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PHASE TRANSFORMATIONS IN TI ALLOYS - A REVIEW OF RECENT DEVELOP--ETC(U)
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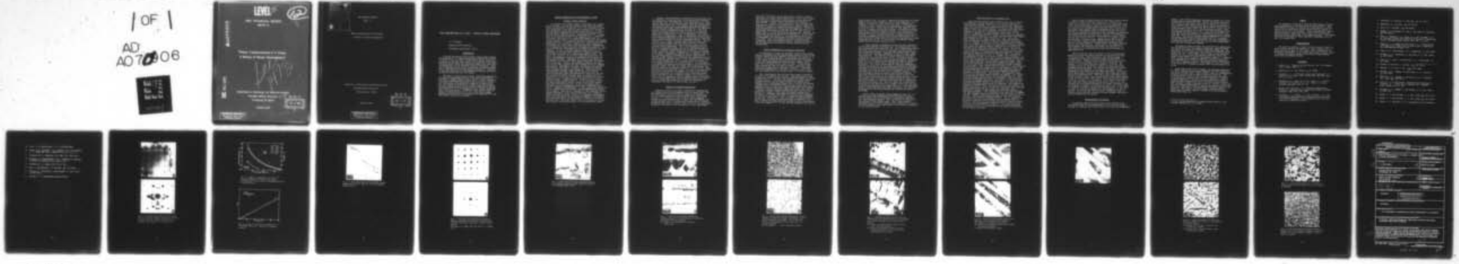

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Department of Metallurgy and Materials Science
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PHASE TRANSFORMATIONS IN Ti ALLOYS - A REVIEW OF RECENT DEVELOPMENTS

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INTRODUCTION

Titanium and titanium alloys exhibit a broad range of phase transformations.(1,2) Some of these transformations are related to the bcc to hcp allotropic transformation, whereas others are precipitation reactions which involve the formation of metastable transition phases and/or the equilibrium phases which occur during the decomposition of the metastable alpha or beta phases. These latter reactions usually occur in more highly alloyed situations. These transformations have been reviewed recently(3,4) and these reviews have shown that the transformational behavior and the resulting microstructures are very complex.

Subsequent to these earlier reviews, significant progress has been made in understanding several of the phase transformation described in somewhat general terms earlier. Further, several of these phase transformations generally are those which influence our understanding of properties of commercial titanium alloys. Thus, this paper will concentrate on these areas where progress has been achieved recently and the reader is referred to the previous papers(1-4) for a more general picture of phase transformations in titanium alloys. In addition, those factors which influence the microstructure of $\alpha + \beta$ Ti alloys during thermo mechanical processing are now reasonably well-understood(5,6) and these factors also will be reviewed.

ATHERMAL DECOMPOSITION OF THE METASTABLE β-PHASE

Athermal ω-Phase Formation

The formation of athermal ω=phase in metastable bcc titanium alloys has been a subject of continuing study, both from experimental and theoretical standpoints.(7-14) The theoretical studies have concentrated on the mode of ω-phase formation(7,9) whereas the experimental studies have examined additional ways to investigate the phase transformation(10-12) and have examined the role of interstitial impurities on the transformation.(11,13) A recent paper by de Fontaine and Buck(7) has suggested that a transformation defect which they call a linear displacement defect can account for the kinetics, crystallography and energetics of athermal ω-phase formation. In support of this point, they have made damping measurements as a function of temperature in several metastable beta-phase alloys which exhibit the reversible $\beta \rightleftarrows \omega$ transformation in the temperature range over which the damping was measured. Thus, they have been able to determine an activation energy for ω-phase formation. In turn, they have proposed a model for the $\beta \rightarrow \omega$ transformation and this model involved the formation, migration and lateral correlation of a linear transformation defect. This defect lies along the <111> bcc directions and provides for the atomic rearrangements necessary to transform the bcc matrix into the mexagonal ω-phase. Agglomeration of these linear displacement defects thus results in small regions which have the ω-phase crystal structure. Further, the estimated energetics for migration of this defect agrees with their internal friction or damping measurements. Subsequently, Williams, de Fontaine and Paton(14) have discussed this subject in terms of the diffraction effects which accompany athermal ω-phase formation. These authors have concluded that the atomic displacements associated with the linear displacement effect can qualitatively account for the complex networks of diffuse intensity which is characteristically observed in selected area electron diffraction metastable β-phase titanium alloys. An example of this is shown in Fig. 1 which exhibits athermal ω-phase formation. On the other hand, Cook(9) has taken issue with the detailed nature of the linear displacement defect mentioned above and, in turn, has suggested that a different type of transformation defect must be responsible for the bcc → hexagonal transformation. It would appear that additional work is required before the correct type of transformation defect can be defined. Sass and his co-workers(12) have performed lattice imaging experiments in the electron microscope in an attempt to directly observe the details of the bcc → hexagonal transformation. While these experiments have produced some impressive micrographs, detailed interpretation of these results is difficult and open to some questions. Thus these results have not yet served to clarify such issues as the detailed nature of the transformation defects.

