Surface Characteristics and Corrosion Properties of Co-Cr Dental Alloys Processed by Laser-based Methods

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Technological developments have led to the implementation of novel digitalized manufacturing methods for the production of metallic structures in prosthetic dentistry, less studied to date. The objective of the study was to assess the morphological characteristics and corrosion properties of selective laser sintered (SLS) and selective laser melted (SLM) cobalt–chromium (Co–Cr) dental alloys related to the surface processing and pH variations. For the experimental analyses metallic specimens made of Co-Cr dental alloys were prepared using SLS and SLM, as indicated by the manufacturers. The morphology and the topography of the samples were investigated by scanning electron microscopy and atomic force microscopy. Electrochemical measurements were made and the values for corrosion potential (Ecorr), corrosion current (icorr) and corrosion rate were calculated. The immanent advantages of additive technologies are accompanied by porosities resulted after the deposition of the fine metallic powder, especially for the SLM method. Considering the corrosion current density value a parameter which provides information on the kinetics of the corrosion process, SLS samples showed better performance under pH variations. Surface processing can result in an improvement in the corrosion performance also for extreme pH values. Given that the microstructure and corrosion behavior was significantly different, further differences in the clinical behavior of prosthetic restorations manufactured using SLS and SLM additive techniques are anticipated.

Keywords: dental alloys, additive manufacturing, surface morphology, corrosion

Technological developments have led to the implementation of novel digitalized manufacturing methods for the production of metallic structures in prosthetic dentistry, less studied to date [1-5]. These technologies can be classified as based on subtractive manufacturing, such as the milling of premanufactured materials assisted by computer-aided design/computer-aided manufacturing (CAD/CAM) systems or on additive manufacturing (AM), such as the recently developed laser-based methods [2, 3, 5-7].

The *p*H within the oral cavity may vary over time and the resulting ion exchange may affect the surface properties of the alloy and potentially modify the corrosion behavior [8, 9]. Corrosion of dental alloys can result in biological, functional and esthetic effects. Metal ions and by-products released in the corrosion process can affect cells and tissues in the immediate environment or disseminate into the organism. Depending on the nature and number of metal ions, risks of sensitization and/or toxic effects can occur with harmful effects for the organism. Thus, the clinical use of metal alloys in dentistry requires extensive investigation of their corrosion properties [10-13].

The objective of the study was to assess the morphological characteristics and corrosion properties of selective laser sintered (SLS) and selective laser melted (SLM) cobalt–chromium (Co–Cr) dental alloys related to the surface processing and *p*H variations.

Experimental part

Materials and methods

For the experimental analyses metallic 12 specimens made of Co-Cr dental alloys were prepared using selective laser sintering (SLS) and selective laser melting (SLM), as indicated by the manufacturers. Round plates of 20 mm diameter and 2 mm thick were fabricated using different technologies.

The laser-sintered and laser-melted specimens were prepared from commercial Co-Cr powder Starbond CoS Powder 16 (S & S Scheftner GmbH, Mainz, Germany) using a dental laser sintering device (PXS Dental System, Phenix Systems, Clermont-Ferrard, France), respective a SLM device MYSINT 100 (Sisma, Piovene, Italy). For scanning the high accuracy D700 scanner (3Shape, Copenhagen, Denmark) and for design Dental System™ CAD Software (3Shape, Copenhagen, Denmark) was used. The alloy is a type 4 alloy according to ISO 22674. Free of beryllium, nickel and cadmium. Nominal values of alloy composition in mass percent: Co 59.0; Cr 25.0; W 9.5; Mo 3.5; Si max. 1; other constituents: C, Fe, Mn, N max. 1.5.

The high power laser beam fused the powder granules homogeneously distributed on a flat building plate guided by a pre-determined pattern by computer aided design (CAD). After exposing to the laser beam, the building plate was lowered by one layer thickness and a new layer of powder granules was loaded on its top. The process was automatically repeated in a layer-by-layer manner. The laser power, scanning speed, and the distance between two scanning line sand layers were the principal parameters in the laser sintering and melting processes. These were set according to two recommendations for dental prostheses, respective metal processing, and using fibre laser for power bed fusion. For SLS samples, the applied laser power was 50 W, and layer thickness 30 μm and for SLM samples, the applied laser power was 80 W, and layer thickness 20 μm.

