Processing of perspective titanium alloy for biomedical applications via powder metalurgy

Ing. Jaroslav Málek

Vedoucí práce: Doc. RNDr. František Hnilica, CSc.

Abstrakt

Titanové slitiny jsou z hlediska svých vlastností (např. vysoká pevnost, dobrá korozní odolnost a nízká hustota) využívány v mnoha aplikacích. V současné době je častá výroba bioimplantátů z těchto materiálů. Pro tyto aplikace je stále nejpoužívanější slitina Ti-Al6-V4. Ta má několik nevýhod (obsahuje zdraví škodlivé prvky jako Al nebo V a má relativně vysoký modul pružnosti). Vývoj se proto v současnosti zaměřuje na slitiny titanu s beta fázovou strukturou, které obsahují výhradně plně biokompatibilní prvky a mají i nižší modul pružnosti. Problémem je jejich vyšší cena. Jedním ze způsobů jak snížit konečnou cenu je příprava těchto slitin práškovou metalurgií. V této práci byla připravena slitina Ti-35,5Nb-5,7Ta metodou CIP a byla studována závislost porozity a mikrostruktury sliny na zrnitosti prášků a době slinování. Zároveň byla zkoumána možnost odstranění zbytkové porozity pro zlepšení mechanických vlastností tvářením slitiny za tepla.

Klíčová slova

Prášková metalurgie, porozita, beta-titanové slitiny, biomateriály

Abstract

Titanium alloys are due to their good properties (high strength, good corrosion resistance and low density) used in many applications. Nowadays they are very often used as biomaterials for production of implants. For these applications the most common Ti alloy Ti-Al6-V4 has still the dominant role in the market. This alloy has several disadvantages for bioapplications (it contains harmful elements V-element with one of the highest cytotoxicity and Al – causes neurological problems and it has also high Young’s modulus). Because of that new titanium alloys with beta-Ti structure are developed. These alloys contain only fully biocompatible elements and have lower Young’s modulus. The reason why they are not often used is their higher price. One of the possibility to decrease the price is preparation via powder metallurgy process. In this paper the Ti-35,5Nb-5,7Ta alloy was prepared via CIP method and the dependence of porosity and microstructure on grain size of powders and on sintering time was studied. Also the possibility of removing the residual porosity by hot forging in order to improve mechanical properties was studied.

Key words

Powder metallurgy, porosity, beta-titanium alloys, biomaterials

1. Introduction

Beta titanium alloys are very perspective materials for bioapplications, because of their excellent biocompatibility and good mechanical properties. They contain only fully biocompatible elements. They have several advantages in comparison with previously used titanium alloys for bioapplications. They have low Young's modulus. Low Young\s modulus is important for as called „biomechanical compatibility“. The bone has low Young's modulus

(10-30 GPa). When using an implant with high Young's modulus, than the bone is unloaded and that can cause in long term use atrophy of the bone. This is called „stress shielding effect“. Previously used materials have Young's high modulus (stainless steel – 210 GPa, Ti-Al6V4 – 110GPa). Beta titanium alloys have the lowest Young's modulus among Ti-alloys. Moreover they have good corrosion resistance and high strength.

Although they have excellent properties as biomaterials, the dominant role in the market has Ti-Al-V4. It is because of its lower price (it is the most common Ti-alloy). Beta-titanium have higher price. One of their problem is the technology of preparation. However they are suitable for forging there can be very high energy costs during their preparation when using conventional technologies (arc melting). They contain elements with high melting point and relatively different densities. So the problem could be chemical heterogeneity and also coarse dendritic structure. The chemical homogeneity can be ensured by remelting for several times. This implies high energy costs. One of the possibilities how to decrease the price is the preparation via powder metallurgy. During powder metallurgy process the chemical homogeneity can be ensured only thanks to thorough mixing of powders. Also the energy costs could be lower. On the other hand the problem could be the porosity, that can influence mechanical properties.

