CHARACTERIZATION OF THE EFFECT OF THE ALPHA-PHASE PRECIPITATION IN HPT-DEFORMED Ti15Mo ALLOY

Kristína BARTHA [1], Josef STRÁSKÝ [1], Anna TERYNKOVÁ [1], Irina SEMENOVA [2], Veronika POLYAKOVA [2], Miloš JANEČEK [1]

[1]*Department of Physics of Materials, Charles University, Prague, Czech Republic, EU*
kristina.bartha@met.mff.cuni.cz

[2]*Institute of Physics of Advanced Materials, UFA State Aviation Technical University, Ufa, Russian Federation*

Abstract

Ti15Mo metastable β-Ti alloy was subjected to severe plastic deformation by high pressure torsion. The microstructure and chemical composition of the studied Ti15Mo alloy was investigated by scanning electron microscope. Furthermore, the microhardness of the non-deformed and deformed material was measured which was influenced by the local features of their microstructure.

The solution treated Ti15Mo alloy after ageing contains acicular α-phase particles along grain boundaries and in the interior of the β-grains. The aged and deformed alloy exhibits an ultra-fine grained duplex (α+β) microstructure. The equiaxed and submicrometer size α-phase particles form by diffusion via expelling a β stabilizer element (in our case Mo). Therefore, the slight difference in the chemical composition can significantly affect the morphology of the α-phase precipitation. The microhardness measurement revealed a remarkable increase of the microhardness of the HPT-deformed Ti15Mo alloy in α+β condition.

Keywords: Metastable beta titanium alloys, high pressure torsion, phase transformations, alpha phase precipitation

1. INTRODUCTION

Metastable β titanium alloys are extensively investigated due to their excellent properties such as high strength, low modulus of elasticity, unique biocompatibility and corrosion resistance [1]. Thanks to the aforementioned properties they are used in a broad field of applications ranging from aerospace to biomedical [2, 3]. These properties are usually achieved by an appropriate tailoring of microstructure of homogenously precipitated α-phase particles in a β-matrix [4]. For medical use especially in orthopedic, high strength is required together with low modulus of elasticity to avoid stress-shielding [5]. To improve the strength of the material without increasing the Young's modulus, severe plastic deformation (SPD) methods can be applied [6]. SPD induce to the materials high strain, thus high density of dislocations which significantly contribute to improving of the strength of the alloys along with grain structure refinement [7]. Moreover, it was also reported that highly deformed materials exhibit lower modulus of elasticity [8].

In our work we examined the effect of the ultra-fine grained (UFG) microstructure on the ongoing phase transformations in metastable β Ti15Mo alloy during heat treatment. The UFG structure of the materials was achieved by SPD method of high pressure torsion (HPT) [6]. In our previous work we investigated the microstructure and mechanical properties of the HPT-deformed Ti15Mo alloy [9]. It was revealed that the deformation induced by HPT results in much higher strength of the material than the precipitation strengthening by nucleation and growth of the α-phase [9]. Nevertheless, the Young's modulus grows with increasing deformation which can be caused by the formation of the ω-phase due to the high strain [10].

It was also previously shown that ultra-fine grained structure accelerates the precipitation of the α-phase [11]. The easy nucleation at lower temperature range (around 400 °C) can be attributed to high amount of nucleation

sites. Dislocations, grain boundaries or even vacancies can be considered as preferential nucleation site since they lead to higher diffusivity [12]. It is well known that ω-phase can also play a role in precipitation of the α-phase [13].

The morphology of the α-phase precipitation in Ti15Mo alloy after HPT was thoroughly investigated in the present study. The microstructure observations showed that local features of the microstructure significantly affect the nucleation of the α-phase.

2. EXPERIMENTAL

Ti15Mo in a form of rod with diameter 10 mm was obtained from Carpenter, Co. The initial, as-received material was subjected to solution treatment at 810 °C for 4 hours. Thereafter, a cylinders with approx. height of 5 mm were prepared from the solution treated (ST) rod. These cylinders were subjected to HPT which results in highly deformed discs with diameter 20 mm and height approx. 1 mm. The HPT deformation was performed at USATU Ufa, Russian Federation. The annealing of the samples at temperatures 400 °C and 500 °C for 16 hours was performed in salt bath in order to avoid contact with the air and to achieve maximum heating rate.

The HPT-deformed Ti15Mo samples were prepared from the periphery part of the disc specimens, where the deformation is the highest [14]. Samples for microstructure observation were prepared by mechanical grinding and polishing ending with the three-step vibratory polishing.

