Study of Gallium Based Restorative Alloy

دراسة سبيكة ترميم ذات أساس كاليوم

Dr. Haydar Hassan Jaber*

Abstract

The purpose of this research is to study the properties of gallium based restorative alloy in vitro and compare with that of high copper dental amalgam . X-ray diffraction analysis and microstructure observation has been performed on gallium restorative alloy to determine and observe the existing phases. The specimens were prepared according to ADA specification No. 1. The specimens have been stored at 37±1 Cº using glass chamber prepared for this purpose. The corrosion test has been carried out according to ASTM standard (G5 – 87) and at 37±1 Cº. Compressive strength, diametral tensile strength, creep, dimensional change and vickers hardness were measured. The value of compressive strength, diametral tensile strength, creep and hardness are considerable, similar to that of amalgam. Corrosion test shows that the gallium restorative alloy less noble than amalgam. Dimensional change of gallium restorative alloy is greater than the allowable A.D.A. limit.

الخلاصة

يهدف هذا البحث إلى دراسة خواص سبائك الترميم ذات أساس كاليوم في المختبر ومقارنتها مع ملغم الأسنان عالي النحاس. أجري تحليل حيود الأشعة السينية وفحص البنية المجهرية على سبائك ترميم ذات أساس الكاليوم لمعرفة وتحديد الأطوار الموجودة. حضرت العينات حسب المواصفة رقم (1) للجمعية الأمريكية للأسنان. حفظت العينات عند درجة حرارة 37±1 Cº باستخدام حجرة زجاجية معدة لهذا الغرض. أنجز اختبار التآكل حسب معيار ASTM (G5 – 87) و عند درجة حرارة 37±1 Cº. قيست كل من مقاومة الانضغاط ومقاومة الشد القطري و الزحف والتغير بالأبعاد والصلادة. كانت قيم كل من مقاومة الانضغاط ومقاومة الشد القطري و الزحف والصلادة كبيرة, مشابهة إلى قيم الملغم. بين اختبار التآكل بأن سبائك الترميم ذات أساس كاليوم هي أقل نبلا من الملغم. كانت قيم التغير بالأبعاد اكبر من الحد المسموح به من قبل الجمعية الأمريكية للأسنان.

Key words: gallium alloy, corrosion resistance, gallium restorative.

Introduction

The search for alternative direct-filling materials to replace silver amalgam, is intensifying. Despite assurances of relative safety, there is continuing controversy over the use of a restorative material containing mercury, and concern about the discharge of amalgam waste. A metallic alternative containing gallium, instead of mercury, was suggested as early as 1928 in Germany, and has been under development since 1956 [McComb, 1998]. The first gallium alloy (in 1956) for dental purposes alloyed liquid gallium with powders of Ta, Cr, Mo, In, Co, Ni, Au and some Cu –Sn alloys. Waterstrat formulated Ga –Pd –Sn alloys and found their strength and setting expansion to be acceptable [Dunne *et al* , 2005].

Two types of Gallium containing alloys became available for clinical use, those containing palladium at 9% (Gallium Alloy GF, Tokurike Honten, Japan) or 2% Gallium GFII and palladium-free alloys namely Galloy (Southern Dental Industries, Bayswater, Australia). Many studies have been performed to evaluate and develop gallium restorative alloys[Horasawa *et al*, 1999, Shaini,*et al*, 2001, Hero, *et al*, 1997, Dunne ,*et al*,2000].Unfortunately, studies with the 9% palladium alloy indicated poor clinical performance with marked discolouration, surface roughness and marginal breakdown. The performance of the reformulated Gallium GFII in laboratory studies was superior, exhibiting fewer defects associated with corrosion, but the setting expansion was much greater than that exhibited by silver amalgam.

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The purpose of the present work is to study the properties of gallium based restorative alloy (designed and prepared by the researcher) in vitro and compare with that of high copper dental amalgam.

