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Oxygen and nitrogen concentrations in the Ti-6Al-4V alloy manufactured by direct metal laser sintering (DMLS) process

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Two machines from two scientific centers (Russia and South Africa) were used for the manufacturing of the Ti6Al4V alloys by the direct metal laser sintering. The chemical composition of powders complies with the ASTM F-136 (grade 5), ASTM B348 (grade 23) standard for medical applications. Analysis of the oxygen and nitrogen contamination in DMLS alloys was done with Van de Graaff accelerator with two Mega Volts. It is found that structures of the samples manufactured with two different machines used the same regimes are close to each other. TEM studies found the metastable martensitic structure and silicon nitride Si_3N_4. It was found that the oxygen and nitrogen contents in both samples are within the normal range for medical grade titanium alloys.

1. Introduction

It is known that above 500 °C oxidation change microstructure and then mechanical properties of the titanium alloys. Oxygen diffusion coefficients for the Ti-6Al-4V alloy were determined as follows: 8×10^{-13} cm^2/s at 600 °C and 1×10^{-11} cm^2/s at 750 °C [1]. Oxygen and nitrogen are strong alpha stabilizers in titanium Ti-6Al-4V alloys and may increase the rate of martensitic $\beta \rightarrow \alpha'$ transformation [2]. Oxygen enriching layer of the titanium ingots promotes to the formation of hard alpha case layer. The depth of the alpha case layer in the titanium Ti-6Al-4V ingots may achieve up to 250 μm [3]. The prevention of alpha case forming is important metallurgical problem. The diffusivity of oxygen being greater than nitrogen in titanium. The effects of nitrogen and oxygen absorption on lattice expansion of Ti-6Al-4V was found in [4]. Cell volume expanded and the c/a ratio changed at increasing temperatures up to 600 °C. This fact was due to both lattice thermal expansion and absorption of oxygen and nitrogen [4]. Oxygen, nitrogen and carbon increase the strength and hardness and decrease the ductility of the alloys [5]. It may be essential effect, because medical titanium alloys should have the high plasticity and low Young's modulus [6].

Direct metal laser sintering (DMLS) is a term suggested for EOS GmbH for the powder bed fusion process. In this process, powder is deposited in layer-by-layer-manner on the substrate. Ti-6Al-4V alloy manufactured by DMLS has high density (about 99.9%) as cast materials [7,8]. Power of the beam and the scan speed, the hatch distance and the layer thickness are the main parameters leads to full density of the samples [6,9,10]. Defects of the powders like voids within powder particles may contain the interstitial elements (nitrogen, hydrogen, carbon) or promote gas absorption under manufacturing [10,11]. Increase in the initial oxygen content in the powder led to higher porosity in the 3D manufactured components [11]. Therefore, it is necessary to investigate the effect of interstitial elements such as oxygen and nitrogen on the structure of the alloys made with a laser manufacturing technology.

The aim of this work is to study the effect of the oxygen and nitrogen contents on the structure of the Ti-6Al-4V alloys manufactured by the direct metal laser sintering.

2. Experimental

Ti-6Al-4V (ELI) has the low density, low elastic modulus and high strength. Biocompatibility of this material allows one to adapt it to human implant production and successfully use in the manufacture of surgical implants. Spherical argon-atomized Ti-6Al-4V (ELI) (45 μm) powder from TLS Technik was used for study. The

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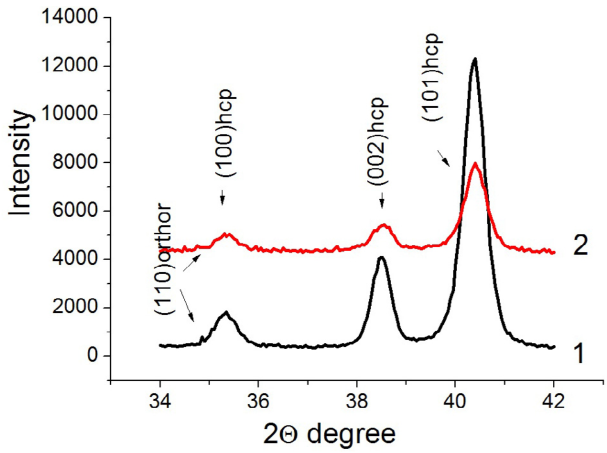

