Research Regarding the Analysis of the Samples Used for Prosthetics and Medical Instruments Obtained by Sintering

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The present paper presents the results of the analysis made on samples obtained by additive manufacturing processes, necessary to realize prostheses and medical instruments. The samples were obtained by melting fine metal powder of Co-Cr by rapid prototyping process - Direct Metal Laser Sintering (DMLS). The examination of the samples (by methods of optical microscopic, scanning electron microscopy (SEM) and the spectroscopy method of X-ray energy dispersion) revealed that the surface of the obtained components contains incomplete melting areas whose size depends on the shape of the surface and the meshing level of the 3D model.

Keywords: prostheses, medical instruments, metal powder, DMLS

Direct Metal Laser Sintering technology fuses metal powder into a solid part by melting it locally using a focused laser beam. The rapid prototyping process requires that the fine metal powder (ex. EOS Ti64, EOS CobaltChrome MP1, EOS CobaltChrome SP2 etc.) be applied in thin layers and completely molten with the help of a laser fascicle in the areas required by the model. With the help of the DMLS process, based on the 3D model of the prosthetic or the medical instrument, complex geometry components can be realized in a much shorter period of time and fully automatic. It is a net-shape process, producing parts with high accuracy and detail resolution, good surface and excellent mechanical properties [1-3].

The Co-Cr super alloy is considered a biocompatible material in medicine and presents a good balance among different properties as strength, toughness and corrosion resistance in different environments. All materials sintered by DMLS present a porous structure that influences the mechanical and corrosion behaviour [4-6].

The chemical composition and microstructure of the alloys have a strong influence on the corrosion behaviour, which can be assessed by chemical or electrochemical tests [7-9].

Due to the formation of a chromium rich passive oxide film (Cr_2O_3) on Co-Cr alloys, they show a high resistance to corrosion. When a metal is in a passive state it will still corrode in a slow and uniform mode, but it will resist the thermodynamic tendency to rapidly dissolve. This condition is achieved when a passive oxide film is formed at the metal surface. Passive oxide films can vary in thickness, chemical composition as well as in oxidation states and are affected by a number of factors, including *p*H, electrode potential and composition of the electrolyte [10-14].

The chemical purity of the powder during processing is also very important. Surface oxidation of the components can alter the superficial tension of the molten material in the process of additive manufacturing and can affect the quality of the components. In welding processes, the oxide layer may lead to the decrease of the material weldability and the occurrence of oxide inclusions in the welded joint. Oxidation also results in poor bonding between sintered lines affecting the manufactured structures, while nitrides reduce the material's corrosion resistance [15].

Some of the possible oxidation reactions that may occur at the surface of the component obtained through DMLS and that can influence the additive manufacturing process are presented in table 1.

Any change brought to the additive manufacturing process can lead to the modification of the component properties [16, 17].

Experimental part

The test samples that were necessary for the analysis were made by the sintering of the Co-Cr powder with the help of the DMLS process. The used Co-Cr powder was EOS CobaltChrome MP1, a Co-Cr alloy powder which has been optimized especially for processing on EOSINT M systems (EOSINT M270).

Parts built from EOS CobaltChrome MP1 are conforming to the chemical composition ASTM F1537 - 11 of wrought

Table 1
THE METAL OXIDATION REACTION

Nr.	Metal oxidation reaction	Corresponding equilibrium reaction
1	$Cr \rightarrow Cr_2O_3/Cr(OH)_3$	$2Cr+3H_2O = Cr_2O_3+3H_2$
		$Cr_2O_3+3H_2O = 2Cr(OH)_3$
2	$Co+CrO_2 \rightarrow CoCr_2O_4$	$Co+CrO_2+3H_2O= CoCr_2O_4+H_2$
3	$Co \rightarrow CoO/Co(OH)_2$	$Co+2H_2O = Co(OH)_2 + H_2$
		$Co(OH)_2=CoO+ H_2O$
4	$Co^{II} \rightarrow Co_3O_4$	$3Co(OH)_2=Co_3O_4+ H_2+ 2H_2O$
		$Co(OH)_2= CoO+ H_2O$
5	$Co^{II} \rightarrow CoOOH$	$2Co(OH)_2= CoOOH+ H_2$
		$Co(OH)_2= CoO+ H_2O$
6	$Cr^{III} \rightarrow Cr^{VI}$	$2Cr(OH)_3+ H_2O=Cr_2O_7^{2-}+ 3H_2+2H^+$
		$Cr_2O_3+3 H_2O=2Cr(OH)_3$

