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Original Article

Clinical and Laboratory Study of Corrosion Resistance of a Base Dental Alloy for Selective Laser Melting

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Abstract

Introduction: CAD/CAM technologies are becoming widely used for the production of metal ceramic dental restorations. Powder Co-based alloys are developed for selective laser melting. The corrosion resistance of the dental alloy affects the biocompatibility, functional suitability, and longevity of the prosthetic restoration.

Aim: The aim of this study was to evaluate and compare the corrosion resistance of a cobalt-chromium dental alloy for porcelain-fused-to-metal (PFM) crowns produced for selective laser melting technique in clinical and laboratory conditions.

Materials and methods: PFM crowns were made for 35 patients using CAD/CAM technology. The metal copings of the crowns were made of the EOS CobaltChrome SP2 alloy (EOS, Germany). Eocp measurements were conducted 2 hours and 7 days after fixing the restorations in oral cavity. The digital files of patients' designed copings were used for the production of another 35 specimens, which were placed in artificial saliva. Eocp measurements were conducted after the same periods.

Results: In vitro studies showed high corrosion resistance after the short 2-hour stay. After 7 days in artificial saliva, the corrosion resistance became even higher probably due to strong passivation. In clinical conditions, Eocp values were slightly higher than the normal range 2 hours after fixing the crowns. Seven days after fixing, the Eocp values showed a decrease of corrosion resistance of the PFM crowns. The cause of the decrease may be interaction with other metal objects or specific conditions of the oral cavity.

Conclusions: The investigated alloy showed high corrosion resistance in in vitro settings. Clinical research revealed that PFM crowns had lower corrosion resistance. Further observation and research are required.

Keywords

cobalt based alloys, corrosion resistance, SLM

INTRODUCTION

Metal-ceramic restorations are fabricated using either the traditional lost-wax method or cutting-edge CAD/CAM techniques. There are two main ways to create the metal copings when using modern digital techniques: milling or 3D printing by selective laser melting (SLM). These two methods provide fast and precise dental restorations.[1]

Structural, mechanical properties, marginal fit, metal ceramic bond strength, and corrosion resistance depend on the composition of the alloy and the fabrication method of the metal copings.[2-4] Powder Co-based dental alloys are most commonly used for SLM.[5]

Corrosion resistance of dental alloys is critical for the biocompatibility and has a direct impact on the functional suitability and longevity of prosthetic restorations.[6] Corrosion is the process by which metal objects deteriorate due to agents in the surrounding environment. Saliva has a strong corrosive effect depending on its pH and chloride ion concentration. When a metal object is immersed in an electrolyte, the surface begins to ionize, metal ion emission is observed, and the metal begins to dissolve. Oxygen molecules are absorbed on the metal surface and, together with metal ions, help to form a surface oxide layer, which inhibits corrosion and confines it to the surface of the metal object.

The oral cavity contains a thin biofilm composed of proteins and glycoproteins from saliva. After fixing a prosthetic restoration in the patient's mouth, this organic layer covers its surface, potentially reducing corrosion. Despite the formation of a passive oxide layer and the presence of biofilm, it is possible that metal objects in the oral cavity will continue to corrode.[7] As a result, metal ions are emitted and digested. They may be the cause of allergic reactions, systemic and local toxicity, and changes in cell structures and functions.[8-10] The increased level of cobalt ions may initiate cell apoptosis and may lead to suppressed lymphocyte proliferation. Co^{2+} and Co^{6+} may inhibit the release of Il-2. It is suggested that even if the concentration of metal ions has no direct cytotoxic effect, it may provoke changes at molecular level and may contribute to alteration in the immune response of patients with cobalt-chromium implants.[11] Electrochemical corrosion is observed in cases where, along with the deterioration of the metal object, an electric load appears on the surface.[12] Corrosion potentials demonstrate the ability of the metal or the metal alloy to dissolve in a specific electrolyte solution. Values of the corrosion potentials represent the ion emission of the metal or the metal alloy and its level is considered crucial for their biocompatibility.[13] According to Botushanov et al.[14], the corrosion potentials of base metal dental alloys have reference values ranging from 0 mV to −150 mV, and the total amount of corrosion potentials in the oral cavity should not exceed 600 mV. In the prosthetic treatment of defects in dental tissues and dental arches, different types of alloys are used, which, when placed in saliva, have electrode corrosion potentials on their surfaces. If the metal objects are in direct contact or become connected through a conductor, such as saliva, blood plasma, or soft gingival tissues, galvanic electrical current flows between them. The process of oral electro-galvanism affects the body mainly because of the ion emission. The increased ion concentration affects the surrounding tissues and distant organs and systems through its allergenic, cytotoxic, and genotoxic effects.[15]

