SYNTHESIZING CONDITIONS AND STRUCTURAL-PHASE STATE OF TI-NB ALLOY WHEN SELECTIVE LASER MELTING

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Keywords: selective laser melting, composite powder, low-modulus Ti-Nb alloy, micro-structure, phase composition, modulus of elasticity, implant materials.

Abstract
A searching experiment aimed at identifying appropriate process conditions to form single tracks of titanium and niobium composite powder is reported to be carried out by an SLM experimental facility. SLM conditions were determined and a set of Ti-Nb alloy multilayer samples was produced relying on the experimental results. Macro-and micro-structures, phase composition of multilayer samples were studied. There are fine-and medium-grained zones detected in selective laser melted Ti-40 wt. % Nb (Ti-40Nb) alloy. Phase composition of the alloy is similar to the main phase of titanium and niobium β-phase solid solution (5–7 μm grains) and non-equilibrium martensite α''-phase (0.1–0.7 μm grains). Grains of α''-phase with low niobium concentration are found on β-phase grain boundaries. Relying on measured modulus of elasticity a low-modulus Ti-Nb alloy is reported to be synthesized in the SLM-process.

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1. Introduction

Bioinert titanium and its alloys, iron-nickel alloys, bio-ceramics, bio-glass ceramics, and bio-polymers are major materials used for implants manufacturing. Titanium and its alloys have a high modulus of elasticity. For instance, modulus of elasticity of titanium BT1-00 and BT1-0 (Grade 1, 2) is reported to be 100–110 GPa. Mechanical compatibility necessitates adequacy of implant mechanical properties and bone tissue characteristics. It is, mainly, compliance with a low modulus of elasticity, 10 - 60 GPa in respect to the bone tissue type. Therefore, Ti-Nb alloys are characterized by higher bio-mechanical compatibility. These alloys, having diverse chemical composition and modulus of elasticity 55-60 GPa, are distinguished by pseudoelasticity, making their properties similar to bone tissue and improving their bio-mechanical compatibility.

Metallurgical manufacturing procedures of these alloys are quite well-known but complex, labor-intensive and expensive, in particular, because of the difference in melting temperatures and density of titanium (1668°C, 4.51 g/cm^3) and niobium (2468°C, 8.57 g/cm^3), and the necessity of applying compound and multistep thermomechanical processing methods to synthesize a sample with homogenous structure and chemical composition. Nearly a half of a sample volume is lost when processing. Thermal properties of titanium and niobium, e.g. thermal conductivity, thermal capacity and coefficient of linear expansion, are pointed out to be considerably different. Thermal conductivity of niobium is much higher as compared with that of titanium, whereas titanium is characterized by better thermal capacity. It also complicates synthesizing technology of alloys based on this system.

In some cases additive technologies, e.g. SLM 3D-printing, are the only alternative to conventional methods of casting or CNC-machining complex parts. Therefore, SLM advance is especially promising for production of medical implants and endoprostheses [1, 2]. Moreover, it allows manufacturing products with a projected porosity [3], which, in turn, is relevant for better osteointegration of implant material with bone tissue.

That is why, SLM updating, improvement of its modes and research into processes of structure and phase formation are vital issues at the moment. The authors of work [4] report preliminary mechanical activation of a powder blend proceeded with selective laser melting of the obtained composite. The samples have low mechanical strength and a high level of porosity. A mechanical Ti and Nb powder blend was used for selective laser melting of samples [5]. A lot of impurities in form of partly melted niobium are found in the low strength and highly porous structure. The most acceptable results are obtained when using gas atomized powder (GAP) of ready-made Ti-45Nb powder [6]. This work is aimed at improvement of SLM modes to produce a low-modulus Ti-Nb alloy, consisting of mono-layers of composite titanium and niobium powder and having a low modulus of elasticity.

2. Material and methods

A selective laser melted layer is formed via line-by-line laser beam melting of a powder. A melted track is formed when displacing a laser beam. It is a top-priority issue to determine modes, providing formation of a uniform and continuous track, which, in turn, is necessary to make a quality layer without big pores and uniform in thickness.

