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Microstructure and properties of CoCr alloys used in prosthetics procedure

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ABSTRACT

Purpose: The aim of this work was to define the influence of manufacturing technology on the chemical composition, surface topography, physicochemical and electrochemical properties of CoCr alloys obtained by casting technology and Direct Metal Laser Sintering.

Design/methodology/approach: This work presents microstructural and chemical compositions obtained by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). Additionally, corrosion pitting analysis and roughness measurement were conducted on the samples.

Findings: On the basis of the investigations, it can be stated that the prosthetic restorations are different depending on the type manufacturing technology. Based on the obtained results it was found that the structures of both materials are chemically inhomogeneous. The investigated alloy exhibited similar polarization curve character.

Practical implications: The rapid prototyping methods are a new technology used for getting details e.g. by CAD/CAM procedure. Using Direct Metal Laser Sintering (DMLS) method can simplify the technology of producing prosthetics restrictions and is an alternate way for standard casting technology.

Originality/value: The paper presents comparative research of two Co-Cr alloys, from which the samples were obtained in conventional casting and DMLS technology.

Keywords: Prosthetic material, SEM, AFM, Roughness, Corrosion tests

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BIOMEDICAL AND DENTAL MATERIALS AND ENGINEERING

1. Introduction

Cobalt based alloys are the most popular metal biomaterials in dental prosthetics applications. Characterized by good corrosion resistance and satisfactory mechanical properties, Co based alloys are inherently related by chemical composition and structure, the latter one being in turn dependent on the type of technology and manufacturing conditions. The majority of conventional cobalt chrome alloys are modifications of CoCrMo and CoCrW triple casting alloys, which are available under different trade's names. Cobalt based alloys are characterized by a dendritic structure of a solid solution of chromium, molybdenum or tungsten in cobalt and micro chemical segregation. Additionally, CoCr alloys during heat treatment in the presence of carbon and carbide forming alloying elements, the precipitates of carbides of a complex $M_{23}C_6$ or M_6C type structure are formed. The carbide precipitates are areas of chemical heterogeneity of the alloy and the structure of alloys are reinforced by them. The cobalt based alloys are used mainly for manufacturing of removable denture frame or metal restorations in ceramic crowns and bridges [1-8,10].

Casting is the most popular method of producing prosthetic dental restorations. These methods are very difficult and their accuracy depends on the precision of the dental technician. Technological developments and increase of prosthetic restorations has resulted in an increasing use of modern CAD/CAM systems based on Rapid Prototyping (3D printing) in dental prosthetics applications. For manufacturing dental prosthetics methods such as Selective Laser Sintering (SLS), Selective Laser Melting (SLM) and the most popular method Direct Metal Laser Sintering (DLMS), which is a variant of the SLS method are used. Fabrication of the metal framework in the DMLS procedure consists of applying a layer of powdered material (usually a cobalt or titanium alloy) to the working platform with a blade and then sintering it selectively with a laser beam guided according to a bitmap that is a virtual recording of the formed element [5,8-16].

DMLS technology is characterized by high repeatability and dimensional accuracy on the order of 0.02-0.01 mm. Moreover, use of three-dimensional printing processes compared to casting procedures reduces the time of prosthetic restoration manufacturing – the manufacturing step for both methods is shown in Figure 1.

The aim of the presented paper is to characterize the structure and determine the surface roughness and corrosion resistance of cobalt based alloys used in prosthetic application, from which the samples are obtained by two technological methods – a traditional casting method and DLMS technology.

