Hodnocení porozity a strukturního složení slitiny TI39Nb připravené práškovou metalurgií

Evaluation of porosity and microstructure of Ti39Nb alloy prepared by powder metallurgy

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Abstrakt:
Beta titanové slitiny jsou v poslední době využívány mimo jiných oblastí zejména pro medicínské využití z důvodu jejich vysoké biokompatibility. Pozornost se soustřeďuje především na slitiny, které neobsahují škodlivé prvky, jako vanad nebo hliník. Kromě toho je důležitá také biomechanická kompatibilita (modul pružnosti blízký modulu pružnosti lidské kosti). Perspektivní metodou přípravy těchto slitin je prášková metalurgie. Výsledné vlastnosti výrobku ovlivňuje zejména kvalita použitých prášků a také způsob přípravy. V této práci byly zkoumány prášky různých zrnitostí (připravené HDH metodou), které byly slisovány za studena (CIP) a následně slinovány při 1400ºC po různé doby. Následně byla hodnocena porozita (kompaktnost) jednotlivých vzorků a také jejich mikrostruktura za účelem určení optimálního postupu jejich přípravy.

Abstrakt:
Beta titanium alloys are recently used especially in medical engineering, because of their very good biocompatibility. Research is focused mainly on alloys not containing elements as V or Al, which can be harmful to human body. Besides the other important property of these alloys is biomechanical compatibility (Young's modulus close to that of bone). One of the most perspective way to process these alloys is powder metallurgy. The properties of product's of powder metallurgy are influenced meanly by quality of used powders and also by parameters of preparing process. In this work powders with various grain sizes (processed via HDH method), were pressed (CIP) and than sintered at and 1400ºC for various time periods. After that the porosity and microstructure of each specimen was studied to point out optimal preparation process.

Key words:
Titanium alloys, powder metallurgy, biocompatibility, α-Ti + β-Ti microstructure.

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 meanly in aerospace and medical applications. Still their disadvantage remains their high cost of raw material and expensive machining operations[1,2].

Titanium has a melting point of 1668°C and hexagonal closed packed (α-Ti) microstructure at room temperature, that changes into bcc (β-Ti) structure at 883°C. β-Ti structure has in compare with α-Ti structure lower elastic modulus[3]. These days titanium alloys with β-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, which means that material of implants should have elastic modulus close to that of bone. When using implant of material with high elastic modulus the implant 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 β-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 β-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 β-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 new techniques as powder metallurgy. That allows to save energy costs during production and obtain near net shape of the final product, so the machining is than much simpler and also cheaper and also the utilization of material is better. As disadvantage can be considered worse mechanical properties of products because of their porosity[9]. Recently due to utilization of powders produced via HDH technology (hydridation of raw material, that causes its brittleness and allows better milling, and subsequent dehydridation in a vacuum furnace of a milled powder [3]) the densities of sintered material about 99% can be reached. Final density depends on used powder, applied pressure and on sintering temperature. Parameters of sintering (time and temperature) influence final microstructure[1,2]. These parameters differ in dependence on used chemical composition.

The goal of this work was to obtain pieces of knowledge, that should allow the production of β-Ti alloys with desired properties via powder metallurgy processes.

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 powder morphology of Nb powder and microstructure of Ti- powder are shown in Fig. 1a and Fig. 1b respectively. Nominal composition of powders are in accordance with the information from the company are in Tab.1.

