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Metal Ion Emission and Corrosion Resistance of 3D-Printed Dental Alloy

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Abstract

BACKGROUND: Prosthetic rehabilitation requires application of materials with different chemical, mechanical, and biological properties which must provide longevity, esthetics, and safe use. Corrosion resistance and metal ion emission are the major factors defining biocompatibility of base dental alloys. Digitalization in dentistry leads to the development of new materials suitable for CAD/CAM technologies. Cobalt-chromium powder alloys are used for additive manufacturing of PFM crowns.

AIM: The aim of this study is to evaluate metal ion emission and corrosion resistance of cobalt-chromium dental alloy for 3D printing.

MATERIALS AND METHODS: Thirty-five metal copings were designed using digital files of intraoral scans of 35 patients. CoCr dental alloy EOS CobaltChrome SP2 (EOS, Germany) was used to produce the copings by direct metal laser sintering. Tests for the presence of free cobalt ions were conducted at several stages of the production process. Open circuit potential measurements were conducted 2 h, 24 h, and 7 days after placing the copings in artificial saliva. Metal ion emission was assessed by inductively coupled plasma mass spectrometry (ICP-MS) after 24 h and 7 days period of stay in the solution.

RESULTS: Tests for free cobalt ions were positive at all stages during production of the metal copings. Eocp measurements showed high corrosion resistance which increased in time. ICP-MS showed significantly higher amount of cobalt and chromium ions after 7-day period of stay compared to 24 h period.

CONCLUSION: Metal ion emission and corrosion resistance are within the accepted range, but the detected ion release from the tested dental alloy for 3D printing requires further clinical investigations on the biological properties.

Introduction

3D printing in the medical field provides fabrication of tissue engineering models, anatomical and pharmacological models, medical devices, and instruments [1]. Prosthetic rehabilitation requires application of foreign to the body materials with different chemical, mechanical, and biological properties. The combined use of materials, different in nature, provides longevity, esthetics, and safe use of the fixed and removable dental restorations.

Biocompatibility is the ability of a material to be accepted in a specific live environment without any harmful or unwanted side effects [2]. Metallic biomaterials for temporary and long-term use are applied in different branches of medicine and dental medicine [3], [4], [5]. All dental alloys must satisfy the requirements of biocompatibility. The most important feature of a dental alloy for its biological safety is its tendency to corrosion [6], [7] because biodegradation leads to metal ion release which is a potential risk for human health. Systemic and local toxicity, allergic reactions, and carcinogenicity could be caused by the metal ion emission from the dental alloy in patient's oral cavity [8], [9], [10], [11], [12], [13].

Corrosion is a process of destroying metals and metal alloys under the influence of agents of the environment. Electrochemical corrosion appears when along with the metal deterioration electrical potentials appear on the metal surface. After placing a metal object in an electrolyte, the surface starts to ionize, metal ion emission is observed, and the metal starts to dissolve. Oxygen molecules are absorbed on the metal surface and together with the metal ions form a surface oxide layer which inhibits the corrosion process and limits it only to the surface of the object. Despite the formation of passive oxide layer, corrosion process of metal objects may continue [14]. Corrosion potential expresses the ability of the metal or the metal alloy to dissolve in a specific electrolyte. The bigger the absolute values of the corrosion potentials, the lower the resistance to corrosion of the material [15]. The reference values of corrosion potentials of base metal dental alloys are within the range from 0 mV to −150 mV [16].

