

THE EFFECT OF pH ON THE CORROSION OF DENTAL METAL ALLOYS

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ABSTRACT

The aim of this study has been to find out the effects of pH degrees of oral environment on the corrosion of dental metals and alloys which have different composition by electrochemical methods. The surface structure of the first and second casting of dental metals and alloys were examined under the Scanning Electron Microscope. Their composition were investigated by the Energy Dispersive X-Ray Analyser system. The rotary disc electrode was prepared by these materials. The potential changes of these electrodes by time were established in three different pH solutions, and their current-potential curves were obtained by the potentiodynamic method. In addition the changes of corrosion potentials due to time was also determined.

INTRODUCTION

The most important properties of dental alloys are their biocompatibilities, corrosion resistances, mechanical features and ease of workability which are provided by various metals included into the alloy.^{1,2}

Despite considerable uncertainties with respect to the biological effects of amalgam fillings currently used in dental medicine and a lively discussion of their use and risks these materials remain the most popular ones for dental restoration. Although the use of heavy, non-noble metals, including mercury and several other metals of high biological toxicity as constituents of dental fillings is not desirable, the lack of alternative materials and the long successful use of amalgams maintains their popularity.³

The microstructure and chemical composition of alloys has great influence on their corrosion behaviours, which can be examined by chemical and electrochemical test methods.⁴

Darwell has explained the corrosion of dental amalgams, due to concentration cells by electrochemical means which gave importance to corrosion potential researches by in-vitro and in-vivo.¹

These researches showed that; dental alloys must resist, to the natural moisture, to the thermal (0-65°C) and pH changes (pH = 2-11) due to food intake and food decomposition in the oral environment.⁵⁻⁸

The corrosion characteristics of metals and alloys depend on; the composition of the alloy, its potential values, the strain, the surface roughness, the degree of oxidation, the pH and the temperature of the media, the mixing velocity of the solution and the presence of the inhibitors.⁹⁻¹⁴

The corrosion tendencies of metals are related to their electrode potentials, whose positions can be seen from the table of electromotive series (Table 1).¹⁵

Metals such as aluminium and titanium which show negative potential values, turn to a passive state because of their protective passivating oxide film layers that form in moist media. Therefore, by obtaining the current-potential curves of materials in the studied media, it can be found out whether they are at their active or passive positions at their equilibrium potentials. Corrosion tendencies of metals and alloys, is defined by the corrosion rates and can be found by various methods.¹⁶

Recently, the corrosion characteristics of dental alloys were performed in artificial saliva, flour and citric acid solutions.¹⁷

In this study, the corrosion tendencies of dental metal and alloys were investigated by measuring the electrode potentials as a function of time and by calculating the corrosion rates from current-potential curves in inorganic solutions at different pH values, which described the effects of alloying elements on the corrosion of dental metal and alloys.

Corrosion tendencies of dental alloys may cause health hazards, weakening and esthetic loss of dental restorations, therefore in this research the corrosion characteristics of dental metals and alloys were examined at different pH values which contained $\text{SO}_4^{=}$ ions.

EXPERIMENTAL PROCEDURE

The studied 21 alloys which were; 3 precious metals, 5 base metals, the second casting of precious and base metals and 5 metals for control groups. The standard potentials, and the chemical composition of these metal and alloys are given in Table 1 and Table 2.

Table 1. The standard electrode potentials of the alloying elements.

REACTION	ELECTRODE POTENTIALS (SCE) (V)
$\text{Au}^+ + e = \text{Au}$	1.43
$\text{Pt}^{2+} + 2e = \text{Pt}$	0.95
$\text{Pd}^{2+} + 2e = \text{Pd}$	0.58
$\text{Ag}^+ + e = \text{Ag}$	0.55
$\text{Hg}^{2+} + 2e = \text{Hg}$	0.55
$\text{Cu}^{2+} + 2e = \text{Cu}$	0.09
$\text{Mo}^{6+} + 6e = \text{Mo}$	-0.25
$\text{Sn}^{2+} + 2e = \text{Sn}$	-0.39
$\text{Ni}^{2+} + 2e = \text{Ni}$	-0.48
$\text{Co}^{2+} + 2e = \text{Co}$	-0.53
$\text{Fe}^{2+} + 2e = \text{Fe}$	-0.66
$\text{Cr}^{3+} + 3e = \text{Cr}$	-0.81
$\text{Mn}^{2+} + 2e = \text{Mn}$	-1.28
$\text{Ti}^+ + e = \text{Ti}$	-1.88
$\text{Al}^{3+} + 3e = \text{Al}$	-1.92
$\text{Be}^{2+} + 2e = \text{Be}$	-1.95
$\text{Ce}^+ + e = \text{Ce}$	-2.59

Table 2. The chemical composition of test samples.

