The Formation of Omega Phase in Titanium and Zirconium Alloys: A Review

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The omega phase is a metastable phase which forms in alloys of titanium and zirconium with most transition metals. In this paper the available data from both alloy systems on the occurrence, the structure, the mechanism of formation, and the morphology of the phase are reviewed and compared. The effect of omega phase on the mechanical behaviour and on the superconducting properties is then discussed. It is concluded that uncertainties still exist on the mechanism of the omega transformation during quenching and on the mechanism of the effect of omega on the mechanical properties.

1. Introduction

Since its discovery in 1954 by Frost *et al* [1] there has been considerable interest in the precipitation of the metastable omega (ω) phase in titanium and zirconium alloys. Initially this interest was motivated by the very marked effect that the phase has on the mechanical properties of the alloys; it causes large increases in strength and large reductions in ductility. More recently interest has been stimulated by the discovery of the marked improvement in the superconducting properties of titanium and zirconium alloys which accompanies omega phase precipitation; large increases in the critical transport current densities in an external magnetic field can be obtained by omega phase precipitation.

Omega phase is a metastable phase which forms in alloys of titanium and zirconium with elements which tend to stabilise the high temperature bcc structure, and depending on the conditions it can form either during quenching from the β-phase region or during ageing of quenched material. It is always metastable with respect to the equilibrium $(\alpha + \beta)$ or $(\alpha +$ intermetallic compound structures).

Reviews of limited scope of omega phase precipitation have been published for titanium alloys [2-4]. In this review studies on both titanium and zirconium systems will be compared. An isolated observation has been made of omega phase precipitation in hafnium alloys [4] but this will not be considered further. The

structure, the conditions and mechanisms of formation and the morphology of the precipitation will be discussed and correlated with the effects on the physical and mechanical properties. It will become obvious that there are still several aspects of this rather unusual precipitation phenomena which are as yet not clearly understood.

2. Occurrence

As mentioned above, the omega phase is observed in all titanium or zirconium alloy systems in which the high temperature bcc phase can be retained in a metastable state at low temperatures by rapid cooling. In both metals the transition metals to the right of titanium in the periodic table, i.e. those of groups VA, VIA, VIIA and VIIIA, are considerably more soluble in β than in α and hence stabilise the β-phase [2, 5]. Two general types of equilibrium phase diagram exist for these systems, depending on whether intermetallic compounds form or not. These are illustrated in fig. 1. In both types the $\beta \rightarrow \alpha$ transition can be suppressed below the equilibrium temperature by quenching; the transformation occurs martensitically at lower temperatures. The M_s temperature is however below room temperature if the alloy content is high enough so that the β-phase can be fully retained at room temperature in a metastable state over a certain composition range.

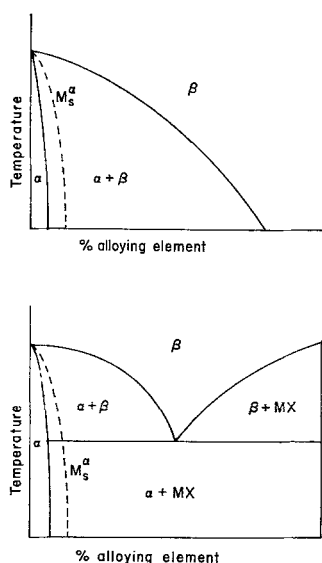Omega phase formation is observed to occur in these systems under three conditions:

Figure 1 Typical phase diagrams for titanium and zirconium alloy systems in which omega phase can be formed. The upper diagram is for a β-isomorphous system (e.g. Ti–V) and the lower for a β-eutectoid system (e.g. Ti–Cr).

(*i*) Over a limited range of alloy content close to the lower limit for retention of the β-phase, omega precipitation occurs during quenching in most systems. The composition ranges over which this occurs have been summarised by several workers (see for instance [3, 6]) but these figures do not have a great deal of significance since they depend on quenching rate and probably on impurity level. Bagaryatskiy and Nosova [7] showed that in a Ti–6 wt % Cr alloy the omega formation was not suppressed even at cooling rates as high as 11 000° C/sec. In some systems, e.g. Ti–Nb [8], omega phase is not observed in rapidly quenched specimens because, as discussed later, in the composition range where it could form, transformation to the hexagonal α' or orthorhombic α'' phase occurs first. However, reheating these alloys above the M_s temperature can result in omega precipitation which is then retained on subsequent cooling to room temperature [8]; quenching at a slower rate allows omega to precipitate during cooling. In addition to its formation in binary alloys, Sass [9] has shown that omega phase can be formed during quenching of Ti–75 at. % Zr alloys if they are contaminated with oxygen. In a pure alloy no omega phase is observed.

