

EFFECT OF OXYGEN AND NITROGEN CONTENTS ON THE STRUCTURE OF THE Ti-6Al-4V ALLOY MANUFACTURED BY SELECTIVE LASER MELTING

ВЛИЯНИЕ КИСЛОРОДА И АЗОТА НА СТРУКТУРУ СПЛАВА Ti-6Al-4V, ПОЛУЧЕННОГО МЕТОДОМ СЕЛЕКТИВНОГО ЛАЗЕРНОГО СПЛАВЛЕНИЯ

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Abstract: Ti6AlV (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 Ti6Al4V (ELI) (45 μm) powder from TLS Technik was used for study. The chemical composition complies with the ASTM F-136 (grade 5), ASTM B348 (grade 23) standard for surgical implant applications. Two machines from two scientific centers (Russia and South Africa) were used for the manufacturing of the alloys. Analysis of the oxygen and nitrogen contamination in SLM alloys was done with Van de Graaff accelerator with 2 Mega Volts. It is found that the oxygen concentration in both samples is about 0.2 wt. % and decreases with the increasing of the sample depth; the nitrogen concentration is about 0,02 wt%. X-Ray results show an absence of beta (BCC) phase in both samples. TEM studies found the metastable martensitic structure and silicon nitride Si3N4.

KEYWORDS: TITANIUM ALLOY, SLM, 3D PRINTING, MICROSTRUCTURE, OXYGEN, NITROGEN

1. Introduction

Oxidation is a central problem in manufacturing of the titanium alloys [1]. Oxygen and nitrogen are strong alpha stabilizers in titanium Ti6Al4V alloys and effect on the rate of martensitic β→α' transformation [2]. Oxygen enriching layer with hard alpha phase is generated by oxidation process. The depth of the alpha case layer in the titanium Ti6Al4V ingots may achieve up to 250 μm [3]. The prevention of alpha case forming is important metallurgical problem. Contents of nitrogen and oxygen effect on the lattice expansion of Ti-6Al-4V alloys [4]. In [5] was demonstrated that these interstitial elements increased the strength and hardness with increasing concentrations and decreased the ductility of the alloys. Nitrogen having the greatest effect followed by oxygen and carbon [5].

Additive technology is a novel surface engineering technique, which allows us to obtained alloys with high density (about 99.9%) as cast materials [6]. However, increase in the initial oxygen content in the powder led to higher porosity in the 3D manufactured components [7].

The main purpose 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 selective laser melting.

2. Experimental

Spherical argon-atomized Ti6Al4V (ELI) (45 μm) powder from TLS Technik was used for study. The chemical composition complies with the ASTM F136 (Grade 5) standard and ASTM B348 (Grade 23) for surgical implant applications. The difference between Ti6Al4V ELI (grade 23) and Ti6Al4V (grade 5) is the reduction of oxygen content to 0.13 % (maximum) in grade 23. 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) 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 operating at 1075 nm wavelength (IPG Photonics Corp.). The laser beam had a TEM00 Gaussian profile and 80 μm spot diameter. In accordance with standard process parameters for a Ti6Al4V alloy, a powder layer thickness of 30 μm, and a back-and-forth scanning by

strips with the hatch distance of 100 μm was applied. The substrate and powder material was similar in chemical composition. Argon was used as the protective atmosphere; the oxygen level in the chamber was 0.07–0.12%. Method of nuclear microanalysis was used to determine the oxygen concentration. Van de Graaff accelerator with 2 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

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 were found in X-ray diffractograms of both samples.

Figures 1-2 shows the results of the nuclear microanalysis of the surface studying of the samples. Increasing of the oxygen concentration in the surface layer (0.5 μm) is connected with the preparation of the samples (polishing). 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.1).

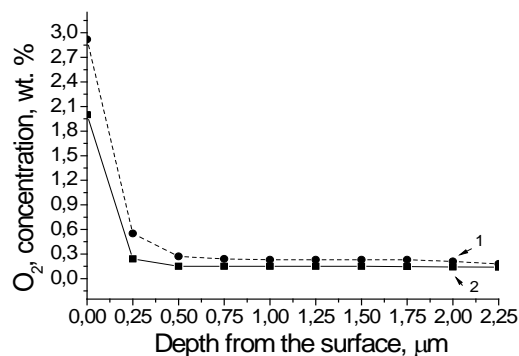


Fig.1 Oxygen concentration in the samples obtained by nuclear microanalysis: 1- grade 23; 2- grade 5

Unlike oxygen behavior, nitrogen concentration increases with the increasing the depth from the surface (Fig.2). 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 [8].

