Frontiers in Dentistry

Corrosion Behavior of a Nickel-Base Dental Casting Alloy in Artificial Saliva Studied by Weight Loss and Polarization Techniques

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Article Info

Article type:
Original Article

Article History:
Received: 16 April 2018
Accepted: 17 November 2018
Published: 20 January 2019

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ABSTRACT

Objectives: Nickel-chromium (Ni-Cr) base dental alloys with desirable properties have been employed in prosthodontics for years. Corrosion behavior of a Ni-Cr base alloy in artificial saliva with different pH values is determined in this work.

Materials and Methods: Corrosion behavior of Ni-Cr alloy was studied in artificial saliva with different pHs (2.5, 5, 7, and 9), using weight loss described by corrosion rate (CR) in mils per year (mpy) and potentiodynamic polarization described by corrosion potential (CP) in mV and current density (CD) in mA/cm^2. Surface morphology was assessed using scanning electron microscopy (SEM). Statistical difference was determined using one-way ANOVA and post-hoc Tukey's honestly significant difference test with a difference significance of 95%.

Results: In the weight loss method, CR was 71.95±3.40, 17.26±1.03, 8.92±0.35, and 6.93±0.54 mpy at pH values of 2.5, 5, 7, and 9, respectively. Significant differences in CR were observed only at pH=2.5, while in CD, they were found at PH=2.5 and 5 ($P<0.05$). In the polarization method, CP values were significantly different. SEM exhibited the formation of preferential sites of corrosion attacks influenced by pH.

Conclusion: Both techniques revealed consistent results. Corrosion resistance increases as pH increases towards less acidic conditions. In more acidic saliva, the corrosion rate is greater. The less acidic saliva leads to formation of a more stable passive film on Ni, and the dissolution of Ni decreases, leading to lower CRs.

Keywords: Corrosion; Nickel-Chromium Alloys; Artificial Saliva; Polarization; Weight Loss

- **Cite this article as:** Moslehifard E, Moslehifard M, Ghasemzadeh S, Ghaiour M, Nasirpouri F. Corrosion Behavior of a Nickel-Base Dental Casting Alloy in Artificial Saliva Studied by Weight Loss and Polarization Techniques. *Front Dent.* 2019;16(1):13-20. doi: 10.18502/fid.v16i1.1104

INTRODUCTION

A variety of metallic alloys is currently available for prosthodontic restorations, among which, nickel-chromium (Ni-Cr) casting alloys are used in dental crown and bridge fabrication. For aesthetic purposes, these alloys are attached to a porcelain veneer fired onto the restoration, i.e. metal-ceramic restoration, known as porcelain-fused-to-metal (PFM) [1].

Ni-Cr casting alloys have been used in dentistry for years. Ni-Cr alloys are a class of base metal alloy system with good corrosion resistance achieved by the formation of a protective oxide film in the oral environment. According to the binary phase diagram of Ni-Cr system, there is an extensive solid solubility of Cr in Ni, and consequently, the binary alloys are not precipitation hardenable. Up to approximately

37 weight percent (wt %), Cr may remain dissolved at room temperature in the matrix, known as gamma phase. One possible solution to strengthen Ni-Cr alloys is to add alloying elements. Cr provides corrosion resistance and some solid solution hardening, while other additives are used to provide more solid-solution hardening or precipitate formation [2]. Various alloying elements may be added to Ni-Cr binary system for different purposes, but molybdenum (Mo) and beryllium (Be) are the most conventional alloying elements added to Ni-Cr binary alloys to modify their properties, forming commercial alloys known as Ni-Cr dental alloys [3]. Ni-base alloys exhibit an appropriate modulus of elasticity compared to gold, which makes thinner sections of the alloy possible to be used, leading to less sound tooth destruction during crown preparation. Furthermore, the thermal expansion coefficient of Ni-based alloys is very close to that of conventional veneering porcelain, which provides a perfect metal/ceramic crown bond during firing without cracking [4]. Therefore, most Ni-Cr restorations perform well clinically. However, they might cause hypersensitivity and other tissue reactions [5]. It is worth noting that the quality of a given dental alloy is influenced by different factors including biologic properties like biocompatibility, material properties such as mechanical strength and corrosion resistance, and technological aspects like fabrication methods [6]. Corrosion behavior of dental alloys during service may exhibit biologic, functional, and aesthetic effects, of which, biologic effects are of greatest significance. When corrosion occurs, metal ions are released and may come into contact with cells and tissues in the immediate environment or may be distributed throughout the entire body [1]. Release of elements during the corrosion process depends on many factors including the material, the amount of release, and the duration of exposure to tissue. This determines the biologic response to the element/alloy [1]. Hence, it is crucial to keep the ion release at a minimum level to improve material function and aesthetic of the restoration [6].

