CORROSION OF AMALGAMS IN ORAL CAVITY

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ABSTRACT

This paper is a study of the effect of natural saliva (oral cavity) and a fluoride mouthwash on dental amalgams .Two types electrodes were made the first was of a high copper amalgam while the second was made from a low copper amalgam. They were immersed in two types of electrolytes for twelve hours and the whole galvanic cell was connected to a computer via a potentiosat. Their corrosion currents, corrosion voltage and corrosion resistance was recorded and compared to find which medium that is usually has the most severe effect on the amalgams corrosion.

الخلاصة

تم في هذا البحث دراسة تأثير محلول الفلورايد واللعاب الطبيعي على سبيكة حشوه السن الزئبقية حيث تم صناعة نوعين من الحشوات الزئبقية الأولى عالي النحاس والثاني واطئ النحاس. تم غرسهما في محلولين المذكورين قابلين للتوصيل الكهربائي لفترة اثنا عشر ساعة وتم إيجاد مقاومتهما للتآكل والتيار المقاوم للتآكل وفولتية التآكل مع المقارنة بينهما وإيجاد إي المحلولين له التأثير الاسوء في عملية التآكل للحشو تين الزئبقيتين.

KEYWORDS:

amalgam, dental materials, corrosion of teeth fillings, saliva effect on amalgams

INTRODUCTION:

Amalgams are found in posterior sites in the mouth. Dental amalgams are alloys that contain Mercury (Hg), Tin (Sn) and Silver (Ag) as the main alloy ingredients. An amalgam means any alloy that contains (Hg) as a major element the major products from the mixing of the amalgam elements is formed of Ag-Hg. the other element particles which have not reacted remain embedded inside the matrix and help mechanical reinforcement (Stephen)..

Dental alloy materials undergo both chemical and electrochemical corrosion in addition to mechanical corrosion (i.e. fretting and stress corrosion). The aim of this paper is to study the electrochemical corrosion since it is the most destructive.

Amalgams (multiple phases) are more electronegative than any other metal they may be in contact with. Anodes and cathodes are generated within the amalgam and this makes them susceptible to relative high corrosion rates. These amalgams undergo galvanic corrosion, local corrosion (Ag-Hg *vs.* Ag-Sn-Cu- phase), crevice corrosion and stress corrosion.

During corrosion dental alloys, release elements into the body over the short term (days) and long term (months). This leads to the roughening of the surface and weakening of the restoration. Corrosion can severely limit the fatigue life and ultimate strength of the material leading to mechanical failure of the implant (gilbert).

GALVANIC CORROSION:

This is due to the difference in electrochemical potentials. Galvanic corrosion occurs when dissimilar elements placed in direct contact within the oral cavity, where the saliva of the mouth plays the role of the electrolyte, a flow of electrical charge occurs due to the stimulation of the oral cavity (M.Karthega 2006). The less noble metal forms the anode while the more noble forms the cathode and the circuit is completed by ion transport through the saliva. Table 1 shows the electro potential of the metals, which form the amalgams that were used in this experiment with respect to the standard hydrogen electrode.

Zinc added to the alloy to absorb oxygen (O_2) during casting. The presence of zinc can be both beneficial and devastating. The devastating effect

is that it can react with water and produce zinc oxide (ZnO_2) and hydrogen gas, if it is produced inside the amalgam and contribute to tooth failure. The beneficial effect is that the zinc makes the amalgams mixture more plastic and easy to handle to mold into any shape that is required.

THE EXPERIMENT:

The Amalgam Mixture:

Two electrodes were fabricated from two different types of amalgam mixtures. The 1st was of a low capper amalgam while the 2^{nd} was of a high (Cu) amalgam. Both these types are used internationally in dental clinics, the particulars of the components used in the composition mixture were Lathe-cut and not spherical. The percentages in weight (%wt) of the mixtures for both types of amalgams are shown bellow:

- 1) 69% Ag + 26% Sn + 2% Cu +3% Zn 1st amalgam (Low Cu amalgam)
- 1^{st} amalgam (Low Cu amalgam)
- 2) 69% Ag + 18% Sn + 6% +1% Zn 2^{nd} amalgam (High Cu amalgam)

As seen from above the other components of the amalgam were fixed in both mixtures with the expectance of copper this was done in order to find the effect of the variation of the copper mixture on the rate of corrosion.

These two types of mixtures were mixed with Hg which forms the matrix that binds the components and solidifies them into one mass. When they are added to the (Hg) any excess Hg is squeezed out and the mass plastizes and begin to solidify.

