306. Usage of the powder metallurgy method for fabrication of titanium implant alloy

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Abstract. In the paper research of the new implant titanium alloy obtained by powder metallurgy method were presented. The Ti15Mo2,8Nb alloy was fabricated from pure alloying component powders. The structure was observed by scanning electron microscope and analyzed by X-ray diffraction. The effect of grinding time of mixtures as well as the size of titanium powder grain on compatibility, compression strength and yield point of sintered alloys was analysed. It was found that grain size has a significant effect on strength properties of the alloy. However, the prolonging of grinding time caused deterioration of compatibility as well as mechanical properties of sinters.

Keywords: biomaterials, titanium alloys, powder metallurgy, structure, mechanical properties.

Introduction

Titanium and its alloys are widely used in medical applications, e.g. in manufacture of reconstructive elements for fixing of bone fragments, prosthetic implants, and joint endoprostheses due to their properties, especially excellent corrosion resistance in physiological fluids as well as the biocompatibility in human cells and tissue environment [1]. The use of titanium and its alloys is limited by a low resistance to friction wear as well as the possibility of passing some alloy components to the surrounding biological environment. Titanium is considered as a neutral metal. However, there is a danger of toxicological reaction of some alloy additives, such as aluminium and vanadium. Depending on obtained structure by appropriate selection of alloy additive, titanium alloys can be divided into one of three groups: single-phase alloys α, diphase alloys α+β, single-phase alloys β.

Recently the most common implant material is pure titanium and Ti6Al4V diphase alloy. However, scientific research carried out in the last decade show advisability of single-phase β-type application especially with molybdenum additive, e.g. Ti15Mo2,8Nb [2].

A separate subject-matter is a problem of titanium implant manufacture. Despite research done over the past fifty years, the technology of titanium still causes many problems.

Specific properties of titanium and its alloys such as high melting and casting temperature, chemical activity of molten metal and low density with high viscosity in liquid state prevent application of conventional melting and casting technology. Processes are carried out in vacuum environment with using of special forms resistant to liquid metal effect. Structural defects and gas porosity cause the necessity of application of further processing of casts [3].

One of the methods for obtaining of titanium products is plastic working. It ensures the best mechanical properties, especially resistance to dynamic loads [4]. However, in case of plastic working there are many requirements that have to be met, concerning temperature regime, heating rate, rate of deformation as well as manufacture of suitable dies and their lubrication [5].

The powder metallurgy method for forming titanium elements is becoming an interesting alternative. Some authors suggest that titanium powder metallurgy is being developed mainly because of its low production costs [6,7]. The products obtained from HDH powders show the properties comparable to products from titanium sponge, combining high resistance with good plasticity [8]. It was shown that Ti6Al4V titanium alloys obtained by PM method have sufficient fatigue strength to be used for automobile part production and airplane engine elements [9,10]. Researches of corrosion resistance also acknowledge suitability of PM for manufacture of materials for biomedical uses [11]. Porous titanium similarly like monolithic shows the ability to produce self-regenerating oxide layers which ensures higher resistance to corrosion in comparison to 316L implant steel.

There are also known interesting works, focused on obtaining of composite materials on the titanium base by PM method by usage of reaction in solid phase [12-14], by gas-solid reduction with formation of Ti-TiC [15] or alloy synthesis in conditions of mechanical activation or mechanical gradation [16,17].

As literature data analysis shows, powder metallurgy allows obtaining titanium materials of required functional qualities for different applications.

The purpose of this work was the assessment of possibilities of implant material production on the base of Ti15Mo2,8Nb titanium alloy by powder metallurgy method in cold moulding and sintering in environment of inert gas atmosphere.