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Table 2
PHYSICAL AND CHEMICAL PROPERTIES OF Co-Cr PARTS

Material	Co [%]	Cr [%]	Mo [%]	Si [%]	Mn [%]	Fe [%]	C [%]	Ni [%]	Density [g/cm³]
EOS CobaltChrome MP1	60…65	26…30	5…7	≤ 1.0	≤ 1.0%	≤ 0.75	≤ 0.16	≤ 0.10	approx. 8.3

Table 3
MECHANICAL PROPERTIES OF PARTS AT 20 °C

No.	Properties	As built	Stress relieved
1.	Tensile strength according to [24] - in horizontal direction (XY) - in vertical direction (Z)	 1350 ± 100 MPa 1200 ± 150 MPa	 1100 ± 100 MPa 1100 ± 100 MPa
2.	Yield strength (Rp 0.2 %) according to [24] - in horizontal direction (XY) - in vertical direction (Z)	 1060 ± 100 MPa 800 ± 100 MPa	 600 ± 50 MPa 600 ± 50 MPa
3.	Elongation at break according to [24] - in horizontal direction (XY) - in vertical direction (Z)	 (11 ± 3) % (24 ± 4) %	 min. 20 % min. 20 %
4.	Modulus of elasticity according to [24] - in horizontal direction (XY) - in vertical direction (Z)	 200 ± 20 GPa 190 ± 20 GPa	 200 ± 20 GPa 200 ± 20 GPa
5.	Fatigue life according to [25] - max. stress to reach 10 million cycles - max. stress to reach 1 million cycles	 approx. 560 MPa approx. 660 MPa	 approx. 560 MPa approx. 660 MPa
6.	Hardness according to [26]	approx. 35 - 45 HRC	approx. 35 - 45 HRC

Table 4
WORKING PARAMETERS OF THE MACHINE

Parameters	Value	
	Hatching	Contouring
Laser power (W)	170	150
Scan speed (mm/s)	1250.0	
Hatching spacing (mm)	0.10	NA
Stripe width (mm)	5.0	NA
Beam offset (µm)	0.015	0.020
Scanning pattern	Rotated	

Cobalt-28Chromium-6Molybdenum alloys for surgical implants. They are nickel-free (< 0.1 % nickel content) and are characterized by a fine, uniform crystal grain structure.

Parts made from EOS CobaltChrome MP1 can be machined, spark-eroded, welded, polished and coated if required. They are suitable for biomedical applications, and for parts requiring high mechanical properties in elevated temperatures (500…1000 °C) and with good corrosion resistance. Due to the layerwise building method, the parts have a certain anisotropy, which can be reduced or removed by appropriate heat treatment [18].

The physical and chemical composition of EOS CobaltChrome MP1 powder parts are presented in table 2 and its mechanical properties are presented in table 3 [18-23].

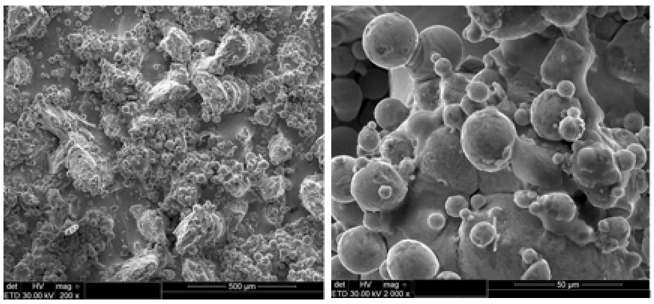
The analysis of the values presented in table 3 indicates that the products obtained through CoCr metallic powder sintering present excellent mechanical properties.

The EOS M270 equipment was used to obtain the Co-Cr sintered metal powder components. The working parameters values of the M270 equipment needed for obtaining the components are presented in table 4.

Results and discussions

To realize the metallographic examination of the samples obtained through DMLS additive manufacturing, they were cut with low speed and continuously cooled to prevent overheating that can lead to structural changes.

