1

Dental casting alloys behaviour during power toothbrushing with toothpastes of various abrasivities. Part II: corrosion and ion release

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Abstract The purpose of this study was to evaluate the long term effect of abrasivity of toothpastes normally used over the corrosion behavior and ion release of the different dental casting alloys. Three dental casting alloys (Ni–Cr, Co–Cr and commercially pure Ti) were studied. Four specimens of each material were immersed, brushed without paste or brushed with one of four toothpastes of different Relative Dentine Abrasivity (RDA 50, 52, 80, and 114). An electric toothbrush with a load of 250 g was used for 420 min. Corrosion behavior was determined by means a potenciostat with high sensitivity and the ion release determined by Inductively Coupled Plasma-Mass Spectrometry. Two-way ANOVA and non-parametric tests were used to detect significant differences. Titanium specimens exhibited the best corrosion behavior after and before the toothbrushed, being the worst of the three alloys the Cr–Ni. Titanium oxide produced spontaneously on the Ti surface is the main cause of the high corrosion resistance of the material. However, the eutectoid of the CrNi with chemical composition between different phases produces pitting on the phases boundaries with an important decrease of the corrosion resistance. Besides, the CrNi produces high values of the Ni and Cr release. Slight increment in roughness were observed after toothbrushing and depended on the material but not on the toothpaste used. The increase of the microhardness (residual stresses) provokes a decrease of the corrosion resistance and an increase of the ion release.

1 Introduction

Corrosion may be described as the deterioration of materials by aggressive action of the environment (atmosphere and oral fluids). This term is used for metals, and the mechanism of corrosion is mainly electrochemical. Corrosion is said to be continuous in the mouth, because these ions are removed with the abrasion of foods, liquids and toothbrushes [1–3].

Corrosion of dental alloys may result in biological, functional and aesthetic effects. Besides, in corrosion processes metal ions are released and may come into contact with cells and tissues in the immediate environment, or be distributed throughout the body, mainly to the intestine canal. If these ions are not biocompatible, then the organism may be injured (toxicity and risk of sensitization) if they are absorbed in sufficient quantity [4–7].

In vitro electrochemical techniques have been proven to be sufficiently sensitive to measure even a low corrosion rate; moreover, they are quick and convenient and are now used by many researchers [1, 5, 6], although the clinical relevance of these techniques is heavily debated.

The aim of this study is to evaluate, in vitro, the effect of toothbrushing on ion release and corrosion resistance of different dental alloys using rotation oscillating toothbrushing and different toothpastes in artificial saliva.

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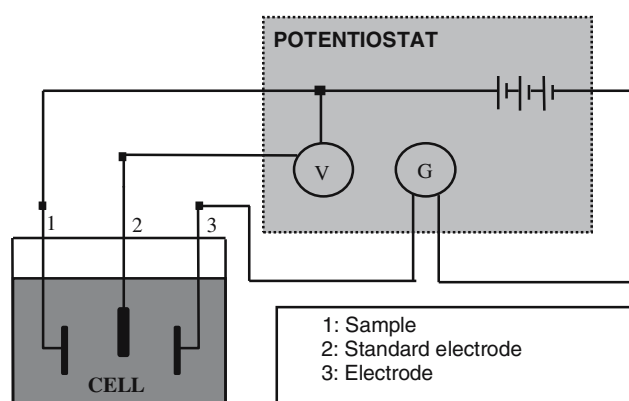A8 Politècnica de Catalunya, Barcelona, Spain

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2 Material and methods

The materials and treatments realized were the same of the Part I of this work.

The schematic electrical set-up used to measure the electrochemical parameters is shown in Fig. 1. The corrosion cell used is a glass cell with the working electrodes and a saturated Ag/AgCl electrode used as a reference (VidraFoc Spain). The distance from the reference electrode to samples was 25 mm. The ratio of anode surface to the cathode surface was equal to one. Dental alloys were kept immersed in the electrolyte for all the measurements taken. The electrolyte is artificial saliva at a temperature of 37°C and pH 6.7 with the composition given in the Table 1. The electrolyte is changed for each experiment. The corrosion tests were realized before and after of the abrasive treatment, described in Part I.

