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Room temperature age-hardening in a ß titanium alloy

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A metastable β titanium alloy containing 10 wt % Zr and 12 wt % V has been found to undergo a substantial age-hardening reaction at temperatures as low as 20° C. The reaction involves continued growth of "athermal" ω-phase particles produced during water quenching from the β-phase field. The morphology of the as-quenched ω is retained, implying the absence of long-range diffusion during ageing: this is consistent with the low value of the activation energy measured (93 kJ kg mol^{-1}). It is suggested that the ω growth is caused by unpinning of ω/β interfaces as a result of the short-range motion of interstitials present in the alloy. The age-hardening produces a severe loss in tensile ductility and inhibition of stress-induced martensite formation.

1. Introduction

ω-phase formation has been extensively studied in a wide range of titanium alloys. Two basic types of ω have been distinguished in the literature. Firstly isothermal ω which is produced during the isothermal ageing of metastable β titanium alloy of low β stabilizing element content. The homogeneously nucleated particles are solute lean and exhibit an ellipsoidal morphology in systems where the ω/β misfit is small and a cuboidal morphology when the misfit is large. The nucleation and growth of this form of ω is of practical importance during ageing treatments both directly, since it generally produces a severe loss in tensile ductility, and indirectly, as a precursor of the equilibrium α-phase which may nucleate on ω dispersions.

The second form of ω has been termed "athermal" since it forms during rapid quenching from the β-phase field. It has been shown to nucleate below a critical temperature ω_s and to increase in volume fraction as the temperature is reduced below this value. ω_s is dependent upon the concentration of β stabilzing elements present and upon interstitial level [1]. The reaction is completely reversible upon reheating. The particle morphology is distinctively different from that of isothermal ω and consists of irregularly shaped domains with less well-defined interfaces with the parent β. Sass and co-workers [2–4] have studied the microstructure of athermal ω in titanium and zirconium niobium alloys in great detail and have shown that the ω is made up of discrete particles 1 to 2 nm in diameter which are regularly spaced in rows along $\langle 1\,1\,1\rangle\beta/[0\,0\,0\,1]\omega$. Aggregates of such rows of particles make up the much larger (up to ~ 50 nm) irregular ω domains observed in the most dilute β alloys. Changes in contrast observed during electron microscopy indicate that individual ω particles nucleate and dissolve dynamically at room temperature. The characteristics of formation indicate the absence of any long-range diffusion and suggest that athermal ω is identical in chemical composition with the parent β phase. The proposed mechanism of formation is non-classical, involving the production of correlated elastic displacement wave packets in the β [5–7]. Although, historically, the two forms of ω were distinguished in the literature, it was shown some years ago that even at temperatures where bulk diffusion can participate in phase transformations (~ 600 to 700 K) the isothermal formation of ω from β is anomalously fast. Microstructural studies [3, 8] have shown that the initially produced ω is microstructurally indistinguishable from the athermal form, including the existence of

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$\langle 1\,1\,1\rangle\beta$ rows of 1 to 2 nm particles within the ω domains, and that chemical equilibration follows the initial nucleation and growth. Internal ordering of ω during ageing has also been reported [3]. Such studies have led Williams and co-workers [9, 10] to propose a mechanism for the initial isothermal formation of ω involving athermal nuclei. It is suggested that the anomalously fast nucleation results from small-scale chemical fluctuations which produce small solute-lean regions where the ω_s is raised locally above the ageing temperature. These regions can then spontaneously undergo the structural transition to ω via the athermal mechanism and then grow slowly via diffusional solute partitioning and equilibration between ω and β. They also propose that interstitials influence ω formation by depressing the ω_s, as observed [1], as a consequence of interacting with the strain fields of the displacement wave packets which constitute the ω nuclei and inhibiting their ordering into the $\langle 1\,1\,1\rangle\beta$ rows and row clusters which constitute the ω domains.

However, there exists in the literature evidence of isothermal changes in metastable β even at room temperature where the compositional fluctuations discussed above cannot be invoked. It has been suggested, without microstructural evidence, that changes in elastic modulus [11] and hardness [12] observed at room temperature in metastable β alloys are due to isothermal ω formation. Further evidence of room temperature time-dependent property changes has been obtained by the present author in a study of stress-induced martensite formation in the Ti–Zr–V system [13]. In that work it was found that as the time interval between quenching the samples after solution treatment and mechanical testing increased the yield strength rose and ductility decreased: ω formation was invoked to explain the observations.

