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THE ω-PHASE REACTION IN TITANIUM ALLOYS

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Introduction

The $\beta \rightleftarrows \omega$ transformation represents a somewhat unusual problem in that it has received significant attention, both theoretically and experimentally, from materials scientists and from materials engineers. The former group view the transformation as a fully reversible, displacement controlled transformation and continue to seek new ways to study the phenomenon. The engineers, on the other hand, view ω-phase formation as the source of embrittlement and, therefore, search for ways to avoid it. As a result of these variour motivations for studying it, the $\beta \rightleftarrows \omega$ transformation is now much better, but still not completely, understood.

In this paper we will first briefly review the general characteristics of the ω-phase. Then we will discuss the current status of the athermal $\beta \rightleftarrows \omega$ transformation and comment on the relationship between this transformation and isothermal ω formation. Finally, we will present some new observations regarding the morphological changes during isothermal ω-phase formation including observations on the relationship between the ω and α phases.

Characteristics of the ω-Phase

The ideal omega structure can be viewed as having a hexagonal (P6/mmm) unit cell, with 3 atoms per cell, positioned at: (0,0,0), (1/3,2/3,1/2), and (2/3,1/3,1/2). The resulting c/a ratio is 0.613. In Ti alloy systems, this ideal structure has been confirmed both by X-ray and electron diffraction [1-3]. In other ω forming systems (based on Zr or Hf), an axial shift of the cell internal atoms has been reported, which results in a (c/a) ratio slightly greater than .613[4].

The ω-phase can form in either of two distinct modes. In relatively dilute alloy compositions, the ω-phase appears during the rapid quenching from the β-phase field to temperatures below the ω start temperature (T_ω). This type of ω is referred to as athermal ω (ω_{ath}). Isothermal aging of these alloys, as well as alloys richer in β stabilizing alloying additions, produces isothermal ω (ω_{iso}).

Isothermal ω is generally reported as having either an ellipsoidal or cuboidal morphology. As will be discussed in this paper, the primary shape controlling factor is the β/ω misfit which in turn is controlled by the solute misfit in the β-phase.

Another aspect of the $\beta \rightarrow \omega$ transformation is observed after quenching alloys slightly too rich to form ω_{ath}. Specifically, a "pre-transition" phenomenon is observed. Although no discrete particles can be visibly associated with this region, streaking in reciprocal space has been observed by both electron and X-ray diffraction. This phenomenon has been the subject of many theoretical and experimental investigations. However, discussions of the "pre-transition" streaking are beyond the scope of this paper[5,6,7].

Although the emphasis of this paper will be on the isothermal formation of ω, we feel that ω_{iso} and ω_{ath} are more closely related than has been previously recognized. Thus, it will first be necessary to review the displacement controlled reaction which is attributed to ω_{ath} formation before presenting our views and evidence which relate the two reaction products, ω_{iso} and ω_{ath}.

The Displacement Controlled Reaction - ω_{ath}

In Figure 1, free energy versus composition curves are represented for the α, ω, and β phases in a hypothetical ω forming alloy system (viz-Ti-V). Although the β+ω common tangent is metastable relative to the α+β tangent, in practice the α-phase precipitates very slowly compared to ω. For the purposes of following discussions, we will focus our attention on ω-formation and ignore the subsequent precipitation of α.

Between compositions A and C of Figure 1, β is energetically unstable with respect to decomposition into the ω and β phases. We should expect that the β-phase will decompose into a β matrix at composition A, with ω particles of composition C. Since this reaction requires diffusion, it can be suppressed by quenching. If the alloy composition falls between A and B, however, a compositionally invariant transformation from β to ω is still energetically favorable. But for this to occur, a diffusionless mechanism for changing the β structure into ω is required.

Experimental evidence for the existence of such a compositionally invariant mechanism is abundant, but the details of the mechanism are much more difficult to determine. The observation that the ω_{ath} reaction cannot be suppressed by quenching rates as high as 11,000°C/sec[8] certainly indicates that a composition change is unlikely. Reversibility studies performed below 0°C with cold stage TEM[9] provide further evidence that the reaction is compositionally invariant. Evidence that the $\beta \to \omega$ reaction does not involve high diffusivity paths is evidenced by the consistently reported uniform nature of ω_{ath}, as well as the extremely high particle density ($\sim 10^{18}/cm^3$) (Fig. 2). The small size and the uniformity of ω, the lack of surface effects, and the short range atom movements associated with the crystal structure change are among those factors which separate the ω mechanism from the classical martensitic reactions which are dominated by lattice shear. The damping associated with the $\beta \rightleftarrows \omega$ reaction also is consistent with an atomic shuffle transformation, rather than a diffusional one.