Metal ceramic fixed prosthetic restorations can be produced either by the classical method of lost wax casting technique or the innovative CAD/CAM technologies. Contemporary digital methods provide fast and precise dental restorations [17]. There are several additive manufacturing methods that can be applied for dental metal alloys and new techniques for 3D printing are being developed [18]. Each 3D printing method has advantages and disadvantages concerning porosity of the structure, dimensional stability, surface roughness, cost, etc. [19]. Selective laser sintering (SLS) is a technique in which the metal alloy particles are bonded to each other in layers by laser energy without reaching the melting temperatures of the components present. This AM method can be applied for different types of alloys such as titanium alloys, CoCr alloys, NiTi alloys, and stainless steel. However, the final product has high porosity, and the method requires post-processing. At selective laser melting (SLM) technique, the laser beam energy is used to fuse the particles in layers after melting all the components of the alloy. It provides production of metal parts with higher dimensional accuracy and better surface roughness [20]. Direct metal laser sintering (DMLS) is technology similar to SLS and may be applied for base dental alloys. The advantage of DMLS to SLM is that it is not necessary to reach the melting temperatures of all components of the alloy to receive the final monolithic object [21]. Powder alloys for metal ceramic dental restorations, most commonly Co based, are developed for SLM and DMLS [22].

Studies show that structure, mechanical properties, and corrosion resistance of metal devices are influenced by the method of manufacturing and different 3D printing techniques (SLM, DMLS, SLS, and electrohydrodynamic redox printing) provide different quality of the final products [23]. Resistance to corrosion of metal specimens produced by additive manufacturing is comparable and even higher than the one of the casted specimens [24], but the parameters of the production process such as building orientation, laser power, laser scan speed, laser spacing, layer thickness, and thermal post-processing may significantly affect structure, mechanical properties, surface roughness, porosity, ion emission, and corrosion resistance of the metal core of final prosthetic metal ceramic restoration [25], [26], [27].

The significance of metal ion emission for the biocompatibility of the dental alloy guided us in defining the aims of the present research.

The aim of this *in vitro* study is to evaluate metal ion release and corrosion resistance of cobalt-chromium dental alloy for DMLS in artificial saliva.

Materials and Methods

Thirty-five metal copings were designed using digital files from intraoral scans of 35 patients (Figure 1). The files of the designed copings were sent to the 3D printer EOS M100 (EOS, Germany), present at the CAD/CAM Center of FDM-Plovdiv, for DMLS. The fabric settings of the 3D printer were laser power – 200W; laser scanning velocity – 7000 mm/s; and layer thickness – 20 μm. CoCr dental alloy EOS CobaltChrome SP2 (EOS, Germany) was used for the production of the metal copings. The composition of the alloy according to the producer is as follows: Co: 63.8 wt-%; Cr: 24.7 wt-%; Mo: 5.1 wt-%; W: 5.4 wt-%; Si: 1.0 wt-%; Fe: Max. 0.50 wt-%; Mn: Max. 0.10 wt-%; and free of Ni, Be, Cd, and Pb according to ISO 22674.

Figure 1: Metal copings after DMLS

After DMLS and thermal stress-relieving regime, the specimens were sandblasted with particles of Al_2O_3, 50 μm in size. The metal copings were placed in a mineral medium resembling saliva, prepared of 0.9% NaCl with acidity adjusted by adding 1% lactic acid and 4% sodium hydroxide up to pH 7.4 ± 0.1 according to standard ISO 2071:2011(E) [28]. The corrosion resistance of the alloy has been assessed according to the values of the open circuit potentials (Eocp) appearing between the metal coping and the passive reference stainless steel electrode placed in the electrolyte at 2–4 mm distance, using apparatus Dentotest Six (Atlantis, Bulgaria) (Figure 2). The

Figure 2: Apparatus Dentotest Six for Eocp evaluation

apparatus is calibrated with voltage calibrator FLUKE SLK 753 and is approved by the standard ISO 13485 (CE 2274). Eocp measurements were conducted after 2 h, 24 h, and 7 days of stay in the medium. Tests for the presence of free cobalt ions using “Chemo Cobalt Test” (Chemotechnique Diagnostics, Sweden) were conducted at several stages of the production process – at the initial powder alloy, before 3D printing, after 3D printing (DMLS), after stress relieving, after preparation for porcelain firing, and after the fabrication of the PFM crowns were completed. Reaction between nitroso-R-salt and free cobalt leads to change in color of the cotton tip from white to reddish-brown [29], [30] (Figure 3).

