

Galvanic Corrosion of Dental Alloys and Amalgam in Artificial Saliva Containing Citric Acid

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ABSTRACT

In this work galvanic corrosion potentials and currents were measured using polarization curves of some dental alloys (amalgam, Co-Cr-Mo, Ni-Cr-Mo, SS 316L, Ti-6Al-4V alloys) in artificial saliva containing citric acid with three concentrations 3,6 and 9 g/l at 37°C. All galvanic corrosion data were measured to coupling of amalgam and other alloys to investigate the galvanic corrosion between filling and other dental devices such as partial-denture framework, crowns, bridges, and endodontic instruments.

The results of galvanic corrosion show that the coupling between amalgam and Ni-Cr-Mo alloy gives higher galvanic corrosion current than other metallic contact, and then the contact between amalgam and Co-Cr-Mo alloy was heavier compared with coupling of SS 316L and Ti-6Al-4V alloy with amalgam. The increasing of corrosion for alloys containing chromium due to rapidly converting of Cr^{6+} to Cr^{3+} and this phenomenon decreases the concentration of chromium ions at surface and then increases the dissolution of metal atoms, while decreasing of galvanic corrosion of Ti-alloy coupled with amalgam due to the passive oxide surface layer (TiO_2).

Keyword: Amalgam, Dental Alloys, Citric Acid, Galvanic Corrosion in Saliva.

التآكل الكلفاني لسبائك طب الاسنان والحشوة الزئبقية في اللعاب الصناعي الحاوي على حامض الستريك

الخلاصة

يتضمن هذا البحث قياس جهود وتيار التآكل الكلفاني باستخدام منحنيات الاستقطاب لبعض السبائك المستخدمة في طب الأسنان كالحشوة الزئبقية وسبيكة كوبلت-كروم-مولبيديوم وسبيكة نيكل-كروم-مولبيديوم والفولاذ المقاوم للصدأ 316 وسبيكة تيتانيوم-المنيوم-فناديوم في اللعاب الصناعي الحوي على حامض الستريك بثلاث تراكيز مختلفة 3 و 6 و 9 غرام/لتر. جميع بيانات التآكل الكلفاني المقاسة تبين بان ازدواج الحشوة الزئبقية والمواد المعدنية الاخرى التي تستخدم في التقويم الجزئي والتيجان والجسور والادوات التجميلية الاخرى تؤدي الى حصول تآكل كلفاني. وتبين النتائج بان الازدواج المعدني للحشوة الزئبقية وسبيكة نيكل-كروم-مولبيديوم تعطي اعلى تيار كلفاني من ازدواج الحشوة الزئبقية مع بقية المواد المعدنية. ان زيادة معدل التآكل للسبائك الحاوية على الكروم يعزى الى التحول السريع لايون الكروم (VI) الى ايون الكروم (III) وهذه الظاهرة تقلل تركيز ايونات الكروم على السطح المعدني وتزيد من ذوبان

الذرات المعدنية، في حين نجد ان نقصان التآكل الكافاني لازدواج الحشوة الزئبقية مع سبيكة تيتانيوم-المنيوم-فناديوم تعزى الى الطبقة الاوكسيدية الحامية من اوكسيد التيتانيوم.

INTRODUCTION

All of the ingredients found in food and drink are capable of becoming incorporated into saliva. However, most of the foods are injected before the breakdown into basic chemicals occurs. Some foods and beverages, though, contain chemicals that are reactive by themselves without any reductions and may become dissolved in saliva and affect the tarnish and corrosion of metallic materials. Some of these include various organic acids, such as lactic, tartaric, oleic, ascorbic, fumaric, maleic, and succinic, as well as sulfates, chlorides, nitrates, sulfides, acetates, bichromates, formaldehyde, sulfoxylates, urea, and the nutrients themselves of lipids, carbohydrates, proteins, vitamins, and minerals [1].

Citric acid exists in greater than trace amounts in a variety of fruits and vegetables, most notably citrus fruits. Lemons and limes have particularly high concentrations of the acid; it can constitute as much as 8% of the dry weight of these fruits (about 47 g/l in the juices)[2]. The concentrations of citric acid in citrus fruits range from 0.005 mol/l for oranges and grapefruits to 0.30 mol/l in lemons and limes. Within species, these values vary depending on the cultivar and the circumstances in which the fruit was grown.

