

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

تأثير إضافة التيتانيوم على مقاومة التآكل لملمع الأسنان عالي النحاس

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Abstract

The purpose of this study is to investigate the effect of Ti additions on corrosion resistance of high copper dental amalgam. Ti addition is added in different percentages of (0.1, 0.2, 0.3, 1, 2, 3 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 at 37 ± 1 C°. Titanium addition with mentioned percentages led to shifting the corrosion potential to positive direction, corrosion rate improvement (91%) at (3% Ti), and passive layer formation increases with increasing titanium content. Vickers hardness has been measured after six months from the end of trituration, and it found that the highest hardness value was of the highest titanium content amalgam.

الخلاصة

تهدف هذه الدراسة إلى معرفة تأثير إضافة عنصر التيتانيوم على مقاومة التآكل في ملاغم الأسنان عالية النحاس. أضيف عنصر التيتانيوم بنسب مختلفة (0.1, 0.2, 0.3, 1, 2, 3 wt%). حضرت العينات حسب المواصفة رقم 1 للجمعية الأمريكية للأسنان (ADA). تم حفظ العينات في درجة حرارة 37 ± 1 C° في حجرة زجاجية معدة لهذا الغرض. اجري اختبار التآكل حسب المعيار ASTM (G5 – 87) و عند درجة حرارة 37 ± 1 C°. إضافة التيتانيوم بالنسب المشار إليها أدت إلى نقل جهد التآكل إلى الاتجاه الموجب، تحسين مقاومة التآكل بنسبة (91%) عند إضافة (3% Ti) وتكوين طبقة خمودية حيث تزداد مع زيادة محتوى التيتانيوم. قيس صلادة فيكرز بعد مرور ستة أشهر من نهاية السحن، ووجد إن أعلى قيمة للصلادة هي للملمع الحاوي على أعلى محتوى من التيتانيوم.

Key words: dental amalgam, corrosion resistance, high copper, admixed Ti.

Introduction

Dental amalgam is a metallic alloy formed by the reaction of mercury with a powder alloy containing silver (40 – 70%), tin (15 – 30%) and copper (10 – 30%), and sometimes also a small percentage of zinc. 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].

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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].

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

Experimental Procedure

1 -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. Titanium powder of 99.99% purity and with 75 μm size was added to powder alloy in different percentages (0.1, 0.2, 0.3, 1, 2, 3 wt%). The chemical composition of the specimens used are shown in Table (1).

2 -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 [ADA, 1974 – 1975]; their dimensions were 4mm in diameter and 8mm in height using steel mould. The specimens have been stored at $37\pm 1\text{ C}^\circ$ in glass chamber prepared for this purpose.

3 -Corrosion test

Potentiostatic polarization was used as the technique for evaluating corrosion resistance for all amalgam alloys tested. Computerized potentiostat (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° 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 $37\pm 1\text{ C}^\circ$ 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 the following equation [Fontana, 1978].

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

where:

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

A = area (cm²).

ρ = density (gm/cm³).

0.13 = metric and time conversion factor.

i_{corr} = current density (μA/cm²).

4- Vickers Hardness test

Vickers hardness of the specimens has been measured using hardness test device type (Digital Display Microhardness Tester Hvs-1000) at 6 months after the end of trituration, the applied load is 0.2 Kg for 10 seconds. Vickers hardness value obtained directly from the device.

5- Microstructure Observation

The microstructure of amalgam G 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]

Result and Discussion

Polarization curve of master amalgam (A) are shown in Figure (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. In cathodic polarization, 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 *etal*, 1982, Fathi *etal*, 2004, Mareci *etal*, 2005].

Figure (2) shows polarization curve of amalgam (B) (0.1 % Ti). In cathodic polarization, the current density decrease with increasing potential until potential reach corrosion potential which shifted to positive direction (-64 mV), where E_{corr} in amalgam A was -103 mV. In anodic polarization, which its behavior is active, after the corrosion potential has passed the current density increase with increasing potential indicating to amalgam dissolution until reach critical value then it remain approximately constant due to barrier film formation. The obtained parameters (E_{corr}, I_{corr}, and corrosion rate) of all tested amalgams are listed in Table (3).

