The Effect of Admixed Al on Corrosion Resistance of High Copper Dental Amalgam

تأثير إضافة الألمنيوم على مقاومة التآكل لملغم الأسنان عالي النحاس

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ABSTRACT

The purpose of this study is to investigate the effect of Al additions on corrosion resistance of high copper dental amalgam. Al addition is added in different percentages of (0.5, 1, 1.5, 2, 2.5 wt%). The specimens were prepared according to ADA specification No. 1. The specimens have been stored at 37 ± 1 C° using glass chamber prepared for this purpose. The corrosion test has been carried out according to ASTM standard (G5 − 87) and at37 ± 1 C°. Aluminum addition with mentioned percentages led to form weak passive layer, there is no improvement in corrosion resistance was found. Vickers hardness has been measured after one month from the end of trituration, and it found that the highest hardness value was of the highest aluminum content amalgam.

الخلاصة

تهدف هذه الدراسة إلى معرفة تأثير إضافة عنصر الألمنيوم على مقاومة التآكل في ملاغم الأسنان عالية النحاس. أضيف عنصر الألمنيوم بنسب مختلفة (0.5, 1, 1.5, 2, 2.5 wt%). حضرت العينات حسب المواصفة رقم ١ للجمعية الأمريكية للأسنان (ADA). تم حفظ العينات في درجة حرارة C° 37 ± 1 في حجرة زجاجية معدة لهذا الغرض. اختبار التآكل اجري حسب المعيار ASTM (G5 − 87) و عند درجة حرارة C° 37 ± 1 . إضافة الألمنيوم بالنسب المشار إليها أدت إلى تكوين طبقة خامدة ضعيفة، ولم يكن هناك تحسين في مقاومة التآكل. قيست صلادة فيكرز بعد مرور شهر من نهاية السحن، ووجد إن أعلى قيمة للصلادة هي للملغم الحاوي على أعلى محتوى من الألمنيوم.

Key Words: dental amalgam, corrosion resistance, high copper, addmixed Al.

ITRODUCTION

   Alloys used in dentistry as restorative materials, like any metal, have a tendency to corrode electrochemically. The nature of dental amalgam to undergo a corrosion process that can lead to ultimate failure of the restoration particularly is important from a clinical standpoint. This failure usually manifests itself as either a bulk fracture of the restoration or as a progressive breakdown of the amalgam along the marginal angles. The resultant " marginal ditch" provides   a nidus for the accumulation of microorganisms that renders the tooth – restoration interface subject to recurrent caries[Holand *et. al.*, 1974]. Oral environment is very susceptible to corrosion products formation. Mouth is always moist and is continually subjected to fluctuation in temperature. Food and liquids ingested have wide ranges of pH. Acids are released during the breakdown of foodstuffs. All of these environmental factors contribute to the degrading process known as corrosion. Corrosion in the specific sense is not merely a surface deposit but is an actual deterioration of a metal by reaction with its environment. It causes severe and catastrophic disintegration of the metal body. This disintegration of the metal may occur through the act of moisture, atmosphere, acids, alkalies or certain chemicals [Anusavice, 1996].

   The possible danger from the internal source of corrosion products, dental amalgam fillings, has been mostly overlooked, this problem is devoted special attention. Through a proof of amalgam

biocompatibility has been presented, amalgam is still by far the most extensively used material for dental restoration [Pleva, 1989].

Tarnish is a surface discoloration on a piece of metal. In oral cavity, tarnish often occurs from the formation of hard and soft deposits on the surface of restoration. The soft deposits are plaques and films composed mainly of microorganisms and mucin. Surface discoloration may also arise on a metal from the formation of thin films, such as oxides, or sulfides. Tarnish is an indication of corrosion [Fathi, 1989].

Sarkar [Sarkar *et. al.* ,1988] studied the improvement of corrosion resistance by Zn addition, and Mahler [Mahler *et. al.* ,1990] studied the effect of Pd on the clinical performance of amalgam.

