Influence of Grain Size and Microstructure on Oxidation Rates in Titanium Alloy Ti-6Al-4V Under Superplastic Forming Conditions

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Ti-6Al-4V (Ti-6-4) sheets of two different grain sizes were exposed to time and temperature conditions representative of superplastic forming (SPF). The influence of SPF conditions on oxidation rates was evaluated in terms of weight gain, α-case depth, and microhardness profile. Differences in the response are related to the difference in grain size between the two lots of Ti-6-4. Fine grain Ti-6Al-4V exhibits faster oxygen diffusion in all three areas examined in this study, weight gain, α-case thickness, and increased microhardness depth. The differences were found to be significant relative to diffusion analysis and processing during manufacturing. Results from this work support reduced temperature SPF using fine grain material and the accompanying benefits in manufacturing superplastic parts.

1. Introduction

Fabricators worldwide use superplastic forming (SPF) to make components for many applications. These applications range from buildings to cookware to automobiles to aircraft (Ref 1). A typical titanium alloy SPF aircraft component is shown in Fig. 1. The door threshold components protect the corners of the doorway in the Boeing 737 and 757 aircraft. Previously, the door threshold parts were composed of several separate pieces that were welded together. The SPF parts reduced cost and weight in addition to improving the appearance of the door threshold, one of the first areas of the aircraft seen by passengers.

Ti-6Al-4V (Ti-6-4) is the titanium alloy most often used to produce SPF components. Recent advances in titanium sheet production have made fine grain sheet material available for SPF. This fine grain material requires a much lower flow stress to accomplish SPF compared with conventional grade Ti-6-4. The reduced flow stress allows SPF to occur at considerably reduced temperatures compared with regular alloy grades, resulting in increased operator safety, reduced maintenance of tooling and forming presses, and longer tool and equipment life (Ref 2-6). The lower forming temperature also results in a smaller amount of brittle, oxygen-enriched material on the sur-

face, and therefore reduced chemical processing is needed to remove the brittle material (Ref 7).

All titanium alloys have in common a tendency to absorb oxygen through surfaces exposed to air during hot production processes, including SPF. This oxygen-rich layer, visible as the light colored layer in Fig. 2, is detrimental to the performance and appearance of the parts and is usually removed by a chemical milling process. The oxygen absorption behavior of regular grade Ti-6Al-4V is fairly well characterized. Increased oxygen levels are associated with increased microhardness and decreased ductility in titanium. Considerable data exist in the literature regarding Ti-6-4 and the influence of oxygen on mechanical properties. A smaller body of data reflects the influence of oxygen contamination on Ti-6-4 formed at its nominal SPF temperature of 900 °C (1650 °F), and there is evidence that the fine grain material will be subject to increased oxygen absorption (Ref 7-12). This paper presents experimental results relating titanium sheet microstructure, specifically the grain size, to oxidation rates under simulated SPF conditions. In addition, the results are analyzed using diffusion theory, and the need for compensation in the production of SPF parts is discussed.

2. Theory

The mass increase of titanium exposed to temperatures in excess of about 650 °C (1200 °F) can be assumed to be due to the diffusion of oxygen. Nitrogen and other diffusing species are much less active than oxygen under the subject conditions. The absorbed oxygen combines chemically with the titanium and other alloying elements to form an oxide layer on the surface, in addition to diffusing interstitially into the metal itself. The diffused oxygen increases the alloy hardness and causes metallurgical changes to occur (i.e., the formation of the α-case). Oxygen content is proportional to hardness in Ti and can be estimated by microhardness measurements (Ref 13). Increased hardness is evident in material with an oxygen percentage below that needed to transform the metallurgical structure to the close-packed hexagonal (cph) (α) matrix. Therefore,

