

Corrosion Study of Ni-Cr-Mo Alloys for Fixed Dental Prostheses in an Aqueous Solution of 0.05% NaF and in Commercial Mouthwashes

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Abstract— *Ni-Cr-Mo alloys have been used as dental prostheses due their properties such as good mechanical strength, high corrosion resistance and also because they are economically viable. The corrosion protection of these alloys in salt solutions which are typical of physiological media is due to the phenomenon called passivation with an oxide superficial layer formation, particularly chromium oxides. This protective film, subjected to mechanical stress in a corrosive environment, can be broken partially releasing ions that have deleterious effects in a human body. Fluoride ions, existent in hygiene products, change the oral environment and their presence may enable the beginning of a localized corrosion process. The objective of this work is to evaluate the corrosion resistance of three Ni-Cr-Mo alloys, of different compositions: SC (73% Ni, 14% Cr, 8.5% Mo, 1.8% Be, 1.8% Al) SB (61% Ni, 25% Cr, 10.5% Mo, 1.5% Si) and W (65% Ni, 22.5% Cr, 9.5% Mo, 1.0% Nb, 1.0% Si, 0.5% Fe) in media containing fluoride which simulate oral rinse solutions. This study has been performed in solution of 0.05% NaF, NaCl 0.05% and commercial mouthwashes on pH 6.0 at 37°C using metallography analyses, immersion techniques, and electrochemical tests, impedance tests and analysis. SC, with the highest nickel and the lowest chromium content, does not passivate in the studied means showing a continuous increase in current density due to increasing potential, while the other alloys exhibit passivation range of 600 mV and passive current density 10^{-6} A/cm². In general, considering the immersion and electrochemical corrosion tests, it is concluded that the worst performance has been attributed to the alloy SC, while W and SB have shown the best performance and very similar behaviors.*

Index Terms—Ni base alloys, Dental prostheses, Corrosion, Mouthwash.

I. INTRODUCTION

Biomaterial can be defined as any synthetic material which replaces or restores the function of body tissues and keeps intermittent or continuous contact with organic fluids. Considering that there is contact with body fluids, it is essential that the material presents biocompatibility, produces no adverse immune response, induces no systemic effects, be not toxic, carcinogenic, mutagenic or antigenic. However, the biomaterials use may cause adverse effects in the human body, due to release of cytotoxic metals. Every implanted metal biomaterial has some interaction with surrounding tissues, by occurring release of ions by dissolution, wear or corrosion. The intra-oral corrosion is considered to be a complex process which depends on composition and thermo

mechanical alloy state, in combination with manufacturing, surface finishing, mechanical aspects, environment and host systemic state [1,2]. Evidence of metallic elements in the human body is often derived from biomaterials implanted in the body. Metal ions can be released from metallic biomaterials, such as orthopedic prostheses, plates, screws, implants, etc.. This metal biodegradation can cause several phenomena such as transport, metabolizing, accumulation of this material in the organs; moreover can cause allergy and carcinomas. A large amount of metal ions released can be detrimental to individual health. The metal ion release from biomaterials should be understood for a better discussion about safety and biocompatibility of these materials [3,4]. Resistance and biocompatibility of some alloys in oral means are of fundamental importance due to formation possibility of allergenic, toxic or even carcinogenic corrosion products [5,6]. Since the development of dental caries results from bacteria accumulation on the teeth and from frequent sugar intake, one of the primary measures for its control would be the periodic removal of dental plaque. Nonetheless, the greatest impact measurement has been attributed to the widespread use of fluoride in several use forms. Saliva naturally protects both enamel and dentin, because it has calcium and phosphate, the main mineral components of crystal structure of teeth. On the other hand, this biological property of saliva is pH dependent. Thus, pH variations will determine the limit of protection capacity of saliva and by considering that nowadays people are exposed to fluoride, either by drinking water or by the use of fluoridated toothpaste, the constant presence of fluoride in saliva changes its physico-chemical properties with respect to critical pH of dissolution [7,8]. Sodium fluoride and other fluorides are often used as prophylactic agents in dental treatments to prevent dental plaque formation and caries development. Fluoride is present in all dental creams that are in general use on the market. Despite being beneficial, it should be used or consumed in the correct dosage, so that prevention does not result in adverse health effects. Creams, gels and mouthwashes are not the only available fluoride sources which population has access to.