The aim of this work is to study galvanic corrosion between amalgam as filling and other dental alloys which used as partial-denture framework, crowns, bridges, and endodontic instruments...etc. when they are contacted in saliva in the presence of different percentage of citric acid at 37°C.

Many authors investigated the corrosion of dental alloys. Chang et al. (2003) studied electrochemical behavior on microbiology-related corrosion of metallic dental materials. They showed that the corrosion behavior of dental metallic materials in the presence of streptococcus mutants and its growth by products is increased [3]. Maruthamuthu (2005) studied the electrochemical behavior of microbes on orthodontics wires in artificial saliva with or without saliva, and he showed that bacteria slightly reduce the resistance and increase the corrosion current [4]. Takemoto et al. (2006) studied corrosion mechanism of Ti-Cr alloys by immersion in solution containing fluoride. They showed by atomic emission spectroscopy (AES) analysis that amount of chromium oxide in the oxide films was correlated with chromium content in the Ti-Cr alloys [5]. Sharma et al. (2008) studied electrochemical corrosion behavior of dental implant alloys in artificial saliva by utilizing electrochemical impedance spectroscopy (EIS), Tafel polarization and cyclic polarization studies. They showed from cyclic polarization studies that all alloys Co-Cr (commercially), Ni-Cr, Co-Cr (indigenously developed by DRDO, India), cp Ti, and Cu-Ni-Al alloys showed active-passive behavior with large potential independent region terminated by a region comprising significant increase in current density except cp Ti [6].

Wang and Zheng (2008) studied the electrochemical behavior and surface analysis in artificial saliva for 50Ti-47.2Ni-2.8Co alloy for orthodontic use by open circuit potential, potentiodynamic and potentiostatic techniques, surface characterization after anodic polarization by (X-rays photoelectron spectroscopy), and metal ions

concentration, measured by ICP/OES [7]. Yfantis (2008) studied corrosion characteristics of base ceramo-metal dental casting alloys, and the vitro corrosion of Ni-Cr and Co-Cr alloys leads to the release of very small amounts of metallic elements (Ni, Co, Cr, Mo) [8].

Zhang et al. (2009) studied effect of silver on corrosion behavior of Ti-Ag alloys in artificial saliva solutions. They showed that addition of silver to titanium is effective in reducing the corrosion current density and increasing the open circuit potential of Ti-Ag alloy in artificial saliva environment. The presence of fluoride leads to higher corrosion current densities and lower open circuit potential for the alloys [9]. Bhola et al. (2009) studied electrochemical behavior of titanium and its alloys as dental implant in normal saline. They showed that in normal saline solution all alloys exhibit a high corrosion resistance and the corrosion rate observed in order, Ti-15Mo > Ti2 > Ti-12Mo-6Zr-2Fe > Ti1 > Ti-6Al-4V > TiOs (Ti-35.5Nb-5.7Ta-7.3Zr). They concluded from cyclic polarization curves the alloys resist localized corrosion [10].

Mareci et al. (2010) studied corrosion behavior for four different Ni-Cr dental alloys. They concluded that very low corrosion current densities, typical of passive materials were obtained for all the samples tested in 0.1 M NaCl solutions. The Cr and Mo contents play a significant role in corrosion resistance. The EIS results show that NiCr-based alloys exhibit passivity at OCP for all samples, the polarization resistance is increasing with the immersion time because of the surface passivation [11].

Mareci et al. (2010) studied electrochemical behavior of two Ag-Pd alloys (Unique white 66% Ag, 22% Pd, 10% Cu, 1% In), (Paliag 50% Ag, 30% Pd, 15.9% Cu, 3% Au, 1% Zn) and one Co-Cr alloy (Vitallium 2000, 63.8% Co, 28.5% Cr, 6% Mo) in Carter-Brugiard/ AFNOR/NF artificial aerated saliva at pH 8.1. Electrochemical measurements were carried out at 25°C under static conditions. They concluded that the open circuit potential of Ag-Pd are attributed to dealloying followed by surface enrichment with Ag and the possible formation of an insoluble AgCl surface film on the respective alloy surfaces [12].

Iijima et al. (2010) studied corrosion behavior of ion implanted Ni-Ti orthodontic wire in fluoride mouth-rinse solutions. The anodic corrosion behavior was examined by potentiodynamic polarization measurements. The surface of the specimens was examined by scanning electron microscopy (SEM) [13].