Figure (3) illustrates polarization curve of amalgam (C) (0.2% T). In cathodic polarization, the current density decrease with increasing potential, current density drops several times with increasing potential to values of (0.22888 and 0.1529 μA) at potential of (-113, -107 and -92 mV), where at -113 and -107 mV current density reach 0.22888 μA, as a result of passive layer formation which break down immediately with increasing potential, where give an indication of layer formed weakness, that titanium is one of its components. The corrosion potential is shifted to positive direction (-83 mV) due to titanium addition. The behavior of anodic polarization is active, in the first part current density increases excessively with increasing potential, and in final part current density increases with increasing potential until reach relatively constant value due to barrier film formation.

Figure (4, 5 and 6) show polarization curve of amalgam (D, E and F) (0.3, 1, 2 % Ti) respectively. It can be seen from these polarizations, increasing of passive layer formation in both anodic and cathodic polarization. The presence of Ti reduces corrosion potential compared with A amalgam as indicated in Table (3).

Figure (7) illustrates polarization curve of amalgam (G) (3 % Ti). In cathodic polarization, the current density decrease with increasing potential where the current density dropped to zero value three times, before reaching the corrosion potential E_{corr} , at potential of (-145, -117 and -104 mV) due to passive layer formation and breaks down several times because of presence of titanium. 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. Titanium addition makes the amalgam more noble than master amalgam A. 2% Ti addition (amalgam F) produce improvement (1%) in corrosion current density of the master amalgam, and 3% Ti addition (amalgam G) produce important improvement (91%) in corrosion current density of the master amalgam, and as a result improvement in corrosion rate of the master amalgam, which is attributable to the concentration of titanium addition to form strong passive layer. The presence of titanium with percentages less than 3% will courage galvanic corrosion in amalgams due to presence of titanium phases and lead to increase current density then corrosion rate as indicated by other researchers [Dingfei *etal*, 2011, Al sarraji *etal*, 2011]. Corrosion potential was shifted to positive direction due to titanium presence which makes titanium containing amalgams more noble than master amalgam.

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 (G) amalgam which contains highest percentage of titanium (3 wt%).

The microstructure of G amalgam illustrated in figure (8), that is similar to microstructure of other studied amalgams. The matrix of the amalgam is γ_1 phase (white regions), the black regions are the η phase (Cu_6Sn_5) and the unreacted particles dark gray regions which consist of γ phase (Ag_3Sn) and ϵ phase (Cu_3Sn), which indicated by other researchers [A.J. McDermott *etal*, 1998].

Conclusion

The conclusion drawn from the present work are as follows:-

- 1- Titanium powder addition to amalgam powder alloy result in layer formation when corrosion test conducted in synthetic saliva.
- 2- When titanium powder concentration increase the layer formation will increase too.
- 3- The corrosion rate will increase (up to 1% Ti) due to presence of multi phases especially titanium phases which courage galvanic corrosion in amalgam.
- 4- Titanium addition with concentration of (2 and 3 wt%) produce corrosion rate improvement (1 and 91%) respectively.
- 5- Titanium addition shifted corrosion potential to positive direction for all amalgams, which means increasing the nobility of titanium containing amalgams with respect to master amalgam.
- 6- Vickers hardness increases with increasing titanium content.

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

Alloys	Ag wt%	Sn wt%	Cu wt%	Ti wt%
A	44.5	30	25.5	0
B	44.45	29.97	25.48	0.1
C	44.41	29.94	25.45	0.2
D	44.36	29.91	25.43	0.3
E	44.05	29.6	25.26	1
F	43.61	29.4	24.99	2
G	43.165	29.1	24.735	3

Table (2) Chemical composition of synthetic saliva.