(*ii*) At higher alloy contents the omega phase forms during ageing in the temperature range

100 to 500° C. The exact temperature range over which omega phase forms varies from one system to another and a possible explanation for this is discussed in section 4. It appears that in those systems where the β-phase is stable at room temperature at high alloy contents, omega phase formation only occurs when the alloy composition is significantly lower than the equilibrium composition, i.e. there is a composition region in which the decomposition proceeds directly to the equilibrium $\alpha + \beta$ structure without forming omega [7, 10]. Continuation of the ageing treatment after omega formation finally causes formation of the equilibrium α-phase. Many workers have constructed TTT type diagrams for these reactions and a typical diagram is shown in fig. 2.
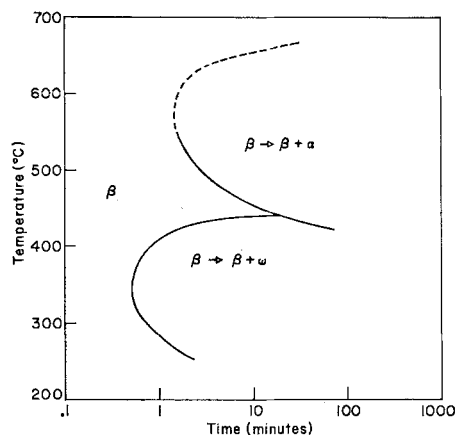

Figure 2 A typical time-temperature transformation diagram for formation of omega phase during ageing in a Ti–20 wt % V alloy (after Harmon and Troiano [17]).

(*iii*) Deformation at room temperature has been shown to produce omega phase under certain circumstances. Bagaryatskiy *et al* [41] showed that omega phase formed during deformation of a quenched Ti–8 wt % Cr alloy. Brotzen *et al* [42] found that compressive deformation of a quenched Ti–15 wt % V alloy caused an increase in the amount of omega phase. However, Silcock [23] could find no effect of deformation in a Ti–20 wt % V or a Ti–13 wt % Mo alloy. Wood [43] suggests that this was due to the preferential formation of martensitic α in these alloys. Wood showed that in a quenched Ti–15 wt % Mo alloy martensitic α forms during the early stages of deformation but that in fine grain

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specimens omega phase formation occurs after about 5% deformation.

In addition to its formation in β-stabilised alloys, omega phase has been observed to form in pure titanium and zirconium under the influence of very high pressures (50 to 80 kbars) [11-13]. Jamieson [11] found that in both titanium and zirconium the transformation from the hcp structure to the omega phase was complete at room temperature and that the omega phase was stable after removal of the pressure. Heating of the titanium for 17 h at 110° C caused complete reversion to α and 4 h at 195° C caused partial reversion of the zirconium. Bundy [13] determined a pressure/temperature phase diagram for titanium which showed the limits of stability of the three phases (α, β and ω).

The effect of α-stabilising additions such as aluminium which are normally present in commercial alloys on the occurrence of the omega phase formation, have been investigated by various workers. Weygand and Dorst [47] observed that aluminium additions to a Ti–9 wt % Cr alloy reduced the volume fraction of omega, increased the incubation times, and reduced the upper temperature limit for formation of omega phase. Aluminium has also been observed to retard the omega phase precipitation in Ti–V alloys [51] and in Ti–Mo–Mn alloys [48] Novikov *et al* [49] observed that oxygen resulted in the formation of less omega phase in a Ti–Cr alloy, but it did not affect the incubation time.

3. Composition

The composition of the omega phase produced in quenched material must be close to that of the matrix alloy, but many workers have noticed that omega precipitation during ageing is accompanied by a shift of the lattice parameters of the β-phase matrix, indicating an enrichment of the β-phase in the alloying element. Hickman [8, 14] has studied this effect quantitatively in various titanium alloys and has shown that omega precipitation during ageing occurs with a composition different from that of the β-matrix, and that on further ageing the alloying element is rejected from the omega phase until a pseudo-equilibrium composition is reached, which is independent of initial alloy content or ageing temperature. These compositions are shown in table I and comparison with data [3] for quenched alloys show that these compositions are at the lower end of the range of alloy contents for which omega phase is formed on

TABLE I Composition of omega phase after ageing.