Fig. 1. X-ray results for samples: 1 – grade 5; 2 – grade 23.

chemical composition complies with the ASTM F136 (Grade 5) standard for surgical implant applications and ASTM B348 (Grade 23) for dental root implants. According to certificate, oxygen content in both batches of powders is less than 0.13%. Nitrogen content in grade 5 (ELI) is less than 0.05% and in grade 23 is less than 0.03%. Two machines from two scientific centers (Russia and South Africa) with the same working regimes were used for the manufacturing of the alloys. Horizontal samples were produced by the EOSINT M280 machines (EOS GmbH) equipped with an Ytterbium fiber laser (IPG Photonics Corp.) operating at 1075 nm wavelength, the laser beam had a Gaussian profile (TEM00 mode) and 80-μm spot diameter. The process parameters for a Ti-6Al-4V alloy are 170 W laser power and scanning speed of 1.2 m/s. Argon was used as the protective atmosphere; the oxygen level in the chamber was less than 0.12%. Powder layer thickness was of 30 μm and a back-and-forth scanning by strips with the hatch distance of 100 μm was applied. Grade 23 was used in Russian machine and grade 5 was used in South Africa machine. The substrate and powder material was similar in chemical composition. Method of nuclear microanalysis was used to determine the oxygen concentration. Van de Graaff accelerator with two Mega Volts was used. The beam diameter was 1 mm. Transmission electron microscopy (TEM) was done with JEM 200CX microscope in the Centre of collective use of the Institute of Metal Physics. X-ray diffractometer DRON-3 with Cu kα radiation was used for study.

3. Results and discussion

Fig. 1 shows the X-ray results for the samples manufacturing with the different machines. We did not found the beta phase lines in the diffraction patterns of both samples. The diffraction lines of HCP alpha phase and a weak diffraction line in the position of the strongest diffraction line of the orthorhombic martensitic α″-phase one can see in both samples. According to many investigations, microstructure of the samples depends on the parameters of DMLS process; martensitic α′-phase is usual for DMLS Ti-6Al-4V alloys and beta phase is rarely observed in DMLS Ti-6Al-4V alloys due to high cooling rates. Higher energy input needed for fully dense material results in increasing of the martensitic lath size [7–9,12].

Fig. 2 shows the results of the nuclear microanalysis of the surface studying of the samples. To obtain the fresh surface, the thin samples with thickness of 1 mm were cut from the center part of the samples manufactured by DMLS. Increasing of the oxygen concentration in the surface layer (0.5 μm) is connected with uncontrolled pollution under preparation of the samples for study as well as with adsorbed oxygen and water molecules. This zone is excluded from the analysis. One can see that oxygen concentration in both samples is about 0.2 wt% and decreases with the increasing of the depth from the surface of the sample (Fig. 2a).

Unlike oxygen behavior, nitrogen concentration increases with the increasing the depth from the surface (Fig. 2b). The same behavior was found for bulk Ti-6Al-4V samples, where authors studied the dependence of the oxygen and nitrogen concentration on the specimen thicknesses at 1000 °C [13]. Difference in oxygen and nitrogen contents in the samples may concerned with difference in both the initial powders and control of the oxygen content within the build chambers of two machines [14].

The diffusivity of oxygen being greater than nitrogen and a thick layer of TiO_2, not TiN, forms on the surface, because of the lower diffusion rate of nitrogen in titanium [15]. Titanium nitrides are formed when nitrogen is absorbed from the nitrogen-enriched atmospheres [16].

Oxygen level above 0.3 wt% and nitrogen level above 0.05 wt% are known to be critical for medical titanium alloys [17]. In our case, the nitrogen and oxygen concentrations of both samples are within the normal range for medical titanium alloys. These results are correlated with observations of [6].

TEM studies of both samples support the X-ray results and show the metastable martensitic structure without any β precipitations (Fig. 3).