Experimental Procedure

1.Preparation of Alloy and its powder

The main elements high purity (99.9 wt%) silver and (99.99 wt%) copper melted using electric furnace and poured into steel mould, the chemical composition of the alloy is shown in Table (1). The obtained ingot heat treated by homogenization at 400 ºC for 4 hours [ASM, 1991] for homogenous and uniform distribution of the ingot elements and phases. The cast transformed to chips by lath cut then ball milled and sieved by 200µm sieve, the resulting powder is annealed at 100 ºC for three hours, to make the condensation easier[ASM, 1998], this alloy, after trituration with liquid gallium alloy, will be designated as (GaSn). Megalloy-EZ, which is high copper dental amalgam made in USA, purchased from the market was used for comparison, its chemical composition illustrated in Table (1).

2 - Specimens preparation

The specimens were made by trituration of equal weight of powder alloy and liquid metal (50:50) by amalgamator type (YDM-Pro) for 35 seconds. The composition and melting point of liquid metal are shown in Table (1).The specimens of creep, compression, diametral tensile, hardness and dimensional tests 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, and dimension of corrosion test specimens were 8mm in diameter and 5 mm in height. The specimens have been stored at 37±1 Cº in glass chamber prepared for this purpose.

3- Microstructure Characterization

- X-Ray Diffraction Analysis

X-ray diffraction analysis has been performed on gallium alloy to determine the existing phases. The X-ray diffraction device used is (XRD-6000,SHIMADZO Japan) supplied with single wave length Cu – Kα – 1.54 Aº, with nickel filter. The range of the diffraction angle was (20º – 90º).

- Microstructure Observation

Optical microscope was used to observe and study the microstructure of silver – copper (powder alloy) and gallium alloys with magnification power of (X 150). Wet grinded using different grades of emery papers (180, 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, 2004].

4 -Corrosion test

Potentiostatic polarization was used as the technique for evaluating corrosion resistance for amalgam and GaSn restorative alloy tested. Computerized potentiostate (Wenking M Lab, Germay) was used for accomplishing the polarization test. The corrosion resistance of the amalgam and GaSn specimens was studied in synthetic saliva, whose composition is shown in Table (2) [Marek, 1990], the pH solution was 6.7 at 37 Cº temperature. The specimens were tested after 1 month form the end of trituration. The upper and side surfaces 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 Cº 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 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 *et al*, 1978].

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

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 ($\mu A/cm^2$).

5- Compressive Strength

Compressive strength was measured by universal testing machine type (WDW-200). The test carried out according to(A.D.A.) specification No.1 for dental amalgam [A.D.A, 1975]. The diameter of the specimens was measured with micrometer (its accuracy is 1 µm) before the test. Specimens have been tested at one week from the end of trituration. The specimen loading speed was for 0.5 mm/min. The compressive strength is calculated by using the following equation [ASM, 1992]:-

$$\text{Compressive strength } (N/mm^2) = \frac{Max.force(N)}{cross\,sectional.area(mm^2)} \quad \text{----------(2)}$$

6- Diametral Tensile Strength

Tensile strength was measured by using the universal testing machine using the diametral tensile test. The test carried out according to(A.D.A.) specification No.1 for dental amalgam [A.D.A, 1975]. The specimen was placed in its lateral side between the flat jaws of the machine. The length and the diameter of the specimens have been measured with the mentioned micrometer , the specimens were padded with two thicknesses of 0.038mm aluminum foil on each side. The specimens were tested at one week from the end of trituration using a loading speed of 0.5 mm/min. Tensile strength is calculated by using the following equation [A.D.A, 1975]:-

$$\sigma_t = \frac{2P}{\pi DL} \quad \text{----------(3)}$$

where

P = load at fracture (N).

D = diameter of specimen (mm).

L = length of the specimen (mm).

σ_t = tensile strength MPa.