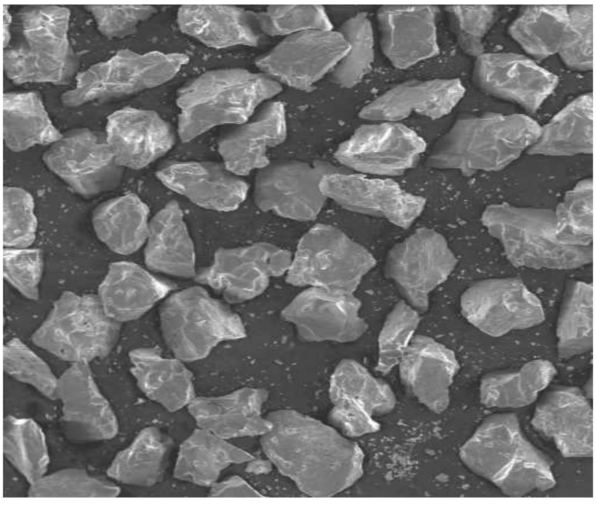

Fig. 1a: *Nb powder with grain size more than 125 µm*

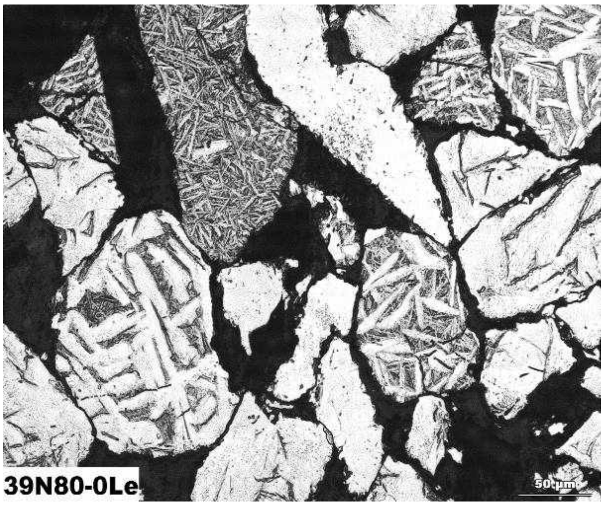

Fig.1b: *Microstructure (α+β phase) of Ti powder with grin size 80-125 µm*

element wt.%	Ti-powder	Nb-powder
Ti	99,095	0,003
Nb	-	99,859
Fe	0,3	0,01
Al	0,06	-
Si	0,1	0,005
O	0,34	0,07
C	0,04	0,04
N	0,05	0,01
H	0,015	0,004
Cu	-	0,003

Tab.1: *chemical composition of powders*

The grain size of powders are -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've 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 less 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. So we've obtained following blends:

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 powders 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 the all 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^{-2}Pa) at 1300ºC and 1400 ºC 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 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 H_2O and 2 ml NH_3. These samples were studied by using optical microscope (OM). Than the samples were 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 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 on computer in program LUCIA G, that allows us to measure the percentage part of pores 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.

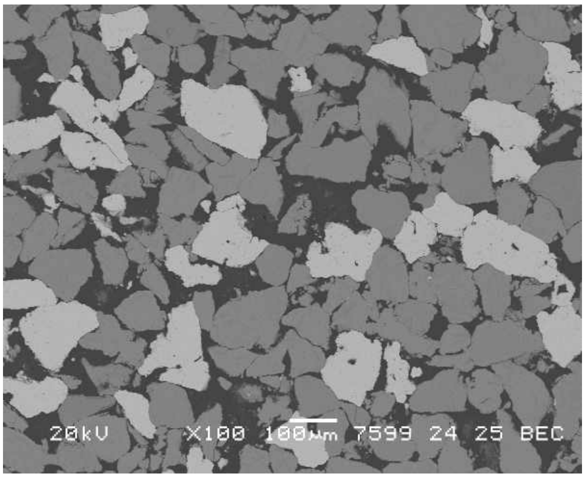

Fig. 2: *SEM micrograph (COMPO) of cold isostatic pressed 39N80 blend.*

Fig. 3: *SEM micrograph (COMPO) of cold isostatic pressed 39Nm50/m40 blend.*

Density of samples depending on grain size fraction, temperature and time of sintering are shown in Fig.4 and Fig.5. At 1300ºC were sintered only samples 39N50/40 and 39N125. In compare with the same samples sintered at higher temperature (1400ºC) 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 has after 30 hrs sintering (at 1300ºC) density 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 1300ºC is insufficient for sintering. Because of that for other experiments were used only samples sintered at 1400ºC.