The object of this paper is to obtain optimal parameters of preparation Ti-35,5Nb-5,7Ta alloy via powder metallurgy process in order to prepare compact (without pores) material with beta-Ti structure.

2.Experimental

Alloy of nominal chemical composition Ti-35,5Nb-5,7Ta (wt.%) was prepared from powders processed via HDH (hydridation – dehydridation) method. The powder grains are irregular shaped with grain sizes -325 mesh (-177μm) for Ti, Nb and Ta powders. From grain size analysis is evident, that powders contain about 50 wt.% of grains with grain size less than 40 μm and about 40% grains with size from 40 to 80mm. There are also about 10 wt.% of grains from 80 to 125 μm and only a very small amount of grains with size over 125 μm. Powders were divided into fractions. Titanium powder with grain size less than 80 μm and unsorted titanium powder. Nb and Ta powders with grain size less than 40 μm. From these powders were prepared two blends:

a) Unsorted Ti-powder (-177μm) with unsorted Nb aTa powders marked as 35N6Tn
b) Ti-powder with grain size from 80μm to 125 μm and Nb and Ta powders with grain size less than 40μm marked as 35N6T80/m40/m40

Powders were weighted and mixed in TURBULA 2F at 40 rpm for 10hours. Mixing was assisted with agate balls. Then the blend of powders was filled in rubber mould. Weighting, mixing and filling was made under argon atmosphere to avoid the oxidation of powders. After that blends were cold isostatically pressed at 400 MPa for 20 s. Then the specimens were sintered in a vacuum furnace under vacuum better than 1.10^{-2}Pa at 1400°C for various times (10, 20, 30 and 40 hours). All of samples were measured by using the equipment Densimeter EW SG of Mirage Trading Co, Ltd. Japan in order to determine their density.

Sintered samples were hot forged in free die. The temperature during heating in furnace was 900°C. Higher temperature causes intensive oxidation of specimen, but the temperature of specimen was above β transus for the period of forging. Reduction section in first step of forging shouldn’t be more than 10%. The total reduction section made in three steps was about 50%.

Metallographic preparation was carried out using conventional techniques: grinding with Al_2O_3 papers from #180 to #1200 and subsequently SiC papers (#2500 – #4000) and polishing with Struers OP-S emulsion in addition of 0,6 ml OP-S, 2 ml H_2O and 2 ml NH_3. These samples were studied by using optical microscope (OM). The samples were than etched with a solution of 100ml HNO_3, 26 ml HF and 84 ml H_2O. Subsequently studying was carried out by using scanning electron microscope in backscattered composition mode (COMPO), which allows us to study the heterogeneity in chemical composition of sintered samples. Chemical composition of certain areas was determined by using energy dispersive analyzer (EDAX). Pictures obtained by OM were analyzed by LUCIA G software. This allows us to measure the percentage part of pores (porosity) in material and their morphology.

3. Results and Discussion

There can be seen the difference in porosity and pore morphology during first ten hours of sintering. After isostatic pressing there is huge amount of large and irregularly shaped pores. After sintering is evident, that the amount of pores decrease significantly and also their dimensions and morphology change significantly.