No.	Constituent	gm/l
1	KCl	1.5
2	NaHCO ₃	1.5
3	NaH ₂ PO ₄ .H ₂ O	0.5
4	KSCN	0.5
5	Lactic acid	0.9

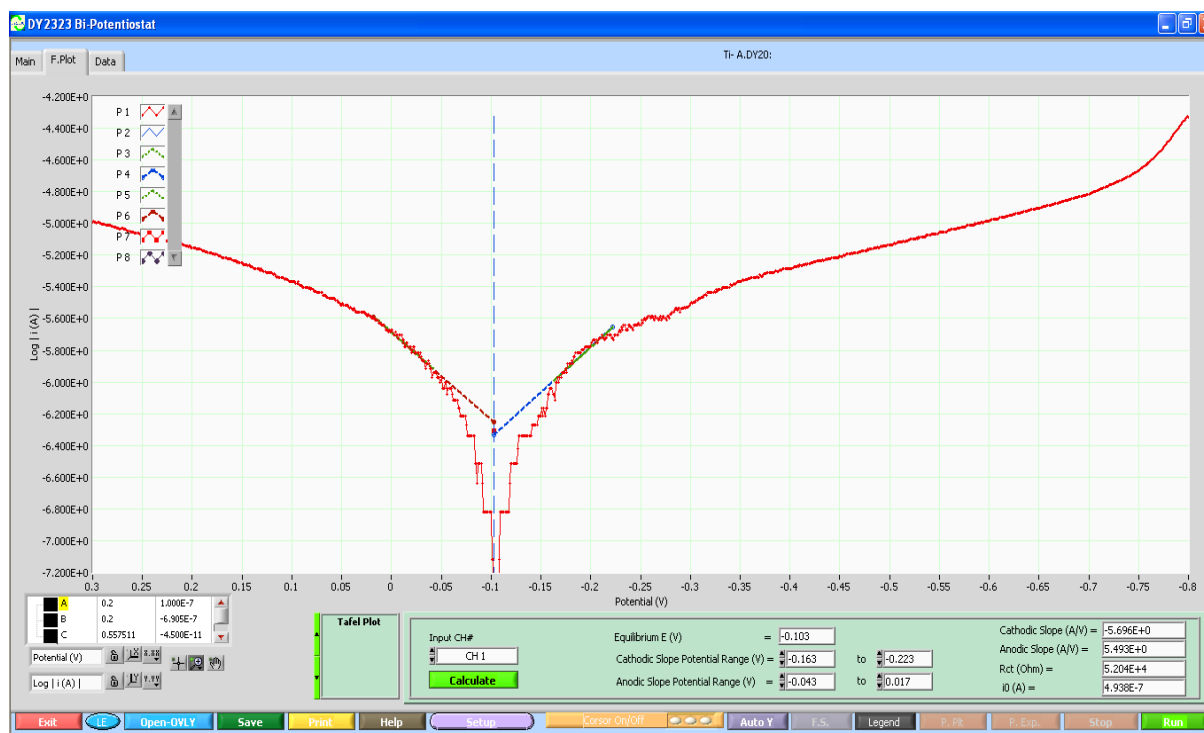


Figure (1) polarization curve of master amalgam A (master alloy) in synthetic saliva at 37 ± 1 C°.