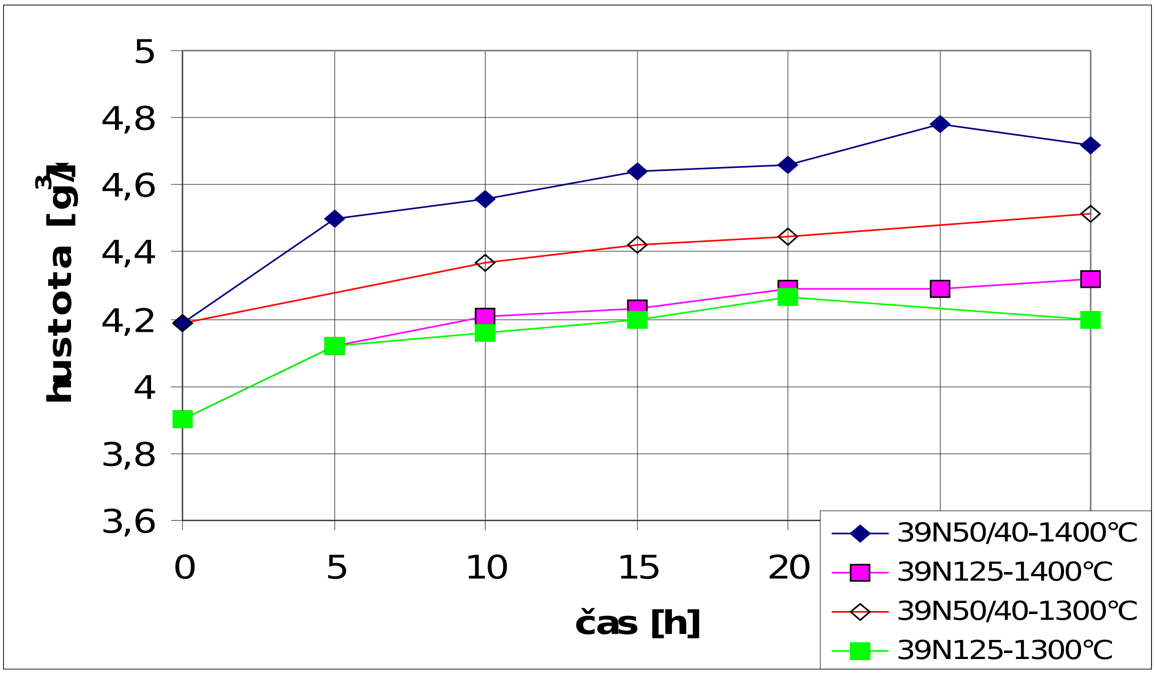

Fig.4: *Density of samples of two grain sizes sintered at 1300 °C and 1400 °C*

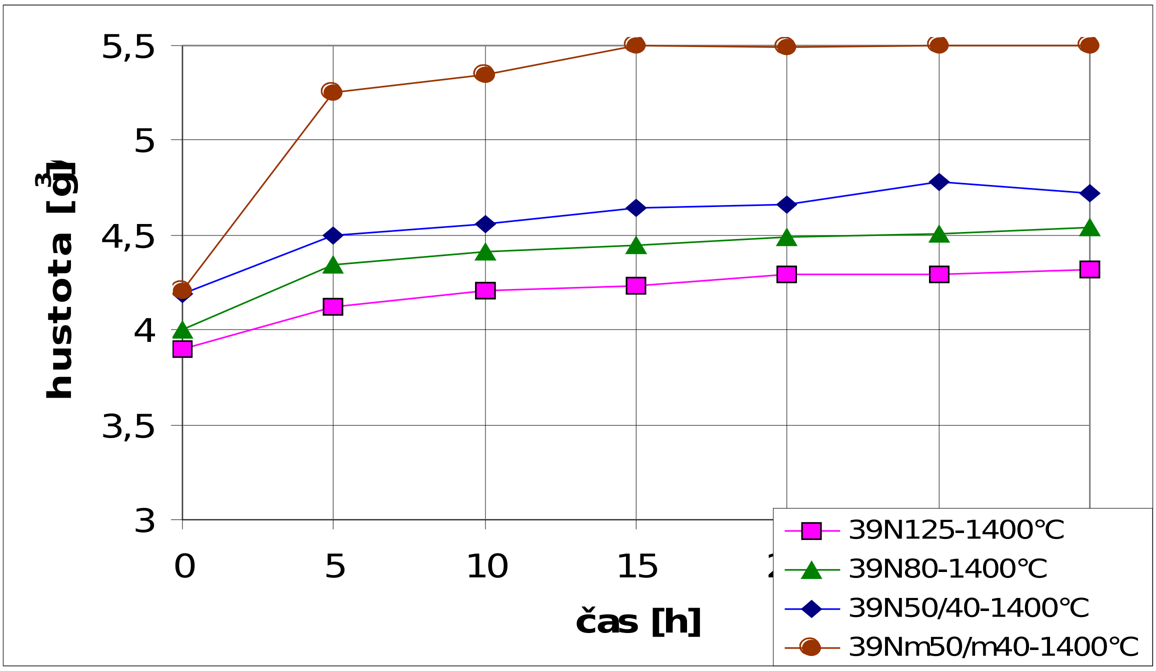

Fig.5: *Density of samples sintered at 1400 °C depending on sintering time*

The density values of samples sintered at 1400°C is in Fig.5. Densities of samples 39N125, 39N80 and 39N50/40 increases during first 15 hours of sintering. Further increase is immeasurable with reference to measurement error. 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 faster increase and after about 15 hours of sintering reaches practically the value of theoretical density of compact material.