Alloy	Composition at. %	
	Hickman [14]	Vanderpuye and Miodownik [10]
Ti–V	13.8 ± 0.3	12–15 at 400° C
Ti–Cr	6.5 ± 0.2	8–9 at 400° C
Ti–Mn	5.1 ± 0.2	≈ 5 at 400° C
Ti–Fe	4.3 ± 0.2	≈ 4 at 400° C
Ti–Nb	9 ± 2	—
Ti–Mo	4.3 ± 0.4	—
Zr–Nb	—	10–11 at 400° C
Zr–Mo	—	2–3 at 400° C
		1–3 at 550° C

quenching. Similar but less precise data was obtained by Vanderpuye and Miodownik [10] from analysis of hardness data on both titanium and zirconium alloys. Their data are also shown in table I.

Cometto *et al* [16] inferred from measurements of the omega phase lattice parameters that a similar process occurred during ageing of Zr–Nb alloys, but they did not obtain a quantitative value for the composition. Blackburn and Williams [15] estimated the volume fraction of omega in Ti–Mo alloys by electron microscopy and deduced a value for the omega composition in reasonable agreement with that found by Hickman.

As has been suggested by several workers [14, 16, 17] a metastable equilibrium diagram can be constructed for the omega phase formation, as shown in fig. 3. It should be noted that the β-phase composition in equilibrium with the omega phase is considerably lower in alloy content than that in equilibrium with α-phase.

Vanderpuye and Miodownik [10], on the basis of their work on zirconium alloys, have proposed a peritectoid type of phase diagram, since they showed that their data for the composition of the ω-phase could be extrapolated to zero alloy content at the same temperature as the β–ω transition on the pressure/temperature diagram extrapolated to one atmosphere pressure (namely 670° C). As discussed by Hickman [8], this concept cannot be applied to titanium alloys since his data showed little consistent variation of the ω-composition with temperature, and the data cannot possibly be extrapolated to zero alloy content at the temperature (450° C) where the β–ω titanium pressure/temperature diagram extrapolates to one atmosphere pressure.

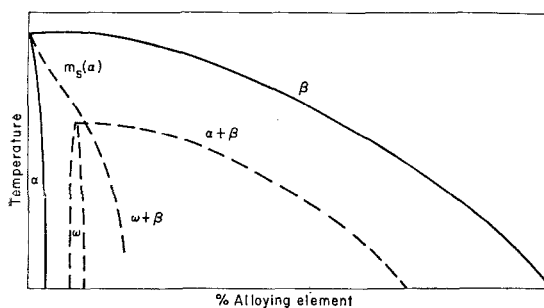The significance of the narrow composition range over which omega is produced during

Figure 3 Metastable phase diagram for omega formation in β-isomorphous systems (after Hickman [8]).

quenching has been discussed by several workers [3, 18, 6]. Bagaryatskiy *et al* [3] collected the available data for titanium alloys and suggested that the omega phase formed when the electron to atom ratio was 4.14 to 4.15. A similar conclusion was reached by Bychkov [6] from an examination of data on zirconium alloys. They conclude from this that omega phase is an electron compound. These conclusions, however, were based on incorrect data and particularly work by Cometto *et al* [16] showed that omega phase formation occurs during quenching over quite a wide composition range in some systems. Luke *et al* [18] suggest that the omega forms over a range of electron/atom ratios of 4.06 to 4.14, but again this conclusion is based on incorrect analysis of the available data. Hickman [8] showed that in several titanium alloys the pseudo-equilibrium composition attained during ageing did not correspond to a constant electron/atom ratio but that the composition did show a definite relation to the position of the alloying element in the periodic table. He suggested that the phase may well be an electron compound but that complications due to the interaction of the various electron energy levels precluded the existence of a constant ratio. Vanderpuye and Miodownik [10] also conclude that a simple electron/atom ratio concept alone cannot explain the range of stability of the omega phase.