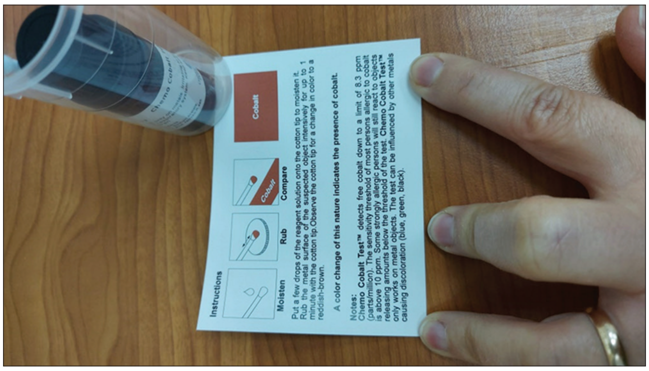

Figure 3: “Chemo Cobalt Test” instructions

Determination of Co and Cr ions in artificial saliva was carried out by inductively coupled plasma mass spectrometry (ICP-MS) after 24 h and 7-day period of stay in the solution using apparatus Thermo Scientific iCAP Qc (Thermo Fisher Scientific Inc., USA), present at the Research Institute at Medical University of Plovdiv.

For statistical processing, SPSS statistical package version 19.0 was used, and parametric independent sample t-test and paired sample t-test were applied.


Figure 4: Positive test of the powder alloy

Results

Tests for free cobalt ions were positive at all stages (Figures 4 and 5) during production of the metal copings (Table 1).

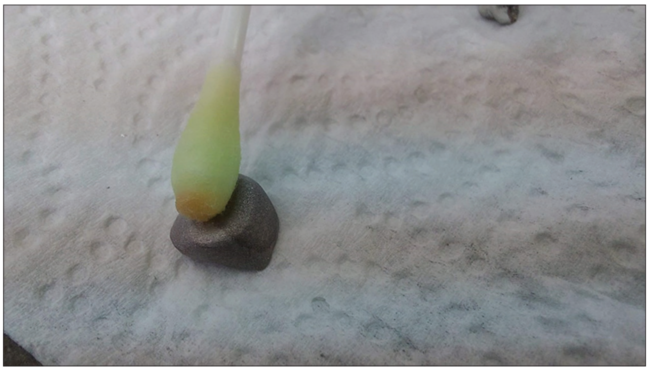
Figure 5: Positive test of the sandblasted coping

Two hours after placing the metal copings in artificial saliva with pH of 7.4 ± 0.1, the Eocp measurements were within the accepted range. There was no statistically significant difference between the received values and the norm of −150 mV.

After 24 h stay and 7-day stay in artificial saliva, the Eocp values were also within the accepted range and decreased significantly (in absolute values) with increasing the period of stay (Figure 6 and Table 2).

ICP-MS analysis showed that the concentration of cobalt and chromium ions in the medium was significantly higher on the 7th day compared to the 24 h period (Table 3).

Discussion

The positive qualitative reaction of free cobalt may be caused by the presence of unstable cobalt oxide on the surface of the powder particles and unwelded particles on the surface of the copings after DMLS.