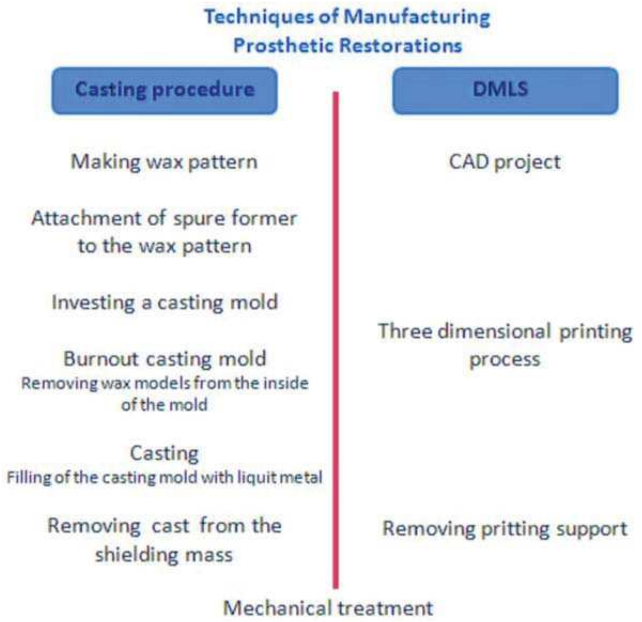

Fig. 1. Manufacturing technologies of the prosthetic restorations

2. Materials and methods

Materials used for testing were two cobalt based alloys in the form of discs of diameter d = 14 mm. The first alloy, Realloy C, obtained from traditional casting methods and the second EOS Cobalt Chrome SP2 obtained from DLMS technology. The chemical compositions of the tested alloys were presented in Table 1.

Table 1.
The chemical compositions of the tested CoCr alloys

Element, %	Realloy C	EOS CoCr SP2
Co	59.00	63.80
Cr	25.00	24.70
Mo	3.90	5.10
W	10.10	5.40
Si	1.60	-
N	0.19	-
S	-	1.00
Fe	-	max. 0.50
Mn	0.75	max. 0.10

The samples were subjected to mechanical treatment, which consisted of two processes: mechanical grinding and mechanical polishing. Grinding was carried out sequentially with the use of abrasives 320, 500, 800 to

1000 grade and the mechanical polishing was carried out with SiO_2 polishing paste was carried out.

The process were performed with the use of polishing-grinding machine TGRAMIN - 30 by STRUERS.

2.1. SEM/EDS analysis

Surface topography analysis before and after pitting corrosion testing was conducted using a ZEISS SUPRA 35, equipped with type SE (Secondary Electrons) detector for secondary electrons imaging in the 200000-100000x magnification range. Additionally, chemical composition analysis was performed using Energy Dispersive X-ray Spectroscopy (EDS). The analysis of the chemical compositions was conducted using a point-by-point method on the surface of the tested alloys. The results of the analysis were presented in the form of characteristic X-ray spectra, also the element contents were determined.

2.2. AFM

In order to determined surface morphology Atomic Force Microscopy (AFM) was performed with an XE-100 by Park System with a non-contact mode. The parameters describing the surface roughness – a Rough Mean Square, (RMS/R_q), the arithmetic average of ordinates profile (R_a) and sum of maximum height and maximum depth (ΔZ) was calculated over three scan areas 25 × 25 μm, 10 × 10 μm and 2 × 2 μm.

2.3. Roughness tests

Surface roughness measurements were made with using contact profilometer Surtronic 3+ by Taylor Hobson. The obtained measurements were determined by R_a parameter.

2.4. Potentiodynamic test

In order to evaluate resistance to pitting corrosion a potentiodynamic method by recording of anodic polarization curves was used. The tests were carried out as recommended by ISO 10993-15 standard [17]. The test stand comprised of a VoltaLab PGP201 potentiostat, a PC computer with VoltaMaster 4 software and a three-electrode system, where the working electrode was represented by the test sample, the auxiliary electrode was a platinum wire (PTP-201) and reference electrode was saturated calomel electrode (SEC KP-113). The corrosion tests were started with determination of open circuit potential E_{ocp} and then anodic polarization curves were recorded from the starting potential $E_{init} = E_{ocp}$ - 100 mV. The potential value changed along the anodic direction at a polarization rate of 3 mV/s. Then, when the anodic current density reached value of 1 mA/cm^3, polarization direction was changed. On the basis of the recorded curves characteristic values describing the pitting corrosion was determined i.e.: corrosion potential E_{corr} (mV), potential of transpassivation E_{tr} (mV). The value of polarization resistance R_p was determined with the use of Stern method and corrosion current density was calculated using the formula $i_{corr} = 0.026/R_p$. The potentiodynamic tests were carried out in artificial saliva (pH = 6.8) at the temperature 37 ± 1°C. The composition of artificial saliva is given in Table 2.