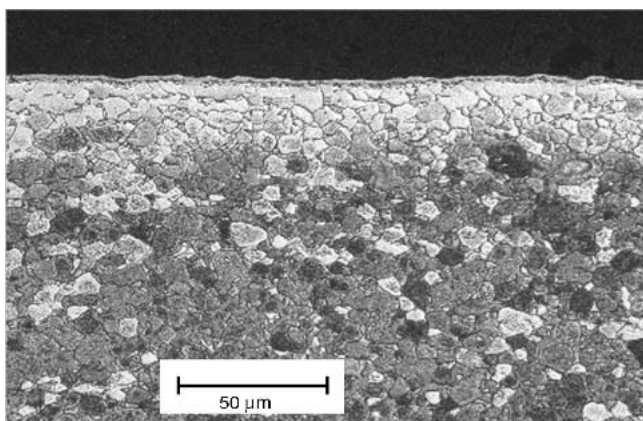**Franna Pitt,** The Boeing Company, Seattle, WA; and **M. Ramulu,** Department of Mechanical Engineering, University of Washington, Seattle, WA 98195. Contact e-mail: franna.s.pitt@boeing.com.
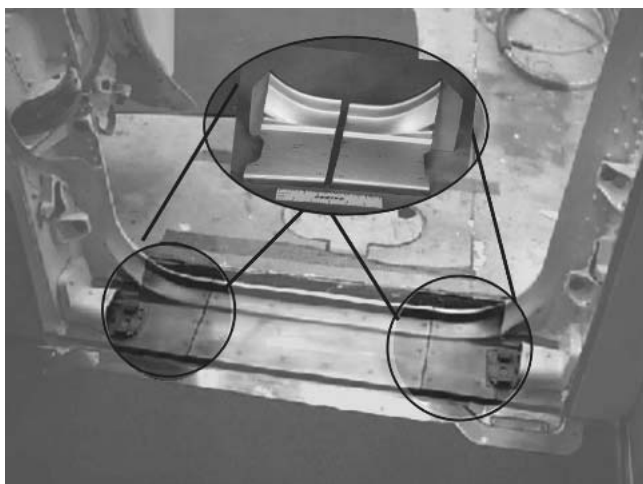
Fig. 1 SPF titanium aircraft door thresholds

Fig. 2 α-case layer on Ti-6Al-4V

increased hardness and decreased ductility in material can be expected when exposed to temperatures in excess of 760 °C (1400 °F) in the presence of air, even though no α-case is evident, as well as in the layer of material below the visible α-case.

Bulk interstitial diffusion in the β structure proceeds at a rate higher than that in the α structure (Ref 14). Diffusion along grain boundaries is also considerably faster than intragranular diffusion (Ref 10-12, 15). At traditional grain sizes of SPF grade Ti-6-4 (8-10 μm), the effect of grain boundary diffusion is normally neglected; however, as the grain sizes approach the nanoscale, grain boundary diffusion influence is expected to be increasingly important and is evidenced by a marked increase in oxygen diffusion.

Oxygen passes readily through the oxide layer, and diffusion into the titanium is comparatively slow, so that saturation (14.3%) is usually assumed at the titanium:oxide interface (Ref 16-18). Therefore, an unlimited supply of oxygen is assumed to be available to diffuse into the titanium matrix.

Initially, diffusion occurs in parallel through the α and β grains and along associated grain boundaries. As the oxygen concentration increases above that needed to convert the β

grains to α (the specific concentration is dependent on the alloy content), a surface layer known as α-case is formed. Diffusion then occurs in series through the α-layer and into the mixed α/β layer. Diffusion through αTi is one to three orders of magnitude slower than through βTi (Ref 14). Thus, diffusion in this dynamic system of titanium in elevated-temperature air is controlled by the presence and thickness of the α-case layer, and theoretically decreases over time as the α-case thickens. Grain growth also proceeds, especially at temperatures higher than those investigated in this paper. The effect of this is to slow the average diffusion of oxygen as the grain boundary paths decrease. In fact, Jenkins (Ref 17) and Kofstad et al. (Ref 18) report a decrease in the diffusion rate of oxygen over time. Additionally, diffusion within the grain increases faster than grain boundary diffusion as the temperature increases (Ref 10); conversely, at lower temperatures grain boundary diffusion becomes more influential.

Traditionally, a single diffusion coefficient (D) describes the average oxidation kinetics in each titanium alloy. Assuming that the effects of the differences in alloy chemistry and percent α between the two subject lots of Ti-6-4 are negligible, any difference in oxygen diffusion as measured by the weight gain, α-case depth, and increased microhardness depth (IMD) can be attributed to the grain size difference.