4. Structure

Frost *et al* [1] on the basis of powder photographs tentatively suggested a cubic structure with $a = 8.00$ Å for the ω-phase in Ti alloys. Subsequently, Silcock *et al* [19] and Bagaryatskiy *et al* [20] simultaneously published the results of investigations using single crystal techniques. Silcock *et al* studied the omega phase in an aged

titanium–16 wt % V alloy and concluded that the structure was hexagonal with $a = 4.60$ Å $c = 2.82$ Å $(c/a = 0.613)$. The atomic positions were 0, 0, 0, ; $\pm$ 2/3, 1/3, 1/2, belonging to the space group D^1_{6H}–$P6/mmm$. Bagaryatskiy *et al* [20] studied the omega phase in a slow-cooled Ti–5 wt % Cr alloy. They agreed with Silcock *et al* [19] that the structure was hexagonal with three atoms per unit cell and obtained the same values for the lattice constants. However, they did propose slight differences in the atomic positions which changed the symmetry and space group. They proposed the atom positions 0 0 0, $\pm$ 2/3 1/3 μ, with $\mu = 0.48 \pm 0.01$, belonging to the space group D^3_{3D} - $P\bar{3}m1$. In a third study, Austin and Doig [21] studied an aged Ti–8 wt % Cr alloy and proposed a body centred cubic cell with $a_\omega \approx 3a_\beta$ and with fifty-four atoms per unit cell (space group $I\bar{4}3_m$).

Bagaryatskiy and Nosova [22] and Silcock [23] subsequently reported further studies to resolve these discrepancies. Bagaryatskiy *et al* [22] show that the choice between the hexagonal and the cubic cell depended on the observation of a very weak (10, 3, 1) reflection made by Austin and Doig. They did not observe this reflection, nor did they observe other stronger reflections required by the cubic structure and they conclude that the structure must be hexagonal. Subsequent electron microscope observations in which four distinct omega phase orientations have been observed (see for instance [24]), and studies on the omega phase in zirconium discussed below would seem to support this conclusion. Silcock studied aged Ti–16 wt % V, 29 wt % V, 13 wt % Mo and 13 wt % Cr alloys and concluded that the structure of the omega phase was the same in all cases and that the rumpling of the central plane proposed by Bagaryatskiy was less than 0.005. All workers agree that in titanium systems the c/a ratio is always 0.613, although the actual values of the c and a parameters depend on the alloying element and alloy content [14].

The structure of the omega phase in zirconium alloys was first studied by Yakel [25] who confirmed that the structure was basically the same as that proposed for the titanium systems, i.e. hexagonal with atom positions 0 0 0 $\pm$ 2/3 1/3 μ. He found that $\mu = 0.45$ in quenched Zr–15 wt % Nb alloy, but that on ageing μ increased to 0.5. Hatt and Roberts [26] studied aged Zr–7 at. % V and aged Zr–Nb alloys containing 8 to 20 at. % Nb. They also found

that in the aged condition $\mu = 0.5$, but that unlike the titanium alloys the c/a ratio was 0.622. As discussed by Hatt and Roberts, it is not possible to index patterns from the zirconium alloys on a cubic lattice with $a_\omega = 3a_\beta$ because the c/a ratio is not 0.613 but 0.622. Hatt and Roberts also studied the omega phase in quenched alloys and agreed with Yakel that in this case μ was considerably less than 0.5. It is possible, therefore that the rumpling of the central planes is a characteristic of quenched alloys and that the apparent discrepancies in the work on the Ti systems are due to the fact that one group studied aged specimens and the other as-cooled specimens. There are two complications which should be kept in mind when assessing these studies. Firstly, since it is not possible to cause complete conversion to omega phase, the "single crystals" used in the above studies actually consisted of oriented particles of the four omega orientations in a β-phase matrix. In addition, in the quenched condition in certain alloys marked reciprocal lattice streaking effects are present. These effects are discussed further in the section on the mechanism of the transformation but it should be noted here that without a detailed explanation of the reciprocal lattice streaking effects any detailed conclusions on the structure are somewhat dubious.

5. Morphology of the Omega Phase

The early X-ray work [19, 20] showed that the orientation relationship between the omega phase and the β-matrix was $[0001]_\omega \,||\, [111]_\beta$ and $(11\bar{2}0)_\omega \,||\, (110)_\beta$. This has since been confirmed a number of times by both X-ray and electron microscopy techniques. There are thus four possible variants of the omega phase particles and in the absence of effects due to deformation, these four variants are equally populated [23].

Direct observation of omega phase has recently been made by a number of workers using transmission electron microscopy. Croutzeilles et al [27] investigated a Ti–15 wt % Mo alloy aged for 4 h at 400° C and observed rod-shaped particles about 40 Å in diameter by 200 Å long.

Brammer and Rhodes [24] studied a Ti–35 wt % Nb alloy, and in the aged condition observed the omega phase as ellipsoids with the major axis parallel to the $[0001]_\omega$ direction. After 24 h at 450° C the particles were approximately 1300 by 500 Å (fig. 4).

