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The effect of metastability on room temperature deformation behavior of β and $\alpha + \beta$ titanium alloys

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Abstract The deformation behavior of single-phase metastable β -titanium alloys and two-phase α +metastable- β alloys strongly depends on the degree of stability of the β -phase. Recently, it has been shown that the tensile deformation behavior, as well as the creep deformation behavior at low temperatures ($<0.25T_{\rm m}$), is strongly influenced by the degree of metastability. For example, the titanium β -alloy Ti–13.0wt%Mn, which has higher stability than the titanium β -alloy Ti-14.8wt%V, deforms by slip only; whereas the latter deforms by slip and twinning. In addition to the mechanical properties, the deformation mechanisms also depend on the degree of metastability. Further, the deformation mechanisms of a given metastable β -alloy depend on whether the β -phase is present by itself as a single-phase alloy, or in the presence of α -phase in the form of a two-phase alloy. For example, it was found that a metastable Ti-V alloy deforms by slip and twinning when it is in the form of a single-phase alloy, but deforms by slip and martensitic transformation when the same metastable β -phase is present in a two-phase $\alpha + \beta$ alloy. The mechanical properties of the metastable β alloys in turn depend on these deformation mechanisms. These recent developments are reviewed in this article.

Introduction

Many previous studies have been performed to examine the low-temperature tensile deformation mechanisms of singlephase α and β , as well as two-phase $\alpha + \beta$ titanium alloys.

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Department of Materials Science and Engineering, University of Maryland, College Park, MD, USA e-mail: ankem@umd.edu These $\alpha + \beta$ and β titanium alloys are specifically important because they have excellent mechanical properties including high strength to weight ratio, biocompatibility, and excellent corrosion resistance [1]. In many of these applications, low temperature creep resistance is an important factor. In this sense, a number of parameters such as grain size and β -phase stability can affect the tensile strength and creep resistance.

In the past two decades, there have been many articles demonstrating the effect of β -phase stability on the mechanical properties of the metastable titanium alloys, but no effort has been made yet to present a comprehensive look at the deformation mechanisms influenced by β -phase stability and grain size in these single-phase β and twophase $\alpha + \beta$ alloys. The aim of this article is to take a comprehensive look at the previous research and put together a methodology for what factors will control β -phase stability, what deformation mechanisms β -phase stability influences, and how these deformation mechanisms affect the mechanical properties of these alloys.

β -Phase metastability

Previous research has well established that the stability of the BCC structure in single and two-phase titanium alloys [2–21] depends on the extent of alloying elements and heat treatments as shown in Fig. 1 [5]. The amount of β stabilizer required to retain 100% of the β -phase at room temperature is defined by the Molybdenum Equivalency (MoE) [2]. MoE is used as a measure for the amount of β stabilizer required to prevent a martensitic transformation when quenching to ambient temperature. The MoE for a given stabilizing element is defined as the ratio of the amount of β stabilizing element to the amount of Molybdenum (Mo)



Fig. 1 A schematic of a pseudo-binary equilibrium diagram showing the ranges of β and ω stability as a function of added β stabilizer [5]

required for the same degree of β -phase stability. A simple formula for Molybdenum equivalency of some of the more common alloying elements of titanium may be derived as:

$$\begin{aligned} MoE &= 1.0(wt\%Mo) + 0.67(wt\%V) + 1.53(wt\%Mn) \\ &+ 0.44(wt\%W) + 1.6(wt\%Cr) + 0.28(wt\%Nb) \\ &+ \cdots \end{aligned} \tag{1}$$

During a quench from the β -phase, there are other nonequilibrium phases that can form including martensites (including α'), ω -phase and β' -phase. Jepson et al. [22] showed that the local effect of alloying inhibits martensitic transformation and the speed of transformation. All β alloys have been found to deform at ambient temperature by coarse and fine slip only [12], by slip and formation of stress-induced plates (SIP) such as twins or martensite [12], or by the formation of new stress-induced metastable phases like the ω -phase [3, 17, 23–27]. It has also been observed that as the alloying element is increased, i.e., the stability of the β -phase is increased; the deformation mode changes from twinning/martensite formation to slip [6, 10, 11, 14]. This review article will also address the effect of the α -phase on the deformation mechanisms of the β -phase, and vice versa, in $\alpha + \beta$ titanium alloys and their relationship to the behavior of single-phase β alloys.