Fick's Second Law of Diffusion describes the interstitial diffusion process in titanium; that is, the rate of transfer of diffusant through the unit area is proportional to the concentration gradient. The proportionality constant is called the Diffusion coefficient, or D (Ref 10). In the case of oxygen diffusion into titanium alloys during SPF, one-dimension diffusion is assumed with the following time-dependent, partial differential equation usually applied:

$$\frac{\delta C}{dt} = \frac{D\delta^2 C}{\delta x^2} \qquad \text{(Eq 1)}$$

In Eq 1, C is the concentration of the diffusant, oxygen in this case, t is the time, D is the diffusion coefficient, and x is the distance from the diffusion surface. In words, the rate of diffusion is related to the concentration gradient through D. D for a given alloy/temperature combination is usually considered constant, although in actuality, it varies with diffusant concentration and internal microstructure (Ref 10).

The concentration of oxygen at the surface is assumed to be constant at the maximum solubility of oxygen in titanium (i.e., 14.3 wt.%). At time zero, constant bulk oxygen can be assumed. Diffusion under these conditions can be considered to occur in a "short" time, that is, not allowing for steady-state conditions to develop. One solution to Eq 1 becomes:

$$\partial = 2D^{-1/2}t^n \qquad \text{(Eq 2)}$$

where δ is the depth of interest (i.e., IMD), D is the diffusion coefficient, t is the elapsed time, and n is a time-independent rate constant that is ideally equal to 2 (Ref 9).

Published estimates of D assume an average bulk diffusion that does not account for differences in diffusion between αTi and βTi or grain boundary diffusion (Ref 11). One such pos-
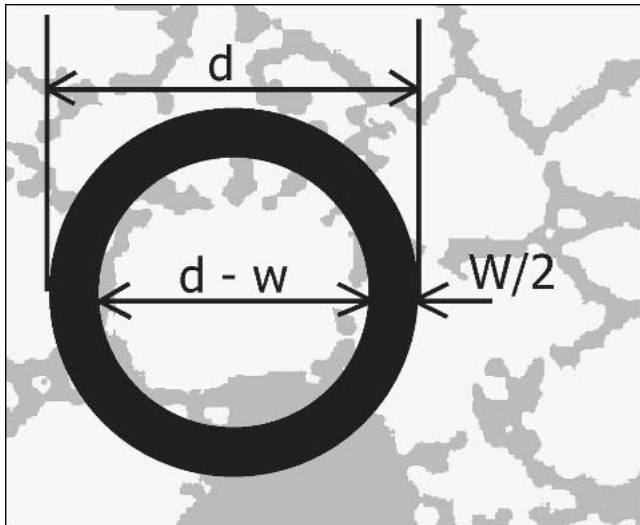
Fig. 3 Illustration of dimensions for grain boundary area calculation
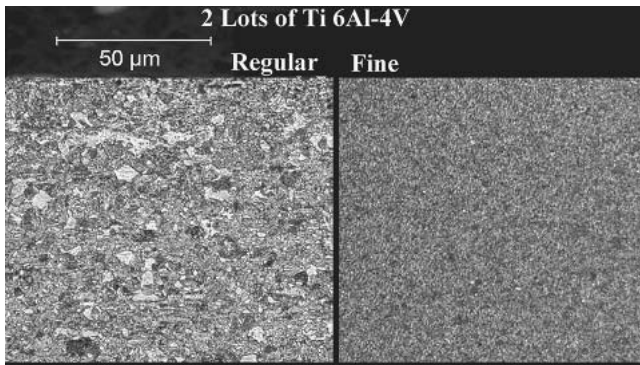
Fig. 4 Comparison of Ti-6-4 microstructures: conventional grain on left, fine grain on right

Table 1 Titanium alloy chemical composition

Ti-6Al-4V properties	Composition, wt.%				Grain size, μm
	Al	V	Fe	O	
Conventional grade	6.23	4.35	0.21	0.160	8.0
Fine grain	6.01	5.43	0.31	0.080	1.0

sible form of a composite diffusion coefficient is given in Eq 3 (Ref 19):

$$D_{bulk} = D_{lattice} (f_{lattice}) + D_{GB} (f_{GB}) \qquad \text{(Eq 3)}$$

where $f_{lattice}$ and f_{GB} represent the fractional area over which each diffusion coefficient acts, D_{bulk} is the diffusion over the total system, while $D_{lattice}$ is the intragranular portion of the system, and D_{GB} is the grain boundary portion of the system.