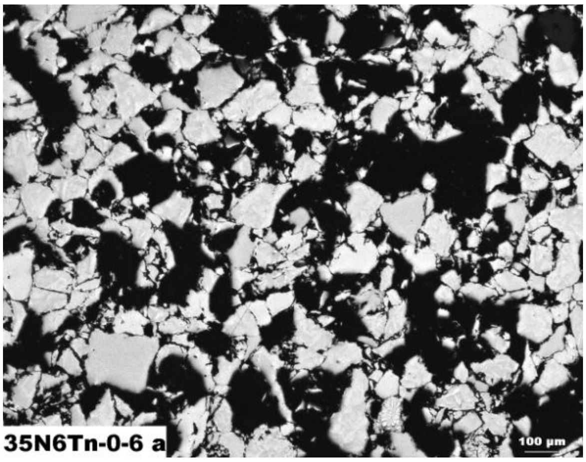

Fig. 1a. *Isostatically pressed specimen of 35N6Tn blend (OM)*

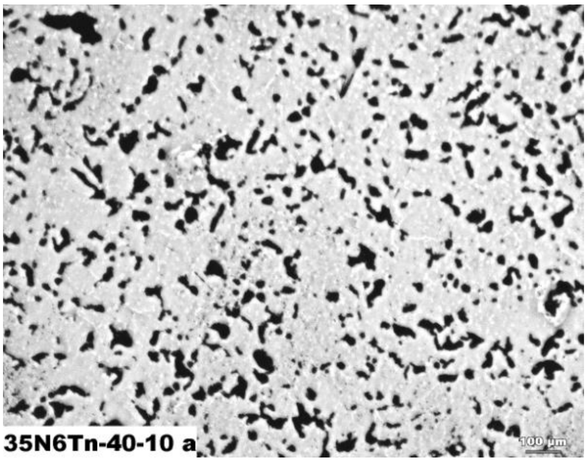

***Fig. 1b**. Porosity of 35N6Tn specimen after 40h sintering at 1400ºC (OM)*

Additional decrease of porosity and further rounding of pores can be seen when compare Fig.1b with Fig.2a. Examples of pores morphology and their amount in various blends specimens sintered for 40 hours are shown in Fig. 2a and 2b. From these pictures is evident that the pores in 35N6Tn specimen are larger than in 35N6T80/m40/m40. The pores of the 35N6T80/m40/m40 specimen are rounder and it is also evident, that the amount of pores is lower for this specimen at the same sintering time. From Fig.2b can be seen slight heterogeneity in pores distribution throughout the specimen of 35N6T80/m40/m40 blend. This heterogeneity can be observed also in others images from this blend.

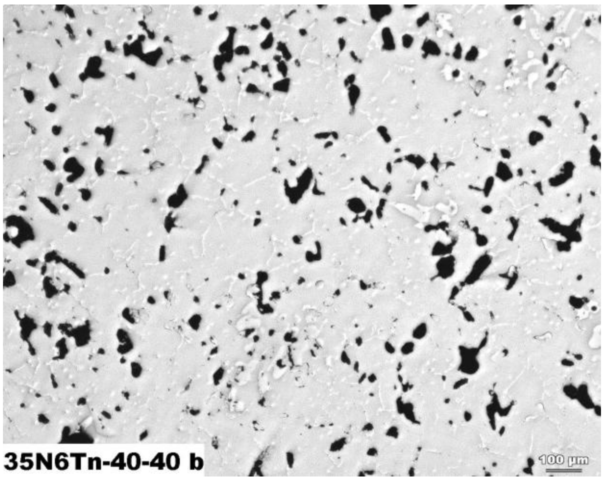

Fig. 2a. *Porosity of 35N6Tn specimen after 40h sintering at 1400°C (OM)*

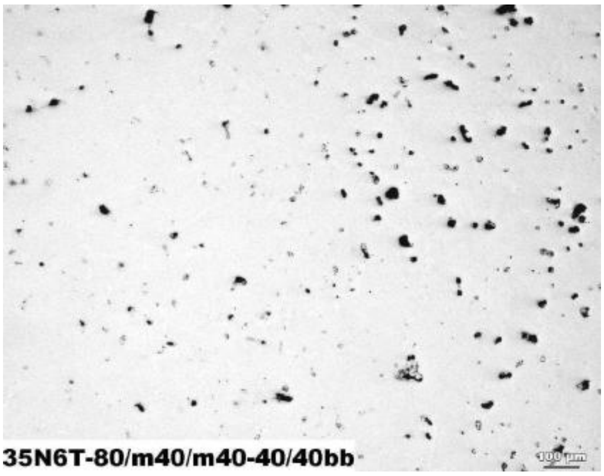

Fig. 2b. *Porosity in specimen 35N6T80/m40/m40 after 40h sintering at 1400°C (OM)*

The dependence specimen density - sintering time is evident from Fig.3 for both blends. Density characterizes the porosity. There can be seen, that the biggest increase in density (reduction of porosity) was obtained during first ten hours of sintering (at 1400°C). After this time the increase becomes slower and at sintering times longer than 20 hours is the density almost constant (with respect to measurement error). So it can be concluded that remained porosity cannot be removed by using longer sintering times. From the graph on Fig. 3 is also clear, that the increase in density of 35N6T80/m40/m40 samples is higher than in 35N6Tn. The porosity (obtained from image analysis) of 35N6Tn is after sintering time longer than 20 hours about 10% while the porosity of 35N6T80/m40/m40 after 20 hours of sintering is approximately 5%.

