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Original Article

Corrosion resistance of cobalt-chromium alloys for metal ceramic dental restorations

Zlatina Tomova[1,2]

1 *Department of Prosthetic Dental Medicine, Faculty of Dental Medicine, Medical University of Plovdiv, Plovdiv, Bulgaria*

2 *Center of Innovative Technologies in Dental Implantology, Research Institute of Medical University of Plovdiv, Plovdiv, Bulgaria*

Corresponding author: Zlatina Tomova, Department of Prosthetic Dental Medicine, Faculty of Dental Medicine, Medical University of Plovdiv, 3 Hristo Botev Bld., 4002 Plovdiv, Bulgaria; Email: zlatina.tomova@mu-plovdiv.bg; Tel.: +359 897 515 526

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Abstract

Introduction: The corrosion of dental alloys can have undesirable consequences. The corrosion properties may be modified by the alloy production method, composition, method of prosthetic restoration manufacturing, and oral conditions.

Aim: The aim of this study was to assess the corrosion resistance of three cobalt-based alloys produced by different methods and indicated for different manufacturing techniques.

Materials and methods: Three groups of specimens were created. Group 1 consisted of 35 specimens produced using direct metal laser sintering (DMLS) with EOS CobaltChrome SP2 (EOS, Germany). Groups 2 and 3 each consisted of 30 specimens produced by a conventional casting technique using Marranium CC (Sintal, Bulgaria) and Wirobond C (Bego, Germany). The former was obtained by powder metallurgy methods, while the latter was obtained by conventional thermal melting and alloying. The specimens were placed in artificial saliva with pH adjusted to 7.4. Open circuit potentials were measured at two time points: two hours and seven days after placement in the medium, using a Dentotest Six apparatus (Atlantis, Bulgaria).

Results: After two hours in artificial saliva, significant differences in the open circuit potential (Eocp) values were observed between the groups. However, after seven days, no significant differences in Eocp were observed.

Conclusion: Corrosion behavior of cobalt-based dental alloys depends on the type of the alloy and the manufacturing methods.

Keywords

corrosion, powder metallurgy, 3D printing

Introduction

The development of numerous diseases in the oral cavity is directly correlated with one's way of life, diet, and oral hygiene habits.[1,2] Nowadays, fashion trends advertise dental grills as a symbol of social status.[3] To restore the function of the masticatory apparatus and improve esthetics, many materials foreign to the human body are used.[4] Despite the advancements in materials science and industry that have led to the production of metal-free dental restorations, there is still no ideal universal dental material, and the use of metal alloys cannot be avoided. Metal-ceramic fixed prosthetic restorations are commonly used, as they provide a combination of high mechanical performance, good esthetics, and acceptable biocompatibility.

The corrosion of dental alloys poses risks of biological, functional, and esthetic changes. Dental metal restorations remain in the oral cavity long term, during which time they are subjected to mechanical forces due to mastication, electrochemical reactions, and general wear.[5]

One of the most important features determining the biocompatibility of dental alloys is corrosion behavior, which results from the interaction between metal objects and environmental factors. Due to corrosion, tribocorrosion, and general wear, metal ions are released from the surface of the metal and may interact with the surrounding oral tissues or distant structures, leading to various pathological consequences. Studies have shown that cobalt-chromium dental alloys can cause transient trace metal accumulation in hepatocytes and renal cells, as well as time-dependent early apoptosis.[6,7] Many researchers have found that these alloys may have cytotoxic effects on human gingival fibroblasts and osteoblasts, as well as induce oxidative stress.[8,9]

According to Marti[10], cobalt-chromium alloys have excellent corrosion resistance. This resistance is determined by the alloy's inner structure, specifically the crystallographic characteristics of the cobalt and the presence of chromium. These characteristics contribute to the formation of hard carbides and a solid solution strengthening effect.[10] Nevertheless, factors such as the production method and composition of the alloy, the method of manufacturing the prosthetic restoration, and oral conditions may modify the corrosion features of dental alloys.[11-14] The diverging conclusions from the studies on cobalt-based alloys and the effect on the human body raise concern about their biocompatibility.

With computer aided design/computer aided manufacturing (CAD/CAM), a new era in dentistry has arrived. Digital workflow offers novel approaches both in clinical and laboratory steps by utilizing intraoral scanning, digital design, materials for subtractive and additive methods of restoration production.[15] Powder cobalt-based alloys are used nowadays for 3D printing of the metal frameworks of dental devices.

Aim

The aim of this study was to compare and assess the resistance to corrosion of three types of cobalt-chromium alloys produced by different methods and indicated for different manufacturing techniques. The defined research hypothesis claimed that the type of the alloy did not influence the corrosion resistance of the restoration.

