INFLUENCE OF THE POWDER GRANULARITY ON THE \( \beta \)-TI ALLOY Ti39Nb INTEGRITY PREPARED BY POWDER METALLURGY METHODS

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Abstract:
\( \beta \)-Ti alloys prepared by using selected biotolerant elements are perspective materials for medical applications (like bone tissues). One of the possibilities of their preparation is powder metallurgy. Basic \( \beta \)-Ti stabilizing and biotolerant element is Nb. In this work the preparation of Ti39Nb alloy was studied. The powders were compacted, after homogenization in argon atmosphere, by cold isostatic pressing and sintering at 1300°C and 1400°C. The dependence of density, porosity, chemical composition homogeneity on temperature and sintering time was observed at blends with various grain size HDH – Ti and Nb powders.

1. Introduction:
Titanium based alloys provide high strength-to-weight ratio, good fatigue strength and high corrosion resistance. Because of that they are widely used mainly in aerospace and medical applications. Still their disadvantage remains their high cost of raw material and expensive machining operations[1,2].

These days titanium alloys with \( \beta \)-structure are developed for biomedical applications because of their expected high biocompatibility and low elastic modulus in compare with conventional titanium alloys. Low elastic modulus is important with respect to biomechanical compatibility. When using an implant with high elastic modulus it overtakes a considerable part of body loading. Then the bone is shielded from necessary stressing required to maintain its strength, density and healthy structure. This effect (usually termed as “stress shielding”) may cause bone loss, implant loosening and premature failure of the implant. Higher biocompatibility of \( \beta \)-Ti alloys is provided due to absence of potential harmful elements in alloys that may cause problems during long term use in the human body. These elements are especially V, which has one of the highest cytotoxicity, and Al, that is suspected from causing neurological problems (Alzheimer disease). For alloying \( \beta \)-Ti alloys are used elements as Nb, Ta or Zr (and some others) that are relatively safe for use in human body. Moreover they in general act as \( \beta \)-Ti stabilizers[4-8].

As it was said the disadvantages of Ti-based alloys are relatively complicated production and resulting higher costs and high reaction with oxygen, nitrogen and other elements during melting process. One of the ways to cost decrease is processing materials via powder metallurgy. That allows to save energy costs during production and obtain near net shape of the final produc. As disadvantage can be considered worse mechanical properties of products because of their porosity[9].

In this work we have obtained some observations which allow the production of \( \beta \)-Ti alloys via powder metallurgy processes with desired properties.

2. Experimental (materials and methods):
The specimens studied in this work were prepared from titanium and niobium powders bought from DAYANG CHEMICALS CO., LTD., China. Powders were processed via HDH method (hydridation of metal, milling and subsequent dehydridation in a vacuum furnace[3]). An example of Nb powder morphology and the microstructure of Ti-powder are shown in Fig. 1a and Fig. 1b respectively.

![Fig. 1a: Nb powder with grain size more than 125 μm](image1)

![Fig. 1b: Microstructure (α+β phase) of Ti powder with grain size 80-125 μm](image2)

The powders have nominal chemical composition- Ti-powder: 99,095 wt. % Ti; 0.30 wt. % Fe; 0.06 wt. % Al; 0.10 wt. % Si; 0.34 wt. % O; 0.04 wt. % C; 0.05 wt. % N and 0.015 wt. % H. Nb-powder: 99,859 wt. % Nb; 0.01 wt. % Fe; 0.003 wt. % Cu; 0.005 wt. % Si; 0.003 wt. % Ti; 0.07 wt. % O; 0.04 wt. % C; 0.01 wt. % Na and 0.004 wt. % H. The powder grains are irregular shaped with grain sizes -80/325 mesh (-177/+44 μm) and -100/325 mesh (-177/+44 μm) for Ti-powder and Nb-powder respectively. Powders were divided into fractions by using grain size analysis under argon atmosphere. So we have obtained four fractions of Ti-powder: powder with grain size smaller than 50 μm, powder with grain size -80/+50 μm, powder with grain size -125/+80 μm and powder with grain size bigger than 125 μm. Also Nb-powder was divided into four fractions: grain size smaller than 40 μm, grain size -80/+40 μm, -125/+80 μm and powders with grain size bigger than 125 μm.

