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Assessment of corrosion resistance of dental cast cobalt- and nickel-chromium alloys in acidic environments

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Abstract

Objective: The aim of this study was the comparison of degradation resistance of nickel-chromium (Ni-Cr) and cobalt-chromium (Co-Cr) alloys used as a base material for partial dentures in contact with saliva.

Methods: Wiron®99 and Wironit extra-hard® were selected as representative casting alloys for Ni-Cr and Co-Cr alloys respectively. The alloys were tested in contact with de-ionised water, artificial saliva and acidified artificial saliva. Material characterisation was performed by X-ray diffractometry (XRD), micro-hardness and nano-hardness testing. The corrosion properties of the materials were then analysed using open circuit potential analysis and potentiodynamic analysis. Alloy leaching in solution was assessed by inductively coupled plasma mass spectrometry techniques.

Results: Co-Cr alloy was more stable than the Ni-Cr alloy in all solutions tested. Leaching of nickel and corrosion attack was higher in Ni-Cr alloy in artificial saliva compared to the acidified saliva. The corrosion resistance of the Co-Cr alloy was seen to be superior to that of the Ni-Cr alloy with the former alloy exhibiting a lower corrosion current in all test solutions. Microstructural topographical changes were observed for Ni-Cr alloy in contact with artificial saliva. The Ni-Cr alloy exhibited microstructural changes and lower corrosion resistance in artificial saliva. The acidic changes did not enhance the alloy degradation.

Conclusions: Ni-Cr alloys are unstable in solution and leach nickel. Co-Cr alloys should be preferred for clinical use.

1. Introduction

Alloys, such as cobalt- and nickel-based alloys, are gaining ~~in~~ popularity for the construction of in their application to both removable and fixed dental prosthesis. This could be a result of the increase in prices of ~~This possibly in light of the fact that~~ prosthesis made from noble metals ~~have risen to prohibitive prices~~ over the past 30 years, due to the swelling price of commodity raw materials [1]. In many countries nickel chromium (NiCr) alloys have been substituted by cobalt chromium (CoCr) alloys owing to growing concerns over the cytotoxic effects of leached nickel ions present when exposing the former alloy to the oral cavity [2]. Nickel is found in very low concentrations in the human body, however, increased concentrations may cause it to become hazardous [3, 4]. Nickel is lately being considered a toxic element and with the Nickel Directive introduced by the European Union in 1994 the position against nickel in materials was further enhanced. Around 1 in every 10 people was found to be allergic to nickel [5] and it is possible that more people suffer from this allergy but due to the non-specific symptoms, the official rate is much lower. A number of systemic disorders have been linked with nickel exposure [6, 7].

Co-Cr alloys exhibit high strength [8] and are non-magnetic. They are also resistant to creep, corrosion and wear [9]. Apart from this, these alloys have been found to be cytocompatible [10-12]. Thus they perform their desired function without inducing an unwanted local or systematic effect in the patient [13]. These properties make them ideal al-

loys to be used in the oral cavity. Co-Cr alloys were also found to be more resistant to corrosion than Ni-Cr alloys [10, 11] as indicated by in vitro potentiodynamic scans testing both alloys immersed in several lactic acid and sodium chloride aqueous solutions. The corrosion of Ni-Cr alloys occurs by preferential dissolution of nickel rich grains, which is very different from the mode of corrosion displayed by Co-Cr alloys, in which no preferential dissolution of Cr rich grains is observed [7, 14]. The casting procedure was reported to have very minimal effect on the corrosion properties of both Ni-Cr and Co-Cr alloys [14]. Temperature and pH both affect the corrosion resistance of Ni-Cr and Co-Cr alloys [15] with Ni-Cr alloy being more susceptible to acid attack.

The high corrosion susceptibility and leaching of nickel from Ni-Cr alloys results in decreased cell viability, increased oxidative and cellular toxicity levels and also an increase in cytokine inflammatory expression [16]. Some authors [17] reported that the effect is enhanced by low pH conditions which results in an increase of nickel ions leached into the simulated oral environment, while another study focused on gastroesophageal reflux disease (GERD), which is generally associated with a lower oral cavity pH found no correlation between people suffering from GERD and the non-sufferers [7].

The objectives of this study was the investigation of the corrosion resistance, surface topographical changes and physical and chemical changes of two base metal alloys in the presence of artificial saliva and acidified artificial saliva. The null hypothesis was that the mechanical properties and electrochemical response of both Co-Cr and Ni-Cr alloys are not affected by saliva and acidified saliva.