The study of the microstructure was performed on scanning electron microscope (SEM) Zeiss Auriga CrossBeam operated at 10 kV and equipped with EDS detector by EDAX. The analysis of the local chemical composition was performed by EDS technique and evaluated using TEAM software. The microhardness of the specimens was measured by Vickers method of automatic evaluation (0.5 kg load, 20 indents per sample) using Qness Q10a instrument.

3. RESULTS AND DISCUSSION

Figure 1a shows the microstructure of the Ti15Mo alloy after solution treatment. The structure is observed due to channeling contrast in BSE micrograph and consists of coarse β-grains. The nanometer size ω_{ath}-phase, which is present in the ST Ti15Mo alloy [11], cannot be observed by SEM. In **Figure 1b** the microstructure of the HPT-deformed alloy after annealing at 400 °C for 16 h is displayed (note the same magnification of **Figures 1a** and **1b**). In addition, brighter and darker areas (hereafter bands) can be also observed in **Figure 1a** (dark bands are indicated by white arrows in **Figure 1a**) thanks to the chemical contrast (Z-contrast) in BSE micrograph. These bands are also observable in HPT-deformed Ti15Mo alloy after annealing at 400 °C for 16 h (marked with arrow in **Figure 1b**) and follow the direction of the torsion during HPT. These bands, especially in ST material, were thoroughly studied by EDS and the results are shown in **Figure 2**. **Figure 2a** shows few β-grains visible due to channeling contrast and darker and lighter bands (visible especially in the top left corner of the image). It was confirmed by EDS that darker bands contain less Mo (**Figure 2b**), thus lower amount of β-stabilizer element. The effect of this local chemical inhomogeneity after HPT deformation was further studied and compared with solution treated material. The bands of local chemical inhomogeneities from ST material persist also in HPT-deformed Ti15Mo alloy moreover they are elongated in the direction of the deformation.

Figure 3 shows BSE micrographs of the annealed Ti15Mo alloy in ST and HPT-deformed condition. **Figure 3a** depicts the ST Ti15Mo alloy after annealing at 400 °C for 16 hours. No visible α-phase particles have been found even at grain boundaries which are considered as preferential sites for α-phase nucleation. In contrast, **Figure 3b** depicts the microstructure of the HPT-deformed material after annealing under the same conditions (400 °C/16 hours). The small (submicrometer) and equiaxed α-phase particles are clearly visible. The heterogeneous microstructure (darker band with more refined α particles) is in accordance with the previously found local chemical inhomogeneities. The α-phase nucleates by expelling the beta stabilizer

elements (in our case Mo), thus the α-phase particles are bigger in zones with lower content of Mo. The zone with bigger α-phase particles in the HPT-deformed Ti15Mo looks brighter and area with lower fraction of α-particles appear darker. The dark (grey) zone is caused by and averaging of the chemical contrast caused by small α-phase particles and β-phase through penetration depth of the electrons (acceleration voltage 10 kV).

In different studies it was claimed that during HPT deformation shear bands are created which affects the morphology and heterogeneity of the precipitation of the α-phase [15, 16]. In our opinion, shear bands can also play a role in heterogeneous nucleation of the α-phase, however, the local feature of the chemical composition also significantly affects the nucleation. Exact explanation of the phenomenon needs further in-situ investigation.

