ω Precipitation in a Beta Metastable Titanium Alloy, Resistometric Study

Frédéric Primâ, Philippe Vermautâ, Denis Anselb and Jean Debuigne1

1GRCM, Laboratoire de Métallurgie, INSA, 20 avenue des Buttes de Coësmes F35043 Rennes, France
2Laboratoire de Métallurgie Structurale, E.N.S.C.P., 11, rue Pierre et Marie Curie, F75231 Paris, France CECM, UPR-CNRS 2801, 15, rue G. Urbain, F94407 Vitré, France

Beta-titanium alloys show an excellent capability for precipitation hardening. The microstructural evolution (i.e., the nature, the morphology, and the degree of coherence of the phases formed during the transformations of the beta phase strongly determines the characteristics of the alloys. It is known that ω precipitates can be formed by: (i) A diffusionless martensitic mechanism during quenching; (ii) a diffusion controlled process during aging; (iii) A stress induced process. The formation of a large volume fraction of ω phase is generally recognised to lead to a drastic reduction in ductility; nevertheless ω crystals are considered as precursors for the α phase at the intermediate aging temperature, allowing in that way the mechanical properties of the (β + α) duplex microstructure to be improved. In the present paper, ω phase precipitation is studied in Ti-6.8Mo-4.5Fe-1.5Al (Low Cost Beta) using a four points resistometric method, as follows: 1-Precipitation ranges are studied during an isothermal aging, 2-Isothermal ω phase is studied during aging between 473 and 523 K and a growth model is proposed, 3-ω phase disappearance is studied and a mechanism linking ωα to α precipitation is discussed.

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1. Introduction

Beta Titanium alloys provide a very good combination of high tensile strength, good corrosion resistance and low density (ρ = 4.9 Mg/m³ for LCB). Moreover beta Ti alloys have an excellent capability for precipitation hardening. One of the methods adopted for strengthening β type Titanium alloys is the thermomechanical processing, in order to change the β structure into a (α + β) structure.2-4 Generally the α phase appears preferentially at grain boundaries, on intragranular defects and along dislocations lines, and therefore it is rather difficult to obtain a finely and uniformly dispersed α phase. Elsewhere it has been shown recently that, at intermediate aging temperatures, the α phase may nucleate uniformly on metastable ω phase crystals, leading to a very fine and dispersed microstructure.5,6

In order to be able to control the process it is necessary to clarify the mechanisms leading to the isothermal precipitation of ω (ωα) and α phases. The present paper describes the investigation of the isothermal kinetics of ωα precipitation through a resistometric method, and a growth model is proposed for an isolated ωα particle. Finally we focus on the α phase precipitation from the ωα particles and we characterized morphologies obtained through aging at intermediate temperatures.

2. Experimental Procedure

The composition (weight/mass) of the LCB Ti rod provided by Timet is 87.2% Ti, 6.8% Mo, 4.5% Fe, 1.5% Al. Samples for metallography and resistivity measurements were cut perpendicularly to the rod axis. Preliminary heat treatment (1.8 ks annealing at 1123 K) was carried out in a high vacuum furnace and followed by water quenching.

A computer driven four point technique eliminating parasitic EMF was used for electrical resistance measurements. The serial electrical circuit used is composed of: the sample (with resistance R), a reference resistor Rref, a d.c. source. At time t, the measured voltages are V across the sample and Vref across the reference resistor. Before starting a run, at the initial time t0, R0 and V0 were respectively the initial resistance of the sample and the initial voltage measured across the sample. We can write:

\[
\frac{V}{V_{ref}} = \frac{R_t}{R_{ref}}
\]

and:

\[
\left(\frac{V}{V_{ref}}\right) = \left(\frac{R}{R_{ref}}\right) = \frac{R}{R_{ref}}
\]

If we neglect the thermal expansion of the sample, we can write: R/R0 = ρ/ρ0 where ρ and ρ0 are the electric resistivities. R/R0 plotted as a function of time for a given temperature shows the structural evolution of the sample and the kinetics of the transformations.

For TEM observation, thin foil samples were obtained by mechanical grinding to 200 μm thickness and twin jet electropolishing (6% perchloric acid in acetic acid; 22 V). TEM observations were carried out on a Topcon 002B high resolution electron microscope operating at 200 kV with a point to point resolution of 0.18 nm (Cs = 0.4 mm).