7- Creep

Creep test accomplished according to A.D.A. specification No. 1 [A.D.A, 1975] at 37± 1 Cº, where allows the maximum of 3% creep. Two hours and 45 minutes after

the end of trituration, the length of the specimen measured with a micrometer caliper. At three hours after the end of trituration the specimen was subjected to a constant axial pressure of 10 MN/m^2. This load was maintained for 21 hours after which the specimen length was measured with mentioned micrometer. Creep percent is calculated by using the following equation [A.D.A, 1975]:-

$$\text{Creep \%} = \frac{L_\circ - L}{L_\circ} \times 100 \qquad \text{----------(4)}$$

where
$L_\circ$ = original length (mm).
L = final length (mm).

8- Dimensional Change

Dimensional change accomplished according to A.D.A. specification No.1 [A.D.A, 1975] at 37± 1 Cº. The initial measurement was taken 30 minutes after the end of trituration. The final measurement was taken at the end of 24 hours. During this test, the temperature of the specimens was maintained at 37± 1 Cº. The dimensional change must be within range of ± 20 µm/cm.

9- Vickers Hardness test

Vickers hardness of the specimens has been measured using hardness test devise type (Digital Display Microhardness Tester HVs-1000) at one week 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 Discussion

Figure (1) shows the diffractogram of GaSn restorative alloy, it can be seen eight different phases in this alloy ($Ag_{0.72}Ga_{0.28}$, $CuGa_2$, Cu_9Ga_4, Cu_3Ga, Cu_6Sn_5, Cu_3Sn, Ag, Cu), the maximum intensity peak was for $Ag_{0.72}Ga_{0.28}$ phase of orientation (300) has 2θ of 40.189º with intensity of 100%, which was the matrix. $CuGa_2$ phase has the intensity peak with orientation(102) has 2θ of 44.576° with intensity of 100%. $Ag_{0.72}Ga_{0.28}$ and $CuGa_2$ have been found in different orientation as shown in Table(3). Cu_9Ga_4, Cu_3Ga, Cu_6Sn_5 and Cu_3Sn phases were detected in different orientations with low intensities, therefore, its amounts thought to be small. Ag and Cu are the unreacted phases detected in low intensity peaks with different orientations, therefore, its existence in the GaSn alloy was thought to be in small amounts. Table (3) indicate the following parameters (2θº, d-spacing, phases, and miller indices (hkl)) of the all the detected phases.

Figure (2) illustrates the microstructure of (Ag – Cu) alloy which consists of two regions. The matrix of the structure as white region eutectic (Ag, Cu) and dark denderitic structure of copper is clearly observed resulting from constitutional supercooling as indicated by equilibrium phase diagram of (Ag – Cu) system[ASM , 1992].

Figure (3) illustrates the microstructure of GaSn restorative alloy, it consists of light gray regions which is the matrix of $Ag_{0.72}Ga_{0.28}$ phase (the highest intensity peak), dark gray regions of (CuGa) phases, black regions of (CuSn) phases and unreacted particles consists of silver and copper surrounded by (AgGa) and (CuGa) phases, these phases are confirmed by X – ray diffraction analysis in Table (3).

Polarization curve of Megalloy-EZ amalgam is shown in Figure (4). From this figure, it can be obtain the corrosion parameters of this amalgam (E_{corr}, I_{corr}, and corrosion rate), which are -252mV, 0.27µA/cm^2 and 3.706 mpy respectively. In cathodic polarization, the current density decrease with increasing potential until

reach value of -338mV where the current remain at constant small value of 0.505 µA due to passive layer formation until potential reach -335 mV value where passive layer breakdown, 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 approved by many researchers [Dingfei *et al*,2011, Al Sarraj *et al*,2011].

Figure (5) shows polarization curve of GaSn restorative alloy. The corrosion parameters of this alloy (E_{corr}, I_{corr}, and corrosion rate), which are -354mV, 13.61µA/cm^2 and 57.468 mpy respectively. In cathodic polarization, the current density decrease with increasing potential until current density increase with increasing potential which mean GaSn dissolution after the corrosion potential has passed, which means active anodic polarization.