The current versus time in the galvanic coupling studied was controlled by a Hewlett Packard potentiostat (USA). The variation of the potentials in an open short circuit was controlled by a Digital Multimeter & Scanner Resistance (Volatalab Radiometer, France). Using this type of assembly it is possible to measure at the same time the current and the common potential (short potential) versus time of the galvanic coupling studied. More or less similar assemblies were used by other authors in measurements of Evans diagrams of galvanic couplings [6, 8–11]. The overall system was controlled using PC-compatible computer. The preparations of the samples and the corrosion test carried out followed the ASTM standards G8 and G15 [12].

The specimens were subjected to the following measuring cycle:

- Immersion in the de-aerated electrolyte for 250 min with recording of the open potential of each electrode.
- By means of a potentiostat the potential at intervals of 50 mV until 1.6 V was increased. Recordings of the variation of the galvanic current density, potential, etc. were obtained and the Tafel slopes were determined from the Evans diagrams. In order to determine these diagrams, it is very important to record the polarization curves in a pseudostationary manner. In this study, the 250 min of immersion of specimens was regarded sufficient.

The microstructure of the different dental materials was observed before corrosion processes by optical microscopy (MEF 4.Olympus, Japan). The corroded surfaces were observed by scanning electron microscopy (JEOL 6400, Japan) in order to observe the pitting zones and by means of X-ray dispersive energy microanalysis (Lynk, USA) to determine the chemical composition of the places more prone to corrosion.

Ten millilitres of solution was extracted before the tooth brushed in order to analyse the metallic ions released. The container was perfectly protected in order that no impurity interfered with the results. The quantification of the ions released was carried out by ICP-MS measurement (Inductively Coupled Plasma-Mass Spectrometry) (IZASA. Spain).

Fig. 1 Schematic electrical set-up used to measure the electrochemical parameters

Table 1 Chemical composition of the artificial saliva

Compound	Composition (g/dm^3)
K$_2$HPO$_4$	0.20
KCl	1.20
KSCN	0.33
Na$_2$HPO$_4$	0.26
NaCl	0.70
NaHCO$_3$	1.50
Urea	1.50
Lactic acid	Until pH = 6.7

3 Results and discussion

Five specimens of each alloy were tested by electrochemical methods. Each specimen was polarized five times and polished before the tests, then the mean values were calculated: the critical current density (i_{cr}), the passive current density (i_p), the corrosion potential (E_{corr}) and the critical pitting potential (E_{cp}), as can be observe in Table 2 for each system (material-paste with different RDA). The light increase of microhardness produces a decrease of the corrosion resistance due to the increase of the surface residual stress by the abrasion process [13, 14]. The different polarization tests for each sample do not showed changes in the results for the different magnitudes.

The material with higher current density at a given potential, is the more prone to corrode. Cp Titanium had

the most passive (0.85 μA/cm^2) and Nickel–Chromium alloy had the most active (1.9 μA/cm^2) critical current density values. The value for the CoCr was 1.11 μA/cm^2. If passive current density is low, the alloy is said to passivate more easily. The passive current density values were 0.68 μA/cm^2 for the Titanium, 0.80 μA/cm^2 for CoCr and 1.00 μA/cm^2 for Ni–Cr alloy was the most active alloy, with a pitting potential value of +90 mV. This potential is +443 mV for CoCr and +555 mV for cp Ti [1, 15].

Titanium is one of the most corrosion-resistant materials used for biomedical applications. The oxide that forms on titanium provides the corrosion resistance under static conditions, and it has often been reported that titanium is not susceptible to pitting and/or crevice corrosion phenomena [16].

In all the cases, the current density increases and the corrosion potential decrease significatively when the abrasivity of the toothpaste is bigger (Table 2). This abrasivity increases the surface microhardness due to the internal stresses produced in the surface of the titanium brushed that favor the corrosion processes [17].