The Temperature Coefficient of Electrical Resistivity (TCR) has been used to monitor minor microstructural changes accompanying β phase decomposition during aging or isothermal transformations. The present study undertakes to assess the evolution of TCR = d(R/R0)/dT for monitoring microstructural transformations. The TCR has been calculated from the slope between 333 and 393 K (during heating and cooling) on the linear portion of the R/R0 curve. TCRheating is the value of the slope during heating up
an "as quenched" sample (this parameter can also be called "initial TCR") or "as quenched" TCR). TCR_{cooling} is obtained during cooling after the thermal cycle. The TCR recovery ratio is defined as $100 \times \text{TCR}_{\text{cooling}} / \text{TCR}_{\text{heating}}$.

3. Results and Discussion

3.1 $\omega_{\text{ath}}$ stability

A thermal cycle ($v = 2 \text{ K/min}$) was carried out on a quenched sample between 300 and 1223 K (Fig. 1). We were focussing on the initial part of the curve (300–723 K), corresponding to the $\omega$ phase evolution.

In "as quenched" metastable beta Titanium alloys the TCR = $d(R/R_\text{i})/dT$ is generally negative, corresponding to an dual ($\beta_m + \omega_{\text{ath}}$) microstructure$^9$ and this Negative Temperature Dependence (NTD) effect is supposed to be linked to the athermal omega phase ($\omega_{\text{ath}}$) which forms during cooling and disappears reversibly upon heating.$^7,8$ The presence of $\omega_{\text{ath}}$ was investigated in as quenched LCB Ti through TEM. Figure 2 shows an electron diffraction pattern of LCB Ti quenched from 1123 K, displaying typical diffuse reflections of $\omega_{\text{ath}}$. The positions of these reflections are consistent with those expected from the hexagonal structure of the $\omega$ phase and with the orientation relations:

\[
(111)_{\omega} // (0001)_{\omega} \\
[110]_{\omega} // [11\bar{2}0]_{\omega}
\]

first reported by Silcock.$^9$

Thermal cycles were carried out on water quenched LCB Ti samples, increasing the aging temperature from 323 to 473 K; the temperature coefficients were calculated at 300 K before and after each cycle. Figure 3 shows the calculated TCR recovery, allowing the determination of the athermal omega phase stability range.

When calculating TCR_{cooling}/TCR_{heating} at each temperature, we consider that we obtain the ratio of $\omega_{\text{ath}}$ reprecipitation after the heat treatment.$^{10}$ We calculate the recovery ratio of the initial TCR as a function of temperature, therefore obtaining the thermal limit of $\omega_{\text{ath}}$ stability.

It can be seen (Fig. 3) that until 423 K the initial TCR (TCR_{heating}) is restored on cooling down; this is corresponding to the complete reprecipitation of $\omega_{\text{ath}}$. Raising the aging temperature above 423 K, only a partial recovery of the quenched TCR is possible, which indicates a microstructural change due to the precipitation of isothermal omega phase from $\omega_{\text{ath}}$. This $\omega_{\text{ath}}$ cannot reprecipitate during cooling.$^7$

3.2 $\omega_{\text{iso}}$ precipitation

The electrical resistivity increases markedly between 473 and 623 K (Fig. 1) owing to the formation of $\omega_{\text{iso}}$ phase, to which some authors$^{11}$ associate a resistivity term $\rho_{\text{def}}$ corresponding to the nature of the interface bonds between the $\beta$ matrix and the coherent $\omega_{\text{iso}}$ precipitates.

To obtain information on the kinetics of the $\omega_{\text{ath}} \rightarrow \omega_{\text{iso}}$ transformation, isothermal heat treatments were carried out at three temperatures in the $\omega_{\text{iso}}$ assumed precipitation range. TCR was determined during heating up the sample (on the linear portion of the $R/R_\text{i}$ curve between 333 and 393 K) and during cooling down (also between 333 and 393 K). Then, the TCR recovery ratio was determined (Fig. 4).

Heating and cooling were fast enough to have a negligible effect with respect to the isothermal aging time.

Assuming that the negative $d\rho/dT$ due to heating is ascribed to the dissolution of reversible (athermal) $\omega$

Fig. 1 Thermal cycle between 300 and 1223 K on the metal quenched from 1123 K.

Fig. 2 TEM diffraction pattern of "as quenched" LCB Ti: [110]$_{\beta}$ zone axis.

Fig. 3 TCR recovery ratio as a function of aging temperature.
Fig. 4 Dependence of the TCR recovery ratio on isothermal aging periods at 523 K (a), 583 K (b), and 613 K (c).