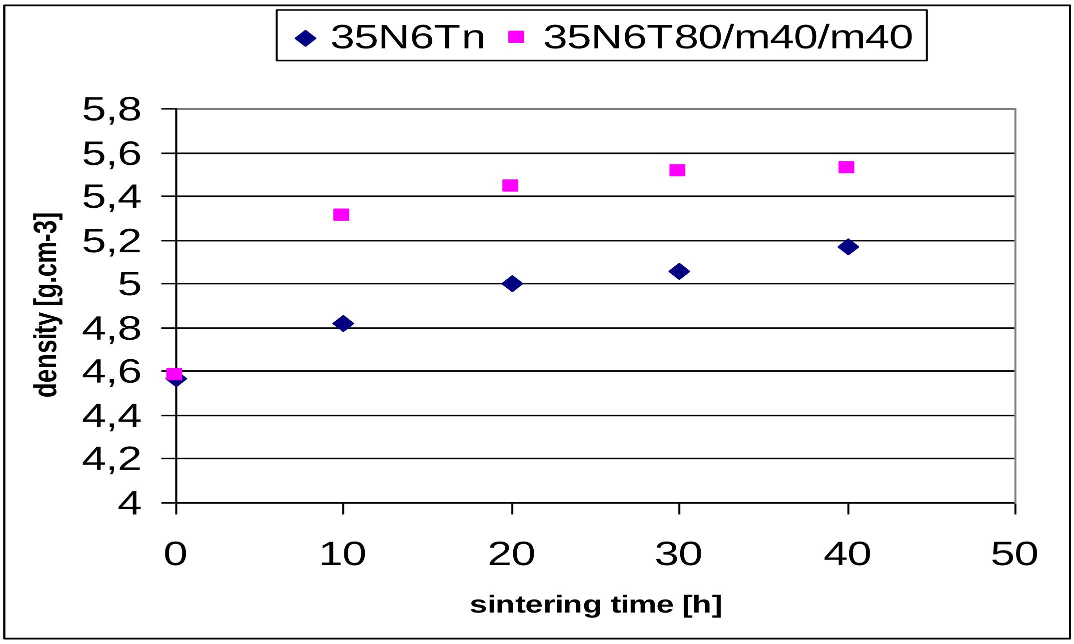

Fig. 3. *Dependence density – sintering time at 1400°C for 35N6Tn and 35N6T80/m40/m40*

The microstructures of specimens sintered at 1400ºC consist of α-Ti phase on grain boundaries of β-Ti phase. In the vicinity of grain boundaries there are lighter areas. This is caused by various etching attached with local chemical heterogeneity. This heterogeneity is probably due to fine precipitates dispersed inside the grains, which cannot be seen on optical microscope. These precipitates are not present around grain boundaries, so we can observe as called “denuded zones”. These zones are due to precipitates on grain boundaries. Their vicinity has higher amount of beta stabilizer because in the precipitates have lower amount of beta-stabilizers. These structures can be seen on Fig. 4a and Fig. 4b for 35N6T80/m40/m40 and 35N6Tn respectively.

