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

Jean Debuigne*1 and Frédéric Prima*2

Groupe de Recherche en Chimie-Métallurgie, INSA, 20 Av des Buttes de Coesmes, 35043Rennes cedex, France

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 \( r_{\text{iso}} \) 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 \( r_{\text{iso}} \propto t \) 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 \( \omega_{\text{iso}} \) particles through the interface between the \( \omega_{\text{iso}} \) particles into the beta matrix is developed. The growth rate slows down when the outward diffusional fields from the particles interact. Oswald 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 (\( \omega_{\text{ath}} \)) by a diffusionless martensitic mechanism during quenching from β phase, that is here from 850°C, and isothermal ω phase (\( \omega_{\text{iso}} \)) during aging, by a diffusion controlled process\(^6\) despite of a possibly displacive stage.\(^2\) These \( \omega_{\text{iso}} \) 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.\(^3\) The control of the \( \omega_{\text{iso}} \) 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 \( \omega_{\text{iso}} \) 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 \( \omega_{\text{ath}} \) 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 \( \beta \) 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 \( dT/dt = 2°C\cdot\text{min}^{-1} \). During heating from room temperature the \( \omega_{\text{ath}} \) phase dissolves, see section I on Fig. 1, reversibly\(^9-11\) till the \( \omega_{\text{iso}} \) particles precipitate, see section II on Fig. 1, taking place seemingly on the \( \omega_{\text{ath}} \) previous sites. The TEM and HRTEM observations show a quasi homogeneous \( \omega_{\text{iso}} \) precipitation as far as the distribution and size are concerned.\(^5,7\) These \( \omega_{\text{iso}} \) particles seem growing simultaneously during isothermal annealing, increasing the \( \omega_{\text{iso}} \)/beta matrix interfacial area and consequently the value of \( R/R_i \).

2. Experimental Results

The \( \omega_{\text{iso}} \) precipitation and growth appear in domain II in Fig. 1. When aging in this temperature range the \( \omega_{\text{iso}} \) 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 \( \omega_{\text{iso}} \) domain. TEM and HRTEM studies\(^5,7\) have shown the development of ellipsoidal \( \omega_{\text{iso}} \) particles we can consider approximately spherical.

---

*1Corresponding author, E-mail: jean.debuigne@insa-rennes.fr
*2Present address: Laboratoire de Métallurgie Structurale, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris cedex 05.

Fig. 1 Normalized resistivity of quenched LCB Ti during a thermal cycle between 30°C and 900°C with \( dT/dt = 2°C\cdot\text{min}^{-1} \).
owing to the small difference between their principal diameters. The nucleation stage for the $\omega_{iso}$ particles is not discussed here. This nucleation seems very fast and cannot be studied using our experimental technique. For the growth stage of the $\omega_{iso}$ 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 interations.11) This effect is rapidly observed at 310°C. Then the $\omega_{iso}$ particles can no more be considered as isolated in an infinite beta matrix. As stated before $\omega_{iso}$ particle may be approximated to spheres with a radius $r$. The overall $\omega_{iso}$/beta matrix interfacial area is then $S_{iso} \propto r^2$. As $R/R_i \propto S_{iso}$ and $R/R_i \propto t^{2/3}$ we obtain $r^3 \propto t$. The particle radius versus time dependence is $r^3 \propto t$.

\(\omega_{iso}\) spherical particle

We propose a very simple mathematical model assuming a quasi-spherical $\omega_{iso}$ 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 $r = r_{iso}$ and $r = R$, around the $\omega_{iso}$ 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 $r > r_{iso}$. It is assumed that the beta matrix absorbs the mean beta stabilizer at a constant rate of $Q$, in atoms/s, at the spherical surface of radii $R > r_{iso}$ concentric to the $\omega_{iso}$ core as on Fig. 4. This model will be valid until the $\omega_{iso}$ diffusion fields interact giving then a slowing down of the growth kinetics.

In this simple model the $\omega_{iso}$ particle of radii $r_{iso}$ 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:

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

The general solution is then:

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

and becomes

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

by considering the boundary conditions. The rate of the volume variation of the $\omega_{iso}$ particle is assumed to be proportional to the flux of beta stabilizer across the interface with a proportionality constant $k_1$.
\[ k_i \frac{dV_{\text{iso}}}{dt} = -D \frac{\partial N}{\partial r} \bigg|_{\text{iso}} \cdot S_{\text{iso}}, \]

with

\[ S_{\text{iso}} = 4\pi (r_{\text{iso}})^2 \]

and

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

The growth rate of the \( \omega_{\text{iso}} \) particles may then be written as:

\[ r_{\text{iso}}^2 \frac{dr}{dt} = \frac{Q}{4\pi k_1} \]

and by integration we obtain:

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

That is: \( (r_{\text{iso}})^3 = r_0^3 + Kt \) which meets the time dependence of \( \bar{r} \) during isothermal annealing.

3. Discussion

The classical sequence for precipitation and growth is not observed here for the \( \omega_{\text{iso}} \) 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 \( \omega_{\text{iso}} \) particle there is no inward diffusion of atom as for the usual precipitation phenomenons and precipitates growths. As the \( \omega_{\text{iso}} \) 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 \( \omega_{\text{iso}} \) but the phenomenon is quite different.

Then it is not necessary to introduce explicitely either the interfacial energy for the interface \( \omega_{\text{iso}}/\beta \) matrix nor the chemical potentials for the various species in the mathematical model. It must be kept in mind that the \( \omega_{\text{iso}} \) 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 \( \alpha/\beta \) alloy with an optimized dispersion of a nanometric \( \alpha \) phase obtained through the transformation \( \omega_{\text{iso}} \rightarrow \alpha^7 \) of the \( \omega_{\text{iso}} \) precipitates formed during heat treatment in the region II in Fig. 1 for LCB Ti initially water quenched from beta.

REFERENCES

2) J. C. Williams, D. De Fontaine and N. E. Paton: Metall. Trans. 4 (1973) 2701.
3) S. Bechet and S. Bein: Beta Titanium Alloys, Ed. by A. Vassel et al., 8 (La revue de Métallurgie, 1994) 83.
18) A. Menand: Private oral communication.