Research on Biocompatible Titanium Alloys Test Samples Obtained by Sintering

CORNELIU RONTESCU[1]*, OANA ROXANA CHIVU[1], ADRIAN PACIOGA[2], GABRIEL IACOBESCU[1], ION MIHAI VASILE[1], DUMITRU TITI CICIC[1], AUGUSTIN SEMENESCU[3]

[1] University Politehnica of Bucharest, Faculty of Engineering and Management of Technological Systems, 313 Splaiul Independentei, 060021, Bucharest, Romania

[2] National Institute for Research and Development in Mechatronics and Measurement Technique, Romania, 6-8 Sos. Pantelimon, 21631, Bucharest, Romania

[3] University Politehnica of Bucharest, Faculty of Material Science and Engineering, 313 Splaiul Independentei, 060021, Bucharest, Romania

This paper presents the results of the analyses conducted on samples made of Ti-6Al-4V biocompatible titanium alloy by using the Direct Melting Laser Sintering (DMLS) process. The results of the analysis methods used in the paper - methods of optical microscopic, scanning electron microscopy (SEM) and the spectroscopy method of X-ray energy dispersion – revealed that at the surface of the sample obtained by sintering there is an incomplete melting area and its size depends on its shape and on the model discretization level. The percentage values of the content of alloying elements in the sample material range within the admissible limits recommended by the producer of EOS Ti64 powder used for making the samples.

Keywords: prosthetic implants, titanium, biocompatibility, DMLS

By the laser sintering process, in the analysed case the Direct Melting Laser Sintering (DMLS) version, the orthopaedic implants are built by layer-by-layer melting in three-dimensional shape. The rapid prototyping process requires that the fine metal powder (EOS Ti64) be applied in thin layers and completely molten with the help of a laser fascicle in the areas required by the model [1, 2].

In order to ensure high precision in the construction of the CAD model, after depositing the powder layer (which is up to 20 microns high) the powder is selectively molten (melting is only done on the areas that are concordant with the CAD model to be carried out) with the help of a precise high-power laser [3].

Due to the oxide passive layer formed in reaction with oxygen in the air, titanium and its alloys present high corrosion resistance and biocompatibility [4, 5]. As it is thermodynamically stable, the TiO_2 oxide (usually with a thickness of 1.5 to 10 nm) has a low tendency to ion release in bioliquids, which leads to a small corrosion rate of Ti and its alloys [6,7].

However, the exposed surface of the titanium is attacked by corrosion in the first part of the exposure to the environment, but the growth of a naturally protective oxide layer (less than 10 nm thick) can prevent its degradation. When titanium is in a fully passive state, the corrosion rates in aqueous media are typically below 40μm/year, values much lower as compared to a value of 130μm/year (generally accepted by designers as standard for general corrosion). The oxide layer occurred in direct contact with the Ti surface consists of TiO; the intermediate layer is composed of Ti_2O_3 and the outer layer is TiO_2 [8-11].

The chemical purity of the titanium powder during processing is also very important. Surface oxidation should be prevented as this increases the surface tension, hindering material from flowing during sintering. Oxidation also results in poor bonding between sintered lines affecting the manufactured structures, while nitrides reduce the material's corrosion resistance [12].

Several reactions taking place at the surface of the titanium alloys that may influence the operating behaviour of the product resulted following the sintering process are presented in equations (1-6).

$$Ti(s) + O_2(g) \rightarrow TiO_2(s) \quad (1)$$
$$TiO_2 + 3H^+ + e^- \rightarrow Ti(OH)^{2+} + H_2O \quad (2)$$
$$TiO(OH)_2 + HPO_4^{2-} \rightarrow TiO(HPO_4) + 2OH^- \quad (3)$$
$$2Ti(s) + N_2(g) \rightarrow 2TiN(s) \quad (4)$$
$$Ti(s) + 2H_2O(g) \rightarrow TiO_2(s) + 2H_2(g) \quad (5)$$
$$2Ti(s) + 12HF(aq) \rightarrow 2[TiF_6]^{3-}(aq) + 3H_2(g) + 6H^+(aq) \quad (6)$$

Experimental part

The test samples that were necessary for the analysis were made by the sintering of the titanium powder with the help of the DMLS process. The used titanium powder was EOS Titanium Ti64, a titanium alloy powder which has been optimized especially for processing on EOSINT M systems (EOSINT M270). Parts built in EOS Titanium Ti-6Al-4V have a chemical composition corresponding to ISO 5832-3, ASTM F1472 and ASTM B348. This well-known light alloy is characterized by excellent mechanical properties and corrosion resistance combined with low specific weight and biocompatibility [13-17].