It is the purpose of the present paper to investigate the isothermal ageing characteristics of a Ti–10 wt% Zr–12 wt% V alloy at temperatures below those at which substitutional diffusion can be involved, to confirm the role of ω formation and to establish a mechanism by which the ageing can occur.

2. Experimental procedure

As part of a wider study of the deformation modes of highly metastable β titanium alloys in the Ti–Zr–V system an alloy of nominal composition Ti–10 wt% Zr–12 wt% V was produced as a 30 g ingot by melting the elemental components in a non-consumable electrode argon arc furnace with a water cooled copper hearth. The actual composition, as measured from the component weights (there being only 0.03% weight change on melting), is precisely the nominal value. The ingot was hot rolled at 873 K to a thickness of 1.2 mm. 0.1 mm was ground from each surface and standard miniature sheet tensile samples of 14 mm gauge length were punched out. The remaining material was cut into 10 mm squares for hardness testing and metallography. The samples were wrapped in thin molybdenum foil and sealed in silica tubes containing 1/3 atmosphere of high purity argon. They were solution treated for 30 min at 1273 K and were quenched into water, the silica being broken on contact with the water. Ageing treatments were carried out in conventional oil baths. Standard electropolishing and electron microscopical methods were employed for the microstructual studies. Tensile testing was carried out at a strain rate of $3 \times 10^{-4}\,\text{sec}^{-1}$ in an Instron test machine. Small coupons 3 mm × 10 mm × 0.25 mm were also tested in a commercial straining stage in a Jeol 35 CF scanning electron microscope.

3. Experimental results

Samples examined immediately after water quenching from the β-phase field exhibited an equiaxed β grain structure with no evidence of any martensite formation. Thin foils contained typical domains of athermal ω (Fig. 1) associated with well-defined ω diffraction patterns. More detailed examination using $\langle 1\,0\,\bar{1}\,0\rangle$ and $\langle 1\,1\,\bar{2}\,0\rangle\omega$ orientations revealed a structure essentially identical to that observed by Sass and co-workers [2–4] in that each domain of ω consists of a series of much smaller particles which, in this work, are approximately 1.5 nm in diameter and are aligned in rows along $[0\,0\,0\,1]\omega$ (Fig. 2). The smallest ω domains consist of single 1.5 nm particles and aggregates of particles rows constitute the largest domains, approximately 20 nm in diameter. Within the larger domains the particle rows are regularly spaced but there was no obvious inter-row correlation of particle positions although substantial overlap of image information in these cases could obscure any such periodicity.

The as-quenched hardness value was 270 Hv. During tensile deformation martensite plates formed throughout the gauge length. Electron

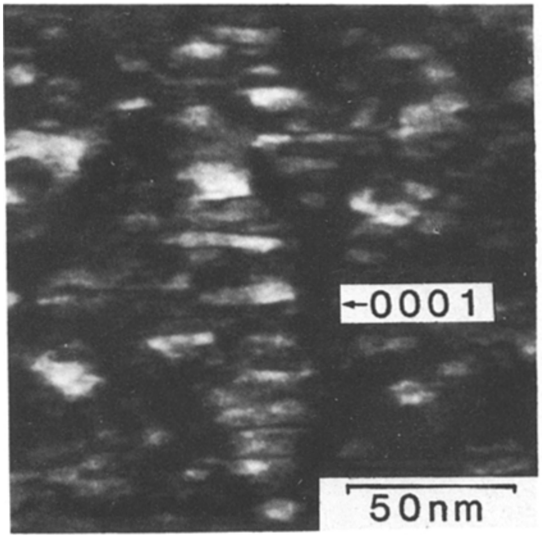

Figure 1 Dark-field micrograph ($g = 0001$) of ω in material quenched from the β-phase field and aged at room temperature for only 5 h. Foil orientation $[10\bar{1}0]\omega$. The morphology of the ω domains is irregular and typical of that of athermal ω.

microscopy showed that the martensite is orthorhombic and is nucleated before any dislocation motion occurs in the β-phase, indicating that the martensite is stress induced. The martensite interfaces shear through and destroy the athermal ω dispersion (Fig. 3). *In situ* straining in the scanning electron microscope demonstrated that the β grains are transformed completely to martensite, which itself deforms by slip and twinning (Fig. 4): This is accompanied by an increase in work hardening rate which eventually saturates resulting in tensile failure at a total strain of ~ 0.33. Ageing in the temperature range 293 to 430 K results in a substantial increase in hardness (Fig. 5) and yield stress and a decrease in tensile ductility. Table I shows the effects of room temperature ageing (293 ± 5 K) on the mechanical properties.