The role of the ω -phase

As can be seen in the previous phase diagram (Fig. 1), the ω -phase would be present for most alloys of titanium using transition metals and tested at room temperature, depending on the stability of the β -phase. The ω -phase is present in the lower stability metastable alloys. For example, when the β stability MoE is 19.9 for a Ti–Mn alloy, only diffuse streaking is observed, indicating that the ω -phase is about to form. However, when the β stability MoE is 9.9 for a Ti–V alloy, the ω -phase is completely formed, as shown in Fig. 2. The ω -phase is metastable with respect to both the α - and β -phases, and is a nanostructured phase present within the β -phase. The ω -phase has been shown to have drastic effects on the mechanical behavior of metastable β titanium alloys [28-31], and so therefore must be also considered here. The ω -phase is formed when titanium is alloyed with β -stabilizers and can form either upon quenching from the β -phase field, or from aging of such a quenched alloy. The ω -phase has a hexagonal structure and forms a coherent interface with a $(110)[111]_{\beta}||(1120)$ $[0001]_{\omega}$ relationship to the surrounding β -phase.



Fig. 2 Selected area diffraction pattern comparing the degree of formation of ω phase in the β -phase of the $\alpha + \beta$ **a** Ti–6.0wt%Mn (β -phase MoE = 19.9) and **b** Ti–8.1wt%V (β -phase MoE = 9.9) alloys. Note pre- ω -phase streaking of ω spots of the β -phase of $\alpha + \beta$ Ti–6.0wt%Mn SADP, which are consistent with incommensurate ω

formation, compared with the sharply defined spots of the β -phase $\alpha + \beta$ Ti-8.1wt%V SADP. The ω -phase indices and orientation are provided. The extra spots in the Ti-8.1V pattern are due to double diffraction [51]

Deformation mechanisms

Single-phase α -Ti alloys

Effect of grain size on creep deformation

The room temperature deformation of single-phase α alloys, such as Ti-1.6V and Ti-0.4Mn, has been extensively covered in the works of Ankem, Greene, and Oberson [32-34] as well as others [35-40]. It was shown first by Ankem et al. [32] that extensive creep deformation can occur at room temperature in coarse-grained alpha titanium alloys, when tested at below the 0.2% yield stress. The phenomena was attributed to slip as well as timedependent $\{1\overline{1}02\}\langle 10\overline{1}\overline{1}\rangle$ or $\{1\overline{1}01\}\langle 10\overline{1}\overline{2}\rangle$ twinning. Later, Neeraj et al. reported that primary creep in single-phase α Ti-6Al alloys can also occur at low temperatures in coarsegrained materials. This phenomenon was attributed to planar slip. These studies therefore show that the alloying elements can determine whether the primary creep at room temperature is due to time-dependent twinning and slip or solely due to planar slip. While these earlier studies show that the timedependent twinning is due to the coarse grain size, the later studies indicated that in the presence of the β -phase, the twinning can also occur even if the α -platelet size is thin in two-phase $\alpha + \beta$ titanium alloys, as described later.

Single-phase metastable β -Ti alloys

Effect of grain size on tensile and creep deformation

Single-phase β alloys have long been shown to have excellent mechanical properties including creep resistance. Additionally, they show a good response to heat treatment and their microstructures can be easily modified. While the deformation modes for β titanium alloys can vary widely depending upon grain size and alloy composition [2, 5–8, 10, 12, 14, 41, 42], one trend involving β stability and resulting deformation mechanisms is apparent and discussed in this article.

While β titanium alloys show good creep resistance in general, it is evidenced from previous research [4, 42], that the net creep strain increases as the grain size increases. There also exists a greater amount of deformation with coarser slip lines in larger grain sized specimens of Ti–13.0Mn, Ti–9.4Mn, and Ti–14.8V [4]. The deformation features observed before and after creep deformation match those observed during tensile deformation and are detailed in the next section. It should be noted that the creep strain for these specimens increases significantly with increasing grain size. This observed at high temperature. This difference in the effect of grain sizes between high temperature

and room temperature has been attributed to the difference in operational deformation mechanisms [4]. Specifically, at high temperatures, the predominant deformation mechanism is grain boundary sliding; where an increase in grain size would result in decreased creep strain.