EXPERIMENTAL PROCEDURE

Preparation of Samples and Electrolyte

The chemical composition of Co-Cr, Ni-Cr, SS 316L and Ti-Al-V alloys are shown in Table (1) by using X-ray fluorescence technique (X-MET 3000TX), in addition to prepare amalgam alloy by amalgamator. All dental alloys were hot mounting to insulate all but one side using formaldehyde (Bakelite) at 138°C for 8 minute, while amalgam was cold mounted using pyrax polymers.

The open side was polished mechanically to a mirror finish, rinsed in distilled water and stored in desiccators. The electrolyte reference used was modified Fusayama artificial saliva [14], which closely resembles natural saliva, with composition of (0.4 g/l KCl, 0.4g/l NaCl, 0.906 g/l CaCl₂.2H₂O, 0.69 g/l NaH₂PO₄.2H₂O, 0.005g/l Na₂S.9H₂O and 1g/l urea). Lactic acid was added to adjust the pH of the solution equal to 4, [15]. To

study the effect of fruit juice, citric acid was added with three concentrations (3, 6 and 9 g/l) to artificial saliva.

Electrochemical Measurements

Polarization experiments were performed in WINKING M Lab 200 Potentiostat/Galvanostat from Bank-Elektronik with electrochemical standard cell with provision for working electrode (dental alloys), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with saturated calomel electrode SCE reference electrode. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 0.5 mA.sec⁻¹.

The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slops by Tafel extrapolation method.

Determination of Galvanic Corrosion Using Polarization Curves

In order to find galvanic corrosion potentials and current densities the anodic polarization curves of the dental material obtained by the Tafel method were superimposed onto each other. The difference in the corrosion potentials and the corrosion currents of the superimposed curves are directly proportional to the magnitude of the galvanic corrosion. In order to find the quantitative value of the galvanic corrosion the coincidence point of the anodic polarization curve with the more negative corrosion potential and the cathodic polarization curve with more positive corrosion potential was determined. The current and potential at this point represent the galvanic corrosion current (i_{couple}) and the galvanic corrosion potential (E_{couple}).

Table (1) Chemical composition of dental alloys.

<i>Types of the alloys</i>	<i>Composition wt%</i>
Amalgam	Ag:56.7, Sn:28.6, Cu:14.7
Co-Cr-Mo	Cr:26.9, Mo:5.27, W:1.01, Mn:0.93, Fe:0.4, Nb:0.16, Co:remaining
Ni-Cr-Mo	Cr:20.9, Mo:9.94, Nb:3.8, Fe:2.4, Cu:0.13, Ni:remaining
SS 316L	Cr:16.0, Ni:12.0, Mo:3.0, Mn:1.5, Si:0.75, N:0.05, C:0.03, P:0.03, S:0.01, Fe:remaining
Ti-6Al-4V	Al:5.54, V:3.6, Cu:0.18, Fe:0.17, Nb:0.01, Ti:remaining

RESULTS AND DISCUSSION

Figure (1) shows the polarization curves of galvanic coupling of amalgam with Co-Cr-Mo, Ni-Cr-Mo, and SS 316L, and Ti-6Al-4V alloys respectively in artificial saliva which show that the galvanic corrosion current density were:

i_{couple} for amalgam contact with Ni-Cr-Mo > Co-Cr-Mo > SS 316L > Ti-6Al-4V

The polarization curve of each dental alloy shows the cathodic and anodic behavior in given environment, and the anodic reactions represent the dissolution of metals in dental alloy according to the general reaction of oxidation:



While the cathodic reaction represents reduction reaction which includes evolution of hydrogen molecules because acidity of electrolyte (artificial saliva) as follows:



And the later reaction can be increased in the presence of citric acid which presence in many drinks or juices, and then increases the rate of reaction as show from the data of polarization curve for each alloy that tabulated in Table (2) especially for amalgam through the data of corrosion rate which calculated according to the following equation [16]:

$$C_R(mpy) = 0.13 \frac{e}{\rho} i_{corr} \quad \dots (3)$$

Where $C_R(mpy)$: corrosion rate in mil per year, e : equivalent weight of alloy (gm), and ρ : density of alloy (gm/cm³).