Table (4) shows corrosion potential (E_{corr}) , corrosion current density (I_{corr}) and corrosion rate (C.R.) for tested alloys (Megalloy-EZ amalgam and GaSn). It can be obtained from Figs. (4 and 5) and Table (4) that the Megalloy-EZ amalgam is more noble than GaSn restorative alloy, where (E_{corr}) for GaSn is more negative than that of the amalgam , and GaSn corrode rapidly than the amalgam where (I_{corr}) and (C.R.) for GaSn are greater than that of the amalgam which confirm by many other researchers [Hero *et al*, 1997, Dunne *et al*, 2005, Chitambar, 2010].

Table (5) illustrates the compressive strength, diametral tensile strength, creep, dimensional change and hardness of Megalloy-EZ and GaSn.

Compressive strength after one week for both Megalloy-EZ amalgam and GaSn restorative alloy are (268 and 263 N/mm^2) respectively, which means the compressive strength of GaSn approximately equal to that of Megalloy-EZ amalgam, where previous works reported that gallium restorative alloys have high strength similar to amalgam[Miller *et al*, 1999, Shaini *et al*, 200].

Diametral tensile strength after one week for both Megalloy-EZ amalgam and GaSn restorative alloy are (22.73 and 21.5 N/mm^2) respectively, which is agree with the result of many researchers [Miller *et al*, 1999, Shaini *et al*, 200].

Creep test for both specimens have been carried out at 37± 1 Cº. The creep percentage are (0.2 and 0.3 %) for Megalloy-EZ amalgam and GaSn restorative alloy respectively. The allowable creep percentage by ADA is 3% [A.D.A, 1975]. GaSn restorative alloy has considerable creep resistance similar to that of amalgam which indicted by Miller *et al* and Shaini *et al* [Miller *et al*, 1999, Shaini *et al*, 200].

From compressive strength, diametral tensile strength and creep tests can be obtain that the GaSn phases have mechanical properties similar to that of amalgam phases (γ, γ_1 and Cu_6Sn_5).

Dimensional change of Megalloy-EZ amalgam and GaSn restorative alloy are (+ 14 and + 94 µm/cm) respectively. According to A.D.A. specification No. 1, the dimensional change must be within range of ± 20 µm/cm [A.D.A, 1975]. The dimensional change of Megalloy-EZ amalgam is within A.D.A. limit, and that of GaSn restorative alloy is out of A.D.A. limit, where GaSn restorative alloy will expand excessively and cause tooth pain, as reported by D. McComb [McComb, 1998].

Vickers hardness of Megalloy-EZ amalgam and GaSn restorative alloy are (158 and 143 Kg/mm^2) respectively. The hardness of GaSn restorative alloy are high enough to withstand force applied by chewing.

Conclusion

From this work, it can be concluded the following:-

1- GaSn restorative alloy has the following phases ($Ag_{0.72}Ga_{0.28}$, $CuGa_2$, Cu_9Ga_4, Cu_3Ga, Cu_6Sn_5, Cu_3Sn, Ag, Cu).
2- The matrix phase in GaSn restorative alloy is $Ag_{0.72}Ga_{0.28}$.
3- GaSn restorative alloy has poor corrosion resistance compared to Megalloy-EZ amalgam.
4- GaSn restorative alloy has high compressive strength.
5- GaSn restorative alloy has high diametral tensile strength.
6- GaSn restorative alloy has high creep resistance.
7- Dimensional change of GaSn restorative alloy is greater than A.D.A. allowable limit.
8- GaSn restorative alloy has high hardness.

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

Name of alloy	**Composition of powder (wt%)**			**Composition and melting point of Liquid Metal (wt%)**			
Alloys	**Ag**	**Sn**	**Cu**	**Ga**	**Sn**	**Hg**	**melting point C°**
Megalloy-EZ	**56.7**	**28.6**	**14.7**	**-**	**-**	**100**	**-38.87**
GaSn	**65**	**-**	**35**	**86.5**	**13.5**	**-**	**20.5**