Effect of β -phase stability on tensile and creep deformation

To demonstrate the effect of β -phase stability on the deformation mechanisms of β titanium alloys, two model systems will be reviewed. Single-phase Ti–V and Ti–Mn β alloys have been selected for review due to the extensive amount of research performed on these alloys by Ankem et al. [4, 5, 12, 42, 43]. In addition, the deformation mechanisms discovered for the single-phase β alloy, Ti-9.4Mn [4] will also be discussed to help illustrate the effect of β stability in one alloy system. The phase diagrams for the Ti-V and Ti-Mn alloy systems are shown in Figs. 3 and 4. By following the phase diagram tie-line, it should be apparent that along the selected heat treatment, whether the alloy is single-phase or two-phase, the β -phase component will have the same amount of β -stabilizer, and therefore the same amount of β -stability. It should be noted here that because of the different amount of β stabilizing element, they also each have a different amount of ω -phase present in the β -phase. As Figs. 2 and 3 show, the β -phase for the Ti–V alloy (whether 50% of the microstructure or 100% of the microstructure) has distinctly defined spots showing the presence of the ω -phase. Conversely, the Ti–Mn alloy only has streaking of the diffraction pattern, suggesting



Fig. 3 Phase diagram showing Ti–V system [12]. Note alloy compositions are marked with *black dots* along *tie-line*



Fig. 4 Phase diagram showing Ti–Mn system [12]. Note alloy compositions reviewed are marked with *black dots* along *tie-line*

incommensurate ω -phase formation. Tensile testing, optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) studies have all been performed during the course of the investigations reviewed. The deformation of single-phase β alloys such as Ti-13.0Mn and Ti-14.8V are dependent upon β -phase stability as well as grain size. The MoE has been calculated as 19.9 for Ti-13.0Mn and 9.9 for Ti-14.8V [4]; therefore the stability of Ti-13.0Mn is much higher than that of Ti-14.8V. During tensile tests conducted at a strain rate of 3.128×10^{-5} s⁻¹, Ti–13.0Mn generated a YS of 940 MPa and deformed solely by coarse and wavy slip [35, 44, 45]. Alternatively, Ti-14.8V exhibited a YS of 774 MPa and deformed by slip and the formation of stress-induced {332}[113] twins [42, 43]. These twins contained two orientations of the ω -phase. Additionally, it was found that the Ti-9.4Mn alloy (MoE = 14.3) [4] had a YS of 1030 MPa with negligible work hardening and deformed by extensive slip [4]. It should be noted now that in the Ti–14.8V alloy (less stable MoE), the modes of deformation were SIP and slip; whereas in the Ti-13.0Mn alloy (more stable MoE), the predominant deformation mechanism was slip [4, 35].

The assumption would be that in an alloy with intermediate stability, there should be slip accompanied by some SIP formation. In the Ti–9.4Mn alloy, there was no SIP observed which suggests that there is some critical β -phase stability above which slip is the only operating mode of deformation [4]. The TEM analysis of the undeformed and deformed Ti–9.4Mn specimen revealed the presence of ω -phase as discrete spots in the BCC β -matrix. These investigations showed no evidence or indication of SIP formation and twinning. The matrix appeared to be unchanged after tensile deformation evidently showing that there is no SIP formation or twining. One should note that in a Ti–14.8V alloy [42], the ω -phase is present before deformation, and in a higher stability Ti–13.0Mn alloy, there is no ω -phase except for a pre- ω -phase streaking. This implies that in a more stable β -alloy, the ω -phase is absent and the deformation is due to slip [4]. These results led to the important conclusion that the formation or presence of ω -phase in the three β -alloys considered here is associated with the stability of β -phase and not a result of deformation [4], additionally, the presence of the ω -phase may also be contributing to the formation of twins.