Materials and methods

The materials for research was titanium alloy with niobium and molybdenum Ti15Mo2,8Nb fabricated by powder metallurgy method. The pure metal powder produced by APS (USA) was used for the study. The purpose of the study was to determine the effect of selected process parameters, especially the grinding time and powder grain size, on compactibility and resistance characteristics of sinters. The grain size of titanium powders was in the range of 45 to 150 μm. The grain size of molybdenum was 3-7 μm and niobium – 1-5 μm. Grinding process was carried out by means of the FRITSCH globular mill. The rotational speed was 300 rpm, grinding time of powder mixtures: 15 min, 1, 2, and 4 hours. Then the cylindrical samples with dimensions of ϕ7x10 mm were formed from the prepared powders. The samples were uniaxially compacted using a hydraulic press at 600 MPa. Sintering process was carried out during 1 hour at the temperature of 950ºC in argon atmosphere.

The microstructure of powder and sintered samples was observed using scanning electron microscope HITACHI SW3000-N. Structural tests were carried out on the X-Ray diffractometer Philips. The resistance properties were tested by means of the universal testing machine INSTRON 8502 during compression test.

Results and discussion

The exemplary microscope images of powder mixtures are presented in figure 1, respectively after 1 and 2 hours of grinding. It can be noticed that during 1 hour grinding size-reduction of titanium powder grains took place regarding to initial material. Subsequent prolonging of the grinding time caused deformation and agglomeration of titanium grains. However, molybdenum and niobium grains stayed practically the same.

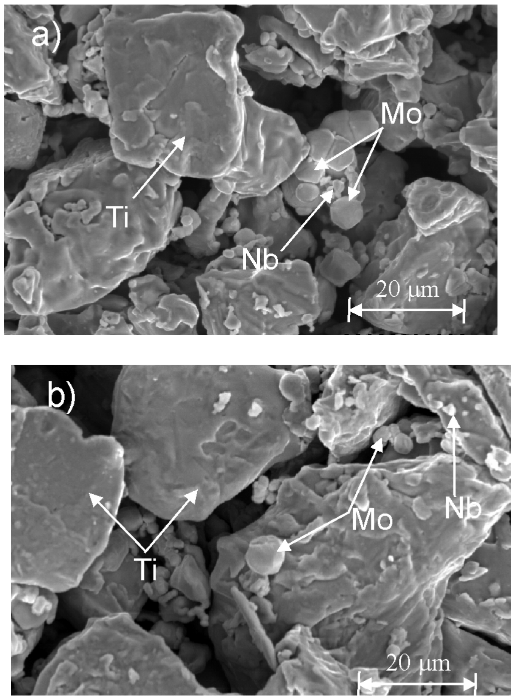

Fig. 1. Morphology of powder particles of Ti15Mo2,8Nb alloy mixture after grinding: a) grinding time - 1 h, b) - 2h

The prepared powder mixtures underwent cold moulding and sintering processes. As a result of sintering in argon atmosphere in 950ºC the partial diffusion of alloy components took place. On the image of sinter microstructure, it is possible to distinguish the presence of the three main phases: phase β - solid solution on titanium base with chemical composition similar to the assumed and the rest of pure titanium, especially inside large particles and agglomerations, as well as the remaining undissolved molybdenum grains (fig.2).

The results of X-ray structural (phase) tests confirmed the fact that during sintering process partial structural transformation of α-Ti in β-Ti took place as a result of diffusion and dissolving of alloy components. On a diffraction pattern of powder mixtures before sintering only peaks characteristic to individual elements α-Ti, α-Mo and Nb (fig.3a) were noticeable. However, additionally peaks characteristic to β-Ti structure appeared on diffractogram of sinters obtained from this powder after sintering (fig. 3b).

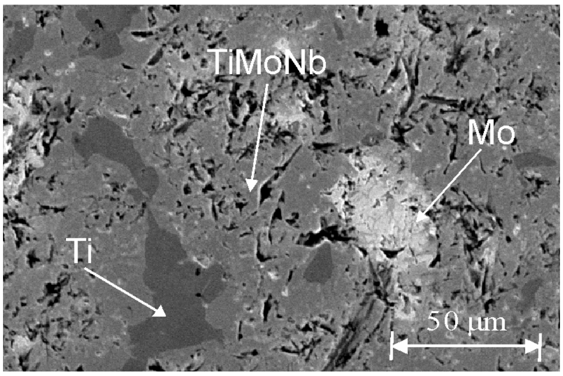

Fig. 2. Microstructures of sintered titanium alloy Ti15Mo2,8Nb with visible phases