2. Material and Methods

2.1 Specimen preparation

Two base metal alloys were investigated. Co-Cr alloy (Co 63.0; Cr 30.0; Mo 5.0; Si 1.1; Mn 0.5; C 0.4 - Wiron 99, Bego, Lincoln RI) and Ni-Cr alloy (Ni 65; Cr 22.5; Mo 9.5; Nb 1; Si 1; Fe 0.5; Ce 0.5, C max. 0.02 - Wironit extra-hard, Bego).

Cylindrical specimens: 8 mm diameter and 1 mm height; and 8 mm diameter and 15 mm height were cast for each material. ~~Wax patterns for each sample were prepared using modelling wax (Bego), sprued and invested with phosphate-bonded investment material (Shera Cast and Shera Liquid, Shera, Lemförde, Germany). The resulting ring was heated in a multidirectional furnace (Dentalfarm Tris, Dentalfarm, Turin, Italy) until reaching 850°C while the alloy was open-flame melted in a muffle with an oxy-propane torch. These were then placed in an electric centrifugal casting machine (Dentalfarm Rotojet, Dentalfarm) and injected into the investment ring when the muffle reached 1500°C. The ring was then left to cool to 20°C and then removed from investment. The cast samples were cut and sand-blasted with 250 µm aluminium-oxide powder (Shera Strahlkorund, Shera) at a pressure of 6 bar. The samples were electrolytically polished (Schuler S-U-Unipol, Schuler Dental, Ulm, Germany) using the electrolyte liquid (Wirolyt, Bego) at 4 A for 3 cycles of 4 minutes each.~~

The cylinders 8 mm in diameter and 1 mm high were used for leachate analysis, phase analysis, microscopy and assessment of micro- and nano-hardness; while cylinders 8 mm diameter and 15 mm high were used for potentiodynamic testing.

2.2 Artificial Saliva Solution preparation

Two solutions were prepared: Fusayama Meyer artificial saliva [18] and acidified artificial saliva. The Fusayama-Meyer artificial saliva includes the right components to mimic the natural oral environment and has also been used for various potentiodynamic scans. The artificial saliva was acidified by adding 8 mL of lactic acid to 1000 mL of artificial saliva solution. This mimics the oral environment after food intake and release of acidic media [19]. The pH of the artificial saliva solution was assessed using a pH meter (Hanna HI 3221, Hanna Instruments, Sigma Aldrich, St. Louis, MO, USA) with a single-junction (Ag/AgCl) ceramic pH electrode (Hanna HI 1131). Temperature compensation was accomplished by simultaneously immersing a temperature probe (HI 7662) in the measurement solution. The pH meter was calibrated using three standard calibrating solutions (pH 4.01, 7.01 and 10.00). The pH of the artificial saliva was 6.7. Addition of lactic acid resulted in a drop in pH with a final pH value of 2.6 for the acidified Fusayama-Meyer solution.

2.3 Material characterisation

The 8 × 1 mm cast cylinders were attached to aluminium sample holders and were ground with progressively finer grits of silicon carbide grinding discs (Struers, Ballerup, Denmark) with a manual grinding machine followed by polishing with 3 µm polycrystalline diamond paste and finished with 1 µm diamond paste. These polished discs were then aged

by immersing them in 5 mL of deionized water (control), Fusayama Meyer artificial saliva and acidified artificial saliva for 30 days. The aged discs were then characterised by X-ray diffraction (XRD), micro- and nano-hardness testing.

2.4 X-Ray diffraction

The diffractometer (Bruker D8 Advance, Bruker, Billerica, MA, USA) used Cu K α radiation at 40 mA and 45 kV and the detector was rotated between 2θ of 35-55° with a step of 0.02° and a step time of 0.6 s. The samples were spun at 15 revolutions per minute around the z-axis. Phase identification was accomplished using a search-match software utilizing ICDD database (International Centre for Diffraction Data).

2.5 Hardness testing

Micro-hardness testing was carried out using the Mitutoyo MVK-H2 (Mitutoyo, Tokyo, Japan) micro-hardness tester with a equipped with a Vickers indenter. Indentations were made on each sample's surface using a load of 0.5 kg. Five hardness readings were taken for each sample and the average hardness was calculated from these readings.