Fig. 5 Dark field images of $\omega_{ab}$ in Ti–6.8Mo–4.5Fe–1.5Al samples aged 10.8 ks at 523 K (a) and 583 K (b).

Fig. 6 Resistometric curve evolution for a 1.8 ks aging at 623 K. Heating and cooling rate, 10 K/min.

out in order to evaluate differences variations in the $\omega_{b}$ crystal dispersion. It can be seen in Fig. 5 that the $\omega_{b}$ dispersion is much more condensed after an aging at 583 K than after aging at 523 K, which indicates that the number of $\omega_{b}$ nucleation sites is very dependent on the aging temperature.

Thus a qualitative correlation can reasonably be made between the aging temperature and the mean distance between neighboring precipitates, in the temperature range from 473 to 623 K.

An isothermal aging at 623 K (matching the maximum of the resistometric curve in Fig. 1) lets a TCR equal to zero: The $\omega_{b}$ precipitation is maximal and there is no $\omega_{ab}$ reprecipitation. The effect of an isothermal aging at 623 K on TCR is exemplified on Fig. 6.

3.3 Isothermal kinetics

Some authors have shown a growth law as $r \propto t^{1/3}$ (where $r$ is the particle radius) with aging time $t$, followed by a size stabilisation. We observed during aging at 473 K (Fig. 7(a)) in the $\omega_{b}$ precipitation range, a resistivity time dependence as $t^{2/3}$. This seems consistent with the previous results, since Ho and Collings interpreted the anomalous resistivity as a $\rho_{int}$ term on the $\beta/\omega$ interface.

Thus the resistivity increases in relation to the total interface area in the considered volume.

We can suggest a model describing the time law of growth of an isolated precipitate.

We assume that the quasi spherical $\omega_{b}$ zones formed by a non-diffusional process grow by outward diffusion of $\beta$ stabilizers into the $\beta$ matrix from the curved $\omega_{b}/\beta$ interface. Using then the Gibbs-Thomson relation with the hypothesis of an average beta stabilizer complying with Henry’s law, we solve the second Fick’s equation in spherical coordinates. The complete calculation will be provided in a further paper. The result is $r^2 \propto D \cdot \sigma \cdot t$, where $r$ is the $\omega_{b}$ radius, $D$ is the mean value of the diffusion coefficient of the $\beta$ stabilizers into $\beta$ phase, $\sigma$ is the interfacial energy $\omega_{b}/\beta$ and $t$ is the time.

We can observe above 508 K a decrease (Figs. 7(b), (c), (d)) and a stabilisation (Fig. 7(d)) of the coarsening process. This is interpreted as attractive elastic interactions between neighboring precipitates resulting from the misfit strain which
arises from differences in the elasticity constants between the precipitates and the matrix.\(^{13}\)

### 3.4 \(\alpha\) phase precipitation

The ability of \(\omega\) to act as a heterogeneous nucleation site for the \(\alpha\) phase has been widely observed in high misfit systems where isothermal \(\omega\) forms as cuboidal precipitates and

where \(\alpha\) phase nucleates at ledges or dislocations on the \(\beta/\omega\) interfaces.\(^{14}\) However, the role played by ellipsoidal \(\omega\) precipitates in low misfit systems (such as LCB Ti) in the nucleation of \(\alpha\) phase has not been clearly defined.

There is an important controversy about the formation mechanism of this \(\alpha\) phase in low misfit systems. According to some authors\(^{15}\) it appears at some distance of the \(\beta/\omega\) interface. It was shown\(^{16}\) that a local enrichment in the \(\alpha\) stabilizer Al (resulting from the interaction of stress fields associated with the \(\beta/\omega\) interface and from the diffusion of solute elements) would provide favourable sites for alpha precipitation.

A direct structural transformation mechanism \(\omega_{\text{iso}} \rightarrow \alpha\) has been assumed elsewhere\(^{17,18}\) taking small atomic displacements and small amount of diffusive transport into account.

Above 623 K a resistivity drop is observed (Fig. 1), and TEM diffraction patterns (Fig. 8) show that this coincides with the formation of the \(\alpha\) phase.

TEM diffraction patterns (Fig. 8) confirm that between 623 and 773 K there is coexistence of the three phases \(\beta\), \(\omega\) and \(\alpha\),

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**Fig. 7** Isothermal evolution of resistivity as a function of the aging temperature: (a) \(T = 473\) K, (b) \(T = 508\) K, (c) \(T = 523\) K, (d) \(T = 583\) K.