From these powders were prepared blends of powders for production of specimens for sintering with a chemical composition Ti-39,3wt.%Nb.

- **a)** Blend of Ti and Nb powders with grain size bigger than 125 μm (marked as 39N125).
- **b)** Blend of Ti and Nb powders with grain size bigger than 80 μm and smaller than 125 μm (marked as 39N80).
- **c)** Blend of Ti-powder with grain size bigger than 50 μm and smaller than 80 μm and Nb-powder with grain size bigger than 40 μm and smaller than 80 μm (marked as 39N50/40).
- **d)** Ti-powder with grain size smaller than 50 μm and Nb-powder with grain size smaller than 40 μm (marked as 39Nm50/m40).

Powders were sorted, weighted and filled into vessel under protective argon atmosphere in order to protect powders from oxidation. Then they were mixed for a 4 hours period in a TURBULA T 2 F mixer with a speed of 40 rpm. The construction of used vessel is hermetic, so all the process of mixing is running under argon atmosphere.

After that the blends were filled into rubber mold (under argon atmosphere) and than they were cold isostatic pressed under pressure 400 Mpa for 20s. Subsequently one
specimen from each blend was stored for further studying of porosity and blend homogeneity after mixing. Other samples from were sintered in a vacuum furnace (under pressure less than $10^{-3}$ Pa) at 1300°C and 1400 °C for 5, 10, 15, 20, 25 and 30 hours and cooled in furnace. All of samples were measured by using the equipment Densimeter EW SG of Mirage Trading Co, Ltd., Japan in order to determine the density of the samples. With regard to high surface porosity it was necessary to avoid the infiltration of the fluid into the specimen. Hence the open surface pores were closed by the nitrocellulose lacquer.

Metallographic preparation was carried out using conventional techniques with $\mathrm{Al_2O_3}$ papers from #180 to #1200 and subsequently SiC papers (#2500 – #4000) and polished with Struers OP-S emulsion in addition of 0,6 ml OP-S, 2 ml $\mathrm{H_2O}$ and 2 ml $\mathrm{NH_3}$. These samples were studied by using optical microscope (OM). Than the samples were etched with a solution of 100ml $\mathrm{HNO_3}$, 26 ml HF and 84 ml $\mathrm{H_2O}$. Subsequently studying was carried out by using scanning electron microscope in backscattered 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, that allows us to measure the percentage part of pores (porosity) in material and their morphology.

3) Results and discussion:

SEM (COMPO) micrographs obtained from a sample cold isostatic pressed are shown if Fig.2 and Fig.3. There can be seen Ti-grains (darker) and Nb-grains (brighter) in the sample 39N80 and 39Nm50/m40 (Fig.2 and Fig.3 respectively). From these micrographs is evident uniform distribution of Nb grains among Ti-grains. This means that blends of all fractions were mixed enough.

![Fig. 2: SEM micrograph (COMPO) of cold isostatic pressed 39N80 blend.](image1)

![Fig. 3: SEM micrograph (COMPO) of cold isostatic pressed 39Nm50/m40 blend.](image2)

The dependence density-time of sintering for specimens of various grain size blends sintered at various temperatures is shown in Fig.4. At 1300°C were sintered only specimens 39N50/40 and 39N125. In compare with the same specimens sintered at higher temperature (1400°C) is their density much more lower and the change of the density with increasing sintering time (from 10 hrs) is inexpressive. Even the sample with relatively small grain size (39N50/40) has after 30 hrs sintering at 1300°C density of about 4,5 g/cm$^3$. That is significantly less than theoretical density of compact Ti39,3Nb alloy (5,5 g/cm$^3$). So it seems that the temperature 1300°C is insufficient for sintering. Because of that for other experiments were used only specimens sintered at 1400°C.
The density values of specimens sintered at 1400ºC is in Fig.5. Densities of specimens 39N125, 39N80 and 39N50/40 increase during first 15 hours of sintering. Further increase is immeasurable with respect to error of measurement. Also is evident that samples from finer fractions has higher density than that ones from coarser fractions. Density of sample with finest grains has the fastest increase and after about 15 hours of sintering reaches practically the value of theoretical density of compact material.

