PHASE TRANSFORMATIONS IN BETA-Ti ALLOYS STUDIED BY IN-SITU ELECTRICAL RESISTANCE MEASUREMENT

Petr HARCUBA, Pavel ZHÁŇAL, Jana ŠMILUEROVÁ

Department of Physics of Materials, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic, EU, Harcuba.p@gmail.com

Abstract

Phase transformations in several metastable β-titanium alloys were studied during linear heating by in-situ electrical resistance measurement. The initial decrease of electrical resistance is caused by a reverse shuffle transformation of athermal ω phase particles to β matrix. The following temperature interval in which a negative dependence of electrical resistance was observed correlates with diffusional stabilization and growth of isothermal ω phase which releases internal stresses in the β matrix. At the temperature of ω phase stability limit (500 - 570 °C, depending on the type of alloy), an abrupt change in electrical resistance is observed. The subsequent β → α followed by α → β transformation may cause an additional local maximum in the electrical resistance, depending on the type of the studied alloy and the kinetics of this transition. Electrical resistance measurement proved to be a very sensitive technique for phase transformation analysis.

Keywords: Metastable beta-Ti alloys, omega phase, electrical resistivity

1. INTRODUCTION

Metastable β-Ti alloys belong to a modern class of materials, finding their use in advanced applications, e.g. in aerospace and biomedical sectors, due to their outstanding mechanical and physical properties. In particular, metastable β-Ti alloys have high specific strength, excellent corrosion resistance and good biocompatibility [1]. Mechanical properties can be further tailored according to specific requirements of particular applications by thermomechanical treatment. The main disadvantage, which hinders a wider use of titanium, is its relatively high cost due to expensive production process [2].

Titanium is an allotropic element. At room temperature and standard pressure, pure titanium crystalizes in a hexagonal close-packed (HCP) structure known as α phase. When heated above 883 °C, so called β transus temperature, its crystallographic structure transforms to a body-centered cubic (BCC) β phase. By adding β stabilizing alloying elements, such as Mo, Fe, Nb or V, the β transus temperature decreases. In metastable β-Ti alloys the content of β stabilizers is sufficiently high to retain the β phase in a metastable state (i.e. the martensitic transformation β → α is suppressed) upon quenching from a temperature above the β transus to room temperature [2].

Depending on the type and content of β stabilizers in metastable β-Ti alloys, particles or precipitates of other metastable phases can form during quenching or further heat treatment. The most important one is the ω phase. In literature, two evolution stages are usually distinguished. The first stage is called athermal ω (ω_{ath}). The ω_{ath} is formed during quenching by a diffusionless transformation described by de Fontaine et. al. [3]. This transformation is accomplished by a collapse of two adjacent $(111)_\beta$ planes into their intermediate position, while one $(111)_\beta$ plane in between two pairs of collapsed planes is left unchanged, creating a hexagonal structure. Particles of ω_{ath} phase are uniformly dispersed in the β matrix and their size is of the order of several nanometers. The ω lattice is coherent with the β phase matrix and the chemical composition of ω_{ath} is identical to the parent phase [4]. It was shown, that this transformation cannot be suppressed even by extremely fast cooling rates [5]. Moreover, it was proved that β ↔ ω_{ath} transformation is partially reversible in a certain temperature interval [6]. During ageing at elevated temperatures, ω_{ath} phase may evolve and grow, resulting

in the so-called isothermal ω (ω_{iso}) phase. This process is diffusion controlled and is accompanied by rejection of β stabilizing elements from the volume of ω_{iso} particles. ω_{iso} particles typically reach the diameter of several tens of nanometers. This process is irreversible [7, 8].

The formation of ω phase particles has a great impact on mechanical properties of metastable β-Ti alloys. ω particles increase the yield strength but also embrittle the material [2, 3]. During subsequent ageing at higher temperatures, thermodynamically stable α phase can form. Finely and uniformly dispersed particles of ω phase formed at a lower temperature serve as nucleation sites for small and homogenously distributed α platelets. This microstructure leads to high yield strength with minimal reduction of ductility [2].

In this work, we investigated phase transformations in several metastable β-Ti alloys by means of in-situ electrical resistance measurement.

2. EXPERIMENTAL

Commonly used abbreviated names of the studied alloys are listed below together with their chemical compositions given in weight percent and calculated molybdenum equivalence (Mo eq.) which helps to compare the β stabilizing effect of different elements in Ti alloys [2]:

- Ti-15Mo,
- LCB - Ti-6.8Mo-4.5Fe-1.5Al (18.4 Mo eq.),
- Ti-5553 - Ti-5Al-5Mo-5V-3Cr (8.15 Mo eq.),
- TNFS - Ti-29Nb-1Fe-0.5Si (11 Mo eq.),
- TNTZ - Ti-35.3Nb-5.7Ta-7.3Zr (13 Mo eq.).