Following the same logic, the bulk diffusion coefficient can be further broken down into α and β constituents, as shown in Eq 4:

$$D_{bulk} = D_{\alpha} (f_{\alpha}) + D_{\beta} (f_{\beta}) + D_{GB} (f_{GB}) \qquad \text{(Eq 4)}$$

where α is the alpha microstructural portion and β is the beta microstructural portion.

Considering that D_{GB} is reportedly larger than either D_{α} or D_{β}, Eq 4 clearly indicates that as the grain boundary area increases relative to the grains themselves, the bulk diffusion coefficient increases.

Equation 3 can be rewritten in terms of two microstructural parameters: the average grain size (*d*) and the grain boundary width (*W*). Assuming that the grains are equiaxed and roughly circular in cross section and the grain boundary width is roughly equal around the grain and shared between two grains, Fig. 3 illustrates the dimensions for the area calculations.

Therefore, in terms of *d* and *W*, Eq 3 can be rewritten as:

$$D_{bulk} = D_{lattice} \left[\frac{(d - W)^2}{d^2} \right] + D_{GB} \left[\frac{(2dW - W)^2}{d^2} \right] \qquad \text{(Eq 5)}$$

The average grain size can be measured (Ref 20), and the expected fraction of α can be obtained from the literature (Ref 13) or measured from micrographs (Ref 21). Diffusion coefficients D_{bulk}, D_{α}, and D_{β} can be obtained from the literature, or measured using empirical data and Eq 1.

3. Experiments

3.1 Materials

Ti-6Al-4V sheet composed of two different grain sizes are examined in this investigation. One is conventional grade Ti-6-4 with an average grain size of approximately 8 μm, and the other is a fine grain material with a grain size of approximately 1 μm (Ref 20). Micrographs showing both grain structures are presented in Fig. 4. The chemical composition of the alloys was evaluated by using inductively coupled plasma (ICP) spectroscopy. Oxygen percentage was measured on a LECO Oxygen/Nitrogen Determinator (St. Joseph, MI). Grain sizes and selected elements of the alloy chemistry are listed in Table 1.

3.2 Experimental Procedure

The material was either machined or sheared into specimens for testing. Specimens approximately 25 by 50 mm (1 by 2 in.) were tagged with unique identification codes, chemically cleaned, measured (length, width, and thickness), and weighed to the nearest 0.1 mg. Specimens were conditioned under the simulated SPF cycle prior to evaluation. Three specimens of fine grain material and one specimen of conventional grade material were in each group. The simulated SPF cycle represents the parameters expected for processing fine grain material. The specimens were conditioned in an air furnace being hung individually on stainless steel wires attached to a stainless steel rack. The rack containing a complete group of specimens was placed into the preheated furnace, soaked for either 30 or 90 min at 760 ± 6 °C (1400 ± 10 °F), then removed from the furnace and allowed to cool in still room air.

The cooled specimens were weighed and subsequently prepared for metallurgical examination using standard metallo-
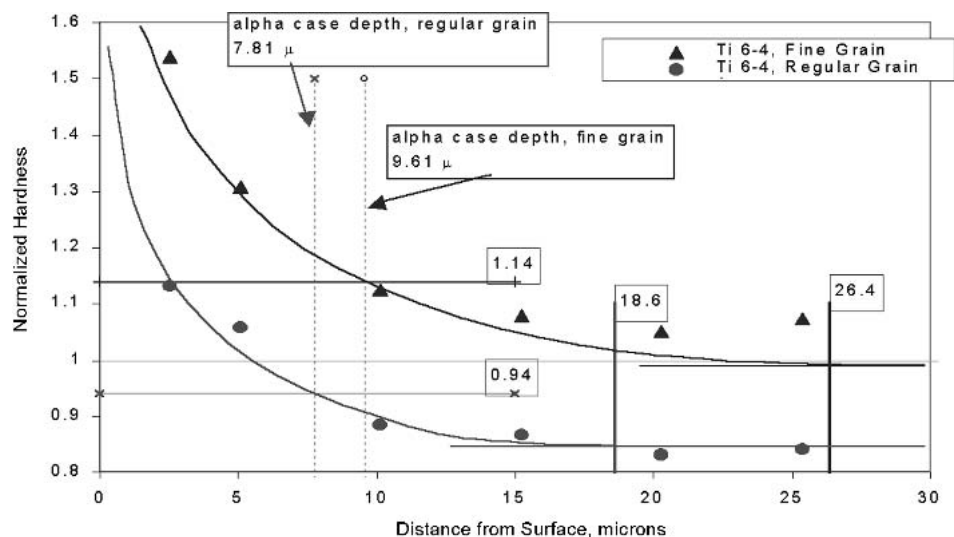
Fig. 5 Estimate of increased microhardness depth at edge of α-case