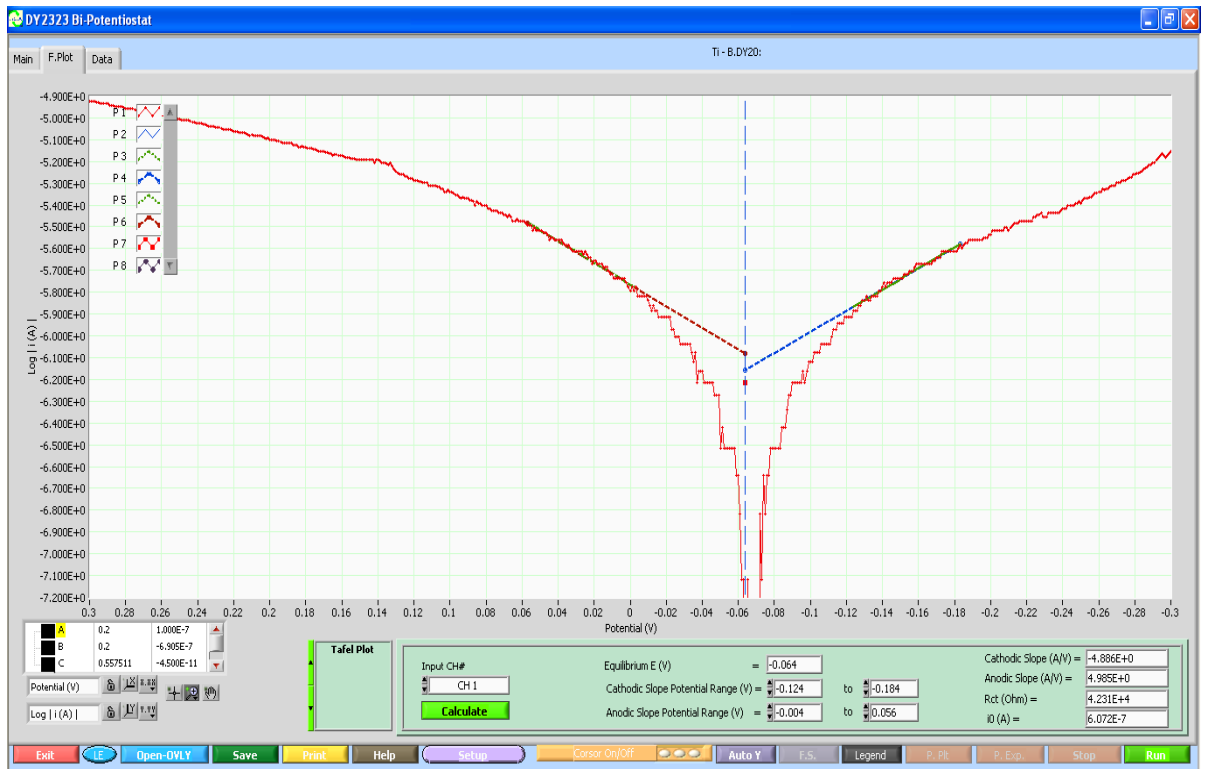


Figure (2) polarization curve of amalgam B in synthetic saliva at 37 ± 1 C°.



Figure (3) polarization curve of amalgam C in synthetic saliva at 37 ± 1 C°.