Simple binary Ti-15Mo alloy was chosen as benchmark material. LCB (stands for Low Cost Beta - an alloy developed by Timet company to address the demand for a less expensive alternative to other metastable β-Ti alloys) and Ti-5553 are structural materials used in demanding aerospace and automotive applications. TNTZ and TNFS are Nb-based metastable β-Ti alloys with exceptionally low elastic modulus and with a high potential in biomedical applications. All alloys were supplied by Timet company except TNTZ alloy which was vacuum arc melted from pure elements in UJP Praha, Czech Republic. The initial state of each material was prepared by β solution treatment at a temperature above the β-transus of each alloy. The solution treatment of the material was done in quartz tubes filled with pure argon, and - was terminated by water quenching.

In order to study phase transformations in these materials, in-situ measurement of electrical resistance during heating was employed. Electrical resistance measurement proved to be an ideal tool for detecting microstructural and phase changes in materials. It usually exhibited higher sensitivity than more commonly used differential scanning calorimetry (DSC) or dilatometry. Flat samples of the thickness of about 1 mm were cut from the studied materials. Series of grooves were cut into the samples to form an “N” shape. This shape was employed to increase the effective length of the sample and consequently the sensitivity of the measurement of electrical resistance. In order to avoid the influence of deformed surface resulting from cutting the sample with a wafering blade, approximately 0.2 mm thick layer was removed by grinding using SiC papers. The four-point method was employed for electrical resistance measurement. The experimental setup allowed the simultaneous measurement of both the voltage and the electrical current using Keithley 2182 nanovoltmeter and Keithley 2400 SourceMeter, respectively. The samples were heated in a specially designed furnace which allowed precisely controlled heating from room temperature to 850 °C with the heating rate of 5 °C/min and 50 °C/min in an inert atmosphere of argon (purity (6N). This setup allows achieve the relative error of the measurement lower than 10^{-4} in each measured point while acquiring 2 points per second. Details about experimental apparatus can be found in [9]. Unfortunately, it is very difficult to determine accurately the electrical resistivity (material constant) with only a small amount of material. Instead, relative electrical resistance normalized to initial electrical resistance ($R(T)/R_0$) was evaluated.

3. RESULTS AND DISCUSSION

The evolution of electrical resistance of metastable β-Ti alloys during heating is usually very complicated. Due to the formation of a large amount of small ω particles (volume fraction of ω phase can reach tens of percent), the crystallographic structure of the material is severely disturbed. This significantly affects the mean free path of electrons and results in high electrical resistance. During heating of common metals and alloys, the increasing scattering of electrons on phonons is the dominant process, leading to an increase of electrical resistance with temperature. In metastable β-Ti alloys, the situation is more complex due to ongoing phase transformations. For example, the reversion of ω phase particles back to the β phase is accompanied by the release of elastic strains arising from the presence of ω particles. Consequently, the mean free path of conduction electrons increases. Similar effect is observed at later stages of ω particle growth. Our hypothesis is that highly strained coherent β/ω interface changes to semi-coherent, which also decreases the resistance to electron motion through the material. These effects which increase electron mean free path may prevail over phonon scattering (increasing electrical resistance with temperature); therefore, we can observe a negative temperature dependence of electrical resistance.

