Microstructure evolution in ultrafine-grained Ti and Ti-6Al-7Nb alloy processed by severe plastic deformation

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Abstract. Unique in-situ electric resistivity measurement was utilized to identify microstructural changes in ultra-fine grained commercially pure titanium and Ti-6Al-7Nb alloy. Both materials were prepared by equal channel angular pressing. Changes in resistivity evolution during in-situ heating were compared to scanning electron microscopy observations. Both materials are stable up to 440°C. Further heating at rate 5°C/min causes recovery and recrystallization of UFG structure. At 650°C the microstructure is fully recrystallized. High resolution in-situ electric resistivity measurement is capable of detecting recovery and recrystallization in UFG CP Ti and Ti-6Al-7Nb alloy.

1. Introduction
The importance of titanium and titanium alloys including their biomedical use is unquestionable [1,2]. The ultra-fine grained (UFG) commercial purity titanium (CP Ti) and Ti-6Al-4V alloy have already been prepared by severe-plastic deformation techniques (SPD) [3,4,5]. UFG commercial purity Ti and Ti alloys became known for their increased strength and enhanced fatigue performance [6]. Moreover, UFG materials exhibit also higher corrosion resistance and improved biocompatibility [7,8]. Recently, biocompatible UFG beta-Ti alloys have also been thoroughly investigated [9,10,11,12]. On the other hand, thermal stability of UFG microstructure in Ti and Ti alloys has been only rarely discussed [13,14], despite its significant importance for material processing and eventual low temperature superplasticity [15]. This investigation focuses on thermal stability of UFG microstructure of commercially pure Ti and biocompatible Ti-6Al-7Nb alloy. Ti-6Al-7Nb alloy has been developed as a biocompatible alternative to the common Ti-6Al-4V alloy. It belongs to α+β alloys consisting of both phases at room temperature. Its beta-transus temperature is 1010 °C [16]. UFG microstructure was obtained by the most popular technique of severe plastic deformation—equal channel angular pressing. The UFG microstructure of this alloy including its thermal stability was investigated by one of the co-authors [14]. The thermal treatment at 500°C is often used to increase the strength of Ti-6Al-4V alloy [17] and the same proved to increase the strength of UFG Ti-6Al-7Nb alloy [14]. The thermal stability of UFG microstructure around this temperature is therefore of major importance.

The principal experimental method used in this study is in-situ measurement of electric resistivity. This method has been successfully used to investigate phase transformations in metastable beta Ti alloys [18]. In this paper, we focus on recovery and recrystallization of microstructure during linear heating. Recovery and recrystallization were studied by in-situ electrical resistivity measurements in copper based alloys and composites [19,20] or in NiTi compound [21]. To our knowledge, there was no attempt up to date to study recovery and recrystallization by in-situ electric resistivity measurements in UFG Ti and Ti alloys.

2. Material and experimental
Two different materials – CP Ti and Ti-6Al-7Nb alloy were prepared by equal channel angular pressing using slightly different procedure. Both materials were procured from ATI Alvac Ltd. in as-rolled condition.

2.1. Preparation of CP Ti
The billets of CP Ti grade 4 were pressed through ECAP die having a round channel and the channel angle Φ = 105° and the corner angle Ψ = 20°. The diameter of the channel was 15 mm. The temperature of the die during pressing was between 300 and 310 °C. The studied billets were pressed 6 times via the route B at a constant ram speed of 1 mm/s. The mixture of 1/3 MoS₂ and 2/3 grease was used as a lubricant. More details about the ECAP processing of CP Ti be found elsewhere [22].

2.2. Preparation of Ti-6Al-7Nb alloy
Ti-6Al-7Nb alloy was at first thermally treated to enable successful processing by ECAP. The thermal treatment consisted of two annealing steps. Initially annealing at a temperature just below β transus was applied for one hour followed by water quenching. In the second step annealing for 4 hours at a temperature of 780 °C was applied. The microstructure after this thermal treatment is standard ‘duplex’ structure consisting of 18 vol.% of primary alpha phase, which allows successful ECAP processing (compared to initial microstructure with more than 60% of primary alpha).

The ECAP die with the diameter of 20 mm angles Φ = 120° and Ψ = 0° was employed. The pressing was repeated six times (6 passes) at 600°C. Finally, extrusion to 10 mm was applied at 300°C. More details on material and its processing can be found elsewhere [14].

2.3. Experimental procedure
Electric resistivity was measured in situ using a self-made experimental setup. DC four-point method and rapid commutation of current were implemented in order to minimize parasitic effects. By utilizing Keithley 2182A nanovoltmeters we are able to achieve measurement with relative error lower than 0.0001 within each measured point while obtaining about 2 points per second. The dynamics of microstructural changes will be thus undoubtedly revealed.