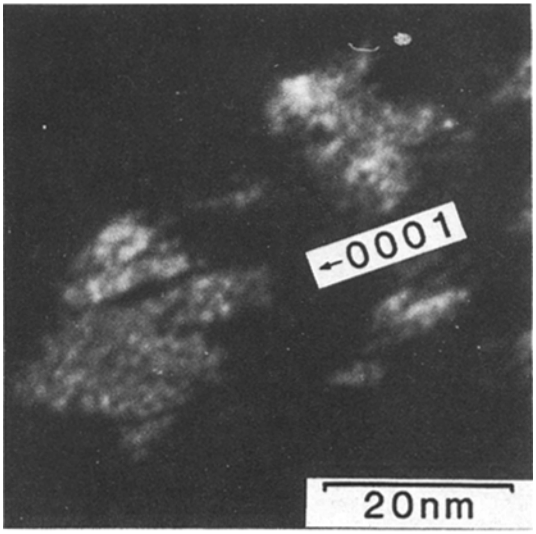

Figure 2 Dark-field micrograph ($g = 0001$) of ω in material aged for 24 h at room temperature. Foil orientation $[10\bar{1}0]\omega$. Individual ω domains can be seen to be composed of much smaller particles aligned in rows along $[0001]\omega$.

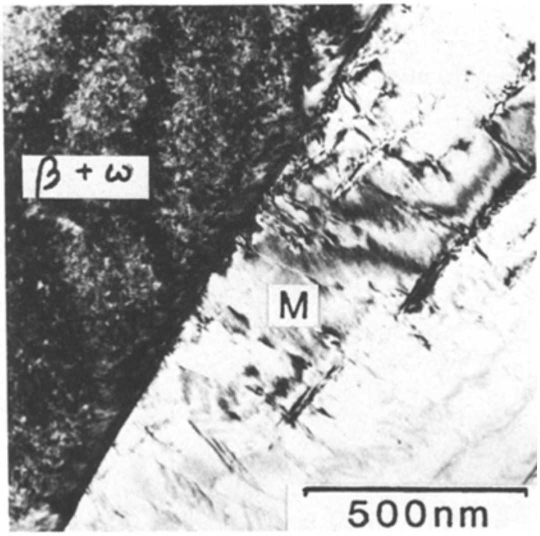

Figure 3 Bright-field micrograph of a martensite/β interface. The high density of ω particles in the β is destroyed by the passage of the interface and conversion of the material to martensite.

Yield is still associated with the formation of the orthorhombic martensite but the greater resistance offered by the hardened β matrix results in the martensite being produced in a work-hardened state with little residual hardening capacity: thus necking resistance and consequent ductility are very low. Although tensile testing was not carried out on specimens aged above room temperature, it was noteworthy that the amount of stress-induced martensite observed at the edges of hardness indentations decreased with increasing ageing time and temperature and ceased when the hardness exceeded approximately 400 Hv, indicating the increasing lattice resistance to martensite formation. Using the age-hardening curves (Fig. 5), and assuming a simple Arrhenius relationship the activation energy was determined (Fig. 6) to be 93 kJ kg mol^{-1}.