AIM

The aim of this study was to determine the corrosion resistance of a cobalt-chromium dental alloy produced for selective laser melting technique in clinical and laboratory environment.

MATERIALS AND METHODS

Porcelain-fused-to-metal crowns were manufactured for 35 patients using CAD/CAM technology. After taking digital impressions **(Fig. 1)**, the metal copings were designed,

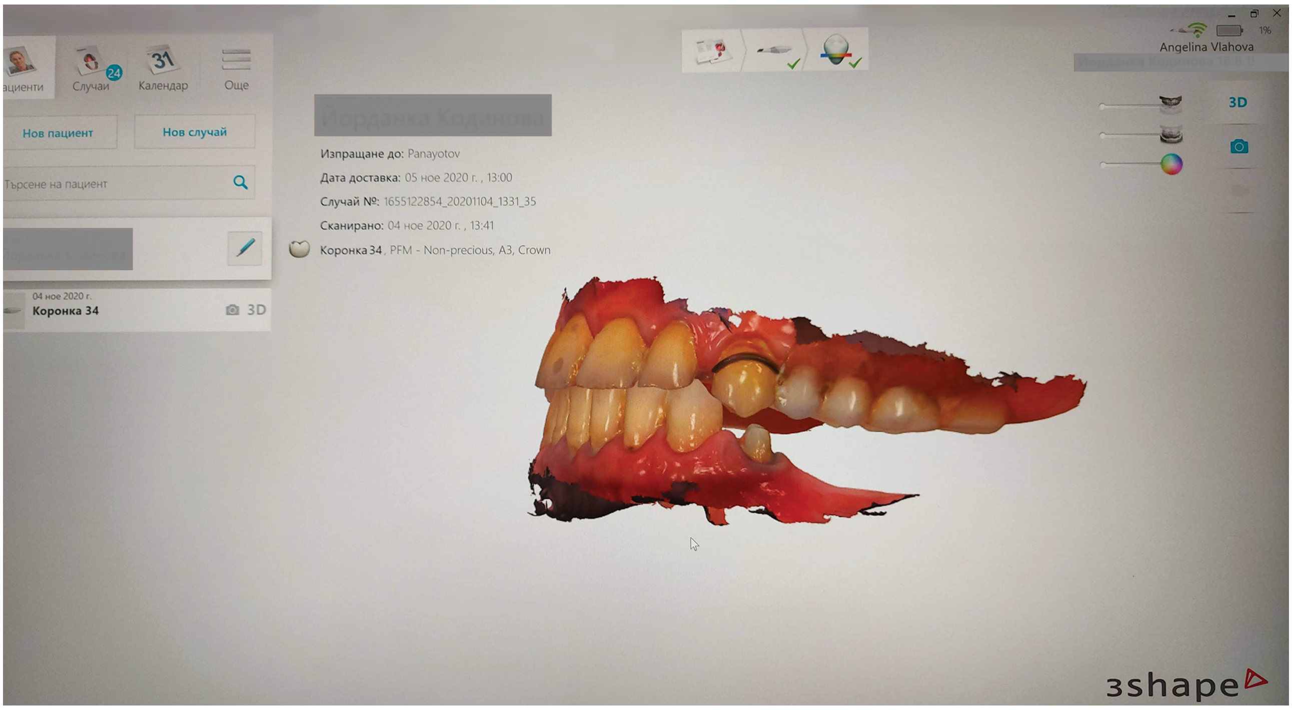

Figure 1. A digital impression.