Searching experiments to determine process conditions of synthesizing multilayer Ti-Nb composite powder were carried out by experimental additive manufacturing facility «VARISKAF-100MB». This facility allows layer-by-layer selective laser melting of powder products with diverse configuration. A powder material can be melted both in vacuum and in various gaseous environments. A basic circuit of facility «VARISKAF-100MB» is outlined in Fig. 1.

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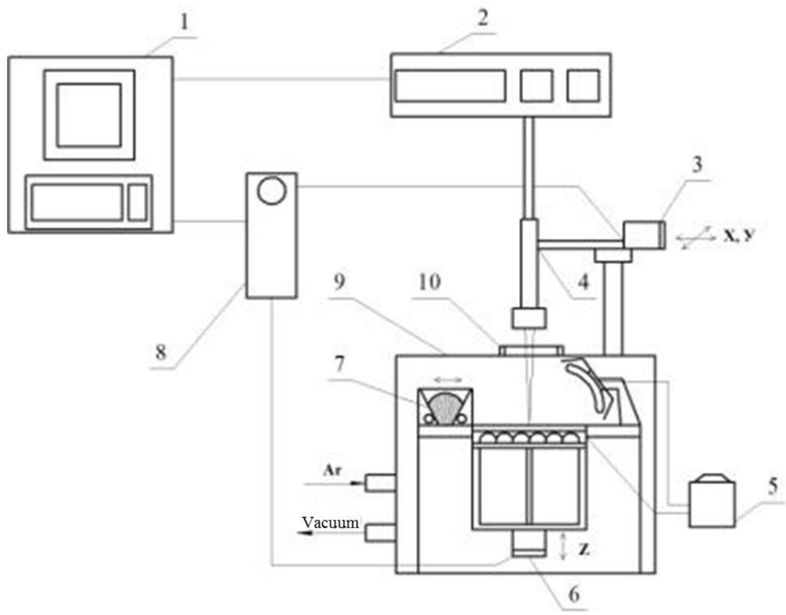

Figure 1. Basic circuit of facility «VARISKAF-100MB». 1 – PC, 2 – ytterbium fiber laser, 3 – assembly for laser displacement in X-Y plane, 4 – collimator, 5 – power source for base pre-heating and infrared heater, 6 – assembly for machine bench Z-displacement, 7 – powder distribution unit, 8 – CNC system, 9 – vacuum chamber, 10 – work opening.

Before SLM-process is started air is pumped out the vacuum chamber (9), so the pressure is ~10^{-4} and oxygen is removed. Afterwards the powder is vacuum-heated up to 200°C by a power source (5). Complete oxygen degassing requires keeping the powder at a certain temperature for 30 min. The chamber is filled with high-purity argon being at excessive vs. atmospheric pressure. The machine bench is moved down at a certain distance by a stepping motor (6). A powder material bunker (7) is displaced over the machine bench. The powder is poured over, making a layer uniform in thickness. Laser output (2) gets into collimator (4) over a fiber-optic canal, and passing through a work opening (10) is focused by lens on the surface of a powder material. A laser beam is displaced by flying optics (3), which is CNC-operated (8) according to the PC software (1).

For the purpose of experiments titanium (60 wt. %) and niobium (40 wt. %) composite powder (average particle size 20 μm) is used.

The first experiment involves melting single tracks in various process conditions: laser power P = 68, 86, 106 W; scanning speed V = 500, 1000, 1500, 2000, 2500, 3000 mm/min; laser spot diameter d = 0.2 mm. The powder was poured over the base, so its thickness varies from 0.1 to 0.4 mm. The pre-heated powder was kept at temperature t = 100°C. Experiments aimed at determining appropriate melting conditions of powder materials were carried out; a detailed consideration of the experimental technique is also provided [7].

