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Characterization of nanophase precipitation in a metastable β titanium-based alloy by electrical resistivity, dilatometry and neutron diffraction

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Metastable β Ti–6Mo–5Ta–4Fe (wt.%) alloy was synthesized by cold crucible levitation melting and then quenched in water from the β-phase field. In order to investigate the transformation sequence on heating, thermal analysis methods such as electrical resistivity, dilatometry and neutron thermodiffraction were employed. By these methods, the different temperatures of transition were detected and solute partitioning was observed in the β matrix during omega and α nanophase precipitation.

Keywords: Titanium; Phase transformations; Neutron diffraction; Electrical resistivity; Dilatometry

Over the last few decades, β Ti alloys have continued to be an increasingly important class of materials because of their unique combination of high strength, excellent hardenability, low density and good corrosion resistance [1]. It has been shown that, in most β Ti alloys, homogeneous nucleation and subsequent growth of a finely dispersed intragranular α phase are accompanied by considerable strengthening and a general increase in mechanical properties (strength and toughness are enhanced while maintaining ductility to an acceptable level) [2]. The persistent problem is that the α phase generally appears preferentially at grain boundaries, on intragranular defects and along dislocations lines, so that it is relatively difficult to obtain uniform and dispersed α-phase distribution. Nevertheless, in metastable β Ti alloys (obtained by quenching the alloy from the β-phase field), the precipitation of nanoscale ω-phase particles is observed on heating in Ti-based alloys containing Fe, Mo, Cr and/or V β-stabilizer elements [3–5]. This additional phase has been widely observed to act as a heterogeneous nucleation site for the α phase [6,7]. By this quenching/heating treatment, a uniform and finer distribution of α precipitates in the β matrix was obtained with Ti–15V–3Cr–3Sn–3Al [8] and 'LCB' Ti–6.8Mo–4.5Fe–1.5Al alloy compositions [9], for example.

The β-phase decomposition of new Ti–Ta–Mo and Ti–Ta–Mo–Fe metastable β alloys was recently investigated by employing electrical resistivity and differential scanning calorimetry [10]. It was shown that the ω and α nanophase transitions could be well detected on heating, particularly by means of the electrical resistivity measurement technique, which is very sensitive to minor constitutional changes produced by quenching, ageing and precipitation [11,12]. In the present study, an investigation of the transformation sequence by additional techniques such as dilatometry and neutron diffraction is proposed. Until now, these methods have never been used to characterize nanophase formation on heating from metastable β Ti-based alloys. The aim of such additional characterization is to validate the resistivity measurements and also try to elucidate the role of the solute elements during ω and α nanophase precipitation. Results concerning the metastable β Ti–6Mo–5Ta–4Fe alloy (wt.%) are presented.

The Ti–6Mo–5Ta–4Fe alloy (wt.%) was synthesized by the cold crucible levitation melting (CCLM) technique. The melting was carried out under a pure Ar atmosphere, which was introduced after several cycles

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of high vacuum pumping, because of the high reactivity of titanium with both oxygen and nitrogen. Notable features of CCLM are that it can melt metals with a high melting point, create an alloy of uniform composition and allow metals to be melted without crucible contamination. The melted alloy was cast into a cylindrical copper mould by removing the copper cold finger situated at the bottom of the cold crucible. Once the generator was switched off, the melt dropped and a cylindrical ingot with a diameter of 8 mm and ~10 mm in length was obtained. The ingot was solution treated at 850 °C under a high vacuum (10^{-6} mbar) for 1 h in a tubular furnace and then quenched in water at room temperature. The purpose of this heat treatment is to produce the desired homogeneous β microstructure alloy with β-stabilizer elements Ta, Mo and Fe.

The transformation sequence of the metastable β titanium alloy was characterized on heating by electrical resistivity measurement and by dilatometry. The electrical resistivity variation of the sample was carried out under high vacuum (10^{-6}–10^{-7} mbar) using a serial electrical circuit set-up composed of the sample (with resistivity ρ), a reference resistor R_{ref} (2 Ω) and a DC source (home-made apparatus). If one neglects the thermal expansion of the sample, the electrical resistivity ratio ρ/ρ_0 or the resistance ratio R/R_0 (R_0 is the initial resistance at room temperature) plotted as a function of temperature (heating rate 5 °C min^{-1}) shows the structural transformations from room temperature to 900 °C. The dilatometry variation $\Delta l/l_0$ (home-made apparatus) of the sample was obtained during continuous heating carried out under high vacuum (10^{-6}–10^{-7} mbar) with a scan rate of 5 °C min^{-1} from room temperature to 900 °C.