Table (2) Chemical composition of synthetic saliva. [Marek, 1990],

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

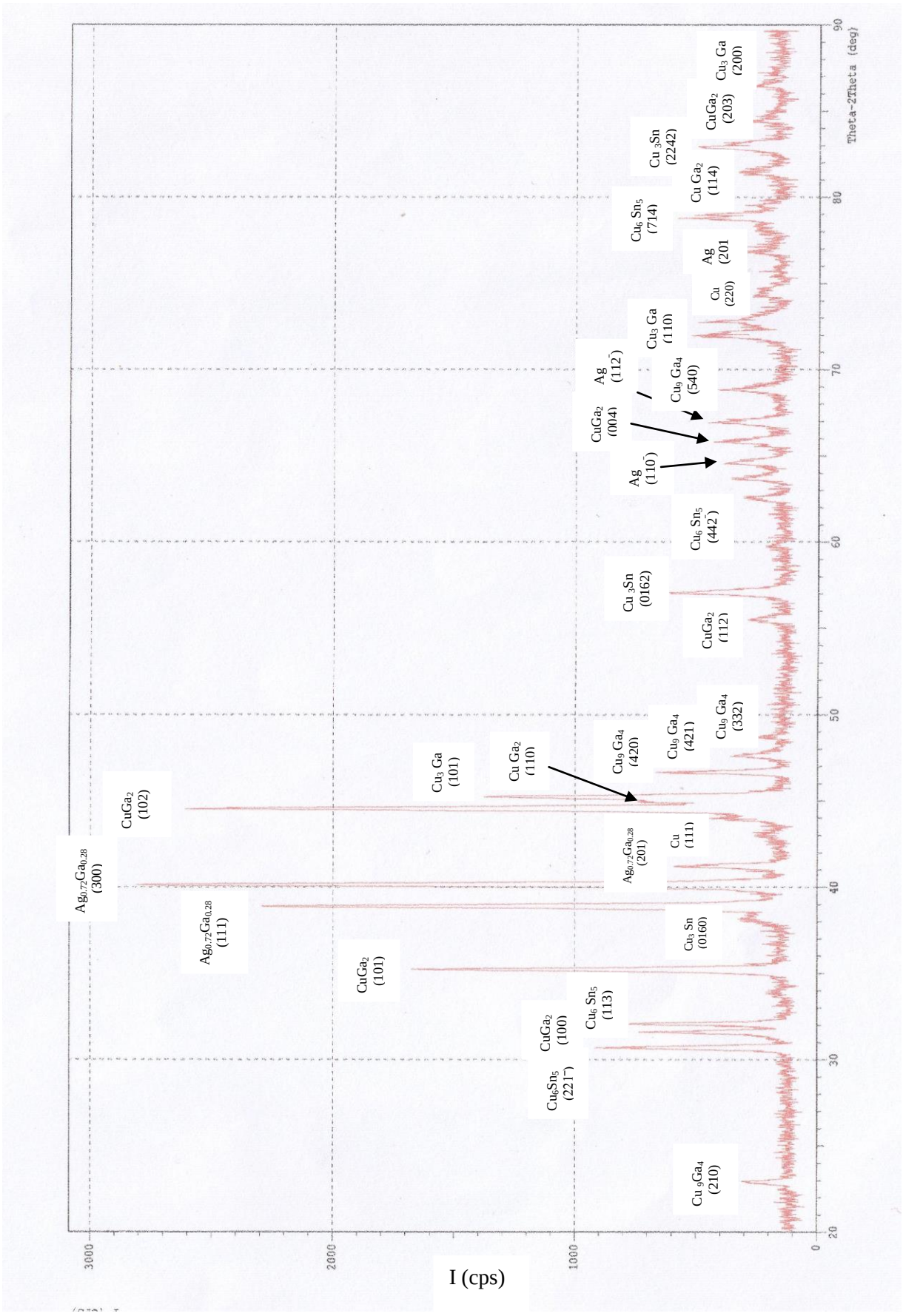

Figure (1) Diffractogram of GaSn restorative alloy

Table (3) shows (2θº), d-spacing, phases, and (hkl) of GaSn restorative alloy.