Table 2 Hardness values at the alpha case thickness depth

Conditioning at 760 °C (1400 °F)

	Knoop hardness, HK	
Ti-6Al-4V lot	30 min	90 min
Conventional	390	406
Fine grain	388	389

Table 3 Hardness values near the surface

Near surface hardness after conditioning at 760 °C (1400 °F)

	Knoop hardness, HK	
Ti-6Al-4V lot	30 min	90 min
Conventional	470	677
Fine grain	524	631

graphic techniques for titanium (Ref 22). A 1% ammonium bifluoride etchant was used on the polished surface to enhance the α grain structure. Alpha-case depths were measured on printed digital micrographs. The mounted specimens were re-polished prior to making microhardness measurements using a diamond Knoop indenter and a 10 g force for 15 s dwell. Average (arithmetic mean) values for the weight gain, α-case depth, and IMD are recorded for each group of specimens.

4. Results

Microhardness profiles were constructed by plotting the measured values of microhardness against the distance from the surface, as shown in Fig. 5. The plotted values of microhardness were then normalized against the average bulk hardness. The depth at which the hardness stabilized was designated the IMD and was estimated from the microhardness profiles.

Figure 6 shows the results for weight gain, α-case thickness, and IMD for SPF exposure times of 30 and 90 min. In all cases, there is evidence that oxygen diffusion proceeds at a faster rate in the fine grain Ti-6-4 than in the conventional grain material; that is, all values for the fine grain material are higher than the values for the conventional grain material.

Within the same alloy, the transition from β to α microstructure should take place at approximately the same oxygen percentage regardless of grain size or length of exposure. Therefore, in these two alloy lots, the hardness at the β to α transition, that is, the α-case depth, should be nearly the same. Table 2 lists the hardness values for the α-case thickness depth. The hardness values are slightly higher in the conventional grain material than the fine grain material, and can be attributed to the small difference in oxygen content and/or measurement error.

Likewise, if one looks at the hardness as close to the surface as possible, the values should be constant if steady state, saturated conditions were present. From the data in Table 3, this is obviously not the case since the hardness is considerably higher in the material conditioned for 90 min compared with the material conditioned for 30 min. Therefore, Fick's Second Law of Diffusion is applicable.

A portion of the micrograph in Fig. 2 has been enhanced to differentiate the contrast between the grains and grain boundaries. The enhanced image is shown in Fig. 7. Measurements taken from this image of the grain boundary width and of the grain diameters are shown in Table 4.

The grain size of 8 μm obtained using the ASTM method (Ref 20) compares favorably to the values reported in Table 4, considering that the grain boundary width is not counted separately from the grains in the ASTM method. To compare the values from Table 4 with the ASTM grain size, the grain diameter is added to the grain boundary width, giving an average grain size of 7.5 μm.
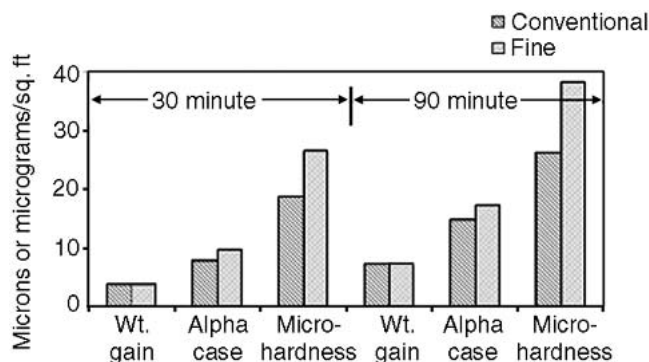
Fig. 6 Graphical results

Fig. 7 Image analysis to estimate grain boundary width

5. Discussion

As seen in Fig. 6, the difference in values between the fine grain and the conventional grain material is small for weight gain and α-case measurements. The IMD, however, shows a much greater difference between the two lots. As is discussed, these results are consistent with grain size being the major difference between the two lots of material.