II. MATERIALS AND METHODS

For this work, it was used three Ni-Cr-Mo alloys used in the dental market: SupremCast, Super Bond (American Dent All, USA) and Wiron 99 (BEGO, Germany). Table 1 shows the chemical compositions provided by the manufacturers. The samples of approximately 1 cm² of exposed area were sanded with sandpapers 80, 220, 600 and 1200, afterwards it was made a polishing with alumina 1μ and then dipped in acetone in an ultrasonic bath Thorton model Metasom -14 per a period of 15 minutes, washed with distilled water, then dried with hot air and then weighed on an analytical balance accurate to 0.1 mg Shimadzu, obtaining the initial mass (m_{initial}). Each sample was hung with nylon and placed in a flask with about 500 mL NaF 0.05% (w/w), pH 6.0 at 37 °C. The specimens were kept in static state for a period of 12 months. After this period, the

samples were removed from the solution, washed with distilled water, dried with hot air and weighed to obtain the final mass (m_{final}). Then the solutions were analyzed by atomic absorption spectrometry for the detection and quantification of ions nickel, chromium and molybdenum. The electrochemical measurements were made using as electrolytes four commercial mouthwashes, a solution of sodium fluoride and another sodium chloride. A solution of sodium fluoride and 0.05% sodium chloride 0.05% were prepared in laboratory with analytical grade reagent using a Shimadzu Analytical Balance for weighing the solute. The pH of this solution was adjusted to a value of 6.0 by adding sodium hydroxide, with the aid of a magnetic stirrer, using a pH-meter model DIGIMED DM20 combined of glass and a magnetic stirrer Model TE-TECNAL 085 [9,10].

Table I - Nominal Chemical Composition of the Alloys (% M/M)

Alloy	Ni	Cr	Mo	Be	Si	Al	Nb	Fe	Ce	C
SC	73	14	8.5	1.8	---	1.8	---	---	---	---
SB	61	25	10.5	---	1.5	---	---	---	---	---
W	65	22.5	9.5	---	1.0	---	1.0	0.5	0.5	<0.02

III. RESULTS AND DISCUSSION

A. Corrosion Tests- Immersion testes

The immersion tests were carried out in NaF solution 0.05% (w/w), pH 6.0, aerated at controlled temperature (37 ± 1) °C using the alloys W, SB and SC and further a solution of NaF 0.05% as a reference standard. After the period of 1 year the alloys were removed, washed with distilled water, dried in an air stream, and finally weighed. It was performed calculus of mass loss using the expression presented in equation (6) and the solutions were analyzed by atomic absorption spectrometry for detection and quantification of ions nickel, chromium and molybdenum. Results indicated that in these alloys the percentage mass loss after immersion is virtually zero, and SC was the one that lost more weight (0.08%), as shown in Table 2. This small mass loss is attributed to formation of surface film composed mainly of Cr oxides, which dissolve and impede the metal contact with the aggressive medium [10,11-13]. In this medium, the solution pH increased as a result of corrosion, the initial pH was 6.0 and the final around 7.92, as displayed in Table 2. Quantitative analysis by flame atomic absorption was made in all solutions, with an average of 3 determinations. The alloy SC showed higher Ni ions concentration in relation to the alloys W and SB. The concentrations of Cr and Mo ions were less than 0.2 mg/L for all alloys, whereas for Ni the amount it was approximately 8.4 mg/L for the alloy SC, as shown in Table 2. This mass loss can also be observed due to a yellow

powder formation in the bottle bottom, probably Ni corrosion products, further emphasizing the low corrosion resistance of this alloy.