The purpose of this study is to investigate the effect of admixed Al on corrosion resistance of high copper dental amalgam.

EXPERIMENTAL PROCEDURE

Powder Alloy Preparation
Ardent amalgam powder alloy made in Sweden which purchased from the market is the master powder alloy used, which is high copper non – gamma 2 alloy, the shape of this powder is a mixture of irregular (atomized) and lathe cut particles. Aluminum powder of 99.99% purity and with 75 µm size was added to powder alloy in different percentages (0.5, 1, 1.5, 2, 2.5 wt%). The chemical composition of the specimens used are shown in **Table (1)**.

Specimens Preparation
The specimens were made by trituration of equal weight of powder alloy and mercury(50:50) by amalgamator type (YDM-Pro) for 35 seconds. The specimens were prepared according to American Dental Association (A.D.A.) specification No.1 for dental amalgam [A.D.A., 1975]; their dimensions were 4mm in diameter and 8mm in height using steel mould. The specimens have been stored at 37 ± 1 C$^\circ$ in glass chamber prepared for this purpose.

Corrosion Test
Potentiostatic polarization was used as the technique for evaluating corrosion resistance for all amalgam alloys tested. Computerized potentiostate (type DY2323 Bi-Potentiostat, USA) was used for conducting the polarization test. The corrosion resistance of the amalgams specimens was studied in synthetic saliva, whose composition is shown in **Table (2)** [Marek, 1990], the pH solution was 6.7 at 37 C$^\circ$ temperature. The specimens were tested after 1 month form the end of trituration. The surface area of the tested specimens is 1cm^2 , the upper and lower surface of the cylinder specimens have been covered with epoxy.

The corrosion test cell used in this study was made according to ASTM standard (G5 – 87) [ASTM, 1988]. The corrosion cell is a beaker of (250)ml capacity with water jacket, the reference electrode is Standard Calomel Electrode (SCE), and Auxiliary Electrode (AUX.E.) is platinum electrode, a lugging capillary was kept in such a way that the working electrode (specimen) and its tip remain at a distance of about 1mm in between to avoid ohmic drop. The corrosion test was carried out at 37 ± 1 C$^\circ$ to stimulate the human body temperature by means of water jacket, which controlled by thermostatic water path.

When the specimen reaches the constant potential, potentiostatic polarization was started from an initial potential of 250 mV below the open circuit potential and the scan was continued up to 250 mV above the open circuit potential[ASTM, 1988], the scan potential may be more than this range when needed. The specimens were scanned in the positive direction at a sweep rate of 1 mV/ Sec and the current was reported to potential by computer. Corrosion rate measurement is obtained by using equation (1) [Fontana *et. al.,* 1978].

$$\text{Corrosion Rate (mpy)} = \frac{0.13 i_{coor}(E.W.)}{A.\rho} \qquad (1)$$

where:

E.W. = equivalent weight (gm/eq.).

A = area (cm^2).

ρ = density (gm/cm^2).

0.13 = metric and time conversion factor.

i_{corr} = current density ($\mu A/cm^2$).

Microstructure Observation

The microstructure of amalgam E has been observed and studied using optical microscope. Wet grinded using different grades of emery papers (220, 800, 1000, 1200), then polished with cloth using alumina liquid of 5μm particle size. The specimens etched with the nitric acid in concentrations of 30% by volume[ASM, 1973].

Vickers Hardness test

Vickers hardness of the specimens has been measured using hardness test devise type (Digital Display Microhardness Tester Hvs-1000) at one month after the end of trituration, the applied load is 0.2 Kg for 10 seconds. Vickers hardness value obtained directly from the devise.