Thin precipitations of silicon nitride Si_3N_4 were found in the sample 1 (grade 5) (Fig. 4). These precipitations look like thin

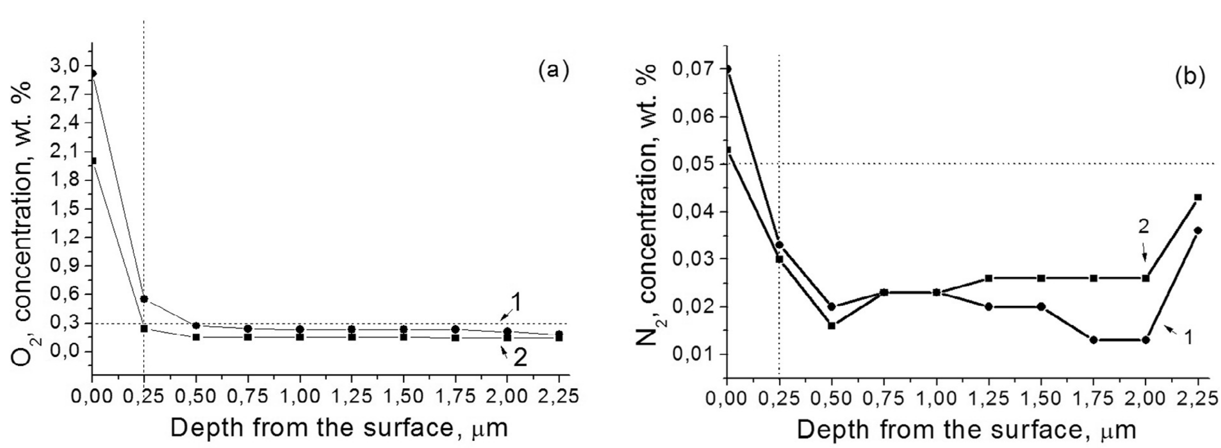

Fig. 2. Results of nuclear microanalysis: a – grade 5; b – grade 23.

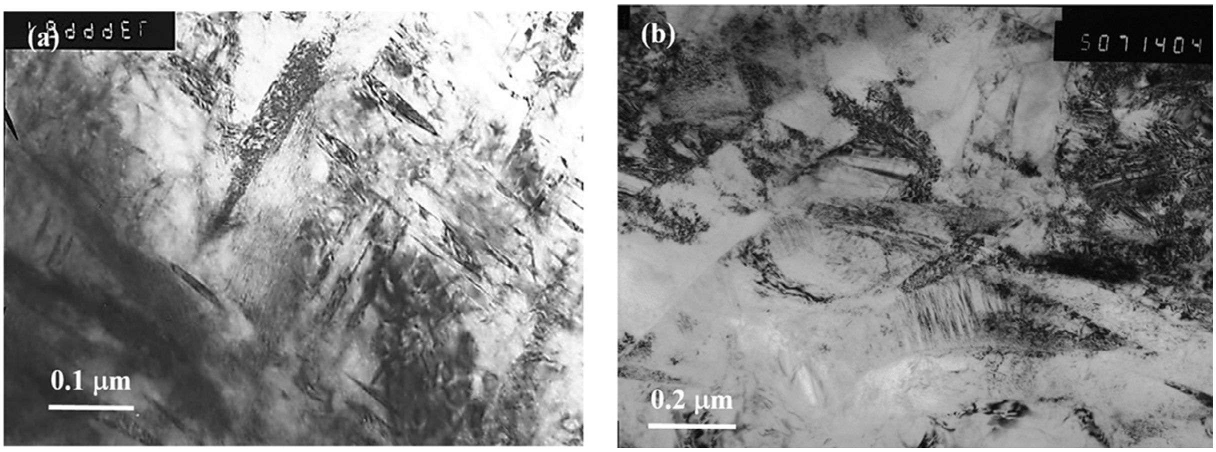

Fig. 3. TEM structure of the samples: a – grade 5; b – grade 23.