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During AM of metals it is necessary to shield the build point from harmful oxidation, by performing the whole operation in an inert chamber or using blown inert gas. In this case nitrogen was used with a debit of 5 L/min for SLS, respective 0.3 L/min for SLM.

Relief-firing was conducted under argon by heating up to 450°C within 60 min, holding for 45 min . The specimens resulted after CAD/CAM technologies were not additional prepared.

Oxide-firing (at 950 – 980°C) was performed, the metal surface was sandblast again with fresh aluminium oxide (approx. 150μm). Half of the specimens were ground until 2000-grit SiC paper, polished with universal polishing paste (Ivoclar Vivadent AG, Schaan, Principality of Liechtenstein). They were after cleaned in alcohol, rinsed in distilled water and dried with adsorbent paper towels. The morphology and the topography of the samples were investigated by scanning electron microscopy with energy dispersive X-ray analysis SEM / EDAX Model INSPECT S (FEI, Oregon, USA) and atomic force microscope AFM Model Nanosurf® EasyScan 2 (Nanosurf AG, Liestal, Switzerland).

The electrochemical measurements were obtained using a potentiostat Voltalab Model PGZ 402 with the software-ul VoltaMaster 4 v.7.09. This software calculated the values for corrosion potential (Ecorr), corrosion current (icorr) and corrosion rate. The electrolyte used was: HCl for *p*H=2; NaOH for *p*H= 10 and KCl for *p*H=6.5-7. For each sample, the open-circuit potential (OCP) vs. time was recorded over 30 min.

Results and discussions

The morphological aspect of the resulting powders was examined by SEM. Depending on the achieving technology and the surface processing of the samples, the morphology was different (fig. 1, 2).

AFM images (fig. 3, 4) of the surface for each of the studied samples were obtained using a scan size of 2 x 2μm. The contact mode cantilever was used to measure the samples.

The surface roughness was calculated with eq. 1 for the average roughness and eq. 2 for the mean square root roughness26.

$$S_a = \frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left|z(x_k, y_l)\right| \quad (1)$$

$$S_q = \sqrt{\frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left(z(x_k, y_l)\right)^2} \quad (2)$$

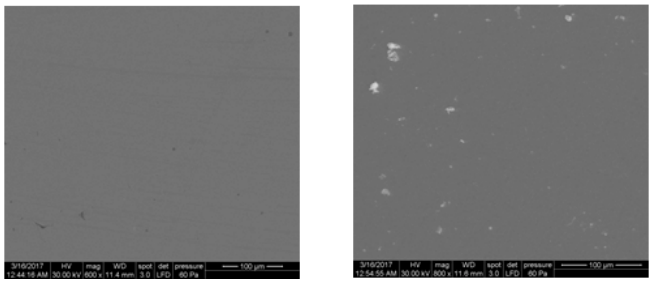

Fig. 1. SEM micrographs showing the structure of polished dental alloys processed by: a. SLS, b. SLM.

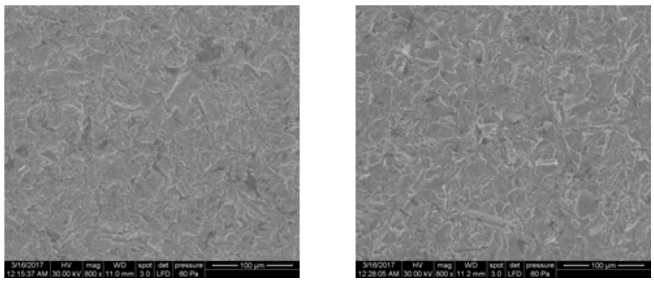

Fig. 2. SEM micrographs showing the structure of sandblasted dental alloys processed by: a. SLS, b. SLM.

where N and M are the crystallites number on x and y axis, z being the medium height of the crystallites, x_k and y_l are the maximum and minimum of the crystallites reported to the average value. The measured values (1.326 pm2 area) of Sa and Sq for the samples are given in table 1.