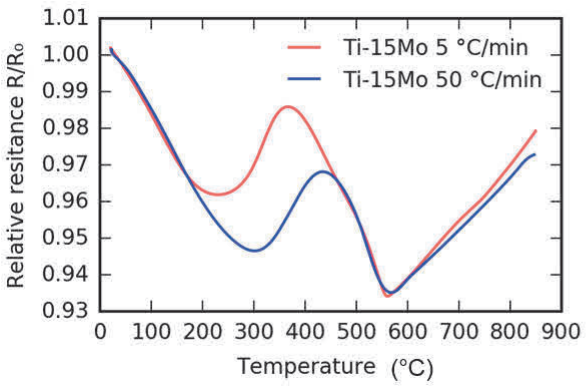

Figure 1 Evolution of electrical resistance of Ti-15Mo

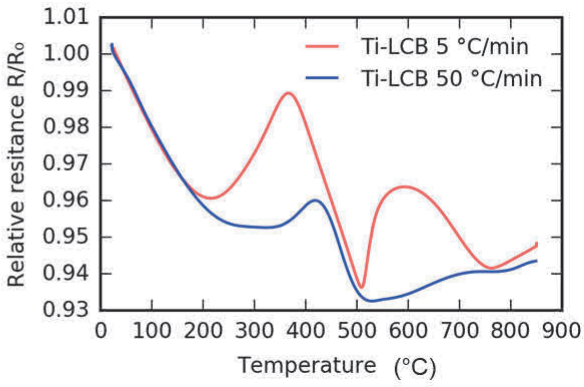

Figure 2 Evolution of electrical resistance of LCB

The evolution of electrical resistance of binary Ti-15Mo alloy during heating with the heating rate of 5 °C/min and 50 °C/min is plotted in **Figure 1**. The initial decrease corresponds to inverse shuffle transformation $\omega_{ath} \rightarrow \beta$. Elastic stresses in the parent β phase which lead to formation of ω_{ath} particles upon quenching are partially released at the beginning of heating which allows ω_{ath} to transform back to β. The periodicity of the crystal structure is increased, resulting in easier electron transport and a decrease of electrical resistance. This process is reversible up to about 110 °C. Above this temperature, the diffusion-driven stabilization of remaining ω particles begins, starting the growth of ω_{iso} particles. During the subsequent temperature interval (250 - 350 °C and 300 - 450 °C for the heating rate of 5 °C/min and 50 °C/min, respectively), an increase of electrical resistance is observed. This increase is caused mainly by phonon scattering. However, it can be assumed that the growth of ω_{iso} also contributes to the increase of electrical resistivity as in the early stages of ω particles growth, the ω lattice is still coherent with the parent β phase (with a small misfit [10]). As ω particles grow, the relative misfit between the two lattices increases, and the resulting larger elastic distortions hinder the motion of conduction electrons. The second temperature interval in which a negative dependence of electrical resistance is observed (350 - 560 °C and 450 - 560°C for the heating rate of 5 °C/min and 50 °C/min, respectively) could be explained by further growth of ω particles. As the size of ω particles increases, the energy associated with the β/ω lattice misfit also increases. At a certain point, the coherent interface between ω and β phases is no longer favorable and it changes to the semi-coherent one [11]. As a consequence, lattice strains are partly released and the electron mean free path increases. Note that both the first local minimum and the first local maximum are shifted to higher temperatures for the higher heating rate.

This is a typical feature of diffusional transformations which is caused by the fact that the diffusion process has less time at any specific temperature. Let us now discuss the first temperature interval (to 250 °C and 300 °C for the heating rate of 5 °C /min and 50 °C/min, respectively) in more detail. It can be seen that up to approx. 110 °C (i.e. the limit for ω ↔ β reversibility), electrical resistance curves for both heating rates exhibit the same temperature dependence. However, at higher temperatures (above 110 °C), different kinetics of ω_{iso} transformation are observed for the two heating rates. At the higher heating rate (50 °C/min) the transformation to ω_{iso} is shifted to higher temperatures due to the reason described above. Therefore, the dissolution of ω_{ath} remains the dominant effect between 110 °C and 250 °C before the diffusion process starts, and the electrical resistance curve continues to decrease. On the other hand, the temperature of the sharp minimum at about 560 °C does not depend on the heating rate. This abrupt change in the dependence of electrical resistance on temperature denotes the limit of stability of the ω phase [3]. At this temperature, all remaining ω phase transforms back to β. It was shown in [7] that α phase starts to form beyond this point. The β transus of Ti-15Mo is at about 775 °C. Exactly at this point a small hump on the resistance curve is seen.

Very similar behavior of electrical resistance can be observed in LCB alloy (see **Figure 2**). At the higher heating rate, transformations in the temperature interval between approximately 200 °C and 400 °C are shifted to higher temperatures compared to the lower heating rate. The limit of the stability of the ω phase is again independent of the heating rate. The most significant difference can be observed beyond the stability limit of the ω phase - a distinct local maximum appears when the slower heating rate is applied. This can be explained by much higher diffusivity of Fe compared to Mo and the presence of α stabilizing Al, resulting in much faster formation of fine α phase particles which in turn causes the increase of electrical resistivity. As the temperature further increases, the equilibrium concentration of the α phase (which has higher electrical resistivity) in the β matrix decreases and the α phase reverts back to β. Decreasing volume fraction of the α phase causes the decrease of electrical resistance in the temperature interval between 600 °C and 750 °C. After the β transus temperature is reached, the material consists of pure β phase and electrical resistance increases due to increasing phonon scattering.