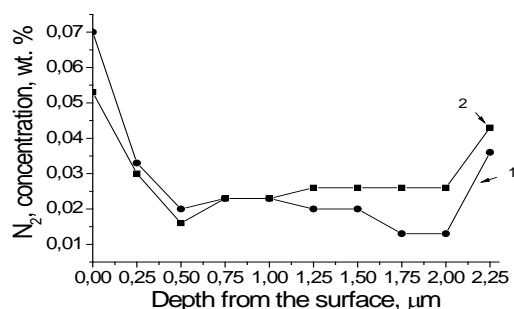


Fig.2 Nitrogen concentration in the samples obtained by nuclear microanalysis: 1- grade 23; 2- grade 5

The diffusivity of oxygen being greater than nitrogen and a thick layer of TiO₂, not TiN, forms on the surface, because of the lower diffusion rate of nitrogen in titanium [9]. Titanium nitrides are formed when nitrogen is absorbed from the nitrogen-enriched atmospheres [10]. It was shown also that titanium nitride is the most suitable to protect the surface of medical implants [11].

In our case, the nitrogen and oxygen concentrations of both samples are within the normal range for medical grade alloys.

TEM studies of both samples showed the martensitic structure without any β precipitations (Fig.3).

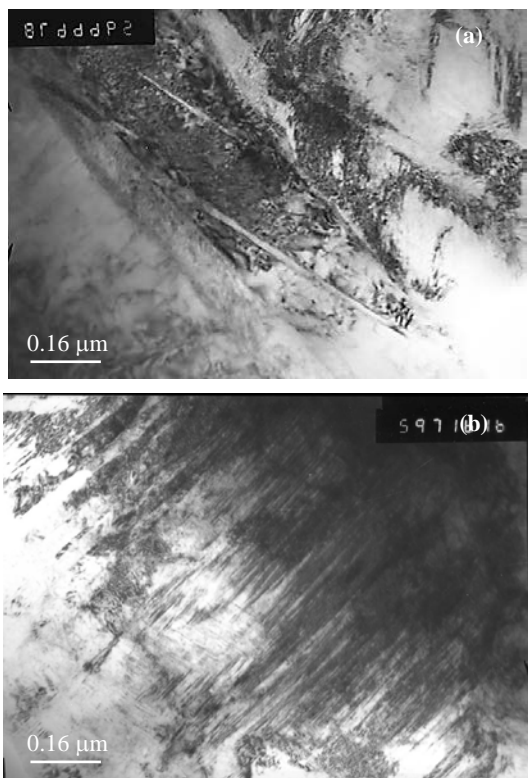


Fig.3 TEM structure of the SLM samples: a- grade 5; b- grade 23

Thin precipitations of silicon nitride Si₃N₄ were found in the sample 1 (grade 5), (Fig.4). These precipitations look like thin needles may be seen inside the HCP region. The morphology of the precipitations is typical for silicon nitride Si₃N₄ [12]. The Si₃N₄ regions are very small and rare in occurrence. 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-SiO₅). Rutile (TiO₂) also contains hundredths of a percent of silicon, leucosene (Fe₂O₃ · nTiO₂) may contain up to 10% of silicon as impurities. Generally, silicon in titanium alloys is a favorable element. Special adding of silicon in titanium alloys gives a good biocompatibility. Silicon in titanium alloys acts as a beta stabilizer, suppresses the formation of the ω-phase and promotes decrease the elastic modulus [13].

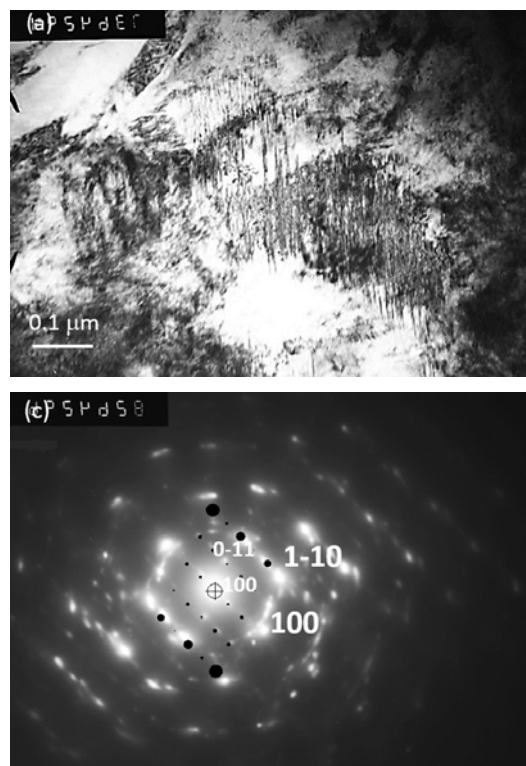


Fig.4 HCP area with silicon nitride Si₃N₄: a- the bright-field image; b- SAED patterns to (a), zone axis [011]Si₃N₄//[001]hcp

4. Conclusion

The effect of oxygen and nitrogen concentrations on microstructure in two different SLM Ti6Al4V samples (grade 5 and grade 23) was investigated in this study. Structures of the samples manufactured with two different machines used the same regimes are found to be close to each other. It was found that the oxygen and nitrogen contents in both samples are within the normal range for medical grade.

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