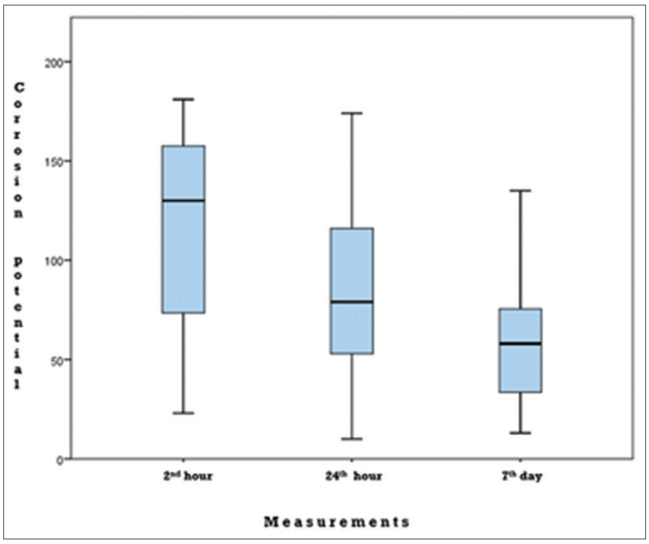

Figure 6: Eocp measurements (in absolute values) on the 2nd hour, 24th hour and 7th day

The copings designed for the patients had different size, weight, and surface, and for that reason, the

Table 1: Reaction for the detection of free cobalt ions

Before DMLS (powder alloy)	After 3D printing	After thermal post-processing	After sandblasting	After porcelain firing
+++	++	++	+	+

Visual determination of color change to reddish-brown: +++: Very intensive color change, +++: Intensive color change, +: Presence of color change, -: Lack of color change.

concentration of the emitted ions in artificial saliva was recalculated from μg/L into μg/g alloy. The significantly higher concentration of the tested ions on the 7th day leads us to conclusion that despite passivation corrosive changes of the alloy continue [14]. It should be stated that the second measurement on the 7th day showed the ion emission concentration for a 7-day period, not just for 1 day. Dividing the mean values of the second measurement by 7, it may be concluded that the speed of ion emission decreases after the 1st day.

Table 2: Dynamics of Eocp mean values

Period of stay	Mean	Std. dev.	Std. error mean	p-value
2 h vs. 24 h	32.5	38.1	6.5	<0.001
24 h vs. 7 days	24.7	37.1	6.3	<0.001

The ICP-MS analysis showed that the level of the cobalt and chromium emission does not correspond to their ratio in the alloy composition. This may be due to the formation of very stable layer of chromium oxides on the coping surface [31]. The concentration of emitted chromium ions was negligibly low, and it may be assumed that it would not cause clinical adverse reactions. Comparing the measured concentration of emitted cobalt ions with derived no-effect level value for cobalt (8.9 μg/kg/day), it can be concluded that a metal ceramic crown with a framework made of the studied alloy would not lead to unwanted biological effects [32].

Table 3: Descriptive analysis of the values of ion emission (μg/g alloy)

Metal ions	Time of measurement	N	Min.	Max.	Mean	SD	p-value
Cobalt	24th h	35	5.736	122.435	42.569	29.701	<0.001
	7th day	35	5.785	249.935	73.117	63.338	
Chromium	24th h	35	0.032	1.941	0.349	0.449	<0.001
	7th day	35	0.113	3.160	0.649	0.638	

According to the measured Eocp values which were within the accepted range, the studied alloy showed high corrosion resistance 2 h after placing the copings in artificial saliva. The formation of passive layer on the metal surface provides good corrosion stability even after this short period of time. After 7 days, the resistance to corrosion becomes even higher probably due to continuing passivation and stable oxide layer. Our studies confirm the results of Alvarez *et al*. which demonstrated that after the initial dissolution of the oxide surface layer, it is restored with time [33]. Corrosion resistance is assessed by evaluating the Eocp measurements received by the apparatus Dentotest Six, designed for clinical use, in “Pathogalvanism” working mode. The device does not provide potentiodynamic testing but would allow making a comparison between laboratory and clinical measurements.

The results from our study correspond to the conclusions of Aldhohrah *et al*., according to which the concentration of the emitted Co and Cr ions is higher on the 7th day compared to the measurement on the 24th h [34].

Conclusion

Metal ion emission and corrosion resistance are within the accepted range, but the detected ion release from the tested dental alloy for 3D printing requires further clinical investigations on the biological properties.

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