Electron microscopy showed that no new

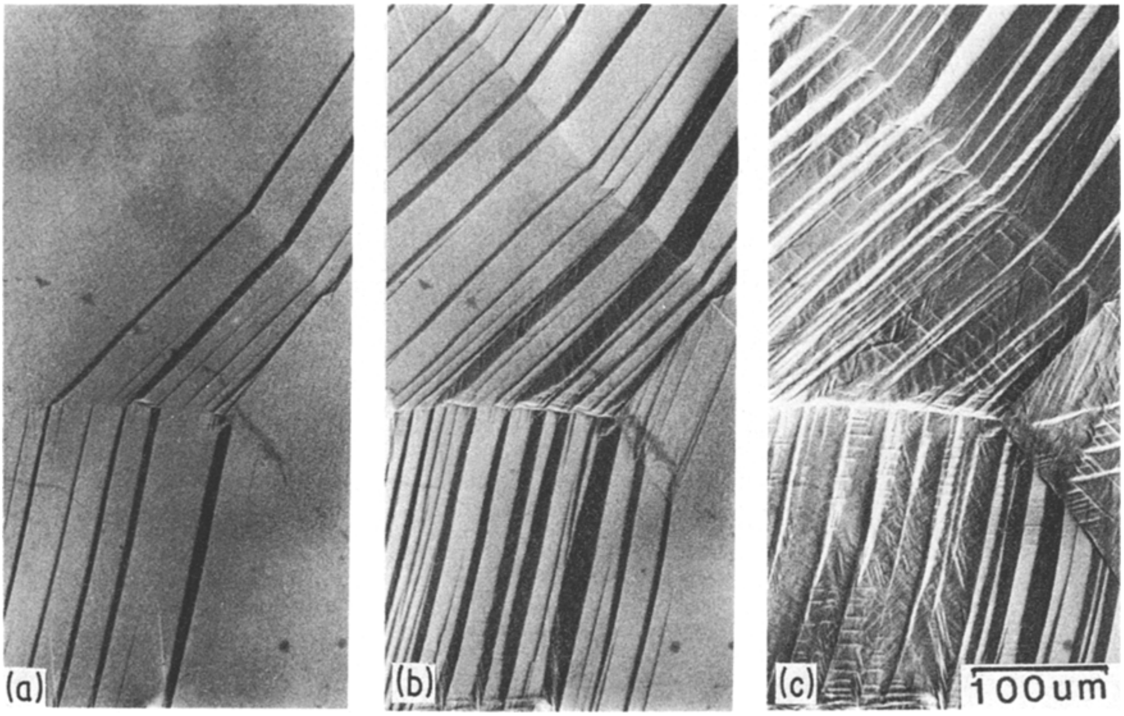

Figure 4 Secondary electron images of a pre-polished surface of solution treated and freshly quenched alloy at increasing levels of strain during *in situ* deformation in the scanning electron microscope. As strain increases (a) → (b) → (c) the martensite plates broaden and deform internally producing the slip steps and twins most clearly seen in (c) when almost complete conversion to martensite has taken place.

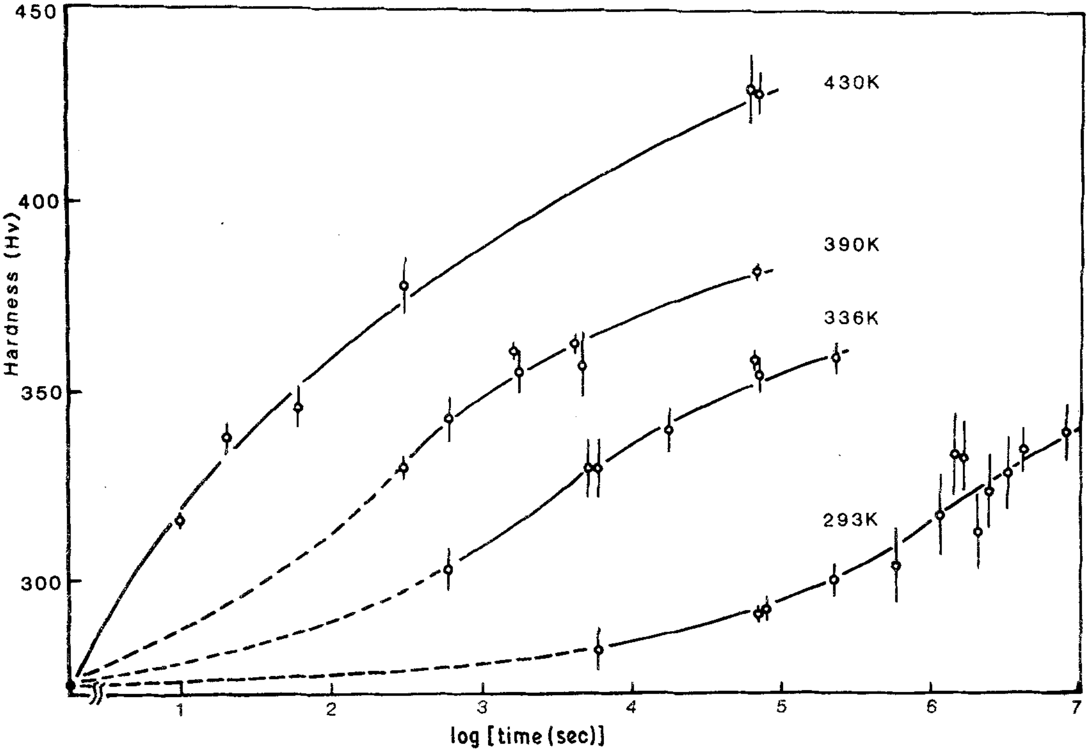

Figure 5 The variation of Vickers hardness with ageing time for Ti–10% Zr–12% V.