Recently, other experimental observations have been made which lend additional insight into some of the factors which influence the athermal $\beta \rightleftarrows \omega$ transformation. These experiments also can be used to infer some of the characteristics which the correct transformation defect must have. For example, Paton and Williams(13) have recently shown that oxygen severely depresses the temperature at which athermal ω-phase starts to form (Fig. 2). Such a depression could be interpreted either in terms of an electronic effect since oxygen can act as a donor and raise the electron: atom ratio of the bcc host lattice. Alternatively, this oxygen effect can be interpreted in terms of a mechanical (elastic) interaction between oxygen atoms in the bcc lattice and the dilatation fields associated with the linear displacement defects. Since the presence of such defects, whatever their detailed nature, gives rise to a damping peak, then such defects must have a stress field which can interact with the oscillation stress field and internal friction experiment. Thus, any transformation defect which can successfully account for all the observed features of the bcc → hexagonal transformation must incorporate a dilational stress field in its overall configuration. In contrast, studies of the effect of hydrogen on athermal ω-phase formation show that the increasing amounts of hydrogen in the bcc β-phase matrix enhances ω-phase formation by increasing the termperature at which the athermal $\beta \rightleftarrows \omega$ reaction begins.(11,15) However, in view of the size of the hydrogen ions, it is considered that this effect is more probably explained on an electronic basis. In this regard, x-ray diffraction studies have been performed on bcc Ti-Mo-H alloys and these studies show that the β-phase lattice undergoes a substantial expansion as hydrogen is added to it (Fig. 3).(15) Since reductions in beta stabilizer content also lead to an expansion of the lattice, the addition of hydrogen to the bcc β-phase can be viewed as equivalent to a reduction in beta stabilizer content. These variations in lattice parameter appear to be isotropic in nature, thus the changes in lattice parameter appear to be related to an ion size change rather than an expansion due to the inclusion of a misfitting interstitial H atom in an octahedral or tetrahedral site such as is the case for C in α-Fe.

Formation of Hexagonal Martensite

Research activity in the area of martensitic transformation in titanium alloys has been somewhat static in recent years. The most notable work on this subject has been that by Shibata and Ono.(16) These workers have used an Eshelby-type strain energy criterion(17) to attempt to account for the crystallographic features of titanium martensites. Indeed, their calculations are in good agreement with the experimental observations of titanium martensite habit planes. However, there seem to be two questionable assumptions involved in their calculations. First, they assume that $(10\bar{1}2)$ twinning is the prevalent mode of lattice invariant deformation in twinned titanium martensites. This is not in agreement with other investigators' observations who have shown that most internally twinned titanium martensites are twinned on $(10\bar{1}1)$(18,19). Secondly, they assume that $\bar{a}$ *slip on prism, basal* and pyramidal planes is the primary mode of lattice invariant deformation in internally slipped titanium martensites. This is in direct disagreement with calculations made earlier by Otte(20) and experimental observations by Williams, et al(21) both of which suggest that $\bar{c} + \bar{a}$ slip should be the dominant mode. Moreover, the calculations of Shibata and Ono(16) assume that all of the strain energy is present in lattice as elastic deformation and this is in disagreement with observations of extensive plastic accommodation strain. Thus, while Shibata and Ono's calculations are interesting, there are unresolved conflicts between calculation and experiment which are worthy of further consideration and reconsiliation.

β-Phase Decomposition by Nucleation and Growth

Precipitation of α-phase in metastable β-phase alloys during aging is responsible for the high strengths observed in most of the solution treated and aged commercial metastable beta alloys.(3) As a result, the detailed kinetics, crystallography and morphology of the α-phase precipitate has been studies in detail to provide a basis for understanding the relatively high strength levels which can be attained in this class of alloys. It has now been shown conclusively that two types of α-phase precipitates form during the decomposition of metastable β-phase(22) These types have been designated type 1 and type 2 according to the orientation relationship which they exhibit relative to the bcc β matrix.

Type 1 precipitates have the weel-known Burger's orientation relation: $(110)_\beta$ $(0001)_\alpha$;$<111>_\beta<1120>_\alpha$. These precipitates occur as monolithic laths or plates with no significant amount of internal structure (Fig. 4). The type 2 precipitates are readily distinguished from type 1 by the complex diffraction patterns which accompany this transformation product (Fig. 5) and by the internal structure which is observable within the type 2 laths (Fig. 6). As suggested by Fig. 5b, the type 2 alpha precipitates have a complex orientation relation between the alpha and the beta, but there is a rational orientation relation between the type 2 and the type 1 precipitates, namely a $(10\bar{1}2)$ twin relationship between type 2 and type 1. Isothermal transformation studies have been conducted and these have shown that the type 2 precipitates form subsequent to the type 1 precipitates. Thus, a rational orientation relation between type 1 and type 2 precipitates might be expected if the type 2 precipitates form within and consume the type 1 precipitates as has been suggested.(22) It has also been shown that the relative rates at which type 1 and type 2 alpha-phase precipitates are formed depends both on alloy composition and on aging temperature. For example, Al additions to the Ti-Mo alloys tend to enhance the stability of type 1 precipitates as does aging at low temperatures in Ti-Mo-Al alloys. Rhodes and Williams(22) have suggested that the type 1 precipitates form first because, although this reaction results in a smaller free energy reduction, it is kinetically much more favorable than the formation of type 2 alpha precipitates. Although the type 2 precipitates contain an extensive internal substructure, presumably various $(10\bar{1}2)$ twin-related variants, the total interfacial energy associated with this transformation product morphology can still be low if the specific interfacial energy between the twin related variants is low.