In figures 4 and 5 the results of relative density of obtained sinters are presented referring to theoretical density of analogical cast alloy. As it can be noticed from the table, titanium alloys of about 65% relative density were obtained as a result of the utilized technological process. The highest density was obtained for sinters produced of the smallest grain titanium powders after 15 min. grinding. Larger grain fractions showed insignificant loss of compactibility which can be caused by formation of stress in powder grains as a result of plastic deformations during grinding as well as the presence of fine Al_2O_3 particles transferred from milling balls.

Resistance tests of sinters were carried out during static uniaxial compressive test. Exemplary diagram of deformation change in the function of load obtained for the sinter № 1 produced from powders after 15 min. grinding is presented in figure 6. The graph of the relationship between load and deformation is characteristic for plastic materials, where in the beginning of the test the range of plastic

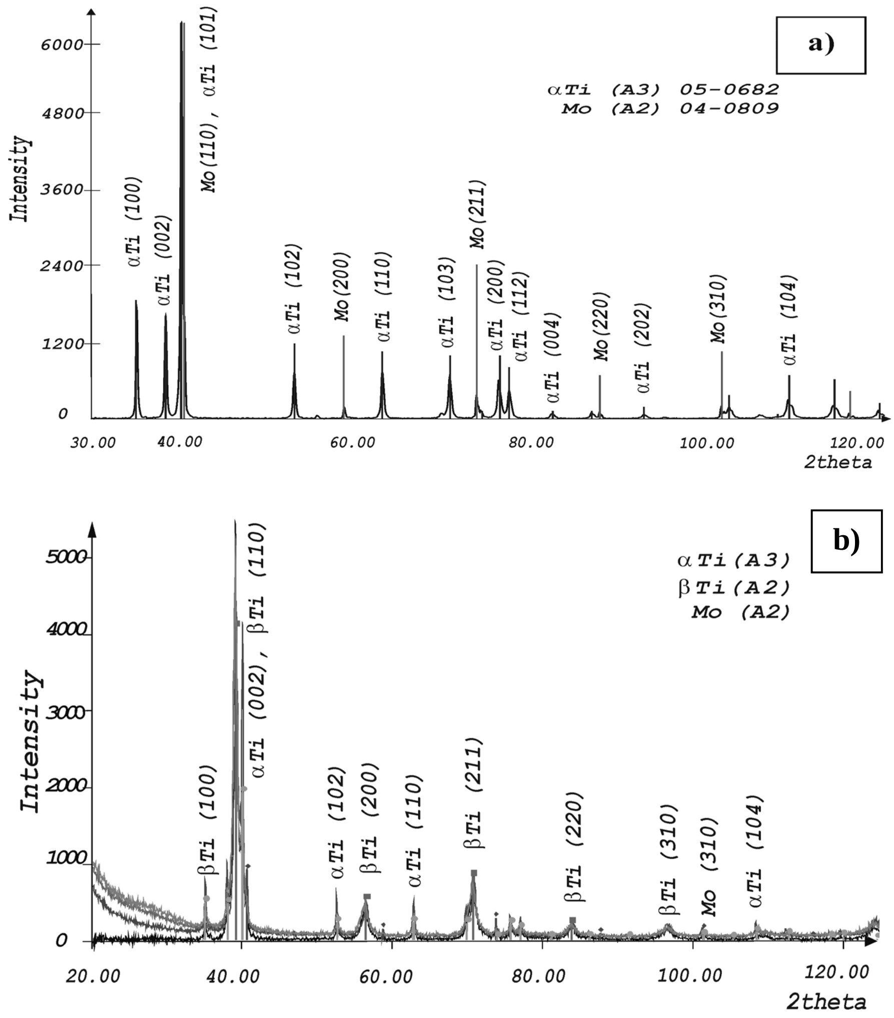

Fig. 3. Diffraction pattern of Ti15Mo2,8Nb alloy: a) powder after grinding, b) material after sintering

