Ultra-fine grained microstructure of metastable beta Ti-15Mo alloy and its effects on the phase transformations

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Abstract. Processing of metastable titanium alloys by severe plastic deformation provides an opportunity to achieve exceptional grain refinement, to enhance the strength and to affect phase transformations occurring during thermal treatment. The main aim of this study is to investigate the microstructure of ultra-fine grained (UFG) material and effect of microstructural changes on phase transformations in metastable β-Ti alloy Ti-15Mo.

Metastable β-Ti alloys are currently the most studied Ti-based materials with prospective use in medicine. Ti-15Mo alloy after solution treatment contains metastable β-phase. Metastable α-phase and stable α-phase particles are formed upon annealing.

Solution treated Ti-15Mo alloy was deformed by high pressure torsion (HPT) at room temperature. Severely deformed structure after HPT with grain size of ~200 nm was studied by transmission electron microscopy. In-situ electrical resistance measurements showed significant changes in undergoing phase transformations when compared to coarse-grained (CG) material. Scanning electron microscopy revealed heterogeneous precipitation of α-particles at grain boundaries (GB). Due to the high density of GBs in UFG structure, these precipitates are very fine and equiaxed.

The study demonstrates that SPD is capable of enhancing mechanical properties due to grain refinement and via affecting precipitation processes in metastable β-Ti alloys.

1. Introduction

Ultra-fine grained (UFG) metallic materials processed by severe plastic deformation (SPD) have attracted significant attention due to the enhancement of mechanical properties as compared to coarse-grained (CG) counterparts [1], which make UFG materials favorable for industrial and medical use [2, 3]. High pressure torsion (HPT) and equal channel angular pressing (ECAP) are the most widely used SPD techniques, producing extreme grain refinement (grain size below 100 nm) [4, 5].

Metastable β-titanium alloys gained significant interest thanks to their excellent mechanical properties [6, 7]. Ti-15Mo (titanium alloy with 15 wt% of molybdenum) is a thoroughly investigated simple binary alloy and a promising candidate for biomedical use [8]. Upon thermal treatment it undergoes several phase transformations. The solution treated (ST) material consists of β-phase with body-centered cubic structure and metastable ω-phase with hexagonal symmetry [9]. The ω-phase is formed already during quenching [10] and is referred to as ωath (ω athermal). ωath-phase particles are coherent with the β matrix and their diameter is only few nanometers [11]. Upon heating ω-particles
become stabilized by diffusion process by expelling Mo atoms (as $\beta$-stabilizing element) – this phase being referred to as $\omega_{\text{iso}}$ ($\omega$ isothermal). The $\omega_{\text{iso}}$ – phase particles grow during annealing and simultaneously become more chemically stabilized [12]. Further annealing of the material leads to precipitation of $\alpha$-phase particles. In some studies, it is claimed that $\omega_{\text{iso}}$ particles serve as nucleation sites for precipitation of the $\alpha$-phase [13]. Alternative preferential precipitation sites of $\alpha$-phase particles are $\beta/\beta$ grain boundaries.

The main aim of this study is to investigate the effect of the UFG structure in the Ti-15Mo alloy on the ongoing phase transformations in the material upon heating.

### 2. Material and experimental

Ti-15Mo alloy supplied by Carpenter Technology Corp. in a form of a rod with the diameter of 10.5 mm was used for this study. The as-received rod was solution treated (810 °C, 20 min) in a protective Ar atmosphere followed by a water quench. It was further cut to cylinders (diameter 10.5 mm, height approx. 5 mm) and pressed in HPT machine at room temperature to obtain the disk-shaped specimen of the diameter of 20 mm. The principle of HPT method is described in detail in [1]. Samples with the thickness of 1 mm were prepared by HPT at Ufa State Aviation Technical University (USATU) Ufa, Russia at room temperature and the pressure of 2 GPa. Sample processed by a single HPT rotation was used for all investigations presented in this study.

Scanning electron images using back-scattered electrons were performed using Zeiss Auriga Compact SEM equipped with the field emission gun (FEG) operated at 10 kV. Samples for SEM observations were prepared by mechanical grinding and polishing followed by a three-step vibratory polishing.