Table 1
THE SURFACE ROUGHNESSES

Samples	Sa (nm)	Sq (nm)
SLS polished	1.4	1.8
SLS sandblasted	5.9	7.9
SLM polished	8.4	9.6
SLM sandblasted	42	46

There was a strong correlation between the aspect of the samples (SEM images) and the roughness. The more uniform samples reflect in the lowest value of roughness and the non-uniform architectures present the highest value of roughness. The roughness is reflected in porous structures.

These findings regarding microstructural properties may have clinical implications. Mechanical properties, electrochemical properties and other properties may be altered by microstructural changes, and further research

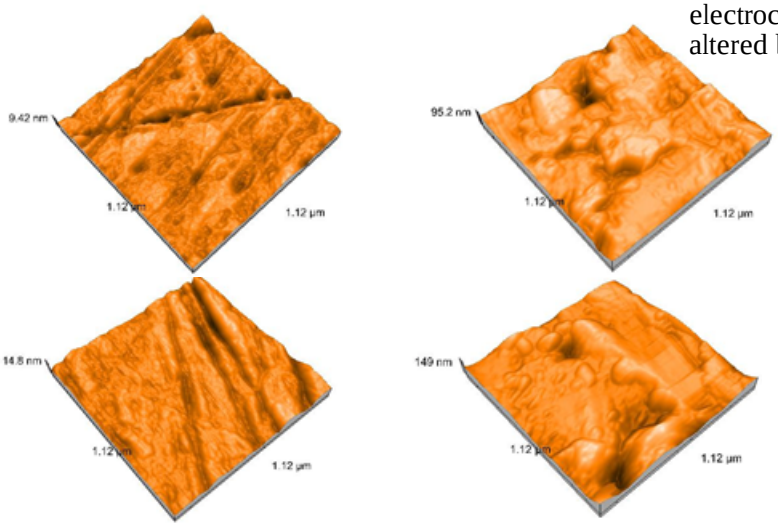

Fig. 3. 3D AFM images of the SLS obtained samples: a. polished, b. sandblasted

Fig. 4. 3D AFM images of the SLM obtained samples: a. polished, b. sandblasted

Sample		SLS M	SLS L	SLM M	SLM L
Ecorr (mV)	pH=2	-378.7	-473.3	-382.9	-415
	pH=7	-915	-1063.2	-921	-1093.5
	pH=10	-980.2	-889	-976.5	-1146.5
Icorr (μA/cm^2)	pH=2	60.24	15.10	61.67	38.99
	pH=7	7.04	13.18	6.19	10.53
	pH=10	13.37	0.81	13.47	7.80
Corrosion rate (μm/Y)	pH=2	704.7	176.6	721.3	456
	pH=7	82.34	154.1	72.49	123.2
	pH=10	156.4	9.55	157.5	91.33

Table 2
ELECTROCHEMICAL PARAMETERS FOR DIFFERENT SAMPLES AND *p*H VALUES

is thus required in this field, for these recently introduced additive technologies.

Open-circuit potential (OCP) allows for the drawing of a relative comparison of the nobility of the alloys in the electrolyte under consideration, being a measurement of the corrosion tendency. Lower OCP values represent a greater tendency toward corrosion. As can be seen in figure 5, for the alloys, a slight increase in potential was observed during immersion in the solutions, indicating that the corrosion tendency of the materials decreased due to the contact with the solution.

Among the different samples, there were differences in the electrochemical potential, which was in the range of -378.7 to -1146.5mV (table 2), the lowest values were registered for *p*H=2.

An increase in the electrochemical potential during immersion can usually be attributed to thickening of the passive film, which becomes more protective. After 30 min of immersion, all of the alloys tended to achieve a steady state.

Considering the potentiodynamic polarization curves plotted in figure 6, the first important remark is that all of the alloys could form a passive film.

The values of the corrosion current (icorr) estimated from the potentiodynamic polarization curves, are summarized in table 2. A higher corrosion current density indicates that the overall corrosion rate will be higher. The corrosion current values were higher for *p*H=2 and sandblasted samples, reflecting a higher corrosion rate.