RESULT AND DISCUTION

Polarization curve of master amalgam (M) are shown in **Fig. (1)**. From this figure, it can be obtain the corrosion parameters of this amalgam (E_{corr}, I_{corr}, and corrosion rate), which are -103 mV, 0.4938 μA and 0.254 mpy respectively. The cathodic polarization behavior are normal where the current density decrease with increasing potential and with active anodic polarization, where the current density increase with increasing potential which mean amalgam dissolution after the corrosion potential has passed until reach approximately constant value of current density indicating to barrier film formation, which is similar to obtained by many researchers [Mahler *et.al.* 1982, Fathi *et.al.*, 2004, Mareci *et. al.*, 2005].

Fig. (2) shows polarization curve of amalgam (A) (0.5 % Al). In cathodic polarization, the current density decrease with increasing potential until potential reach -415 mV at which current density drop to 0.9918 μA value, then return current density to normal value with increasing potential, this is due to passive layer formation and breaks down immediately. In anodic polarization, which its behavior is active, after the corrosion potential has passed the decreasing current density to (0.2288 and 0.3051 μA) at (-404 and -401 mV) potential respectively indicating to layer formation and breaks, then current increase with increasing potential because of the dissolution amalgam until reach critical value then it remains approximately constant due to barrier film formation. The obtained paramete (E_{corr}, I_{corr}, and corrosion rate) of all tested amalgams are listed in **Table (3)**.

Fig. (3) illustrates polarization curve of amalgam (B) (1% Al). In cathodic polarization, the current density drops several times with increasing potential, until current density reaches zero value at potential of 187, 183 and 182 mV befor reaching corrosion potential, this is due to passive layer formation and breaks down, where give an indication of layer formed weakness, which aluminium is one of its components. The behavior of anodic polarization is similar to that of amalgam M and A.

Fig. (4) shows polarization curve of amalgam (C) (1.5 % Al). In cathodic polarization, the current density decrease with increasing potential until potential reach zero value at E_{corr} potential, while when anodic polarization, which its behavior is active, the current density increase with potential due to the dissolution of amalgam, until reach critical value then it remains approximately constant due to barrier film formation.

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Fig. (5) shows polarization curve of amalgam (D) (2 % Al). In cathodic polarization, the current density drops several times with potential increasing due to passive layer formation and breaks. In anodic polarization, after the corrosion potential has passed, current density drops several times to (2.3651, 1.9836 and 1.4496 μA) at potential of (-612, -607 and -599 mV) respectively, which indicate to layer formation and break down. With potential increasing, it can be seen increasing of current density as a result of amalgam dissolution, until reach critical value due to barrier film formation.

Fig. (6) illustrates polarization curve of amalgam (E) (2.5% Al). In cathodic polarization, the current density decrease with increasing potential where the current density dropped to zero value four times, before reaching to corrosion potential E_{corr}, at potential of (-477, -432, -390, -378 and -372 mV) due to passive layer formation and breaks down several times because of presence of aluminum addition. The anodic polarization shows formation and break down of weak layer with increasing potential. The last part of anodic behavior indicates that current density is relatively constant due to formation of barrier film.

Table (3) shows corrosion potential (E_{corr}) , corrosion current density (I_{corr}) and corrosion rate for all tested amalgam, the corrosion potential of master amalgam is more noble than other amalgams which contain Al, corrosion current density of the master amalgam is the lowest value, and as a result the corrosion rate of the master amalgam is the lowest value, which can be attributable to low concentration of aluminum addition to form strong passive layer and the presence of aluminum phases will courage galvanic corrosion in amalgam and lead to increase current density then corrosion rate as indicated by other researchers [Dingfei *et. al, 2011*, Al Sarraj *et.al., 2011*].

Fig. (8) shows the microstructure of E amalgam, where γ_1 phase (Ag_2Hg_3) is the matrix of the amalgam (white regions), the black regions are the η phase (Cu_6Sn_5) and the unreacted particles dark gray regions which consist of γ phase (Ag3Sn) and ε phase (Cu3Sn), which indicated by other researchers [A.J. McDermott *etal*, 1998].