Transmission electron microscope (TEM) Jeol JEM 2200 operated at 200 kV was used for detail microstructure observation. Thin foils for TEM observations were prepared by electrochemical thinning using Tenupol-5 jet polishing unit at -20°C followed by ion polishing using Leica EM RES102 ion polisher.

The four-point method was employed for electrical resistance measurements of samples during heating [14]. This experimental set-up allows simultaneous measurement of the voltage and the electrical current. The samples of the thickness of approximately 0.7 mm and the size of 6.5x15 mm were cut to a special ‘U’ shape [15] and mechanically grinded. The electrical resistance of the samples was measured in-situ during linear heating up to 750 °C and 800 °C with the heating rate of 5 °C/min.

### 3. Results and discussion

#### 3.1. Microstructure of HPT-deformed Ti-15Mo alloy

TEM images in Figure 1 show the periphery part of the sample of the HPT-processed (N = 1) Ti-15Mo alloy. Figure 1(a) shows the bright field (BF) image of the severely deformed microstructure. The corresponding dark field (DF) image from the $\beta$$(110)$ reflection as well as selected area electron diffraction (SAED) pattern is shown in the Figure 1(b). The non-uniform contrast in the bright regions in Figure 1(b) and a distortion of a diffraction spots in SAED pattern reveal the lattice distortion associated with the high internal stress [16]. The individual grains in the UFG microstructure cannot be distinguished due to their overlapping through the thickness of the sample and the bright areas in the DF image are parts of grains rather than individual grains [17]. No $\omega_{\text{iso}}$-particles were observed by TEM, which is in contrast to statements in previous report [16]. Wang et al. explained the absence of the $\omega$-phase in the UFG material by occurrence of reverse $\omega$-$\beta$ transformation due to ultra-fine grains and high dislocation density [18].
3.2. In-situ electrical resistance measurement

The relative electrical resistance was measured during two heating cycles for each studied specimen. Each run consisted of heating up to 750 °C and cooling back to room temperature. The evolution of relative resistance \( R(T)/R_0 \), where \( R(T) \) is the electrical resistance measured at the temperature \( T \) and \( R_0 \) is the resistance at room temperature after the second cycle, was studied. The selection of ‘normalization constant’ \( R_0 \) is based on assumption that after two heating cycles runs, the material is fully recovered and recrystallized and therefore both original HPT processed and solution treated conditions are comparable. Figure 2 shows the evolution of relative resistance of solution treated (solid line) and HPT processed (dashed line) Ti-15Mo alloy during linear heating up to 750 °C (first cycle) with the constant rate of 5 °C/min. The resistance evolution of ST specimen may be divided into four temperature zones (regions). Initially, the relative resistance of ST material decreases to the temperature of 255 °C – this stage is referred to as zone I. The decrease in \( R/R_0 \) can be attributed to the dissolution of the \( \omega_{\text{ath}} \) [9, 19]. Near the coherent \( \beta/\omega \) interfaces elastic strain field is formed which acts as scattering zone for conducting electrons. In the absence of these interfaces (after dissolution of \( \omega_{\text{ath}} \)) the elastic strain field is released which allows smooth electron drift associated with the decrease of the electrical resistance [20]. The electrical resistance of the HPT material also decreases in zone I. However, the decrease is less pronounced than in the ST specimen. It suggests that the HPT material contains less \( \omega_{\text{ath}} \) particles due to high deformation of the parent \( \beta \)-phase. On the other hand, some \( \omega_{\text{ath}} \) must be present in the material after HPT to cause initial resistance decrease.

In the zone II (255°C – 360°C) the relative resistance of ST material increases with increasing temperature. In this range the \( \omega_{\text{iso}} \)-particles grow due to diffusion-driven chemical stabilization [11]. In contrast to the previous case, the amount of \( \beta/\omega \) interfaces increases raising the electrical resistance [21]. In the HPT deformed material, the resistance increase is again much less pronounced when compared to the ST condition. The lack of \( \omega_{\text{ath}} \) nuclei reduce the formation of \( \omega_{\text{iso}} \)-particles and furthermore the outset of the recovery processes may reduce the resistance increase.