Materials and methods

Three types of cobalt-chromium alloys indicated for manufacturing of metal ceramic restorations were evaluated in this laboratory study: EOS CobaltChrome SP2 (EOS, Germany), Marranium CC (Sintal MM, Bulgaria) and Wirobond C (Bego, Germany). The composition of the alloys was as follows:

- EOS CobaltChrome SP2 (weight %): Co: 63.8; Cr: 24.7; Mo: 5.1; W: 5.4; Si: 1.0; Fe: max. 0.50; Mn: max. 0.10; without presence of Ni, Be, Cd and Pb according to ISO 22674.
- Marranium CC (weight %): Co: 57.5; Cr: 31.5; Mo: 4.5; W: 3.5; Si, Mn, FeCe: 3.0 (total).
- Wirobond C (weight %): Co: 63.3; Cr: 24.8; W: 5.3; Mo: 5.1; Si: 1.0.

The alloys chosen for this study are produced using different methods. The Wirobond C alloy is produced through conventional thermal melting and alloying. Marranium CC is produced using powder metallurgy methods. Fine metal powders are mixed, densified, and vacuum sintered into ingot shapes without reaching the melting temperatures of their constituent elements. EOS CobaltChrome SP2 is a powder alloy produced by atomization processes. The initial components are melted to form the alloy, which is then melted again and pulverized into small droplets to create the final powder state.[16] Marranium CC and Wirobond C are used to produce metal restorations using the conventional lost wax technique. A wax pattern of the future object is created and invested in an appropriate refractory material, which is then cast from a melted alloy. EOS CobaltChrome SP2 is a powder alloy used in direct metal laser sintering (DMLS), a widely used additive manufacturing technique with increased implementation of CAD/CAM technologies.

Three groups of specimens were created. Group 1 consisted of 35 specimens produced by 3D printing and direct metal laser sintering (DMLS) from EOS CobaltChrome SP2. After a stress-relieving regimen, the specimens were sandblasted with 50-μm Al_2O_3 particles. Groups 2 and 3 each consisted of 30 specimens produced by the conventional casting technique using Marranium CC and Wirobond C, respectively.

The metal specimens were placed in artificial saliva prepared with 0.9% NaCl. The acidity was adjusted by adding 1% lactic acid and 4% sodium hydroxide until the pH reached 7.4±0.1, according to the ISO 2071:2020(E) standard. The containers were stored at a room temperature of 22°C. This study used the Dentotest Six apparatus (Atlantis, Bulgaria). The voltage calibrator FLUKE SLK 753 was used to calibrate the device according to ISO 13485 (CE 2274).[17] Corrosion resistance was evaluated by the open circuit potential (Eocp) that appeared between the reference stainless steel electrode placed in the medium and the active electrode in contact with the metal surface of the specimen. Measurements were conducted after a 2-hour and a 7-day stay in the artificial saliva.

Statistical analysis

A statistical analysis was performed using the SPSS statistical package, version 19.0. Since the sample sizes differed among the three groups studied and the number of specimens in each group was relatively small, the nonparametric Kruskal-Wallis test was applied. The level of significance was set at 0.05.

Results

The descriptive statistics of the acquired results are presented in **Table 1**.

Table 1. Results for the Eocp obtained after the specimen was left in artificial saliva for 2 hours and for 7 days

Type	Duration	min	max	med
EOS	2 hours	−181	−23	−130
EOS	7 days	−135	−13	−56
Marranium CC	2 hours	−105	−1	−47.50
Marranium CC	7 days	−130	−5	−69
Wirobond C	2 hours	−220	−80	−149.5
Wirobond C	7 days	−107	−10	−59

The Eocp measurements received from the three alloys studied are shown in **Fig. 1**. There was no significant difference in Eocp measurements between the two time points for the Marranium CC group (p=0.954). However, statistically significant differences were observed in the EOS CobaltChrome SP2 and Wirobond C groups between the Eocp values received after a 2-hour and a 7-day stay in the medium (p<0.001).

A statistical analysis confirmed that there was a significant difference in Eocp values between groups of alloys after a two-hour stay in artificial saliva. After a seven-day period in the medium, no significant difference in Eocp existed **(Fig. 2)**.

With the non-parametric Kruskal-Wallis test, the research null hypothesis that the corrosion resistance depends on the type of alloy was tested. At p-value set at 0.05, the results appeared statistically significant for the

