Fine alpha in current and newly developed Ti alloys

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M. Wang[1], Y. Lu[1,] B. Pang[1], Z. T. Kloenne[2], H. L. Fraser[2], Y. L. Chiu[1], M. H. Loretto*[1]

[1]Metallurgy and Materials, The University of Birmingham, Edgbaston, B15 2TT,
[2]Center for the Accelerated Maturation of Materials, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43212

M.Wang.8@bham.ac.uk; Y.Lu.2@bham.ac.uk; b.pang89@hotmail.com; kloenne.2@buckeyemail.osu.edu; fraser.3@osu.edu; y.chiu@bham.ac.uk; M.H.Loretto@bham.ac.uk

Abstract

Analytical transmission electron microscopy has been used to determine the chemical compositions of beta grains in samples of HIPped powder Ti6Al4V, cooled in the HIP at approximately 5°C/min in order to understand their different microstructures. It has been found that beta grains, which contain a high density of fine secondary alpha phase, have compositions (wt%) of about 81%Ti; 3%Al; 14%V and 2%Fe. This analysis includes both the fine secondary alpha and the beta in the grain and thus corresponds to the composition of the parent beta grain. Grains of retained beta, which do not contain any fine secondary alpha, are stabilised by a much higher V-content and contain about 75%Ti; 3%Al, 20%V and 2%Fe. The diffraction patterns from the grains that contain secondary alpha show maxima from several habits of alpha as well as beta maxima, whereas the beta grains, which contain no secondary alpha, show only beta maxima together with diffuse scattering. These observations provide the data needed to understand the factors that lead to the different microstructures observed in beta grains in slowly cooled HIPped powder Ti64 and suggest that an alloy, of a composition close to that of the beta grains in Ti64, which contain fine secondary–alpha, should also contain a large fraction of fine alpha, when slowly cooled. This has been confirmed and the microhardness of slowly cooled samples has been shown to be higher than that of air-cooled Ti64.

*Corresponding author MH Loretto. Email M.H.Loretto@bham.ac.uk.
Phone +44 121 414 5214 FAX +44 121 414 7890

Introduction

A considerable amount of work has been published, where it has been reported that fine and coarse secondary alpha can be formed in transformed beta grains when Ti alloys are cooled after high temperature processing. [e.g 1, 2, 3,4]. Collins et al [3] showed that the fraction of secondary alpha in functionally graded Ti-V alloys, prepared using a LENS™ facility, increased with V-content, until at about 20wt%V when the alloy was fully beta. The hardness increased as the fraction of secondary alpha increased. In the case of Ti64, it was shown in [2] that cooling at 0.1°C /min, from above the transus to 700°C, followed by cooling at 5°C/min resulted in a microstructure in which many of the beta grains contained fine secondary alpha. More recently Lu et al [5] have studied the role of cooling rate on the nature of the secondary alpha in HIPped powder Ti64 and have found that slow cooling at about 5°C /min from below the transus resulted in the formation of a small fraction of fine secondary alpha. This small fraction of fine secondary alpha does not lead to significant strengthening. In contrast, Lu et al [5] showed that air cooling Ti64 from just below the transus, where the rate of cooling varies from about 600°C/min to 200°C/min, leads to a very high fraction of coarser secondary alpha and to significant improvements in properties. Cooling at this rate limits the section size of components that could be heat treated in this way to improve properties. The long-term aim of the current research is to develop a solution to this limitation, and consists of three tasks. Firstly, to understand the factors that lead to the formation of some grains which contain fine secondary alpha in slowly cooled Ti64, secondly, to use that information to design an alloy which should contain a high fraction of fine alpha on slow cooling and thirdly, to assess the mechanical properties of this new alloy. This paper covers the first two aims.

Experimental

The Ti64 alloy used was supplied by TLS as powder of composition shown in Table 1, which was HIPped (Hot Isostatically Pressed) in an EPSI Lab facility at 930°C for 4h at 100MPa and slowly cooled in the HIP at about 5°C/min.

Table 1 Chemical analysis (wt.%) of EIGA (Electrode Induction-melting Gas Atomisation) powder supplied by TLS.

	Al (%)	V (%)	Fe (%)	C (%)	H (ppm)	N (%)	O (%)	Ti (%)
Sample	6.31	3.92	0.19	0.012	34.8	0.013	0.10	Bal.