De Fontaine[10] first pointed out that a $\vec{k} = \frac{1}{3}$ <112> transverse bcc lattice displacement wave of the proper amplitude would convert the bcc β-phase to the ideal ω structure. Further, he showed that such a mechanism would result in the observed orientation relation:

$$[111]_\beta \| [0001]_\omega$$
$$(1\bar{1}0)_\beta \| (11\bar{2}0)_\omega$$

Figure 3 demonstrates this by viewing the $(1\bar{1}0)$ plane of the β matrix (closed circles), during passage of a $\underset{\rightarrow}{k} = \frac{1}{3}[11\bar{2}]$ sinusoidal transverse displacement wave. The displaced atomic positions resulting from such a wave are shown by the open circles. This displaced, or periodically disturbed, structure is then the $(11\bar{2}0)$ plane of the ω structure.

De Fontaine was able to show by harmonic lattice theory that minimum stability contours in the bcc structure fell along the {111} octahedral planes in reciprocal space. Further, that the stability minimums corresponded to $\underset{\rightarrow}{k} = \frac{1}{3}\langle 112\rangle$ transverse waves, which can be equivalently viewed as 2/3 <111> longitudinal waves.

Harmonic theory was not, however, able to account for several aspects of the β→ω transformation. Specifically, it provided no activation barrier for the lattice displacement. The implications of this were that nothing would prevent the ω reaction from going to completion. Also, there was no preference provided for phonons of the specific wave amplitude required to form ω from β. This problem was corrected by Cook[11,13], who used an anharmonic approximation of lattice energy. Cook's approximation of lattice energy took the form:

$$F \simeq \frac{1}{2}\gamma_{ij}U_iU_j + \frac{1}{3!}\gamma_{ijk}U_iU_jU_k$$

where γ_{ij} and γ_{ijk} are coupling parameters, and are physically the second and third derivatives of the lattice free energy-F with respect to the planar displacements - U_i, U_j and U_k. It is the second term, the anharmonic term, of this expression that drives the ω reaction. This third order coupling term appears to be important only at low temperatures. (Graphically we can visualize this by studying Figure 4). Plotted are the lattice energy and displacement amplitude for a transverse wave of $\underset{\rightarrow}{k} = \frac{1}{3}\langle 112\rangle$. Below the omega start temperature - T_ω, the energy minimum corresponding to the ω structure must lie below that for the β structure. Separating the β and ω energy wells, there must be an activation energy barrier and an activated complex state - β^*. The$_*$reversibility and quenching studies discussed above are evidence that F^* must be very small. Above T_ω, the energy minimum associated with the ω structure may still exist, but is now metastable to the β. From Figure 4, we can see that a wave of amplitude greater than A^* is required to form ω. To achieve this, Cook[11] has proposed that the amplitude of the above displacement wave be thermally modulated. The result is pictured in Figure 5, as regularly spaced wave packets. Since the amplitude of the modulated displacement wave alternates polarity from packet to packet, every other wave packet is out of phase by 180° with the required ω displacement. Thus every other packet is a potential ω former. If the envelope amplitude is above A^*, ω will form. A phonon flipping mechanism[11] could subsequently transform the remaining packets to ω. The end result, as predicted by this model, is a field of ω particles spaced periodically along the <111> directions (Fig. 5b), with a spacing controlled by the envelope frequency or, in this case, by the temperature.

Finally, it is useful to examine the sequence of events occurring as an ω forming alloy is rapidly heated to an aging temperature - $T_a > T_\omega$. During heating, the ω free energy curve of Figure 1 will rise relative to the β curve. This is qualitatively equivalent to shifting our alloy composition to the right in Figure 1. Above T_ω, our alloy composition must lie to the right of composition B. Between compositions B and C, the β structure is energetically preferable to ω, assuming, of course, local composition changes by diffusion are suppressed.

From both Figure 1 and Figure 4, we do not then expect to observe the athermal ω reaction above T_ω. Cold stage microscopy has revealed, however, that the reversion of ω to β occurs over a range of temperatures[9]. Diffuse neutron scattering work[14] has shown that ω particles are present well above T_ω, even though no particles were visible in TEM. Cook[13] has stated that this presents no theoretical difficulties. The apparent contradiction between microscopy and neutron scattering can be understood in terms of particle lifetime. Fluctuations between the β and the quasi-static ω structures could be too rapid for detection using microscopy, but could be readily found by neutron scattering[14]. Moreover, these heterophase fluctuations above T_ω should be expected, since an ω energy well in Figure 4 still exists, and because β-ω_{ath} strain fields are likely to be extremely small. For the purposes of the following discussion, it will be necessary to assume that the ω structure can persist above T_ω in a steady state equilibrium, but that the number of ω particles decreases as $(T-T_\omega)$ increases.