Sample No	Mass %													
	Au	Ag	Pd	Cu	Sn	Cr	Ni	Si	Mo	Fe	Al	Co	Ti	Hg
1	81			19										
1*	83.6			16.4										
3	34		51.8		14.2									
3	36.4		48.6		15.1									
*		86	17											
4		76.8	23.2											
4*														
5						18.3	80.6	0.34	0.79					
5*						18.5	80.4	0.32	0.84					
6						23.5	65.9	0.25	1.26	9.12				
6*						23.9	65.3	0.21	1.44	9.19				
7						23.9	70.8	0.13	4.6	0.66				
7*						27.8	64.4	0.19	2.54	5.16				
8						21.8	70.7		2.08	5.4				
8*						22	70.6		2.28	5.11				
12						25.7			1.18	0.73		72.4		
12*						62.7		0.52	4.65	1.72		30.4		
13													99.5	
14		88.7		11.3										
15				99.5										
16		16.3		8.86	17.5									57.4
17		17.2		4.24	10.5									68.1

* : refers to the second casting of the same numbered alloy.

The samples were prepared by wax-lost system and induction casting technique due to the directions of the manufacturers. Amalgam samples were obtained by condensation of the amalgam material into teflon moulds. Each sample was designed in the form of cylinders, with 2 mm diameter and 1 cm length (Figure 1). Studied examples were embedded into epoxy resin material using teflon moulds for preparing rotary disc electrodes, the rotation speed of the working electrode was chosen to be 2000 rpm.

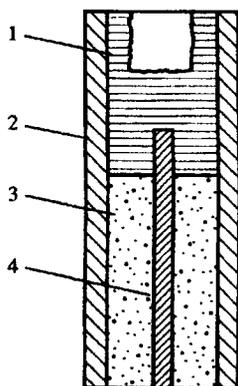


Figure 1. Working electrode: 1-brass; 2-Teflon; 3-epoxy and 4-sample.

Three different corrosive media were prepared for testing the corrosion resistance of dental metal and alloys, which were Na_2SO_4 (pH = 5.6), $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH = 2.4) and $\text{Na}_2\text{SO}_4 + \text{NaOH}$ (pH = 10.8) solutions. The solutions were prepared with double distilled water using Merck grade chemicals. During the tests, platinum plate as a counter electrode and Standart Calomel Electrode (SCE) as a reference electrode were used. All potentials were given against SCE.

Test electrodes were polished with emery paper washed with double distilled water and put into the test cell at the constant temperature (37°), which was open to air. Corrosion potentials were measured after each five minutes during the 30 minutes periods (Table 4). After measuring the potentials, the current-potential curves of the rotary disc electrodes were determined by the potentiodynamic method.

The experiments were carried out with a potentiostat (Wenking 70 HV1, G. Bank Electronic, Göttingen, Germany), a voltage generator (Wenking SMP 69, G. Bank Electronic, Göttingen, Germany), a labograph recorder (Metrohm E 478, Switzerland), a thermostat (Nel Electronic, Ankara Turkey) and with a rotary electrode (Tacussel EDI Solea, Paris, France).

RESULTS

The corrosion potentials measured at the 30 th. minute (E_{cor}), the corrosion rates (i_{cor}) obtained from current-potential curves and the calculated cathodic Tafel slope (β_c) are given for 21 electrodes in Table 3, 5, 6 in Na_2SO_4 (pH = 5.6), $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH = 2.4) and $\text{Na}_2\text{SO}_4 + \text{NaOH}$ (pH = 10.8). These values are the average of the five consecutive measurements.

Table 3. Corrosion characteristics of precious alloys in different media.

Sample No	$\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH=2.4)			Na_2SO_4 (pH=5.6)			$\text{Na}_2\text{SO}_4 + \text{NaOH}$ (pH=10.8)		
	E_{cor} (mV)	i_{cor} ($\mu\text{A}/\text{cm}^2$)	β_c (mV)	E_{cor} (mV)	i_{cor} ($\mu\text{A}/\text{cm}^2$)	β_c (mV)	E_{cor} (mV)	i_{cor} ($\mu\text{A}/\text{cm}^2$)	β_c (mV)
1	+30	1.75	-180	-85	5.2	-254	-37	3	-200
1*	+19	0.9	-225	+19	1.9	-263	+19	1.03	-249
3	+47	6.9	-205	-15	6.4	-179	-31	5.4	-168
3*	+19	3.9	-170	+19	3.3	-170	+19	2.3	-160
4	-135	1.7	-250	-135	1.14	-240	-179	0.53	-200
4*	+175	3.1	-260	+19	2.1	-252	+19	2.2	-250

Corrosion potential of metal and alloys with respect to time are given in Table 4.