Analytical transmission electron microscopy was carried out at 200kV on a JEOL 2100, which was interfaced to an INCA EDX system and on a Thermo Fisher Scientific Talos F200X with a Super-X EDS system operating at 200kV. Scanning electron microscopy (SEM) was carried out using a TESCAN MIRA-3 (SEM) equipped with an Oxford Instruments XMax silicon drift detector (SDD) for energy dispersive X-ray spectroscopy (EDS), which was operated at 10kV. A focused ion beam SEM (FIB/SEM, FEI Quanta 3D FEG) was also used to prepare TEM specimens from specific positions.

Results

Electron microscopy observations

A typical SEM image of an as-HIPped sample cooled in the HIP at about 5°C/min is shown in Figure 1, where the bright phase is beta. The beta is present in three different forms. It is present as thin regions of interfacial beta, which are the remnants of the beta grains that were present at the HIP temperature and is also present as two different types of roughly equiaxed regions at triple points; some are featureless, whereas others clearly contain a second phase. High magnification images of the thin regions of interfacial beta do not reveal any further structure, but as shown in Figure 1(b) there is fine secondary alpha present in the beta at triple points, but this is not observed at all triple points. The grains that contain secondary alpha show bright contrast along their boundary with alpha. Similar observations have been made earlier [e.g. 2]. In this SEM image, it appears that fine secondary alpha is not present in the whole of the equiaxed beta grain, but closer inspection reveals faint contrast throughout this beta grain. The region shown in Figure 1(b) has been excised using a dual beam FIB and examined in the Talos. The TEM section shown in Figure 2 taken from the dashed rectangle in Figure 1(b) confirms that fine secondary alpha is present in the whole of this beta grain.
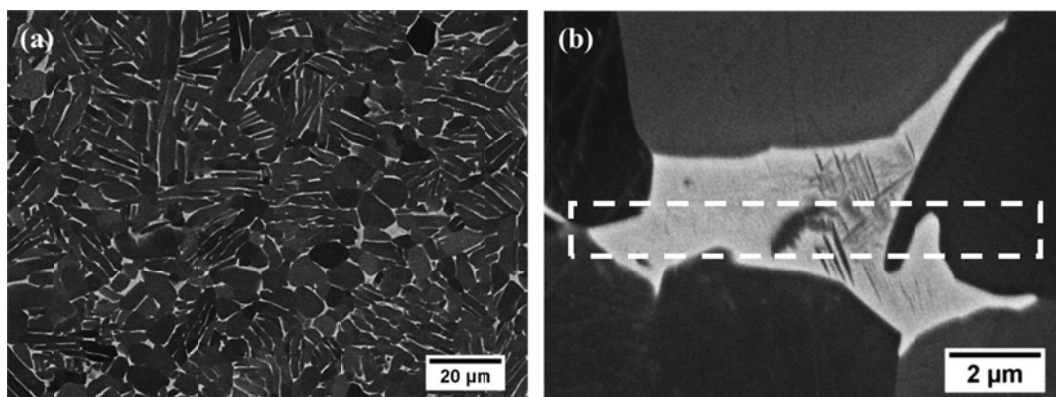

Figure 1 (a). Back scattered SEM image of Ti64 powder, HIPped at 930°C for 4h at 100MPa and cooled in the HIP at about 5°C /min. (b) High magnification of a region of beta, which contains fine secondary alpha. The dashed rectangle indicates the position of the vertical section that was prepared for TEM (see below)

Importantly, as noted above some beta grains do not contain any fine secondary alpha. Areas of beta, which contain fine secondary alpha and areas of beta that did not contain any fine secondary alpha, have been examined using analytical transmission electron microscopy.

A TEM high-angle annular dark-field (HAADF) image of the beta grain, that contains fine secondary alpha, is shown in Figure 2, together with composition maps for V, Al and Fe. It is clear from the HAADF image and from the EDX maps that the composition of the secondary alpha laths is different from that of the beta between the alpha laths, so that there is clearly time for some diffusion to take place during this transformation.

Figure 2. (a) HAADF image of a grain of beta containing fine secondary alpha. (b), (c) and (d) EDX maps for V, Al and Fe.

