

TITANIUM ALLOYS FOR HIGH TEMPERATURE

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Introduction

The last decade has seen the evolution of two simple criteria on which successful high temperature titanium alloy design is based. The first determines the framework within which the composition of the alloy may be manipulated: Rosenberg's α - equivalent[1]; the second relates to structure: β -annealed alloys exhibit superior combinations of creep resistance, fracture toughness and fatigue crack growth resistance properties[2]. The first part of this paper outlines the problem areas which the titanium metallurgist must look to within the essentially restrictive framework of the first criterion. In the latter portion we outline possible approaches to break out of this framework.

The Composition of High Temperature Titanium Alloys

The compositions of several high temperature titanium alloys are indicated in Table 1, together with some relevant properties:

Table 1 Composition and Properties of High Temperature Ti Alloys[3]

Designation	Al	Sn	Zr	Mo	Nb	Si	Bi	UTS (RT) N/mm ²	Creep: Total plastic strain after 100 hr at 500°C
IMI 685	6.0	-	5.0	0.5	-	0.25	-	992	0.204
IMI 829	5.5	3.5	3.0	0.25	1	0.30	-	962	0.122
Ti 11	6.0	2.0	1.5	1.00	-	0.35	0.1	903	0.219
VT 9	6.5	-	1.0	3.00	-	0.25	-	-	-

These alloys fall into the class of alloys called near- α , or super- α alloys; the volume fraction of β is extremely low but nevertheless it may be an important microstructural constituent as we shall see later. The composition may be characterised in terms of its α -equivalent[1] given by the empirical relationship: $\alpha_{eq} = Al + Sn/3 + Zr/6 + 10(O)$ (Wt%). The α -equivalent of all near- α alloys approach the empirically determined upper bound of 9. Beyond this value, precipitation of the embrittling Ti_3Al intermetallic compound occurs during creep exposure. Aluminium, tin, zirconium, molybdenum and niobium act as solid solution strengtheners; strong partitioning of molybdenum to the β -phase and aluminium to the α -phase is expected. The role of silicon is of great importance and appears now to be fairly well understood. It either precipitates on moving dislocations or provides an atmosphere drag[4].

Microstructure

The microstructure of these alloys are controlled by processing variables such as forging temperature and the solution treatment. The high α alloys are generally β forged and β solution treated so as to carefully control the β grain size. The cooling rate from the solutionising temperature is an important parameter since it affects the scale of the transformed β structure; that is, the α lath size, the widmanstatten colony size, and the grain boundary α thickness. Recent electron microscopic investigations[5] into the structure of the alloys IMI 685 and VT 9 show the presence of an interface phase at the α lath/retained β interfaces (Fig.1). The interface phase has been found to have an fcc structure with two orientation relationships to the α phase: $(\bar{1}\bar{1}0)_{fcc} // (\bar{1}\bar{1}00)_{\alpha}$; $[001]_{fcc} // [0001]_{\alpha}$ (Type A fcc) and $(111)_{fcc} // (0001)_{\alpha}$; $[\bar{1}\bar{1}0]_{fcc} // [11\bar{2}0]_{\alpha}$ (Type B fcc). The origin of the fcc phase is not yet clear. However, the crystallography is totally incompatible with the suggestion[6] that it forms as a transitional phase in the $\beta \rightarrow \alpha$ transformation. It is clear[7] that the phase has precipitated on the α side of the α/β interface, and in fact, the orientation relationships and the lattice parameter ($\sim 4.4\text{\AA}$) indicate a high possibility that the phase is titanium hydride.

Tensile properties

The tensile properties, yield stress and ductility, of the β -annealed structures compare unfavourably with the 'equiaxed α in transformed β ' structure of the $\alpha+\beta$ treated alloy. The mechanism of void nucleation and growth in such structures has been characterised[8]. It appears that grain boundary α can act as sites for void nucleation provided that the interface is incoherent with the adjacent β . If the interface separates Burgers related α and β , the basal planes of α (which are the predominant slip planes) and the $(110)_{\beta}$ planes are parallel, and no obstacle exists to slip transfer. Thus widmanstatten α lath interfaces are not sites for void nucleation. Void growth occurs by extension of the main void along the grain boundary α interface, and therefore, a continuous grain boundary α film provides an easy path for crack growth across the entire sample. The role of alloying additions on grain boundary α structure in high α alloys remains to be investigated in detail. However, comparative studies of alloys IMI 685 and VT 9 [9] indicate that higher molybdenum contents promote the formation of discontinuous grain boundary α allotriomorphs (which extend into widmanstatten laths) under identical cooling rates (Fig.2). The discontinuous α structure may offer increased ductility.

