Effect of high pressure torsion on the aging kinetics of β-titanium Ti-15Mo alloy

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Abstract. This paper focuses on the study of the aging kinetics of the β-titanium Ti-15Mo alloy prepared by high pressure torsion. The experimental methods of differential scanning calorimetry and transmission electron microscopy were used for structural investigations. It was established that during aging at 500 and 550 °C, in the ultrafine-grained (UFG) alloy, the precipitating α-particles have mostly equiaxed morphology, in contrast to the needle-like and lens one in the coarse-grained (CG) alloy. There have been identified differences in the aging kinetics of the Ti-15Mo alloy in the UFG state identified by a decrease in microhardness within the first 30 minutes of heating, as opposed to the CG alloy coarsening. The influence of morphological features of the alloy microstructure on the strengthening effect after aging is discussed.

1. Introduction
The Ti-15Mo alloy is a typical representative of metastable β-titanium alloys, which has high biocompatibility, corrosion resistance and in the β-phase state is characterized by a low elastic modulus. However, in modern medicine, in order to fabricate multiaxial orthopedic implants, the material strength increase is a very urgent task [1]. High specific strength of the material allows creating products with improved design that are capable of withstanding prolonged cyclic loads [1, 2]. Strengthening of β-titanium alloys can be achieved by thermal and/or thermomechanical treatment as a result of structural phase transitions [3, 4]. However, after aging a significant strength increase is accompanied by a decrease in plastic properties due to the precipitation of secondary α-particles, which in a coarse β-grain are plate-like and lens-shaped. In particular, the Ti-15Mo tensile strength after aging increases up to 1400 MPa, but the total elongation drops to very low values (δ ≤ 5 %) [3]. This limits the practical application of β-Ti alloys in the aged condition.

A new approach how to increase mechanical properties of metals and alloys is the formation of ultrafine-grained (UFG) structures by severe plastic deformation (SPD) [5]. In β-titanium alloys the fabrication of UFG structures solves the problem of increasing strength characteristics without a drastic reduction of plasticity. It is known that SPD can also have a significant impact on mechanisms of phase transitions occurring in metals and alloys during straining and also during subsequent heat treatment. Particularly, SPD, along with the formation of ultrafine grains, is accompanied by precipitation of secondary phases, the morphology of which essentially differs from the shape and size of phases precipitations during normal aging. Such observations have been made on a number of aluminum alloys and steels [6, 7], and the nature of unique transformations is associated with the
dynamic aging occurring during SPD. The change in the precipitation morphology in these alloys as a result of SPD-processing is extremely important for enhancing their mechanical properties, as it increases the strength and retains good ductility of these materials. It should be also noted that the ultrafine grain contributes to a more homogeneous diffusion decomposition of $\beta$-phase, which is impossible to achieve in a conventional coarse grain \cite{8, 9}.

In this paper, high pressure torsion (HPT) and subsequent aging were employed to form an UFG structure in the Ti-15Mo alloy. The main objective of this work is to study the influence of the UFG structure on the distribution and morphology of the second phases’ particles precipitating in Ti-15Mo during aging, and also on the mechanical properties of the alloy.

2. Material and experimental

The rods of a metastable$\beta$-titanium alloy Ti-15Mo were solution treated at 810 °C for 20 minutes and then water quenched. The material consists of $\beta$-phase only. The polymorphic transformation temperature was determined by differential scanning calorimetry (DSC) on Netzsch Geraetebau STA 409 PC/4/H, the samples were heated up to 1200 °C at a rate of 10 °C/min. The quenched billets were subjected to 5 HPT rotations at 200 °C with an applied pressure of 6 GPa. The aging of samples after solid solution treatment and straining was carried out at 500 and 550 °C for 0.5, 2 and 4 hours in electric furnaces in the air. The microstructure was investigated on a transmission electron microscope JEM 2100 (TEM) with the accelerating voltage of 200 kV. Microhardness was measured on the microhardness tester Omnimet (Buehler) with a load of 300 g and a holding time of 10 seconds. X-ray phase analysis (XRD) was performed on a diffractometer DRON-3, copper radiation was employed.