Quantitative EDX analysis has been carried out on this region and on grains of alpha and of beta that did not contain any secondary alpha. Area scans were carried out on the beta grains that contain secondary alpha, so that the composition of the parent grain could be obtained. Additionally, analyses were carried out on individual alpha laths and the beta between laths. The results are shown in Table 2.

Table 2 showing TEM/EDX analyses (wt%) of the structures in a sample of Ti64 cooled at 5°C/min after HIPping at 930°C for 4h at 100MPa. The table also shows the measured scatter of compositions of primary alpha grains.

Area in grain which contains secondary alpha	Ti	V	Al	Fe
β grain with no fine secondary α	74.46	20.53	2.87	2.14
β grain with fine secondary α	80.95	13.53	3.71	1.81
Secondary α laths in β grain	91.68	2.94	5.16	0.22
β between secondary α laths	75.28	19.54	2.66	2.42
α matrix grain	89.85	2.89	7.15	0.11
Average of β grains containing secondary α	81.1	13.5	3.6	1.8
Measured scatter of compositions of alpha grains				
Analyses carried out in different grains and in different positions within individual α grains.	88.8 to 90.3 ± 0.3	2.5 to 3.4 ± 0.2	6.9 to 8.2 ± 0.2	0 to 0.3 ± 0.1

In addition, as shown in the Table 2, the variability of the composition of alpha grains has been measured in order to assess the significance of any differences observed between the measured composition of the fine alpha laths and of primary alpha grains. The difference in Al-content in alpha grains and in the fine alpha laths is in fact significantly larger than the scatter between the Al-contents within alpha grains, whereas the V and Fe-contents of fine alpha laths are within the range found in alpha grains and are therefore not significant. The most obvious difference between beta grains that contain fine secondary alpha from those that do not, is the very high V-content of the grains free of secondary alpha, but differences in Al and Fe-contents are not significant. Similarly the analyses of beta between the fine alpha laths do not differ significantly from that of beta grains that contain no alpha.

Line scans were also taken from beta grains that contained secondary alpha, and ones that did not, to adjacent alpha grains, as shown in Figures 3 and 4. The profiles shown in Figures 3 and 4 are very different, with diffusion causing broadening of the profiles in Figure 3 taken from the beta grain that contains fine secondary alpha, in contrast to the sharper composition profile across the boundary of the beta grain that contains no secondary alpha. It should be noted that the profiles will be influenced by the inclination of the different boundaries to the electron beam and the differences in these profiles may be influenced by this factor. However the interface between the alpha/beta grains that contain secondary alpha shows very different contrast from the interior in back scattered images (see figure 1(b)). No such difference is observed on the alpha/beta interface in the beta grains that contain no secondary alpha. On that basis the different EDX profiles are caused, at least in part, by different composition gradients.
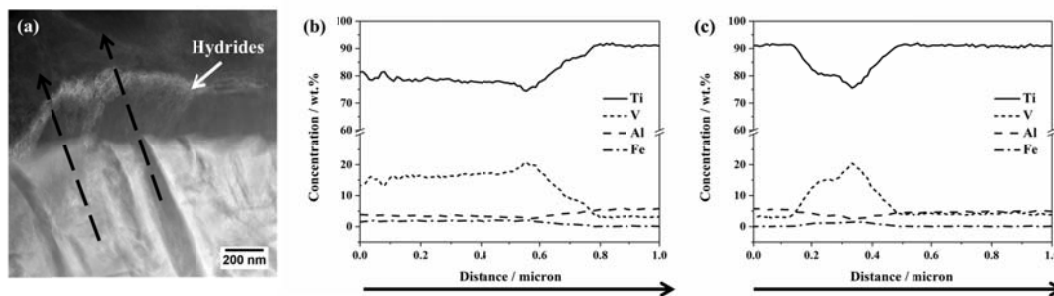
Figure 3 (a) HAADF image of a grain that contains fine secondary alpha. EDX line traces taken (b) along a region of beta in the beta grain to the adjacent alpha matrix (left hand arrow) and (c) along an alpha lath within the grain to the adjacent alpha matrix grain. Arrows show scan positions and directions. Hydrides are also arrowed.