5.1 Weight Gain

The weight gain results show that the fine grain material gained more mass than the conventional grain material under the simulated SPF conditions. However, this difference does not appear to be significant. Weight gain results are an indicator of oxygen incorporated into both the surface oxides and diffused into the base metal. The oxide on the surface is a chemical combination of oxygen and titanium atoms. It is a surface phenomenon and would not be influenced by grain boundary diffusion. The α-case, as discussed in the next section, is related to diffusion within the grain and is only partially influenced by grain boundary diffusion. As such, the other avenues of weight gain would overshadow differences in weight gain resulting from grain boundary diffusion alone.

5.2 α-Case

As shown in Fig. 6, the α-case thickness is greater for the fine grain material than the conventional material by 23% after 30 min and by 16% after 90 min. The change to α structure from β structure is a material property and based on the chemistry of the alloy. In this case, it is based on an increase in oxygen content (an α stabilizer). The oxygen percentage at the interface of the α-case and base microstructure should be nearly the same from sample to sample of the same alloy. In addition, the oxygen must have diffused within the grain interiors to effect the change in structure. The α-case thickness is an indication of diffusion within the grains, although diffusion along grain boundaries gives the oxygen access to grains well away from the surface. Differences in the α-case thickness, therefore, are a combination of the diffusion within grains, which should be similar between these two lots of titanium, and to a lesser extent, the diffusion along grain boundaries, which are more numerous in the fine grain material.
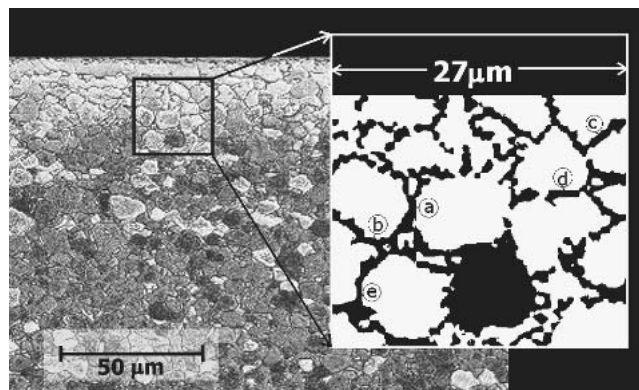
Table 4 Measured grain boundary width and grain diameters from Fig. 7

Location	Grain boundary width, μm	Grain diameter, μm
a	0.815	8.58, 6.30
b	0.706	7.39, 5.43
c	1.000	5.92, 5.54
d	0.858	7.44, 6.95
e	0.739	· · ·
Average	0.824	6.69

Note: 27 μm = 497 pixels

5.3 Microhardness

The difference in IMD between the two lots is considerably greater than either the weight gain or the α-case thickness. At 42% and 46% increases in IMD of the fine grain material over the conventional material for 30 and 90 min conditioning cycles, respectively, the difference is very significant. Of the three parameters measured in this study, microhardness is most directly a measure of oxygen content and comprises discrete measurements. Thus, a microhardness profile gives a much more accurate representation of oxygen diffusion in the material than either weight gain or α-case measurements.

The individual microhardness measurements are subject to variation. This variation is due to the small size of the Knoop indenter relative to the grain size of the material, the experimental technique used, and various other factors. The Knoop indenter is advantageous, however, in obtaining measurements near the titanium surface. On the other hand, Knoop hardness measurements can be skewed by a single "harder" or "softer" grain in the indentation volume. The small 10 g load, again advantageous for obtaining data close to the surface, is very sensitive to external influence during the indentation operation. Small vibrations in the equipment can make a large difference in the size of the indent and, thus, cause an erroneous hardness value. The obviously larger or smaller values can be double-checked, although minor variations will go unnoticed and contribute to variation in the final results. Indentations that are within about 25 μm (0.001 in.) of the surface are also influenced by the "softer" mounting material, though they are valuable when comparing similarly located or adjacent data points.
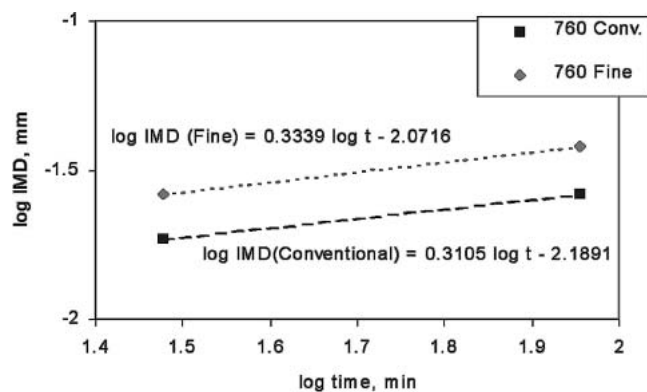
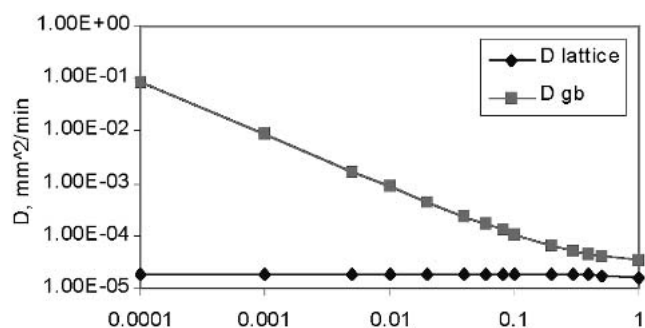**Fig. 8** IMD results plotted for conventional and fine grain material