A uniform in thickness and density layer of powder material was poured over the titanium BT1-0 base when forming single mono-layers. The following process conditions of forming single mono-layers were determined in view of conducted searching experiments: scanning speed V = 1500 and 2000 mm/min, laser power P = 68, 86 and 106 W. Scanning pitch and laser spot diameter were 0.1 mm, and 0.2 mm, respectively. Thickness of the layer was ~1 mm with its upper surface melted by laser beam to avoid heat passing through the base in the melting zone. Laser beam scanning pattern of the powder material surface is a line-by-line zigzag (Fig. 2).

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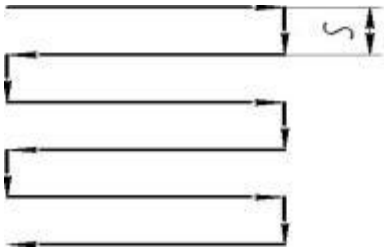

Figure 2. Scanning pattern.

Assessment of mechanical characteristics required indentation of 10×10 mm mono-layer samples by Nano Hardness Tester NHT-S-AX-000X (CSEM, Switzerland). The assessment involves analysis of time-dependent load vs. penetration depth and indentation area (Vickers Pyramid). Structure and phase composition of the samples were studied by optical metallography, scanning electron microscopy (SEM), energy-dispersive micro-analysis (EDMA) and X-ray structural analysis with such instruments as Altami MET 1 MT, LEO EVO 50, and DRON-7 in the Shared Use Center «NANOTECH», Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences.

3. Results

The searching experiment results in a set of melted powder tracks. All tracks are of diverse structure and geometry. The tracks appears to consist of a drop fraction, uniform, and combined (drops and smoothly melted track) structures. Tracks with the most uniform and combined structures were made in process conditions, given in Fig. 3.

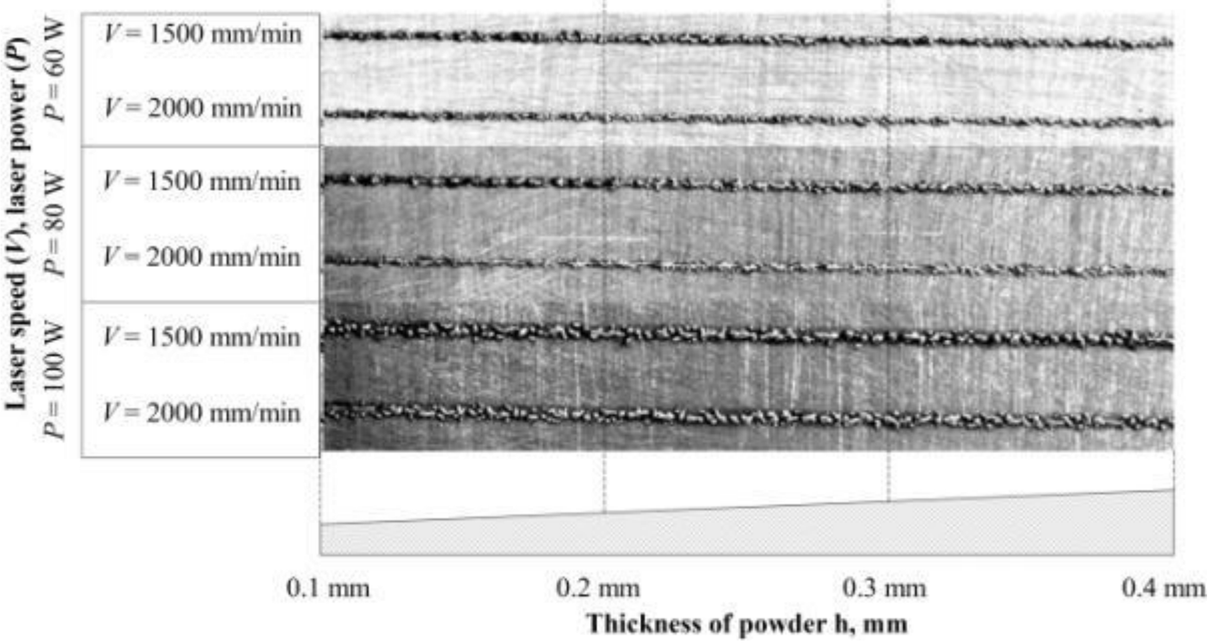

Figure 3. Tracks with uniform and combined structures.