TABLE I Tensile properties of Ti–10 wt % Zr–12 wt % V

Condition	Hardness	Yield stress (MPa)	Tensile stress (MPa)	Strain
Freshly quenched	270	490	695	0.33
Quenched and aged 49 days at 293 K	338	620	675	0.05

phases were produced by ageing for the times and at the temperatures employed here. ω morphology remained precisely the same as that observed immediately after quenching and the size range also remained unchanged. In specimens aged above room temperature for the longest times the ω particle density was observed to be increased and more ω domains lay at the upper end of the size range. It was very difficult to establish consistently identical imaging conditions in areas of constant thickness in separate foils and thus small changes in particle distributions could not be measured. It was consequently not possible to prove conclusively that the same changes occurred on ageing at room temperature, although subjectively the same trend appeared to be followed (Fig. 7), and the ω domains consisted of clusters of the 1.5 nm particles as observed in the freshly quenched material (Fig. 2). In no condition of ageing were forbidden $10\bar{1}0$ or $20\bar{2}0\omega$ reflections observed except as a consequence of double diffraction, thus indicating that the property changes were not attributable to any internal ordering of the ω particles.

4. Discussion

The ageing response in the temperature range examined here is clearly associated with the ω-phase since no other phase transformation occurred as a result of heat treatment. The hardening cannot be associated with the development of internal order within the ω particles which has been reported for ω formed at higher temperatures [3] since no superlattice reflections were detected. The microstructural results indicate that the ω volume fraction increases upon ageing but without any significant increase in the maximum size of the ω domains beyond that observed in freshly quenched material. The internal structure of the domains is also unchanged and remains typical of the athermal form of ω. The development of ω of the athermal form with essentially identical substructure has previously been reported by Balcerzak and Sass [3] for Ti–Nb alloys aged for short times at 623 K and associated with the anomalously fast growth regime discussed by Williams and coworkers [9, 10]. The Williams model is directed to systems aged above, but close to, ω_s. Nucleation is

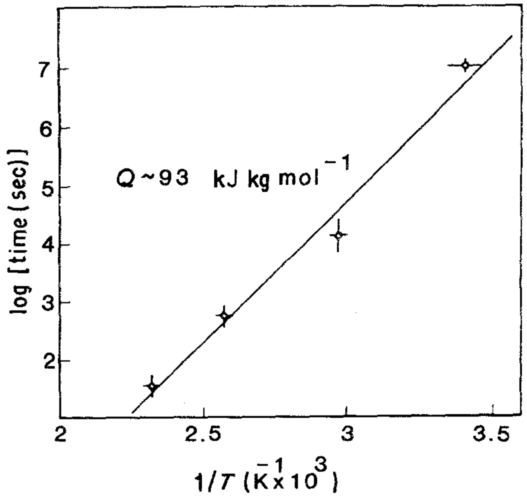

Figure 6 A graph showing the relationship between the time required to achieve a hardness value of 340 Hv as a function of ageing temperature. Assuming a simple Arrhenius relationship the activation energy for the ageing is 93 kJ kg mol^{-1}.

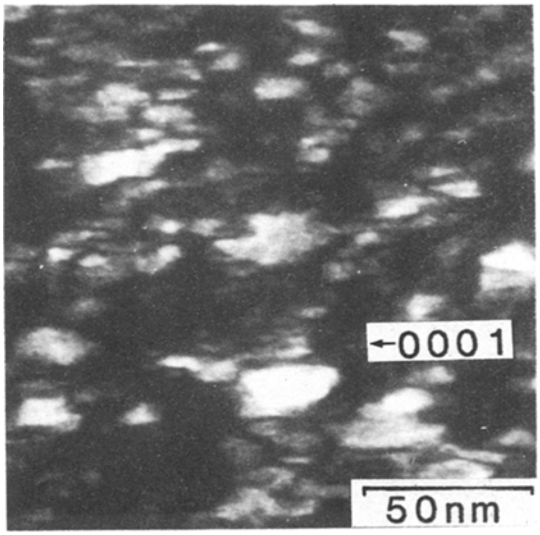

Figure 7 Dark-field micrograph (g = 0001) of ω in material aged at room temperature for 10^7 seconds (125 days). Foil orientation [$10\bar{1}0$]ω. The morphology of the ω is indistinguishable from that shown in Fig. 1.