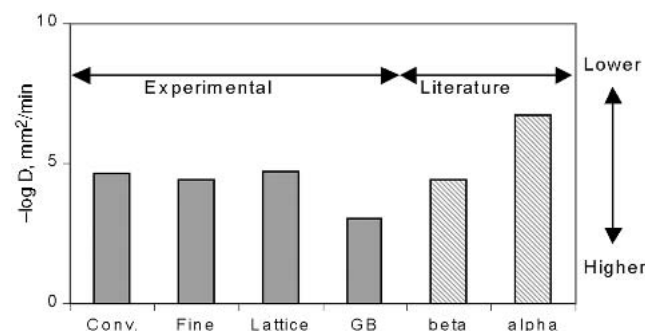**Fig. 9** Lattice and grain boundary diffusion coefficients as a function of grain boundary width

Fig. 10 Comparison of diffusion coefficients, experiment and literature values (Ref 14). Note negative log scale for *D*

5.4 Diffusion

The diffusion results are used to estimate the relationship between grain boundary width and grain boundary diffusion. The results shown in Fig. 6 are plotted in log/log space in Fig. 8. The values of *D* for each material are then determined from the slopes and intercepts from Fig. 8 and Eq 2. The values are 2.09×10^{-5} and 3.60×10^{-5} mm^2/min for the conventional and fine grain material, respectively.

Possible values for the grain boundary width can be bounded by 1 μm at the largest (it is obviously less than 1 μm, as the fine grain material is measured at 1 μm grain size) and the size of a single grain, herein estimated at 1Å. The calculated values for *D* in Eq 5, and the assumed widths for the grain boundary, result in calculated values for the diffusion coefficient along the grain boundaries and within the grains, as shown in Fig. 9. The lattice diffusion coefficient varies little throughout the range of 0.0001 to 1 μm grain boundary widths. The grain boundary diffusion coefficient, however, increases significantly as the grain boundary width decreases.

Assuming an intermediate value of 10 μm for the grain boundary width, the diffusion coefficient for grain boundary diffusion would be 8.86×10^{-4} mm^2/min. This value compares to published values of diffusion coefficients for αTi and βTi and the measured bulk coefficients for the materials in this investigation as shown in Fig. 10.

As can be seen from Fig. 10, the bulk diffusion coefficients are similar to the calculated lattice diffusion coefficient, and intermediate between the published α and β diffusion coefficients. The grain boundary coefficient is likewise higher than that of any of the others. These results show that as the grain size approaches the grain boundary width, grain boundary diffusion becomes more influential and increases the overall diffusion.

5.5 Material Removal Criteria

It is current shop practice for titanium alloys to remove a certain amount of material after high-temperature exposure in air. For traditional SPF the removal criteria were determined by measuring α-case following processing. Removal of 150% of the measured maximum α-case, or a minimum of 0.127 mm (0.005 in.), has been standard practice. With the introduction of

fine grain titanium alloys that superplastically form at considerably lower temperatures with resulting very small amounts of visible α-case, these criteria were challenged to avoid the unnecessary loss of "good" material. The minimum mandatory material removal has been revised in some cases to be 0.024 mm (0.001 in.) even in the presence of no visible α-case. However, as the data in Fig. 11 and 12 show, this material removal criterion may not be adequate.