Attempts were made to analyse the interfacial region between the beta grains that contain secondary alpha and the adjacent grains, which as shown in Figure 1(b) show bright contrast in back scattered images. No useful data could be obtained, but the profiles provide information about the difference in the extent of diffusion across the interface in the beta grains, which do or do not contain fine secondary alpha.
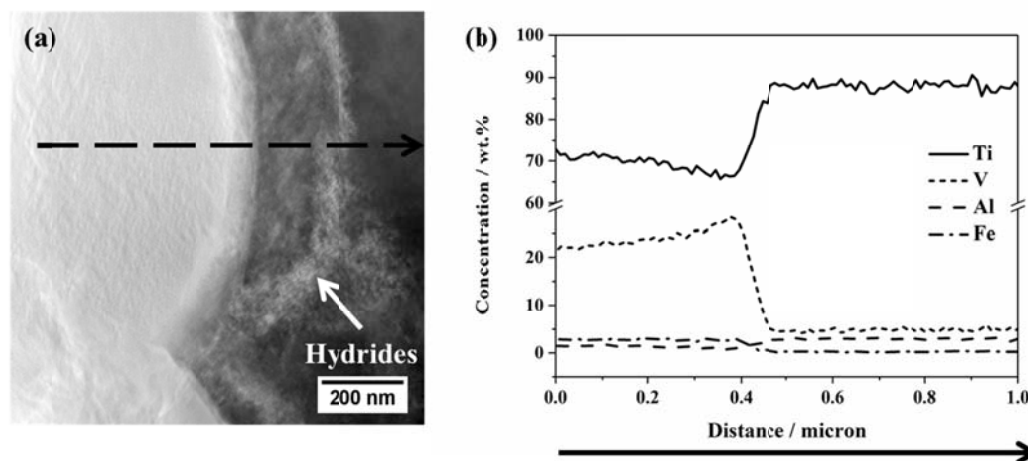
Figure 4 (a) HAADF image of a beta grain that contains no fine secondary alpha. (b) EDX line traces taken from the beta to the alpha. Arrows show scan positions and directions. Hydrides are also arrowed.

In addition to the EDX data, diffraction patterns and dark field images using selected diffracted beams were obtained from the beta grains that contained secondary alpha and from the beta grains that contained no secondary alpha. Diffraction patterns and a dark field image, obtained from a grain that contained secondary alpha, are shown in Figures 5(a) and (b).

As expected the pattern, shown in Figure 5(a), which was obtained using a small diffraction aperture that covered several alpha laths and the inter-lath beta is complex and obviously as well as beta maxima, shows maxima from several habits of alpha. The dark field image shown in Figure 5 (b) using closely spaced alpha reflections, confirms that the pattern contains maxima from alpha.
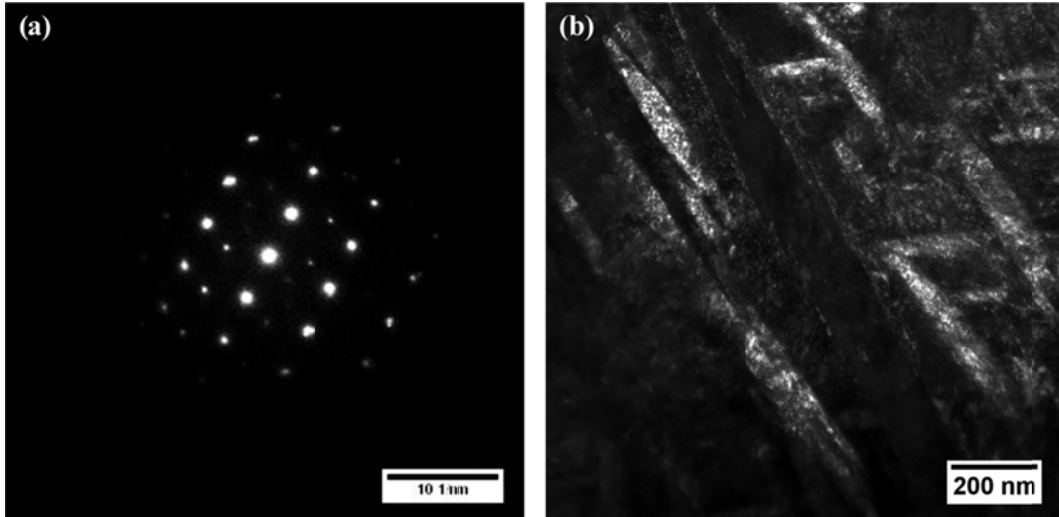
Figure 5 (a) Selected area electron diffraction pattern taken along <110> beta from a grain containing secondary alpha; (b) dark field image taken using alpha reflections.