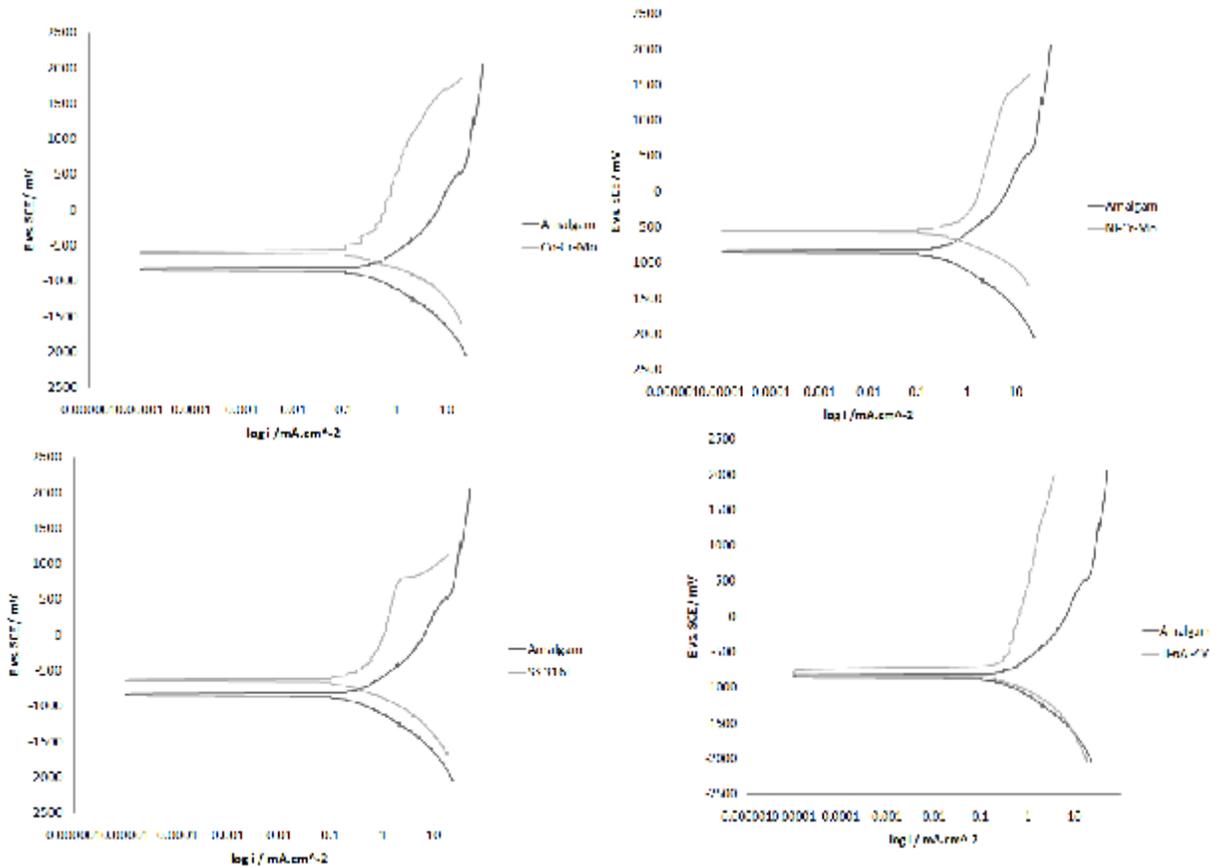


Figure (1) galvanic corrosion current density and galvanic corrosion potential for dental alloys and amalgam in artificial saliva at 37°C.

Table (2) Corrosion parameters of dental alloys in artificial saliva at pH=4 and temperature 37°C in the absence and presence of citric acid with three percent.

