Growth Kinetic Model for Isothermal Omega Phase Particles in Low-Cost Beta Titanium Ti–6.8Mo–4.5Fe–1.5Al Alloy

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The growth kinetics of the isothermal omega phase in Ti–6.8Mo–4.5Fe–1.5Al can be monitored by the continuous measurement of the electrical resistivity as shown in our previous publication in this Journal. The rate law for the growth of these isothermal omega particles radius r_{iso} is obtained assuming the resistivity to be proportional to the surface of the interface between the beta matrix and the quasi spherical isothermal omega particles. The rate law $r_{iso}^3 \propto t$ is observed at the beginning of the growth process, that is before the interaction of the outward diffusion fields from the particles. A mathematical model based on a diffusional transfer of the beta stabilizers from the ω_{iso} particles through the interface between the ω_{iso} particles into the beta matrix is developed. The growth rate slows down when the outward diffusional fields from the particles interact. Ostwald ripening is not observed.

(Received July 9, 2004; Accepted May 10, 2005; Published June 15, 2005)

Keywords: beta titanium alloy, isothermal omega phase, electrical resistivity, nanophase, precipitate growth

1. Introduction

The low cost metastable beta alloy LCB Ti (Ti–6.8Mo–4.5Fe–1.5Al) alike the other metastable β -Ti alloys precipitate athermal ω phase (ω_{ath}) by a diffusionless martensitic mechanism during quenching from β phase, that is here from 850°C, and isothermal ω phase (ω_{iso}) during aging, by a diffusion controlled process¹⁾ despite of a possibly displacive stage.²⁾ These ω_{iso} precipitates could behave as nucleation sites of an extremely fine and dispersed α phase at intermediate aging temperatures leading to higher yield strength $\alpha + \beta$ duplex alloys.^{3–5)} The control of the ω_{iso} particles growth is therefore very important. The structural transformations of LCB Ti studied here can be monitored by electrical resistance measurements. TEM and HRTEM studies are reported elsewhere^{6,7)} and showed that the ω_{iso} particles are practically identical in shape and dimensions. A computer driven four points technique eliminating parasitic EMF gives R/R_i as a function of temperature and also as a function of time. R_i is the electrical resistance of the sample either at room temperature or at the beginning of the experiment and R is the resistance at temperature T and time t . According to Ho *et al.*⁸⁾ the electrical resistivity depends on the nature of the interfacial bonds between the matrix and the ω precipitates and its variation is proportional to this interface surface variation. The electrical resistance measurement during the growth of ω_{iso} precipitates allows then the monitoring of the kinetics of growth of these precipitates, for example during isothermal heat treatments. Figure 1 shows the variation of R/R_i for a sample initially water quenched from β as a function of temperature during a thermal cycle corresponding approximately to the sequence 30°C–900°C–30°C for a temperature variation speed $dT/dt = 2^\circ\text{C}\cdot\text{min}^{-1}$. During heating from room temperature the ω_{ath} phase dissolves, see section I on Fig. 1, reversibly^{9–11)} till the ω_{iso} particles precipitate, see section II on Fig. 1, taking place

Fig. 1 Normalized resistivity of quenched LCB Ti during a thermal cycle between 30°C and 900°C with $dT/dt = 2^\circ\text{C}\cdot\text{min}^{-1}$.

seemingly on the ω_{ath} previous sites. The TEM and HRTEM observations show a quasi homogeneous ω_{iso} precipitation as far as the distribution and size are concerned.^{6,7)} These ω_{iso} particles seem growing simultaneously during isothermal annealing, increasing the ω_{iso} /beta matrix interfacial area and consequently the value of R/R_i .

2. Experimental Results

The ω_{iso} precipitation and growth appear in domain II in Fig. 1. When aging in this temperature range the ω_{iso} particles grow and reject beta stabilizers atoms into the beta matrix whose lattice parameter decreases^{6,7)} owing to this beta matrix enrichment in alloying elements such as molybdenum and iron with atomic radii lower than the titanium's one. Quasi-symmetric XRD peaks are observed. A typical X-Ray diffraction diagram is given in Fig. 2 for a sample cold rolled, water quenched from 850°C and annealed at 350°C at the extremum of the ω_{iso} domain. TEM and HRTEM studies^{5,7)} have shown the development of ellipsoidal ω_{iso} particles we can consider approximately spherical

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Fig. 2 X-ray diffraction ($\lambda = \text{Cu K}\alpha_1$) on LCB Ti with ω_{iso} precipitates after annealing at 350°C at the extremum of the ω_{iso} domain. We put marks only on the β phase spectrum for this highly textured sample.

Fig. 3 Time dependence of R/R_i at 200°C, 235°C and 250°C. The straight line parts satisfy the rate law $r^3 \propto t$.

owing to the small difference between their principal diameters. The nucleation stage for the ω_{iso} particles is not discussed here. This nucleation seems very fast and cannot be studied using our experimental technique. For the growth stage of the ω_{iso} particles the isothermal evolution of R/R_i during isothermal annealing in the temperature range 200–310°C are reported as a function of $t^{2/3}$ (t is the time in seconds). Typical results are shown on Fig. 3.