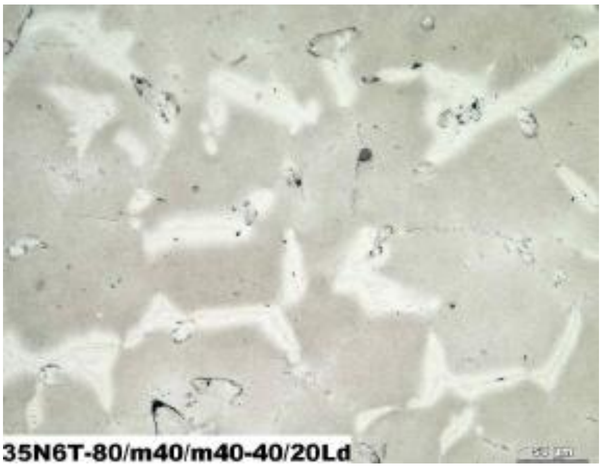

Fig. 4a. *Microstructure of 35N6T80/m40/m40 after 20h sintering at 1400ºC (OM)*

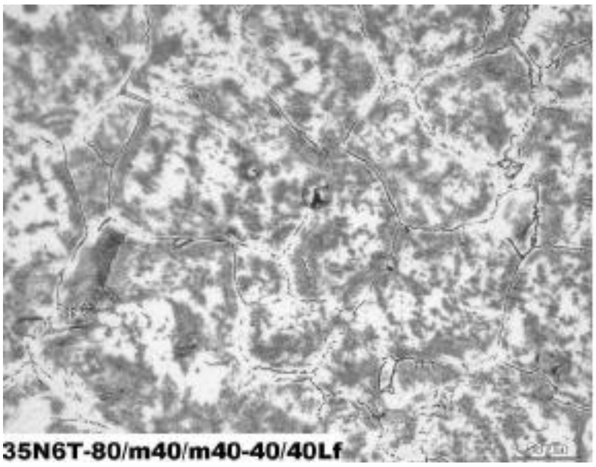

Fig. 4b. *Microstructure of 35N6T80/m40/m40 after 40h sintering at 1400ºC (OM)*

The changes in chemical composition during sintering can be seen in Fig.5a and Fig.5b. These images were made in backscattered COMPO mode. White areas have higher average atomic number than darker areas. This implies the presence of higher amount of heavier elements (Nb or Ta) than in the matrix (Ti). These places are original Nb or Ta particles, which has not yet been completely dissolved (Fig.4a). The dissolution is evident also from the diffusion borders where white color changes to gray continuously. After 40 hours of sintering (Fig.4b), there were observed areas with slightly lighter color. That means that Nb and Ta particles are almost dissoluted. But the diffusion of Ta is relatively low and this causes longer times necessary for fully homogeneous structure. The presence of higher Ta and Nb content was also confirmed by the local chemical analysis (EDAX), where in area 1 in Fig. 4b the chemical composition is (52,2% Ti, 36,6% Nb and 11,2% Ta) and in area 2 (58,8%Ti, 35,1% Nb and 6,1% Ta).