The neutron thermodiffraction experiments were performed on the D1B two-axes diffractometer at the Institut Laue-Langevin, Grenoble, France. The neutron spectra were collected, placing the 400 cell multidetector in a cylindrical geometry centred at the sample. The angular span was 80°, with steps of 0.2° and a 2-θ starting angle of 40°. A graphite monochromator (002) was used, producing a $\lambda = 2.52$ Å wavelength. The sample was heated from room temperature to 900 °C (heating rate 3 °C min^{-1}) in a furnace working under a vacuum of 10^{-4}–10^{-5} mbar. The neutron flux on the sample was ~10^6 n (s cm^2)$^{-1}$, which allowed the evolution during heating to be monitored by diffraction patterns collected every 5 min. Finally, the samples were naturally cooled down to room temperature.

For transmission electron microscopy (TEM) observations, thin foil samples were obtained by mechanical grinding to 200 μm and twin jet electropolishing (6% perchloric acid in acetic acid; 22 V). Conventional TEM observations were carried out using a JEOL 120CX II Electron Microscope operating at 120 kV.

In order to investigate the phase transformation sequence from the β as-quenched state, the alloy was first characterized on continuous heating (heating rate of 5 °C min^{-1}) by electrical resistivity and dilatometry measurements. Figure 1 shows the electrical resistivity (in grey) and the dilatometry (in black) variation curves for the Ti–6Mo–5Ta–4Fe alloy.

It has already been reported that the negative temperature dependence observed on the resistivity curve at low temperature is due to the presence of the athermal omega phase (ω_{ath}), which is formed during quenching and disappears reversibly on heating [3,12,13]. A (1 1 1)β plane collapse model has been proposed to explain the β/ω_{ath} displacive transformation: the ω lattice can be obtained by collapsing one pair of (1 1 1) planes to the intermediate position, leaving the adjacent (1 1 1) planes unaltered. [14]. The interatomic distances of the quenched ω_{ath} phase have been recently characterized by neutron diffraction in the Ti–V system [15].

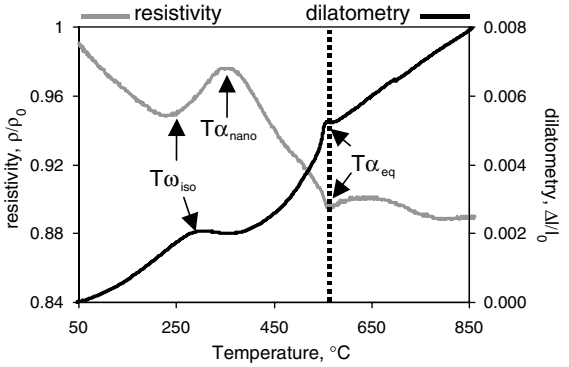

Figure 1. Electrical resistivity (grey curve) and dilatometry (black curve) variations of the metastable β Ti–6Mo–5Ta–4Fe alloy on heating (heating rate 5 °C min^{-1}).

At higher temperatures, the ω_{iso} hexagonal phase can precipitate irreversibly, implying diffusional phenomena. The formation of this ω_{iso} phase on heating is shown to occur at 260–280 °C (identified by $T\omega_{iso}$ in Fig. 1), where an increase in the resistivity and a decrease in the dilatometry curves are observed simultaneously.

This ω_{iso} phase is nanometre in size, and TEM is required for its observation. The bright-field TEM micrograph presented in Figure 2 corresponds to the Ti–6Mo–5Ta–4Fe alloy, which was annealed at 300 °C for 1 h. The size of the observed ω_{iso} particles (dark) is ~20–30 nm, which is in good agreement with the size found in the literature [6–10].

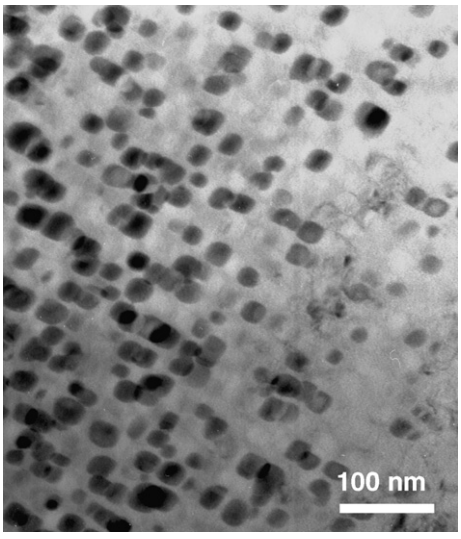

Figure 2. Bright-field TEM image showing the ω_{iso} nanoprecipitates in the Ti–6Mo–5Ta–4Fe alloy annealed at 300 °C for 1 h.