Corrosion resistance of Ni-Cr dental alloys relies on their passivation associated with the formation of a thin superficial oxide layer. Cr is the main alloying element in Ni-based alloys and is added to promote the formation of a stable passive oxide layer that is highly resistant to corrosion. Molybdenum (Mo) is also frequently added to promote resistance to pitting and crevice corrosion [3,4]. Beryllium (Be) improves both the alloy castability and adherence of the veneering porcelain. However, it significantly decreases alloy corrosion resistance, and its content should be less than 0.6 wt% [3,4]. On the other hand, Ni-Cr dental alloys are exposed to different service conditions which affect their corrosion behavior. Significant factors to take into account are the humidity, the change in temperature inside the mouth from 0 to 70˚C, and also, pH change from 2 to 11, which happens during the chewing process inside the mouth [3,4].

Different categories of food, oral hygiene products, age, periodontitis, oral habits such as smoking, systemic disease, infection, and salivary gland radiation contribute to the changes in the salivary pH [7-9].

Little information exists on the effect of pH on the corrosion properties of Ni-Cr alloys. de De Micheli and Riesgo [10] reported that the anodic corrosion behavior of commercial Be-free Ni-Cr alloys was not affected by heat treatment. In a study by Qiu et al [11], the corrosion rate of a Be-free Ni-Cr alloy increased significantly after porcelain firing. Wataha et al [12] studied element release from base metal alloys. They found that reducing the pH significantly increased Ni release. But they did not evaluate the corrosion behavior of the alloy at different pH levels. Wylie et al [4] ascribed the corrosion behavior to the content and distribution of Cr in the microstructure.

The aim of this study was to investigate the corrosion behavior of Ni-Cr alloy in artificial saliva at 37˚C as a function of pH values (2.5 to 9) using two different techniques including weight loss and polarization.

MATERIALS AND METHODS

Ni-Cr alloy discs (Thermabond alloy super cast, MFG, Los Angeles, CA, USA) with the chemical composition of 75% Ni, 15% Cr, 5% Mo, and 1.6 Be, and dimensions of 8 mm in diameter and 1 mm in thickness were formed by melting. The melt was prepared by a propane/oxygen flame, and the cast was achieved using a centrifugal casting machine (Motorcast, Degussa, Germany) in accordance with the manufacturer's instruction. All samples were mechanically polished using grinding papers (#320, #400,

#600, #80; Sandpaper 991 A, Softflex, Wasserfest, Germany) and polishing cloths (Bego, Bremen, Germany) with diamond paste to obtain a mirror surface. Samples were ultrasonically cleaned with deionized water (Ultrasonic Processor, Hielscher, Germany). Finally, they were washed by isopropanol (70% vol) and acetone, each for 10 minutes, and finally dried using hot air.

The corrosion specimens were divided into four groups to investigate the effect of pH in each group. The groups included different pH values of 2.5, 5, 7, and 9. The composition of the artificial saliva used was KCl (0.4 g/l), NaCl (0.4 g/l), CaCl2.2H2O (0.906 g/l), NaH2PO4.2H2O (0.690 g/l), Na2S.9H2O (0.005 g/l), and urea (1 g/l) [9]. The composition of this solution closely resembles that of human natural saliva. To obtain a more acidic artificial saliva solution, lactic acid was added in 1 ml increments, and to obtain a more basic artificial saliva solution, sodium hydroxide (NaOH) was added in 1 ml increments. To evaluate the pH, a digital pH meter (Metrohm's 827 pH Lab meter, Poland) was used.