A closely related transformation product has been reported to occur at the alpha/beta interfaces in $\alpha + \beta$ titanium alloys which have Widmanstatten microstructures.(23) This transformation product occurs as a thin layer at the α/β interfaces as shown in Fig. 7. This transformation product layer has been termed interface phase and consists of a feathery arrangement of very fine type 2 alpha phase platelets. The formation of this structure is preceded by a monolithic fcc transition phase.(23,24) The details of this products are somewhat less clear, although the paper by Rhodes and Paton(24) in this conference proceedings describes the interface phase reaction in greater detail than has been done elsewhere previously. Also, Kelly and Williams(25) have used transmission electron microscopy and the associated microdiffraction techniques available with a STEM (scanning transmission electron microscopy) attachment to analyze the detailed crystallography of the interface phase and to verify that it has a hexagonal structure. They have succeeded in obtaining single crystal patterns from the individual 100Å particles of the interface phase and have been able to index these patterns as hexagonal α-phase patterns. These investigators have also shown that increasing oxygen content enhances the formation of interface phase and tends to suppress the fcc transition product.(25) Thus, one useful set of experiments which has not been done would be to attempt to show that the type 2 alpha phase precipitates are oxygen stabilized. Such experiments would be a good application for some of the new in situ analytical techniques which are being developed for transmission electron microscopy.

Recent studies of fatigue crack propagation rates in $\alpha + \beta$ titanium alloys with Widmanstatten microstructures have shown that cracking at the α/β interfaces is a significant feature of the crack propagation process. Such cracking may be affected by the presence of the interface phase. Thus, a more detailed understanding of the factors which control formation(26) of interface phase appears to have application in the control of properties in this class of alloys.

Ordering Reactions in Titanium Alloys

There have been several recent studies in the role of ternary and quaternary alloying additions to Ti-Al alloys containing 25 atomic percent aluminum. These alloys are based on the composition Ti_3Al which are the ordered α_2 phase which has the DO_{19} structure. These α_2 alloys have a high strength, a low density and high elastic modulus. Thus, they are in principle, attractive for elevated temperature applications. Unfortunately, binary Ti_3Al is very brittle. Accordingly, numerous studies, some of which are described below, have been initiated in an attempt to improve the room temperature ductility of this class of alloys. The α_2 alloys, like other ordered alloys, exhibit planar slip. Thus, one promising means of improving the ductility would be refinement of the grain size (slip length). Secondly, since the ordering reaction in binary Ti_3Al is so rapid that it cannot be suppressed,(27) alloying addition which retard the ordering kinetics would also be desirable since they provide for additional microstructural control. To this end, Ti-Al-Nb alloys have been investigated. In contrast to Ti_3Al, which orders completely even during rapid quenching from 1200°C, niobium additions as small as 2.5at% have significant effect in reducing the ordering kinetics(28). (Fig. *). Further, the allotropic $\beta \rightarrow \alpha$ transformation in Ti_3Al occurs martensitically during quenching, but the martensitic product has a lath or packet morphology in the binary alloy. This morphology has an attendent large slip length. With increasing Nb additions, the martensite morphology rapidly changes from a lath martensite to an acicular martensite thereby reducing the slip length. Thus, niobium additions appear to be very beneficial in controlling the slip length as well as the degree of order. Subsequent annealing of Ti-Al-Nb alloys as high temperatures restores the order and imparts attractive elevated temperature mechanical properties of these alloys. Unfortunately, the martensitic structures are also microstructurally unstable and undergo a self induced or autorecrystallization reaction during aging(28) (Fig. 9). This recrystallization reaction leads to a coarsening of the microstructure with an attendent increase in slip length. To retain the micro structural refinement gained by Nb additions, it is clear that the autorecrystallization reaction must be suppressed. Such suppression requires an understanding of the driving force for the reaction. Two possibilities exist. First, the degree of long range order increases during recrystallization and, second, the interfacial area is dramatically reduced. These possibilities have been examined using step aging experiments. Such experiments have shown that low temperature heat treatments permit the ordering to proceed without recrystallization. However, high temperature aging of this fully ordered structure still results in recrystallization. Thus it appears that the strain energy and high interfacial area associated with the martensitic structure is the driving force for the recrystallization reaction. Thus the martensitic product should be avoided in these alloys dur to microstructural instability. Nucleation and growth transformation of β to α_2 should lead to more stable microstructures and thus appear promising.

Another class of ordered alloys are those which contain between $\sim$ 40 and $\sim$ 50 atom % Al and which consist of a mixtures of α_2 (Ti_3Al) and γ (TiAl).(29) The γ phase has the $L1_o$ structure. These alloys are microstructurally stable but the room temperature of the $\alpha + \gamma$ alloys is not significantly better than that of the α_2 alloy. Thus these alloys required further development before they will be attractive. Nevertheless, these two phase alloys have the potential for microstructural variations by heat treatment and processing. The annealed structure of these alloys consists of alternating α_2 and γ laths (Fig. 10) which have the orientation relation $(0002)_{\alpha_2} \parallel (111)_\gamma$ and $<11\bar{2}0>_\gamma \parallel <110>_\gamma$. Since the γ is ordered to the melting point, it always is well-ordered whereas the α_2 regions have a variable degree of order, depending on thermal history. Thus the α_2 phase frequently contains thermal anti-phase boundaries whereas the γ phase does not. Variations in alloy composition, heat treatment and processing thus creates the potential for a wide range of $\alpha_2 + \gamma$ microstructures which may hold promise for improved ductility.