Nano-hardness of the alloys was assessed by indenting with a Berkovich indenter using a NanoTest nanoindentation system (Micro Materials Ltd., Wrexham, UK). 30 indents per sample were made, in the shape of a grid with indents spaced 30 μ m apart in both the x- and y-directions. The parameters were as follows: Initial load 0.03 mN, loading and unloading rate 0.8 mN/s with a 1s dwell time at maximum load of 40 mN.

2.6 Immersion Corrosion testing

Co-Cr and Ni-Cr cast discs 8 mm in diameter and 1 mm height were immersion aged at room temperature in air (control), Fusayama Meyer artificial saliva and acidified artificial saliva for 30 days. The solutions had a volume of 5 mL and were placed together with the coupons in a sealed container. The surfaces of these specimens post-immersion were characterised using a scanning electron microscope (SEM) coupled with an energy dispersive spectroscope (EDS). For scanning electron microscopy, the specimens were removed from the soaking solutions and dried in a vacuum desiccator. The specimens were then mounted on aluminium stubs and viewed under a scanning electron microscope (Zeiss MERLIN Field Emission SEM, Carl Zeiss NTS, Oberkochen, Germany). Scanning electron micrographs of the different material microstructural components at different magnifications in secondary electron mode were captured.

2.7 Assessment of leaching

Co-Cr and Ni-Cr cast discs 8 mm in diameter and 1 mm height were immersed in 5 mL of deionized water (control), Fusayama Meyer artificial saliva and acidified artificial saliva for 30 days. At the end of the soaking period the solutions were tested for traces of nickel, chromium, cobalt and molybdenum using inductively coupled plasma (ICP) spectroscopy.

2.8 Potentiodynamic testing

The 8 x 15 mm cast cylinders had a blind hole measuring 2 mm in diameter and 5 mm deep prepared on one end. These cylinders in multiples of four were then immersion aged at room temperature in air (control), Fusayama Meyer artificial saliva and acidified

artificial saliva for 30 days. Following ageing a brass cylinder 2 mm in diameter and 4.5 mm deep with a threaded blind hole was press fitted in the cast Co-Cr and Ni-Cr cylinders. This was done to have an electrical circuit connection for the working electrode. The brass cylinder was totally isolated from contact with the solution thanks to the O-rings shown in Figure 1.

The air aged cast cylinders were potentiodynamic tested in a 9 g/L sodium chloride testing solution (control). The cast cylinders aged in the Fusayama Meyer artificial saliva and acidified artificial saliva were potentiodynamic tested in a testing solution with an identical composition of that used for ageing.

The experiments were conducted following ISO 16428:2005 [20] and BS EN ISO 17475:2008 [21]. Potentiodynamic testing was performed using a potentiostat (Gamry Interface 1000, Gamry, Warminster, PA, USA). The setup ~~as of the working electrode is~~ shown in Figure 1 ~~shows.~~ ~~Aa EuroCell™ electrochemical cell kit was used for these tests. The cell~~ ~~was~~ ~~which~~ ~~was~~ filled with 150 mL testing solution and was kept at $37^{\circ}\text{C} \pm 1^{\circ}\text{C}$ via a heating jacket. The solution was deaerated by bubbling with nitrogen gas for an hour at a flow rate of 1 L/hr. Following the termination of bubbling the specimen (Working Electrode; WE) assembly was inserted in the solution via the central 24/40 port through the two ace thread ports. The cell also contained a glass frit isolated platinum wire (Counter Electrode; CE) and a potassium chloride (3 g/L) fitted Luggin capillary, saturated calomel electrode (SCE) assembly (Reference Electrode; RE).

The time to set-up the cell was kept constant and testing commenced by measuring the open circuit potential (OCP) for an hour. At termination of the OCP test a potentiodynamic test was performed between a voltage of -100 mV vs OCP and 1000 mV vs Reference at a scan rate of 0.17 mV/s.

Each solution was tested with 4 individual samples of each alloy. Graphs of current density (A/cm^2) against linear voltage (V) were plotted. Current density was calculated by dividing the current recorded from the potentiostat by the surface area of the area specimen in contact with the solution.

In order to calculate the corrosion current density (i_{corr}) for each of the samples, a number of steps were undertaken: (1) The graph of $\log(i)$ against potential was plotted for each of the representative potentiodynamic plots. (2) The gradient of the tafel slopes was then calculated by differentiating each of them at a region around the OCP voltage. The polarization resistance of each sample along with the gradient of the tafel slopes was then be used to determine the actual corrosion current (i_{corr}) according to Equation 1 [22].

$$\left[\frac{d(\Delta E)}{di} \right]_{\Delta E=0} = R_p = \frac{b_a b_c}{2.303(b_a + b_c) i_{corr}} \quad \text{Equation 1}$$

Where b_a and b_c are the gradients of the anodic and cathodic regions respectively.