Blackburn and Williams [15] studied a Ti–11.6 wt % Mo alloy at various stages of ageing and observed a similar ellipsoidal morphology with the major to minor axis ratio of about 2.2 and with the major axis again parallel to the $[0001]_\omega$ direction. The particle sizes varied from less than 60 Å in the as-quenched condition to a maximum of 3000 Å immediately before the transformation to α started to occur. These workers also studied an aged Ti–20 wt % vanadium alloy and in this
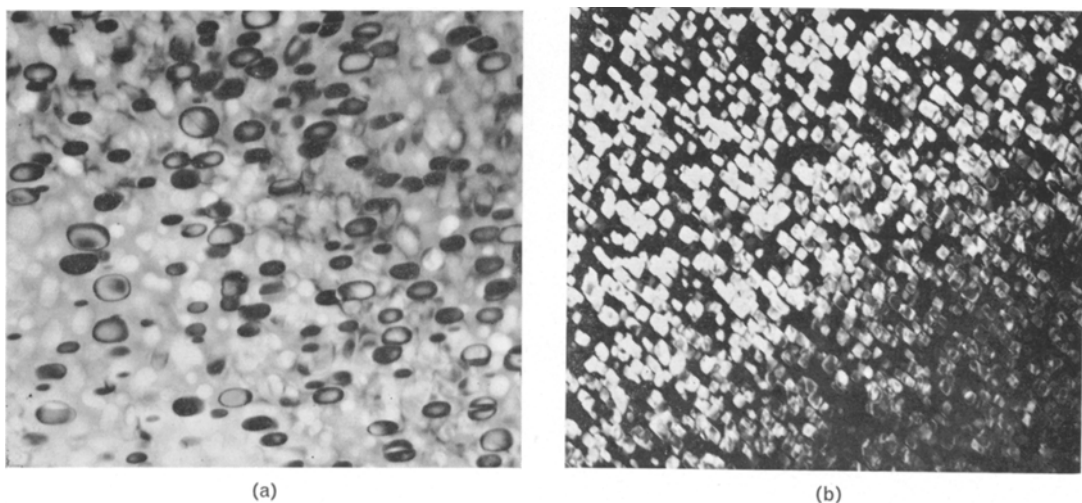

(a) (b)

Figure 4(a) Electron micrograph showing ellipsoidal omega precipitates in a Ti–35 wt% Nb alloy (after Brammer and Rhodes [24]) (×10000). (b) Electron micrograph showing cube shaped omega precipitates in a Ti–20 wt% V alloy (after Blackburn and Williams [15] (× 25000).

case the omega precipitates were approximately cube shaped with the sides of the cubes parallel to $(100)_\beta$, i.e. parallel to $(20\bar{2}1)_\omega$ (fig. 4). Hickman [14] reports a similar observation on a Ti–25 at. % V alloy. Hickman [14], using X-ray diffraction techniques on Ti–V alloys showed that the particle size of the omega phase increased with increasing ageing temperature, but that once precipitation was complete at any given ageing temperature particle coarsening does not occur. Blackburn and Williams [28] have reported that the omega particles are also cubes in Ti–Fe, Ti–Cr and Ti–Mn and this was confirmed by Hickman [8].

The only reported observation in zirconium alloys is that by Stiegler *et al* [29]. They studied a Zr–15 wt % Nb alloy in a fully aged condition and observed omega phase in the form of platelets 1000 Å in diameter by 200 Å thick lying parallel to $\{111\}_\beta$ planes. They also observed an intensity modulation within the retained beta phase which they attributed to a "coherent diffuse omega" phase. Recent work by Cometto *et al* [16] on the same alloy suggests that this is in fact an athermal form of omega which precipitates during cooling from the ageing temperature (see section 6).

The question of the coherency of the omega precipitates in aged alloys has been discussed by Stiegler *et al* [29] and by Blackburn and Williams [15]. Stiegler *et al* [29] stated that the aged omega particles were incoherent because of the sharpness of their images. Blackburn and Williams, however, suggested that in the Ti–V and Ti–Mo alloys that they studied, the particles are coherent They based this conclusion on the lack of any observable misfit dislocations associated with the boundaries and they also observed some contrast effects which could be the δ fringes arising from coherency strains. In X-ray diffraction studies of the Ti–Nb system, Hickman [8] observed lattice parameter changes during the early stages of omega precipitation which he concluded could only be due to coherency strains. The magnitude of the contraction agreed closely with the predicted value for coherency strains.