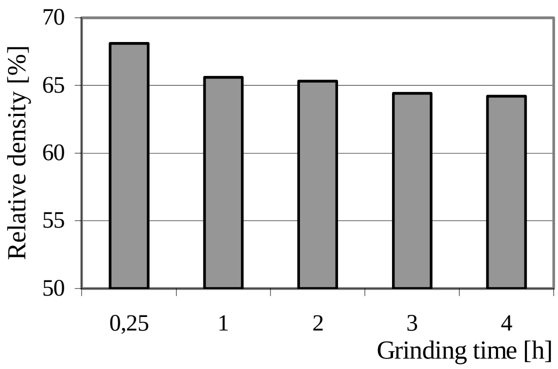

Fig. 4. The influence of grinding time of powder mixtures on compactibility of sintered alloys

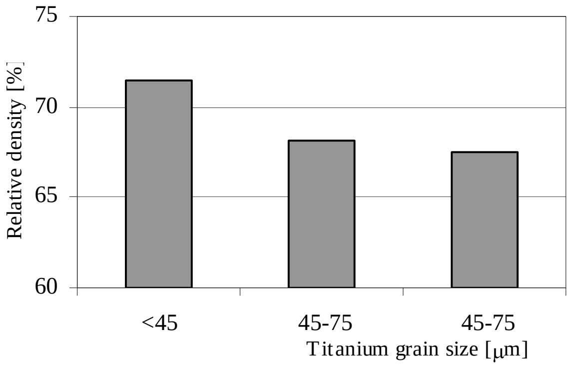

Fig. 5. The influence of titanium powder grain size on compactibility of sintered alloys

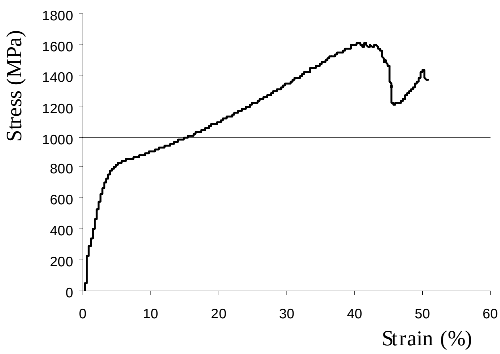

Fig. 6. Typical stress-strain curve for sintered titanium alloy Ti15Mo2,8Nb (compression test)

deformations and a clear yield point can be noticed. This is confirmed by the macroscopic observation of sample № 1 after compression (fig. 7a). So it can be stated, that the employed conditions of sinter formation (powder grinding and sintering in argon atmosphere process) allowed obtaining alloys characterized by good plasticity. Only in samples obtained from powders after a longer grinding time – 4 hours the brittle cracking during strength tests was observed (fig.7b). This can be caused by large stress appearing in grains of titanium powders during grinding. Another reason for brittleness of these sinters could be the presence of small Al_2O_3 particles, transferred from the material of the grinding container. The analysis of the chemical composition (EDS) of investigated samples showed the presence of aluminium in sinters rising with the time of powder grinding.