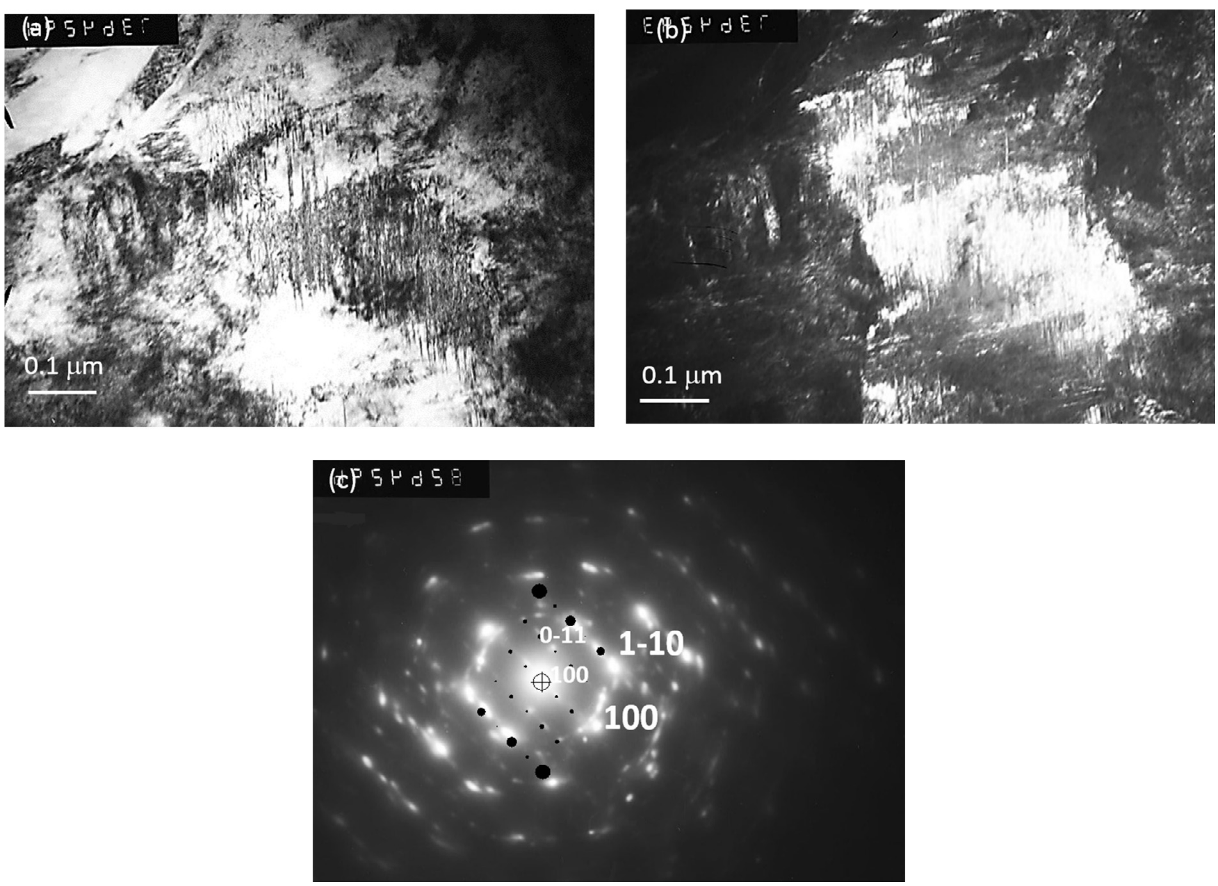

Fig. 4. HCP area with silicon nitride Si_3N_4: a – the bright-field image; b – the dark-field image taken with (2-22)Si_3N_4 reflexes; c – SAED patterns to a–b, zone axis [0 1 1] Si_3N_4//[0 0 1]hcp.

needles may be seen inside the HCP region. The morphology of the precipitations is typical for silicon nitride Si_3N_4 [17]. The Si_3N_4 regions are very small and rare in occurence. Because, we suppose that the silicon contamination may be remained from the powder. Small silicon content in the titanium alloys may be retained from its manufacturing, because silicon is contained in titanium ore such as sphene (CaTi-SiO_5). Rutile (TiO_2) also contains hundredths of a percent of silicon, leucoxene (Fe_2O_3 ·nTiO_2) may contain up to 10% of silicon as impurities. Generally, silicon in titanium alloys is favoral element. Special adding of silicon in titanium alloys gives a good biocompatibility. Silicon in titanium alloys acts as beta stabilizer, suppresses the formation of the ω-phase and promotes decrease the elastic modulus [18].

4. Conclusion

The oxygen and nitrogen concentrations in two different Ti-6Al-4V samples (grades 5 and 23) manufactured by DMLS were investigated in this study. The following results were obtained.

1. Structures of the samples manufactured with two different machines, used the same regimes, were close to each other. TEM analysis showed martensitic structure. No β phase was detected.
2. It was found that the oxygen and nitrogen contents in both samples are within the normal range for medical grade Ti-6Al-4V alloys.
3. Silicon nitride Si_3N_4 region was found in the sample manufactures with South Africa machine. It was supposed that silicon remained from titanium powder.

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