B. Measurements of open-circuit potential

A comparison of stability of the alloys W, SB and SC in medium 0.05% NaF pH 6.0 at 37 °C in aerated system can be seen in Fig. 1. The potential values about 200 mV more positive to alloys W and SB were achieved at steady state. It is important to note that this significant increase in values of open-circuit potential is consistent with the increase in the alloy chromium content. The SC alloy which has a lower percentage of chromium presented the lowest potential in the whole time interval, indicating that the passive film is less protective, which makes this alloy less corrosion resistant [14,15].

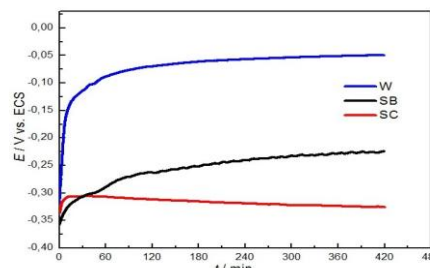


Fig. 1 – Curves of Open Circuit Potential With Time Of Alloys W, SB And SC In 0.05% Naf.

Alloys	Ni	Cr	Mo	Total	Concentration (mg.L ⁻¹ cm ⁻²)	Mass Loss	pH increase
SC	8.4 ± 0.1	< 0.2	< 0.2	< 8.9	8.3x10 ⁻¹	8.0x10 ⁻²	1.92
SB	< 0.2	< 0.2	< 0.2	< 0.6	7.9x10 ⁻²	5.4x10 ⁻²	1.92
W	< 0.2	< 0.2	< 0.2	< 0.6	7.6x10 ⁻²	8.6x10 ⁻³	1.13
NaF	---	---	---	8.3 < % < 8.9	---	---	1.12

Table II – Results of quantitative analysis by atomic absorption and weight loss calculations for all the three alloys

Table III shows the stabilization potentials for the alloys W, SB and SC in all studied media, thus it can be seen that the alloy SC has a lower stabilization potential for all media showing that it really has the lowest corrosion resistance.

C. Potentiodynamic polarization curves.

The potentiodynamic polarization curves obtained with a scan rate of 20 mV/min in NaF 0.05%, 0.05% NaCl and different commercial mouthwashes, aerated at 37 °C for the alloys W, SB and SC are shown in Fig 2.

Table III – Apparent stabilization potential (V/SCE) for alloys W, SB and SC.

Media used	W	SB	SC
NaF 0.05%	-0.08	-0.04	-0.30
NaCl 0.05%	-0.15	-0.15	-0.25
CP	-0.05	-0.14	-0.43
NS	-0.05	-0.20	-0.33
L	-0.12	-0.26	-0.30
C	-0.32	-0.20	-0.35

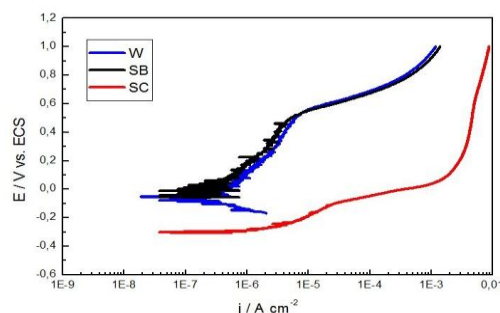


Fig. 2 - Potentiodynamic polarization curves of alloys W, SB and SC in 0.05% NaF.

Table IV - Parameters Obtained From Potentiodynamic Polarization Curves Of The Alloys W, SB And SC.