Creep

Creep exponents and activation energies of alloys such as IMI 685 and Ti-11 at temperatures around 700K have high values ranging from 7 - 11 for η and >100 Kcal/mole for Q . The rate controlling mechanisms for creep appear to be the overcoming of silicide precipitates and atmosphere drag at low strain rates and the cross-slip of extended dislocations on the basal planes to prismatic and pyramidal planes at higher strain rates[4,10]. All these mechanisms require a threshold stress to be overcome before dislocations may become mobile, thus explaining the apparent high values of η and Q [11]. Clearly at high strain rates the influence of alloying

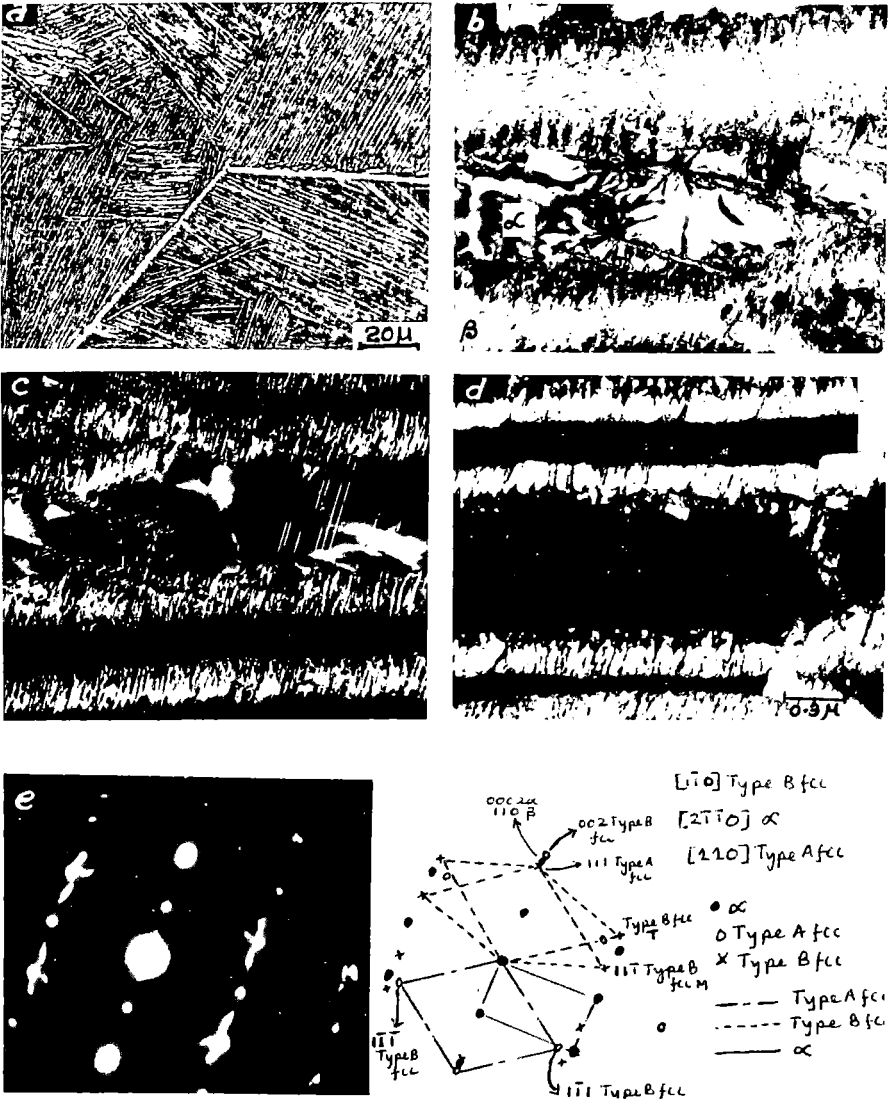


Fig.1: VT 9, β -annealed and argon cooled [5].
 a) Optical micrograph b) Bright field TEM of interface phase
 c) Dark field of Type B fcc d) Dark field of Type A fcc
 e) SADP of interface area showing the orientation relationships of fcc phase.

elements on the stacking fault energy is an important factor. Aluminium, in this respect, must be a potent creep strengthening element.