The corrosion rates of the dental metal and alloys were obtained by extrapolating the anodic and cathodic Tafel lines of the current-potential curves to the corrosion potential, whereas for the passive metal and alloys only cathodic Tafel lines, have been extrapolated (Figure 2).

Table 5. Corrosion characteristics of the base metal alloys in different media.

Sample No	Na ₂ SO ₄ +H ₂ SO ₄ (pH=2,4)			Na ₂ SO ₄ (pH=5,6)			Na ₂ SO ₄ +NaOH(pH=10,8)		
	E _{cor} (mV)	i _{cor} (μA/cm ²)	β _c (mV)	E _{cor} (mV)	i _{cor} (μA/cm ²)	β _c (mV)	E _{cor} (mV)	i _{cor} (μA/cm ²)	β _c (mV)
5	-170	4,1	-300	-80	1.8	-250	-80	0.92	-240
5*	-220	1.9	-310	-34	1.5	-280	-156	0.42	-250
6	-135	3.5	-280	-157	2.6	-250	-195	0.3	-200
6*	-165	2.5	-240	-122	0.45	-189	-263	0.21	-170
7	-195	3.4	-315	-118	1.1	-220	-132	0.97	-200
7*	-39	1.35	-320	-42	0.64	-305	-248	0.32	-170
8	-75	0.21	-110	-75	0.32	-200	-322	0.4	-210
8*	-69	0.57	-106	-27	0.62	-180	-210	0.72	-200
12	-180	0.52	-230	-112	0.4	-220	-202	0.36	-200
12*	-29	0.54	-280	-47	0.96	-300	-221	0.46	-270

Table 6. Corrosion characteristics of the metal and alloys in the control group in different media.

Sample No	Na ₂ SO ₄ +H ₂ SO ₄ (pH=2,4)			Na ₂ SO ₄ (pH=5,6)			Na ₂ SO ₄ +NaOH(pH=10,8)		
	E _{cor} (mV)	i _{cor} (μA/cm ²)	β _c (mV)	E _{cor} (mV)	i _{cor} (μA/cm ²)	β _c (mV)	E _{cor} (mV)	i _{cor} (μA/cm ²)	β _c (mV)
13	-240	1.3	-200	-130	1.2	-180	-348	0.8	-166
14	-08	7	-270	0	3	-220	+05	2.3	-210
15	-40	3.2	-210	-08	0.9	-180	+26	1.15	-200
16	-43	8.6	-300	-69	5.2	-240	-106	6	-200
17	-115	2.7	-220	-45	3.8	-280	-182	2.25	-200

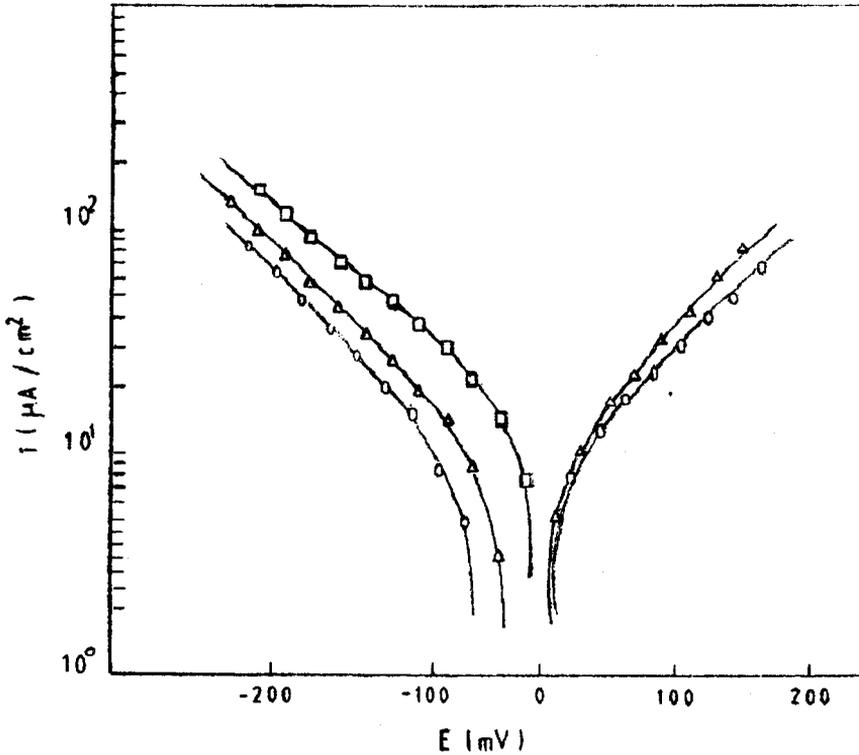


Figure 2. Polarization curves of alloy sample 3 in Na_2SO_4 (Δ), $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (\square) and $\text{Na}_2\text{SO}_4 + \text{NaOH}$ (\circ).