3. Results of research

Figure 1,a shows the DSC signal during heating of the coarse grained Ti-15Mo alloy after solid solution treatment. We see that in the initial quenched state an athermal $\omega_{\text{ath}}$-phase is present in the $\beta$-phase. When the alloy is heated to relatively low temperatures, the reverse transitions occurs, the $\omega_{\text{ath}}$-phase disappears \cite{10}. When the heating temperature increases in the areas with a low concentration of $\beta$-stabilizers, an isothermal $\omega_{\text{iso}}$-phase is formed by shear. Obviously, this leads to a release of some energy, which characterizes the first exothermic peak at 300 °C on the DSC curve (figure 1a). At the next stage of decomposition of the supersaturated solid solution, when the heating temperature increases, the $\omega_{\text{iso}}$-phase is replaced by the $\alpha$-phase. On the DSC curve, the formation of the exothermic peak, associated with $(\beta+\omega_{\text{ath}}) \rightarrow (\beta+\alpha)$-transformation, starts at a temperature of 500 °C and has a maximum at 550 °C. Exothermic peak 3 is obviously associated with a complete polymorphic transformation at 790 °C.

Based on the obtained critical temperatures of phase transformations determined in the alloy, the HPT was carried out at 200 °C, when the athermal and/or isothermal $\omega$-phase is minimal. The presence of $\omega$-phase is known to greatly reduce the alloy ductility \cite{3, 10}. Subsequent aging was conducted at temperatures of 500 and 550 °C, which correspond to the $\alpha$-phase precipitation providing additional strength improvement.

After quenching from 810 °C, the Ti-15Mo alloy has a coarse grained structure with an average size of $\beta$-grains 33 $\mu$m (figure 1b). Subsequent deformation by HPT led to the microstructure refinement, and the average size of structural features determined by dark-field images was 0.13 $\mu$m (figure 1c). We observed high internal stresses and high defect density in the microstructure, as evidenced by a strong contrast of TEM images and azimuthal blur of spots on the electron diffraction pattern (figure 1d).
Further heating during the alloy aging, both in the CG and UFG condition (after HPT processing) led to structural and phase changes. The analysis of TEM images of the microstructure after aging revealed significant differences in the shape and size of $\alpha$-phase particles precipitated in the CG and UFG structure. In particular, already after 30 minutes of heating at 500 °C, in the CG alloy the fine ellipsoidal $\alpha$-particles were observed and their shape was close similar to the shape of $\omega$-particles, which, were the sites of $\alpha$-phase nucleation (figure 2a). The size of these particles was less than 80 nm. After ageing for 4 hours, apprat of ellipsoidal particles of $\alpha$-phase, the $\alpha$-particles with needle-like morphology were detected. These particles precipitated primarily along the grain boundaries were also formed in the alloy (figure 2b,c). Thus, 500 °C can be considered as the temperature of the $\alpha$-phase precipitation. This fact is also supported by the DSC analysis (figure 1a).

In contrast to the CG alloy, in the UFG structure equiaxed $\alpha$-phase particles having the average size of about 150 nm were also identified (figure 2d). Some coarsening of $\alpha$-particles was observed after aging for 2 and 4 hours (figure 2e,f).

Figure 1. The DSC curve of Ti-15Mo after solid solution treatment (a) and the microstructure of Ti-15Mo: b) after solid solution treatment at 810 °C – coarse-grained state (CG); c, d) after 5 HPT rotations at 200 °C (UFG); c – bright-field; d – dark-field image

Figure 2. The microstructure of Ti-15Mo after aging at 500 °C: a, d – for 0.5 hours; b, e – 2 hours; c, f – 4 hours; a, b, c – CG state; d, e, f – UFG state
Figure 3 shows TEM micrographs of the CG and UFG microstructure after aging at 550 ºC. After 30 minutes of the CG alloy heating the $\alpha$-particles of needle-like morphology and the width of 0.03-0.07 µm were found along the boundaries and within the $\beta$-grains in the CG alloy, (figure 3a). In the UFG condition the $\alpha$-phase particles had an equiaxed shape, and their average size was about 0.2 µm (figure 3b). After aging for 2 and 4 hours, some coarsening of $\alpha$-particles was observed, but these particles maintained their shape, the needle-like and equiaxed in the CG (figures 3b,c) and in the UFG conditions (figures 3e,f), respectively.

Some differences were also observed in the kinetics of $\alpha$-phase precipitation in the CG and UFG alloys. Figure 4a,b shows the dependence of the volume fraction of the precipitated $\alpha$-phase in CG and UFG samples on the duration of aging. It is clearly seen that after heating for 30 minutes, there is a sharp increase in the $\alpha$-phase fraction in UFG samples, in contrast to the CG ones. This is probably caused by the high extent of grain/subgrain boundaries and high dislocation density that can be the nucleation sites of $\alpha$-phase precipitation. Upon further heating, the growth rate of the $\alpha$-phase reduces in both conditions. Apparently, in a UFG alloy during the first 30 minutes the proportion of $\alpha$-phase enhances due to the nucleation of new particles, and for longer annealing times due to the increase in their size [10].