After the cutting process, the samples were cleaned from impurities and subject to a polishing process using metallographic paper with different granulations; finally, the samples were subjected to polishing with abrasive diamond paste. The obtained SEM metallographic images are presented in figure 1 [27].



a) b)

Fig. 1.SEM micrographs of melted EOS CobaltChrome MP1 alloy powder: a – magnification by 200x; b – magnification by 2000x

After analysing the metallographic images, it can be noticed that the surface of the analysed components is a porous surface that presents incomplete melting areas of the Co- Cr powder. The incomplete melting was noticed at the surface of the sample and at the passing area between the successive layers deposited by selective melting. The size of the incomplete melting zone and the roughness of the surface depend largely on the complexity and meshing level of the 3D model.

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.

Following the analysis of figure 2 and of the values presented in table 2 it can be seen that the average values of the alloying elements are close to the maximum limit

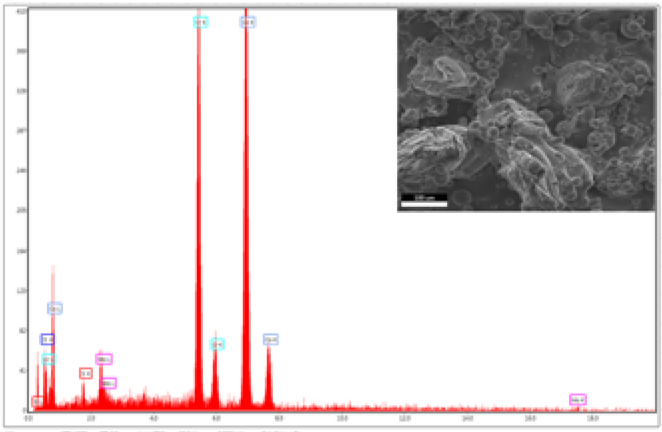


Fig. 2. The energy dispersive x-ray spectra of the laser-sintered Co-Cr powder surface test sample

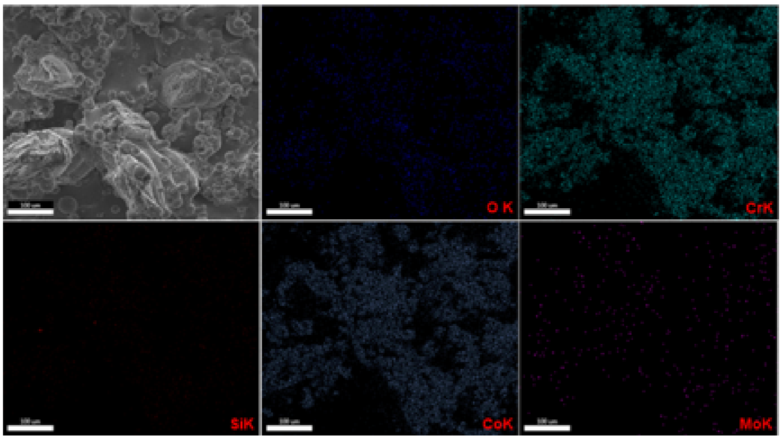


Fig. 3. EDAX mapping distribution of principals chemical elements over the laser-sintered material scanned area

presented by the producer of CobaltChrome MP1 alloy powder.

Figure 3 presents EDAX mapping distribution of the main chemical elements of the laser-sintered material.

After analysing the images presented in figure 3, the homogeneous distribution of the main chemical elements : Cr, Si, Co, Mo on the entire melted area can be observed. This homogeneous distribution of the alloying elements offers the possibility to obtain constant values of the mechanical properties in the entire mass of the component.

Conclusions

From the analysed samples it can be seen that as a result of the Co-Cr powder sintering process by DMLS additive manufacturing, the chemical composition has changed to the downside amount of Fe, C and Ni. This can lead to the modification of the mechanical properties of the component.

Also, an increase of the oxygen content could be observed, fact that can be explained by ensuring inadequate protection to the inert atmosphere needed to carry out the manufacturing process. The oxide layer can also be a result of the component surface processing for micrographic examination.

The quality of the surface of the components depends largely on the complexity and meshing level of the 3D model.

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