The processing method (SLS or SLM) had no significant influence on the obtained electrochemical values, only the *p*H values. Surface finishing is important especially for *p*H=2 and *p*H=10, for the neutral solution is less essential.

It is known that the mouth is an ideal environment for the biodegradation of metals, exposing patients to their corrosion products [14]. Metallic alloys corrode in the oral cavity, even when covered with a passive film. However, the corrosion rate of a given material will depend on the environmental conditions of its surroundings [15]. High corrosion resistance, resulting in low ionic release, is a requirement for dental alloys.

Generally, a high OCP indicates a high tendency to resist corrosion. An increase in Ecorr can usually be attributed to an increase in the thickness of the oxide passive film. Ecorr measurements do not provide any information on the

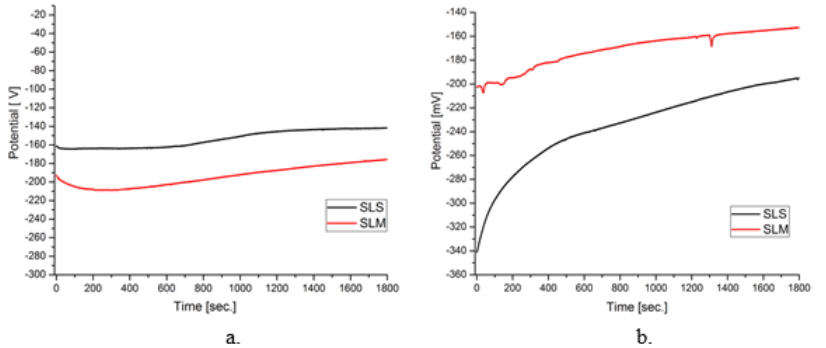

Fig. 5. Curves of the evolution of the open-circuit potential with time, at a *p*H of 6.5-7, for: a. polished samples, b. sandblasted samples

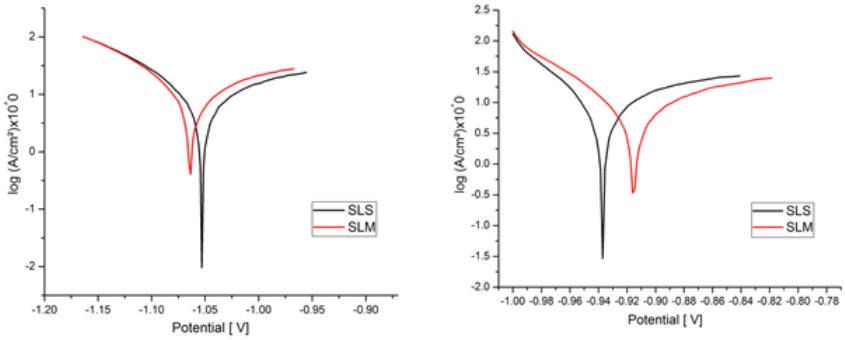

Fig. 6. Potentiodynamic polarization curves obtained at a *p*H of 6.5-7, for: a. polished samples, b. sandblasted samples.

kinetics of the corrosion process. This information can be obtained from the corrosion current density (icorr). From the thermodynamic point of view, the acid environment leads to a thinner oxide passive film, reflected through higher corrosion current density values and corrosion rates. For *p*H variations it would be advisable to polish the metallic surfaces. SLS obtained samples perform better under *p*H variations.

An additional important concern when considering dental restorative metallic materials is that the chemical and electrochemical environment in the oral cavity is very complex and can have enormous variations within the same individual as a function of time. Variations in pH, temperature, composition or the amount of microorganisms adhering to the dental surface are expected. In this context, the electrochemical potential of the material can change [10].

Taking into account the many benefits of AM technologies, and the findings regarding the studied structural and morphological characteristics of Co-Cr dental alloys processed by alternative manufacturing techniques, more research is required in order to understand the influence of microstructure on restoration properties, further veneering procedures of the frameworks, and last but not least the clinical behavior.

Conclusions

The immanent advantages of additive technologies are accompanied by porosities resulted after the deposition of the fine metallic powder, especially for the SLM method.

