Influence of ECAP on the structure and properties of 
Ti18Zr15Nb and Ti10Mo8Nb6Zr alloys for medical application

A A Churakova12, D V Gunderov12, G I Raab2, S D Prokoshkin3, V A 
Sheremetyev3, Paulo N Lisboa Filho4, João Pedro4, Ana Paula Rosifini Alves 
Claro4

1Institute of Molecule and Crystal Physics, Ufa Federal Research Center RAS, Ufa, 
Russia
2Ufa State Aviation Technical university, Ufa, Russia
3NUST «MISiS», Moscow, Russia
4São Paulo State University, São Paulo, Brazil

*Corresponding author: churakovaa_a@mail.ru

Abstract. Studies of the influence of ECAP on the structure and properties of the metastable β- 
Ti alloys Ti18Zr15Nb and Ti10Mo8Nb6Zr have been carried out. The XRD data shows that the 
BCC β is the main phase in the initial alloys and alloys after ECAP. As a result of ECAP, the 
strength and yield stress of the alloys increases significantly due to the refinement of the 
structure. After ECAP, UTS and YS of the Ti10Mo8Nb6Zr alloy increase more noticeably than 
the Ti18Zr15Nb alloy, but after 7 ECAP cycles according to the regimes used (n = 6 T 250 °C + 
n = 1 350 °C), the Ti10Mo8Nb6Zr alloy becomes brittle. The increment in the yield point of the 
Ti18Zr15Nb alloy after ECAP processing together with the preservation of the β-state, allows 
one to expect an increase in the functional properties of the alloy.

1. Introduction
Titanium and its alloys are the most preferred materials for medical implants, due to their unique 
biocompatibility, good corrosion resistance, high specific strength [1, 2]. However, the large difference 
between the Young's modulus of the implant material and Young's modulus of the bone leads to “stress 
shielding” phenomenon, and bone resorption around the implant.

Metastable β-Ti alloys, including the Ti18Zr15Nb (at.% hereinafter) alloy, developed at NUST 
MISiS [3-6] and the Ti10Mo8Nb6Zr alloy, developed by the team of São Paulo State University, are 
the preferred materials for medical implants. These alloys do not contain toxic components, have low 
Young's modulus (high biomechanical compatibility with bone tissue) [3-5]. In the Ti18Zr15Nb alloy, 
recoverable thermoelastic β ↔ α” martensitic transformation provides the superelasticity and shape 
memory effects [3].

It was shown in [7-9] that due to SPD in pure titanium and its alloys, a significant increase in their 
properties for biomedical application is possible. The SPD method, which makes it possible to obtain 
relatively large samples for practical use, is equal channel angular pressing [9]. The results of studies of 
 ultra-fine-grained (UFG) CP Ti and Ti-alloys processed via equal channel angular pressing (ECAP) are
presented in particular in the review [9]. New modifications of ECAP processing is an ECAP-Conform (ECAP-C) technique that allows fabricating an UFG microstructure in long-length rods (up to few meters long) suitable for commercial applications [7,8]. A number of previous works also showed the possibility of increasing due to ECAP the strength and functional characteristics of the Ti-6Al-4V titanium alloy for medical applications [10] and low-modulus β-Ti alloy based on Ti-Mo [10]. However, studies of the effect of ECAP on the Ti18Zr15Nb and Ti10Mo8Nb6Zr alloys have not been conducted.

2. Experimental
ECAP was performed on a die-set with a diameter of the channel of 10 mm and an angle of the channels’ intersection of 120°, route Bc. ECAP of Ti18Zr15Nb was performed at T = 250 °C, n = 4 and n = 7. A relatively low ECAP temperature (250 °C) was used to prevent the β-α transition. ECAP of Ti10Mo8Nb6Zr was carried out at a temperature of T = 250 °C, n = 4 and another sample - six ECAP cycles at a temperature of T = 250 °C, n = 6 and the seventh ECAP cycle at a temperature of T = 350 °C (on the last cycle they had to raise the temperature to 350 °C due to the hardening of the sample in the previous 6 cycles).

X-ray studies were carried out on a Rigaku Ultima IV diffractometer under Cu radiation. The tensile tests at room temperature were carried out on flat samples with a gauge section of 1x0.25x4 mm at a tension rate of 3.10-3 s⁻¹ using an INSTRON tensile testing machine. Three or two samples were tested per one condition.

3. Results and discussion
Analysis of the XRD data shows that the BCC β is the main phase in the initial alloys and alloys after ECAP. Weak diffraction lines of the secondary α”-martensite phase or α are observed as well in Ti18Zr15Nb and Ti10Mo8Nb6Zr alloys, but the amount of α”-martensite phase or α-phase is insignificant both in the initial state of the alloy and after ECAP. The X-ray line width of the β-phase abruptly increases after ECAP (Table 1) pointing to an increase in dislocation density or/and grain refinement.

Table 1. Results of mechanical tests of alloys before and after ECAP and data of XRD at half-width of (FWHM) of the 110 β-phase line.

| State                  | UTS  | YS   | ε, % | FWHM(deg) 110β |
|------------------------|------|------|------|----------------|
| Ti18Zr15Nb Initial     | 630  | 510  | 27   | 0.28           |
| Ti18Zr15Nb ECAP n=4    | 880  | 855  | 6    | 0.63           |
| Ti18Zr15Nb ECAP n=7    | 990  | 960  | 4    | 0.66           |
| Ti10Mo8Nb8Zr Initial   | 710  | 430  | 30   | 0.29           |
| Ti10Mo8Nb8Zr ECAP n=4  | 1280 | 1270 | 6    | 0.57           |
| Ti10Mo8Nb6Zr ECAP n=7  | 1515 | 1420 | 5    | 0.51           |

The results of mechanical tests of the alloys before and after ECAP are presented in Figure 1 and Figure 2.
Mechanical test data showed that as a result of ECAP, the strength and especially the yield stress of the alloys increases significantly due to the refinement of the structure. As the number of ECAP cycles $n$ increases from 4 to 7, the strength properties of the alloys continue to increase. The yield stress of the Ti10Mo8Nb6Zr alloy increases especially significantly (almost threefold) as a result of ECAP $n = 7$. But the material becomes brittle. If in the initial state the strength properties of the initial Ti18Zr15Nb and initial Ti10Mb8Nb8Zr alloys are close, then after ECAP, UTS and YS of the Ti10Mb8Nb8Zr alloy
increase significantly more noticeably than the Ti18Zr15Nb alloy. The nature of this result requires additional investigation, including fine TEM studies of the structure with phase analysis. The increment in the yield point of the Ti18Zr15Nb alloy after ECAP processing together with the preservation of the $\beta$-state, allows one to expect an increase in the functional properties of the alloy.

4. Conclusions

Analysis of the XRD data shows that the BCC $\beta$ is the main phase in the initial alloys Ti10Mo8Nb6Zr, Ti18Zr15Nb and alloys after ECAP. As a result of ECAP, the strength and yield stress of the alloys increases significantly. As the number of ECAP cycles $n$ increases from 4 to 7, the strength properties of the alloys continue to increase. After ECAP, UTS and YS of the Ti10Mo8Nb8Zr alloy increase much more noticeably than the Ti18Zr15Nb alloy, but the Ti10Mo8Nb8Zr alloy after ECAP $n=7$ becomes brittle.

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