2θ°	**d-spacing A°**	**Phase**	**hkl**	**2θ°**	**d-spacing A°**	**Phase**	**hkl**
40.189	2.242	$Ag_{0.72}Ga_{0.28}$	(300)	45.545	1.99	Cu_3 Ga	(101)
38.922	2.312	$Ag_{0.72}Ga_{0.28}$	(111)	72.673	1.3	Cu_3 Ga	(110)
41.245	2.187	$Ag_{0.72}Ga_{0.28}$	(201)	86.519	1.124	Cu_3 Ga	(200)
44.576	2.031	$CuGa_2$	(102)	43.297	2.088	Cu	(111)
35.235	2.545	$CuGa_2$	(101)	74.130	1.278	Cu	(220)
31.6	2.829	$CuGa_2$	(100)	64.526	1.443	Ag	(110)
55.658	1.65	$CuGa_2$	(112)	67.526	1.386	Ag	(112)
63.684	1.46	$CuGa_2$	(004)	76.807	1.24	Ag	(201)
45.305	2	$CuGa_2$	(110)	22.723	3.91	Cu_9Ga_4	(210)
81.587	1.179	$Cu\ Ga_2$	(114)	46.534	1.95	$Cu_9\ Ga_4$	(420)
84.648	1.144	$CuGa_2$	(203)	47.568	1.91	$Cu_9\ Ga_4$	(421)
30.092	2.9672	Cu_6Sn_5	(221^{-})	48.929	1.86	$Cu_9\ Ga_4$	(332)
32.378	2.7627	$Cu_6\ Sn_5$	(113)	68.997	1.36	$Cu_9\ Ga_4$	(540)
62.636	1.4819	$Cu_6\ Sn_5$	(442^{-})	57.557	1.6	Cu_3Sn	(0162)
78.999	1.211	$Cu_6\ Sn_5$	(714)	83.217	1.16	Cu_3Sn	(2242)
				57.557	2.38	Cu_3Sn	(0160)

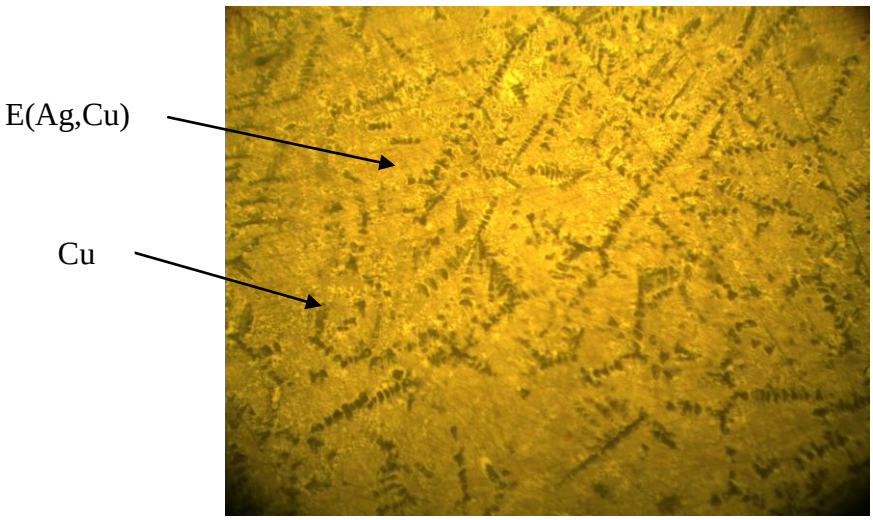

Figure (2) The microstructure of (Ag – Cu) alloy. (X 150)