Statistical analyses

The data was evaluated using SPSS (Statistical Package for the Social Sciences) software (PASW Statistics 18; SPSS Inc.). Parametric tests were performed as Kolmogorov-Smirnov tests on the results indicated that the data were normally distributed. Analysis of variance (ANOVA) with $P = 0.05$ and Tukey Tukey post-hoc test were used to perform multiple comparison tests.

3. Results

3.1 Phase Analysis

The X-ray diffraction plots for both alloys in contact with the different soaking solutions are shown in Figure 2. The Co-Cr alloy shown in Figure 2a is a dual phase alloy, which contains face centred cubic (FCC) α phase (largest quantity) and an ϵ hexagonal closed packed (HCP) phase. The Ni-Cr alloy (Figure 2b) has a face centred cubic (FCC) structure. Both alloys did not exhibit any phase changes in contact with the soaking solutions.

3.2 Hardness testing

The mean micro- and nano-hardness of each alloy after a 30-day immersion in different solutions are shown in Figures 3a and 3b respectively. It can be clearly seen that the

Co-Cr alloy has a higher value of hardness than Ni-Cr alloy. Furthermore there was no difference in hardness when comparing the same alloy in different media ($P > 0.05$) for both micro-hardness and nano-indentation. This means the media had no effect on the surface hardness of the alloys.

3.3 Immersion Corrosion testing

The scanning electron micrographs of Co-Cr and Ni-Cr alloys exposed to different solutions are shown in Figure 4. The corrosion attack on the Co-Cr in all solutions and on the Ni-Cr in the acidified saliva was very minimal. On the other hand the Ni-Cr alloy exposed to artificial saliva had a greater tendency for dissolution with more evident surface depressions when compared to the other sample electrolyte combinations.

3.4 Assessment of leaching

The leaching of trace metal ions in the various solutions is shown in Figure 5. The release of nickel was particularly high in the Ni-Cr alloy immersed in artificial saliva followed by acidified saliva whilst the least amount of leaching was obtained from the control sample. Some leaching of chromium and cobalt were demonstrated in the cobalt-chromium alloy.

3.5 Potentiodynamic testing

The results of potentiodynamic assessments for both CoCr and NiCr alloys in different electrolyte solutions are shown in Figures 6a and 6b respectively. A comparison between the materials can be found in Figure 7. The scan can be split in four regions namely cathodic, OCP, passive and transpassive. The OCP is the point at which the current density

dips to virtually zero. The cathodic region lies at potentials lower than that of the OCP whilst the passive part (anodic) lies at potentials higher than the OCP. The passive region is a region of a stable low current while the transpassive region occurs after an approximate voltage of 700 mV.

As shown in Figure 8a, both alloys subjected to artificial saliva reached OCP at a lower voltage than the control (specimens tested in 9 g/L NaCl) and the alloy tested in acidified artificial saliva. When exposed to the control solution, both alloys were observed to have higher passive current densities compared to the same alloys in both test media. As shown in Figure 8b, the highest corrosion current density was produced when the NiCr alloy was exposed to artificial saliva. A lower value was then obtained when the same alloy was exposed to acidified artificial saliva and the control solution. The Co-Cr alloy generally showed a very low corrosion current density in all solutions tested.

4. Discussion

Potentiodynamic scans (Fig. 6 and 7) provided information on the corrosion rate, pitting susceptibility and passivity. Both alloys exhibited transpassive dissolution in all media as indicated by a sudden increase in corrosion current at similar potentials in the region of 700 mV/SCE. Oxidation of chromium from Cr^{3+} to Cr^{6+} has already been reported at these potentials in other works [23]. However, no evidence of pitting could be found from the same potentiodynamic scans.

The corrosion resistance of the Co-Cr alloy was seen to be superior to that of the Ni-Cr alloy in all solutions tested as shown by the lower OCP corrosion current densities plotted in Figure 8b. The most pronounced difference could be observed in artificial saliva, in

which the Ni-Cr alloy had a corrosion current, which was approximately 350% greater than that of Co-Cr in the same solution. This was reflected in the quantity of ions released into solution as shown in Figure 5, where the Ni-Cr alloy can be seen to release far greater flux of ions compared to the Co-Cr alloy in each solution respectively. This is mainly due to the amount of Ni released into solution.