Isothermal ω

The nucleation of ω during isothermal aging appears to progress independently of both grain boundaries and dislocations. Further, recent work[15] has demonstrated that residual solute depleted zones (resulting from a phase separation reaction in the Ti-Cr system) do not seem to effect ω nucleation. We suggest that at aging temperatures near T_ω, growth may continue from the quasi-static ω_{ath} particles which remain after heating to T_a. Figure 6 supports this view. The size consistency of the isothermal ω indicates that all nucleation events were essentially simultaneous. Also shown in Figure 6 is hyperfine ω; ω_{ath} that has reprecipitated during the requench of T_a. If this nucleation model is correct, re-aging at a lower temperature would mean that fewer ω_{ath} particles revert to β, and more would become available as nuclei for ω_{iso} growth. Thus, a bimodal size distribution should be expected and, in fact, is found (Fib. 7). If the original T_a is lowered, we should expect and find a higher number density of particles (Fig. 8).

A mechanism of isothermal growth is now required. The apparent anomalously rapid growth of ω after only 1 minute at 400°C (Fig. 6) cannot be analyzed using diffusional growth. That is, simple calculations of diffusion at such low temperatures indicates that precipitation by solute segregation to the β+ω tie line compositions of Figure 1 is impossible. Furthermore, the displacement controlled mechanism applied to athermal ω formation is energetically unfavorable in this regime.

To surmount these difficulties, we visualize a β compositional fluctuation in the vicinity of a quasi-static ω_{ath} particle. This would reduce the ω free energy with respect to β. In terms of Figure 1, the local β composition would enter the A-B regime. Following this event, growth by the displacive mechanism could then proceed as already discussed. We should thus observe a rapid physical growth of the ω-phase, followed by a gradual chemical equilibration to the β-ω tie line compositions A and C. Such a process was alluded to by De Fontaine et al[9].

Note also, that in alloy compositions just to the right of 'B' in Figure 1, particle growth will be far more rapid than chemical equilibration, while in heavily β-stabilized compositions (near composition C of Figure 1), particle growth and chemical equilibration should correlate reasonably well. In fact, precipitation in these latter solute rich compositions should begin to approach the classical diffusion controlled nucleation and growth.

There is experimental evidence for this in the literature. Hickman[16] measured changes in β lattice parameters during ω precipitation in Ti-V alloys of several compositions. Since V markedly contracts the Ti lattice, he was able to use lattice parameter and volume fraction data obtained from X-ray diffraction to follow changes in β and ω compositions during aging. The physical growth of ω was, in fact, observed to occur over a shorter time scale than the solute rejection of ω. Recent Mössbauer work[17] in Ti-7.1wt%Fe shows a similar effect.

Perhaps the most definitive support for the diffusionally assisted, displacement controlled growth of ω can be found in Figures 6 and 7. It has been a generally accepted observation that low misfit ω forming systems such as Ti-Mo and Ti-Nb form ellipsoidal ω_{iso} with the major axis of the ellipsoidal lying along the "elastically soft" $\langle 111 \rangle_\beta$ direction[18,19]. High misfit systems such as Ti-Fe, Ti-V, Ti-Cr, Zr-Nb, Ti-Mn form cuboidal ω with the cuboid faces lying parallel to $\{100\}_\beta$ planes[19]. The generally accepted explanation of this phenomenon is that high misfit systems must assume a shape minimizing strain energy, while low misfit systems take on a shape minimizing surface energy. The observation of ellipsoidal ω in the high misfit Ti-10V-2Fe-3Al alloy (Fig. 6) can only be explained by the incomplete solute segregation between β and ω. Continued aging (and continued solute segregation) then converted the sllipsoids to the anticipated cuboids (Fig. 7). It was necessary to lower T_a from 400°C to 300°C during the second aging treatment in order to suppress α formation.