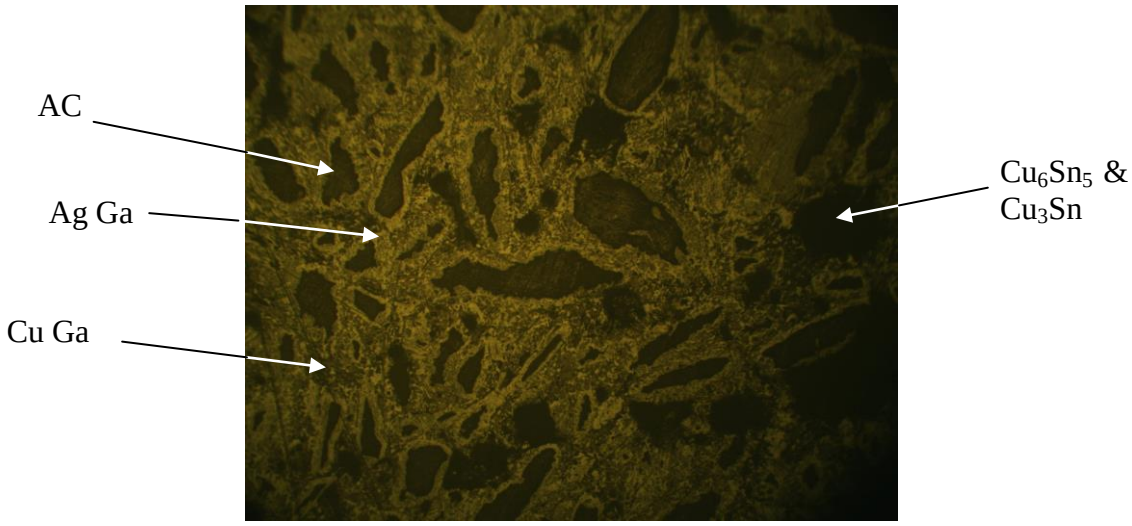

Figure (3) The microstructure of GaSn restorative alloy. (X 150)
AC = Ag – Cu unreacted particles.

Table (4) The corrosion potential (E_{corr}) , corrosion current density (I_{corr}), corrosion rate of the amalgam and GaSn .

Alloy	**E_{corr} (mV)**	**I_{corr} (µA/cm^2)**	**Corrosion Rate (mpy)**
Megalloy-EZ	-252	0.27	3.706
GaSn	-354	13.61	57.468