Table 2.
Composition of artificial saliva by ISO 10271 [11]

Component	Quantity, g/l
$CO(NH_2)_2$	0.13
NaCl	0.70
$NaHCO_3$	1.501
Na_2HPO_4	0.26
K_2HPO_4	0.20
KSCN	0.33
KCl	1.20

3. Results

3.1. SEM/EDS analysis

Based on microscopic observation of surface topography of Realloy C material before and after the pitting corrosion test (Fig. 2.) it can be concluded, that corrosion resistance does not affect the quality of surface to a large degree.

Additionally, in the both cases microscopic observations showed the structure of Realloy C material occurrence of many precipitates. Based on local chemical analysis (Fig. 3, Tab. 3), the increased concentration of molybdenum and tungsten in the precipitates were found, while in the matrix (Fig. 3), higher concentrations of cobalt (ca. 62 at %) and lower concentrations of molybdenum, tungsten and silicon was found.

The obtained SEM image of the surface of the EOS CoCr SP2 material is shown in Figure 4. Surface microscopic observation after potentiodynamic testing relative to surface before testing showed presence of more precipitates.

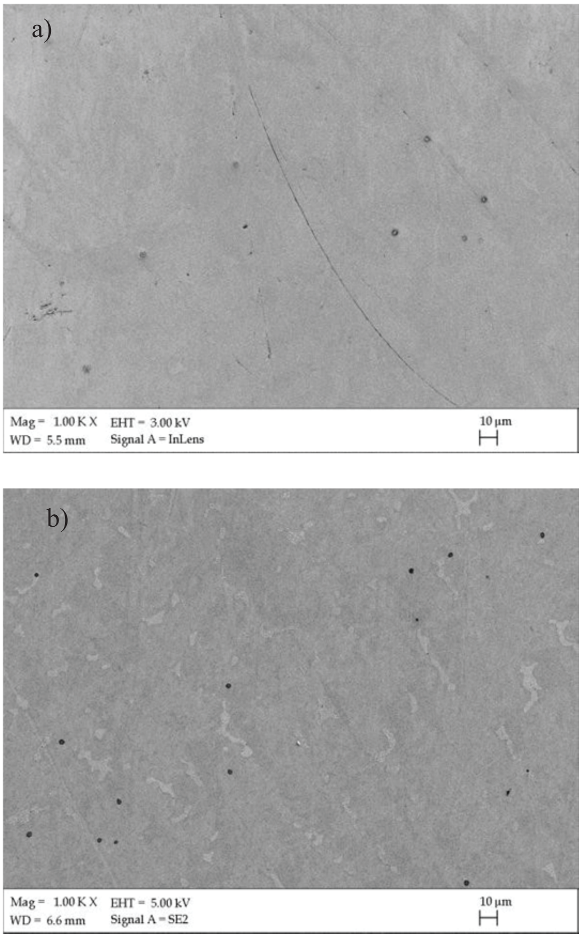

Fig. 2. SEM image of the surface of the Realloy C, a) before, b) after the potentiodynamic test