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

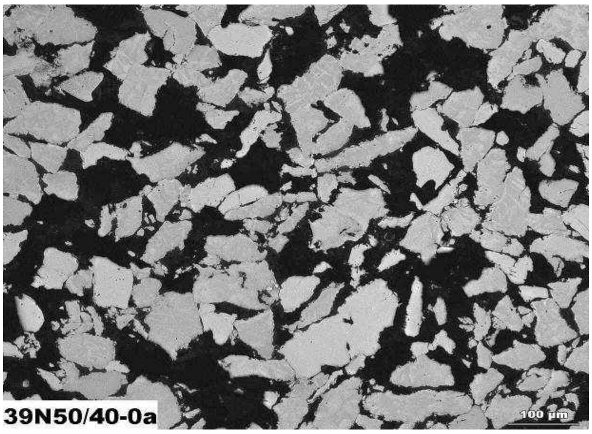

Fig.6a: *Cold isostatic pressed 39N50/40 sample (OM)*

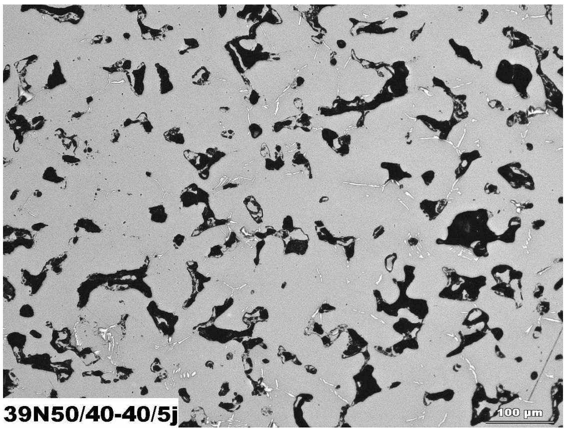

Fig.6b: *Sintered (5h at 1400 °C) 39Nm50/m40 sample (OM)*

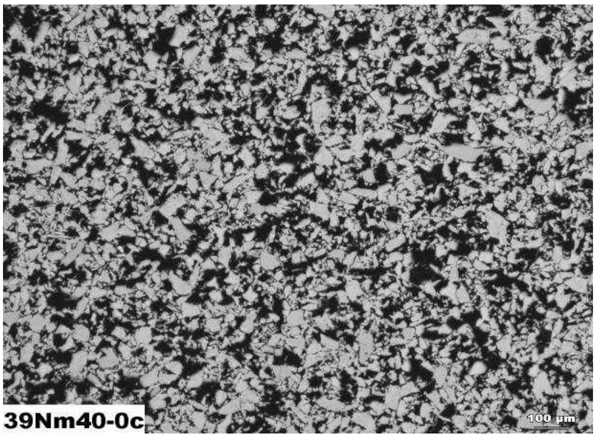

Fig.7a: *Cold isostatic pressed 39Nm50/m40 sample (OM)*

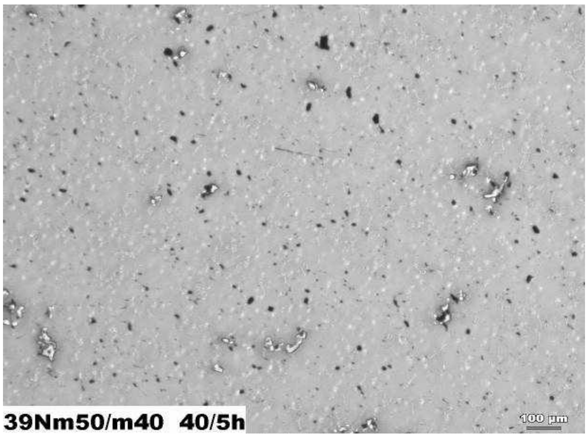

Fig.7b: *Sintered (5h at 1400 °C) 39Nm50/m40 sample (OM)*

Results of pores quantity are shown in Fig.8. With increasing time of sintering decreases the quantity of pores in all of used samples. The most significant decrease of porosity is during first 5 hours of sintering and then the decrease rate slows. The rate of decrease also depends on grain size of blend. In sample 39N125 the porosity decrease only during first 5 hours of sintering and further