There is one last class of ordered Ti alloys which deserves mention since they may provide the basis for an even wider range of microstructures. These are based on the ordered β phase (designated β_2) originally reported by Bohn and Lohberg(30) in Ti-Mo-Al alloys. Recent work on Ti-Al-Mo(31) and Ti-Al-Nb alloys has shown that the β_2 phase can be retained by quenching, for example, in a Ti-Al-Nb alloy which contains $\gtrsim$ 12 at% Nb. This metastable phase can subsequently undergo nucleation and growth decomposition during aging. The subsequent decomposition products which form during aging are the α_2 phase, the α phase or both, depending on alloy composition and aging temperature. These alloys can be duplex aged to provide complicated, but potentially strong and ductile microstructures. Thus these alloys would appear to be worthy of further study. Such studies should include investigations of the structure of the β phase and of the microstructural stability of the $\beta_2 + \alpha_2$ and $\beta + \alpha + \alpha_2$ mixtures. With regard to the structure, Bohn and lohberg reported the β_2 phase to have a CsCl (B2) structure but an alternate possibility for ternary compounds of the type Ti_2MoAl or Ti_2NbAl is the Heusler structure ($L2_1$). With regard to structural stability, the most obvious application for this class of alloys is at elevated temperatures, thus stuability is very important. As with any new class of alloys, fundamental study of these and other areas must accompany the most pragmatic application related characterization studies.

Thermomechanical Processing

An expanded range of microstructures can be attained in α+β and β-phase alloys if controlled amounts of hot work (by rolling or forging) are combined with careful control of the hot work temperature regime. Such combined thermal and mechanical treatments are called thermomechanical processing (TMP). Because TMP permits the microstructure to be altered and controlled to a degree not possible by heat treatment alone, many Ti users are now specifying microstructures which can only be achieved by TMP in order to achieve the improved properties which result from these microstructures. Since the final microstructure is a result of the $\beta \rightleftarrows \alpha$ transformation and simultaneous recrystallization, it is appropriate to briefly consider the factors which affect the final microstructure of an alloy after TMP. These factors include; working temperature* for isothermal working, starting and finishing temperature* for continuous working operations, amount of deformation, the rate of deformation, starting microstructure, cooling rate from the final working operation and post working heat treatment.

The extent to which $\alpha+\beta$ alloy such as Ti-6Al-4V is worked below the β-transus controls the primary α morphology. Material worked less than $\sim$ 50% retains an elongated α-phase morphology (Fig. 11a). Working 50% or more results in a fully spherical or equiaxed morphology (Fig. 11b). Since dynamic recovery always occurs during hot working, the rate at which the working is done also affects the amount of work needed to produce the equiaxed primary α. In general, faster working rates followed by immediate cooling require lower total deformations to effect the same microstructural change since this tends to minimize recovery. The maximum work rate is limited by the occurrence of adiabatic heating, which is quite severe in Ti alloys.

Again using Ti-6Al-4V as an example, the finishing temperature for the hot working operation also influences the final microstructure since finishing above $\sim$ 900°C (1650°F) results in a Widmanstatten $\alpha+\beta$ matrix structure such as shown in Figures 11a and 11b. This structure becomes coarser as the finishing temperature increases. If the material is finished above the final annealing or solution treatment temperature a triplex structure consisting of primary α, coarse secondary Widmanstatten and a transformed β matrix results. This structure is shown in Figures 11a and 12. Finally, cooling rate from the finishing temperature affects the microstructure since cooling at very slow rates ($\sim$ 50°C/hr) permits diffusional growth of the primary α. This leads to relatively large, equiaxed primary α-phase grains with small regions of β-phase at the grain boundary triple points (Fig. 13).

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* In this context temperatures are always quoted relative to the β-transus temperature, e.g., T_β-50°F.

SUMMARY

The progress in achieving an improved understanding of several phase transformations in Ti base alloys has been reviewed. These transformations include the athermal $\beta \rightleftarrows \omega$ transformation, the formation of an α/β interfacial reaction product and the ordering reactions in both the α and β-phases. Other transformations, such as hydride formation, where significant progress also has been made have been deleted, largely due to the length limitation. This length limitation is necessary if these conference proceedings are to be kept to a sensible size.