When comparing results from the acidified artificial saliva with those of the non-acidified artificial saliva, Figure 8b shows that the difference in corrosion current is negligible when considering Co-Cr alloys. This ~~matches well~~ is in accordance with ~~to~~ previous findings ~~by previous researchers [7] ⁷ who showing that~~ no differences ~~arises when consider-~~ ing Co and Cr concentrations in saliva from patients with metal dentures suffering from GERD compared to those who do not suffer from GERD. Contrarily however, a major difference could be found when comparing the corrosion current and OCP potential of the Ni-Cr alloy when exposed to acidified and non-acidified artificial saliva. This is partially in contradiction to the work presented by Borg et al. [7] who also state that no difference could be found in the amount of nickel ions released from Ni-Cr alloy dentures into saliva when comparing patients suffering from GERD versus the control. This may be due to the difference in exposure time to the lower pH environment, which as stated by the same authors, requires monitoring within a clinical trial.

The surface irregularities observed in Figure 4d on the Ni-Cr alloy samples after a 30 day immersion in artificial saliva are indicative of preferential corrosion from Ni-rich zones due to preferential segregation of nickel-rich phase during solidification of the alloy [24]. These nickel-rich regions appear to suffer localised selective dissolution as also re-

flected in clinical trials conducted by Borg et al. [7] on Ni-Cr alloy dentures and in vitro experiments [14] on a similar alloy. This is once again confirmed in results from ion leaching experiments (Fig. 5), which show that in all media leaching of nickel was high in comparison to other metal ions. On the other hand, when considering the Co-Cr alloy, no evidence of preferential corrosion could be observed. All this leads the authors to the rejection of the null hypothesis.

On the other hand, cobalt and chromium ions were still released into solution during the in vitro testing as can be observed in Figure 5. This is also demonstrated in the in vivo environment, as suggested by a recent clinical study in which patients wearing metal prosthesis had higher levels of cobalt and chromium than non-denture wearers [7]. The similar results obtained also show the robustness of the in vitro methods used in the current study.

Conclusions

Both alloys exhibited adequate corrosion resistance with Co-Cr having a higher corrosion resistance when compared Ni-Cr alloy across all solutions tested. The largest difference in corrosion resistance was found to be produced in artificial saliva where the Ni-Cr alloy gave a corrosion current 350% greater than that given by the Co-Cr alloy. The electrolytic solutions were found not to modify the alloy's mechanical properties. Furthermore, the Ni-Cr alloy suffered from a higher corrosion attack in artificial saliva as when compared to an acidified artificial saliva. Surface topographical changes were observed in Ni-Cr alloy in

contact with artificial saliva due to larger Ni dissolution. The null hypothesis thus was thus rejected.

Declaration

The authors declare no conflict of interest

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Figure legends

Figure 1: Working electrode assembly

Figure 2: X-ray diffraction patterns for the (a) CoCr and (b) NiCr alloys after exposure to de-ionised water, artificial saliva and acidified saliva showing the main crystalline phases present in the alloys and no phase changes on exposure to the different solutions

Figure 3: (a) Micro indentation data and (b) Nano hardness indentation data for CoCr and NiCr alloys after exposure to de-ionised water, artificial saliva and acidified saliva. Error bars representative of $n=5$ indents for (a) and $n=30$ indents for (b) $p>0.05$ standard deviation.

Figure 4: Surface scanning electron microscopy image after exposure of the CoCr and NiCr alloy to air, artificial saliva and acidified saliva.

Figure 5: Concentration of Cr, Co and Mo ions leached from the (a) CoCr and (b) NiCr alloy after exposure to de-ionised water, artificial saliva and acidified saliva.

Figure 6: Representative potentiodynamic plots for the (a) CoCr and (b) NiCr alloy exposed to 9 g/L NaCl, artificial saliva and acidified saliva. $n = 4$ repeats

Figure 7: Representative, comparative potentiodynamic plots for the CoCr alloy and NiCr alloy exposed to (a) 9 g/L NaCl; (b) artificial saliva; (c) acidified saliva $n = 4$ repeats

Figure 8a: Average OCP potential of the CoCr and NiCr alloys in 9 g/L NaCl, artificial saliva and acidified saliva. Error bars representative of the range of $n = 4$ repeats.

Figure 8b: Median corrosion current density, of the CoCr and NiCr alloys in 9 g/L NaCl, artificial saliva and acidified saliva. Error bars representative of inter quartile range.