During creep tests, the single-phase alloy, β -Ti-13.0Mn (β -phase of Ti-6.0Mn), with a grain size of 200 μ m, showed negligible creep strain of only 0.03% strain over a test period of 400 h and deformed only by rare coarse slip, with no observed twinning [5, 32]. Conversely, the singlephase alloy β -Ti-14.8V (β -phase of Ti-8.1V) crept to a strain 0.101% and deformed by slip, instantaneous twinning, and time-dependent twinning [46]. For comparison, the Ti-9.4Mn alloy crept to a strain of ${\sim}\,0.07\%$ and deformed by slip. A comparison of the three alloy's creep strain as a function of their β stability is shown in Fig. 5. The time-dependent twinning phenomena exhibited by the β -Ti-14.8V alloy is shown in Fig. 6. The deformation features for the creep tested Ti-9.4Mn alloy were very similar to those observed during tensile deformation. Only slip was observed in the Ti-9.4Mn alloy, and from micrographs taken during the test, it was determined that most of the slip lines were generated in the first few minutes of the test [4].

Other β alloys have been shown to behave similarly. Specifically, research performed by Xu et al. [14], Grosdidier et al. [6, 47], Zhao et al. [15], and Kim et al. [8] have presented similar results. Explicitly, the work of Grosdidier et al. showed that microstructure as well as β stability plays



Fig. 5 Creep resistance of three β Ti alloys as a function of MoE [4]

Fig. 6 Interrupt creep test, Ti-14.8V, 350- μ m grain size. a Interrupt I: time = 3.62 min, strain = 0.056%; b interrupt II: time = 1.68 h, strain = 0.07%; c interrupt III: time = 8.13 h, strain = 0.075% d unloading: time = 200 h, strain = 0.101%. Note growth of SIP denoted by A in a, and formation of new SIP denoted by B in d [42]



an important role in controlling the formation of martensite in a Ti β -Cez alloy. For example, large β grains favor the formation of stress-induced martensite (SIM), but a decrease in the martensitic temperature as controlled by a higher β stabilized alloy inhibits the formation of SIM [6, 47]. In regards to the newly developed Ti–Nb–Ta–In/Cr β alloys, Xu et al. showed that the lower β stability In based alloy deformed by martensite formation, twinning, and slip; whereas, the higher β stability Cr based alloy only deformed by slip [14].

Two-phase α -metastable β Ti alloys

Effect of β -phase stability on tensile and creep deformation

Many investigations have studied the tensile and creep deformation mechanisms of various two-phase Ti alloys. For reference, a few of these alloys will be discussed here. To demonstrate the effect of β -phase stability on the deformation mechanisms of $\alpha + \beta$ titanium alloys, twophase Ti–V and Ti–Mn alloys have been selected for review such that the chemistry of the single-phase β alloy reviewed earlier would match the component β -phase in the two-phase alloy. Ti–6.0Mn and Ti–8.1V are two titanium alloys whose component β -phases have the same chemistry and therefore same MoE as the single-phase Ti–13.0Mn and Ti–14.8V alloys. This is due to the fact that all of the single and two-phase alloys were heat treated or annealed at the same temperature where the phase composition is determined by the tie-lines. Tensile testing, creep testing, optical microscopy, SEM, and TEM have all been performed during the course of the investigations reviewed.

It should be noted that all of the two-phase titanium alloys reviewed for this article exhibited similar behavior in regards to grain size and β stability effects on the resulting deformation products. To illustrate this, the research of Ankem et al. [17-20, 33, 34], Balcerza et al. [23], and Gerland et al. [35], who investigated the interactions between the two phases, is reviewed. During tensile tests conducted by Jaworski and Ankem [44, 45], a twophase alloy Ti–6.0Mn (higher MoE of metastable β -phase) demonstrated a YS of 623 MPa and showed some amount of strain hardening. The $\alpha + \beta$ Ti-6.0Mn alloy demonstrated fine slip in the α -phase and some limited α -phase $\{10\overline{1}2\}$ type twin formation and interphase interface sliding [44, 45]. In contrast, a $\alpha + \beta$ Ti-8.1V alloy (lower MoE of metastable β -phase) yielded at approximately 597 MPa, showed no significant strain hardening, and showed many coarse deformation products [44, 45]. After SEM and TEM analysis of the $\alpha + \beta$ Ti–8.1V alloy, these products were shown to be twins in the α -phase and SIM in the β -phase, which spanned many grains of the specimen, not shown here [44, 45]. Additionally, it should be noted that TEM analysis also revealed the presence of the ω phase in the lower stability alloy, as shown in Fig. 2.