Corrosion studies:

The corrosion behavior of Ni-Cr in the artificial saliva was studied using two different methods including weight loss and potentiodynamic polarization curves according to standard procedures ASTM-G31-72 and ASTM G61 described by the American Society for Testing and Materials (ASTM). In weight loss method, corrosion specimens were weighed using a high-accuracy balance (accuracy of ±0.1 mg) before and after immersion in the artificial saliva for 5 weeks, and the experiment was repeated three times. Corrosion rate (CR) was then determined in mils per year (mpy) using the following equation [13]:

$$\mathrm{C.R.} = \frac{534\ \mathrm{W}}{\mathrm{D.A.T}}$$

Where W is weight loss measured in mg, D is the density of alloy in g/cm3, A is the surface area of the specimen exposed to the solution in cm2, and T is the time in hour. In the polarization method, the tests were conducted in a conventional three-electrode electrochemical cell and repeated three times for each group.

The corrosion cell held 100 ml of the artificial solution. A saturated calomel electrode (SCE) was used as the reference electrode (RE), a graphite rod was used as a counter electrode (CE), and a potentiostat/galvanostat instrument (Zahner-Elektrik, Kronach, Germany) was used to carry out the corrosion measurements. Corrosion specimens were mounted to restrict the surface area to 1 cm2. A time duration of 30 minutes was adjusted as the rest time for the initial stabilization and heating of the solution to 37°C to simulate the normal body temperature. Polarization curves were recorded at a scan rate of 1 mV/s. Corrosion parameters were extracted from the polarization curves including corrosion potential (CP) which is known as Ecorr, corrosion current density (CD) which is also known as Icorr, and passivation current density (Ep) of anodic and cathodic slopes according to the Stern-Geary method.

Surface characterization:

Surface morphology of corrosion specimens before and after immersion in the artificial saliva was characterized using scanning electron microscopy (SEM; Cam Scan MV2300, Oxford, UK).

Statistical analysis:

Statistical assessments were performed by SPSS software (Version 13; IBM Co., Chicago, IL, USA). After testing, all results were analyzed by

Statistical methods:

Mean, standard deviation (SD), minimum and maximum in each group were calculated, and the normal distribution curve was evaluated. Kolmogorov-Smirnov test was used to evaluate normal distribution. The corrosion parameters, including Ecorr (corrosion potential), Icorr (corrosion current density), and also, corrosion rate obtained by weight loss were analyzed. Statistical analysis of the obtained results for each test group was conducted using a one-way analysis of variance (ANOVA) for analyzing how pH affects the corrosion parameters. Tukey's HSD (honestly significant difference) test was chosen as the multiple-comparison technique. Statistical significance was set at P<0.05.

RESULTS

The corrosion behavior of Ni-Cr base alloy in artificial saliva at different pH values was evaluated using two different methods. Table 1 summarizes experimental data obtained from both weight loss and dynamic potentiodynamic polarization tests.

Figure 1 shows the dynamic potentiodynamic polarization curves recorded at different pH values of artificial saliva and the corresponding data including corrosion potential and corrosion current density.

Statistical evaluation was performed based on Kolmogorov-Smirnov for corrosion parameters achieved by each technique and showed that the data are parametric. In order to determine the statistical difference, ANOVA was employed in each group, and then, Tukey's HSD test was used for comparison. Figure 2 shows the variation of measured parameters along with the statistical calculations including the mean and SD. Corrosion potential values measured at different pH levels were significantly different.