envisaged to occur by small thermal compositional fluctuations locally producing β sufficiently solute-depleted that ω_s is raised above the ambient temperature. Athermal ω nucleates rapidly in such solute-depleted regions and then grows slowly by normal diffusional processes involving solute partitioning and equilibration between ω and β. It is most unlikely that this model could be extended to the temperature range encompassed in the present work. Extrapolation of high temperature diffusion data for both substitutional species present implies their total immobility at room temperature and times of the order of 10^7 seconds for migration by only one atomic spacing at the highest ageing temperature employed. Therefore neither the nucleation of additional ω particles nor the growth of quenched in ω domains can involve substitutional solute diffusion.

Since the ageing occurs below ω_s the ω structure must have a lower chemical free energy than that of β at the composition of the alloy. The fact that β only partially decomposes into ω on quenching indicates the presence of a barrier to its growth. It has been suggested, as noted in the introduction, that interstitials may provide such barriers by interaction with the strain fields at the ends of the displacement wave packet-induced defects in the β structure which act as ω particle nuclei. The interstitials inhibit the growth of the defect into an ω particle and development of the $\langle 1\,1\,1\rangle\beta$ rows and production of inter-row correlation necessary to produce domains of ω. The interstitials cannot be irreversibly trapped since it has been shown by Sass and co-workers that the 1 to 2 nm particles which make up the $\langle 1\,1\,1\rangle\beta$ rows are dynamic in nature at room temperature. In the present case dynamic trapping and detrapping must lead to a net increase in the amount of ω since a detrapping event which produces an ω particle, especially in a row or inter-row correlated position, results in a reduction in volume free energy and such a particle will be stabilized against reversion to β. A mechanism thus exists for the isothermal increase in volume fraction of athermal ω at temperatures too low for substitutional diffusional processes. The relatively low value of the activation energy measured ($93\,\text{kJ}\,\text{kg}\,\text{mol}^{-1}$) is consistent with such an interstitial migration-controlled mechanism: oxygen is the major interstitial impurity in the alloy (~ 2000 ppm) and is therefore considered to be responsible for the mechanism of ω growth. Indeed it is possible that this mechanism also applies in cases where ageing is carried out above ω_s. As noted in [1] for Ti–17% V an increase in oxygen content from 250 to 1750 ppm depresses ω_s from nearly 700 K to only 100 K. If this is due, as proposed in that paper, solely to interstitial pinning of the displacement defects which constitute ω nuclei and not to an oxygen-induced change in the relative free energies of ω and β phases then, in the temperature range up to at least 700 K, ω has a lower free energy than β at the composition Ti–17% V. Hence ageing in this range could produce ω which is athermal in form via the mechanism proposed in the present work. At the upper end of the temperature range it offers an alternative to the Williams model which is restrictive in the composition range to which it applies and is more complex in that it requires first the creation of thermally induced compositional fluctuations of a size at least as large as an ω embryo (1 to 2 nm) and the creation and growth of a displacement wave packet in that region to produce an ω particle. This can only occur if the lifetime of the compositional fluctuation is long in relation to the frequency of formation of displacement wave packets.

At a practical level the low temperature isothermal formation of ω-phase has been demonstrated to inhibit markedly the production of stress-induced martensite and reduce tensile ductility. In order to exploit potential transformation induced plasticity (TRIP) effects in this and related β alloys, it will be necessary to prevent ω formation. The addition of more β stabilizer is not practical since this would also inhibit martensite formation. Neutral or α stabilizing elements such as tin and aluminium may be beneficial and are the subject of further study.

5. Conclusions

1. The age hardening of Ti 10 wt % Zr 12 wt % V in the temperature range 293 to 430 K is due to the formation of ω-phase which exhibits a morphology of the athermal type.

2. The ω formation inhibits the production of stress-induced martensite and is highly deleterious to the tensile ductility.

3. It is proposed that the ω formation is controlled by the unpinning of ω embryos from interstitial oxygen atoms and that this process may also control the previously reported fast formation of ω isothermally at temperatures above ω_s.

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