Creep tests performed by Jaworski and Ankem [45] resulted in similar deformation features to the tensile tests.

Fig. 7 SEM micrographs of α -β Ti–8.1V **a** before and **b** after creep deformation at 95% YS for 280 h to 0.52% plastic strain. Note the coarse deformation products spanning multiple α (*light*) and β (*dark*) grains. The deformation has been identified as a combination of stress-induced martensite in the β-phase and slip or twinning in the α-phase [44, 45]



The $\alpha + \beta$ Ti–8.1V alloy (total creep strain $\varepsilon = 0.37\%$) exhibited 16% greater creep strain compared to the $\alpha + \beta$ Ti–6.0Mn alloy ($\varepsilon = 0.22\%$) [45]. Creep deformation in the $\alpha + \beta$ Ti–6.0Mn alloy has been primarily attributed to fine slip in the α -phase and some infrequent interphase interface sliding in SEM micrographs. In stark contrast, the deformation products in $\alpha + \beta$ Ti–8.1V are highly visible and travel over the distance of many grains as shown in Fig. 7. Using TEM analysis, these deformation features have been identified as slip bands or twins in the α -phase and stressinduced hexagonal martensite in the β -phase [45].

The additional creep strain experienced by the $\alpha + \beta$ Ti-8.1V over alloys such as β Ti-13.0Mn or even $\alpha + \beta$ Ti-6.0Mn over the same test period can be explained by the difference in deformation mechanisms, specifically the formation of SIM in the β -phase and a greater number of twins in the α -phase of $\alpha + \beta$ Ti-8.1V [45]. In both the $\alpha + \beta$ Ti-8.1V and $\alpha + \beta$ Ti-6.0Mn alloys, the α -phase deformed by extensive fine slip with some coarse slip also observed in the $\alpha + \beta$ Ti-8.1V alloy [45].

The TEM analysis of the $\alpha + \beta$ Ti-8.1V specimens as conducted by Jaworski and Ankem [44, 45] revealed that the coarse lines visible in SEM micrographs were actually a combination of stress-induced hexagonal martensitic plates (α') in the β -phase and either twins or coarse slip in the α -phase as shown by Fig. 8 [44]. However, the single-phase β -Ti–14.8V, which has the same chemical composition as the β -phase of the $\alpha + \beta$ Ti-8.1V, only showed timedependent {332} twinning and no martensite was observed as shown in Figs. 6 and 7 [48]. In metastable β alloys, two types of SIM are common: hexagonal martensite (α') and orthorhombic martensite (α''). The plates in this alloy were confirmed to be hexagonal with selected area diffraction patters, not shown here. Additionally, the Burgers orientation relationship was obeyed between the martensite and the β -phase, and the martensite was not internally twinned with a straight α'/β interface which suggests a habit plane. These results clearly showed that the deformation mechanisms in the two-phase alloy could differ from those of the singlephase alloy even when the component phase chemical



Fig. 8 TEM micrograph of Ti–8.1V following tensile deformation showing stress-induced hexagonal martensite plates in the β -phase and twins in the α -phase [44]

composition is equivalent to the single-phase alloy. The phenomenon of interest is the formation of SIM in the β -phase of $\alpha + \beta$ Ti–8.1V as opposed to twins in the single-phase alloy, as well as the formation of twins in the single-phase α -alloy even though the platelet size was small (<5 µm). Twinning and martensite formation become the dominant mechanisms at low β stability even though there are many slip systems to accommodate deformation. In order for SIM to occur in the place of twinning, the relative activation energy must be lowered relative to twinning or additional stresses must be applied.

Discussion

The role of β -phase stability on tensile deformation mechanisms

Single-phase β -Ti alloys

In single-phase β titanium alloys, the role of β -phase stability and the role of the ω -phase on the stability of the

 β -phase are not very clear. It is known that as the stability of the β -phase is lowered through the lowering of the amount of a stabilizing element, or the use of a lesseffective β -stabilizer, the deformation products change from slip to twinning. There are at least three reasons why the mechanisms of single-phase metastable β alloys can be different. The first reason is related to the fact that in the higher stability alloys, the weight percent of alloying elements is higher. It is possible that the addition of alloying elements can hinder the formation of twins more effectively than opposing slip; therefore, it is possible to have only slip as you increase β -phase stability.