Current density values measured at pH of 2.5 and 5 were significantly different in all groups. However, current density values measured at pH of 7 and 9 were not significantly different (P>0.05). Corrosion rates measured by weight loss method at pH of 2.5 and 5 were significantly different from that of other groups. But those measured at pH of 7 and 9 were not significantly different (P>0.05). This was the same for weight loss values. Surface morphology of Ni-Cr base alloy was examined using SEM before and after immersion for 5 weeks in artificial saliva at different pH values as shown in Figures 3 and 4, respectively. As is evident from Figure 4, partial dissolution of metal has taken place in some preferential places, the amount of which changes with pH.

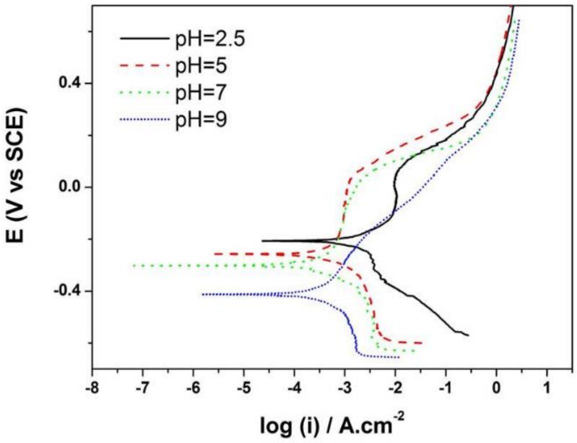


Fig. 1: Potentiodynamic polarization curves recorded on nickel-chromium (Ni-Cr) base alloy in artificial saliva at different pH levels

Table 1. Parameters determined according to the polarization curves of nickel-chromium (Ni-Cr) alloy in artificial saliva

pH	Corrosion parameter	Mean±SD	Minimum	Maximum
2.5	Corrosion potential (mV)	-207±3.7	-211	-202
	Corrosion current density (mA/cm2)	1.74±0.08	1.65	1.85
	Corrosion rate (mpy)	71.95±3.40	68.2	76.4
	Weight loss (mg)	0.64±0.15	0.48	0.80
	Passivation current density Ip (mA/cm2)	9.79	---	---
	Transpassive potential (mV)	39.6	---	---
5	Corrosion potential (mV)	-249.5±4.6	-256	-245
	Corrosion current density (mA/cm2)	0.41±0.02	0.39	0.45
	Corrosion rate (mpy)	17.26±1.03	16.12	18.61
	Weight loss (mg)	0.20±0.03	0.17	0.24
	Passivation current density Ip (mA/cm2)	1.01	---	---
	Transpassive potential (mV)	33.1	---	---
7	Corrosion potential (mV)	-298.5±6.9	-305	-289
	Corrosion current density (mA/cm2)	0.21±0.01	0.20	0.22
	Corrosion rate (mpy)	8.92±0.35	8.47	9.3
	Weight loss (mg)	0.10±0.01	0.08	0.12
	Passivation current density Ip (mA/cm2)	0.97	---	---
	Transpassive potential (mV)	-0.45	---	---
9	Corrosion potential (mV)	-416.7±6.9	-425	-410
	Corrosion current density (mA/cm2)	0.16±0.01	0.15	0.18
	Corrosion rate (mpy)	6.93±0.54	6.24	7.52
	Weight loss (mg)	0.09±0.02	0.07	0.13
	Passivation current density Ip (mA/cm2)	1.11	---	---
	Transpassive potential (mV)	-0.12	---	---

DISCUSSION

Corrosion is generally defined as the deterioration of materials by aggressive action of the environment (atmosphere and oral fluids).

This definition is used for metals, where the mechanism of corrosion is mainly electrochemical. Corrosion of metals in oral conditions takes place continuously because these ions are removed through abrasion by foods, liquids and tooth brushing [14]. Corrosion of dental alloys may result in destructive biological, functional, and aesthetic effects. Furthermore, metal ions are released in corrosion processes and may come into contact with cells and tissues in the immediate environment or be disseminated throughout the body, mostly to the intestinal canal.