After 30 min exposure, either removal criterion removes all α-case, and the 0.001 in. minimum removal criteria removes all oxygen-enriched material in the conventional grain material. Some oxygen-enriched material remains on the fine grain material. This remaining enriched material is the leading edge of the oxygen diffusion front, so it is minimally enriched. However, enrichment in the grain boundary region has been implicated in enhanced fatigue crack growth (Ref 11).

After 90 min exposure, as shown in Fig. 12, neither removal criteria removes adequate material to eliminate the oxygen-enriched zone, although very little of it remains on the conventional material. The current removal criteria are, therefore, inadequate in defining the amount of material that must be removed to eliminate the oxygen-enriched zone, especially in the fine grain material.

Using the values determined in this study, a grain boundary width of only 2% of the grain diameter is large enough to cause equal diffusion via the grain boundaries and the lattice. As shown in Fig. 11 and 12, the IMD is roughly double the depth of measured α-case and is most likely attributed to diffusion along grain boundaries.
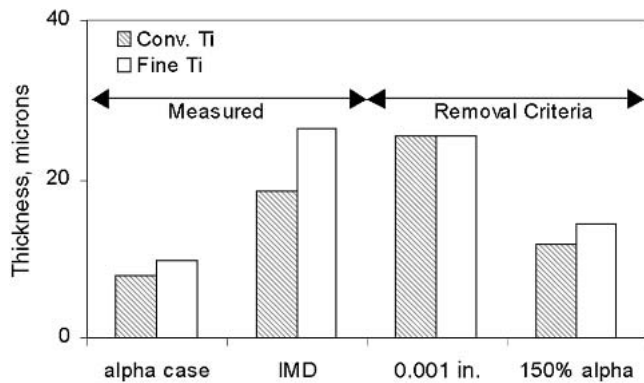
Fig. 11 Comparison of measured oxygen contamination after 30 min exposure with current material removal criteria
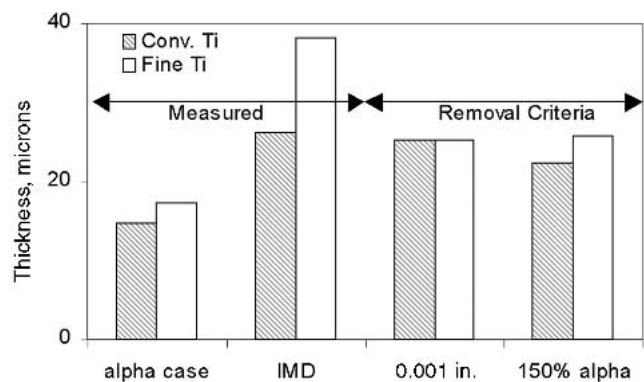
Fig. 12 Comparison of measured oxygen contamination after 90 min exposure with current material removal criteria

6. Conclusion

New processes are being developed to take advantage of lower temperature forming SPF titanium alloys and improve the efficiency of SPF. An experimental investigation was conducted to study the grain size effects on oxidation rates in fine grain and conventional Ti-6Al-4V. Based on this study the following conclusions were made:

- Fine grain Ti-6Al-4V exhibits faster oxygen diffusion in all three areas examined: weight gain, α-case thickness, and increased microhardness depth.
- The IMD shows the largest increase at 42% and 46% increase over conventional Ti-6Al-4V after conditioning times of 30 and 90 min, respectively, at 760 °C (1400 °F) in air.
- The α-case thickness is 23% and 16% greater in the fine grain material compared with the conventional grain material under the same conditions of time and temperature, and this is a significant result.
- The weight gain is the least-sensitive measure, and the difference reported herein is not significant.
- Grain size influenced oxygen diffusion in titanium, that is, as the grain size decreased, the rate of oxygen diffusion increased considerably. Current manufacturing practices need to be revised to account for this enhanced diffusion.

- Accurate modeling of the expected oxygen diffusion and/or microhardness testing will be more valuable than α-case thickness measurements to determine the amount of material that must be removed due to oxygen contamination.

Determination of the effect of minimal amounts of oxygen-enrichment on the mechanical and fatigue properties of SPF titanium is needed to assess the impact of these results. Investigation of additional grain sizes, alloys, and combinations of time and temperature conditions are recommended, as is the formulation of a mathematical model that can accurately predict the oxygen diffusion in these nonconventional materials.

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