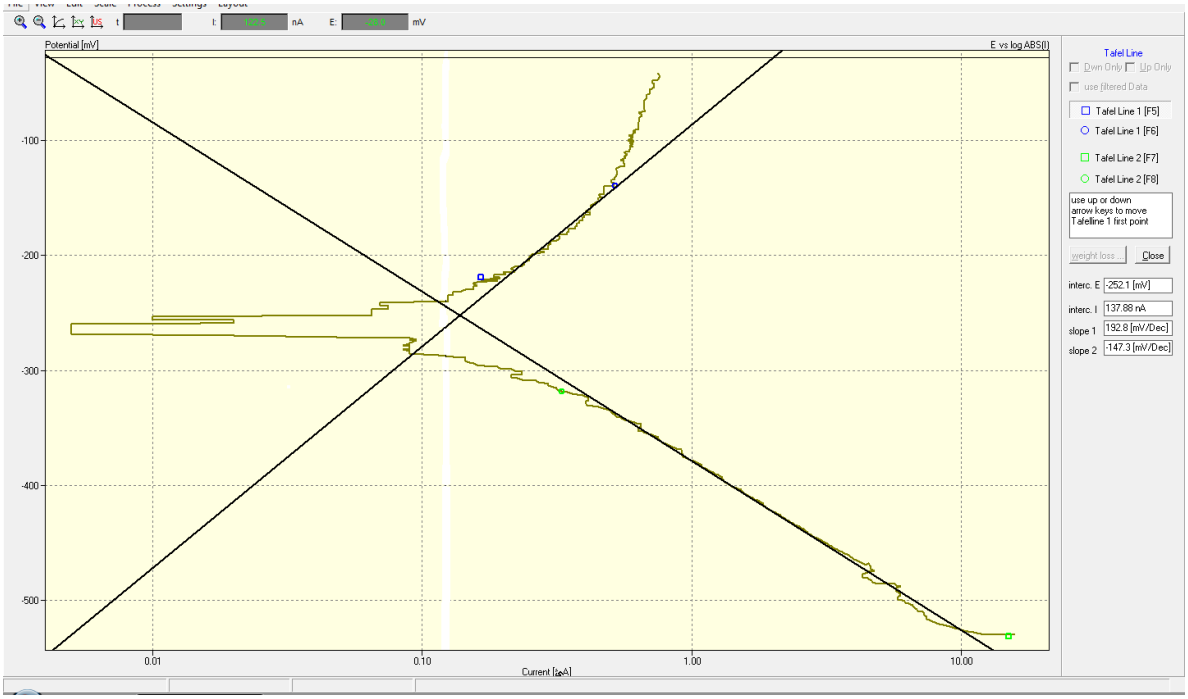

Figure (4) polarization curve of Megalloy-EZ amalgam in synthetic saliva at 37±1 Cº.

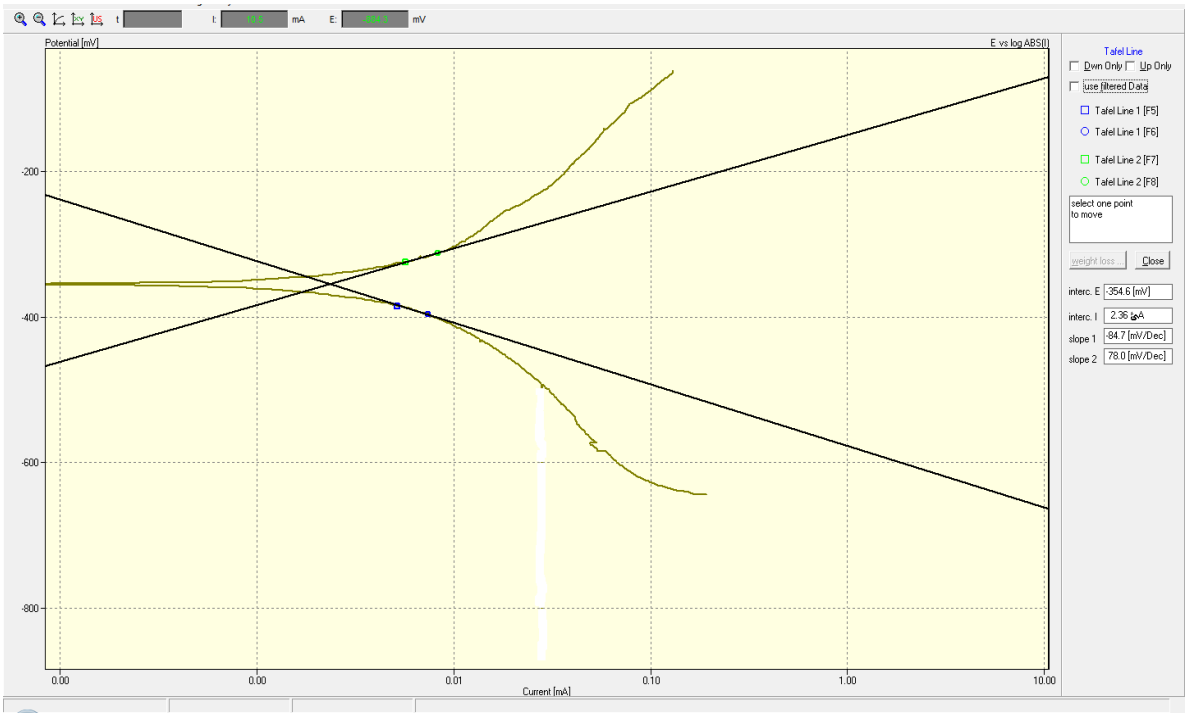

Figure (5) polarization curve of GaSn restorative alloy in synthetic saliva at 37±1 Cº.

Table (5) the compressive strength, diametral tensile strength, Creep, Dimensional Change and Hardness of Megalloy-EZ and GaSn.

Amalgam	compressive strength **(**N/mm^2**)**	diametral tensile strength	Creep (%)	Dimensional Change (μm/cm)	**Hardness Hv** (Kg/mm^2)
Megalloy-EZ	268	22.73	0.2	+ 14	158
GaSn	263	21.5	0.3	+ 94	143