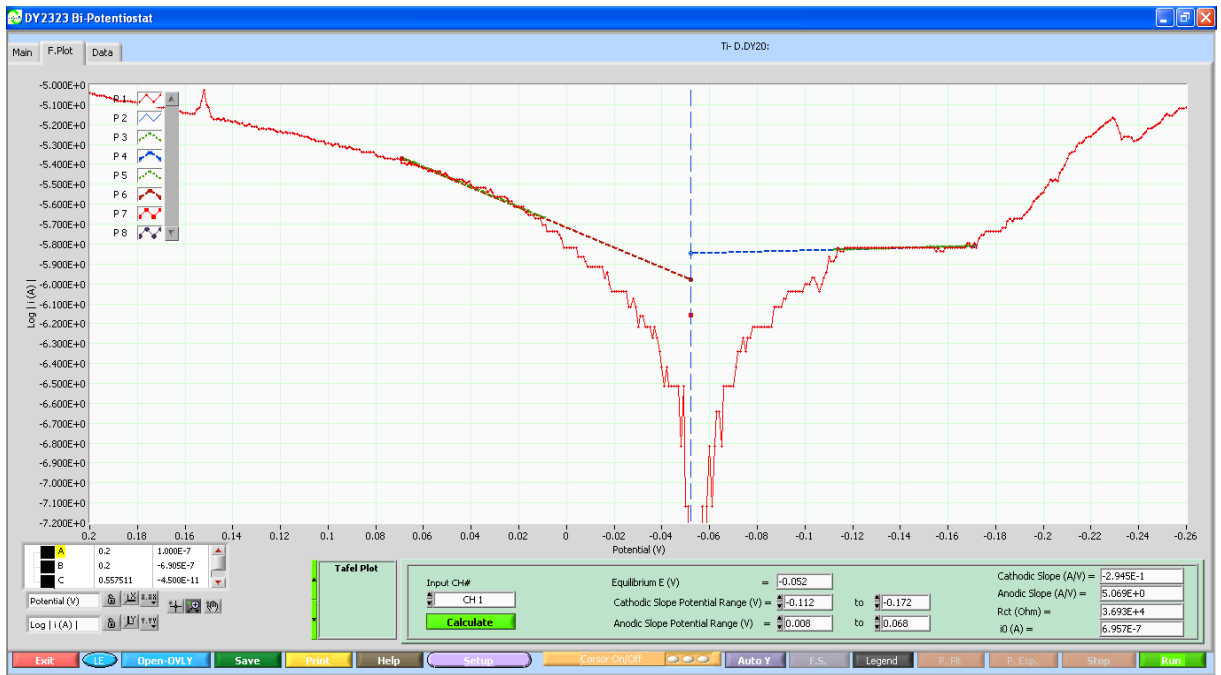


Figure (4) polarization curve of amalgam D in synthetic saliva at $37\pm 1\text{ }^{\circ}\text{C}$.

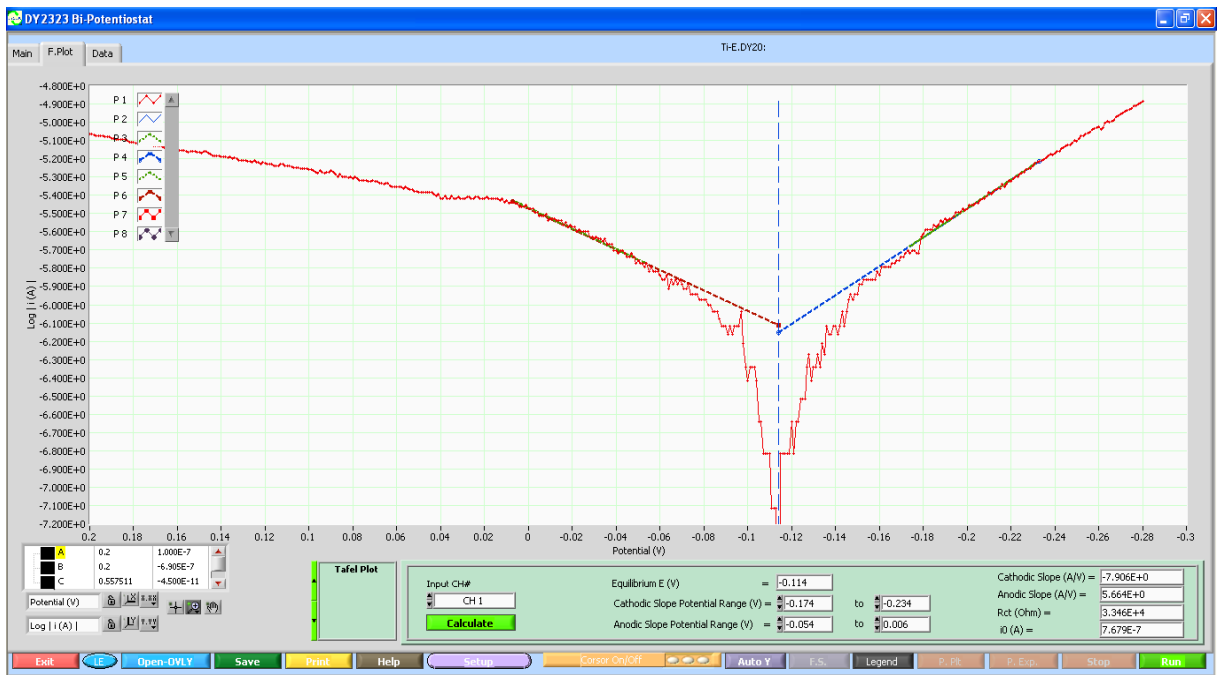


Figure (5) polarization curve of amalgam E in synthetic saliva at $37\pm 1\text{ }^{\circ}\text{C}$.