As it’s seen in Fig. 3, melted tracks get wider due to rising laser power. Increasing width of melted tracks has a positive effect on layer formation, since track width exceeds the laser spot. It allows complete melting and re-melting of adjacent tracks. Melted track width vs. laser power dependence is shown in Fig.4.

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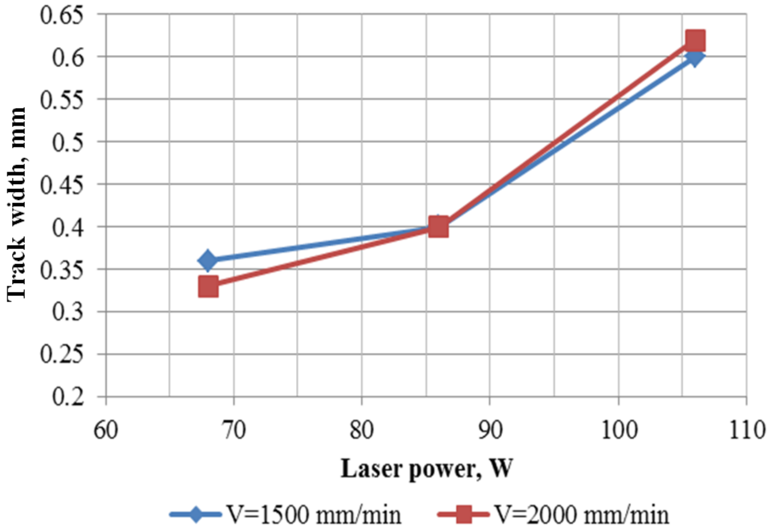
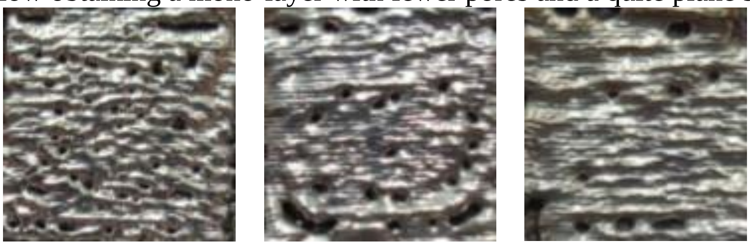


Figure 4. Melted track width vs. laser power dependence.

The surfaces of monolayer samples produced in process conditions, assigned in the searching experiment, are given in Fig. 5. A surface porosity is detected when analyzing the images of monolayer samples. The number of surface pores is reduced when increasing the laser power at scanning speed *V*=1500 mm/min. A certain alignment of the sample surface is registered (Fig. 5 a, b, c). The growth of speed up to V=2000 mm/min results in changing surface porosity. The number of pores is decreased but they gain in size in conditions of growing laser power P=68 to P=106 W (Fig. 5 d, e, f).

The decrease in the number of surface pores under power augmentation is conditional on growing heat input in the melting zone [8]. The melted zone gets significantly extended as compared with the laser spot (Fig. 4). Heat conditions have a positive effect on melting or re-melting of adjacent tracks. However, the growth of scanning speed has an inverse effect. An exposure time of a powder surface section is shortened, heat input is decreased, and the effect of re-melting declines, so tracks are melted worse with each other. As a result, surface pores are upsized. Having carried out the analysis above, appropriate process conditions are determined: scanning speed *V*=1500 mm/min and laser power *P*=106 W, which allow obtaining a mono-layer with fewer pores and a quite plane surface.



V=1500 mm/min, *P*=68 W a) | *V*=1500 mm/min, *P*=86 W b) | *V*=1500 mm/min, *P*=106 W c)

V=2000 mm/min, *P*=68 W d) | *V*=2000 mm/min, *P*=86 W e) | *V*=2000 mm/min, *P*=106 W f)

Figure 5. Optical images of mono-layer sample surfaces

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Having SM-analyzed the cross-section structure of mono-layer samples, a monolayer is detected to be made of completely melted and crystallized material, comprising two zones (Fig. 6). The lower part of a mono-layer is a fine-grained zone; the most grains are 2 to 8 μm. The fine-grained structure changes for the medium-grained one with the grain size 7–24 μm. There are pores detected throughout the mono-layer section.

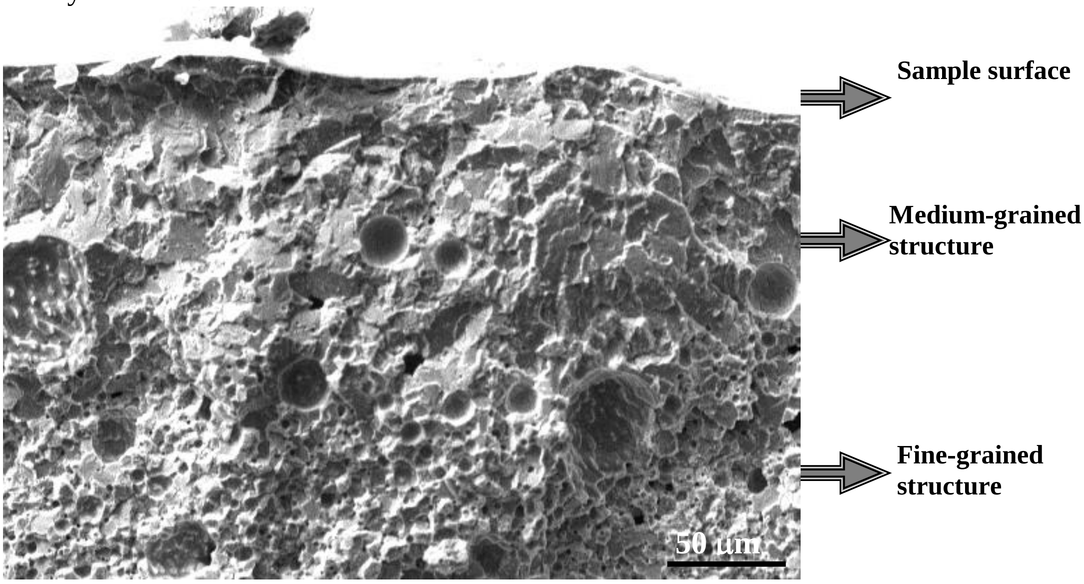

Figure 6. REM –images of fractured monolayer surface cross-section

Taking into account specifics of zone structures, the process of mono-layer formation can be described as follows. Powder material near the heat source is melted under the laser beam action. When cooling the melted material zone, heat is removed towards the solid-powder and the base. Crystallization occurs backwards from the powder material layer. When laser output contacts with the surface of material a zone of melted material – a crystallizing pool is formed. A fine-grained structure with tiny gaseous pores on grain boundaries is generated due to high cooling speed in the low part of the pool. In the upper part of the crystallizing pool, where heat removal is complicated, cooling conditions further more balanced crystallization of material. As a result a low-porosity zone with bigger grains is formed in the upper part of a mono-layer.

Therefore, a sample has inhomogeneous structure due to various SLM temperature and time conditions of powder melting, crystallization and cooling.

Main phases, their morphology and localization in the fine-grained melted zone were detected by optic metallography (Fig. 7a), X-ray structural analysis (Fig. 7b) and transmission electron microscopy [9]. β-phase and α''-phase are formed in the melt when selective laser melting (Fig. 7b). 5-7 μm β-phase grains, containing up to 45 wt. % niobium, are decorated by finer grains of metastable 0.1-0.7 μm α''-phase of titanium (Fig. 7a, [9]). Concentration of niobium in α''-phase grains is low; approximately 15-20 wt. %.

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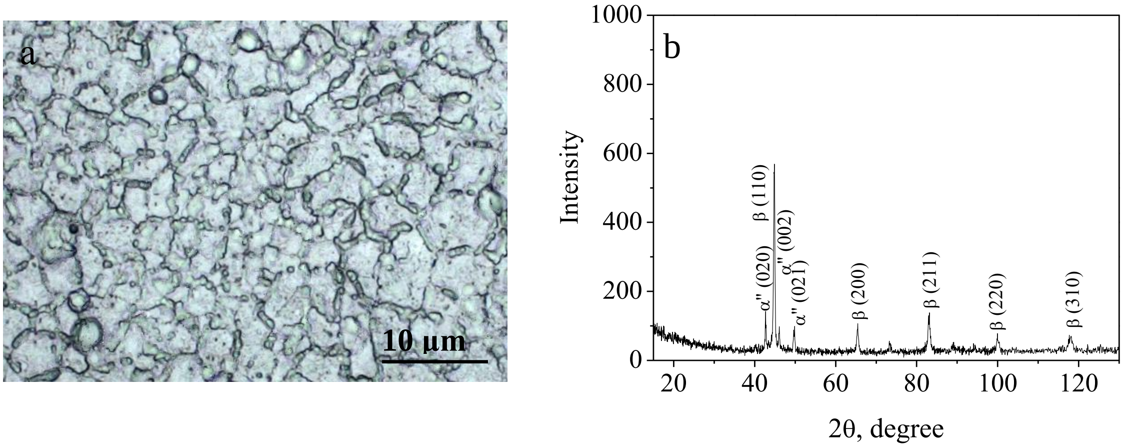

Figure 7. Optical images of the micro-structure (a) and X-ray diffractogram fragment of the sample (b)

Samples synthesized at scanning speed *V*=1500 mm/min and laser power P = 68, 86, 106 W were used to measure Young's modulus. The measurement results are given in Fig. 8.

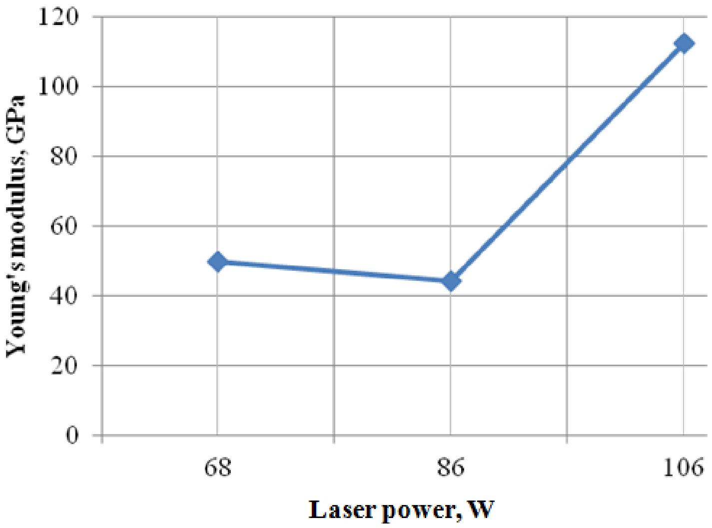

Figure 8. Young's modulus vs. laser power dependence

The values of Young's modulus of samples synthesized at laser power P = 68 and 86 W are 49 and 44 GPa, respectively. These values are comparable with the modulus of elasticity for low-modulus Ti-(40-45) wt. % Nb alloys [10]. Further increasing laser power causes the growth of Young's modulus up to 114 GPa. The measurement results of Young's modulus (Fig. 8) and X-ray structural analysis (Fig. 7) sustain formation of a low-modulus alloy when selective laser melting composite Ti-60 wt. % and Nb 40 wt. % powder in the assigned process conditions P=86 W and V=1500 mm/min.

4. Conclusions

Ti-40Nb alloy in form of a mono-layer is SLM-synthesized of composite Ti-60 wt. % and Nb 40 wt. % powder. The mono-layer has an inhomogeneous structure, being fine-grained to medium-grained throughout the section. The inhomogeneity of mono-layer structure is caused by changing conditions of heat removal from alloy formation zone in the process of crystallization and cooling. It is revealed that the quality of obtained mono-layer and Young's modulus values can be varied broadly by laser power and exposure time.

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