Alloys	Conc. of citric acid in saliva (g/l)	$-E_{corr}$ (mV)	i_{corr} ($\mu A.cm^{-2}$)	$-b_c$ (mV.dec ⁻¹)	b_a (mV.dec ⁻¹)	C_R (mpy)
Amalgam	0	834.1	288.78	524.5	711.5	386.10
	3	434.3	156.73	224.2	354.3	209.55
	6	1309.2	200.78	908.3	1377.0	268.44
	9	655.4	261.17	312.9	391	349.18
Co-Cr-Mo	0	577.8	191.92	323.2	1114.6	83.101
	3	114.0	362.09	678.2	1822.7	156.78
	6	507.0	269.25	219.3	773.6	116.59
	9	512.7	337.48	245.5	1248.1	146.13
Ni-Cr-Mo	0	549.9	336.91	335.2	514.4	128.03
	3	91.3	378.2	254.5	755.6	143.72
	6	529.6	563.5	139.8	414.3	214.13
	9	546.7	424.6	172.6	272.4	161.348
SS 316L	0	642.0	279.16	419.6	991.0	127.57
	3	171.8	279.74	306.5	757.1	127.84
	6	596.5	557.71	295.0	437.0	254.87
	9	254.4	537.49	311.1	877.8	245.63
Ti-6Al-4V	0	772.7	265.11	441.6	2020.6	183.46
	3	197.6	321.19	460.8	1650.0	222.26
	6	621.2	265.17	300.0	1391.8	183.50
	9	21.3	685.97	217.1	550.5	474.70

The galvanic corrosion can be increase in the presence of citric acid as shown in Figure (2) to (4) and Table (3). The galvanic corrosion current densities take the sequence of increment in the presence of citric acid C.A.:

Artificial saliva containing 3g/l C.A. Ni-Cr-Mo > Co-Cr-Mo > SS 316L > Ti-6Al-4V
 6g/l C.A. Ni-Cr-Mo \simeq Co-Cr-Mo > SS 316L > Ti-6Al-4V
 9g/l C.A. Ni-Cr-Mo > Co-Cr-Mo \simeq SS 316L \simeq Ti-6Al-4V

These results indicate that Ti-Al-V alloy is extremely resistant against corrosion and Ti-alloy owes this corrosion resistance to the passive oxide surface layer (TiO₂)[17]. Also other alloys can be form protective layer on its surface, but the protective layer on Ti-alloy surface more stable than these formed on SS and the later more stable than that of Co- and Ni- alloys. Also can be observing the end of anodic curves for dental alloys

where increases of dissolution can occur with clear difference among the behavior of these alloys.