and the files were sent to the 3D printer (EOS M100, Germany) available at the CAD/CAM Center of the Faculty of Dental Medicine in Plovdiv for selective laser melting of the dental alloy **(Fig. 2)**. The 3D printed resin models were used for completing the PFM restorations **(Fig. 3)**. Co-Cr dental alloy EOS CobaltChrome SP2 (EOS, Finland) was used for the production of the metal copings. The composition of the alloy according to the producer is: 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-%; free of Ni, Be, Cd and Pb according to ISO 22674.

Informed consent was obtained from all patients included in the study. None of the patients reported symptoms of gastric disorders and no signs of acidic erosion on the hard dental tissues were observed. The crowns were fixed with resin-modified glass ionomer cement Ketac Cem Plus (3M ESPE, USA) **(Fig. 4)**.

The tests were conducted in the morning. Before the measurements, patients were instructed not to consume any food or drink other than water. The corrosion resistance of the alloy in clinical conditions was assessed according to the values of the open circuit potentials (Eocp) appearing between the visible metal edge of the PFM crown and the gingiva at a distance of 2-4 mm using a Dentotest Six apparatus (Atlantis, Bulgaria). The apparatus was calibrated with a voltage calibrator FLUKE SLK 753 and was approved by the standard ISO 13485 (CE 2274). The measurements were conducted 2 hours after fixing the crowns into the patients' oral cavities and after a period of 7 days.

Figure 2. 3D printed metal copings.

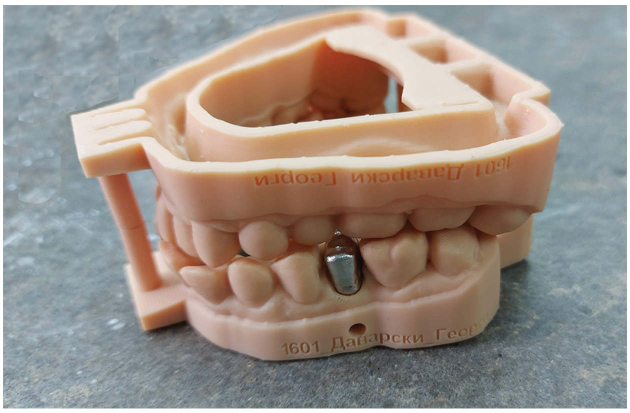

Figure 3. A metal coping on a 3D printed resin model.

Figure 4. A PFM crown on tooth 14.

For the in vitro measurements, the patients' digital files of the designed copings were used and another 35 metal specimens were produced from the same alloy using SLM and 3D printing. After selective laser melting and stress-relieving regime, the specimens were sandblasted with 50-μm Al_2O_3 particles. The metal copings were immersed in artificial saliva **(Fig. 5)**, 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).[15] Containers were stored in steady room temperature of 22°C. Eocp measurements were conducted after 2 hours, and a 7-day stay in the medium using the same apparatus (Dentotest Six, Atlantis, Bulgaria) **(Fig. 6)**.

For statistical analysis, SPSS v. 19.0 was used, applying the parametric independent sample *t*-test and the paired sample *t*-test.

RESULTS

The results of the open circuit potential measurements of the specimens placed in artificial saliva and the Eocp values

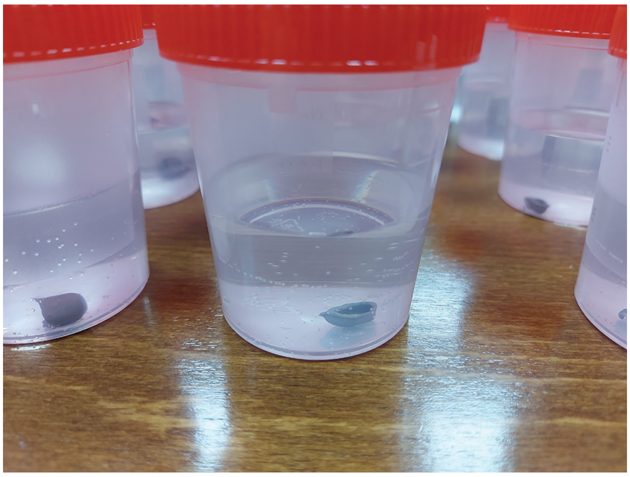

Figure 5. Metal specimens in artificial saliva.