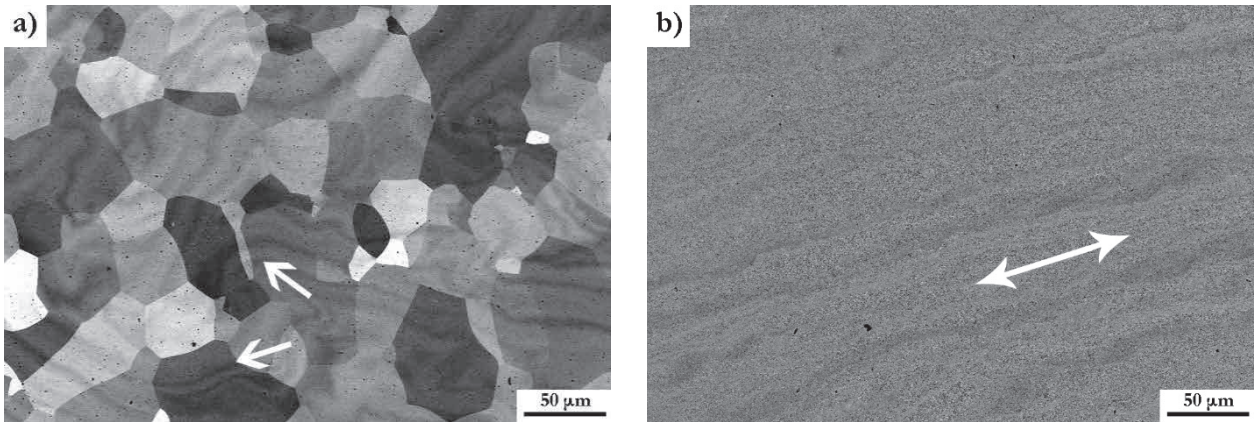

Figure 1 Overview BSE micrograph of the Ti15Mo after solution treatment (white arrows indicate the "dark bands") (a) and overview BSE micrograph of the Ti15Mo alloy after *N* = 5 HPT turns (white arrow indicate the direction of the HPT deformation) (b)

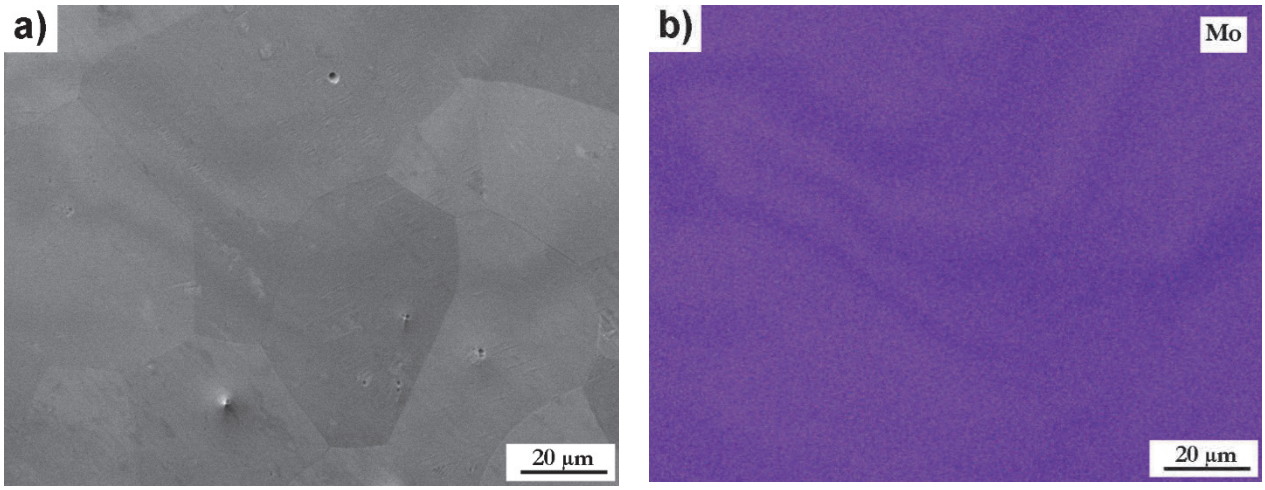

Figure 2 Local chemical inhomogeneity in ST Ti15Mo alloy: a) SE micrograph of the area of interest, b) relative chemical content of Mo (EDS map)

In **Figure 3c** the microstructure of ST TI15Mo alloy after annealing at 500 °C for 16 hours is shown. The grain boundary α-phase as well as the lamellar structure of the α-phase particles are visible inside the β-grains. The difference between **Figures 3a** and **3c** is clearly observed, annealing at 500 °C for 16 hours is sufficient for a nucleation and growth of the α-phase on grain boundaries and even in the interior of the β-grains. On **Figure 3d** the HPT-deformed alloy after annealing at 500 °C for 16 hours is displayed. In comparison with the

microstructure seen on **Figure 3b** material became more homogenous. The α-phase particles are bigger but still not exceed the size of hundreds of nanometers.