**Figure 3.** The microstructure of Ti-15Mo after aging at 550 ºC: a, d – for 0.5 hours; b, e – 2 hours; c, f – 4 hours; a, b, c – CG state; d, e, f – UFG state

**Figure 4.** Effect of heating time on kinetics of the $\alpha$-phase volume fraction (%) growth in the CG and UFG Ti-15Mo alloy
Figure 5 shows the results of microhardness (HV) measurements of CG and UFG samples after different aging time.

![Microhardness (HV) measurements](image)

**Figure 5.** Dependence of the Ti-15Mo microhardness on the aging time

It is apparent that as a result of the UFG structure formation in the alloy by HPT, microhardness values reached 5250 MPa, compared to 3100 MPa in the quenched condition, which is typical for metals subjected to SPD [5] (figure 5). The behavior of CG and UFG alloy during subsequent aging varies considerably, especially in the first 30 minutes of heating when the HV of the CG alloy increases, and in the UFG one – reduces. Apparently, this phenomenon is explained by the difference in phase and structural transformations that occur during heating. In the CG alloy the volume fraction of α-particles during aging increases gradually (figure 4), which results in the strengthening of the alloy β-matrix (figure 5). Aging for 4 hours leads to the α-phase coarsening (figures 2c and 3c), thus, contributing to a certain microhardness reduction. At the same time, alongside with second phase precipitates, competing recovery processes take place during annealing of UFG alloy. They result in density decrease of dislocations accumulated during SPD. Reduction of dislocation density is a dominating process, as a result of which significant microhardness reduction is observed. Increase of heating time causes α-phase growth, which also leads to further microhardness reduction (figures 2f and 3f).

4. Discussion of results

The possibility of forming an ultrafine-grained structure in the β- Ti-15Mo alloy by severe plastic deformation is documented. The average grain/subgrain size of the β-phase reached 130 nm the hardness increased almost 1.5 time sowing to the structure refinement with a minimum volume of ω-phase. A similar result was reported in [11] for the β-alloy TNTZ via the formation of a nanostructure by HPT. The possibility to achieve high strength and to retain low elastic modulus and excellent biocompatibility was demonstrated in TNTZ alloy. This proves the high application potential of nanostructured β-Ti alloys in medicine. The results obtained in this study also show the influence of severe plastic deformation on the aging mechanisms in the β-alloys, which is related to the initial β-grains sizes, the presence of dislocation substructure and morphology of precipitated particles of the secondary α-phase. The change in the α-phase morphology of the strained samples in comparison with the quenched ones may be due to several reasons. Firstly, the high dislocation density in the UFG alloy increases the number of nucleation sites of α-particles during aging, and, secondly, a small size of β-grains impedes the growth of α-precipitates. Both factors contribute to the formation of mostly equiaxed particles. Similar patterns were observed in steels and aluminum alloys subjected to ECAP and subsequent aging [6, 7]. Note also the unusual behavior of the UFG alloy, associated with softening within the first 30 minutes of aging, as opposed to the conventional coarse-grained material. It is known that large degree of accumulated strain considerably increase the internal energy of the material due to high defect density. This may affect the kinetics of precipitation of secondary phases’ particles during subsequent thermal
treatment [6]. Apparently, when the UFG alloy is heated to 500 and 550 °C the hardness degradation is faster than in the quenched state, which is caused by the competition with aging earlier processes of recovery and recrystallization. In particular, in aluminum alloys [12, 13] and the alloy Ti LCB [9], the microhardness maximum shifts after SPD towards lower aging temperatures. This may be explained by earlier formation and development of the second phases’ particles via greater stored internal energy. Apparently, in the Ti-15Mo alloy after HPT the aging effect appears below 500 °C. The optimization of the aging treatment to achieve the best combination of strength and ductility requires a more detailed consideration of structural phase transformations at lower temperatures, which will be demonstrated in our further work.

5. Conclusions
1. It is shown that severe plastic deformation at 200 ºC allows producing an UFG (β+ω) structure of the Ti-15Mo alloy with the average grain/subgrain size of 0.13 µm, which led to the strengthening of the material by 1.5 times.
2. A considerable influence of the Ti-15Mo alloy SPD on the morphology and volume fraction of the precipitated α-phase was identified. In particular, during aging at temperatures of 500 and 550 ºC the α-particles in the UFG alloy mostly have an equiaxed morphology, as compared to the needle-like and lens shape ones in the CG alloy.
3. The processes occurring during aging of the Ti-15Mo alloy in an UFG state at 500 and 550 ºC were determined and explained by microhardness reduction within the first 30 minutes of heating, as opposed to a coarse-grained alloy. The microhardness in an UFG alloy after aging is significantly higher than in a CG alloy.

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