Diffraction patterns have also been taken from regions of beta that did not contain any secondary alpha, as shown in Figure 6. Diffraction patterns were taken using either a small probe to define the area precisely or, to obtain patterns with higher angular resolution an aperture was used to define the area and a defocussed beam used.

Figure 6 (a) Microdiffraction pattern and (b) selected area pattern taken from a beta grain that contained no fine secondary alpha.

These patterns contain diffuse scattering, which is more obvious in Figure 6 (a) and attempts have been made to obtain dark field images from the diffuse scattered intensity, but no useful

images could be obtained . This diffuse scattering was not obvious in the grains that contained secondary alpha, but with 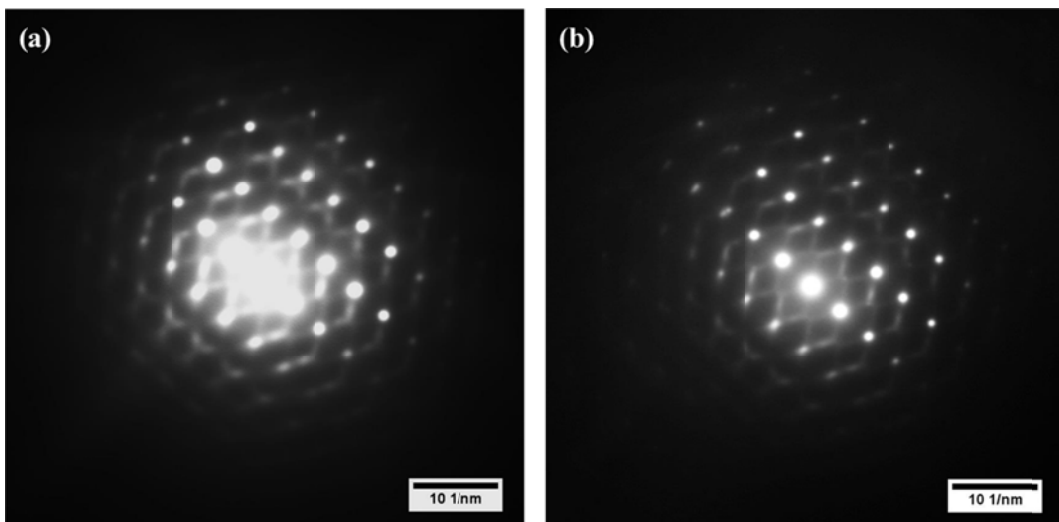the complex patterns obtained with several habits of alpha and the matrix beta, it would be more difficult to observe any diffuse scattering.

Interestingly it has been observed in samples prepared using a FIB that beta grains that do not contain any fine secondary alpha commonly contain a high dislocation density as illustrated in Figure 7. The presence of dislocations is unfortunately quite common when using FIB, where beta is retained, but we do not know the source of these dislocations. In this connection the interfacial regions in figure 7 and in figures 3 and 4 show contrast similar to that seen in earlier work [6] where samples were electropolished, in what appeared to be an interfacial phase, but was in fact shown to be a region with hydrides [6]. Some hydrides can in fact be seen in figures 3 and 4
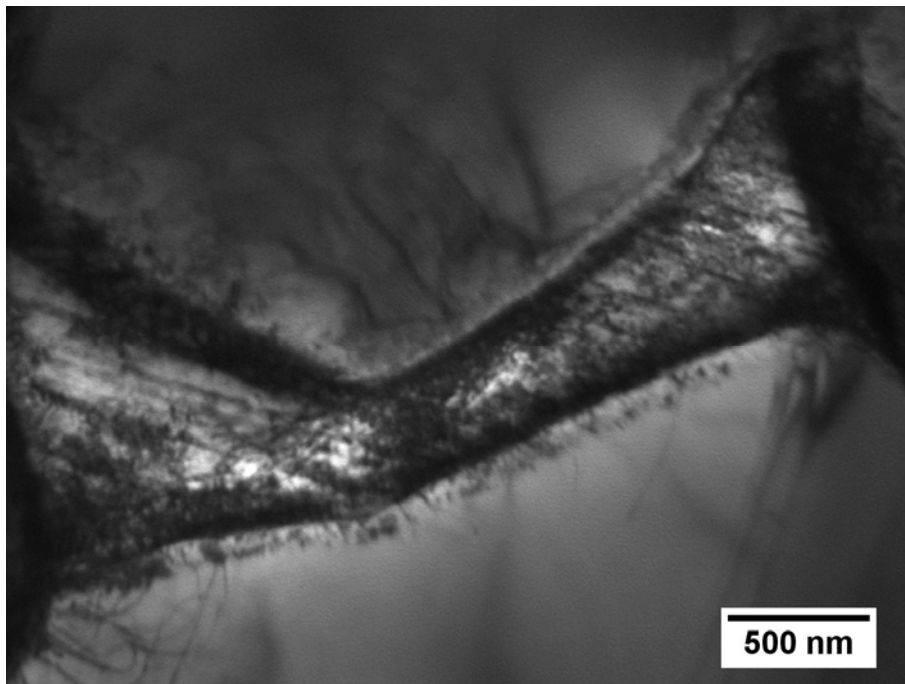
Figure 7 Many-beam bright field TEM image of a beta grain in Ti64V cooled at 5°C/min, showing a high density of dislocations. The sample was thinned using FIB. Note the diffuse contrast associated with the interface.