If these ions are not biocompatible and are absorbed in sufficient quantity, the organism may be damaged due to the toxicity and risk of sensitization. Therefore, corrosion of metallic dental alloys like Ni-Cr base alloys makes them susceptible to failure and the consequent problems [14].

Most dental alloys are corroded in the oral cavity although the extent of this corrosion depends on the type of alloys and compounds. For instance, alloys with a high-gold content exhibit no evidence of damage to health resulting from this alloy group. By contrast, in Ni-base alloys, the degree of damage is plausible.

The extent of metal ion released during corrosion depends substantially on the chemical composition and microstructure of the alloy and on the production and processing conditions; however, these processes are also dependent on the particular characteristics of different oral environments (saliva, dental plaque, bacteria, gastric acid reflux, etc.) [3].

In order to achieve desirable properties like castability, mechanical strength, corrosion resistance, etc., dental alloys comprising of a variety of metals have been developed. The biocompatibility of a given casting alloy correlates directly with its corrosion properties and the consequent ion release [1]. In terms of the structure, it has been found that single phase alloys are more corrosion-resistant, whereas varying grain composition in multiphase alloys tends to facilitate corrosion reactions by imposing differential electrochemical potentials and a corrosion driving force.

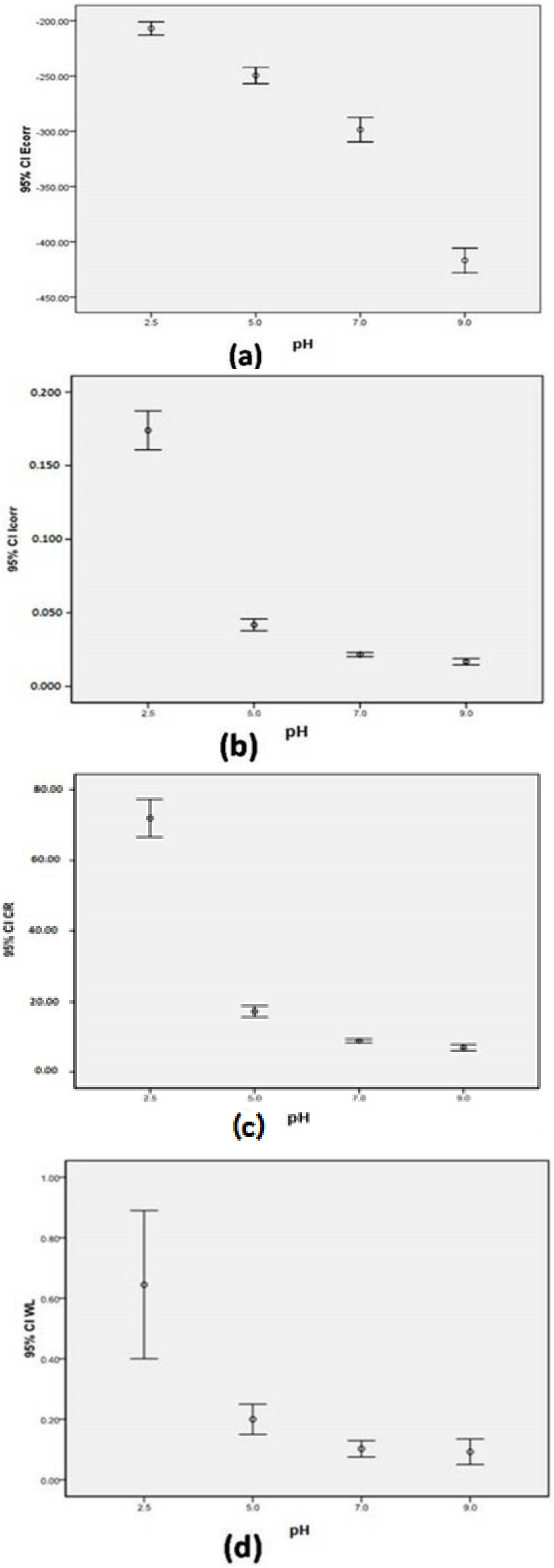


Fig. 2: Error bar of the mean and 95% confidence interval of corrosion parameters measured using two different corrosion tests in artificial saliva. (a) Corrosion potential. (b) Current density. (c) Corrosion rate by the Stern-Geary method. (d) Corrosion rate by weight loss