Vickers hardness of all tested amalgam have been shown in **Table (3).** It can be seen from the table that the hardness increases with increasing titanium content, where the lowest hardness value was of master amalgam (A) which is titanium free, and the highest hardness value was of (E) amalgam which contains highest percentage of aluminum (2.5 wt%).

CONCLUSION

The conclusion drawn from the present work are as follows:-
1- Aluminum powder addition to amalgam powder alloy result in layer formation when corrosion test conducted in synthetic saliva.
2- When aluminum powder concentration increase the layer formation will increase too.
3- The addition of Al with concentration of up to 2.5 wt % led to weak passive layer formation.
4- The corrosion rate will increase duo to presence of multi phases especially aluminum phases where courage galvanic corrosion in amalgam.
5- Vickers hardness increases with increasing aluminum content.

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Table (1) The chemical composition of the used alloys.

Alloys	Ag wt%	Sn wt%	Cu wt%	Al wt%
M	44.5	30	25.5	0
A	44.27	29.85	25.38	0.5
B	44.04	29.7	25.26	1
C	43.82	29.53	25.15	1.5
D	43.59	29.38	25.03	2
E	43.36	29.23	24.91	2.5

Table (2) Chemical composition of synthetic saliva.[6]

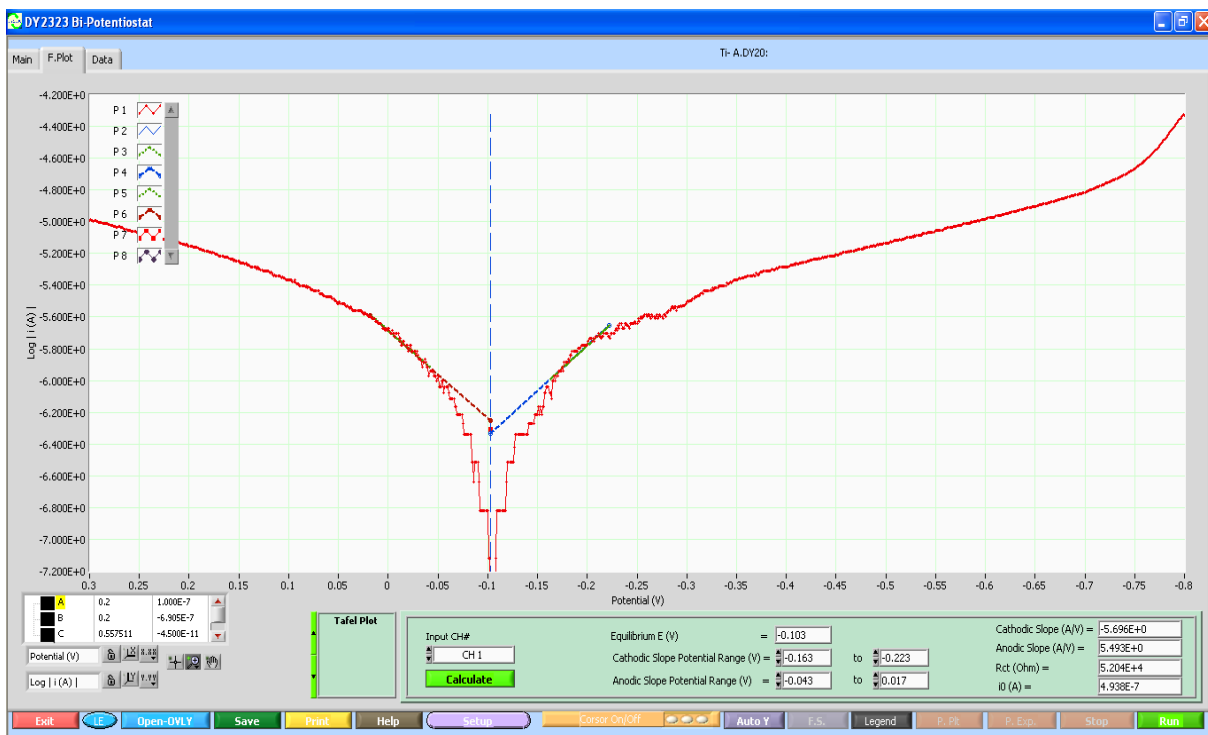| No.	Constituent	gm/l
1	KCl	1.5
2	$NaHCO_3$	1.5
3	$NaH_2PO_4.H_2O$	0.5
4	KSCN	0.5
5	Lactic acid	0.9