The second factor is related to the presence of the ω -phase. As mentioned before, in the lower stability alloys, the ω -phase is present. It is possible that this ω -phase is responsible for twinning in lower stability alloys. It should be noted that coinciding with this transformation from slip deformation to twinning and martensite deformation is the appearance of the ω -phase in the β microstructure. This suggests that the ω -phase is playing a critical role to the deformation of the phase. However, after twinning, the ω -phase is still present within the twinned region of the grain. During a martensitic transformation, both the ω -phase and the β -phase would be consumed. The presence of the ω -phase within a twin suggests two possible scenarios. Either the ω -phase sheared along with the β -phase, or it dissolved during twinning and recrystallized along its preferred directions within the twin after twinning was complete. It may be impossible to determine which of these mechanisms is operating. Alternatively, it may be possible that the ω -phase is acting as a nucleation site for the twinning process. Being that the ω -phase is an intermediate phase between the stable α -phase and the metastable β -phase, it may be possible that twinning is occurring in the low stabilized alloys because the ω -phase is lowering the τ_{crss} for twinning close to or lower than slip. The mechanisms for this, however, are not known and further investigations are needed.

The third reason for the change in deformation mechanisms may be related to the chemical free energy difference between the metastable β -phase and the martensite (α') phase. As the stability decreases, the chemical free energy difference between these two phases increases. Therefore, any minor stresses developed because of various reasons, including cooling from high temperatures or applied stresses, can promote the formation of martensite.

Two-phase $\alpha + \beta$ -*Ti alloys*

In addition to the factors mentioned above for single-phase metastable β alloys, additional factors come into play in regard to the two-phase α +metastable- β alloys. These include elastic and elasto-plastic interaction stresses

between α and β phases, crystallographic relations between phases, and residual stresses due to cooling from high temperatures. It is quite possible to have residual stresses in the microstructure because the coefficient of thermal expansion is different between α and β phases; however, observations of the microstructures of the as-quenched alloys reviewed showed no twins and no martensite, indicating that these residual stresses may not be significant enough to produce these transformations.

Initially, interaction stresses develop at the α/β interfaces due to different amounts of strains for the same applied stress. At lower stresses, for a given amount of applied stress, the β -phase deforms more than the α -phase because the β -phase is elastically softer than the α -phase, as shown in Fig. 10. Therefore, at the α/β interface, the stress on β has to come down and the stress on the α -phase has to go up so that the interfacial strain will be the same, to maintain compatibility. This means that the β -phase can apply a stress, in addition to the applied stress, on α -phase causing slip or twinning in the α -phase. This can explain why twinning can be seen in the α -phase even though the α platelet size is very small. Consequently, once slip or twinning initiates in the α -phase, it can apply very strong interaction stresses on the β -phase in addition to the applied stress, see Figs. 9 and 10. Such interaction stresses are found to be significantly higher in the martensitic system in the β -phase as opposed to twinning in the β -phase [44, 45]. This is one of the reasons why martensite forms in β instead of twinning in the presence of α -phase.

The third reason that martensite (α') may form in the β -phase is related to the templating effect. It was found that the martensite in the β -phase and the α -phase have a twin relationship. This interface between α and α' has a lower misfit orientation than the α - β interface and so a martensitic formation is favored. The additional stresses from slip and twinning in the α -phase that act on the $\beta \rightarrow \alpha'$ transformation, as noted before, are only present in the two-phase alloys. This is why twinning is the predominant mechanism in the single-phase alloy Ti-14.8V rather than SIM seen in the $\alpha + \beta$ Ti–V alloys. Where β -stability comes into play is when SIM is formed in the β -phase of Ti-8.1V but not in the β -phase of Ti-6.0Mn or Ti-9.4Mn. SIM occurs because the stress applied effectively raises the martensitic transformation temperature to ambient temperature. The change in Gibbs Free Energy for a martensitic transformation is:

$$\Delta G = A\gamma + \Delta G_{\rm S} - V \Delta G_{\rm V} \tag{2}$$

In comparing β titanium alloys with different stabilities, the less stable alloys will have a greater change in volume free energy upon transformation, resulting in a greater likelihood of martensitic transformation.