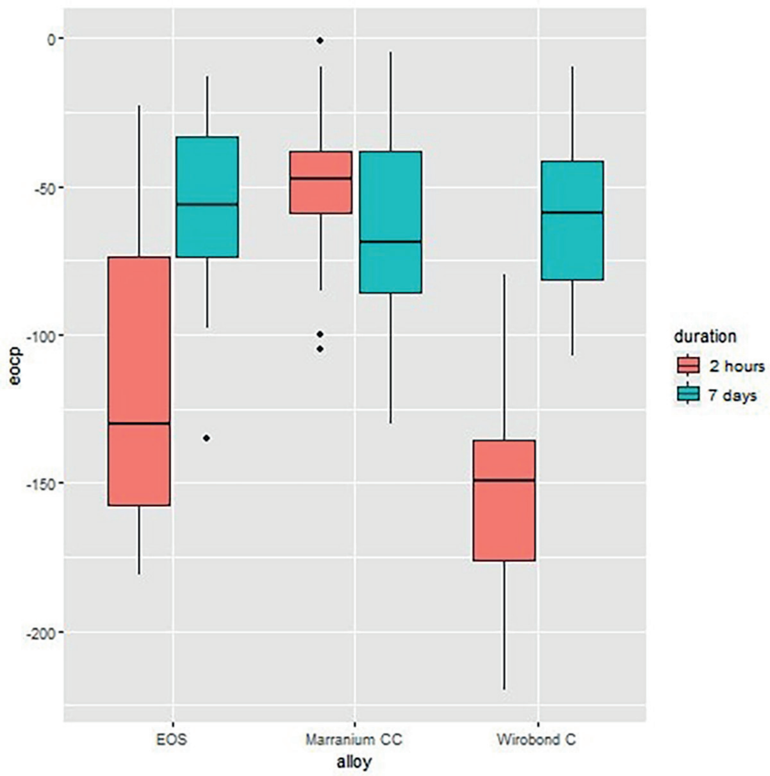

Figure 1. Eocp values at 2 hours (red color) and at 7 days (blue color)..

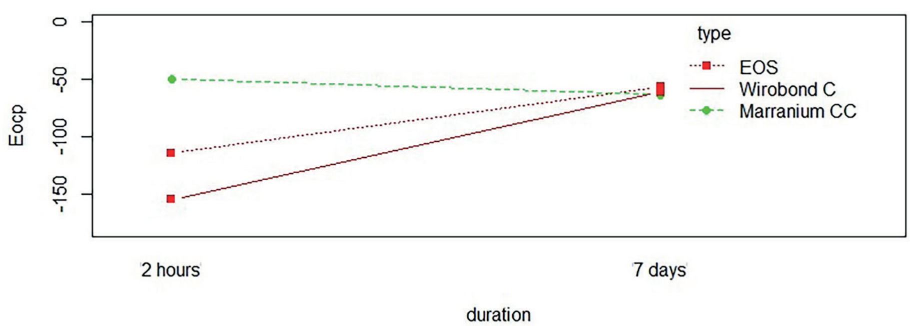

Figure 2. Dynamics of Eocp values appearing between the two studied time points.

2-hour period (Kruskal-Wallis chi-squared =50.025, df = 2, $p<0.001$) and there was no significant difference for the results received for the 7-day period of stay in artificial saliva (Kruskal-Wallis chi-squared =1.525, df = 2, $p=0.466$).

Discussion

Once placed in the oral cavity, the metal object begins to oxidize on its surface. The passive layer, which is composed primarily of dichromium trioxide, provides corrosion resistance to cobalt-based dental alloys. This layer prevents the release of metal ions from the alloy by creating a barrier and incorporating the ions into its structure.[10,18] The speed and characteristics of surface oxidation depend on the alloy's composition, surface morphology, internal structure, and the distribution of alloy elements within the final metal object.[19]

The results of the study showed that there was no significant difference in the corrosion resistance of Marranium CC after a 2-hour or 7-day period in artificial saliva. This alloy's high, stable, and constant corrosion properties are due to its production method. Powder metallurgy provides an exact and even distribution of elements in each ingot of the alloy and in the final metal device.[20] Two hours after placement in artificial saliva, Eocp values measured in the group of specimens produced by DMLS from EOS CobaltChrome SP2 were smaller (in absolute values) than the ones measured in the group of specimens, produced by conventional casting from conventionally produced alloy (Wirobond C). The superior corrosion properties of 3D printed specimens may be due to the thermal post-processing, which is an obligatory step in metal additive manufacturing methods, providing relieving of internal stresses and forming homogenous internal structure and grains with uniformly distributed crystal orientation.[21] Seven days after placement in the chosen medium, Eocp values of the three alloys were similar and within the accepted range.[22] The finding that a change and improvement of corrosion behavior of dental alloys appear with increasing the period of stay in the medium and that this may be attributed to the formation of a stable passive oxide layer on the metal surface aligns with the results from other researchers.[14,23,24] According to our results, a two-hour period is insufficient for complete passivation of the metal surface when Wirobond C or EOS CobaltChrome SP2 is used to produce the dental device. There is a risk of potentially harmful cobalt release in the first few days after the restoration is placed in the oral cavity. Further research is necessary to develop strategies that accelerate the passivation of exposed metal surfaces. Including additional laboratory surface oxidation in the restoration production process may prevent the risk of metal ion emission in the first hours after placement in the oral cavity.

The research hypothesis that corrosion resistance does not depend on the alloy type was rejected for the 2-hour period of stay. For the 7-day period, the null hypotheses cannot be rejected.

Conclusion

The corrosion behavior of cobalt-based dental alloys depends on the type of alloy and the manufacturing method used. Powder metallurgy alloys exhibit high corrosion resistance and fast passivation of exposed surfaces. The development of additive manufacturing has led to the creation of powder metal materials with superior properties compared to conventional cobalt-based alloys.

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Competing Interests

The authors have declared that no competing interests exist.

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