The decrease of relative resistance in zone III (360°C - 560°C) in ST material is attributed to the coarsening and continuous dissolution of \( \omega_{\text{iso}} \)-particles in the ST material [22]. The decrease is even more significant in the HPT deformed material. Considering that the HPT deformed material contains lower fraction of \( \omega_{\text{iso}} \)-phase, the resistance decrease is therefore related mainly to the recovery and recrystallization.
The abrupt increase of the relative resistance of ST material above 560 °C (zone IV) was observed. Distinct change of slope at 560°C is associated with the sudden dissolution of ωiso-particles [9]. On the other hand in HPT material, the resistance decrease becomes slower between 450°C and 500°C, which suggests that the recovery and recrystallization processes become exhausted. In the zone IV, the resistance increase in the ST material is linear, which corresponds to the common electron phonon interaction in the absence of any phase changes. It is therefore assumed that α-phase particles do not homogeneously precipitate in the coarse-grained material during heating with the rate of 5 °C/min. On the other hand, small peak in the zone IV observed in resistivity evolution of HPT deformed material suggest increasing volume fraction of α-phase up to the temperature of 650°C. This behavior is typical also for other β-Ti alloys, e.g. TIMETAL LCB [23].

The effect of the ultra-fine grained microstructure prepared by HPT on the phase transformations upon thermal treatment was also studied in other materials [24].

![Figure 2](image_url)

**Figure 2.** The dependence of the electrical resistance on the temperature of heating for ST and HPT-processed one.

### 3.3. Microstructure of annealed Ti-15Mo alloy after HPT deformation

Based on the measurement of the dependence of the electrical resistance on the heating temperature, the annealing temperatures of 400°C and 500°C and annealing periods of 1 and 16 h were chosen for the investigation of the microstructure by SEM. Samples from the periphery part of the HPT material after N=1 HPT rotation were annealed to chosen temperatures in Ar atmosphere and subsequently water quenched. The back-scattered electron images in the Figure 3 clearly show the precipitation of the α-phase in the HPT deformed and annealed samples. It can be observed that the α-phase precipitates form already after annealing at 400 °C for 1h (Figure 3(a)). The α-particles are ultra-fine and equiaxed. Coarsening and further growing of α-particles can be observed after further annealing, see the Figure 3(b). After annealing at 500°C for 1 and 16 hours (Figure 3(c) and (d)) the α-phase particles are larger; moreover, enhanced contrast suggests that α-phase is more chemically stabilized (i.e. Mo depleted). Associated Mo diffusion to β-phase causes its stabilization and may cause reverse ω to β transformation.

The size of α-phase particles significantly differ in different regions. The origin of such more-refined and less-refined areas remains unclear. The size of the α-phase is still in sub-micrometer range. Note,
that no $\alpha$-phase form in some areas (for instance in Figure 3(b)). Jiang et al. [16] claim that $\alpha$-phase precipitates in so-called shear bands which are formed during HPT straining. These shear bands are surrounded by alpha-free zones. For the detail explanation of this phenomenon further investigation is needed by in-situ methods.

The shape of $\alpha$-precipitates is rather polygonal than round or plate-like. It is well known that $\alpha$-phase precipitate heterogeneously at GBs [23, 25]. Therefore, we assume that all $\alpha$-phase particles formed during annealing of HPT processed material precipitated as grain boundary $\alpha$-phase.

4. Conclusions

The microstructure of ultra-fine grained metastable beta Ti-15Mo alloy and its effect on the ongoing phase transformations in the material were investigated. The following conclusions can be drawn from this experimental study:

- Transmission electron microscopy proved severely deformed nanocrystalline microstructure.
- In-situ electrical resistance measurement indicated that ultra-fine grained structure has a significant effect on the phase transformations in metastable $\beta$-Ti alloys. High deformation and easy precipitation of GB $\alpha$-phase suppress the formation of $\omega_{\text{sat}}$-phase and subsequent evolution of $\omega_{\text{iso}}$-phase, respectively. More exact explanation of ongoing processes requires further investigations, in particular in-situ scanning and transmission electron microscopy.
- Annealed samples at 400°C and 500°C contain the high volume fraction of homogeneously distributed, sub-micrometer sized equiaxed $\alpha$-phase particles which precipitate as GB $\alpha$-phase.
This study shows that SPD processing is capable of complete alteration of phase transformations and precipitation sequence in metastable β-Ti alloys. The resulting microstructural condition is promising for achieving high strength.

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