INFLUENCE OF GRAIN SIZE ON MICROSTRUCTURE AND POROSITY OF BIOMATERIAL Ti-35.5Nb-5.7Ta ALLOY PROCESSED VIA POWDER METALLURGY

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Abstract

Beta-titanium alloys containing only fully biocompatible elements are very perspective materials for production of bioimplants. They have good properties for use as biomaterials, including above mentioned biochemical compatibility, low elastic modulus (important for biomechanical compatibility), in comparison with previously used alloys. Moreover they are suitable for forging. Perspective method with respect to final price is powder metallurgy. There are several advantages in compare with usual methods like arc melting. On the other hand the problem of powder metallurgy could be the porosity of the final product after sintering.

In this paper, the influence of the grain size and parameters of sintering used during the preparation of biocompatible Ti-35.5Nb-5.7Ta alloy on its microstructure and compactness, which influence properties of the alloy, were studied. Measurements of porosity depending on sintering time at 1400°C were made. Furthermore the microstructure of specimens and local chemical composition were observed. The object was to obtain fully compact specimen without pores by hot forging of specimens prepared via CIP method (cold isostatic pressing and subsequent sintering).

Keywords: Porosity, powder metallurgy, beta-titanium alloys, biomaterials

1. INTRODUCTION

Titanium and its alloys are nowadays used in many applications because of their good mechanical properties, good corrosion resistance and low density. They are very often used in aerospace and aeronautical industry. These alloys are used also in biomedical applications. The most common titanium alloy Ti-Al6-V4 was developed in 1950’s for aeronautical industry and it has been also using as a biomaterial [1]. Although it has dominant role in the market of biomaterials because of its low price, it has also some disadvantages. It contains vanadium, which has high cytotoxicity and aluminium – element that can cause some neurological problems such as Alzheimer disease. Moreover it has relatively high value of Young’s modulus (about 110GPa). This is more than that of bone (10-30GPa). High elastic modulus of implant material can cause “stress shielding effect”. This means that the load is in general carried by the implant and surrounding bone is unloaded. This causes atrophy of the bone [1-4].

In the past decade the research of other alloys for bioapplications with better biomechanical compatibility and improved biocompatibility was started. These alloys contain only fully biocompatible elements (Nb, Ta,Zr…). These elements act as beta-stabilizers in titanium alloys. Alloys with β-Ti microstructure have lower modulus in comparison with α+β-Ti alloys (Ti-Al6V4…) and good ductility [1-7]. Despite of these alloys have very attractive properties their use is limited because of their higher price. There are some problems when using common techniques of preparation (arc melting). These alloys contain metals with various density and relatively high melting point and are very reactive with oxygen. This causes the risk of chemical inhomogeneity and coarse dendritic structure. Because of that these materials are often remelted several times to ensure the homogeneity. This implies high energy costs during processing. Other way of preparation is powder metallurgy. Chemical homogeneity can be ensured by mixing the powders and also energy costs are lower. The problem is the porosity, which can influence mechanical properties of final
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 80μm. There are also about 10 wt.% of grains from 80 to 125μm and only a very small amount of grains with size over 125μm. 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 10 hours. 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 Al₂O₃ 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 H₂O and 2 ml NH₃. These samples were studied by using optical microscope (OM). The samples were than etched with a solution of 100ml HNO₃, 26 ml HF and 84 ml H₂O. 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

Examples of pores morphology and their amount in sintered specimens are shown in Fig. 1a and 1b. 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.
The dependence specimen density - sintering time is evident from Fig. 2 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). Than 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 longer sintering times. From the graph on Fig. 2 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%.

The microstructures of specimens sintered at 1400°C 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 structures can be seen on Fig. 3a and Fig. 3b for 35N6T80/m40/m40 and 35N6Tn respectively.

The changes in chemical composition during sintering can be seen in Fig.4a and Fig.4b. 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 dissolved. 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).

The changes in chemical composition cause also changes in microstructure. The microstructure of this alloy is shown in Fig. 5. 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. 6, 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.

![Image 1](Fig.5. SEM image of 35N6T80/m40/m40 after 30 hours of sintering)

![Image 2](Fig.6. 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.7 and Fig. 8 that the pores disappeared after forging. This is evident when comparing Fig. 8 with Fig. 1b. 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. 8, 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.

![Image 3](Fig.7. Surface layer of hot forged specimen 35N6Tn (OM))

![Image 4](Fig.8. 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.

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

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LITETRATURE REVIEW