The electric resistivity was measured during linear heating with the rate of 5°C/min up to 700°C and 800°C for CP Ti and Ti-6Al-7Nb alloy, respectively. UFG conditions of both materials were investigated along with their annealed counterparts in which no microstructural transformations occurred.

Microstructure changes in both materials were observed by high resolution scanning electron microscope FEI Quanta 200 FEG operated at 20 kV using backscattered electrons. Employing of Z-contrast allowed distinguishing α and β phases in Ti-6Al-7Nb alloy and the channeling contrast revealed the grain structure. The microstructure of both the as pressed materials and its evolution after subsequent heating were investigated. The samples for SEM observations were heated in the furnace with the rate of 5°C/min up to selected temperatures (see the section Results) and then water quenched. This heating procedure aims to mimic the thermal processing during resistivity measurements. Specimens were then prepared by automatic grinding in Struers Automet 50 precision cut-off machine (0.3 mm removed), followed by standard metallographic grinding and vibratory polishing in three 8-hour steps using successively 0.3 µm alumina, 0.05 µm alumina and colloidal silica.

3. Results
3.1. In-situ electrical resistivity measurements
Fig. 1 shows the dependence of relative resistivity of CP Ti after ECAP and of the annealed material. The resistivity increases almost three times during heating to 700°C. Initially, the resistivity increases linearly, above 300°C the course slightly deviates from linearity. Small
difference between annealed and ECAP samples is observable. In order to see the difference
more clearly, the first and the second derivatives were computed numerically using Savitzky-
Golay algorithm with smoothing. Fig. 2 shows the first derivative of electrical resistivity. The
course of both curves is similar with two small deviations at about 500°C and 600°C. Those
deviations appear as clear peaks in the plot of the second derivative of relative resistivity
which is shown in Fig. 3. Based on the assumption that these peaks correspond to undergoing
microstructural changes, the temperatures of 440°C, 520°C and 640°C were chosen for
subsequent SEM observations.

The results of resistivity measurements of Ti-6Al-7Nb alloy are processed and presented in
the similar way. Fig. 4 shows the temperature dependence of relative resistivity for the UFG
material after ECAP and also in the as-annealed condition. The relative resistivity increases
only by approx. 10%, which contrasts to the CP Ti. The difference of the ECAP and as-
annealed condition is therefore well visible. The course of both curves is similar (concave) up
to 650°C. For higher temperatures, the electrical resistivity even declines. Fig. 5 shows the
first derivative with two distinct peaks around 500°C and 650°C for the material after ECAP.
The differences between the two conditions are accentuated by plotting the second derivative of electrical resistivity as shown in Fig. 6. The temperatures of 440°C, 550°C and 660°C were chosen for microstructure observation by SEM.

3.2. SEM observations

Based on resistivity measurements, four conditions were chosen for SEM observations in each material; namely the as-ECAPed condition and three annealed conditions – samples heated up to selected temperatures.

Fig. 7 displays the microstructure of CP Ti. In Fig 7a the ultra-fine grained microstructure of as-ECAPed material is shown. It is a typical heavily deformed structure and the grains of the average size of 1 µm [3, 22]. No significant change of the microstructure was observed in the sample heated to 440°C, see Fig. 7b. On the other hand, the microstructure in Fig. 7c (condition after heating up to 520°C) differs significantly. Individual grains are much clearer, which indicates that some recovery process occurred during heating between 440°C and 520°C. Grain size is also slightly increased indicating some grain growth. The dark spots in
the micrograph are relics from polishing – in fact parts of grains that fell out from the surface during vibratory polishing - those relics should be excluded from the consideration. Microstructure in the condition after heating to the highest temperature (640°C) is shown in Fig. 7d. It is a completely recrystallized microstructure with grains of the average size of approximately of 5µm.

![Fig. 7a CP Ti – as-ECAPed condition](image1)

![Fig. 7b CP Ti – heated up to 440°C](image2)

![Fig. 7c CP Ti – heated up to 520°C](image3)

![Fig. 7d CP Ti – heated up to 640°C](image4)

The microstructure of Ti-6Al-7Nb alloy after ECAP and annealed conditions are shown in Fig. 8. In Fig. 8a the typical microstructure of the ultrafine-grained material after ECAP and extrusion is shown. Lower magnifications (not presented here) show that the microstructure can be described as duplex with approx. 20% of heavily deformed primary alpha phase and fragmented α + β region. The microstructure is significantly less deformed then after processing by HPT [23]. Fig. 8b shows microstructure after deformation and subsequent heating up to 440°C. The microstructure is similar as the as ECAPed one (cf. Figs. 8a and 8b). Large (~5 µm) alpha grain remains heavily deformed. Surrounding α + β region is fragmented and contains slightly elongated beta phase particles appearing white. Fig. 8c
corresponds to the material heated to 550°C (after the first ‘peak’ in second derivative of resistivity). Detail inspection of the micrograph reveals that a negligible fraction of small grains in α + β region are non-deformed (clear contrast) and the higher proportion of beta phase particles are more equiaxed. Finally, Fig. 8d shows partly recrystallized microstructure of the condition heated up to 660°C containing bigger and more equiaxed beta phase particles.