The hyperfine particles of Figure 6 demonstrate still more support for the diffusionally assisted displacement controlled growth process. During requenching, a uniform distribution of ω_{ath} appeared throughout the untransformed β matrix. The lack of an ω_{ath} free zone around ω_{iso} particles demonstrates solute rejection could not have been extensive during ω_{iso} growth. Note that the ω_{ath} is absent in Figure 7 because the β matrix is now enriched in solute due to diffusional partitioning.

The ω_{iso} final particle size appears to be dependent on temperature more than time. We can visualize four possible reasons that an isothermal ω particle could stop growing.

1. Chemical stabilization of the β matrix
2. Coherency strains
3. Dilatation strain fields overlap

The first of these is likely to be controlling when the aging times are very long, or when the alloy composition is far to the right of composition 'B' in Figure 1. Coherency strains, on the other hand, will tend to limit growth at high temperatures and short times when the alloy composition is near composition 'B' of Figure 1. In this situation, the β matrix remain chemically unstable relative to the ω structure, but the increase in strain energy that would result from further growth outweighs the chemical energy gains of transforming the β structure to ω. It is yet unclear what magnitude or even what sense the dilatational strain fields surrounding a growing ω particle might have. It may be that when the particle density is high (Fig. 8), growth is limited by the interaction of such strain fields. Perhaps it is this interaction which prevents high ω dispersion densities from adopting a specific particle shape.

Conclusions

A model for the isothermal precipitation of ω in Ti alloys has long been presented, which utilizes chance compositional fluctuations to set the stage for a compositionally invariant growth mechanism. In heavily β-stabilized alloys, this type of growth does not differ from "classical" diffusion controlled growth. As the alloy content becomes leaner (or the β structure less stable), the compositionally invariant growth mechanism begins to dominate, and certain "unusual" growth phenomenon is observed, which distinguishes the β→ω reaction from most others. For example, a morphology transition from ellipsoids to cuboids was noted in Ti-10V-2Fe-3Al at a constant size. It was proposed that this could result from a rapid, chemically invariant ω particle growth, followed by a slow composition equilibration.

Acknowledgments

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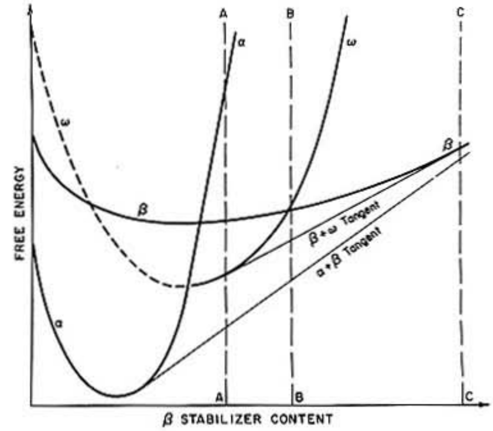


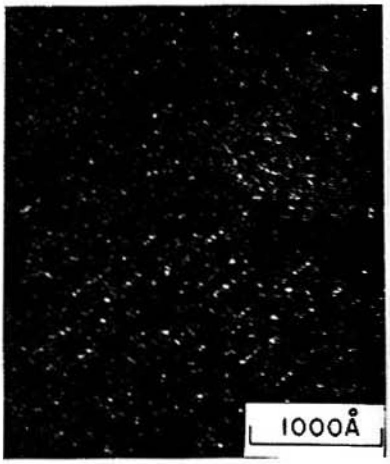


Fig. 1 - Schematic free energy curves for the α, β, and ω phases in a β stabilized Ti alloy.

Fig. 2 - Athermal ω in β-ST and water quenched Ti-10V-2Fe-3Al shown by dark field TEM.

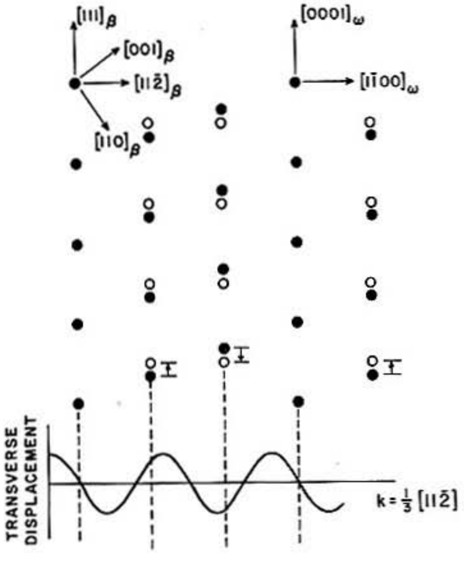


Fig. 3 - Representation of the atomic "shuffles" involved in the β-ω transformation. Closed circles represent ω lattice positions, and open circles represent the displaced, or ω lattice sites. The $(1\bar{1}0)_\beta$ plane is shown with the atoms displaced by a $\underline{k} = \frac{1}{3}\ [11\bar{2}]$ wave.