Fig. 10 Elastic interaction stress on α and β phases of a titanium alloy. The interaction of the stronger but lower modulus β -phase with the α -phase initially increases the stress in α . Once significant plastic deformation occurs in α , elasto-plastic interaction stresses act on the β -phase [44, 45]

A fourth reason for the differing mechanisms between single-phase metastable β alloys and two-phase $\alpha + \beta$ alloys may also be due to the presence of the ω -phase in the β -phase of these alloys. Kuan et al. [26] suggest that the metastable ω -phase which is also present in Ti–8.1V, is an intermediate phase between the α - and β -phases. This intermediate phase would effectively lower the free energy change required to form martensite. Because of the lack of ω -phase in the Ti–6.0Mn alloy, stresses required to form SIM are higher. The presence of the ω -phase is illustrated by Fig. 2 [44]. To properly address the relationship of β -phase stability and deformation mechanisms, various other Ti–V alloys were reviewed. Ramesh et al. [42] found {332}[113]-type twins containing two variants of the ω -phase in single-phase Ti–14.8V alloy, with the same chemistry as the β component of the Ti–8.1wt%alloy. This result is consistent with the results of Oka and Teniguchi [41] in a Ti–15.5V alloy. Kouland and Breedis [9] found that the SIP in Ti–16.2V were hexagonal martensite (α'). Menon and Krishnan [49] investigated Ti–V alloys with 5, 10, and 20wt%V, and found SIM in the Ti–20V alloy. Ling et al. [10] investigated Ti–V alloys ranging from 20 to 40wt%V and found that, as the solute concentration was increased, the deformation mechanisms changed from twinning in the 20wt%V alloy to fine slip and finally coarse slip in the Ti–40wt%V alloy. Additionally, Xu et al. [14] found that in two β alloys with differing β -phase stability, the stability of the second phase played a crucial role in whether a martensitic transformation would occur under room temperature stresses.

Both oxygen and hydrogen have marked effects on the ω -phase. Oxygen depresses the temperature at which it forms and hydrogen enhances thermal ω -phase formation. These effects are important because the levels of these two elements can vary from alloy to alloy and would therefore affect the variation in the literature results mentioned above. The interactions between the α -phase and ω -phase become possible because of the high concentration of ω -phase within these lower stability β alloys. The observations in this article suggest that the activation energy for twinning can decrease in the presence of ω -phase in the case of single-phase alloys. In addition, the activation energy for the formation of martensite is also decreased in the presence of the intermediate ω -phase. It is reasonable to believe that the activation energy for the formation of martensite is lower than that for the formation of twinning. If the activation energy is met by the interaction stresses between α - and β -phases, which are much more prevalent on the martensite system as compared to twin system, then one can explain why martensite has formed in the presence

of α -phase even though only twins are found in the singlephase β alloys.

Additionally, because the misfit strain between the α and ω phases is high, the places along the α/β -phase interface where α and ω phases interact, the plastic deformation of the α -phase places high stresses on the ω -phase planes and directions which facilitate a $\omega \rightarrow \alpha'$ transformation. Because the resolved shear stresses from α -phase slip or twinning act more strongly on the ω -phase shear systems than the β -phase twinning systems, SIM becomes far more likely to occur. It should also be considered that there are four main orientations of the ω -phase present in the β -phase; of these, slip in α affects two of them and twinning in α affects the other two; so no matter the primary deformation mechanism in the adjacent α -phase of a twophase alloy, martensite will form in the β -phase. It has been shown here how the SIM may form, but the question as to how the martensite propagates through the β -phase must also be considered. If one looks at the orientation relationship between the ω - and β -phases, $\{\overline{1}010\}\langle 0001\rangle_{\omega}$ $\{\overline{1}12\}\langle 1\overline{1}1\rangle_{B}$, it becomes apparent that each shear system for a $\omega \rightarrow \alpha'$ transformation is exactly parallel to the $\beta \rightarrow \alpha'$ shear system. What this means is that once the transformation is started, it will propagate through the β -phase along parallel systems.

Conclusively we can say that the deformation products for metastable β titanium alloys are dependent upon the amount of stabilizing element, hence, as the stability is increased, the mechanisms change from SIM to twinning to slip.