The role of microstructure on creep rates is not as well established. It has been shown that creep rates increase with the increase of the mean free path in the α phase[12]. This implies that the widmanstatten α /retained β interfaces act as obstacles to dislocation motion in some manner. The effect of the interface phase in slip transfer across the α/β interface merits greater attention. However the type B orientation provides parallelism of the $(111)_{\text{fcc}}$ slip plane to the $(0001)_{\alpha}$ and $(110)_{\beta}$ planes, and thus the interface phase may not be an ineffective obstacle[13]. The thickness and strength of the interface phase may be the other important factors. Of particular importance to creep is structural stability above 500°C. Above these temperatures, recrystallisation occurs by the spheroidisation of the continuous β film and the interface phase at the α lath interfaces as shown in Fig.3. The mean free path in the α phase thus increases, rendering the alloy unstable to creep. This effect is compounded by the removal of silicon from solution and its precipitation as coarse particles at the plate interfaces.

Fatigue

Fatigue crack propagation studies indicate that β -annealed alloys are far superior to equiaxed α structures in this respect. This has been clearly established as being due to the existence of a structure-sensitive mode of crack propagation in the β -annealed alloys[14,15]. Below a critical stress intensity, when the plastic zone ahead of the crack tip is smaller than the α colony size, crack propagation occurs by crystallographic bifurcation at the colony boundaries. This bifurcation reduces the effective stress intensity ahead of the crack tip. Studies of the crystallographic features of crack growth within an individual colony[16,17] show that the crack prefers to travel along a line almost normal to the α -phase axis, with no deviation at the α/β interfaces. This leads to the formation of facets extending across entire colonies on the fracture surface which have been shown to lie on the basal plane of the α phase[16]. While the reason for this is not very clear, we would like to suggest a possible role for hydrogen in this process. In situ electron microscopy straining studies of IMI 685 show hydride precipitation on basal planes in the α phase ahead of the crack tip[18] in an alloy containing 70 ppm hydrogen. The basal plane of the α phase lies at 10-20° to the plate axis (see Fig.1) which is approximately the angle at which the cracks propagate across the colony[17]. It is likely therefore that hydrogen migrates to the stressed area ahead of the fatigue crack tip and precipitates as hydride. This promotes cleavage on basal plane in this region at hydride plate interfaces, and the main crack may thus propagate across the colony on the basal plane in a brittle fashion, by joining up with the cleavage cracks (Fig.4). It is interesting to note that the type B fcc acts as a nucleating point for the hydride[18]. This is strong evidence that the interface phase in these alloys may itself be titanium hydride. It is likely that this mechanism of crack propagation may not be operative at higher temperatures where hydrogen has much larger solubilities in the α phase.



Fig.2: Discontinuous grain boundary α in VT 9, β -annealed and argon cooled [5].

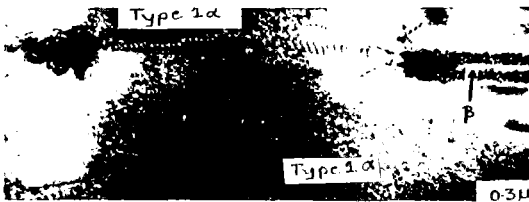


Fig.3: Spheroidisation of β and interface phase, VT 9, β -annealed, argon cooled, aged 600°C for 16 hr[5].

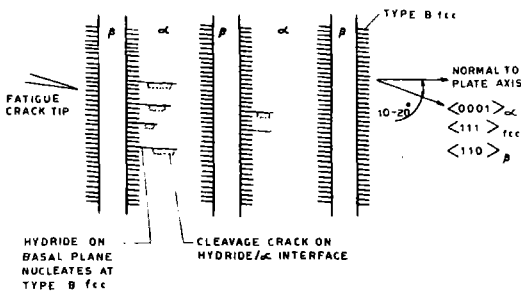


Fig.4: Fatigue crack growth mechanism across a widmanstatten α colony.

The Future of High α Alloys

While the preceding discussion outlines certain areas for further study in high α alloys, it is clear that these alloys face an upper limit of temperature capability in service. Their potential at temperatures above 550°C appears to be mainly limited by the degradation of creep properties. It appears that creep stability can only be ensured by raising the α/β transus by the addition of α -stabilisers such as aluminium. The restriction on this however is the formation of the intermetallic Ti_3Al which embrittles the alloy. Further increases in temperature capability may well depend on identifying alloying additions which significantly retard Ti_3Al precipitation kinetics, and which may therefore be added concomitantly with increasing aluminium contents. It is worth noting that the oxidation resistance of this class of alloys may then become an important parameter.

