Phase Transformations in Ti–15Mo Investigated by *in situ* Electrical Resistance

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In this study phase transformations in metastable beta Ti–15Mo alloy were investigated by an *in situ* electrical resistance measurement in a wide range of temperatures from –196 °C to 850 °C. Different temperature ranges of the evolution of electrical resistance were correlated with underlying phase transformations. In the low temperature range, stage I (from –196 °C to 220 °C) the decrease of electrical resistance with increasing temperature is caused by the dissolution of ω_{ath} (formed during quenching by athermal shuffle transformation) which is accompanied by the relaxation of lattice strain, while the diffusional assisted growth of ω_{iso} in the range from 220 °C to 380 °C (stage II) is the main mechanism causing the increase of resistance. Another decrease of the resistance in the range from 380 °C to 550 °C (stage III) is explained by the dissolution or transformation of ω_{iso}. The increase of resistance above 550 °C (stage IV) is related to the growth of α-phase particles. The fully reversible character of ω_{ath} growth and dissolution during heating and cooling in the stage I up to 100 °C was confirmed by temperature cycling during repeated *in situ* resistance runs from RT. Pre-ageing of samples at 300 °C promotes the formation of ω_{iso} particles. Subsequently, ω_{ath} particles are not created, which is fully consistent with electrical resistance measurements. The presence of ω_{ath} and the orientation relationship between ω and β were identified by the electron diffraction.

1. Introduction

Titanium and its alloys exhibit high specific strength, excellent corrosion resistance, and enhanced biocompatibility. Due to the low specific density, which is approximately half of that of steels and Ni-based superalloys, titanium alloys are successfully used in the aerospace, chemical industry and biomedicine. A wide range of application of titanium may be also found in other branches such as architecture, chemical processing, medicine, power generation, marine and offshore, sports and leisure, and transportation [1]. The only disadvantage, which hinders wider use of titanium, e.g. in automobile industry, is its comparatively high cost, which is caused by high processing costs. This paper presents a study of phase transformations, which occur in the metastable β-Ti alloy Ti–15Mo (titanium alloy with 15 wt% (8.1 at.%) of molybdenum). Ti–15Mo alloy was chosen for this experimental study, because it is designed for biomedical use [2], and represents a simple binary system that has been already widely investigated [3, 4] and undergoes several phase transformations. A detailed understanding of these transformations is of particular importance due to the impact of the resulting microstructures on the mechanical properties of the alloy.

Titanium is a polymorphic material. The high-temperature phase has the body-centered cubic structure and is referred to as β-phase. The ambient temperature phase has the hexagonal close-packed structure and is referred to as α-phase. Recently, the main interest focuses on development and investigation of the so-called metastable β alloys. These alloys contain sufficient amount of β-stabilizing elements such that β-phase can be retained at room temperature after quenching. The β-phase is in a metastable state and ultimately equilibrium $\alpha + \beta$ composition can be achieved by annealing treatment [5]. Several other structural phases can be found in metastable β-Ti alloys. In the investigated Ti–15Mo, the formation of ω-phase is an important process for controlling microstructure. The ω-phase has a hexagonal symmetry and is formed by a diffusionless shuffle transformation described in [6]. This phase is formed already during quenching and is referred to as ω_{ath} (ω athermal). The formed particles are coherent, few nanometers in diameter and considered to have the same chemical composition as the β-matrix [7]. Upon subsequent ageing (around 300 °C), ω particles become chemically stabilized by expelling β-stabilizing elements — Mo in the case of Ti–15Mo alloy. This phase is referred to as ω_{iso} (ω isothermal). Particles ω_{iso} grow during annealing and become more chemically stabilized — i.e. they differ from surrounding β-matrix in composition [8]. Upon further annealing (around 500 °C), α-phase particles precipitate. ω particles serve as preferential nucleation sites for α-phase particles precipitation and therefore the size and mainly the distribution of α-phase particles can be controlled by controlling the formation of ω-phase particles. The principal experimental method employed in the present study is the electrical

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resistance. It was shown that the electrical resistance is very sensitive to ω-phase evolution during heating [9].