In the other hand, chromium is added to the nickel-based alloys to improve the alloy's ability to form a protective oxide film on the surface. It has been suggested that chromium content from 16% to 27% will provide an optimum corrosion resistance for the nickel-based alloys, while the addition of molybdenum will also further enhances the corrosion resistance [17–19]. Alloys with lower chromium content may not be able to develop oxide films adequate for corrosion resistance. The microstructure of the nickel-chromium alloy before corrosion test is shown in the Fig. 2. This reveals its dendritic structure and an eutectic phase, which is susceptible to preferential corrosion [20]. It can be observed in the Scanning Electron Microscopy that an etched surface is showing corrosion of the preferential phase of the eutectic and thus a disruption of the oxide film (Fig. 2). This alloy presents localized corrosion phenomena. The phases formed by the minor alloying elements have been shown to

Table 2 Corrosion parameters analysed for the different metals and alloys with different toothpastes

| Alloys	Microhard. (HVN)	E_{nat} (mV)	i_{cr} (μA/cm^2)	i_p (μA/cm^2)	E_{CORR} (mV)	E_{cp} (mV)
Ti	480.5	0.024	0.85	0.68	−20	+555
Ti abraded RDA 50	499.0	0.022	1.02	0.78	−30	+550
Ti abraded RDA 52	503.2	0.020	1.15	0.82	−32	+540
Ti abraded RDA 80	510.2	0.019	1.19	0.85	−35	+536
Ti abraded RDA 114	515.6	0.016	1.21	0.90	−41	+530
CrCo	527.8	−0.121	1.11	0.80	−45	+443
CoCr abraded RDA 50	543.2	−0.223	1.21	0.90	−52	+343
CoCr abraded RDA 52	545.0	−0.225	1.31	0.95	−55	+312
CoCr abraded RDA 80	550.1	−0.235	1.43	0.99	−62	+301
CrCo abraded RDA 114	559.2	−0.289	1.56	1.10	−71	+298
NiCr	312.7	−0.130	1.90	1.00	−100	+90
NiCr abraded RDA 50	339.6	−0.144	1.99	1.20	−110	+78
NiCr abraded RDA 52	340.2	−0.158	2.08	1.25	−125	+69
NiCr abraded RDA 80	351.6	−0.168	2.14	1.30	−130	+60
NiCo abraded RDA 114	370.0	−0.171	2.30	1.33	−134	+58

**Fig. 2** Microstructure of NiCr alloy
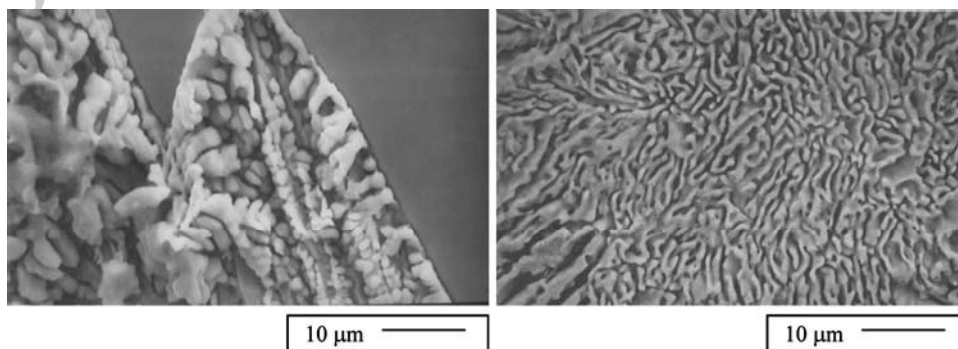
have a significant effect on the corrosion properties of the nickel-based alloys [20]. The corrosion results can be observed in Fig. 3 for the NiCr alloy brushed. Ti and CrCo present only one phase in their microstructures and consequently there are not differences in the chemical composition in the material. This fact produces an important increase in the corrosion behavior.

The results of the ion release are shown from Fig. 4. It should be emphasized, in the first place, that the ion release in the titanium material does not reach 40 ppb after tooth brushed. This low release is due to the passivating film of titanium oxide (inert coating) that reduces the metallic ion diffusion to the external environment [21].