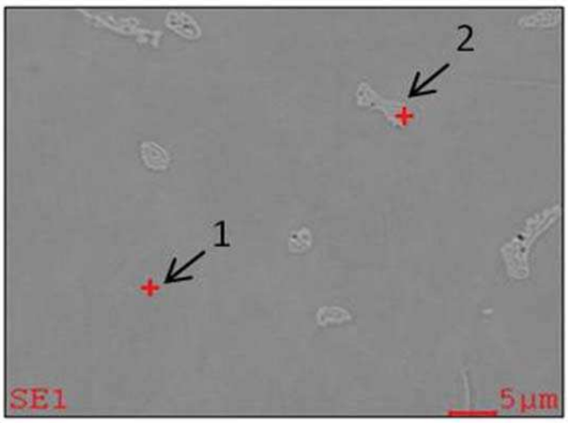

Fig. 3. SEM image of the surface of the Realloy C material with arrows pointing to the chemical composition analysis 1 – matrix, 2 – precipitates

Table 3.
Chemical microanalyses of Realloy C material obtained for the points 1 and 2

Point				
	1		2	
Element	% weight	% atomic	% weight	% atomic
Mn	0.69	0.78	0.45	0.53
Si	0.80	1.75	1.94	4.47
Mo	3.02	1.93	10.66	7.20
W	9.99	3.33	15.50	5.46
Cr	23.32	27.51	25.77	32.11
Co	62.17	64.71	45.68	50.22

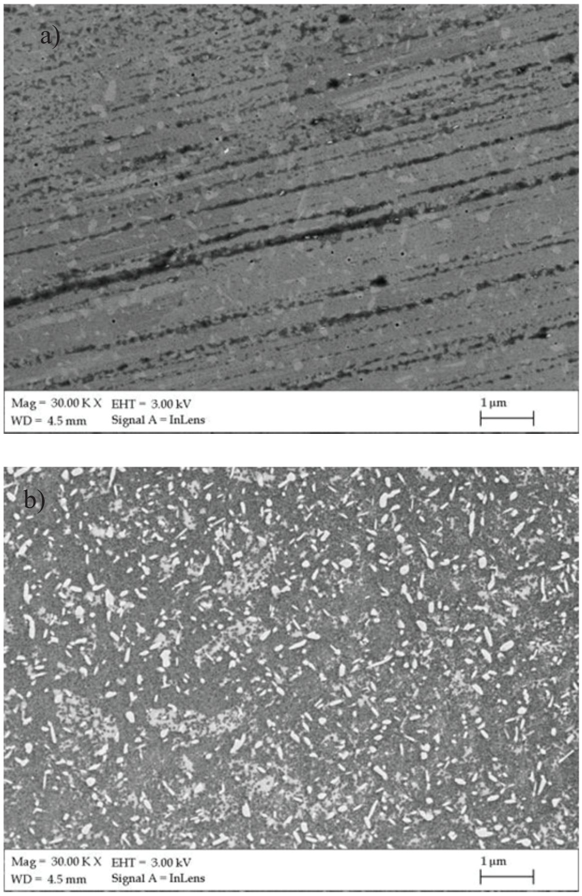

Fig. 4. SEM image of the surface of the EOS CoCr SP2 material before, b) after the potentiodynamic test

Chemical analysis of EOS CoCr SP2 material after pitting corrosion tests (Fig. 5) showed similar results to the analysis of Realloy material – in the matrix reduced concentrations of molybdenum and tungsten, whose decidedly major part was bound in the precipitates (Tab. 4).

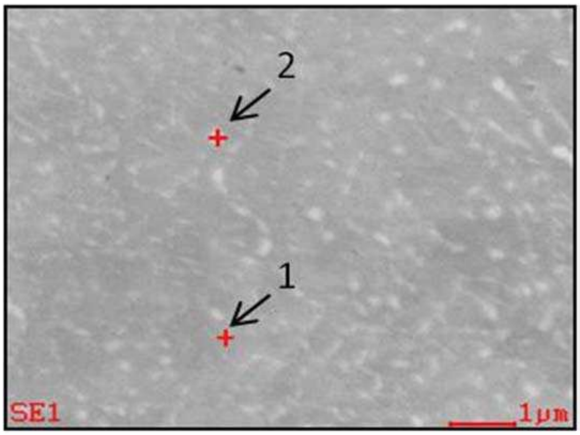

Fig. 5. SEM image of the surface of the EOS CoCr SP2 material arrows pointing to the chemical composition analysis 1 – matrix, 2 – precipitates