Occurrence of pores in specimens and their morphology was studied by analyzing photographs from optical microscope (OM). Quantity and morphology of pores in specimens with coarse grains does not change very much. Despite there is evident diffuse rounding of
pores surface and decrease of their amount. In specimen 39N80 the change becomes more significant. The porosity and morphology of specimens 39N50/40 and 39Nm50/m40 is shown in Fig.6 and 7 respectively. The change of porosity and morphology of pores during first 5 hours of sintering for these specimens can be seen when comparing Fig.6a and 6b (or 7a and 7b). There is a significant decrease in porosity especially for the finest grains and also the morphology after sintering is much more different.

Results of pores quantity are shown in Fig.8. With increasing time of sintering the quantity of pores decreases in all of observed specimens. The most significant decrease of porosity is during first 5 hours of sintering and then the decrease rate slows down. In sample 39N125 the porosity decreases only during first 5 hours of sintering and further decrease is not significant because of scatter of experimental values. While the porosity of specimen with the finest grain size (39Nm80/m40) falls to less than 1% after 5 hours of sintering at 1400ºC. Specimen porosity and rate of its decrease also strongly depends on the grain size of sintered specimens. After about 15 hours of sintering 39N50/40 sample reaches the porosity of about 10%, the porosity of 39N80 sample is about 22% and for 39N125 sample is about 28%. This is caused by higher amount of grains in sintered volume of blends with finer grain size and resulting larger surface of grains and more contact areas, which enables easier and faster diffusion of Ti and Nb atoms along grain boundaries. So the diffusion distances are shorter.
Very important role for the quality of the final product plays chemical homogeneity reached during the sintering process. That is the reason why the chemical composition and phase microstructure were studied besides porosity. The origin microstructure of Ti-powder was \( \alpha \)-Ti + \( \beta \)-Ti microstructure (Fig.1b).

An example of microstructure (COMPO) of the coarsest blend (specimen 39N125) after 5 hours sintering is shown in Fig.9. Brighter areas that with higher content of Nb (element with higher atomic mass than Ti). Whereas originally Ti-grains are darker. In the vicinity of Nb-particles can be seen gray areas. This is a proof of dissolving of Nb into Ti-rich regions.

In other SEM micrographs (Fig.10 and 11) are details of areas from the specimen shown in Fig.9. The former shows \( \alpha \)-Ti+\( \beta \)-Ti microstructure. Analysis of chemical composition (EDAX) confirmed content of Ti higher than 60%. The latter figure shows area
consists entirely of β-Ti microstructure. In this case the EDAX analysis showed much higher content of Nb. So it is evident that Nb acts as β-Ti phase stabilizer.

During phase study from photographs obtained by OM from etched specimens was observed the decrease of amount areas consisting of α-Ti+β-Ti microstructure, which were replaced by areas with β-Ti microstructure, with increasing sintering time. There is an optical micrograph of sample 39N125 sintered for 15 hours in Fig.12. There can be seen areas with pure β-Ti phase (bright ones) and areas consisting of α-Ti+β-Ti microstructure (darker). In specimens with coarse grains (39N125, 39N80) was not reached fully β-Ti microstructure (there were always some areas of α-Ti+β-Ti microstructure) even after 30 hrs. of sintering. On the other hand in the 39N50/40 specimen was reached wholly β-Ti microstructure after 20 hours of sintering, and in the specimen with the finest grains was reached fully β-Ti microstructure after 5 hours of sintering. This is caused by easier and faster diffusion of Nb into Ti-particles in material with finer grains as was said.

4) Conclusions:

In terms of results mentioned above imply:

1. Study of pressed specimens structure showed, that the mean and parameters of blending powders are suitable for homogeneous distribution of Ti and Nb particles in used blend with composition of 39,3 wt.% Nb and 60,7 wt.% Ti.
2. The temperature 1300°C is not sufficient for sintering, because of high porosity and small density of sintered material.

3. Detailed study of microstructure, local chemical composition and the density has offered the dependencies of porosity, structure and chemical homogeneity on sintering time at 1400°C for blends with various grain size.

4. For totally compact material it is necessary to insert subsequent heat forging operation, which only can provide additional decrease of porosity. Only after studying forged samples will be possible to analyze acceptable and most suitable range of grain size in blends, regarding the lowest price of final product.

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Literature review:


