IN-SITU SYNTHESIS OF TITANIUM ALLOYS FROM ELEMENTAL POWDERS BY LASER ADDITIVE MANUFACTURING

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Abstract

Additive manufacturing offers great potential for producing metal parts with a high degree of geometrical complexity and high mechanical properties. However, the number of alloys in the form of powder material that can be applied in these technologies are limited at the moment. A solution for this problem might be found by utilizing a mechanical mixture of elemental powders for manufacturing parts by laser additive manufacturing which would result in the in-situ synthesis of the required alloy. This work presents the results of the study of the in-situ synthesis of Ti-5Al, Ti-6Al-7Nb and Ti-22Al-25Nb alloys by laser additive manufacturing, i.e. selective laser melting (SLM) from elemental powders. Titanium, aluminum, and niobium powder particles were used as initial powders, which were mechanically mixed to prepare powder mixtures of the corresponding alloys. It was shown that SLM technology can be successfully utilized to synthesize α-titanium Ti-5Al alloy from elemental powders with homogeneous chemical composition and high mechanical properties. In order to fully dissolve niobium particles and achieve a homogeneous chemical composition and microstructure of Ti-6Al-7Nb and Ti-22Al-25Nb alloys heat treatment of bulk samples after SLM is required. The microstructure, phase composition of the obtained material before and after different heat treatments were studied, also the mechanical properties of the obtained alloys were investigated.

Keywords: Additive manufacturing, selective laser melting, titanium alloys, in-situ synthesis

1. INTRODUCTION

Titanium alloys are widely used in different industries, for example, for producing aviation parts due to its high specific strength, corrosion resistance and its ability to withstand relatively high temperatures. In the recent years, there is a tendency for increasing a fraction of titanium parts in the total mass of a gas-turbine engine. However, the problem of developing high-temperature titanium alloys which could have a working temperatures 600 - 750 °C has not been solved yet. Orthorhombic titanium alloys based on a Ti_2AlNb-phase are considered to be most promising materials for manufacturing parts of a last stage compressor and a turbine of a new generation engine due to their high specific strength and a working temperature higher than 600 °C [1]. However, a possibility of utilizing such alloys in additive manufacturing technologies has not been studied.

Modern industry development rates require introduction of advanced manufacturing techniques for metal parts. One of them is additive manufacturing which combines digital design for creation a CAD-model of a future part and production of the part by adding material layer-by-layer using special equipment [2, 3]. Selective laser melting (SLM) of metal powders is one of the most accepted and advanced technique for manufacturing of metal parts by additive manufacturing.

Metal powders are used for the initial feedstock material in SLM technology. The powders for additive manufacturing are usually produced by gas of plasma atomization methods. Due to difficulties in manufacturing of powders of complex alloys for additive manufacturing, a range of commercially available materials is limited.

A solution for this problem might be found by applying alternative methods for producing titanium alloys parts by additive manufacturing. One of these methods is utilizing a mechanical mixture of elemental powders for manufacturing parts by layer-by-layer synthesis which would result in in-situ synthesis of the required alloy [4]. At the moment, there several studies which describe investigations of a layer-wise in-situ synthesis for such systems as Ti-Ni [5], Ti-Ta [6, 7], Ti-Al-V-Mo [8]. These papers usually show that SLM technology can be successfully used for in-situ synthesis of alloys which are not available in the form of a pre-alloyed powder.

The aim of this work is to investigate and evaluate the possibility of a layer-by-layer in-situ synthesis of different types of titanium alloys from elemental powders by SLM. Using Ti-5Al, Ti-6Al-7Nb и Ti-22Al-25Nb elemental powder mixtures we synthesized bulk specimens with two lasers of different power and spot diameter. The microstructure, phase composition of the obtained material before and after different heat treatments were studied, also the mechanical properties of the obtained alloys were investigated.

2. MATERIALS AND METHODS

Three titanium alloys were chosen for study of in-situ synthesis from elemental powders: Ti-5Al (wt.%), Ti-6Al-7Nb (wt.%), Ti-22Al-25Nb (at.%). The initial powders used for preparing powder mixtures of Ti-5Al, Ti-6Al-7Nb, and Ti-22Al-25Nb alloys were titanium (CP Ti Grade 2), aluminum (99.9% purity) and niobium (99.7% purity). The images of the initial powder particles are shown in **Figure 1**. Titanium and aluminum powder particles have spherical shape while niobium particles have an irregular shape.

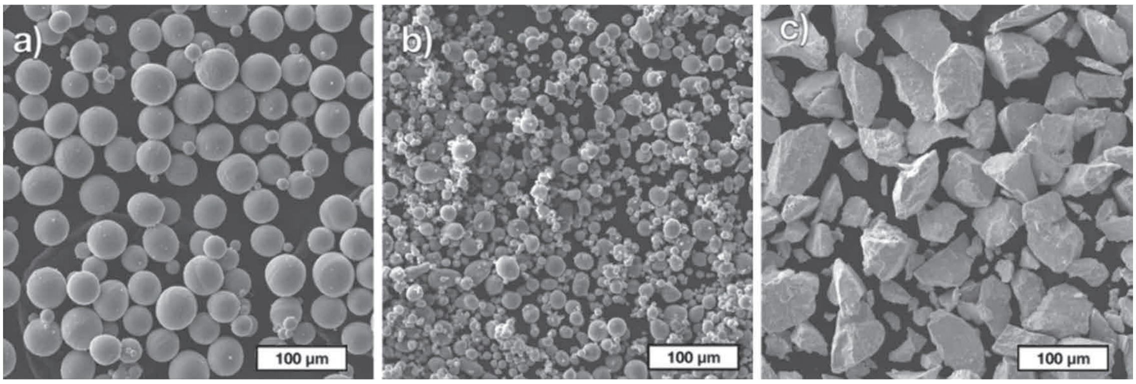


Figure 1 Images of the initial powder particles: Ti (a), Al (b) and Nb (c)

Particle size distribution of the powders was measured by laser diffraction technique with Analysette 22 NanoTec plus. The information about particles size distribution of the powders is presented in **Table 1**.

Table 1 Particle size distribution of the initial powders

Powder	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
Ti	23.8	44.6	76.1
Al	8.5	21.2	41.1
Nb	15.1	32.9	65.1

The powder mixtures were prepared from initial powders by mixing them in a tumbler mixer for 12 hours. The time of mixing was chosen so that to obtain an uniform distr ibution of several elements in the mixture. SLM Solutions 280 HL machine was used to synthesize bulk samples. The synthesis of the samples was carried out on a titanium base plate. A thin powder layer was deposited on the platform. The deposition is carried out by a special recoater device, which contains powder and distribute the powder to create a smooth layer. After that the layer is processed by laser irradiation. A laser beam is being focused on the surface of the powder layer, creating a laser spot. The laser beam is moved with a mirror system accordingly to the computer file. By applying laser irradiation, the powder layer is melted and then creating a solidphase structure. After that the platform is lowered by one layer thickness and a new powder layer is deposited. This process is repeated until the final part is produced. The synthesis of the samples was carried out in an argon atmosphere. The SLM 280 HL machine is equipped with two fiber lasers with 1.07 μm wavelength and maximum power 400 W and 1 kW. The laser with 400 W maximum power has a laser spot with a diameter about 80 μm and a Gaussian intensity profile, while the laser with 1 kW maximum power has a laser spot diameter about 700 μm and a uniform intensity profile. To study microstructure, phase composition of the synthesized material bulk samples of 10x10x10 mm size were produced. For mechanical tests, cylindrical specimens of 12 mm diameter and 90 mm length were manufactured and then machined to size according to ISO 6892-1. The SLM process parameters used in this work to produce bulk samples are presented in **Table 2**.

Table 2 SLM process parameters used to produce bulk samples

Laser profile	Laser power (W)	Scanning speed (mm/s)	Hatch distance (μm)	Layer thickness (μm)	Volume energy density (J/mm^3)	Laser spot diameter (μm)
Gaussian	275	760	120	50	60.3	~80
uniform	950	350	450	100	60.3	~700

The microstructure studies were carried out with a scanning electron microscope (SEM) TESCAN Mira 3 LMU using both secondary electrons (SE) and backscattered electrons (BSE). This microscope is equipped with an energy-dispersive X-ray spectroscopy (EDS) option which was used for local chemical analysis of the samples. The phase composition was analyzed with a Bruker D8 Advance X-ray diffraction (XRD) meter using CuKα (λ = 0.15418 nm) irradiation. The mechanical tensile tests were carried out at room temperature and 400 ºC according to GOST 1497-84 (ISO 6892 «Metallic materials - Tensile testing») and GOST 9651-84 (ISO 783 «Metals. Methods of tension tests at elevated temperature») using Zwick/Roell Z050 testing machine. The samples made from Ti-5Al mixture were heat treated in a MTI VBF-1200X vacuum furnace. They were annealed at 750 ºC for 1 hour and furnace cooled. Ti-6Al-7Nb and Ti-22Al-25Nb samples were sealed in quartz tubes in vacuum and heat treated in a KJ-1700X muffle furnace. They were annealed at temperatures from 1050 ºC to 1350 ºC for 1 to 4 hours with furnace cooling.

3. RESULTS AND DISCUSSION

Figure 2 shows the image of Ti-5Al powder mixture after mixing for 12 hours. Titanium and aluminum powder particles kept their spherical shape, which is important for the flowability of the powder. Aluminum particles have smaller size compared to titanium and are uniformly distributed in the mixture. However, there are some coagulated fine particles of aluminum in some places of the mixture.

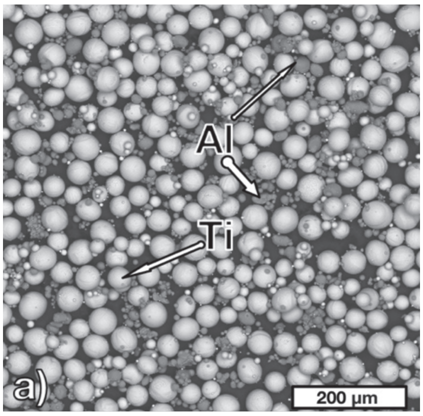
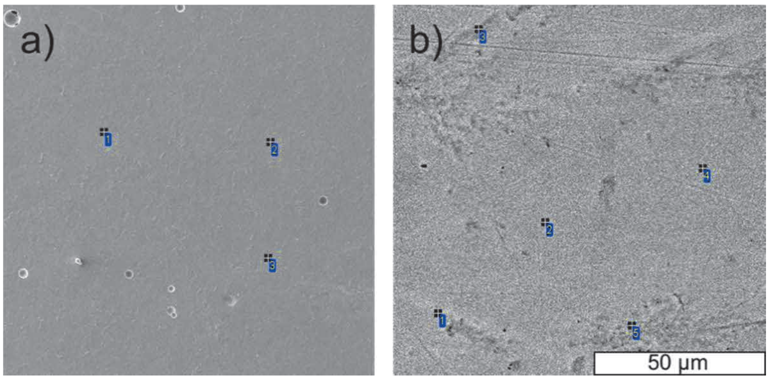


Figure 2 Ti-5Al powder mixture

The SEM-images of the non-etched sample surface in BSE are shown in **Figure 3**. There are no visible areas with separate unmelted particle of Ti or Al. The relative density of sample, measured by the Archimedes method, is 98.97±0.07 %. The EDS analysis in different points showed that aluminum particles were fully dissolved in titanium matrix during the SLM process both using 275 W and 950 W laser power. However, the content of aluminum for 275 W samples is closer to the initial aluminum content of the powder mixture, while 950 W samples have slightly lower aluminum content, which might be the result of its evaporation during the SLM process.

a)

Al (wt.%)	Ti (wt.%)
4.9	95.1



b)

Al (wt.%)	Ti (wt.%)
4.55	95.45

Figure 3 SEM-images of the non-etched samples' surfaces produced from Ti-5Al powder mixture with 275 W (a) and 950 W (b) laser power. EDS analyses - mean values of concentrations

The XRD results (**Figure 4**) showed that the samples produced from Ti-5Al powder mixture with a laser with a big spot diameter and 950 W as well as with a small spot diameter and 275 W power have only HCP-titanium phase with aluminum dissolved in it.

The microstructure of the bulk samples (**Figure 5**) consists of α-titanium equiaxed grains of different size. The grain size tends to be bigger with using the higher laser power, which can be caused by difference in cooling rates during the SLM process. While using 275 W laser with a Gaussian intensity profile the samples are more prone to cracking during the SLM process compared to 950 W laser with a uniform intensity profile, which is a result of higher cooling rates in case of the laser with a small spot diameter. In this regard, the samples for mechanical tests were produced using 950 W laser power.

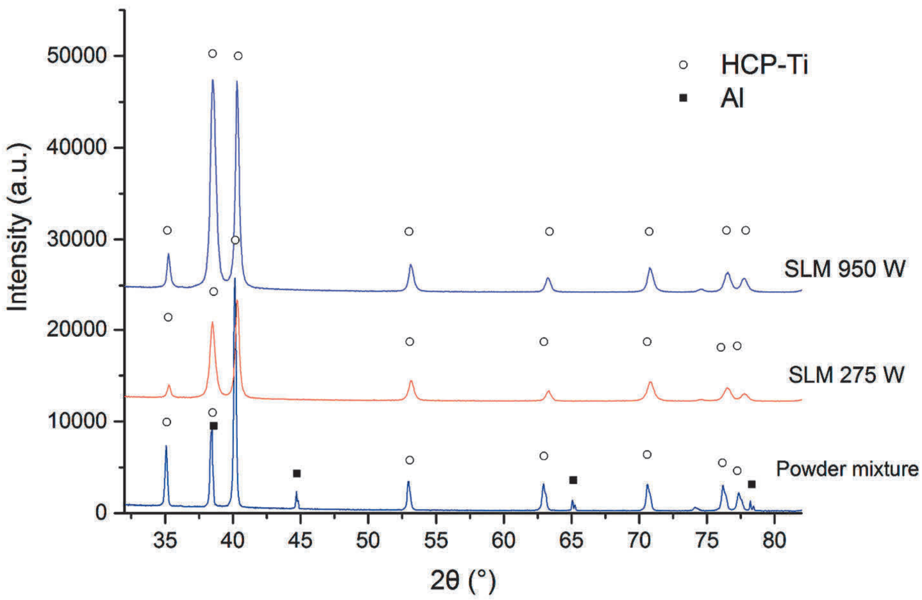


Figure 4 The XRD results for Ti-5Al powder mixture and bulk samples produced by SLM

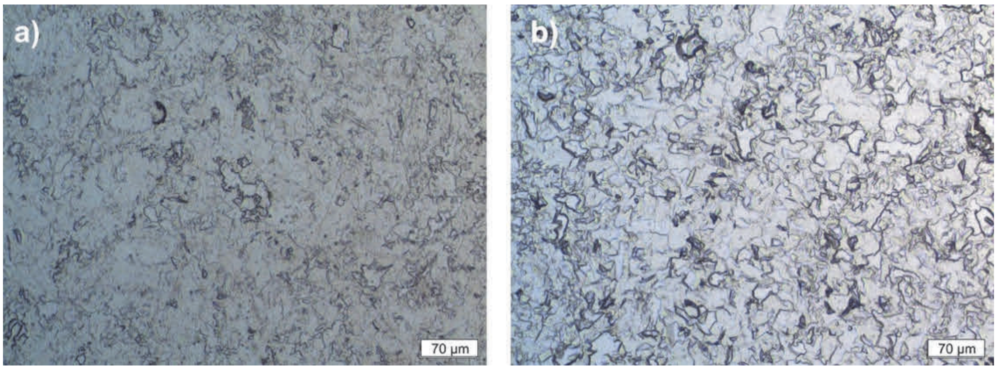


Figure 5 The microstructure of the Ti-5Al samples produced with 275 W (a) and 950 W (b) laser power

The results of mechanical tests of the specimens after annealing at 750 °C for 1 hour and comparison with the properties of conventionally manufactured material are shown in **Table 3** The tensile strength of the synthesized material at room temperature is 897±7 MPa with the elongation at break 5.0±1.2 %, which is comparable to conventionally produced Ti-5Al alloy. The tensile strength at 400 °C is 521±12 MPa, which is higher than tensile strength of a casted Ti-5Al alloy and in the order of hot-rolled material.

Table 3 Mechanical properties of Ti-5Al alloy, obtained from elemental powder mixture by SLM and their comparison with the properties of conventionally produced Ti-5Al alloy

Testing temperature (°C)	Alloy	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
20	Ti-5Al (SLM after annealing)	855 ± 15	897 ± 7	5.0 ± 1.2
	Ti-5Al casted [9]	-	800	6
	Ti-5Al hot rolled and annealed [10]	-	685-735	6-8
	Ti-5Al (powder sintering at 1300-1400 °C) [9]	-	590-830	0.7-6.9
400	Ti-5Al (SLM after annealing)	412 ± 10	521 ± 12	9.7 ± 1.1
	Ti-5Al casted [10]	-	350	10
	Ti-5Al hot rolled and annealed [9]	-	520	-

During the SLM of Ti-6Al-7Nb powder mixture titanium and aluminum particles were fully melted, while niobium particles (white areas) were only partially melted (**Figure 6**). The synthesized material obtained by SLM consists of a solid solution of alloying elements in titanium with separate niobium particles. The maximum relative density of the synthesized material is 98.9 %.

Point	Al (wt.%)	Nb (wt.%)	Ti (wt.%)
1	0.2	98.2	1.6
2	0.5	94.2	5.3
3	6.5	7.2	86.3
4	5.9	5.5	88.6

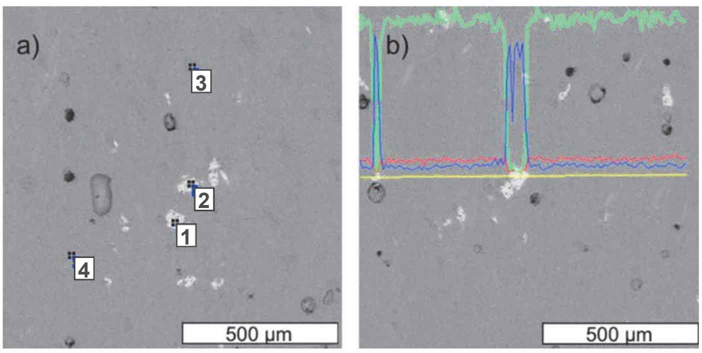


Figure 6 SEM-images of the non-etched sample surface produced from Ti-6Al-7Nb powder mixture with 950 W laser power (green line corresponds to Ti concentration, red - Al, blue - Nb). EDS analyses - mean values of concentrations

In order to dissolve niobium particles and achieve more homogeneous chemical composition in the synthesized material, the specimens were annealed at conditions. The microstructures of the synthesized Ti-6Al-7Nb alloy are shown in **Figure 7**. If the annealing temperature were lower than 1350 ºC niobium particles did not dissolve in the matrix. At 1350 ºC and soaking time 3.5 hours separate niobium particles were not seen in the material. The alloy features (α+β)-lamellar microstructure. The presence of α- and β-phases is also confirmed by the results of XRD analysis (**Figure 8**). Increasing the annealing temperature and time leads to higher volume content of β-phase and thicker α-plates.

The results of mechanical tests for Ti-6Al-7Nb specimens after annealing at 1350 ºC for 3.5 hours are shown in **Table 4**. The yield and tensile strength of the material are 770 and 850 MPa correspondingly with the elongation at break 2 %. The strength of the obtained alloy is in the order of Ti-6Al-4V alloy produced by conventional sintering of powders.

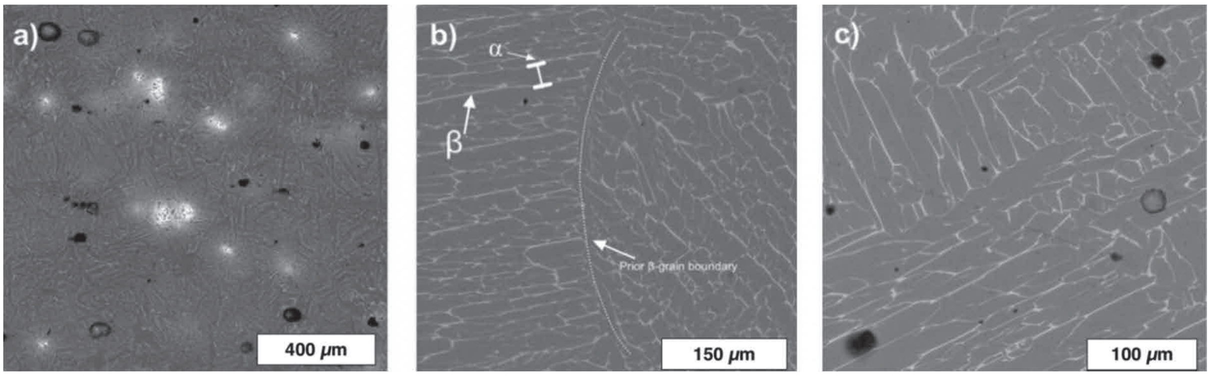


Figure 7 The microstructure of the Ti-6Al-7Nb alloy after annealing at different conditions: (a) 1050 °C, 1 hour; (b) 1350 °C, 2.5 hours; (c) 1350 °C, 3.5 hours

The Ti-22Al-25Nb powder mixture was used to produce bulk specimens with 950 W laser power. Their maximum relative density is 97.3%. The polished surface of the Ti-22Al-25Nb specimen features separate niobium particles (white colour) which are nonuniformly distributed in the material (**Figure 9**). There are some areas where all elements were melted during the SLM process, but were not fully interfused during melting and crystallization. That resulted in areas with unevenly mixed elements, which can be seen in the BSE-image. These areas could be formed as a result of Marangoni convection induced by surface tension gradient in the melt pool. Melted components of the mixture are mixed under the influence of the capillary forces which leads to mixing of the elements during the SLM process.

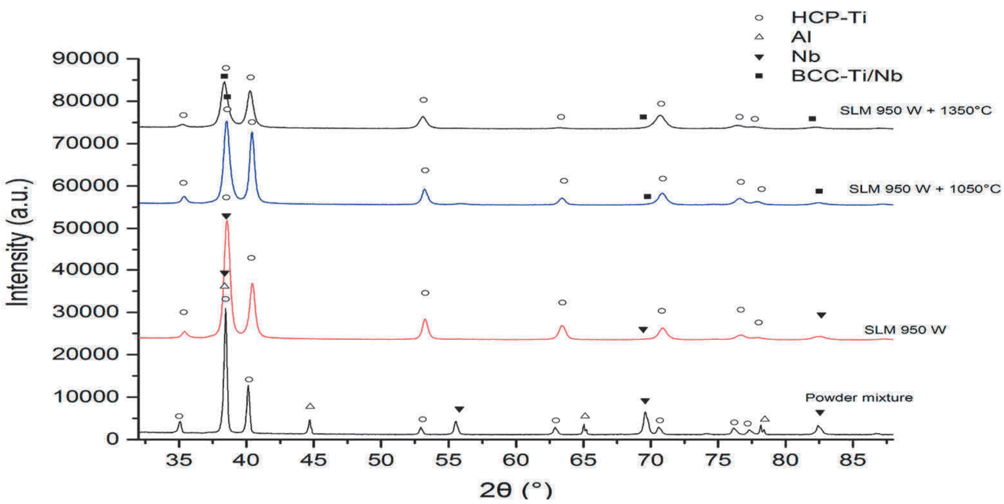


Figure 8 The XRD results for Ti-6Al-7Nb powder mixture and bulk samples produced by SLM before and after heat treatment

Table 4 Mechanical properties of Ti-6Al-7Nb alloy, obtained from elemental powder mixture by SLM, and their comparison with the properties of other alloys, testing temperature: 20 °C.

Alloy	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
Ti-6Al-7Nb elemental powders (SLM after annealing)	774 ± 10	850 ± 10	2.0 ± 0.2
Ti-6Al-7Nb pre-alloyed powder (SLM after annealing) [11]	1360 ± 30	1480 ± 26	1.4 ± 0.6
Ti-6Al-4V (VT6) (sintering) [9]	740	830	5

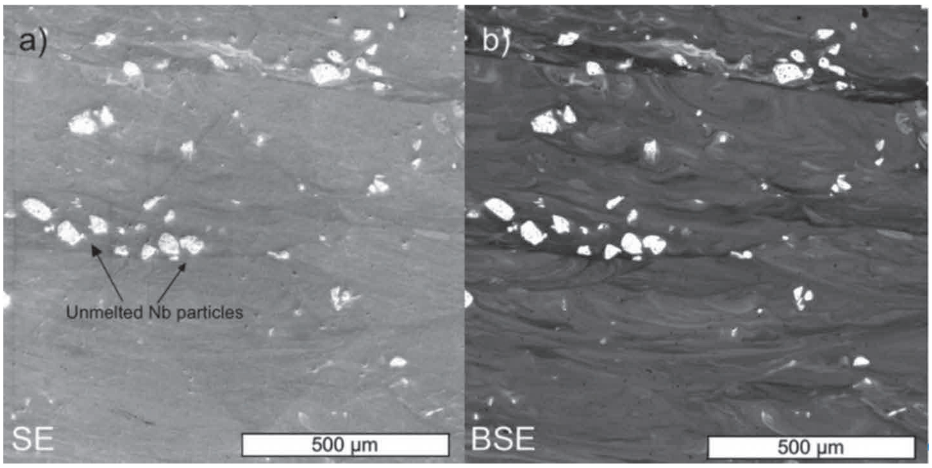


Figure 9 SEM-images in SE (a) and BSE (b) of the Ti-22Al-25Nb alloy obtained by SLM from elemental powders

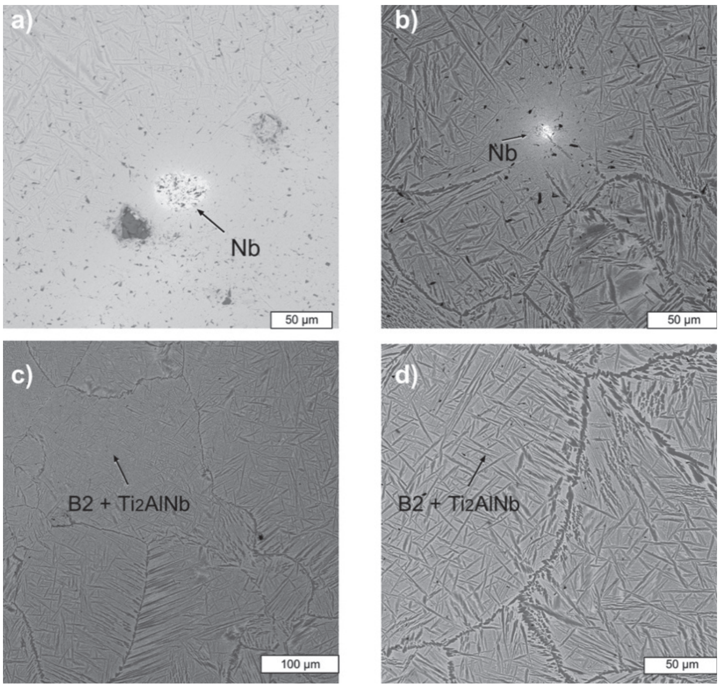


Figure 10 The microstructure of the Ti-22Al-25Nb specimens after annealing at different conditions: (a) 1250 °C, 2.5 hours; (b) 1250 °C, 4 hours; (c) 1350 °C, 2.5 hours; (d) 1350 °C, 3.5 hours

In order to further dissolve niobium, Ti-22Al-25Nb samples were annealed at 1250-1350 ºC for 2.5-4 hours. The microstructures of the material after heat treatment are shown in **Figure 10**. Annealing at 1250 ºC did not result in diffusion of niobium in the matrix. After annealing with furnace cooling the areas with already dissolved alloying elements feature acicular precipitates of Ti2AlNb-phase. Increasing the annealing temperature to 1350 ºC with 2.5 hours holding time resulted in diffusion of niobium, however there are areas with higher niobium content where there are no secondary phase precipitates. Increasing annealing time to 3.5 hours led to fully dissolved niobium without areas with its higher content. The microstructure of the material consists of B2/β-grains with Ti2AlNb-precipitates in form of needles.

4. CONCLUSION

Selective laser melting can be successfully utilized to synthesize titanium alloys from elemental powders. In case of Ti-5Al alloy the microstructure of the material consists of α-titanium grains. The tensile strength is 897 ± 7 MPa with the elongation at break 5.0±1.2 %. In case of Ti-5Al alloy grain size is bigger with higher laser power. While using 275 W laser power with the Gaussian intensity profile and small laser spot the samples are more prone to cracking during the SLM process compared to 975 W laser power with the uniform intensity profile and big laser spot due to higher cooling rates in case of the first one. Selective laser melting can be used to synthesize Ti-6Al-7Nb alloy from elemental powders, however the material features separate non-melted niobium particles inside areas with a uniform distribution of Ti, Al and Nb. After heat treatment at 1350 °C niobium particles dissolve in the matrix with the formation of (α+β)-lamellar microstructure. The tensile strength of the alloy is 850 MPa with the elongation at break 2 %. In case of orthorhombic Ti-22Al-25Nb alloy obtained from elemental powders by SLM, the material consists of B2/β-phase with uniformly distributed non-melted niobium particles. After annealing niobium dissolves in the matrix with the formation of needle-shaped Ti_2AlNb precipitates.

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