Blackburn and Williams [28] have suggested that the particle morphology is related to the misfit strains. In Ti–Nb and Ti–Mo systems the misfit is small and the particle shape (ellipsoids) is determined by the minimisation of surface energy which is anisotropic. In the Ti–V, Ti–Mn, Ti–Fe and Ti–Cr systems (cubes) the misfit is greater and the particle shape is determined by the minimisation of the elastic strains in the matrix. Hickman [8] agreed with this conclusion and showed that the critical misfit for the change from ellipsoidal to cubic morphology was about 0.5% (see table II). A similar consideration

TABLE II Computed lattice misfit for omega phase in various titanium alloys (compositions are in at. %).

| Alloy | Lattice misfit % | |
	Initial	Final
Ti–8 % Mo	+ 0.36	+ 0.88
Ti–10 % Mo	+ 0.42	+ 0.88
Ti–6 % Fe	+ 1.04	+ 2.85
Ti–9.3 % Cr	+ 0.88	+ 1.65
Ti–25 % Nb	− 0.23	− 0.45
Ti–20 % V	+ 1.08	+ 2.85
Ti–8 % Mn	+ 0.4	+ 2.80

would seem to apply in Zr–Nb but in this case because the c/a ratio is 0.622 the effect is anisotropic and platelets result.

Blackburn and Williams [28] further suggest that the upper temperature time limits of stability are determined by the degree of misfit. In systems with low misfit (niobium and molybdenum) the omega is stable for higher temperatures and longer times than in systems with high misfit (e.g. vanadium).

6. Mechanism of Formation of Omega Phase

It is generally agreed that the omega phase which forms during ageing is produced by a conventional nucleation and growth process. The evidence for this is as follows:

(*i*) Composition changes occur *during* precipitation [8, 14].

(*ii*) The kinetics of the ageing process depend on the solution treatment temperature and quenching rate [30]. This implies that the vacancy concentration in the specimen is affecting the nucleation and growth process by its effect on diffusion rates.

The possibility that the phase forms by a spinodal decomposition has been suggested; a phase separation could occur at the ageing temperature and the omega phase could form in the solute poor regions, either at the ageing temperature or during subsequent cooling. The very fine scale and the regularity of the omega particle distribution suggests a homogeneous nucleation process. (Several workers have com-

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mented that omega phase formation does not appear to be associated in any way with heterogeneities in the structure, e.g. grain-boundaries, sub-grain-boundaries, or dislocations.) A chemical spinodal is predicted to exist in at least some of these alloy systems [31] and evidence has been presented for a phase separation in zirconium-niobium alloys at high niobium contents [32, 5]. The reversion at high temperatures and the continuous composition changes during ageing would also appear to be compatible with a spinodal mechanism. However, Silcock [23] and Hickman [8] have shown by X-ray diffraction studies at the ageing temperature that the omega phase intensities are comparable at the ageing temperature and at room temperature, i.e. no transformation occurs on cooling. It appears, therefore, that at least during the later stages of ageing, spinodal decomposition is not involved.

The mechanism of omega formation during quenching has been the subject of much discussion and speculation. The following experimental observations must be taken into account in considering this question:

(*i*) Omega phase only forms during quenching over a limited composition range.

(*ii*) Bagaryatskiy and Nosova [7] showed that in a Ti–Cr (6 wt %) alloy, quenching rates as high as 11 000° C/sec did not suppress the transformation.

(*iii*) The omega phase diffraction pattern in quenched materials generally shows extensive reciprocal lattice streaking in the (0001) direction of the omega reciprocal lattice.

(*iv*) In most systems the omega phase appears to form during quenching at around 400° C, i.e. at the same order of temperature as it forms during ageing. However Cometto *et al* [16] showed that in the Zr–Nb system the temperature for the beginning of omega formation during quenching varied with composition from 460° C at 7.5 wt % Nb to 125° C at 17.5 wt %, and similar results were reported by Stewart *et al* [33].