ACKNOWLEDGMENTS

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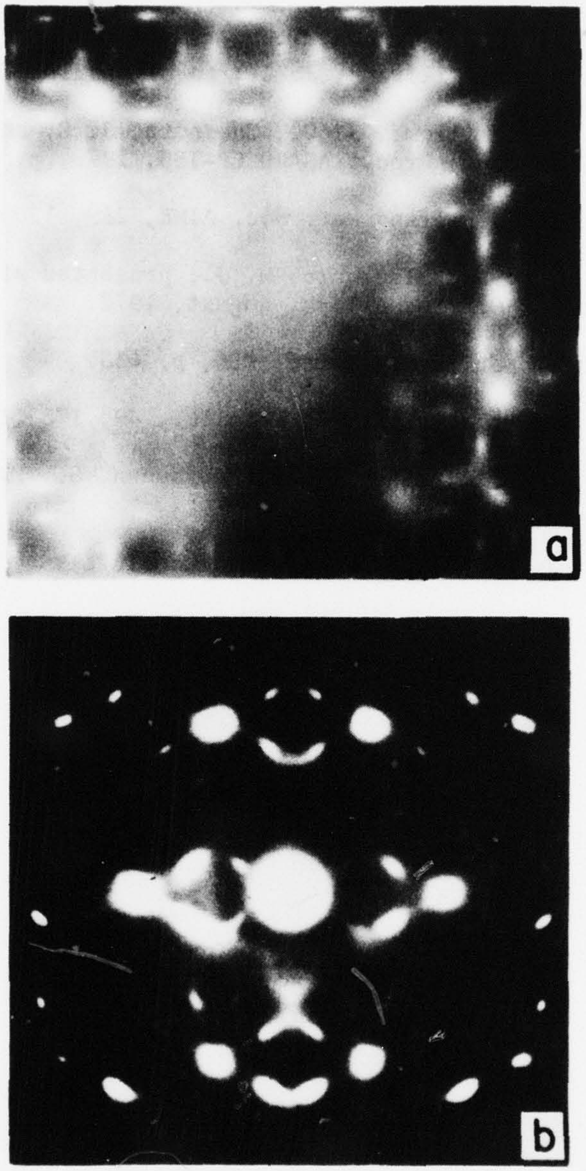


Fig. 1 - Selected area electron diffraction patterns showing complex networks of diffuse streaking due to ω-phase transformation defects. (a) $[100]_\beta$ Z.N. (b) $[210]_\beta$ Z.N.

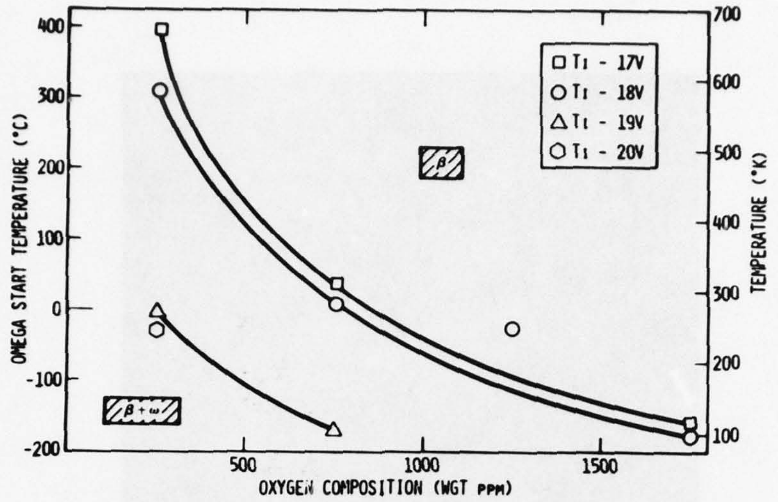


Fig. 2 - Graph of temperature for onset of athermal ω-phase as a function of oxygen concentration in Ti-V alloys containing different V concentrations.

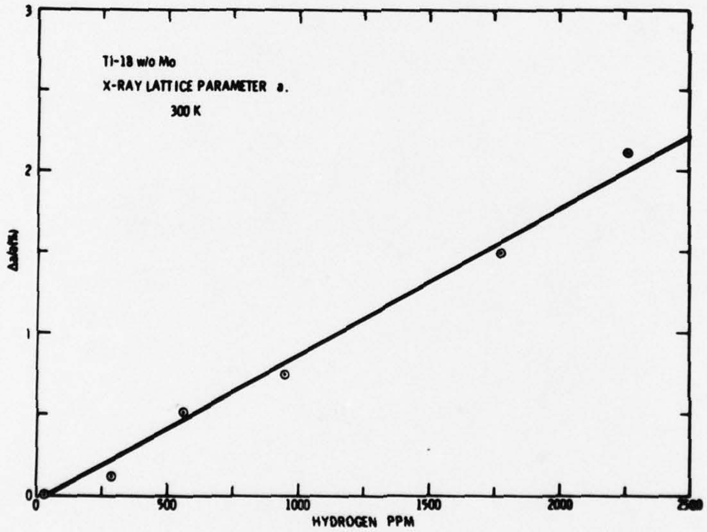


Fig. 3 - Graph of the lattice parameter of a Ti-18wt%Mo alloy as a function of hydrogen content.

Fig. 4 - Dark field electron micrograph showing monolithic laths of type 1 α in a Ti-12wt%Mo-6wt%Al alloy.