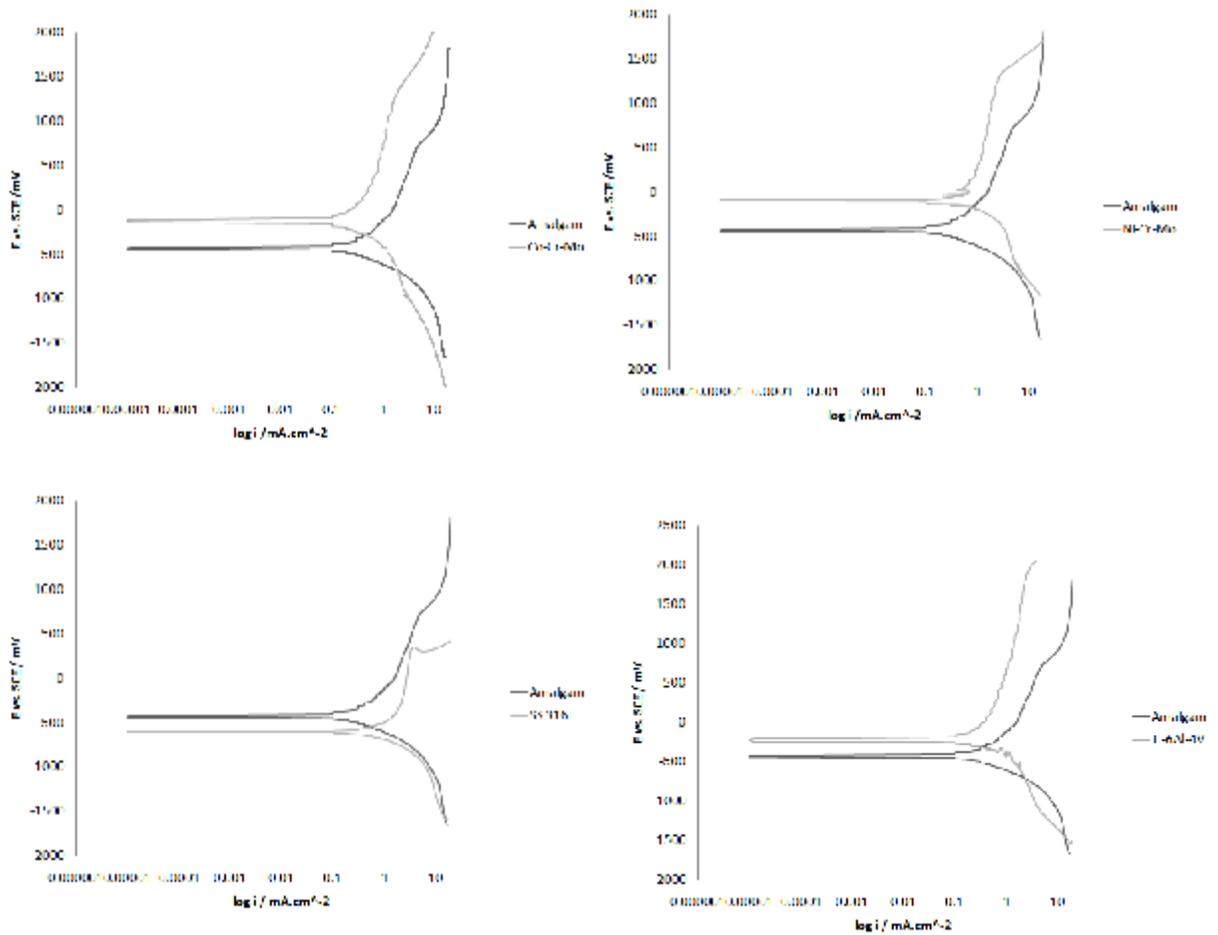


Figure (2) galvanic corrosion current density and galvanic corrosion potential for dental alloys and amalgam in artificial saliva containing 3g/l citric acid at 37°C.