decrease is not significant because of scatter of experimental values. While the porosity of sample with the finest grain size (39Nm80/m40) falls to less than 1% after 5 hours of sintering at 1400ºC. Porosity of samples also strongly depends on the grain size of sintered samples. 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 closer.

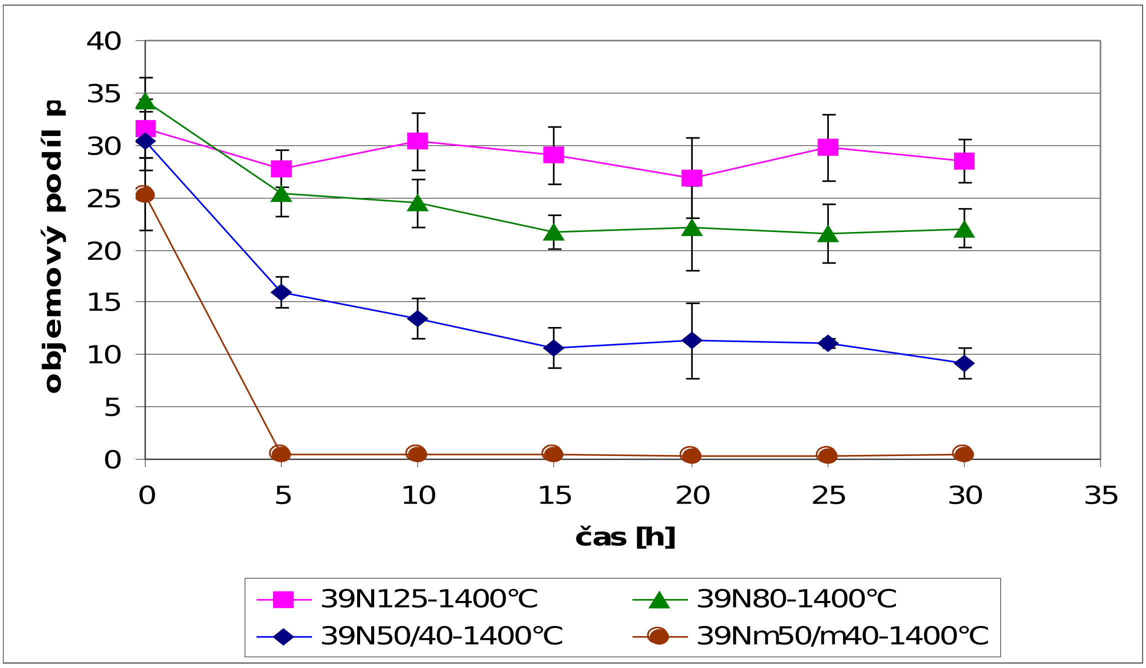

Fig.8: *Porosity of blends sintered at 1400 °C depending on sintering time*

Very important role for the quality of the final product processed via powder metallurgy 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 α-Ti + β-Ti microstructure (Fig.1b).

An example of microstructure (COMPO) of the coarsest blend (sample 39N125) after 5 hours sintering is shown in Fig.9. Brighter areas are 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 titanium-rich regions.