Figure 6. The Dentotest Six apparatus.

received from the crowns in the oral cavity are presented in **Table 1**.

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 staying 7 days in artificial saliva, the Eocp values were also within the accepted range and were significantly lower (in absolute values) than the Eocp values received after the 2-hour stay **(Fig. 7)**.

Two hours after fixing the PFM crowns in the oral cavity, 19 of the crowns (54.3%) had higher than 150 mV Eocp values. The mean was −166.6±61.2 which is insignificantly higher than the norm of −150 mV (p=0.119).

After staying 7 days in the mouth, an increase of the corrosion potential mid values was detected, but it was not significantly higher than the values measured after a 2-hour stay (p=0.149) **(Fig. 8)**. There was, however, a statistically significant difference between the accepted norm of −150 mV and the Eocp measurements received at the 7th day (p=0.009). An increase of the number of cases with Eocp values exceeding the accepted range of 0 mV to −150 mV was registered, compared to the 2-hour period (p=0.090) **(Table 2)**.

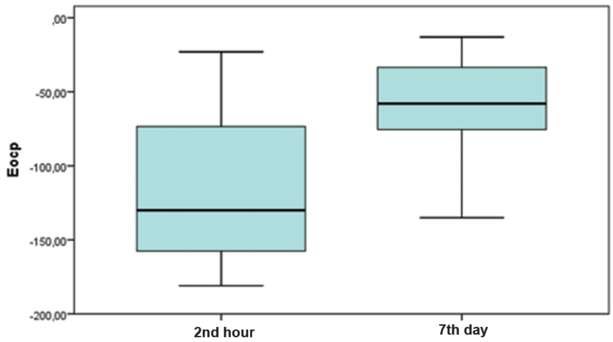

Figure 7. Eocp values after 2 hours and after 7 days in artificial saliva.

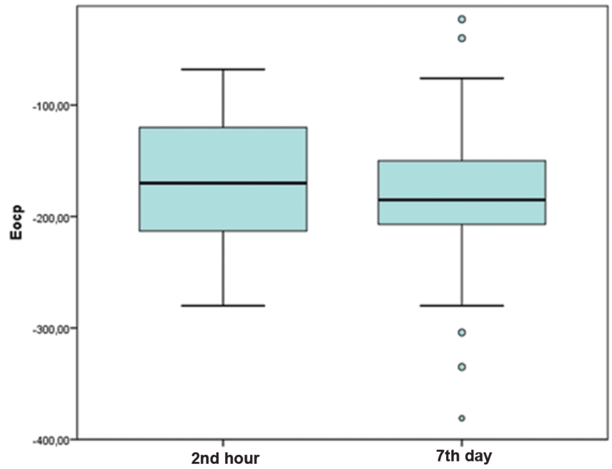

Figure 8. Eocp values after 2 hours and after 7 days in the oral cavity.

Table 1. Descriptive analysis of the Eocp values measured in artificial saliva (AS) and in the oral cavity (OC) (mV)

	Duration of stay	min	mean	max	Standard deviation
AS	2 hours	−188.00	−114.80	−23.00	49.00648
	7 days	−135.00	−57.54	−13.00	26.78
OC	2 hours	−68	−166.6	−280	61.2
	7 days	−23	−188.7	−410	83.3

Table 2. Crosstabulation: Eocp values after a 2-hour stay in oral cavity/Eocp values after a 7-day stay in the oral cavity

Eocp within normal range N		**7 days after fixing**		**Total crowns N (%)**	***p*-value**
		Eocp above normal range N			
2 hours after fixing	Eocp within the normal range	8	8	16 (45.7)	0.090
	Eocp above normal range	4	15	19 (54.3)	
Total crowns N (%)		12 (34.3)	23 (65.7)	35 (100.0)	

DISCUSSION

The in vitro studies have shown high corrosion resistance of the alloy 2 hours after placing the copings in artificial saliva. The formation of a 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 or due to the stable oxide layer.

