diffusion coefficient at 635° C can be obtained by comparing the profiles at the beginning (Fig. 3a) and the end (Fig. 3d) of the diffusion process. At time $t = 0$ the 635° C equilibrium composition occurs in Fig. 3a at about 6 μm from the interface. If we assume that the composition at this point remains constant during annealing at 635° C the solute flow is equivalent to diffusion across a fixed interface as Ti diffuses from the Al_3Ti surface and peritectic envelope to raise the matrix concentration above 0.15% Ti. A standard solution for Fick's Law for these conditions is

$$\frac{C_x - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (1)$$

where $C_s = 1\%$ Ti, being the composition at the interface, $x = 0$, chosen as a plane 6 μm from the Al_3Ti platelet surface, $C_0 = 0.15\%$ Ti, being the initial composition at a point x in the matrix (as determined in [1], Fig. 5). The point x is chosen as $x = 14\,\mu$m (20 μm from the Al_3Ti in Fig. 3a). $C_x = 0.75\%$ Ti, being the final composition at $x = 14\,\mu$m after annealing at 635° C for time $t = 24$ hours.

Equation 1 yields a value of 2×10^{-11} cm^2 sec^{-1} for the diffusion coefficient of Ti in Al at 635° C. This value compares favourably with the values of 2.7×10^{-11} cm^2 sec^{-1} for Zr in Al at 635° C [11] and 2.03×10^{-11} cm^2 sec^{-1} for Co in Al at 635° C [12].

5. Conclusions

The thermal stability of phases has been observed in an Al–2wt% Ti alloy.

(a) Al_3Ti particles are stable for a holding time of 24 hours, up to a temperature of about 500° C. Above 500° C there is a tendency towards spheroid formation.

(b) In the alpha solid solution intercellular microsegregation persists after annealing for 24 hours at 635° C. Pronounced concentration gradients between peritectic envelopes and the matrix alpha lead to substantial redistribution of the dissolved Ti, the nature of which is dependent on the annealing temperature. Solute redistribution was still in progress after 24 hours at any temperature, but an approach to homogeneity was achieved at 635° C.

(c) Al_3Ti precipitation is required for equilibrium at the lower temperatures, but was not observed. It was concluded that the large composition change required in the alpha phase prior to precipitation, combined with very slow diffusion rates, makes precipitation difficult.

(d) An approximate value for the diffusion coefficient for Ti in Al at 635° C was found to be 2×10^{-11} cm^2 sec^{-1}.

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