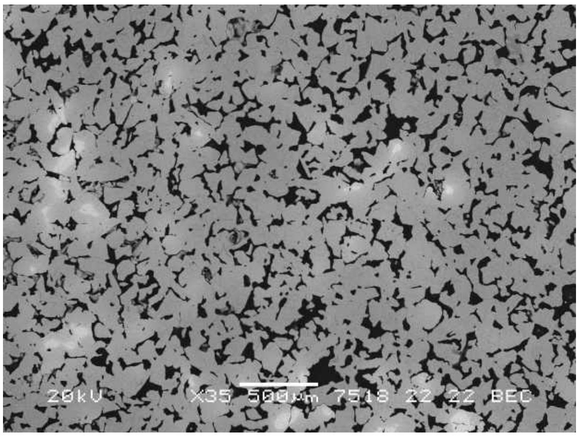

Fig.9: *SEM micrograph of 39N125 sample sintered for 5 hrs. at 1400 °C (COMPO)*

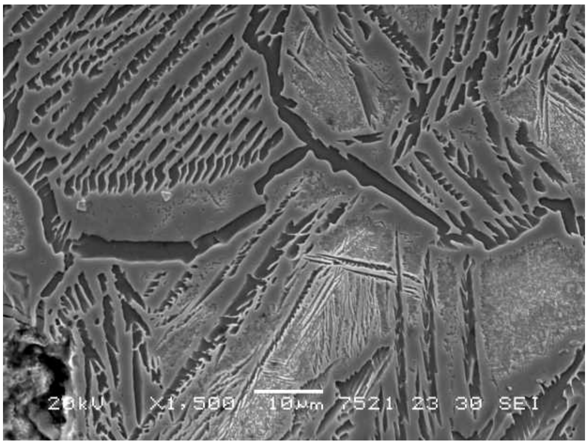

Fig.10: *Detail of α-Ti + β-Ti phases in sample 39N125 sintered at 1400 °C/5 hrs.*

In other SEM micrographs (Fig.10 and 11) are details of areas from the sample shown in Fig.9. The former shows α-Ti+β-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.

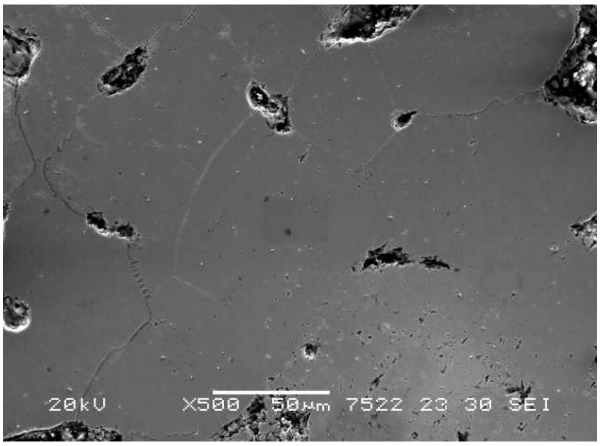

Fig.11: *Detail of β-Ti phase microstructure of 39N125 sample sintered at 1400 °C/15 hrs.*

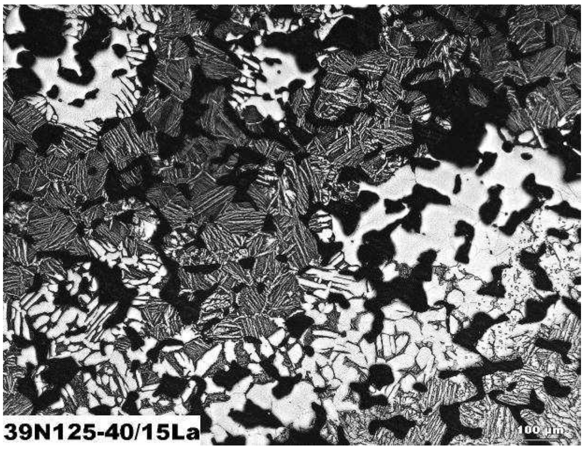

Fig.12: *Microstructure of an 39N125 sample sintered at 1400 °C/15 hrs. (OM)*

During studying phases from photographs obtained by OM from etched samples was observed with increasing sintering time decrease of amount areas consisting of α-Ti+β-Ti microstructure, which was replaced by areas of β-Ti microstructure. 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 samples 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 sample 39N50/40 was reached wholly β-Ti microstructure after 20 hours of sintering. and in the sample 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.