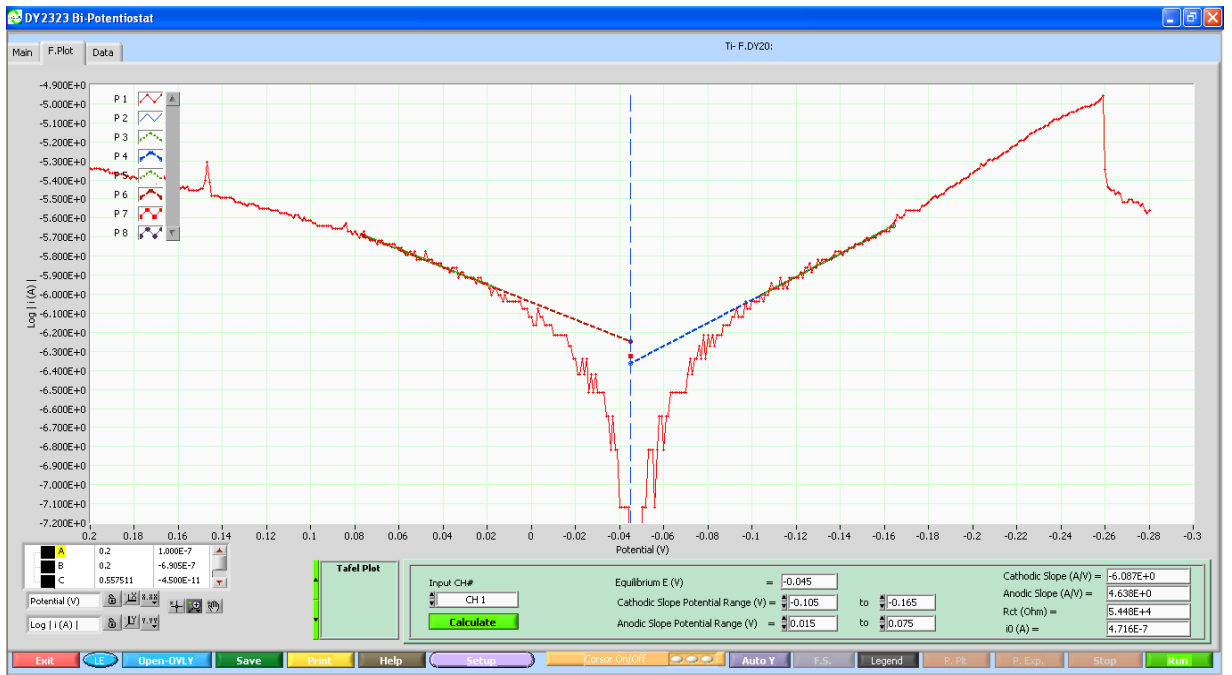


Figure (6) polarization curve of amalgam F in synthetic saliva at 37 ± 1 C°.