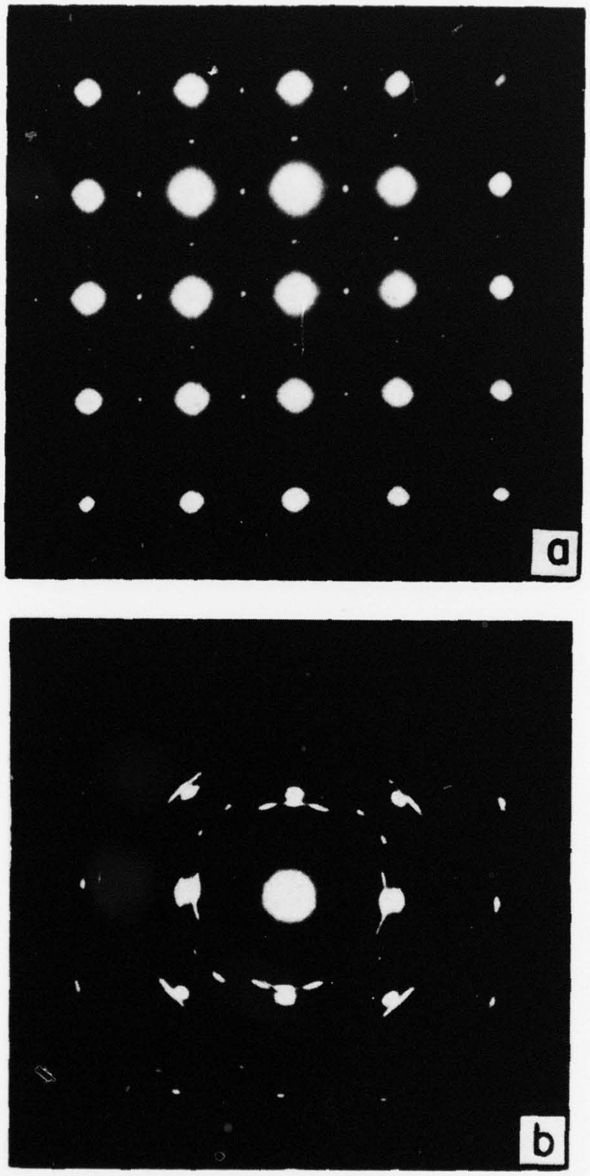


Fig. 5 - Selected area electron diffraction patterns showing the difference in diffraction effects from type 1 and type 2 α-phase precipitates.
(a) type 1 α, $[100]_{\beta}$ Z.N. (b) type 2 α, $[100]_{\beta}$ Z.N.

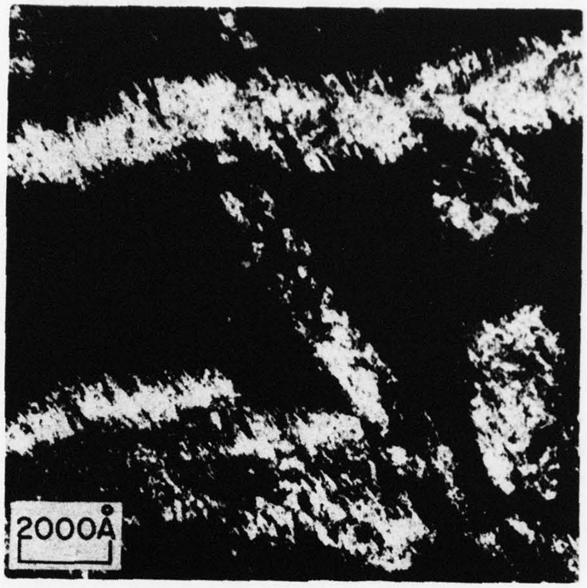


Fig. 6 - Dark field electron micrograph showing the internal structure within type 2 α laths in a Ti-12wt%Mo-6wt%Al alloy.

Fig. 7 - Electron micrographs showing the interface phase at α/β interfaces in Ti-6Al-4V.
(a) Bright field micrograph
(b) Dark field micrograph of interface phase only.

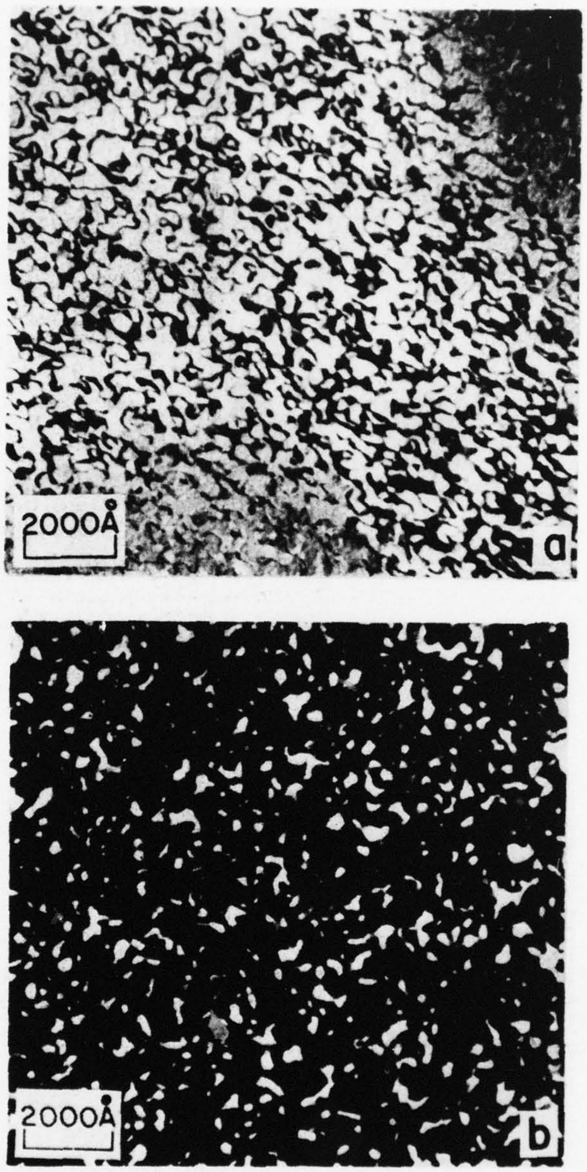


Fig. 8 - Dark field electron micrographs showing ordered α_2 domains in binary and ternary Ti_3Al alloys quenched from 1200°C. These show the effect of Nb additions on the formation of α_2 during quenching.
(a) Ti-25at%Al (b) Ti-25at%Al-2.5at%Nb