Table 4.
Chemical microanalysis of EOS CoCr SP2 material obtained for the points 1 and 2

	Point			
	1		2	
Element	% weight	% atomic	%weight	% atomic
Mo	5.53	3.57	12.10	8.41
W	8.86	2.99	14.37	5.21
Cr	23.76	28.34	20.86	26.76
Co	61.85	65.09	52.66	59.61

3.2. AFM

Results of observation using the atomic force microscopy are presented for Realloy C alloy and for EOS CoCr SP2 alloy respectively in Figure 6 and Figure 7. While the characteristic values describing surface roughness are shown in Table 5. The highest values of surface roughness were recorded for the cast samples. The mean values of surface roughness parameters for Realloy C alloy in the output state of scan areas were: for 25 x 25 μm scan areas ΔZ_{max} = 1915 nm, R_q = 97 nm and R_a = 84 nm, for 10 x 10 μm scan areas ΔZ_{max} = 1358 nm, R_q = 78 nm and R_a = 67 nm and for 2 x 2 μm Z_{max} = 316 nm, R_q = 26 nm and R_a = 19 nm. The lowest values for EOS CoCr SP2 alloy were recovered: for 25 x 25 μm scan areas ΔZ_{max} = 265 nm, R_q = 83 nm and R_a = 67 nm for 10 x 10 μm scan areas ΔZ_{max} = 273 nm, R_q = 39 nm and R_a = 32 nm and for 2 x 2 μm Z_{max} = 89 nm, R_q = 19 and R_a = 17. For the both analysed alloys, the values of roughness parameter for smallest scan areas were decreasing. Based on obtained results, it was found that the type of manufacturing technology does not significantly affect the quality of the surface topography.

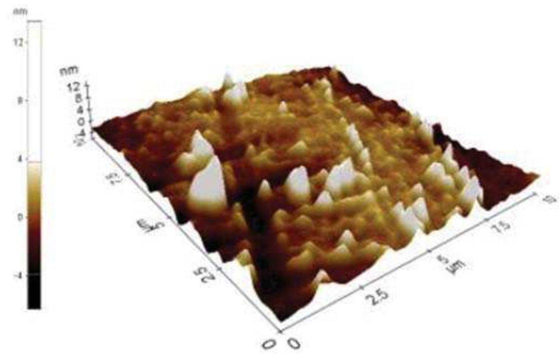

Fig. 6. Image of the Realloy C material, 10 x 10 μm

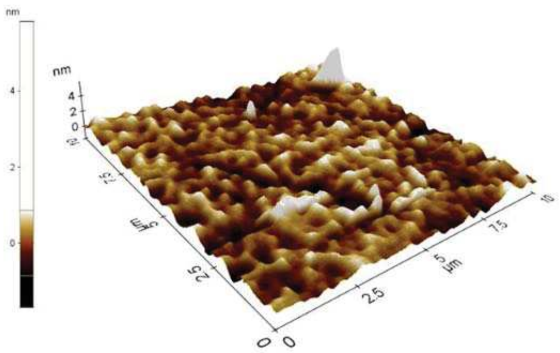

Fig. 7. Image of the EOS CoCr SP2 material, 10 x 10 μm

Table 5.
Results of surface roughness by the AFM method

Area	Parameters, nm	Realloy C	EOS CoCr SP2
25 x 25, μm	ΔZ_{max}	1915	265
	R_q	97	83
	R_a	84	67
10 x 10, μm	ΔZ_{max}	1358	273
	R_q	78	39
	R_a	67	32
2 x 2, μm	ΔZ_{max}	316	89
	R_q	26	19
	R_a	19	17

3.3. Surface roughness results

The tested cobalt based alloys are characterized by different surface roughnesses, despite sharing the same parameters for surface grinding and polishing. For the Realloy C material the mean value of R_a parameter was 0.37 μm and the obtained values were higher comported to EOS CoCr SP2 materials, the values of which were R_a = 0.07 μm.