(*v*) Cometto *et al* [16] reported experiments in which in a Zr–17.5 wt % Nb alloy the intensity of the omega phase X-ray reflections increased with decreasing temperature down to − 196° C, and that this transformation was completely reversible without hysteresis. They showed that this type of omega formation could occur in the matrix of an aged alloy during cooling, and have suggested that the intensity modulations between aged omega particles observed in transmission electron microscopy by Stiegler *et al* [29] were

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due to this form of omega. Hickman [8] looked for a similar effect in several titanium alloys but could not observe it. Nelson *et al* [50] have studied the acoustic relaxation processes in a Zr–17.5 wt % Nb alloy and observed relaxations at 160 and 40° K which they attribute to the β to ω transition. In this context it should be noted that most of the titanium and zirconium alloys in which omega phase can be formed, show a negative temperature coefficient of electrical resistivity. Cometto *et al* [16] and Gardner and Raub [52] suggest this is due to electron scattering from omega phase formed in a reversible manner during cooling. However, Luhman *et al* [53] conclude that in Ti–Cr alloys the negative temperature coefficient is still observed in alloys in which omega phase does not form. A negative coefficient is also observed in Ti–Mo [54] and Ti–V alloys [55] in composition and temperature ranges where omega formation is known not to occur [8]. It appears therefore that although omega phase may contribute to the effect in Zr–Nb alloys, its formation cannot be used to explain the negative coefficient in all systems.

(*vi*) Hatt and Roberts [26] showed that the omega structure could be formed from the bcc β-phase by gliding on the $\{112\}_\beta$ planes, the glide component being 0, $+ g$, $- g$ on alternate planes where g is the glide component which glides a $\{112\}_\beta$ plane by $1/6\sqrt{3}/2a_\beta$ in the $<111>_\beta$ direction contained in that plane. They suggest that the reciprocal lattice streaking effects are compatible with faults arising from such a transformation model.

(*vii*) Apart from the experiment referred to above in a Zr–17.5 wt % Nb alloy, there have been no convincing demonstrations of the reversibility of the transformation. Reversion has certainly been observed, but only during relatively slow heating experiments where diffusion could have occurred.

Whilst many workers have assumed that the transformation during quenching is "martensitic" it is not at all clear that this is a valid conclusion. Certainly the transformation does not exhibit many of the features normally associated with shear type transformations. In particular:

(*i*) Nucleation is homogeneous rather than heterogeneous.

(*ii*) The transformed regions are very limited in extent and do not interact.

(*iii*) Surface relief effects do not occur because of this small extent (typically less than 50 Å) of the transformed regions.

(iv) The alternative shears in different directions proposed by Hatt and Roberts [26] are rather unique.

It appears that the mechanism of transformation is certainly not "martensitic" in the normally accepted use of this term. As the transformed regions are of such small extent and no compositional changes need occur, it is virtually impossible to determine the exact nature of the atomic mechanisms involved; that is, whether a co-operative shear or random atom shuffles are involved. More work is obviously needed in this area, particularly to establish whether the athermal type of reaction observed by Cometto et al [16] is peculiar to the Zr–Nb system or is of more general occurrence.

7. Relationship between Omega Phase and the Equilibrium Alpha Phase

There appears to be two different mechanisms for the formation of the equilibrium $\alpha + \beta$ structure from the $\beta + \omega$ structure in the β-isomorphous alloys. In titanium–molybdenum [15] and titanium–niobium [24] the $\alpha + \beta$ structure grows by a cellular reaction from the grain-boundaries consuming the $\beta + \omega$ structure. In titanium–vanadium, however, Blackburn and Williams [15] have shown that α-phase platelets are nucleated at omega-beta boundaries and these then grow at the expense of the omega phase to give a very fine distribution of α-phase, which subsequently coarsens during further heat treatment. Hickman [14] found supporting evidence for this mechanism of transformation from X-ray studies. These are the only detailed studies of this aspect of the transformation although many workers have noticed that there is a stage in the ageing process when the α, β, and ω phases coexist.

8. Effect of Omega Phase on the Properties of Titanium and Zirconium Alloys

8.1. Superconducting Properties

Many β-stabilised titanium and zirconium alloys have superconducting transition temperatures above $4.2°$ K and the superconducting properties of several of these alloys have been extensively investigated. These alloys are generally Type II superconductors and with suitable metallurgical preparation they have the ability to sustain a high maximum zero resistance transport current (J_c) in a high applied magnetic field (H) due to the presence of microstructural features which can pin lines of magnetic flux and prevent Lorentz-force-induced motion with concomitant energy dissipation. These microstructural features are referred to as pinning sites and reviews of these concepts have been given by Livingston and Schadler [34] and by Anderson and Kim [35]. As mentioned earlier, several workers have shown that omega phase precipitates act as particularly effective pinning sites and result in large increases in the critical transport current.