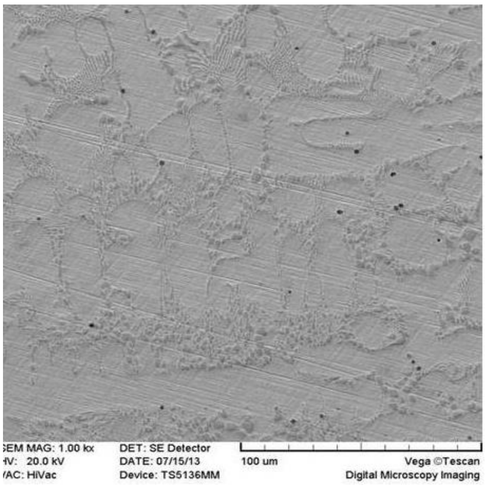
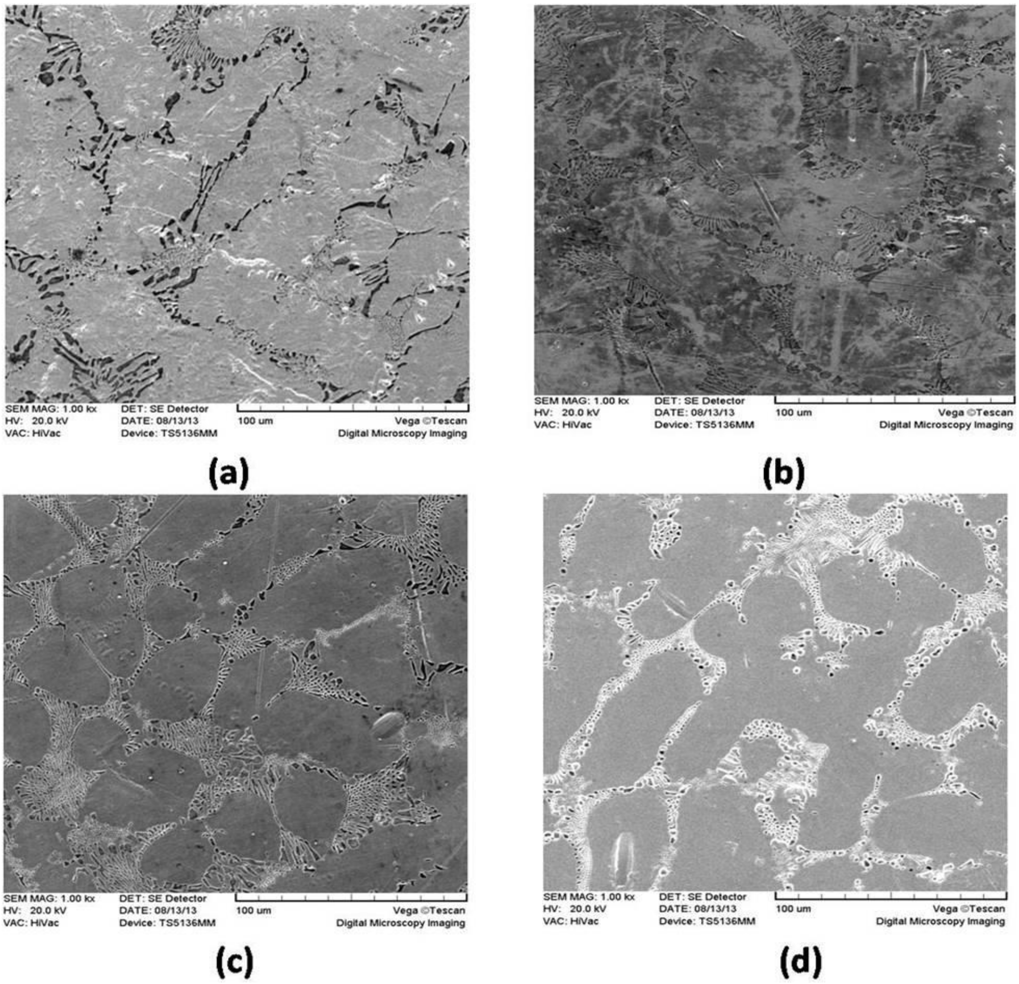