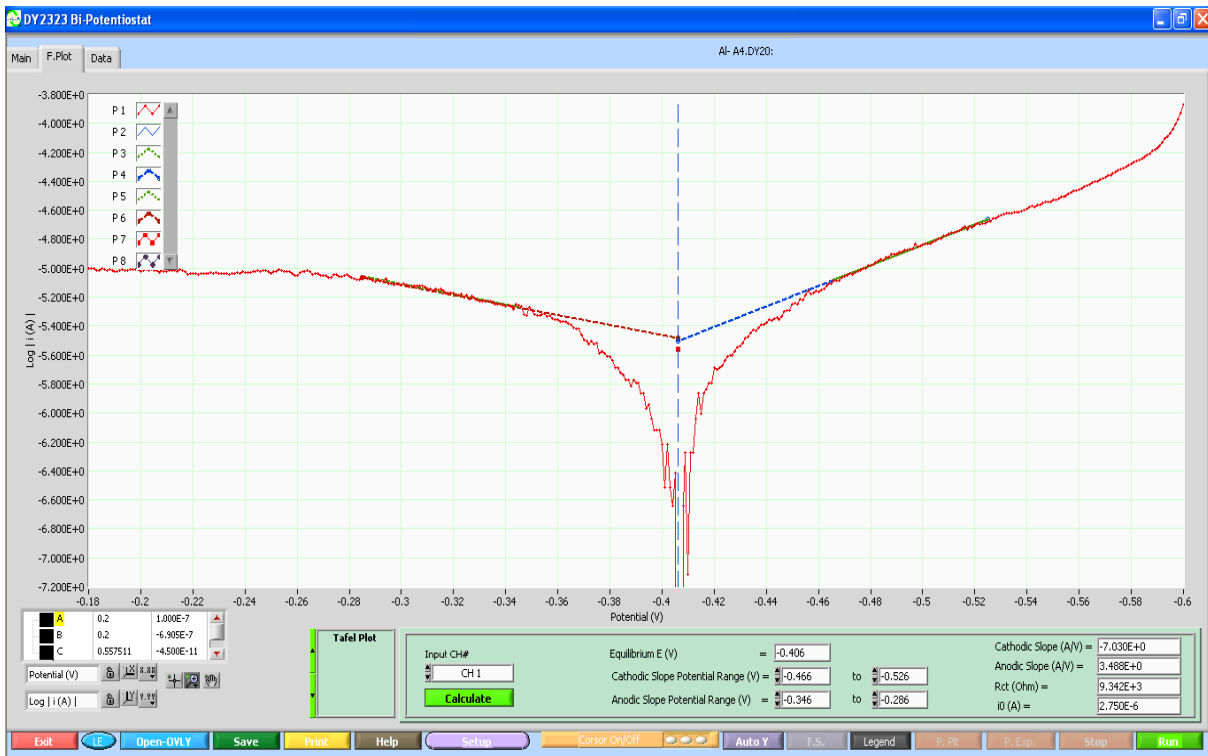**Fig. (1)** polarization curve of master amalgam M (master alloy) in synthetic saliva at 37±1 C°.