Used media	W			SB			SC		
	j _{pass} (A cm ⁻²)	E _{rup} -E _{corr} (V)	E _{rup} (V)	j _{pass} (A cm ⁻²)	E _{rup} -E _{corr} (V)	E _{rup} (V)	j _{pass} (A cm ⁻²)	E _{rup} -E _{corr} (V)	E _{rup} (V)
NaF	2.0 x 10 ⁻⁶	~0.6	~0.5	1.0 x 10 ⁻⁶	~0.6	~0.5	10 ⁻⁵	~0.2	
NaCl	2.0 x 10 ⁻⁶	~0.8	~0.6	5.0 x 10 ⁻⁶	~0.6	~0.8	5x 10 ⁻⁶	~0.3	
CP	1.2 x 10 ⁻⁶	~0.5	~0.5	1.0 x 10 ⁻⁶	~0.7	~0.5	1.0 x 10 ⁻⁵	~0.9	~0.5
NS	1.1 x 10 ⁻⁶	~0.7	~0.6	1.0 x 10 ⁻⁶	~0.8	~0.6	5.0x 10 ⁻⁵	~0.5	~0.2
L	1.0 x 10 ⁻⁶	~0.8	~0.6	1.0 x 10 ⁻⁶	~0.8	~0.6	5.0 x 10 ⁻⁶	~0.9	~0.6
C	1.1 x 10 ⁻⁶	~0.7	~0.5	1.9 x 10 ⁻⁶	~0.7	~0.5	5.0 x 10 ⁻⁵	~0.9	~0.5

Table IV shows the parameters, passivation current density (j_{pass}), passivation range (E_{rupture}-E_{corr}), rupture potential (E_{rupture}), obtained from potentiodynamic polarization curves of the alloys W, SB and SC in different media.

C. Cyclic voltammetry

In Fig. 3, the cyclic voltammograms of alloys W, SB and SC in 0.05% NaF, pH 6.0 were obtained in potential region

between -0.6 V and 0.6 V (SCE) with scan starting towards positive potentials at a speed of 10 m V s⁻¹. This potential range covers the main electrochemical processes, such as formation and increase of oxide in passive region. The scan reversal was taken in the material dissolution region. It is observed, according to this figure, alloys W and SB display a

passive region in this medium, with the greatest passivity range for the alloy W, while the SC is not passive [16].

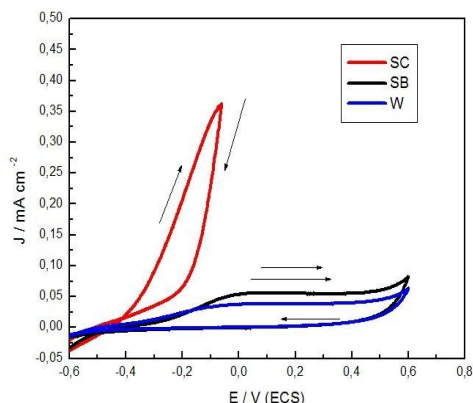


Fig. 3 - Cyclic voltammograms of the alloys W, SB and SC, with $v = 10 \text{ mV/s}$ in 0.05% NaF.

IV. CONCLUSION

The alloys that have higher chromium concentration, as for instance the alloy W (22.5%) and SB (25%), have a higher corrosion resistance compared to the SC with lower Cr content but containing Be due to the passivation phenomenon attributed to formation of a protective layer of chromium oxide, thus inhibiting the corrosion process continuation. The percentage mass loss of the alloys W, SB and SC after immersion was virtually zero, being the latter which the most weight lost (-0.05%), which suggests that this alloy is even the least corrosion resistant due to the lower chromium concentration. Analyzing the measurements carried out in open circuit as well as the potentiodynamic profiles, there is a clear distinction among the electrochemical behaviors corresponding to the SC as compared to the two other alloys. In general, the alloys W and SB displayed very similar responses and good corrosion resistance, being the worst performance for the SC. Moreover, the results obtained by these electrochemical techniques traditionally carried out to evaluate corrosion resistance of metals and alloys in aqueous media are in agreement with those of immersion. Given the results, it is evident that the best alloy for dentures fixed manufacture in terms of corrosion resistance is W and the worst is SC.

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