Fig. 3. Scanning electron microscopic (SEM) image of nickel-chromium (Ni-Cr) base alloy before corrosion test



(a) (b) (c) (d)

Fig. 4: Scanning electron microscopic (SEM) image of nickel-chromium (Ni-Cr) base alloy after immersion for 5 weeks in artificial saliva at (a) pH=2.5, (b) pH=5, (c) pH=7, and (d) pH=9

In Ni-based alloys containing small amounts of Cr and Mo, corrosion readily occurs, which can be associated with the risk of a sensitizing effect of depleted Cr regions under thermal or heat treatment. However, no evidence of this is available to date in dental application [3].

Corrosion resistance of the most commonly used metallic materials depends on their passivation capability defined as the formation of a thin oxide insulating surface layer. This layer of oxide, known as the passive film, acts as a protecting interface between the metal structure and the environment such as saliva [10]. However, it has been shown that corrosion resistance can be altered by the passivation mechanism depending on irregularities and porosities of the oxide layer formed on the alloy surface [15]. Ni-Cr alloys exhibit active-passive-transpassive corrosion behaviors.

Figure 1 shows the potentiodynamic polarization curves recorded in the artificial saliva at different pH levels. In the pH range studied, although the Ni-Cr alloy shows active-passive-transpassive behaviors, it exhibits significant changes in passivation current density and potential. The magnitude of passivation parameters is indicated in Table 1. As is evident, the lower the pH, the weaker the passive film formed on the Ni-Cr alloy. At pH of 2.5, the passivation current density is the highest, indicating that the passive film is not an adherent, firm and compact film on the surface as will be discussed later using weight loss and morphological observations. The passivation current density is reduced as the pH increases, meaning that either the passivation process is improved or the passive film is strong. It has been established that Cr, Mo, and manganese (Mn) are the most effective elements in preventing pitting of a series of Ni-Cr dental castings. It has been indicated that Ni-rich interdendritic zones appearing during solidification were preferentially dissolved above the breakdown potential [6,9]. Reclaru and Meyer [16] studied the effects of fluorides on titanium and other dental alloys. If fluoride ions are present, the dental alloys tested undergo pitting and crevice corrosion processes as soon as the pH drops to below 3.5 [16,17].

Our results indicate that the corrosion behavior of Ni-Cr alloy is affected by pH levels of surrounding artificial saliva. It is observed that corrosion rate and passivation current density decrease by increasing the pH of the artificial saliva from 2.5 to 9 according to SEM images taken from the sample immersed for 5 weeks in the artificial saliva.

CONCLUSION

It is shown that the corrosion behavior of Ni-Cr alloy investigated by weight loss and polarization techniques depends on the pH level of artificial saliva and the alloy phase microstructure. The results obtained by both techniques are consistent. Corrosion rate as a function of weight loss (mpy) or corrosion current density increases against the pH of the artificial saliva. In acidic saliva with pH of less than 7, the corrosion rate is higher owing to the higher dissolution rate of Ni determined by the weak passivation behavior. However, the less acidic saliva leads to formation of a more stable passive film on Ni, and therefore, the dissolution of Ni decreases, leading to lower corrosion rates.

ACKNOWLEDGMENTS

This article was written based on a dataset from one DDS thesis entitled “Evaluation of corrosion behavior of nickel-chromium alloy in artificial saliva” registered at Tabriz University of Medical Sciences Faculty of Dentistry. The thesis was supported by the Vice Chancellor for Research at Tabriz University of Medical Sciences.

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