The microhardness of the non-annealed samples and samples annealed at 400 °C and 500 °C for 16 hours was measured and compared (see **Figure 4**). The solution treated Ti15Mo alloy exhibit a microhardness of 278 HV. The deformation by HPT increases the microhardness of the material up to 400 HV (this value is valid for the periphery part of the sample). The microhardness significantly increases after annealing at 400 °C for 16 hours for both ST and HPT-deformed Ti15Mo alloy. The HPT-deformed material after annealing (400 °C/16 h) shows a microhardness ~600 HV, the solution treated one after annealing ~530HV. This rapid growth of the microhardness can be attributed to the significant amount of the hard and brittle ω_{iso} (isothermal)-phase which forms during annealing [17]. Material after similar annealing conditions exhibits a low ductility [18]. Further increase of the annealing temperature up to 500 °C leads to decrease of the microhardness of both ST and HPT-deformed material. The reason should be the continuous dissolution of the ω-phase as well as growth of the α-phase. For both ST and deformed Ti15Mo alloy the microhardness after annealing at 500 °C for 16 hours is above the microhardness of non-annealed ones.

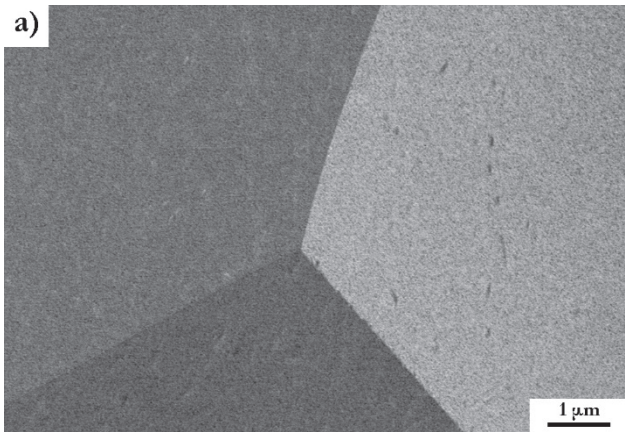

Figure 3a Detail BSE micrograph of the Ti15Mo alloy after solution treatment and subsequent annealing at 400 °C for 16 hours

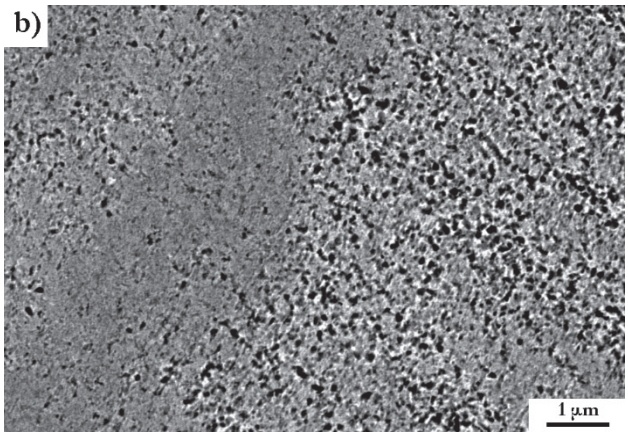

Figure 3b Detail BSE micrograph of the Ti15Mo alloy after *N* = 5 HPT turns and subsequent annealing at 400 °C for 16 hours

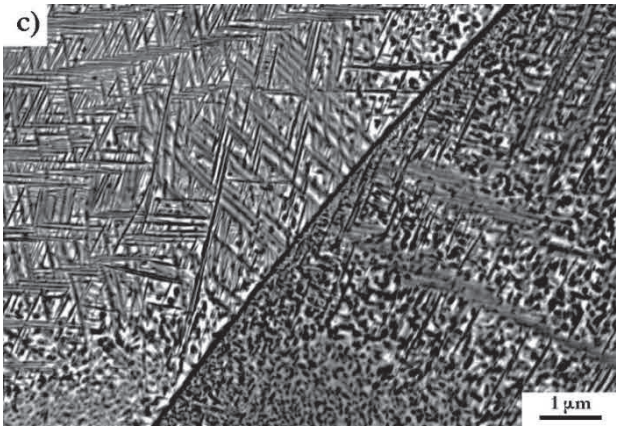

Figure 3c Detail BSE micrograph of the Ti15Mo alloy after solution treatment and subsequent annealing at 500 °C for 16 hours

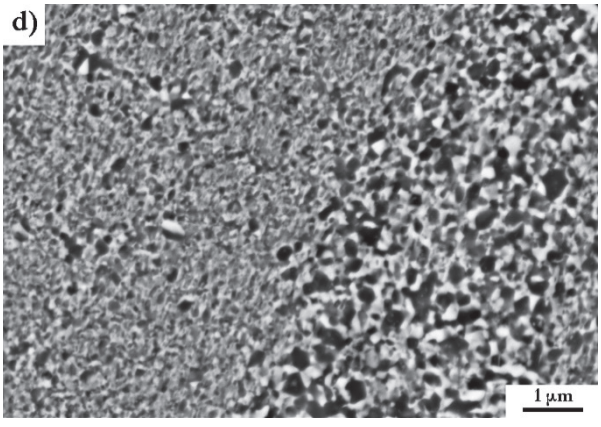

Figure 3d Detail BSE micrograph of the Ti15Mo alloy after *N* = 5 HPT turns and subsequent annealing at 500 °C for 16 hours