3.4. Potentiodynamic tests

Results of potentiodynamic tests carried out to evaluate the pitting corrosion resistance are presented in Figure 8 and Table 6. For both the examined groups of materials, the polarization curves had a similar character. The progression of the curves was characteristic for materials with a high corrosion resistance – no hysteresis loops were recorded. Basing on the obtained polarization curves existence of transpassivation potential E_{tr} has been stated. For the Realloy C material mean value of transpassivation potential was E_{tr} = 837 mV and for EOS CoCr SP2 was similar E_{tr} = 875 mV. Furthermore, it was stated that the mean values of the corrosion potential for Realloy C was E_{corr} = -182 mV and the obtained value was higher comported to EOS CoCr SP2 materials, the value of which was E_{corr} = -273 mV. It was stated that the value of the polarization resistance R_p for the cast samples was equal 15 kΩ/cm^2 and for the printing samples the mean value was 490 kΩ/cm^2.

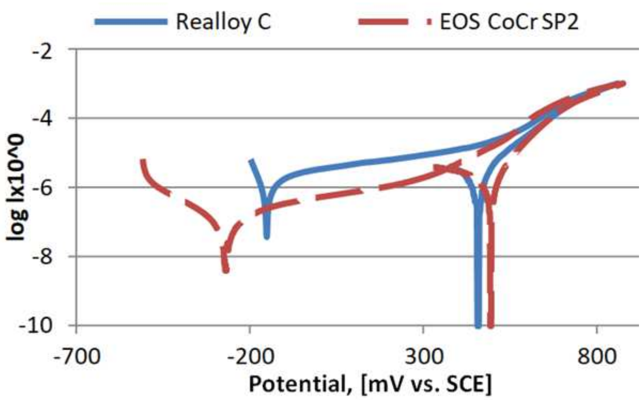

Fig. 8. Examples of the polarization curves for Realloy C and EOS CoCr SP2 materials

Table 6.
Results of potentiodynamic tests

Material	E_{kor}, mV	E_{tr}, mV	R_p, kΩ/cm^2
Realloy C	-182	837	15
EOS CoCr SP2	-273	875	490

4. Conclusions

Examined dental alloys are safe for use in the oral applications. However, based on obtained results, it can be concluded, that type of manufacturing technology have significantly affected of the final quality of the dental materials. Taking into consideration the accuracy of details, DMLS technology is more effective in terms of quality and dimensionality.

- For both materials chemical analyses revealed highest concentrations of molybdenum and tungsten in the precipitates.
- The microscopic observation of the surface topography for cast samples and samples obtained from the DMLS technology indicate the significant differences in the nature of the carbide precipitates.
- For the Realloy C alloy, the precipitates were mainly concentrated in eutectics. While for the EOS CoCr SP2 alloy the occurring precipitates were characterized by an irregular distribution in the entire volume of the material.
- The topography of the surface of the Realloy C material, before and after the corrosion resistance test was not different. For the EOS CoCr SP2 material after pitting corrosion tests a presence of more precipitates was observed, which did not affect corrosion resistance.
- Based on AFM results the quality of the examined alloys exhibited a repetitive surface quality regardless of scanning areas.
- The highest values of roughness surface parameter R_a were obtained for the Realloy C. The lower values of surface roughness parameters for materials used in dental application are most favorable. It reduce the ability of bacterial to adhesion to the surface of material.
- The alloys were characterized by similar corrosion resistance. The transpassivation potential obtained for Realloy C alloy E_{tr} = 837 mV and for EOS CoCr SP2 E_{tr} = 875 mV.

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