**Fig. 8** A TEM diffraction pattern on LCB Ti quenched and aged at 683 K, showing the presence of 3 phases: \(\{110\}\) \(\beta\) zone axis (\(/ / [1120]_\beta / / [0001]_\beta\) (a), key of the diffraction pattern showing the 3 phases spots indexing (b).
with the classical Bürgers orientation relations:

\[
\begin{align*}
(111)_\beta &= (0001)_\omega, \\
(110)_\beta &= (11\bar{2}0)_\omega, \\
(110)_\beta &= (0001)_\omega, \\
(111)_\beta &= (11\bar{2}0)_\omega.\n\end{align*}
\]

The important resistivity drop seems to suggest the progressive vanishing of \(\omega\) through reversion into \(\beta\) phase between 623 and 773 K. The \(\omega\) phase becomes energetically metastable above 623 K, strengthened by the stored coherence elastic strain energy arising from the lattice accommodation across the \(\beta/\omega\) coherent interface.

We presently think that the precipitation of \(\alpha\) phase is clearly separated into two stages. The displacive reversion \(\omega \rightarrow \beta\), much faster than diffusion mechanisms, can produce locally depleted \(\beta\) zones (since the \(\omega\) growth process is controlled by outward diffusion of \(\beta\) stabilizers).

TEM observations (Fig. 9) show an actually dispersed \(\alpha\) platelets as large as the preceding \(\omega\) particles (Fig. 10).

In order to investigate the localization of \(\alpha\) phase precipitation (which constitutes the second step of the process), \(\alpha\) phase lattice parameters were calculated from X-ray diffraction patterns. Considering \((100)_\alpha\), \((002)_\alpha\), \((101)_\alpha\), \((102)_\alpha\), \((110)_\alpha\) and \((200)_\alpha\) peaks, anomalous lattice parameters \(a_\alpha = 0.294 \text{ nm} \pm 0.002\), and \(c_\alpha = 0.471 \text{ nm} \pm 0.002\) (on a quenched and aged 10.8 ks at 683 K LCB Ti) were displayed. Comparison with those obtained on a fully recrystallised LCB Ti alloy with \(\alpha\) and \(\beta\) in quasi equilibrium: \(a_\alpha = 0.294 \text{ nm} \pm 0.002\) and \(c_\alpha = 0.468 \text{ nm} \pm 0.002\) supports the proposition that the \(\alpha\) phase nucleates in \(\beta\) zones where lattice parameter is quite large, rather than at \(\beta/\omega\) interfaces (as assumed by previous studies) where the \(\beta\) phase, contracted by Mo and Fe enrichment, has a small lattice parameter.

Consequently, the \(\omega(\alpha)\) (Fig. 10) can be considered as the precursor phase for \(\alpha\) at the intermediate aging temperatures, but through an indirect way.

Nevertheless the hypothesis of a direct \(\omega(\alpha) \rightarrow \alpha\) transition involving collective and coherent motion of neighboring atoms can’t be completely rejected, but the mechanism already proposed elsewhere doesn’t lead to Bürger’s relationships between the two phases.

Experimental confirmation of this transition process will have to be provided by an extensive High Resolution Electron Microscopy study. Experiments are in progress and will be the subject of other publications.

4. Summary

We know that the \(\omega(\alpha)\) phase governs the precipitation of a dispersed \(\alpha\) phase at medium annealing temperatures. In order to control this \(\alpha\) precipitation, we tried to provide evidences of the various mechanisms controlling the \(\omega(\alpha)\) precipitation. It appears that:

1. The \(\omega(\alpha)\) precipitates completely below 423 K; no \(\omega(\alpha)\) can be observed (total recovery of the TCR).
2. The \(\omega(\alpha)\) precipitates in the temperature range 423–623 K. The experimental results allow us to determine the volume fraction of the precipitates as a function of temperature.
3. The \(\omega(\alpha)\) evolution is controlled by diffusion of the beta stabilizers (Mo, Fe) into the matrix. A kinetic model is proposed.
4. The precipitation process of the \(\alpha\) phase follows a dual mechanism: (i) The vanishing of \(\omega(\alpha)\) above 623 K (evidenced by a resistivity decrease); (ii) The diffusion controlled precipitation of the \(\alpha\) phase in domains of the \(\beta\) phase depleted in \(\beta\) stabilizers.

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