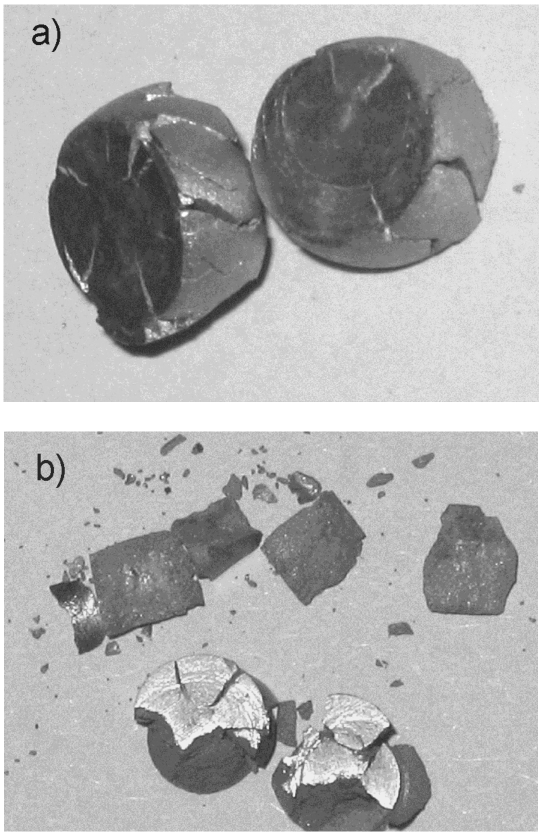

Fig. 7. The view of sinters after compression tests: a) serie № 1, b) serie № 5

Table 1. Results of compression test of sintered alloy Ti15Mo2,8Nb

№ series	Grain size	Grinding time	Relative density ρ_w	Compression strength Rc	Yield strength $Rc_{0,2}$
	μm	h	%	MPa	MPa
1	<45	0,25	71,5	1681	682
2	45-75		68,1	1652	617
3	75-150		67,5	1388	376
4	45-75	1	65,6	1512	577
5		2	65,3	1503	606
6		4	64,4	757	626

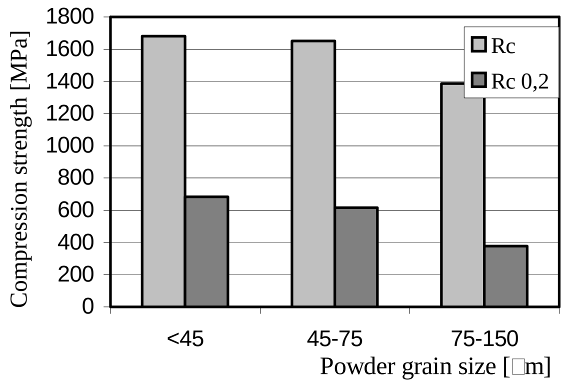

Fig. 8. The influence of titanium powder grain size on mechanical properties of sintered alloy Ti15Mo2,8Nb

The values of compressive strength R_C and yield point $R_{C0,2}$ were calculated basing on the obtained graphs. The results of comparative tests of investigated materials are presented in table 1 and in figures 8 and 9. The sinters fabricated of small fraction powders after a short grinding time showed highest strength properties. In case of samples produced from large-grain titanium powder (fraction 75-150 μm) the compressive strength as well as the yield point had clearly lower values. Prolonging the grinding time of powder mixtures also does not influence positively the strength properties. In case of sample № 6 made of powder grinded 4-hour – brittle cracking was observed under loading of 757 MPa.

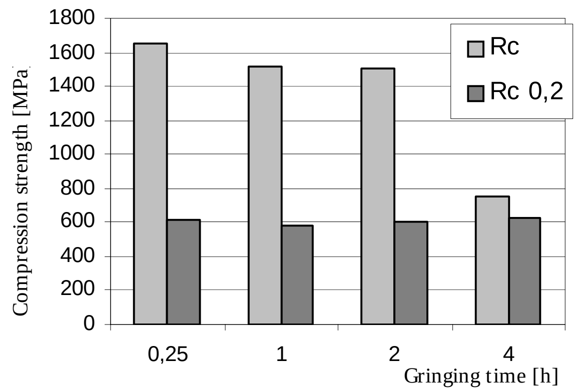

Fig. 6. The influence of grinding time of prowder mixtures on mechanical properties of sintered alloys Ti15Mo2,8Nb

Summary

The purpose of the study was assessment of possibilities of implant material manufacture on base of Ti15Mo2,8Nb titanium alloy by means of powder metallurgy method. Basing on the obtained results it can be concluded that the utilized parameters of the technological process allow producing sinters, characterized by good plasticity. Comparative tests of the influence of grain size of titanium powders and grinding time allow choosing optimal conditions. The highest compactibility and strength properties are shown by sinters of titanium powders with the smallest grains. Use of large grain fraction caused substantial decrease in strength properties. Prolonging the grinding time of powder mixtures does not influence positively compactibility and strength of sinters. This fact can be explained by the presence of Al_2O_3 particles and formation of stress in titanium grains as a result of prolonged grinding.

Acknowledgments

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