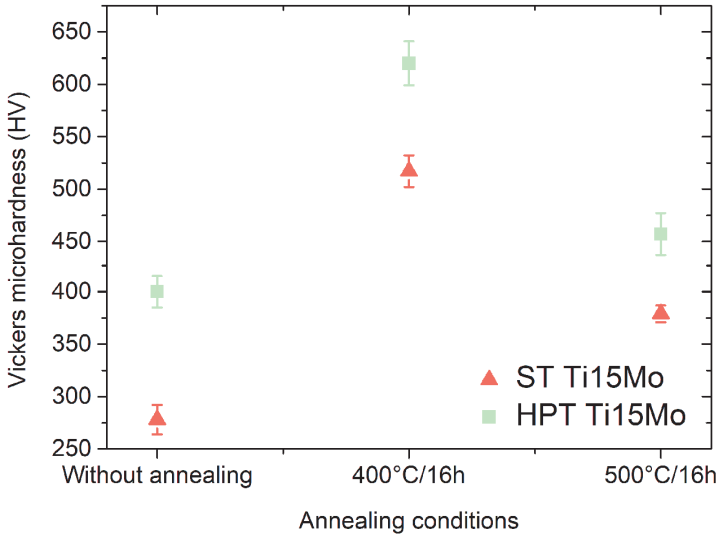

Figure 4 The microhardness of ST and HPT-deformed Ti15Mo alloy depending on the annealing conditions

4. CONCLUSIONS

The morphology of the α-phase precipitation in Ti15Mo alloy after deformation by high pressure torsion (HPT) as well as its effect on the microhardness evolution were investigated. The most important conclusion of this study can be summarized as follows:

- The solution treated Ti15Mo alloy contains local chemical inhomogeneities which persist in the HPT-deformed material and follow the direction of the torsion.
- The local features of the microstructure and chemical composition of the material significantly affect the phase transformations, especially the nucleation and growth of the α-phase.
- In a highly deformed Ti15Mo alloy, equiaxed and nanometer size α-phase particles precipitate.
- The microhardness of the alloy increases by the HPT deformation and reaches values of ~600HV for α+β+ω condition of the HPT-deformed material.
- With continuous dissolution of the hard ω-phase, the microhardness decreases, however, it is still higher for α+β condition in comparison with the microhardness of the alloy without annealing.

ACKNOWLEDGEMENTS

This work was financially supported by Ministry of Education Youth and Sports, project No. LTARF18010. Partial financial support by Czech Science Foundation, project No. 17-04871S and ERDF Project No. CZ.02.1.01/0.0/0.0/15003/0000485 is also gratefully acknowledged. K. B. acknowledges by the Grant Agency of Charles University, project No. 1106216.

REFERENCES

[1] LEYENS, Christoph and PETERS, Manfred. *Titanium and titanium alloys: fundamentals and applications*. Wiley-VCH, 2003. p. 37-57.

[2] BOYER, Renee R. An overview on the use of titanium in the aerospace industry. *Materials Science and Engineering: A*. 1996. vol. 213, no. 1, pp. 103-114.

[3] GEETHA, Manivasagam, SINGH, Anjuvan K., ASOKAMANI, Rajamanickam and GOGIA, Ashok K. Ti based biomaterials, the ultimate choice for orthopaedic implants - A review. *Progress in Materials Science*. 2009. vol. 54, no. 3, pp. 397-425.

[4] MAKINO, Takehiko, CHIKAIZUMI, R., NAGAOKA, T. and FURUHARA T. Microstructure development in a thermomechanically processed Ti15V3Cr3Sn3Al alloy. *Materials Science and Engineering: A*. 1996. vol. 213, no. 1, pp. 51-60.

[5] KURODA, Daisuke, NIINOMI, Mitsuo, MORINAGA, Masahiko, KATO, Yosihisa and YASHIRO, Toshiaki. Design and mechanical properties of new β type titanium alloys for implant materials. *Materials Science and Engineering: A*. 1998. vol. 243, no. 1-2, pp. 244-249.