High Temperature Alloy Alternatives

If there is a limit to the temperature capability of the high- α alloys, is it possible to design ductile alloys containing the brittle $Ti_3Al(\alpha_2)$ and $TiAl(\gamma)$ phases? Extensive research has been carried out to answer precisely this problem. We describe here two alloy types, one consisting of α_2 dispersed in the α -Ti matrix, and the other lying in the two phase, $\alpha_2+\gamma$, region of the Ti-Al binary system. We note that a great deal of work has also been carried on single phase α_2 [19-22], single phase γ [23-25], and three phase, $(\alpha+\alpha_2)$ dispersed in a β matrix, alloys [26]. All these alloy types offer significant high temperature strength advantages over the high- α class and even some nickel base alloys [27].

1. $\alpha + \alpha_2$ Alloys

$\alpha+\alpha_2$ alloys in the binary Ti-Al system (7-12 Wt%Al) display attractive microstructures consisting of very uniform coherent or semicoherent α_2 dispersions in the α matrix (Fig.5). The analogy to the γ/γ' system in nickel-base alloys is readily apparent. These alloys however possess no ductility at all at room temperature and limited ductility at higher temperatures. Lutjering and Weissmann [28] have however shown that it is possible, by careful adjustment of interparticle spacing and size of the α_2 particles, to introduce an appreciable measure of ductility while retaining high strength values [28-30]. At low interparticle spacing and size, slip in these alloys is planar and inhomogeneous, leading to high stress concentrations at dislocation pile-ups and resultant crack formation. At high particle spacing dislocations bow out between the particles; the slip distribution now being more homogeneous, some ductility is gained. The problem then is one of retaining the necessary interparticle spacing at service temperatures. This problem has two aspects: one pertains to the significant changes in volume fraction of α_2 with temperature due to the shape of the $\alpha/(\alpha+\alpha_2)$ solvus; the other relates to coarsening rates of the α_2 precipitates. Coarsening beyond the critical particle spacing would lead to strength decrements. While the latter is now being evaluated [31], investigations on the effect of alloying additions on the slope of the solvus are also essential to arrive at suitable compositions which will show a limited dependence of the volume fraction of α_2 on temperature.

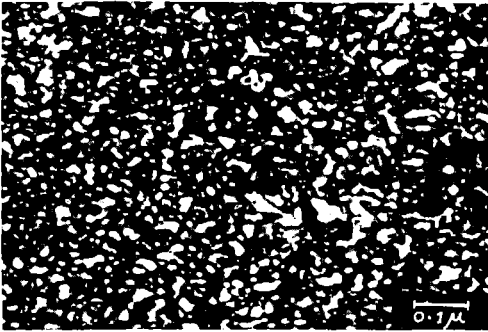


Fig.5: Dark field of α_2
dispersed in a α matrix:
Ti-9Wt%Al [31].



Fig.6: Dark field of γ plates
in an α_2 matrix.



Fig.7: γ phase precipitated in
a α_2 matrix in Ti-31Al-13Mo [33].

2. $\alpha_2 + \gamma$ Alloys (26-36 Wt%Al)

The brittle behaviour of this class of alloys is attributed to extreme anisotropy in the structure[32]. The γ phase precipitates in α_2 in the Ti-Al binary as plates extending from one end of the α_2 grains to another (Fig.6). This is due to the close matching between the close-packed planes of the two phases which results in (a) a plate-shaped γ nucleus with a habit of $(111)\gamma$ or $(0001)\alpha_2$ and (b) anisotropic growth of the plate due to the low mobility of the semi-coherent interface[33]. Some unsuccessful attempts have been made to alter the anisotropy with alloying additions[32]. However recent results[34] show that in Ti-Al-Mo alloys with high molybdenum (the β phase is also stabilised), γ phase precipitation in α_2 at temperatures below 600°C is dictated by strain energy considerations. This leads to formation of γ plates with much lower aspect ratios on habit planes of the type $\{10\bar{1}0\}$, $\{11\bar{2}0\}$ and $\{1\bar{3}20\}$ (Fig.7). The results however await confirmation in binary alloys with trace molybdenum additions.

3. Summation

Considerable work has been carried out to ductilise alloys containing the α_2 and γ intermetallic compounds of the Ti-Al system but no commercially viable alloy composition has so far been reported. However the increased availability of attractive powder technologies for processing brittle materials with superior properties indicate a reappraisal of the problem.

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