4. Discussion

4.1. Overall resistivity evolution

The increase of electric resistivity of pure Ti during heating to 700°C (three times) is reasonable and depends on the amount of impurities, mainly the oxygen content [24]. Much smaller increase of resistivity (by only 10%) in Ti-6Al-7Nb alloy confirms also for Ti-alloys the well-known fact that the structural/compositional component in alloyed systems is of higher importance than the temperature dependent component [25]. The decrease of the resistivity in Ti-6Al-7Nb alloy above 700°C is caused by increased amount of beta phase. Similar alloy - Ti-6Al-4V - contains around 15% of beta phase at 750°C
and 20% of beta phase at 800°C and that this difference causes the decrease in resistivity [26].

4.2. Microstructural changes identified by resistivity measurements and SEM observations in CP Ti

SEM observations of CP Ti did not reveal any microstructure change after heating to 440°C. It is consistent with resistivity measurements and in perfect agreement with other authors [13]. No thermally activated process is observable by SEM or identifiable by in-situ resistivity measurement in CP Ti during heating to 440°C. Further heating to 520°C caused significant recovery and possibly even the initial stage of recrystallization/grain growth. Heating up to 640°C caused complete recovery and significant grain growth. These processes were apparently detected by in-situ measurement of electric resistivity. Recovery processes were identified by electric resistivity measurements in copper alloys [19], copper-based composites [20] and in NiTi alloy [21]. Some differences in resistivity between severely deformed material and solution treated material were found in [27], however, only for isothermal high-temperature annealing of a beta titanium alloy. Our results proved that high sensitivity in-situ measurement of electric resistivity is capable of detecting recovery and/or recrystallization processes in temperature regions that are decisive for microstructure stability of UFG pure Ti.

4.3. Microstructural changes identified by resistivity measurements and SEM in Ti-6Al-7Nb

The comparison of resistivity measurements and SEM observations is less convincing in Ti-6Al-7Nb alloy. The microstructure remains unchanged after heating up to 440°C, which is consistent with resistivity measurements. However, no obvious microstructure changes were observed in the condition after heating up to 550°C despite resistivity evolution suggests some microstructural transformation to occur. (Note that the sample heated up to 550°C was exposed to temperatures above 500°C only for 10 minutes.) The same alloy annealed at 500°C for 1 hour showed recovery process (identified by X-ray diffraction) and the beginning of recrystallization (observed by TEM) [14]. Fig. 8d shows partly recrystallized structure of the sample heated to 660°C, which is consistent with resistivity measurements and observations of material annealed at 600°C for 1 hour [14]. We believe that resistivity measurements captured the recovery and recrystallization processes also in Ti-6Al-7Nb, despite that the beginning of the process cannot be unambiguously proven by SEM observations.

4.4. Open issues and future work

Resistivity measurements show two distinct peaks. However, recovery and recrystallization processes seem to operate simultaneously. The distinction between both effects might be revealed by isothermal annealing similarly to [21]. Microstructural observations require samples prepared with precise temperature control and should include TEM and/or in-situ microstructural observations. The possible effect of the rearrangement of beta phase particles during annealing of Ti-6Al-7Nb alloy on electrical resistivity remains also unclear.

5. Conclusions

The following conclusions can be drawn from this experimental study

- In-situ measurements revealed differences in electrical resistivity between UFG and annealed condition obtained by linear heating of both CP Ti and Ti-6Al-7Nb alloy
- The effects in electrical resistivity evolution of UFG condition of CP Ti were identified by SEM observations as recovery and recrystallization.
- Similar effects observed in Ti-6Al-7Nb alloy occur in the range of temperatures where recovery and recrystallization were also identified
- UFG structure of CP Ti and Ti-6Al-7Nb alloy is stable up to 440°C.

**Acknowledgements**

This work was financially supported by Ministry of Education, Youth and Sports under the project Kontakt II LH12217. Partial support by GACR under the project 14-36566G is also acknowledged. The authors wish to express their thanks to Dr. Kaveh Hazijadeh for ECAP processing of CP Ti.

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