The most related study to the present work identifies ω_{ath} dissolution, ω_{iso} formation and α precipitation by *in situ* electrical resistance measurements in a TIMET LCB titanium alloy [10]. The evolution of electrical resistivity in this alloy that undergoes similar consequent phase transitions is further discussed using more direct methods as transmission electron microscopy (TEM), X-ray diffraction (XRD) and neutron-diffraction [9, 11, 12]. Very similar Ti–12Mo alloy was investigated in [13].

2. Experimental

The metastable Ti–15Mo (with 15 wt% (8.1 at.%) of Mo) was used in this investigation. The material was sealed in a quartz tube and solution treated (ST) at $900\,^{\circ}$C for 4 h and subsequently quenched in water.

The four-point method was employed for electrical resistivity measurements allowing simultaneous measurement of the voltage and the electrical current. The sample of approximate thickness of 1 mm and the size of 20×10 mm^2 is cut to a special shape to increase the effective length of the sample for current flow and four contacts are appropriately jointed. The sample is then placed in a specially designed furnace which allows precise heating of the sample in a protective argon atmosphere up to high temperatures as well as defined cooling back to room temperature. The cooling can be further extended to $-200\,^{\circ}$C (liquid nitrogen, LN). By utilizing Keithley 2182A nanovoltmeters we are able to achieve measurement with relative error better than 0.0001 within each measured point while obtaining about 2 points per second [14]. The evolution of relative resistivity (related to room temperature (RT) resistivity) can be evaluated from measured data.

Thin foils for TEM were prepared by mechanical grinding on fine emery papers to the thickness of 150 μm followed by ion polishing. TEM observations were performed on JEOL JEM 2000FX microscope at 200 kV.

3. Results and discussion

The presence of the ω-phase in the ST specimen was proved by TEM. The detailed inspection of electron diffraction patterns revealed the extra spots corresponding to the ω-phase [8] and confirmed the orientation relationship between the hexagonal ω and bcc grains [15], see Fig. 1:

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

The evolution of electrical resistance was measured *in situ* during linear heating with the heating rate of $5\,^{\circ}$C/min from RT to $850\,^{\circ}$C. The result of this measurement is shown in Fig. 2. The solid line corresponds to the resistivity evolution. Dashed line is the first derivation of the same curve — computed numerically. Furthermore,

the evolution of resistivity was also measured during cooling from room temperature to approximately $-196\,^{\circ}$C. This is illustrated in Fig. 2 by a dotted line. Several stages corresponding to the monotonous increase and/or decrease of the resistance can be identified during heating from RT. At low temperatures (RT–$220\,^{\circ}$C) — stage I — the decrease of electrical resistance with increasing temperature was observed. This can be attributed to the dissolution of ω_{ath}. In the vicinity of the coherent β/ω interface, the elastic strain field is formed which acts as the scattering zone for conducting electrons [16]. Therefore, during the dissolution of ω_{ath} phase particles, the elastic strain fields are released, which clears the matrix for electron drift. This leads to the decrease in conduction electron scattering and therefore to the resistance drops.
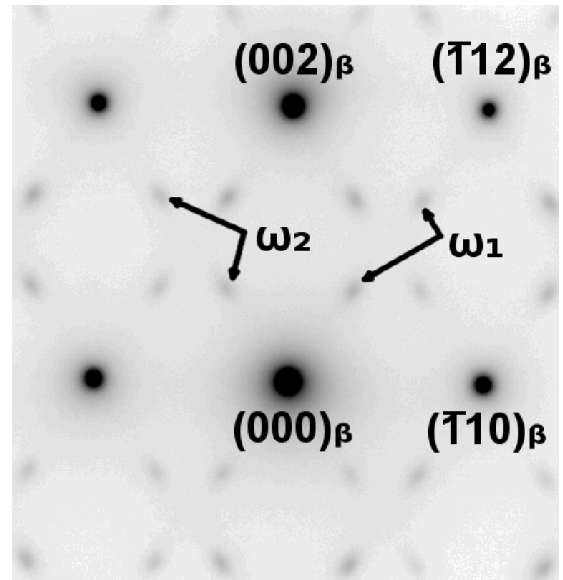