[6] ZHILYAEV, Alexander P. and LANGDON, Terence G. Using high-pressure torsion for metal processing: Fundamentals and applications. *Progress in Materials Science*. 2008. vol. 53, no. 6, pp. 893-979.

[7] KAWABE, Yoshinuki and MUNEKI, Seiichi. Strengthening and Toughening of Titanium Alloys. *ISIJ International*. 1991. vol. 31, no. 8, pp. 785-791.

[8] LEBEDEV, Alexander B., BURENKOV, Yu A., ROMANOV, Alexei, KOPYLOV, Vladimir I., FILONENKO, Vladimir P. and GRYAZNOV, V. G. Softening of the elastic modulus in submicrocrystalline copper. *Materials Science and Engineering: A*. 1995. vol. 203, no. 1, pp. 165-170.

[9] VÁCLAVOVÁ, Kristína, STRÁSKÝ, Josef, POLYAKOVA, Veronika, STRÁSKÁ, Jitka, NEJEZCHLEBOVÁ, Jitka, SEINER, Hanuš, SEMENOVA, Irina and JANEČEK, Miloš. Microhardness and microstructure evolution of ultra-fine grained Ti-15Mo and TIMETAL LCB alloys prepared by high pressure torsion. *Materials Science and Engineering: A*. 2017. vol. 682, pp. 220-228.

[10] TANE, Masakuzu, OKUDA, Yosiyuki, TODAKA, Yoshikazu, OGI, Hirotsugu and NAGAKUBO, Akira. Elastic properties of single-crystalline ω phase in titanium. *Acta Materialia*. 2013. vol. 61, no. 20, pp. 7543-7554.

[11] VÁCLAVOVÁ, Kristína, STRÁSKÝ, Josef, ZHÁŇAL, Pavel, VESELÝ, Josef, POLYAKOVA, Veronika, SEMENOVA, Irina and JANEČEK, Miloš. Ultra-fine grained microstructure of metastable beta Ti-15Mo alloy and its effects on the phase transformations. *IOP Conference Series: Materials Science and Engineering*. 2017. vol. 194, no. 1, p. 012021.

[12] LEGROS, Marc and DEHM, Gerhard. Observation of Giant diffusivity along dislocation core. *Science*. 2008. vol. 319, pp. 1646-1649.

[13] PRIMA, Frédéric, VERMAUT, Philippe, TEXIER, Gwénaël, ANSEL, Denis and GLORIANT, Thierry. Evidence of α-nanophase heterogeneous nucleation from ω particles in a β-metastable Ti-based alloy by high-resolution electron microscopy. *Scripta Materialia*. 2006. vol. 54, no. 4, pp. 645-648.

[14] VALIEV, Ruslan Z., IVANISENKO, Yulia, RAUCH, Edgar F. and BAUDELET, Bernard. Structure and deformaton behaviour of Armco iron subjected to severe plastic deformation. *Acta Materialia*. 1996. vol. 44, no. 12, pp. 4705-4712.

[15] XU, Wei, WU, Xiaolin, STOICA, Mihai, CALIN, Mariana, KÜHN, Utha, ECKERT, Jürgen and XIA, Kenong. On the formation of an ultrafine-duplex structure facilitated by severe shear deformation in a Ti-20Mo β-type titanium alloy. *Acta Materialia*. 2012. vol. 60, no. 13, pp. 5067-5078.

[16] JIANG, Baozhen, TSUCHIYA, Koichi, EMURE, Satoshi and MIN, Xiaohua. Effect of High-Pressure Torsion process on precipitation behavior of α phase in β-type Ti-15Mo alloy. *Materials Transactions*. 2014. vol. 55, no. 6, pp. 877-884.

[17] NG, Hoi P., DEVARAJ, Arun, NAG, Suomya, BETTLES, Colleen J., GIBSON, M. A., FRASER, Hamish L., MUDDLE, Barrington C. and BANERJEE, Rajarshi. Phase separation and formation of omega phase in the beta matrix of a Ti-V-Cu alloy. *Acta Materialia*. 2011. vol. 59, no. 8, pp. 2981-2991.

[18] OZAN, Sertan, LIN, Jiying, LI, Yuncang, ZHANG, Yaowu, MUNIR, Khurram, JIANG, Hongwei and WEN, Cuie. Deformation mechanism and mechanical properties of a thermomechanically processed β Ti-28Nb-35.4Zr alloy. *Journal of the Mechanical Behavior of Biomedical Materials*. 2018. vol. 78, pp. 224-234.