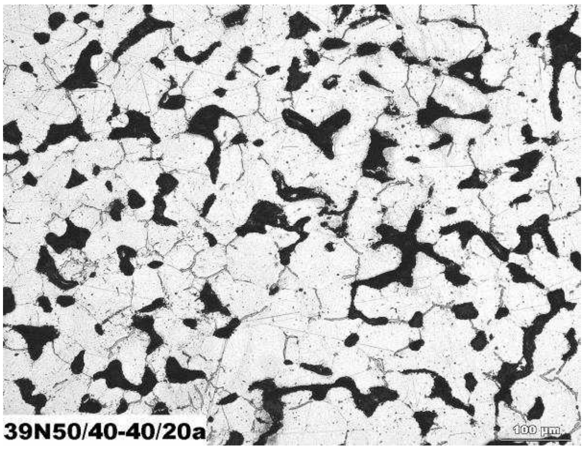

Fig. 13*: β -Ti phase of 39N50/40 sample sintered at 1400 °C/20hrs.*

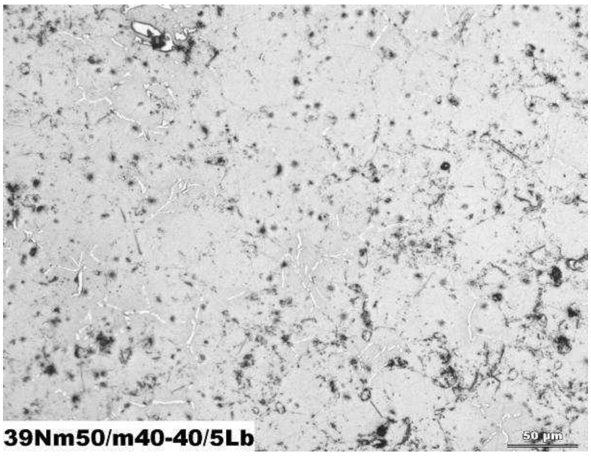

Fig. 14: *β -Ti phase of 39Nm50/m40 sample sintered at 1400 °C/5hrs.*

4) Conclusions:

In terms of results mentioned above imply:

1) Study of pressed samples structure showed, that the mean and parameters of blending powders are suitable for homogenous distribution of Ti and Nb particles in used blend with composition of 39,3 wt.% Nb and 60,7wt.% Ti.

2) The temperature 1300ºC is not enough for sintering this alloy, because of high porosity and small density of sintered material.
3) For reaching almost compact material after sintering at 1400ºC is necessary to use powders with grain size smaller than 50 µm and 40 µm for Ti and Nb powders respectively. In this case is sintering time about 5 hours sufficient.
d) By using the finer grain size material is after 5 hours sintering the microstructure fully β-Ti.

For totally compact material it is necessary to insert subsequent heat forging operation, which can as unique subsequent operation provide the 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.

Literature review:

[1] E.B. Taddei, V.A.R. Henriques, C.R.M. Silva, C.A.A. Cairo: Production of new titanium alloy for orthopedic implants. Materials Science and Engineering C 24 (2004) 683-687.
[2] D.R. Santos, M.S. Pereira, C.A.A. Cairo, M.L.A. Garca, V.A.R. Henriques: Isochronal sintering of the blended elemental Ti-35Nb alloy. Materials Science and Engineering A 472 (2008) 193-197.
[3] J.P. Beckman: Powder metallurgy/1137. Metals Handbook, 9th Edition, Vol. 7.
[4] M.C. Bottino, P.G. Coelho, M. Yoshimoto, B. Konig Jr., V.A.R. Henriques, A.H.A. Bressiani, J.C. Bressiani: Histomorphologic evaluation of Ti-13Nb-13Zr alloys processed via powder metallurgy. Materials Science and Engineering C 28 (2008) 223-227.
[5] V.A.R. Henriques, C.E. Bellinati, C.R.M. da. Silva: Production of Ti-6%Al-7%Nb alloy by powder metallurgy (P/M). Journal of Materials Processing Technology 118 (2001) 212-215.
[6] F.A. Muller, M.C. Bottino, L. Muller, V.A.R. Henriques, U. ohbauer, A.H.A. Bressiani, J.C. Bressiani: In vitro apatite formation on chemically treated (P/M) Ti-13Nb-13Zr. Dental Materials 24 (2008) 50-56.
[7] J. Svoboda, H. Riedel, H. Zipse: Equilibrium pore surfaces, sintering stresses and constitutive equations for the intermediate and late stages of sintering.Acta metall. mater. Vol.42 No.2, pp. 435-443, 1994.
[8] V.A.R. Henriques, H.R.Z. Sandim, G.C. Coelho, C.R.M. da Silva: Microstructural evolution during hotpressing of the blended elemental Ti-6%Al-7%Nb alloy. Materials Science and Engineering A347 (2003) 315-324.
[9] V. N. Anciferov, V.C. Ustanov, Y.G. Olesov: Spetchenye splavy na osnove titana, Metallurgia. Moscow 1984.