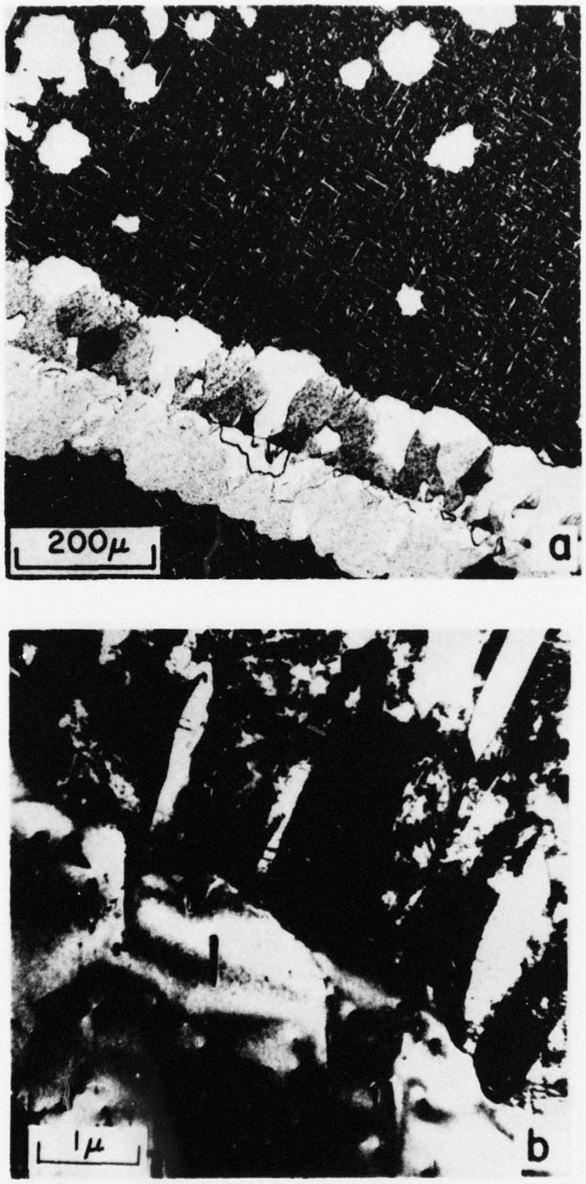


Fig. 9 - Showing the autorecrystallization reaction in a Ti-25at%Al-5at%Nb alloy quenched from 1200^{o}C and aged in the single phase α_2 region.

(a) light micrograph showing light etching recrystallized regions.

(b) electron micrograph showing boundary between martensitic structure and the recrystallized α_2 region.

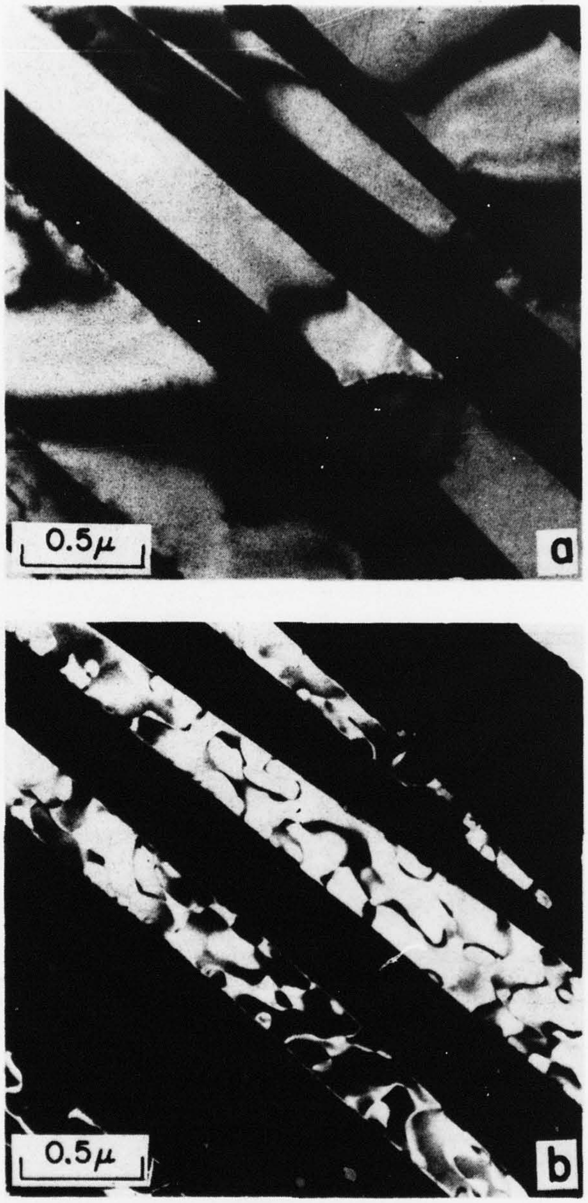
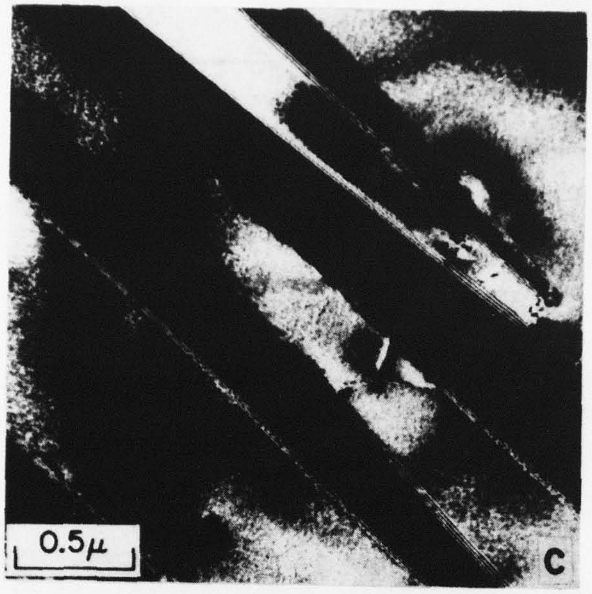