Kramer and Rhodes [36] studied a Ti–22 at. % Nb alloy and they showed that ageing to produce omega phase precipitation caused an increase in J_c from 10^3 up to 10^5 A/cm^2 in fields of 40 K gauss. They observed a maximum in their curves of J_c versus H which they attributed to either: (i) the condition that the precipitate spacing equalled the fluxoid (quantised flux line) spacing. Optimum pinning is obtained under these conditions and using transmission microscopy they showed that for various heat treatment conditions the field at which the maximum occurred correlated reasonably well with the condition when the fluxoid spacing equalled the precipitate spacing; or (ii) that the omega phase became non-superconducting at low values of the magnetic field and hence became more effective as a pinning site. The only reported measurement of the superconducting properties of ω-phase itself was by Tittmann et al [12] who measured the transition temperature of the ω-phase produced in pure zirconium at high pressures and found it to be $0.62°$ K. In Kramer and Rhodes' experiments the ω-phase would contain at least 13 to 15% niobium and the effect of this on the superconducting transition temperature is not known, although an increase in T_c would be expected from the electron concentration considerations discussed by Matthias [56].

Kramer and Rhodes [36] noticed that for a given precipitate distribution the omega was a more effective pinning agent if the ageing conditions were such as to produce a larger composition difference between the omega phase and the matrix.

Hehemann and Zegler [37] studied the transition temperature of zirconium-niobium alloys as a function of ageing conditions and found that precipitation of omega phase caused an increase in T_c. They attribute this simply to the composition change in the matrix. They could not detect any separate transition attributable to the ω-phase.

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King *et al* [38], Bychkov *et al* [39] and Baranov *et al* [40] studied the critical current versus magnetic field in zirconium-niobium alloys and found the same effect as Kramer and Rhodes found in titanium alloys, viz. a marked increase in the critical current was associated with the formation of aged omega phase precipitates.

8.2. Mechanical Properties

Although the basic reason for the interest in the omega phase arises from its effect on the mechanical properties, there have not been any detailed studies of this aspect and most reports are limited to studies of hardness changes. Increases in hardness due to omega precipitation can be very marked, e.g. in Ti–V alloys hardnesses of up to 600 VPN are obtained [42]. Typical hardness/ageing time curves are shown in fig. 5. It is generally supposed that the hardening effect is associated with normal precipitation
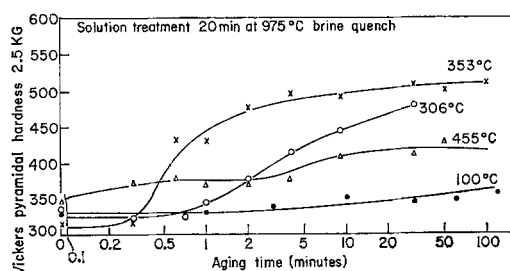
Figure 5 Typical hardness ageing time curve for a Ti–20% V alloy (after Brotzen *et al* [42]).

hardening phenomena and Hickman showed that there was a reasonable qualitative correlation between the omega phase distribution and the hardness changes in Ti–V alloys, i.e. that the peak hardness which occurs at intermediate ageing temperatures is associated with a high volume fraction of smaller particles. At lower ageing temperatures the precipitation is incomplete, and hence the volume fraction is lower. At higher ageing temperatures the volume fraction is also lower and the particle sizes are larger. Associated with these high hardness values is a virtual complete loss of ductility.

Silcock [23] discusses the mechanism of hardening and points out that slip in bcc titanium occurs predominantly in the $[111]$ direction on a number of slip planes. For slip in a given $[111]_\beta$ direction, only one of the four omega orientations will have the close packed (0001) direction favourably oriented and the

other three omega orientations will have irrational directions parallel to $[111]_\beta$ and hence would be expected to act as barriers to slip. However, nothing is known about slip mechanisms in the omega structure (it has never been possible to grow large enough omega particles to make any observations of dislocation structures in the microscope). An additional complication is that Hickman [44] and Williams and Blackburn [45] have observed that little or no loss of ductility or increase in yield strength occurs in certain alloys (Ti–V and Ti–Mo) when omega phase is formed during quenching or during the early stages of ageing, although this is not the case in other alloys (Ti–Mn and Ti–Cr, for instance). Further, Williams *et al* [46] have shown that even in the highest strength condition when the ductility as measured in a tensile test is negligible, the fracture surface still exhibits the dimple rupture appearance characteristic of a ductile failure. In the case of the Ti–Mo and Ti–V alloys, it appears that either the composition changes or increased misfit which occurs on ageing are required to produce the hardening effect. Obviously further work is needed in this area. A better understanding of the hardening mechanism may allow the development of alloys in which desirable mechanical properties would be obtained by controlled omega phase precipitation.

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