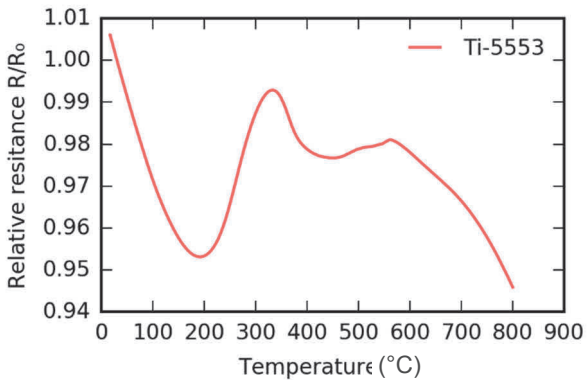

Figure 3 Evolution of electrical resistance of Ti-5553

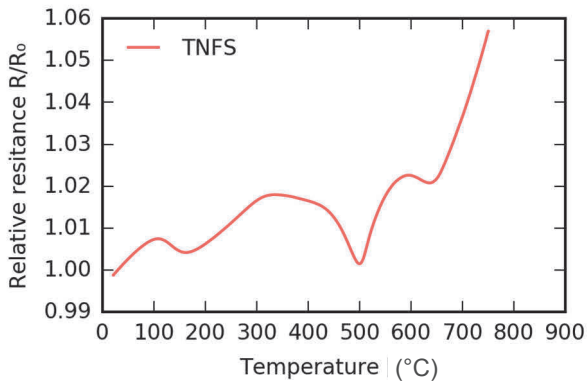

Figure 4 Evolution of electrical resistance of TNFS

The dependence of electrical resistance of Ti-5553 on temperature during heating is shown in **Figure 3**. An initial drop by approximately 5% followed by an increase of electrical resistance is very similar to that observed for both previously discussed alloys. Contrary to the other alloys, in which the stability limit of ω phase particles manifests itself as a local minimum, this process occurs at a local maximum at about 560 °C for Ti-5553. Furthermore, it is observed at much higher relative resistivity compared to Ti-15Mo and LCB. Ti-5553 is much less β stabilized than Ti-15Mo and LCB and contains a significant amount of α stabilizing Al. Therefore, α phase may form much easier during heating before the ω stability limit is reached. In this alloy, the α phase has a significantly larger resistivity than the β phase. In the temperature interval of 560 - 800 °C, the volume

fraction of α continuously decreases which causes a decrease of electrical resistance. The β transus temperature of Ti-5553 is about 860 °C which exceeds the limit of the employed apparatus; therefore, we cannot observe the final increase of resistance in the pure β phase. Negative dependence of electrical resistance above 600 °C was also observed in α + β alloy Ti-6Al-7Nb [12].

The main difference in the temperature dependence of electrical resistance of TNFS compared to the aforementioned alloys is the initial increase of resistance. High Nb content in metastable β-Ti alloys hinders the formation of the ω phase. The increase of resistance from RT to 120 °C might be caused by a low volume fraction of ω_{ath} phase particles which are more stable in this temperature interval. The inverse shuffle transformation $\omega_{ath} \rightarrow \beta$ accompanied by a decrease of electrical resistance may therefore start at higher temperatures. The stability limit of the ω phase is detected at 500 °C. Above this temperature, rapid formation of α phase particles manifests itself as another local maximum at 600 °C, similar to LCB alloy.

The temperature dependence of electrical resistance of TNTZ alloy looks very different as it can be seen in **Figure 5**. The addition of Zr very effectively inhibits the formation of ω_{ath} phase particles upon quenching, as reported by Pang et al. [13]. Due to the absence of ω particles, the initial decrease of electrical resistance observed in the previously discussed alloys and caused by partial dissolution of these particles is not detected in the case of TNTZ alloy. Electrical resistivity of TNTZ increases continuously with increasing temperature as the dominant effect is classical phonon scattering which increases with temperature.

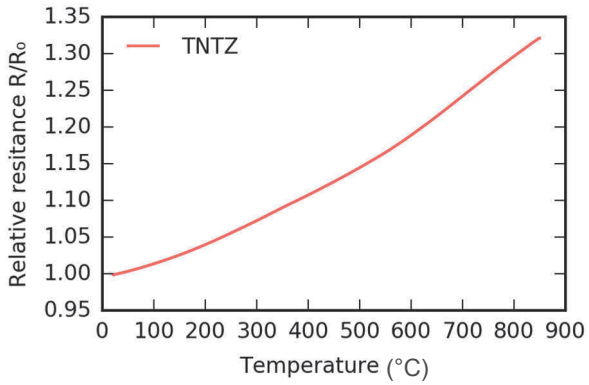

Figure 5 Evolution of electrical resistivity of TNTZ

4. CONCLUSION

Phase transformations in metastable β-Ti alloys occurring during heating were studied using in-situ measurement of electrical resistance. Temperature dependences of electrical resistance of selected alloys exhibit very complex behavior. In certain temperature intervals, phase transformations in these materials result in inversion of common increasing trend of this dependence. Large number of tiny ω phase particles in these alloys severely affects the periodicity of the crystal lattice and reduces the mean free path of conduction electrons. Therefore, any change of these particles has a significant effect on electrical resistance of the material. In-situ electrical resistance measurement proved to be an ideal tool for studying phase transformations and their kinetics in metastable β-Ti alloys. It is a simple and very straightforward method which could help to design thermal treatment regime to achieve desired properties of these class of materials by modification of morphology and volume fraction of individual phases.

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