Regarding the results in clinical conditions, it can be concluded that two hours after being placed in the patient's mouth, the PFM restoration with a substructure of the studied alloy had low corrosion resistance; furthermore, the Eocp values were close to the risky –150 mV. A one-week period was not enough for passivating the alloy surface and improving its corrosion resistance. It can be assumed that during the studied period, ion emission is high and the biocompatibility of the restoration is under consideration. The passivation process of the metal surface and the formation of a biofilm are not strong enough to improve the corrosion resistance of the alloy within the first 7 days in the mouth.

The differences between the clinical and laboratory results may be explained with the specific conditions in the oral cavity including the variable pH, temperature, and masticatory pressure. The presence of microorganisms in the oral cavity, *Streptococcus mutans* and *Candida albicans*, has a negative effect on the corrosion resistance.[16] In addition, other metal objects in the patients' oral cavities influence the corrosion resistance of the studied alloy.[17] The acidity of the saliva may also affect the corrosion resistance of the dental alloys. The lower pH values due to gastro esophageal reflux disease, bulimia or other pathological conditions may lead to a decrease of the corrosion resistance of the metal restorations.[18]

CONCLUSIONS

The obtained results suggest that the Cobalt-Chromium alloy EOS SP2 (EOS, Germany) has a higher corrosion resistance in the laboratory settings than in the oral environment.

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Conflict of Interest

The authors have declared that no competing interests exist.

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Клинико-лабораторное исследование коррозионной стойкости базового стоматологического сплава для селективного лазерного плавления

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Резюме

Введение: Технологии CAD/CAM находят всё более широкое применение для производства металлокерамических реставраций зубов. Порошковые сплавы на основе кобальта разработаны для селективного лазерного плавления. Коррозионная стойкость стоматологического сплава влияет на биосовместимость, функциональную пригодность и долговечность протезной реставрации.

Цель: Целью данного исследования было оценить и сравнить коррозионную стойкость кобальт-хромового стоматологического сплава для металлокерамических коронок, изготовленных методом селективного лазерного плавления в клинических и лабораторных условиях.

Материалы и методы: Металлокерамические коронки были изготовлены 35 пациентам с использованием технологии CAD/CAM. Металлические колпачки коронок изготовлены из сплава EOS CobaltChrome SP2 (EOS, Германия). Измерения Eocp проводились через 2 часа и 7 дней после фиксации реставраций в полости рта. Цифровые файлы разработанных пациентами колпачков были использованы для изготовления ещё 35 образцов, которые были помещены в искусственную слюну. Измерения Eocp проводились через те же интервалы времени.

Результаты: Исследования *in vitro* показали высокую коррозионную стойкость после короткого 2-часового пребывания. После 7 дней пребывания в искусственной слюне коррозионная стойкость стала ещё выше, вероятно, за счёт сильной пассивации. В клинических условиях значения Eocp были несколько выше нормы через 2 часа после фиксации коронок. Через семь дней после фиксации значения Eocp показали снижение коррозионной стойкости металлокерамических коронок. Причиной снижения может быть взаимодействие с другими металлическими предметами или специфические состояния полости рта.

Заключение: Исследуемый сплав показал высокую коррозионную стойкость в условиях *in vitro*. Клинические исследования показали, что металлокерамические коронки имеют более низкую коррозионную стойкость. Требуются дополнительные наблюдения и исследования.

Ключевые слова

сплавы на основе кобальта, коррозионная стойкость, SLM