The properties of EOS Titanium Ti64 powder are presented in table 1 and its chemical composition is presented in table 2 [17].

Table 1
PROPERTIES OF EOS TITANIUM Ti64 POWDER ACCORDING TO [17]

Material (DMLS)	Tensile strength R_m [MPa]	Yield strength $Rp_{0.2}$ [MPa]	Elongation [%]	Modulus of elasticity [GPa]	Hardness [HRC]
Ti64 POWDER	1150 ± 60	1030 ± 70	11 ± 2	110 ± 15	31-35

* corneliu.rontescu@upb.ro

Table 2
CHEMICAL COMPOSITION OF EOS TITANIUM TI64 POWDER ACCORDING TO [17]

Material	Al [%]	V [%]	Ti [%]
Ti64 powder	5.5-6.75	3.5-4.5	balance

Results and discussions

After making the samples by using the DMLS process, in order to subject them to the metallographic analysis process, the samples were cut using a special cutting system at low cutting speeds with continuous cooling so as to prevent the analysed area from being affected by the heat. After the cutting process the samples were cleared of impurities [18]. The obtained SEM metallographic images are presented in figure 1.

In order to obtain the local chemical composition of the laser-sintered samples an energy dispersive X-Ray analysis was performed. The spectrum in figure 2 shows the chemical composition of the laser-sintered material. The average values of the chemical composition of the sintered material – presented in table 3 – resulted following the conducted analysis. The quantity of alloying elements influences the mechanical properties, biocompatibility, corrosion resistance and specific strength of the prostheses made by sintering.

Following the analysis of figure 2 and of the values presented in table 3 it can be seen that the average values of the alloying elements are close to the maximum limit presented by the producer of Ti-6Al-4V powder.

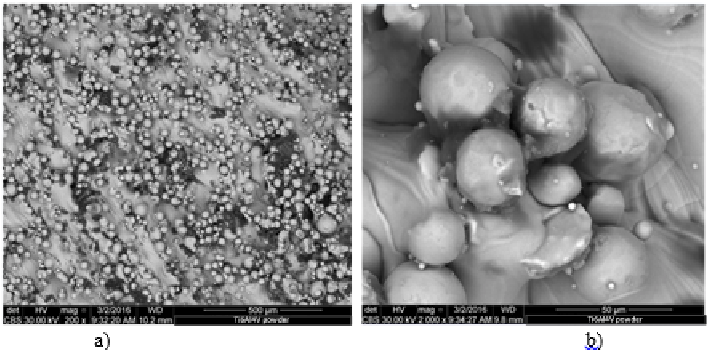

Fig. 1.SEM micrographs of melted EOS Titanium Ti64 titanium alloy powder: a – magnification by 200x; b – magnification by 2000x

Table 3
CHEMICAL COMPOSITION OF LASER-SINTERED MATERIAL

Material	Al [%]	V [%]	Ti [%]
Ti64 powder	5.5-6.75	3.5-4.5	balance
Laser-sintered Ti64 powder	6.35	4.23	balance

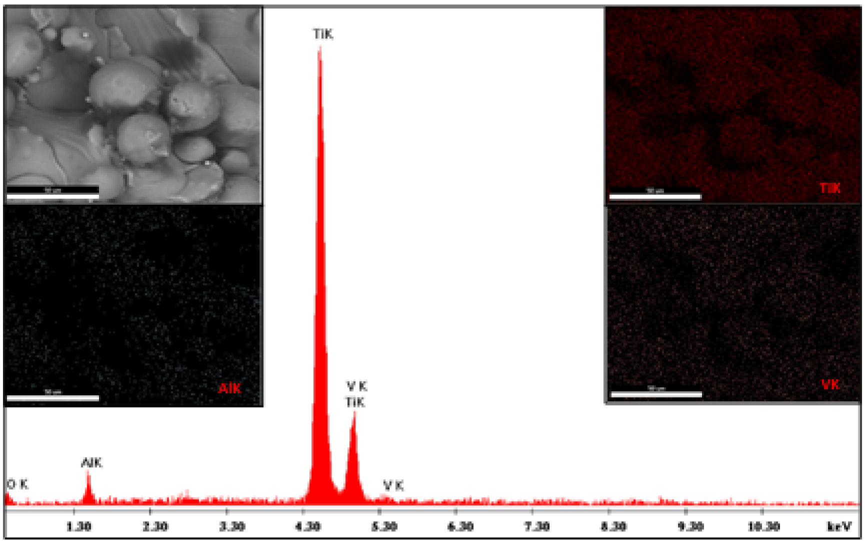

Fig. 2. The energy dispersive x-ray spectra of the laser-sintered Ti-6Al-4V powder surface test sample

Following the analysis of the metallographic images taken on the surface of the test sample obtained by sintering, it can be noticed that there is an incomplete melting area of the titanium powder. The incomplete melting was noticed at the surface of the sample, at the passing area between the successive layers deposited by selective melting; the size of the area depends on the sample shape but also on the discretization level of the 3D model.