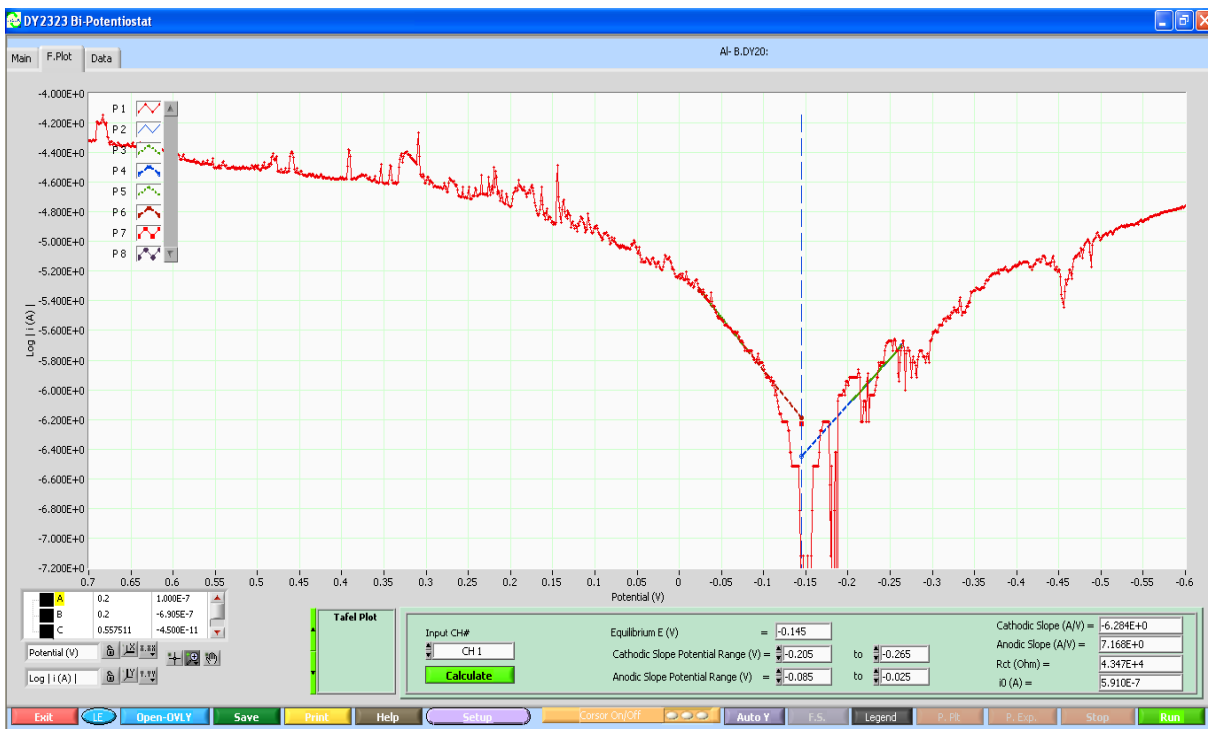**Fig. (2)** polarization curve of amalgam A in synthetic saliva at 37±1 Cº.