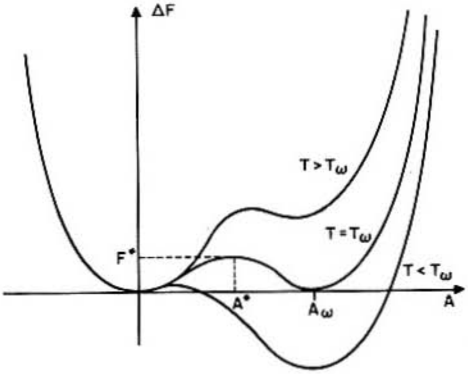


Fig. 4 - Schematic representation of a free energy versus wave amplitude curve for a $\underset{\sim}{k} = \frac{1}{3} <11\bar{2}>$ transverse wave.

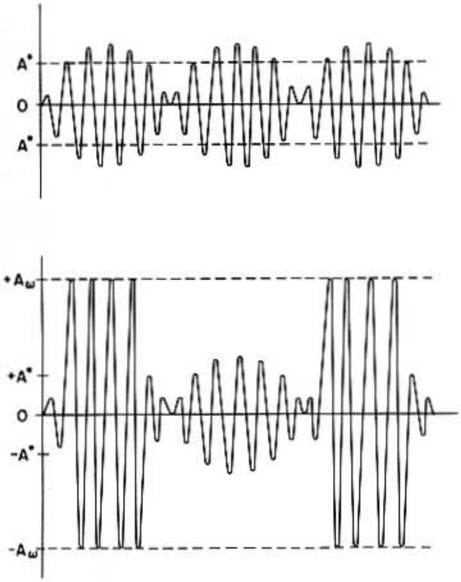


Fig. 5 - (a) Modulated sinusoidal wave, forming wave "packets" of alternating "sense", and (b) the growth of discrete ω particles from the above packets. The displacements of the center packet are 180° out of phase with the "proper" ω displacements, and are therefore unstable.

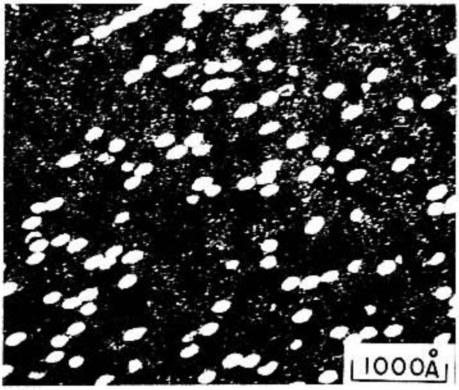
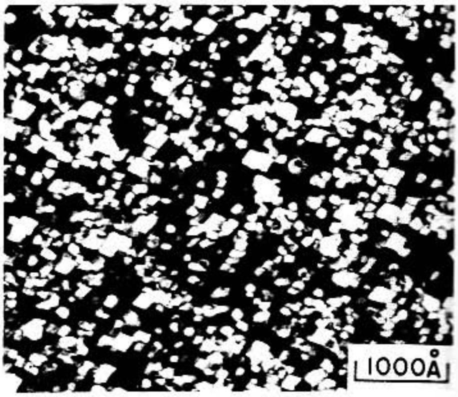


Fig. 6 - Ellipsoidal isothermal ω in β-ST Ti-10V-2Fe-3Al aged at 400°C for 1 minute.

Fig. 7 - Cuboidal isothermal ω, in β-ST Ti-10V-2Fe-3Al duplex aged at 400°C for 1 minute, and 300°C for 45 minutes.



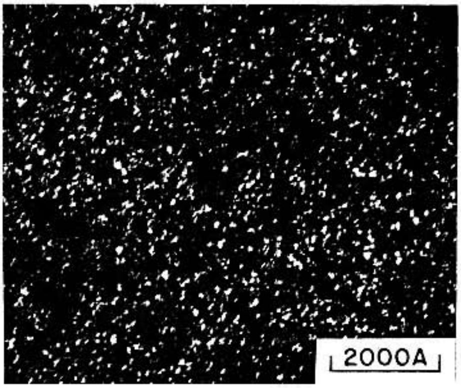


Fig. 8 - Isothermal ω of non-descript form, in β-ST Ti-10V-2Fe-3Al aged at 260°C for 10,000 mins.