The reaction of these mixtures is shown bellow (Stephen):

$$1^{st}$$
 amalgam :
Ag₃ Sn + Hg \longrightarrow Ag₂ Hg₃ + Sn₇ – Hg
+ Ag₃ Sn (untreated)
(1)

 2^{nd} amalgam: $Ag_3 Sn + Ag Cu (Eutectic) + Hg \longrightarrow$ $Ag_3 Hg_3 + Cu_6 Sn_5 + Ag_3 Sn (untreated)$ + Ag Cu (untreated) (2)

Zinc was originally added to the alloy to absorb (O_2) during manufacturing. The devastating effect is that it can react with water and produce hydrogen gas. If this is produced inside the amalgam, it results in delayed expansion of the amalgam.

The beneficial effect is that Zinc makes the amalgam mixture more plastic and easy to handle.

The Electrolytes:

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The electrolytes used in the experiment were two types:

The 1st electrolyte was natural saliva accumulated in a sucker obtained from a dental clinic. The composition of the saliva was shown in Table2.

The second electrolyte was a mouthwash used for dental hygiene (pH=3.9), which had the composition shown in Table3.

The second type of electrolyte used to find the effect of dental mouthwash on dental amalgams, since most mouthwashes and toothpaste contain fluoride.

The Electrochemical Corrosion Apparatus:

The apparatus used in the experiment consisted of a glass container with three openings at the top. The 1st opening was for a rotating disc electrode, the 2nd for platinum electrode and the 3rd was for a standard calomel electrode (SCE). The electrodes used were maintained at body temperature ± 2 °C to maintain oral conditions. the entire assembly was connected to a computer controlled potentiosat. the electrolyte was circulated inside the container at a speed of 450 rpm,as shown in Fig 1.

Data Collection:

The data collected was from a twelve-hour period. The polarization curves in which the current is a function of electrical potential:

$$I=F(E) \tag{3}$$

were plotted so as to determine the corrosion resistance of the amalgams in the electrolytes. the polarization curves & Stern – Geary relationship were used to find the current density for the corrosion current (I_C) and the polarization resistance R_P (Milton 2007).

$$R_{\rm P} = B/I_{\rm corr} \tag{4}$$

While all laboratory corrosion tests require accelerating corrosion processes, only electrochemical tests can directly amplify the impact corrosion process. this is because all electrode kinetics associated with corrosion process to qualify corrosion rates. The amplification of the electrical signals generated during these tests has permitted very precise and sensitive measurement. For this reason this part was conducted in the UAE since Iraq lacks such devices.

$$B = \frac{ba \cdot bc}{2.3(ba+bc)}$$
(5)

B: Can be calculated form (ba) & (bc) which are the slopes of anodic and cathodic Tafel slopes respectivly.

Corrosion Rate Determination

The rate of corrosion was gained by

- Plotting the obtained data from the current-potential curves that were obtained, and then extrapolating the cathodic and anodic Tafel lines to current potation so as to obtain the slope at that point.
- The Tafel slops of the anodic and cathodic curve can be used in the stern-Geary eg. to determine the corrosion rate.

THE RESULTS:

The corrosion resistance of the two different amalgams that were immersed in the two different electrolytes was measured after 12 hr's and their results are shown in table 4 & 5. Their corrosion curves are given in figures 2 & 3.

Low Copper Amalgams.

In the natural saliva the low copper amalgam started with a very high corrosion resistance but after 3 hr's started to drop and at the end of the 12 hr period it had reached (200) mV/SCE, whereas it went much more severe corrosion relatively when it was immersed in a fluoride mouthwash (fig 3).it did not start with a very good corrosion resistance and dropped even more at the end of the experiment and stabilized at (-350) mV/SCE.

In addition, the polarization resistance was much higher in the natural saliva in accompany to a lower corrosion current (table 5) than it had in the fluoride solution.

High Copper Amalgam.

For the natural saliva, in the first 4 hrs the high copper amalgam had a lower corrosion resistance (Fig 3) but in due time it increased gradually and stabilized at a higher corrosion resistance of (230) mV/SCE, whereas in the fluoride electrolyte its corrosion resistance dropped severely and stabilized at (-350) mV/SCE. It had a much higher corrosion resistance in natural saliva than in the fluoride solution, showing a higher corrosion current (table 5) in the fluoride mouthwash than in the natural saliva.