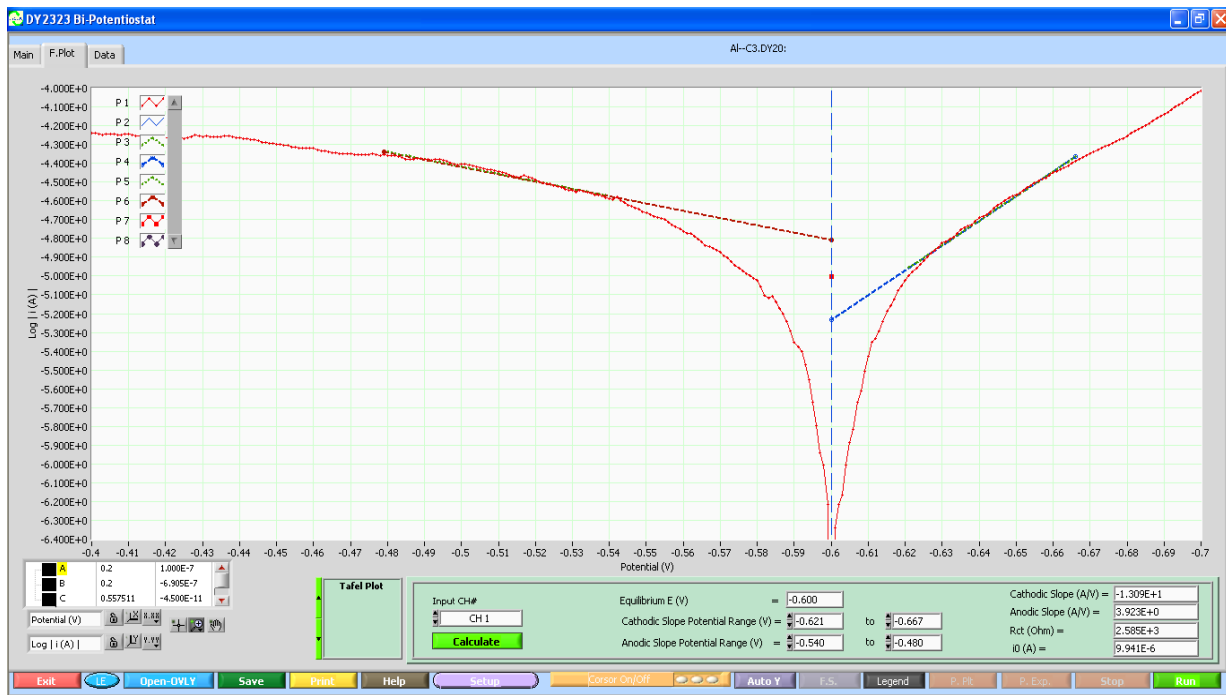**Fig. (3)** polarization curve of amalgam B in synthetic saliva at 37±1 Cº.

Fig. (4) polarization curve of amalgam C in synthetic saliva at 37±1 Cº.

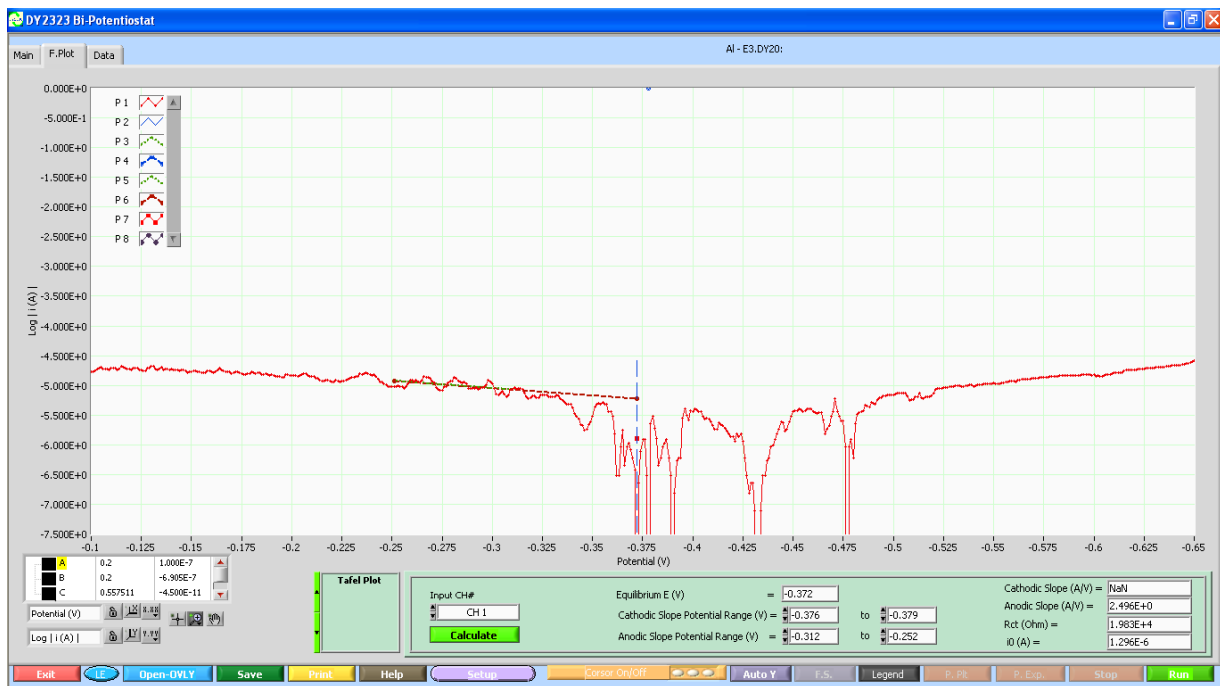**Fig. (5)** polarization curve of amalgam D in synthetic saliva at 37±1 Cº.