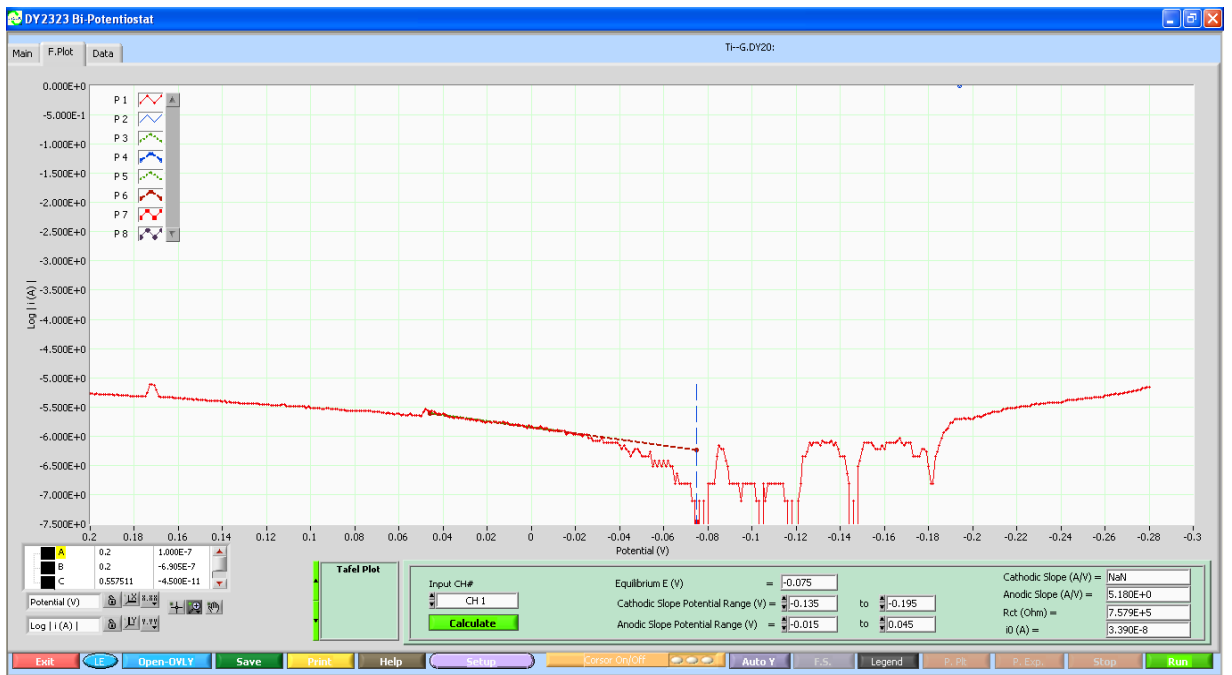


Figure (7) polarization curve of amalgam G in synthetic saliva at 37 ± 1 C°.

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

Amalgam	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion Rate (mpy)	Improvement percentage %	Hardness Hv (Kg/mm^2)
A (master)	-103	0.4115	0.254	0	193
B	-64	0.6072	0.3	0	195
C	-83	1.296	0.64	0	198
D	-52	0.6957	0.522	0	229
E	-114	0.7679	0.513	0	251
F	-45	0.4716	0.251	1	263
G	-75	0.0339	0.022	91	290

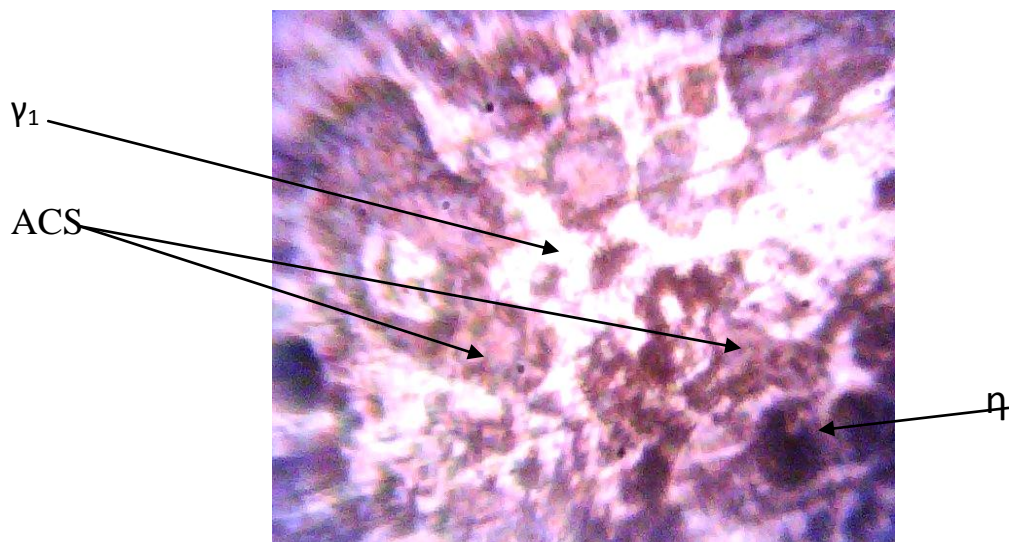


Figure (8) The microstructure of (G) amalgam. ACS = Ag – Cu – Sn unreacted particles. (X 150)