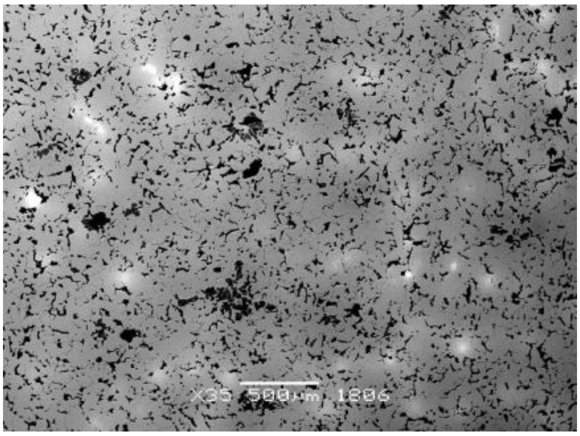

Fig. 5a. *SEM image of 35N6Tn after 10 hours of sintering (COMPO)*

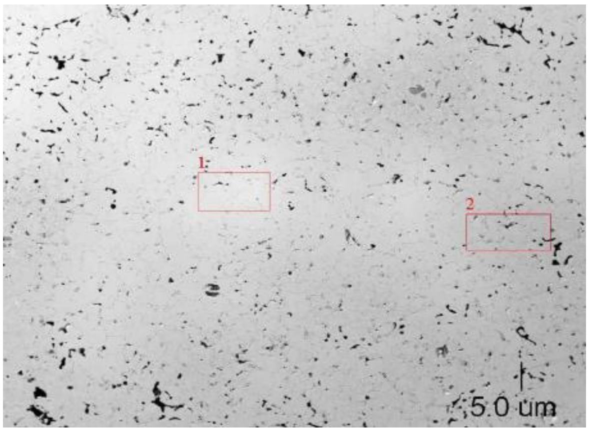

Fig. 5b. *SEM image of 35N6Tn after 40 hours of sintering (COMPO)*

The changes in chemical composition cause also changes in microstructure. The microstructure of this alloy is shown in Fig. 6. It consists of α-Ti phase (low content of beta stabilizers – Nb and Ta) on grain boundaries of β-Ti phase as was said. Moreover in more detailed image in Fig. 7, there can be seen fine precipitates inside β-Ti grains. These precipitates have also lower content of β-stabilizers. So they are supposed to be α-Ti phase, however they haven't been identified in this work.

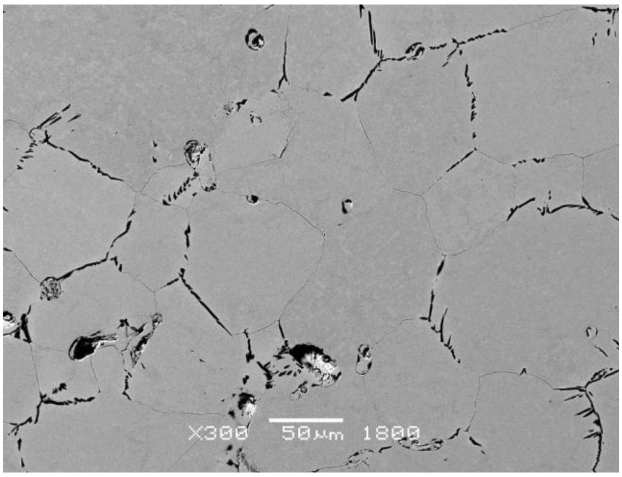

Fig.6*. SEM image of 35N6T80/m40/m40 after 30 hours of sintering*

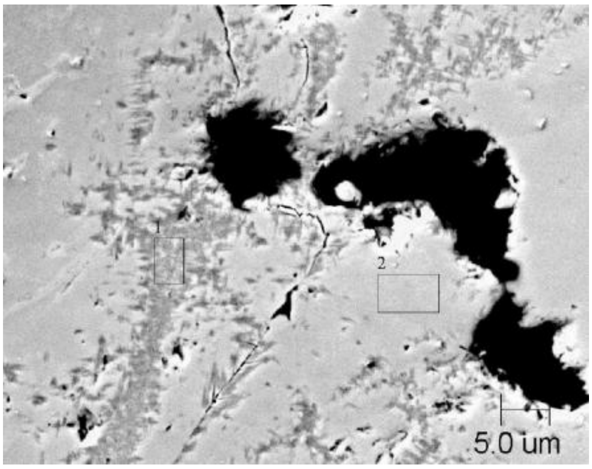

Fig.7. *SEM image of 35N6Tn after 10 hours of sintering*

In order to completely remove the pores, the material was hot forged in a free die. There were made some tests of hot forging. It can be seen from Fig.8 and Fig. 9 that the pores disappeared after forging. This is evident when comparing Fig. 9 with Fig. 2a. But There are still some defects (cracks, corrosion products…) remained in a surface layer (see Fig.7). But these defects are only in very thin surface layer and because of that they can be removed very easily. The microstructure after hot forging and subsequent air cooling is in Fig. 9, where can be seen the microstructure consisted of α -Ti grains on grain boundaries of β-Ti grains. Inside β-Ti grains can be seen very fine precipitates.