Fig. 10 - Electron micrographs showing the lamellae $\alpha_2+\gamma$ structure in Ti-48at%Al.
(a) bright field showing both phases
(b) dark field showing α_2-phase with thermal antiphase boundaries
(c) dark field showing γ-phase.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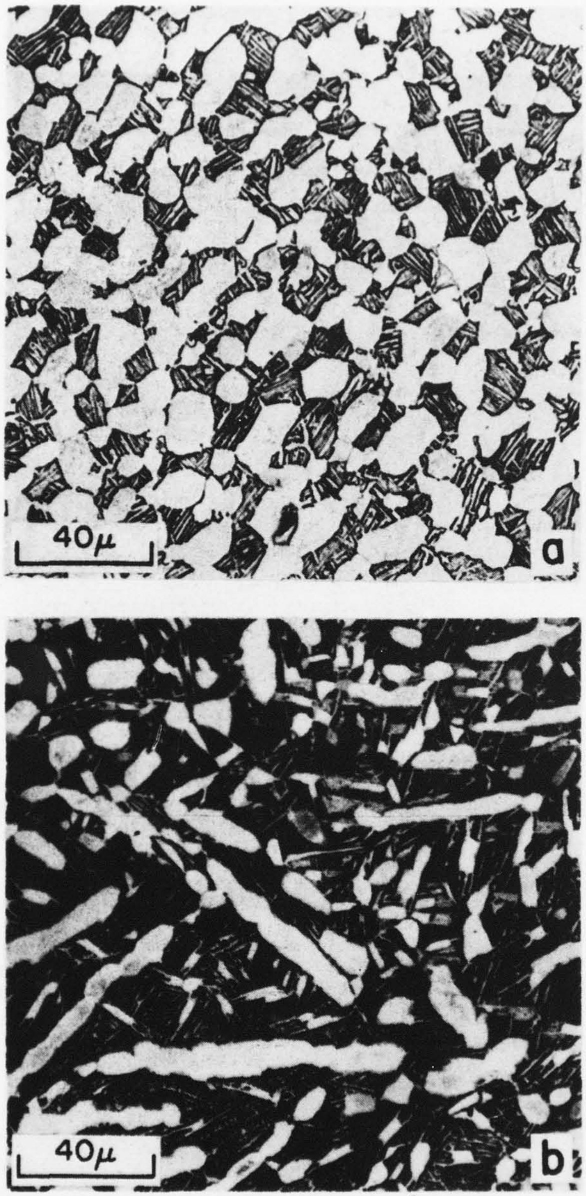

Fig. 11 - Light micrographs of Ti-6Al-4V forgings showing the effect of TMP schedule of microstructure.

(a) worked ∿50% in the $\alpha+\beta$ phase field, finished at ∿1650°F

(b) worked ∿50% in the $\alpha+\beta$ phase field, finished at ∿1700°C.

Fig. 12 - Triplex microstructure in Ti-6Al-4V worked ~50% in the α+β phase field and finished at ~1750°F.

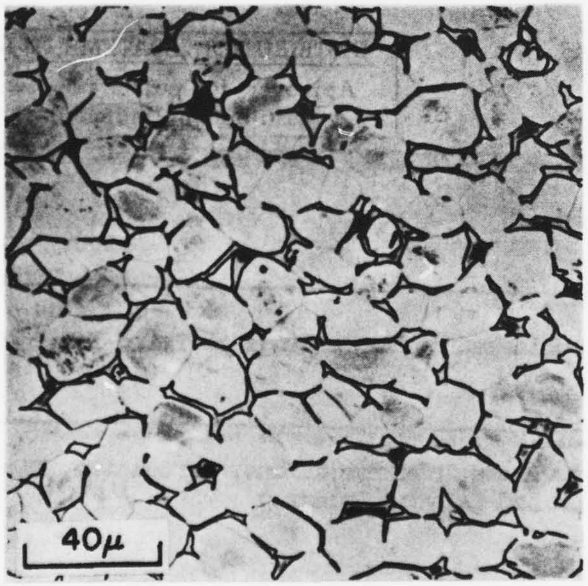

Fig. 13 - Recrystallization annealed Ti-6Al-4V worked ~50% in the α+β phase field, reheated to 1700°F for 4h and cooled at ~90°F/h to 1400°F then air cooled.

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The phase transformations in Ti alloys are reviewed. This review augments earlier reviews and emphasizes several transformations which have recently received attention. These include athermal ω- phase formation, martensitic transformations, nucleation and growth decomposition of the β-phase, the ordering reaction in hcp and bcc Ti alloys and the effects of processing history on microstructure.

omega

beta

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