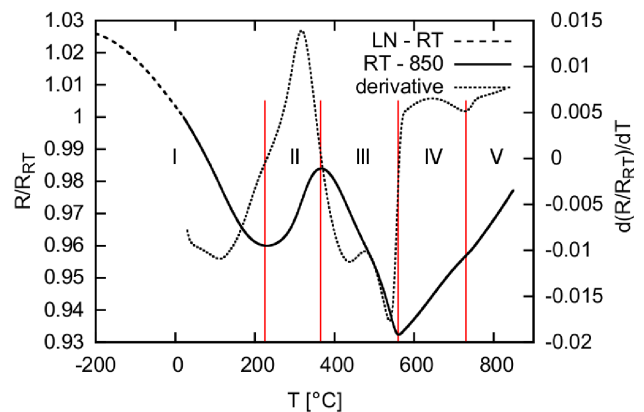Fig. 1. TEM diffraction pattern of solution treated Ti–15Mo, showing the presence of two phases: β and ω.

Fig. 2. The dependence of electrical resistance on temperature for ST sample and its derivative.

In stage II ($220\,^{\circ}$C–$380\,^{\circ}$C) the resistance increases

with increasing temperature. In this temperature range, particles, referred to as ω_{iso}, grow due to diffusion-driven chemical stabilization [7]. This process is accompanied by the increasing amount of β/ω interfaces, and therefore resistivity increases [13]. Note that resistivity also partly increases during heating due to lattice vibrations.

In stage III (380 °C–550 °C) the resistance declines with increasing temperature. The main reason is the decreasing volume fraction of semicoherent ω_{iso} particles. This can be caused either due to precipitation of α particles [13] (sometimes referred to as α-nano [10]) or simply by dissolution of ω_{iso} particles back to β matrix due to lower stability of the ω-phase in this temperature range [17].

The dissolution of ω particles can be also confirmed from dilatometry measurements [9]. In stage IV, the α-particles precipitate and grow directly in β-matrix [13] until the equilibrium volume fraction of α-phase is reached. The volume fraction of α-phase is decreasing towards the β-transus temperature that was found at 730 °C. This agrees well with the β-transus temperature given in the binary equilibrium phase diagram of Ti–Mo system [18].

The *in situ* measurement of electrical resistance of ST sample was extended to the cryogenic range from –196 °C to RT. As seen from left-hand side of Fig. 2 the resistance in the cryogenic range decreases with increasing temperature up to RT and merges smoothly the curve in stage I to 225 °C.

It is argued that even more ω_{ath} phase particles are formed during cooling from RT to –196 °C. The dissolution of these particles with increasing temperature causes the resistance decrease and even dominates over the common resistance increase with temperature due to lattice vibrations. Furthermore, it can be concluded that no α-phase particles are formed even at –196 °C. This proves that no α phase is created martensitically during cooling from RT to –196 °C in Ti–15Mo alloy.

Figure 2 also shows the derivative of the resistance evolution. The change of the slope in the resistance evolution as described above suggests that a new process already dominated over the previous one (e.g. more $\beta/\omega_{\mathrm{iso}}$ interfaces are formed than $\beta/\omega_{\mathrm{ath}}$ interfaces disappear). On the other hand, the onset of the new process can be identified as the peak of the first derivative. Therefore it can be concluded that ω particles become chemically stabilized already from 110 °C. Similarly the dissolution (or transformation) of ω_{iso} particles starts at 340 °C.

The minimum at the derivative of the resistivity curve in stage I (see Fig. 2) at around 110 °C also suggests that the resistance evolution up to this temperature should be reversible. This was indeed experimentally proven by cyclic repeated heating and cooling (heating/cooling rate of 5 °C/min) of the sample in a sequence up to 80, 90, and 100 °C. The results in Fig. 3 show that the lines for cooling and heating follow the same path and the resistance always returns to its original value. The minimum at the derivative of the resistivity curve (see Fig. 2)