DISCUSSION

The corrosion rates (i_{cor}), corrosion potentials (E_{cor}) and cathodic Tafel slopes (β_c) of the first and second casting (samples such as 1-4 and 1* -4*) of precious alloys in Na_2SO_4 , $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4 + \text{NaOH}$ solutions are shown in Table 3. The dissolution of precious metals containing gold, platinum, silver, copper and tin is dependent on the composition of the working media and recycling times of the metals. It is shown in the potential-pH equilibrium diagrams that the palladium is in metallic form depending on the pH of working solutions. Copper is at the metallic form or dissolves as Cu^{2+} ions at $\text{pH} < 4$ whereas it is passive at $\text{pH} > 4$. On the other hand, tin is in its passive form at $\text{pH} = 2.4$ and

pH = 10.8.¹⁸ It was observed that the dissolution rates of the samples containing gold, platinum and silver were low, but the dissolution rates of the samples containing copper and tin were high.¹⁹⁻²¹ This situation is suitable with the electrode potentials of the alloying elements (Table 1).¹⁵ According to the electrode potentials, gold is the most noble and tin is the least noble. For this reason, sample 1 corroded minimal and sample 3 corroded maximum.¹⁷

The dissolution of gold electrode containing copper increases as the pH increases then gradually decreases as expected from potential-pH equilibrium diagrams (Table 3). This event is most probably related to the passivation of alloys with the increasing pH.

At each pH value, the examples containing gold, palladium and tin are in passive form so that a small difference can be seen at the dissolution rates of alloys. Materials containing silver and palladium are in the metallic form at the potential-pH diagrams, however metallic palladium can be changed to the PdH₂ depending on the studied solutions. Dissolution rate of alloys were increased depending on the percentage of palladium in alloys (samples 4 and 4*).²²

Dissolution rates of precious metals were decreased in the second casting form with the decreasing of active elements in the alloys which are oxidized at the casting process (1*, 3* and 4*). In addition, it can be said that dissolution of the precious metals decreases with the increase of the pH.

Corrosion characteristics of the base metal alloys in the same media are given in table 5. At the studied solutions in some metal alloys which contain chromium, chromium is in passive form in the potential-pH equilibrium diagrams. Nickel is in the passive form at pH = 10.8, but it dissolves as Ni²⁺ ions at pH = 2.4 and 5.6. Molybdenum is also active at pH = 2.4 but it is in passive form in the other studied solutions. It can also be seen from potential-pH diagrams of iron and cobalt that they are active at pH = 2.4 and 5.6, but passive at pH = 10.8.¹⁸

Dissolution rates of the base metal alloys are varied depending on the corrosive media. Increasing percentage of iron is caused by the

changing of the corrosion rates of alloys in each studied media. It can be observed that dissolution rates of the base metal alloys in basic media is a result of the iron's passivation effect. In the same manner; the dissolution of the alloys 7 and 8 is dependent on the nickel, chromium and iron percentages,²² when the percentage of iron was increased with increasing pH.

According to the results of the dental base metal alloys, nickel, chromium and iron dissolve as Ni^{2+} , Cr^{3+} and Fe^{2+} ions in every studied solution. Addition of the molybdenum and cobalt into the alloy increased the resistance of the alloy against the corrosion.²³⁻²⁵

The dissolution rates of the control group metal alloys is dependent on the inclusion, of the working media and alloys. Increasing the percentage of copper and tin in the alloys which are used as alloying elements increased the corrosion rates of the control group metals,¹⁹⁻²¹ because these elements are being either active or passive, but mercury is a noble metal. When we look at the corrosion rates of the examples containing copper, we can see the dissolution depending on the corrosion rates and the pH.

The corrosion characteristics of the metals and alloys in the control group are also given in Table 6.

In this group, active dissolutions are done by copper, silver and tin in acidic media.

Addition of copper, silver and tin made the amalgams active at the process of dissolution^{20,21,26} (Table 6). Titanium is the least dissoluble alloy in the studied solutions.^{22,27} This fact can be explained by the covering of the metal surface with a good passive layer.

CONCLUSION

- Ion dissolution was observed for all studied alloys.
- Titanium alloy dissolves less at each studied pH media. So, it can be used against the corrosion.

- Chromium and nickel alloys show resistance against the corrosion.
- Tin and copper contained in the alloys increase the dissolution of the dental metal alloys.
- Dissolution of the precious metals increase with the increasing percentage of the noble metals in the alloys.
- The dissolution resistance of the second casting alloys against corrosion were increased with the increase of the percentage of the noble metals.
- Silver, copper and iron increased the dissoluability of alloys in acidic solution.
- Addition of the alloying elements cobalt and molybdenum into the alloys made the alloys resistant against the corrosion in all studied solutions.

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