Discussion

The first aim of the work reported in this paper was to understand why different beta grains in slowly cooled Ti64 showed such different microstructures, varying from retained beta grains to beta grains that contain a high density of fine secondary alpha. The observations have shown that this difference is associated with the fact that the compositions of beta grains present after slow cooling powder-HIPped Ti64 can be very different, ranging in V-content from about 13wt% to over 20wt%. It is important to understand how these differences arise. It

should be noted that beta is preferentially polished away when samples are produced by electropolishing and the data obtained from beta grains has been taken from samples prepared using FIB. Only two or three grains have been analysed in addition to the beta within grains that contain fine alpha and presumably if more were analysed other beta grains of different mean compositions, which transform to form fine secondary alpha, would be found and/or the range of compositions of retained beta grains increased. The compositions of beta range from 19.5 to 20.5wt%, which is a significant difference. The analysis of parent beta grains, that form fine alpha internally, is influenced by the extent of the scanned area since for slight changes the amount of fine alpha contributing to the analyses would vary. It is thus not straightforward to detect small changes in the compositions of parent beta grains, which contain fine alpha. There is the possibility that powders produced by the EIGA process will have liquid droplets of different composition. Because of this possibility, HIPped AP&C plasma atomised, Tekna plasma atomised and spheroidised powders and of TIMET PREP powder have been examined, and it was found that they all have both types of beta grains; those that contain secondary alpha and those that are retained beta. It has also been suggested by one of the referees that the microstructures of powder particles can vary, with particles below 50μm containing no martensite and particles above about 150 μm containing only a limited fraction of martensite. Such differences could lead to significantly different behaviour during heating in a HIP, resulting in local compositional differences. It is not clear if these differences would be retained during the HIP cycle of 4h at 930°C, but we have confirmed that for our powders the structure of as-atomised powder appears to be fully martensitic over the whole size range we used, which was between 45 and 180μm. It is thus concluded that the different compositions are not produced during atomisation, but arise in the solid state during cooling from high temperatures. The way in which these composition differences arise during slow cooling is explained below.

The amount of retained beta when slowly cooling Ti64 from 930°C at 5°C /min has been measured recently as 11% on the same HIPped powder as used in the present work [5]. Calphad calculations[1] predict that about 4% of beta is the equilibrium amount at room temperature and that 11% of beta is present at 870°C. Assuming that Calphad calculations are not too far in error it thus follows that the proportions of alpha and beta present in Ti64 at 870°C are frozen in. However, it is clear that the composition of beta can change very significantly during cooling below 870°C since although some grains have about 13%V (the amount expected at 870°C), some have over 20%V, which corresponds to the equilibrium concentration at about 790°C. Because the fraction of alpha is about 90%, any diffusion

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[1] The calculations do not include the small Fe-content of the alloy and correspond to an alloy with 6wt%Al and 4wt%V, so that the temperatures discussed may be slightly different for this alloy.

to/from alpha from/to beta, which could cause detectable changes in the beta grains, would therefore not necessarily give rise to detectable changes in the alpha composition.