In relation to the Nickel–Chromium alloy produces the largest amount of ion release, as can be appreciated in
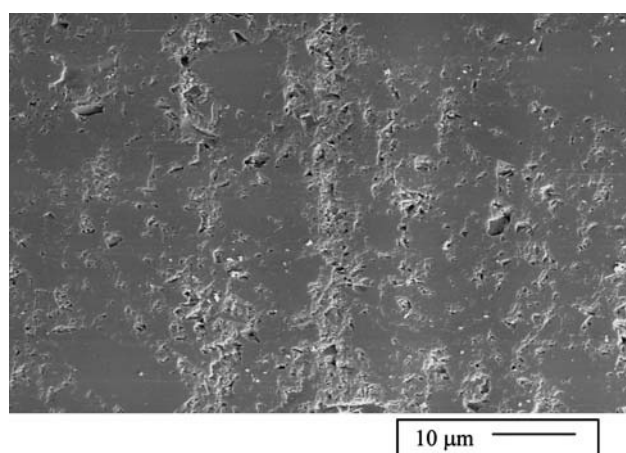
Fig. 3 Corrosion localized for the NiCr alloy
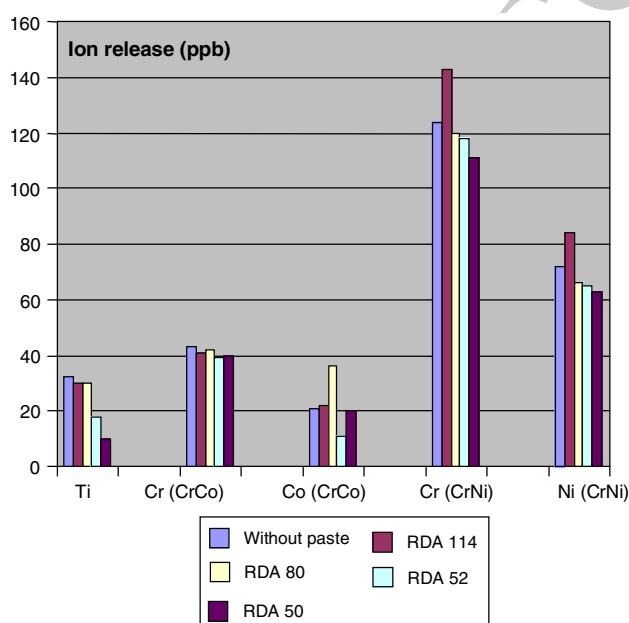
Fig. 4 Ion release for each alloy and toothpaste used

Fig. 4. This greater ion release in the environment can be justified because this alloy presents the least resistance to corrosion and accordingly presents a larger amount of products of corrosion released to the environment [22].

The Nickel–Chromium alloy microstructure is not single phase and accordingly does not present chemical homogeneity in all its structure like the other alloys studied. The Chromium–Nickel alloy presents solidification dendrites and around these a laminar eutectic structure. This means in effect that there are plates one beside the other with a different chemical composition, so accordingly the structure acts as if it were an electrochemical cell [23]. The alloy should be chemically homogenized at high temperature to improve the performance against corrosion and the ion release of the alloy, followed by a rapid cooling to avoid metallic diffusion and to produce a chemically homogeneous structure.

Although the quantity of Ni ions released is much below the 300–500 µg corresponding to the critical concentration to induce allergy [24], even in the case of untreated surfaces, this quantity might be enough to induce long-term inflammatory responses or alter cells behavior. Sun et al. [25] showed that even at subtoxic concentrations, metal ions can alter osteoblast behavior. For Ni ions, a significant decrease in Alkaline Phosphatase Activity (ALP) and DNA synthesis has been observed. Other works have shown that Ni ions could be responsible for inducing the secretion of different cytokines involved in the inflammatory process. Wataha et al. [26] observed an increase of IL1β secretion by macrophages at Ni concentrations known to be released by NiTi dental materials. Moreover, in another study [27], they also demonstrated that the quantity of IL1β secreted from monocytes due to Ni ions release (7.2 µg/ml) was sufficient to indirectly induce ICAM1 (Intracellular Adhesion Molecules that are involved in the recruitment of other inflammatory cells) secretion on endothelial cells. Finally, Cederbrant et al. [28] showed that even a quantity as small as 1.2 µg/ml of Ni could induce an increase in lymphocytes proliferation and IL10 secretion in subjects allergic to Ni. Thus, the results obtained might be of great importance to improve the long-term biocompatibility properties of the material and to reduce sensitization to Ni and allergies.

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