The role of β -phase stability on creep deformation mechanisms

Similarly to tensile tests which have been performed, deformation mechanisms during creep in the two-phase alloys differed from those observed in the single-phase alloys. Creep test results mirrored the results of the tensile testing for Ti-8.1V and Ti-14.8V (same composition β -phase). In the single-phase alloy, the SIP responsible for deformation were {332} type twins; whereas in the twophase alloy, stress-induced martensitic (α') plates were formed in the β -phase. As a single-phase alloy, Ti–14.8V has a martensite start temperature low enough to prevent a martensitic transformation; however, the presence of α -phase raises the temperature high enough that martensite can form during creep. Specimens tested under creep conditions differ from tensile testing in that the load is constant and any additional stresses required to initiate creep must come from internal stresses. Therefore, interaction stresses are even more important. Schematics of the orientation relationship between the two phases and the interaction stresses experienced by the two phases are shown in Figs. 9 and 10 [44, 45]. For twin nucleation and growth in the α -phase (which is preferred), the β -phase must strain to accommodate the α -phase strain. If the β -phase is stable enough, it will retard the growth of twins as evidenced by the two-phase alloy Ti-6.0Mn. The limited interphase interface sliding in Ti-6.0Mn is not enough to accommodate the growth in the α -phase, which limits the overall creep strain. The creep results of the single-phase β alloys: Ti-9.4Mn, Ti-14.8V, and Ti-13.0Mn were also compared. It has been hypothesized [34, 50] that interstitial oxygen atoms act as pinning sites at the twin/matrix interface to control time-dependent strain. This diffusion of oxygen atoms away from the twin front would explain the increase in twin width with time for the β alloys. A similar mechanism would also be possible for Ti-9.4Mn as well. However, since slip was much more prevalent in Ti-9.4Mn than in Ti-13.0Mn, the pinning sites are not oxygen because the systems should respond in the same way [4]. TEM diffraction patterns showed ω -phase spots before and after deformation in Ti-9.4Mn but were absent in the stable Ti-13.0Mn. This means that the ω -phase could be responsible for pinning of slip lines and creep strain results from slip lines intersecting with the ω -phase and dissolution of the ω -phase [4, 51].

Summary

This study was undertaken to gather together the information regarding the effect of the metastable β -phase on deformation in single-phase and two-phase titanium alloys. As of yet, there had not been a comprehensive review of these relations, nor postulations as to how they affect the alloy's final microstructure and mechanical properties. The magnitude of metastability of the β -phase plays a significant role on the deformation mechanisms and the deformation behavior during tensile and creep deformation. The effect of metastability on single-phase β alloys appears to be threefold. The first reason is related to simply the amount of stabilizers added to the titanium. Since the higher stability β -alloys have more alloying elements, it is quite possible that the alloying elements can interfere more strongly with twinning as compared to slip. Therefore, slip can be preferred in very highly stabilized alloys as compared to twinning. As the stability decreases, it was found that ω -phase is present. This ω -phase can also act as nucleation sites for twinning thereby promoting twinning in the lower stability β -alloys. It is to be noted, however, that slip is an operating mechanism even though twinning is present. As the stability is decreased further, the chemical free energy difference between the metastable β and martensite becomes so high that any kind of disturbance can result in the initiation/formation of martensite.

In two-phase α +metastable- β alloys, additional factors come into play. These include interaction stresses between the two phases and crystallographic relationships between the two phases. Therefore, some of the deformation mechanisms which have been observed at much lower stability in single-phase β alloys can also be seen in the higher stability two-phase $\alpha + \beta$ alloys. For example, the α -phase can act as a template for the martensite in β , promoting its formation; where in the absence of α , this may not happen for the given stability of β -phase.

In regard to the creep deformation behavior, the deformation mechanisms are similar to tensile tests; however, the time-dependent effects are important to recognize. Given that for example the twinning in α can be a time-dependent phenomenon, it is quite possible that the growth of the martensite in β in the lower stability alloys is also time-dependent. While these suggestions need to be confirmed experimentally, it is very important to recognize at this time how the two-phase alloys deform so that optimal chemistry and microstructure of the two-phase $\alpha + \beta$ alloys can be selected for various structural applications.

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