For the short immersion times tested in this work, no significant differences were observed in the electrochemical behavior when comparing SLS and SLM processing methods in neutral solution.

Considering the corrosion current density value a parameter which provides information on the kinetics of the corrosion process, SLS samples showed better performance under *p*H variations.

Surface processing can result in an improvement in the corrosion performance also for extreme *p*H values.

Given that the microstructure and corrosion behavior was significantly different, further differences in the clinical behavior of prosthetic restorations manufactured using SLS and SLM additive techniques are anticipated.

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References

1.AL JABBARI, YS, KOUTSOUKIS, T, BARMPAGADAKI, X, ZINELIS, S, Metallurgical and interfacial characterization of PFM Co-Cr dental alloys fabricated via casting, milling or selective laser melting, Dent Mater, **30**(4), 2014, p. 79.
2.VAN NOORT, R, The future of dental devices is digital, Dent Mater, **28**, 2012, p. 3.
3.QUANTE, K, LUDWIG, K, KERN, M, Marginal and internal fit of metal–ceramic crowns fabricated with a new laser melting technology, Dent Mater, **24**, 2008, p. 1311.
4.TRAINI, T, MANGANO, C, SAMMONS, RL, MANGANO, F, MACCHI, A, PIATTELLI, A, Direct laser metal sintering as a new approach to fabrication of an isoelastic functionally graded material for manufacture of porous titanium dental implants, Dent Mater, **24**, 2008, p. 1525.
5.MIYAZAKI, T, HOTTA, Y, CAD/CAM systems available for the fabrication of crown and bridge restorations, Aust Dent J, **56**(1), 2011, p. 97.
6.WILLER, J, ROSSBACH, A, WEBER, HP, Computer-assisted milling of dental restorations using a new CAD/CAM data acquisition system, J Prosthet Dent, **80**, 1998, p. 346.
7.ALT, V, HANNIG, M, WOSTMANN, B, BALKENHOL, M, Fracture strength of temporary fixed partial dentures: CAD/CAM versus directly fabricated restorations, Dent Mater, **27**, 2011, p. 339.
8.WYLIE, CM, SHELTON, RM, FLEMING, GJP, DAVENPORT, AJ, Corrosion of nickel-based dental casting alloys, Dent Mater, **23**(6), 2007, p. 714.
9.AL-HITY, RR, KAPPERT, HF, VIENNOT, S, DALARD, F, GROSGOGEAT, B, Corrosion resistance measurements of dental alloys, are they correlated? Dent Mater, **23**(6), 2007, p. 679.
10.GALO, R, ROCHA, LA, FARIA, AC, SILVEIRA, RR, RIBEIRO, RF, DE MATTOS, MDGC, Influence of the casting processing route on the corrosion behavior of dental alloys, Mater Sci Eng C Mater Biol Appl, **45**, 2014, p. 519.
11.XIN, XZ, CHEN, J, XIANG, N, GONG, Y, WEI, B, Surface characteristics and corrosion properties of selective laser melted Co-Cr dental alloy after porcelain firing, Dent Mater, **30**(3), 2014, p. 263.
12.HANCU, V., COMANEANU, R.M., COMAN, C., FILIPESCU, A.G, GHERGIC, D.L., COTRUT, M.C., In vitro study regarding the corrosion resistance of NiCr and CoCr types dental alloys, Rev. Chim. (Bucharest), **65**, no. 6, 2014, p. 706.
13.COMANEANU, R.M., HANCU, V., BARBU, H.M, COMAN, C., COTRUT, C.M., TARCOLEA, M., HOLICOV, A.M., ORMENISAN, A., Comparative assessment of biocompatibility of NiCr and CoCr alloys used in metal fused-to-ceramic technology, Rev. Chim. (Bucharest), **66**, no. 3, 2015, p. 312.
14.CANAY, S, HERSEK, N, CULHA, A, BILGIÇ, S, Evaluation of titanium in oral conditions and its electrochemical corrosion behavior, J Oral Rehabil, **25**(10), 1998, p. 759.
15.BERGMAN, M, Corrosion in the oral cavity—potential local and systemic effects, Int Dent J, **36**(1), 1986, p. 41.

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