Fig.8. *Surface layer of hot forged specimen 35N6Tn (OM)*

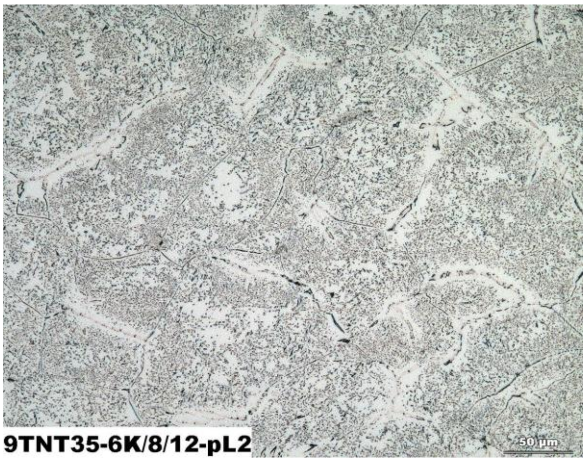

Fig.9. *Microstructure of hot forged specimen 35N6Tn (OM)*

4. CONCLUSIONS

On the basis of results mentioned above we can conclude that:

a) The porosity of specimens prepared from unsorted powders (35N6Tn) is higher than the porosity of blend from Ti powder with grain size from 80 to 125 μm and Nb and Ta powders with grain size lower than 40 μm (35N6T-80/m40/m40), when sintered for the same time.

b) Pores cannot be completely removed by sintering at 1400°C, because the porosity decreases very slow after 20 hours of sintering.

c) There is still some heterogeneity in local chemical composition (Ta amount) even after 40 hours of sintering.

d) Pores can be removed during hot forging, but there are still some defects in a thin surface layer of the specimens, but this layer can be removed.

e) The microstructructure of sintered and forged specimen consists of β-Ti grains with fine precipitates inside them. On grain boundaries there are α-Ti particles.

ACKNOWLEDGMENTS:

Works presented in this article were made thanks to a financial support of Ministry Of Industry and trade of the Czech Republic within the project „Trvalá prosperita č. 2A – 2TP1/073“.

LITETRATURE REVIEW

[1] GEETHA, M., SINGH, A.K., ASOKAMANI, R., GOGIA, A.K.: Ti based biomaterials, the ultimate choice for orthopaedic implants – A review. Progress in Materials Science 54 (2009) 397-425.

[2] QAZI, J.I., MARQUARDT, B., ALLARD, L.F., RACK, H.J.: Phase transformations in Ti-35Nb-7Zr-5Ta- (0,06-0,68)O alloys. Materials Science and Engineering C 25 (2005) 389-397.

[3] GEETHA, M., SINGH, A.K., GOGIA, A.K., ASOKAMANI, R.: Effect of thermomechanical processing on evolution of various phases in Ti-Nb-Zr alloys. Journal of Alloys and Compounds 384 (2004) 131-144.

[4] NIINOMI, M.: Mechanical biocompatibilities of titanium alloys for biomedical applications. Journal of the Mechanical Behavior of Biomedical Materials I (2008) 30-42.

[5] BANERJEE, R., NAG, S., STECHSCHULTE, J., FRASER, H.L.: Strengthening mechanisms in Ti-Nb-Zr-Ta and Ti-Mo-Zr-Fe orthopaedic alloys. Biomaterials 25 (2004) 3413-3419.

[6] EISENBARTH, E. et al: Biocompatibility of beta-stabilizing elements of titanium alloys. Biomaterials 25 (2004) 5705-5713.

[7] NIINOMI, M.: Mechanical properties of biomedical titanium alloys. Materials Science and Engineering A243 (1998) 231-236.

[8] TADDEI, E.B., HENRIQUES, V.A.R., SILVA, C.R.M., CAIRO, C.A.A.: Production of new titanium alloy for orthopaedic implants. Materials Science and Engineering C 24 (2004) 683-687.

[9] SANTOS, D.R., et al.: Isochronal sintering of hte blended elemental Ti-35Nb alloy. Materials Science and Engineering A 472 (2008) 193-197