may be therefore considered as the limit of reversibility. Above this point ($T > 100$ °C) the diffusion controlled (thus irreversible) growth of ω phase resumes.
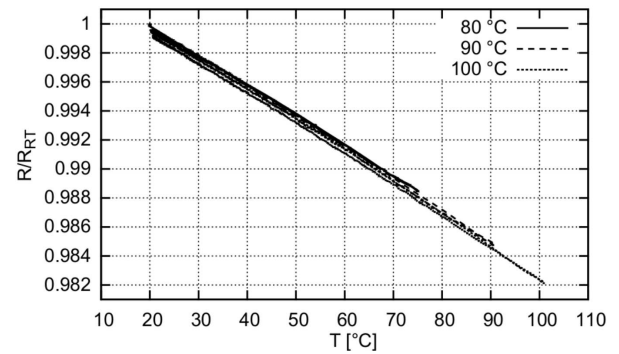

Fig. 3. The electrical resistance (normalized to R at RT) dependence on temperature during heating and cooling.
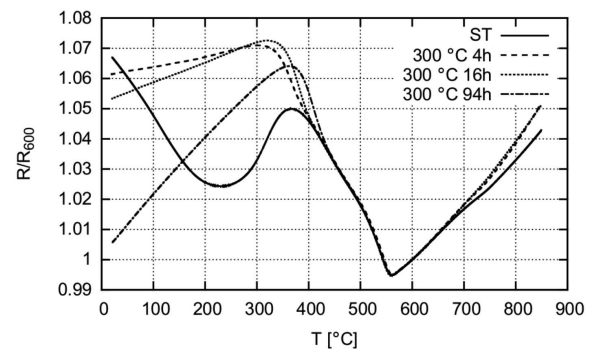

Fig. 4. The electrical resistance (normalized to R at 600 °C) dependence on temperature for samples aged at 300 °C for 4, 16, and 94 h compared with solution treated state.

We have already discussed that the course of resistivity curve in stage II is influenced by the growth of ω_{iso} phase and that this growth is irreversible. The slope of the resistivity curve at the stage II may be related to the transferred volume of ω_{iso}. In order to inspect this influence we have pre-aged solution treated specimens at 300 °C for 4, 16, and 94 h. These samples must differ in the volume fraction and in sizes of ω_{iso}. The resistivity curves measured in these specimens from RT to 850 °C are shown in Fig. 4. Note that since the microstructural conditions at room temperature are very different, it is more reasonable to normalize the relative resistance at temperature of 600 °C. At this temperature we assume similar microstructural condition in all samples, because the ω_{iso} particles created during pre-ageing are completely dissolved. As a result we can compare the different evolution in the lower temperature ranges.

For pre-aged samples we do not observe any resistivity decrease with increasing temperature. The ω_{ath} particles are obviously not formed in pre-aged samples that contain ω_{iso} particles. Furthermore, the decreasing slopes of these curves with increasing time of preaging in stage

II may be directly related to the increasing volume fraction of ω_{iso} after pre-ageing. The sample pre-aged for 94 h shows only slight increase of resistivity up to 350 °C. This means that either only very limited amount of ω_{iso} particles is formed or this increase can be attributed to common thermal increase of resistivity due to lattice vibrations.

4. Summary

The main results of the present work can be summarized as follows:

- The evolution of *in situ* resistivity of Ti–15Mo alloy was measured from −196 °C to 850 °C.

- During heating from room temperature, the temperature ranges of consequent processes can be identified, namely I: ω_{ath} particles dissolution, II: ω_{iso} particles formation, III: ω_{iso} particles dissolution, IV: α particles precipitation and finally V: α particles dissolution.

- Cooling to cryogenic temperatures showed that more ω_{ath} is created during cooling from RT. Furthermore, it is suggested that no α phase is created martensitically during cooling from RT to −196 °C in Ti–15Mo alloy.

- The dissolution of ω_{ath} is fully reversible below 110 °C.

- During pre-ageing at 300 °C the ω_{iso} particles are created. Therefore ω_{ath} are not created at room temperature, which is fully consistent with electrical resistance measurements. The longer the time of pre-ageing the lower the resistivity increase, because less ω_{iso} particles are created during *in situ* measurement.

- The resistance drop starting at approximately 350 °C is caused by dissolution or transformation of ω_{iso} particles.

- The β-transus was detected at 730 °C.

Acknowledgments

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