Conclusions

The employed analysis methods offer us important information on the quality of the surfaces of the test samples obtained by using the rapid prototyping process called DMLS.

The optical microscopic and electronic methods showed that at the surface of the test samples there is a partially molten powder area, and the size of the area depends on the shape of the surface.

Using the x-ray spectroscopy method with energy dispersion provides us with information on the content of alloying elements of the laser-sintered test samples area, elements that, depending on the percentage, influence the mechanical properties, biocompatibility, corrosion resistance and specific strength of orthopaedic implants.

References

1. GH. I. GHEORGHE, D. D. PALADE, A. MOLDOVANU, D. CIOBOTA, A. PACIOGA; Rapid Prototyping Advanced Microtechnologies by Selective Laser Sintering, 2010,

2. A.I. PACIOGA, Research on the Development of a New Conceptual Base in the Design and Manufacture of Hip Prosthesis Through Customization, PhD Theses, Bucharest, 2011

3. *** Information on: http://bavaria-medical.ro/, accessed on 11.02.2016

4. H. GULERYUZ, H. CIMENOGLU, Effect of thermal oxidation on corrosion and corrosion-wearbehaviour of a Ti-6Al-4V alloy", in Biomaterials, vol. 25, 2004, pp. 3325-3333

5. B. FENG, J.Y. CHEN, S.K. QI, L. HE, J.Z. ZHAO, X.D. ZHANG, "Characterization of surface oxide films on titanium and bioactivity", in J. Mater. Sci. Mater. Med., vol. 13, 2002, pp. 457-464

6. MINDROIU, M., CICEK., E.,MICULESCU,F.,DEMETRESCU,I., The influence of thermal oxidation reatment on the electrochemical stability of TiAlV and TiAlFe alloys and their potential application as biomaterials, Rev. Chim.(Bucharest), **58**, no. 9, 2007, p. 898

7. D. BAJENARU-GEORGESCU, D. IONITA, M. PRODANA, I. DEMETRESCU, Electrochemical and antibacterial characterization of thermally treated titanium biomaterials, U.P.B. Sci. Bull., Series B, Vol. 77, Iss. 4, 2015

8. ALDEA,E., BADEA, N., DEMETRESCU, I., Evaluating Titanium Alloys Bioactivity in Terms of Hydroxyapatite (HA) Forming Capability, RRev. Chim. (Bucharest), **58**, no. 9, 2007

9. POPESCU, S., MANOLE, C.C., PIRVU, C., Surface Features Changes and Corrosion Stability of Titanium Surfaces by Suitable Treatments, Rev. Chim. (Bucharest), **64**, no.8, 2013, p. 796

10. M.J., DONACHIE, Titanium: a Technical Guide. ASM International. 2000

11. S., MINAGAR, C. C., BERNDT, J., WANG, E., IVANOVA, C., WEN, Acta Biomater. 8, 2012, p.2875.

12. H. Bissett, I.J. van der Walt, J.L. Havenga, J.T. Nel, Titanium and zirconium metal powder spheroidization by thermal plasma processes, The Journal of The Southern African Institute of Mining and Metallurgy, vol. 115, October 2015

13. *** Information on: http://www.astm.org, accessed on 12.02.2016

14.*** EN ISO 5832-3: 2012 - Implants for surgery. Metallic materials. Wrought titanium 6-aluminium 4-vanadium alloy;

15.*** ASTM F1472: 2014 - Standard Specification for Wrought Titanium-6Aluminum-4Vanadium Alloy for Surgical Implant Applications

16.*** ASTM B348: 2013 - Standard Specification for Titanium and Titanium Alloy Bars and Billets;

17. *** Information on: http://www.eos.info, EOS Titanium Ti64 data sheet; accessed on 12.02.2016

18. I. VOICULESCU, C. RONTESCU, L. I. DONDEA, Metalografia îmbinãrilor sudate, Ed. Sudura, Timisoara, 2010

Manuscript received: 22.04.2016