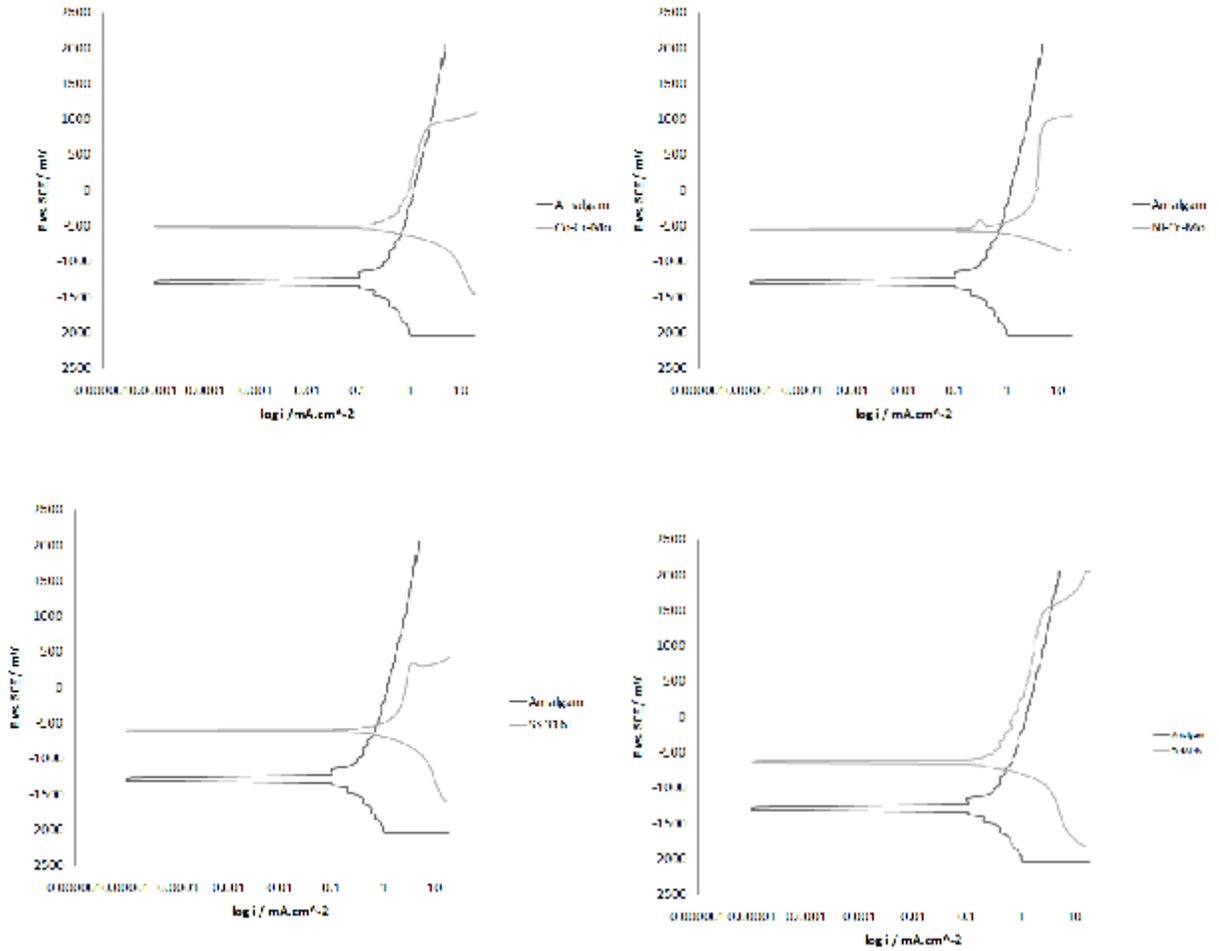


Figure (3) galvanic corrosion current density and galvanic corrosion potential for dental alloys and amalgam in artificial saliva containing 6g/l citric acid at 37°C.