R/R_i is a linear function of $t^{2/3}$ during aging at 200°C whereas for higher temperatures the same linear dependence is observed for a shorter time only. After that the evolution rate decreases due to overlapping of the diffusion fields from the particles and also elastic interactions.¹¹⁾ This effect is rapidly observed at 310°C. Then the ω_{iso} particles can no more be considered as isolated in an infinite beta matrix. As stated before ω_{iso} particle may be approximated to spheres with a radius r . The overall ω_{iso} /beta matrix interfacial area is then $S_{\text{tot}} \propto r^2$. As $R/R_i \propto S_{\text{tot}}$ and $R/R_i \propto t^{2/3}$ we obtain $r^3 \propto t$. The particle radius versus time dependence is $r^3 \propto t$.

ω_{iso} spherical particle

Fig. 4 Growth of a spherical ω_{iso} particle of radius $r_{\omega_{\text{iso}}}$ in a β matrix with constant flux transfer of beta stabilizer into the β matrix.

We propose a very simple mathematical model assuming a quasi-spherical ω_{iso} particle growing into an infinite beta matrix. The limiting kinetic step is the transfer of solute atoms into the beta matrix through and from a limited region, between $r = r_{\omega_{\text{iso}}}$ and $r = R$, around the ω_{iso} particle which is growing at the expense of this region. The solute transfer is assimilated to a diffusion process of a mean atom with an apparent diffusion coefficient D . The concentration of this mean diffusing atom is noted N_r for $r > r_{\omega_{\text{iso}}}$. It is assumed that the beta matrix absorbs the mean beta stabilizer at a constant rate Q , in atoms/s, at the spherical surface of radii $R > r_{\omega_{\text{iso}}}$ concentric to the ω_{iso} core as on Fig. 4. This model will be valid until the ω_{iso} diffusion fields interact giving then a slowing down of the growth kinetics.

In this simple model the ω_{iso} particle of radii $r_{\omega_{\text{iso}}}$ is assumed to be homogeneous.

Using the approximation of the stationary interface the concentration distribution of the mean beta stabilizer is given by the solution of the steady state one dimensional diffusion equation in spherical coordinates:

$$\Delta N = \frac{\partial^2 N}{\partial r^2} + \frac{2}{r} \frac{\partial N}{\partial r},$$

where N is the number of diffusing species per unit of volume, with the boundary conditions in the interfacial region:

$$N(r = r_{\omega_{\text{iso}}}) = N_{r_{\omega_{\text{iso}}}} \quad \text{and} \quad -D \left. \frac{\partial N(r)}{\partial r} \right|_R \times 4\pi R^2 = Q.$$

The general solution is then:

$$N(r) = A + \frac{B}{r}$$

and becomes

$$N(r) = N_{(r_{\omega_{\text{iso}}})} - \frac{Q}{4\pi D} \cdot \left(\frac{1}{r_{\omega_{\text{iso}}}} - \frac{1}{r} \right)$$

by considering the boundary conditions. The rate of the volume variation of the ω_{iso} particle is assumed to be proportional to the flux of beta stabilizer across the interface with a proportionality constant k_1 :

$$k_1 \frac{dV_{\text{iso}}}{dt} = -D \left. \frac{\partial N}{\partial r} \right|_{\text{iso}} \cdot S_{\omega_{\text{iso}}},$$

with

$$S_{\omega_{\text{iso}}} = 4\pi(r_{\omega_{\text{iso}}})^2$$

and

$$V_{\omega_{\text{iso}}} = \frac{4}{3} \pi (r_{\omega_{\text{iso}}})^3.$$

The growth rate of the ω_{iso} particles may then be written as:

$$r^2 \left. \frac{dr}{dt} \right|_{\omega_{\text{iso}}} = \frac{Q}{4\pi k_1}$$

and by integration we obtain:

$$(r_{\omega_{\text{iso}}})^3 = r_0^3 + \frac{3Qt}{4\pi k_1}.$$

That is: $(r_{\omega_{\text{iso}}})^3 = r_0^3 + Kt$ which meets the time dependence of $\frac{R}{R_i}$ during isothermal annealing.

3. Discussion

The classical sequence for precipitation and growth is not observed here for the ω_{iso} particles. Particularly Ostwald ripening doesn't take place here. TEM observations show particle of the same radii, keeping an uniform radii while growing through rejection of beta stabilizers into the beta matrix. During the growth of an ω_{iso} particle there is no inward diffusion of atom as for the usual precipitation phenomenons and precipitates growths. As the ω_{iso} particles grow through the outward diffusion of alloying elements any interfacial energy effect acts then in favor of the production of particles of the same size.

The mean radius growth rate law given by the LSW theory^{12,13} and more recently re-discussed^{14–17} has the same time dependence as for the ω_{iso} particle but the phenomenon is quite different.

Then it is not necessary to introduce explicitly either the interfacial energy for the interface ω_{iso} /beta matrix nor the chemical potentials for the various species in the mathematical model. It must be kept in mind that the ω_{iso} particles are

nanophases for which interfacial energy and chemical potentials are not trivial to formulate as far as classical chemical thermodynamics is considered.

Our mathematical model is a realistic one representing very well the experimental growth law without inconsistencies with the physical observations such as X-ray diffraction, transmission electron microscopy, atomic probe results.¹⁸⁾ Moreover the relation derived from our model is very useful for the determination of the heat treatment path giving rise to an α/β alloy with an optimized dispersion of a nanometric α phase obtained through the transformation $\omega_{\text{iso}} \rightarrow \alpha^7$ of the ω_{iso} precipitates formed during heat treatment in the region II in Fig. 1 for LCB Ti initially water quenched from beta.

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