Fig. (6) polarization curve of amalgam E in synthetic saliva at 37±1 Cº.

Table (3) The corrosion potential (E_{corr}) , corrosion current density (I_{corr}) and corrosion rate of the amalgams.

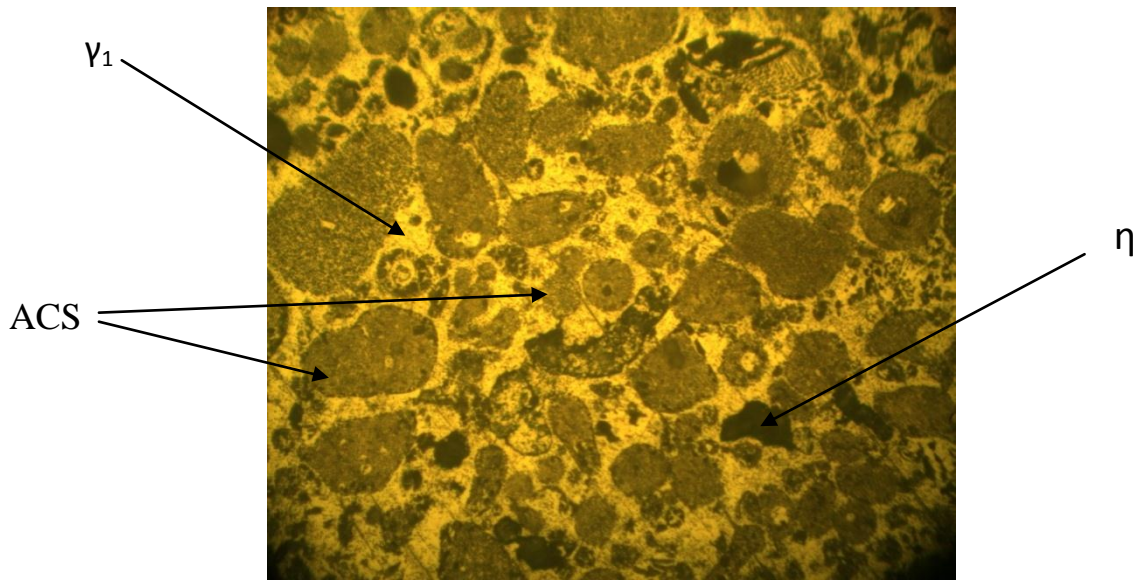| Amalgam	E_{corr} (mV)	i_{corr} (µA/cm^2)	Corrosion Rate (mpy)	Hardness Hv (Kg/mm^2)
M (master)	-103	0.4115	0.254	193
A	-406	2.8947	2.256	195
B	-145	0.5472	0.377	203
C	-600	9.3783	6.6	214
D	-621	12.1047	8.138	221
E	-372	1.628	1.428	247

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Fig. (7) The microstructure of (E) amalgam. ACS = Ag – Cu – Sn unreacted particles.(150 X)