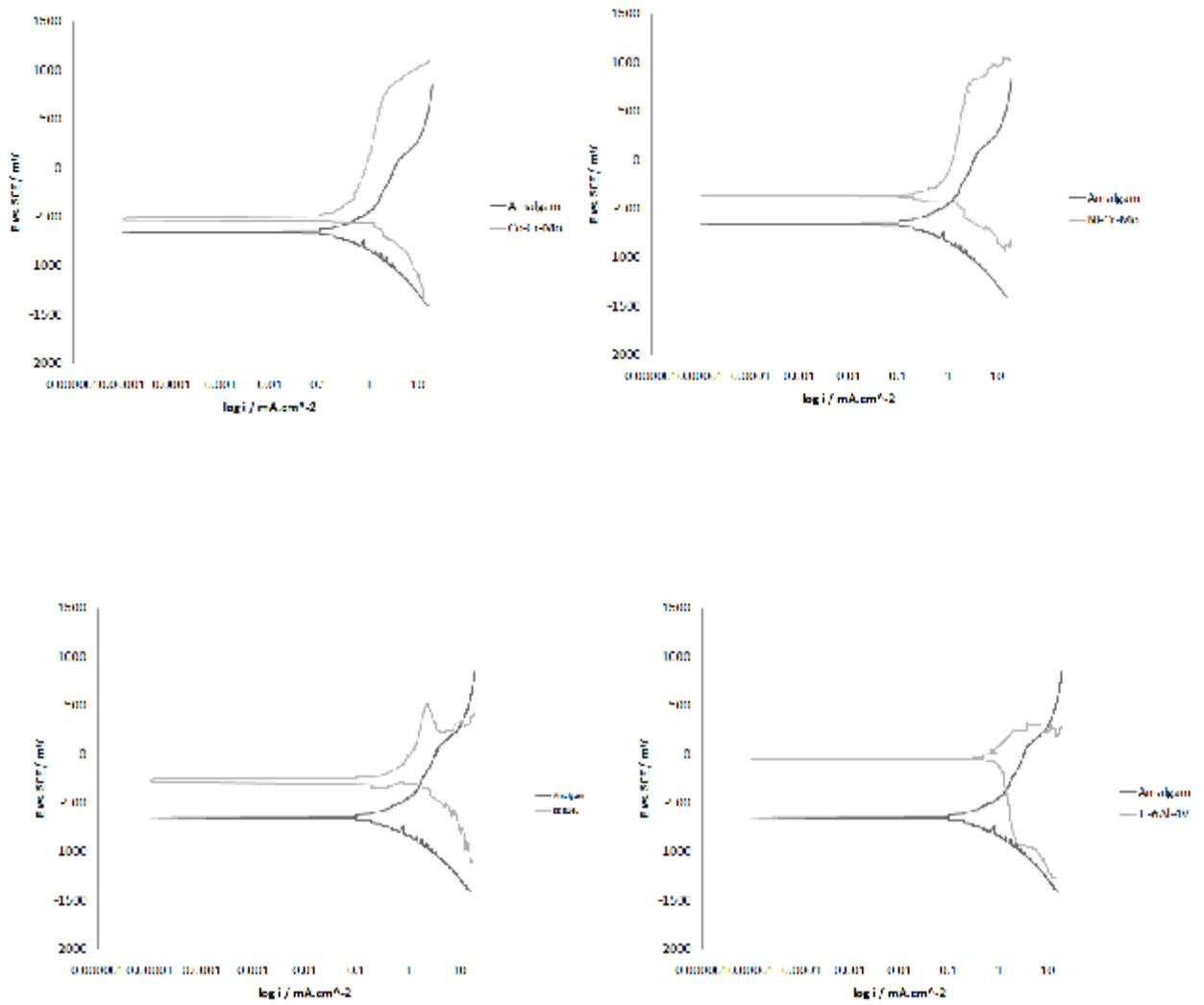


Figure (4) galvanic corrosion current density and galvanic corrosion potential for dental alloys and amalgam in artificial saliva containing 9g/l citric acid at 37°C.

Table (3) galvanic corrosion potentials and current density of various dental materials coupled with amalgam in the absence and presence of citric acid in artificial saliva at 37°C.

Dental alloys	Conc. of citric acid	E_{couple} / mV	$i_{couple} / \mu A.cm^{-2}$
Co-Cr-Mo	0 g/l	-735	0.4
Ni-Cr-Mo		-700	0.8
SS 316L		-759	0.3
Ti-6Al-4V		-	-
Co-Cr-Mo	3 g/l	-293	0.5
Ni-Cr-Mo		-193	0.9
SS 316L		-564	0.4
Ti-6Al-4V		-337	0.4
Co-Cr-Mo	6 g/l	-629	0.8
Ni-Cr-Mo		-606	0.8
SS 316L		-667	0.7
Ti-6Al-4V		-738	0.5
Co-Cr-Mo	9g/l	-562	1.3
Ni-Cr-Mo		-431	1.5
SS 316L		-370	1.3
Ti-6Al-4V		-326	1.3

The causes of this behavior can be interpret by the interactions (affinity) between released metal ions from (Co-Cr-Mo and Ni-Cr-Mo alloy) and species in saliva more than that observed from Ti-Al-V alloy and SS 316L. Ni-Cr-Mo, Co-Cr-Mo alloys and SS 316L consist of chromium and produce chromium oxide, but the only ion taken up intracellular by red blood cells following corrosion of alloy is Cr^{6+} , which is then rapidly converted to Cr^{3+} . This phenomenon decreases the concentration of chromium ions at surface and then increases the dissolution of metal atoms.

Morais et al. [18] found that chromium and nickel are retained in bone marrow.

Nickel is very small and has a low affinity for blood cells. Cobalt binds to both red blood cells and white blood cells. Although only very small quantities of Cr^{3+} bind to cells, Cr^{6+} binds very strongly to red blood cells and white blood cells [19]. This phenomenon lead to resist the surface of Ti-alloy more than other alloys when its coupled with amalgam.

Roughness and pitting of the surface of amalgam as a result of chemical attack from component in food or saliva, and corrosion may by the result of galvanism. The gamma 2 (Sn_7Hg) [20] phase of conventional amalgam is the most electrochemically reactive. For higher copper amalgam the Cu_6Sn_3 phase forms the anode but less corrosion occurs than conventional amalgam because absence of gamma 2 phases [20].

The rate of corrosion is accelerated when the amalgam filling is contact with gold or old restorations. Corrosion will cause roughness of the amalgam which may lead to plaque and bacterial accumulation and inflammation of the soft tissue also will cause

poor appearance of the filling surface and may affect the mechanical properties of amalgam. Level of corrosion may be minimized by polishing the surface of restoration. Corrosion has one advantage that corrosion products thought to be gathered at the restoration–tooth interface (seal the gap) to prevent or decrease microleakage.

Corrosion products (Ni^{2+}) can lead to toxicity symptoms and allergic reactions, Schiff et al. indicated that the NiTi/CoCr combination might be more susceptible to corrosion in (fluoridated mouthwash) than in (chlorhexidine mouthwash) [21]. Finally, corrosion products consistent with artificial saliva as well as deposits possibly related to the organic component of natural saliva.

CONCLUSIONS

From the data of galvanic corrosion measurements, we can conclude that the metallic contact of amalgam as filling with Ti-6Al-4V alloy give better galvanic corrosion resistance than the coupled of Co-Cr-Mo, Ni-Cr-Mo, and SS 316L with amalgam in the absence and presence of citric acid.

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