The fact that beta grains exist at 790°C which have very different V-concentrations, is clear evidence that diffusion occurs very differently in different volumes of a sample below 870°C. In some beta, the V-content increases by diffusion from the adjacent alpha, to 20wt% so that it forms retained beta, although the temperature at which it reaches this composition is not known. In other grains, of average V-content of about 14wt%, the composition of the beta between the alpha laths of 20wt%V is reached by diffusion within those grains, associated with the precipitation of fine alpha, but this must occur below about 760°C, the estimated transus of this alloy. It thus appears that the rate of diffusion of V from alpha to beta is very different in different beta grains, because some beta grains reach 20wt% by diffusion from the surrounding alpha and others by diffusion within the beta grain. The factors that could lead to the differences in the extent of diffusion, which underlie the different microstructures observed, are considered below.

There are several factors that could locally influence the diffusion rate. Thus, the work of Elmer et al [7] referred to above, showed that significant changes in unit cell volumes of beta occur during heating or cooling as the V-content changes, leading to high internal stresses, which, in the present work, may lead to a high dislocation content in some beta grains, as in Figure 7. If these are formed by internal stresses during cooling, rather than being introduced by electropolishing and/or FIB preparation of foils [6], they could change local diffusion rates; the extent of the influence depending upon the dislocation density. Diffusion will also be influenced by the misorientations between the beta and the alpha grains that replace the beta during cooling and by the corresponding structures of the boundaries, which migrate during the transformation. In addition the different curvatures of the interface between the alpha and beta could lead to compositional differences

These factors, different dislocation densities, different misorientations between different alpha and beta grains and the associated difference in boundary structure and curvature appear to be the factors which could lead to compositional differences between different alpha grains and between different beta grains. Because of their different stability during cooling, these differences in composition between beta grains lead to the different microstructures observed of retained beta grains and beta grains that contain fine secondary alpha. Thus it should be understood, that any initial small differences in V-content between different beta grains would tend to increase during cooling because any grain that has a slightly low V-content will have a higher transus and form some alpha in that grain, increasing the V-content of the beta in that

grain. Other grains, with a slightly higher V-content, will have a lower transus and will, as they cool, continue to increase their V-content from the remaining alpha, thus further increasing their stability. These differences will continue to increase on further cooling until no further diffusion can occur and the final microstructure will contain beta grains, with an average composition of about 14wt% V that have formed fine alpha, and retained beta grains containing 20wt% V. The large difference in V-contents observed, thus develop gradually during cooling and the different grains are locally in equilibrium.

This sequence of events could lead to the perimeter of grains that contain secondary alpha being rich in V and depleted in Al due to diffusion to/from the surrounding alpha, whilst the fine alpha precipitated internally. Once fine alpha is totally formed, the beta within that grain has a V-content of about 20wt% so that further diffusion to/from the surrounding alpha will cease leaving the Al-depleted and V-enriched perimeter, which would explain the presence of the bright perimeter visible in figure 1(b). This mechanism can also explain the diffusion profiles in Figures 3 and 4, which are very different. The grains that contain fine secondary alpha show a more diffuse change in composition across the adjacent alpha/beta boundary than the retained beta grains. Thus, if the initial diffusion of V into the beta and Al from the beta ceases when the secondary alpha forms, this will lead to composition profiles related to the distance over which diffusion has occurred, before the formation of beta with 20%V caused by formation of alpha within the grain, brings diffusion to an end. In contrast, diffusion of V and Al continues in the retained beta grains until the temperature is so low that diffusion ceases and these grains will have time to become more homogeneous.

The diffusion to/from the surrounding alpha makes local precipitation of alpha at the boundary less likely because it is effectively beta-stabilised, leading to the zone depleted of alpha at the boundary. If the diffuse scattering shown in Figure 6 is due to the presence of fine omega, the secondary alpha may then be nucleated on this omega as observed in beta alloys [8]. Whether that is possible depends upon the temperature at which fine alpha is formed during cooling at 5°C /min and the stability of omega in this alloy. We know neither of these facts and at this stage we cannot decide whether or not omega can play a part, although with a transus of about 750°C it may be that the alpha forms at a temperature above that at which omega is stable.