DISCUSSION

From the obtained results it is obvious that corrosion occurs within an amalgam which make up a tooth filling the corrosion was much more severe in the fluoride mouth wash than in natural saliva. The purpose of the fluoride substance is to kill bacterial growth, yet while it is doing this it corrode any amalgam fillings in the mouth. This will eventually lead to the failure of the alloy due to It being subjected to alternate stresses from chewing food in addition to its corrosion

Early dental amalgams contained less than 5% copper had limited corrosion resistance (Stephen) as it was proven in the experiment. The higher copper amalgam had a much higher corrosion resistance in natural saliva then in the fluoride mouthwash.

In a high copper amalgam the Ag-Sn-Zn irregular particles are mixed with the Ag-Cu to produce the amalgam alloy. Mixed with Mercury (Hg), Ag-Hg and Sn-Hg phases form almost as quickly as Sn-Hg forms, and then the released Hg reacts with more Ag-Sn to produce predominately Ag-Hg. Therefore little or no Sn-Hg resides in the set amalgam.

Of special interest is the actual geometry in the phases involved. The Ag-Hg (γ_1) crystals are relatively equi-axed. Contrary to these grains Sn-Hg (γ_2) crystals are elongated and look like tongue depressor blades. This has a major consequence for corrosion. While the Sn-Hg crystals represent little volume of the mixture they tend to touch

(connected) through the entire dental amalgam allowing penetrating corrosion to take place.

Shifting to high copper amalgam has both the advantage that Cu-Sn is less corrosion prove and the grains do not routinely touch each other so that only superficial corrosion occurs (Stephen).

All amalgams leak mercury into the mouth to some extent. (R.C House 1980).

In addition to Sn-rich corrosion products of high copper amalgams, Cu-rich amalgams also form Cu- containing corrosion product. Two products were identified Cu2O a red product and CuCl₂.3Cu(OH)₂ a green product.

As soon as an amalgam is filled into the moth it starts corroding. This is one reason why amalgam fillings have to be replaced when they became in our mouths we also have the chemical corrosion that can be caused by electrical activity previously discussed. We have both these factors increasing the corrosion of the amalgam, which is process of releasing metal ions into our saliva.

In addition to the weakening of the amalgam strength due to corrosion the mercury into the body have disastrous health effects. Research show that mercury is associated with disorder such as multiple sclerosis, Alzheimer's disease depression and reduced immune functioning Mercury exposure also presents a risk to fetuses in mothers who have amalgam fillings and may cause birth defects.(N.K. Sarkar 2000)

CONCLUSION

- Each and every person who has an amalgam filling has a battery constantly working in his/her mouth releasing metallic toxic ion into the body.
- Both high and low copper amalgam under corrosion, but high copper amalgam has more corrosion resistance.
- While fluoride solution are for oral hygiene. They are more useful to people with healthy teeth. Where as any one who has fillings made from amalgam, the will corrode much faster when using fluoride dental products Fluoride may act bacterial growth on teeth yet it also corrodes amalgam a much faster rate.

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NOMENCLATURE

Ag: Silver Cu: copper H₂: Hydrogen Sn: tin Zn: zinc Hg: mercury O₂: oxygen I_c: corrosion current in mA/cm² R_p: polarization resistance in Kohm.cm² E_{corr}: voltage corrosion in volts b_a:anodic slope b_c:cathodic slope γ : gamma phase

Silver (Ag)	+0.80
Copper(Cu)	+0.52
Hydrogen (H ₂)	0.00
Tin(Sn)	-0.14
Zinc(Zn)	-0.76

Table 1: electro potential of the elements that make up a typical amalgam (Raymon 1973)

Table 2: composition and concentration of elements for natural saliva

Element	Concentration mmol/L
sodium	2-2
potassium	36
calcium	2.8

magnesium	0.5
chloride	40
bicarbonate	25
phosphate	39

Table 3: composition and concentration of mouth wash

Compound	Concentration ppm
Amine Fluoride Dafour	95
Sodium Fluoride	150





Table (4): Corrosion potential (Ecorr) of the specimens in different electrolytes after aperiod of 12 hr`s

Electrolytes	Ecorr (mv/sce)		
Electrolytes	Low Cu Amalgam	High Cu Amalgam	
1. Natural Saliva	200	230	
2.Fluoride Mouthwash	-370	-350	

 Table (5): Corrosion current densities icorr (mA/cm²) and polarization resistance R.p (Kohm.cm²)

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Amalgam Nat	Natural Saliva		Fluoride Mouthwash	
	i _{corr}	Rp	i _{corr}	Rp
1.Low Cu Amalgam	1.36	500	2.8	160
2.High Cu Amalgam	2.2	550	3.0	165

Polarization Cures for Natural Saliva





Time Polurization curve for Flouride Mouth wash



Fig 3