The only beta remaining at room temperature, when cooled at 5°C /min, has a V-content close to 20%. If this formation of secondary alpha, which occurs in beta of about 14wt%V, did not occur, X-ray diffraction and even electron diffraction would reveal a spread in lattice parameter of beta at room temperature, because as noted above, changes in V-content give

rise to significant changes in the volume of the unit cell of beta; such a spread in the lattice parameter of beta in Ti64 at room temperature is not observed [7].

The second aim of this paper was to define the composition of an alloy that should transform to produce a microstructure with a very high volume fraction of fine alpha. Since the mean composition in Ti64 of grains that transform to produce fine secondary alpha is about 81%Ti; 3%Al; 14%V and 2%Fe, it follows that alloys with this composition would be expected to produce the desired microstructure. Some preliminary work has been carried out on as cast, coarse grained (several 100 microns) buttons of alloys close to this composition cooled from 930°C at 5°C/min and heat treated at 900°C to homogenise them. As shown in Figure 8(a), the microstructure consists of a high density of fine alpha laths, separated by beta. The microhardness (VHN) of this sample is 474, which is higher than the value of 444 found in samples heat treated to coarsen the microstructure (see figure 8(b)) and higher than the value of 374 reported in Ti64 air-cooled from 980°C, which has a microstructure which contains 80% of beta grains that contain secondary alpha laths [5]. The interest in this composition is that a fine microstructure is observed when cooling as slowly as 5°C /min, which corresponds to cooling in a typical HIP. Somewhat slower cooling of large forgings, of castings, or of components cooled in larger HIPs would result in some coarsening of the microstructure and further work is needed to ascertain the extent to which the properties are influenced by the extent of coarsening.
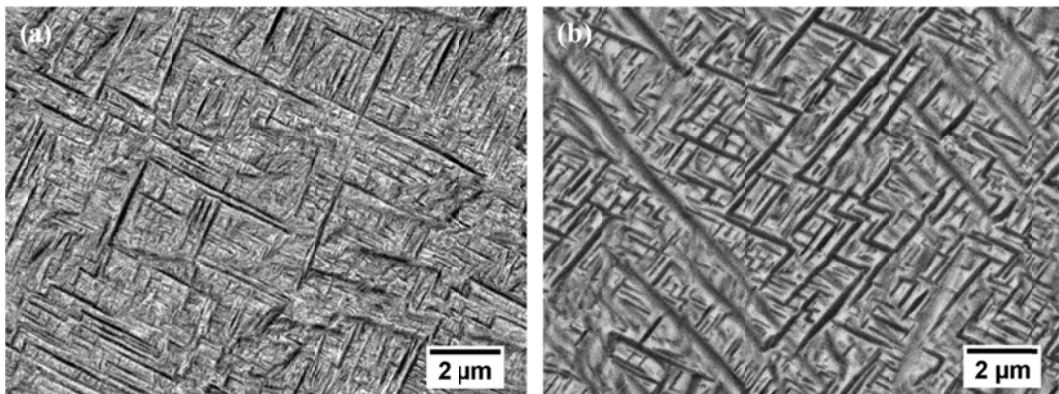

Figure 8. Back scattered SEM images of samples of about 79.1%Ti; 15.5%V, 3.6%Al; and 1.8%Fe; (a) a slowly cooled sample which contains fine alpha. (b) Slowly cooled sample held for 2h at 600°C to coarsen the microstructure, before cooling to room temperature.

The interest from the present point of view is that the composition of beta grains, that form fine alpha when slowly cooling Ti64, has been defined and an alloy of that composition has been shown to contain a very high fraction of fine alpha. The aim of future work is to optimise the microstructures of alloys close to this composition and to assess their properties.

Conclusions

(1) The parent beta grains that transform to fine secondary alpha contain about 14wt% V.

(2) The grains, in Ti64, which did not contain any secondary alpha, contain about 20wt% V and are thus stable as beta.

(3) These V-rich grains show diffuse scattering, which may mean that omega acts as nuclei for the secondary alpha, because the composition at the interface of beta grains that contain secondary alpha are such as to limit the driving force for precipitation at the boundary.

(4) An alloy, with the same overall composition as the grains that in Ti64 transform to produce fine secondary alpha, has the microstructure predicted of 100% fine alpha laths separated by beta and has high microhardness.

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