Study of ($Ag_{0.72} Ga_{0.28}$ and $CuGa_2$) Gallium Restorative Phases

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دراسة أطوار ترميم كاليوم ($Ag_{0.72} Ga_{0.28}$, $CuGa_2$)

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Abstract

The purpose of this research is to study the properties of gallium restorative phases ($Ag_{0.72} Ga_{0.28}$ and $CuGa_2$) in vitro. X-ray diffraction analysis and microstructure observation have been carried out on (Ag – Ga and Cu – Ga) alloys to determine and observe the existing phases. The specimens prepared according to ADA specification No. 1 and kept at 37 ± 1 Cº. The electrochemical tests have been done according to ASTM standard (G5 – 87). Compressive strength, diametral tensile strength, dimensional change and vickers hardness have been measured, which indicated that the $Ag_{0.72} Ga_{0.28}$ phase stronger than $CuGa_2$ phase. Dimensional changes of both phases are within the allowable A.D.A. limit. OCP shows that the $CuGa_2$ phase superior to $Ag_{0.72} Ga_{0.28}$ phase due to passive film formation. Polarization tests show that both phases are corrosion prone, and $CuGa_2$ phase nobler than $Ag_{0.72} Ga_{0.28}$ phase.

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الخلاصة

يهدف هذا البحث إلى دراسة خواص أطوار ترميم الكاليوم ($Ag_{0.72} Ga_{0.28}$، $CuGa_2$) في المختبر. أجري تحليل حيود الأشعة السينية وفحص البنية المجهرية على سبائك (Ag – Ga , Cu – Ga) لمعرفة وتحديد الأطوار الموجودة. حضرت العينات حسب المواصفة رقم (1) للجمعية الأمريكية للأسنان وحفظت العينات عند درجة حرارة Cº 37 ± 1. أنجزت الاختبارات الكهروكيميائية حسب معيار ASTM (G5 – 87) . قيست كل من مقاومة الانضغاط ومقاومة الشد القطري والتغير بالأبعاد والصلادة والتي تشير الى ان طور($Ag_{0.72} Ga_{0.28}$) هو أقوى من طور ($CuGa_2$). كانت قيم التغير بالأبعاد لكلا الطورين هي ضمن الحد المسموح به من قبل الجمعية الأمريكية للأسنان. بين اختبار جهد الدائرة المفتوحة (OCP) بأن طور ($CuGa_2$) يتفوق على طور($Ag_{0.72} Ga_{0.28}$) بسبب تكوين طبقة خامدة. بين اختبار الاستقطاب بان لكلا الطورين ميل للتآكل، وان طور ($CuGa_2$) أكثر نبلا من طور($Ag_{0.72} Ga_{0.28}$).

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Key words: gallium alloy, gallium restorative, $Ag_{0.72} Ga_{0.28}$ phase, $CuGa_2$ phase, gallium phases.

Introduction

Gallium, like mercury, has a low melting point and at room temperature reacts with other metals to form a workable materials that hardens over time. The application of gallium alloys as a filling material and alternative to amalgam has received increased attention. Two gallium alloys have approved on the market, one of them has been approved by the Japanese government for clinical use [Hero, *et al*, 1997].

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Gallium restorative alloy consists of several phases such as ($Ag_{0.72} Ga_{0.28}$, $CuGa_2$, $Cu_9 Ga_4$ and $Cu_3 Ga$). The behavior of a restorative alloy depends on its phases. Properties of Gallium restorative alloys, such as corrosion resistance, mechanical strength, creep resistance and dimensional change have been studied [Hero, *et al*, 1997, Horasawa, *et al*, 1999, Shaini, *et al*, 2001, Dunne, *et al*, 2000]. The strength properties of gallium alloys have been reported to be comparable to those of amalgam. The dimensional change property measurement reveals that gallium alloys have excessive post placement expansion and it is capable of cracking dental structures [Ballester, *et al*, 2001]. Corrosion resistance of gallium alloys has been studied *in vitro* and *in vivo* and great corrosion was found compared with dental amalgam.

The purpose of the present work is to study the properties (electrochemical and mechanical) of gallium restorative alloy phases *in vitro*.

Experimental Procedure

1 - Specimens preparation

High purity (99.9 wt %) silver (powder of 53 μm in size), (99.99 wt%) copper (powder of 40 μm in size) and (99.99 wt%) gallium are used. Ag - Ga specimens were made by trituration of 72wt% Ag powder and 28 wt% Ga liquid metal for 30 seconds. Cu - Ga specimens have been made by trituration of 33 wt% Cu powder and 67 wt% Ga liquid metal for 400 seconds. **Table 1** shows the chemical composition of the used alloys. The amalgamator used was type (YDM-Pro). The specimens were prepared according to American Dental Association (A.D.A.) specification No.1 [A.D.A, 1975] for all tests using steel mould, and its height and diameter were (8x4 mm) respectively. The specimens have been kept at 37 ± 1 C°.

2- Microstructure Characterization

- X-Ray Diffraction Analysis

X-ray diffraction analysis has been performed on (Cu - Ga and Ag – Ga) specimens to determine the existing phases. X-ray diffraction device used is (XRD-6000,SHIMADZO Japan) supplied with single wave length Cu – Kα – 1.54 A°, with nickel filter. (20° – 90°) was the range of the diffraction angle.

- Microstructure Observation

Microstructure observation has been accomplished by using optical microscope to observe and study the (Cu - Ga and Ag – Ga) specimens 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 nitric acid in concentrations of 30% by volume was the specimen's etchant [ASM, 2004].

4 – Electrochemical Test

- Open Circuit Potential (OCP)

The OCP – time curve is recorded for (Cu - Ga and Ag – Ga) specimens. Synthetic saliva was the solution of the electrochemical test; **Table 2** shows its composition [Marek, 1990], the solution pH was 6.7 at 37 C°. Saturated calomel electrode was the reference electrode (SCE). One week from the end of trituration was the age of tested specimens. The full time period for this test was 125 minutes with interval of five minutes, where the potential is approximately stable.

- Potentiostatic polarization

Evaluation of corrosion resistance for (Cu - Ga and Ag – Ga) specimens has been performed using Potentiostatic polarization. Computerized potentiostate (Wenking M Lab, Germany) was used for accomplishing the polarization test. The age of tested specimens was one-week 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, the reference electrode is Standard Calomel Electrode (SCE), and the Auxiliary Electrode (AUX.E.) is platinum electrode.

The constant potential obtained by OCP – time curve, 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. Corrosion rate measurement is obtained by using the following equation [Fontana,*etal,* 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 ($\mu A/cm^2$).

5- Compressive Strength

The universal testing machine type (WDW-200) was used to evaluate the compressive strength. The test carried out according to (A.D.A.) specification No.1 [A.D.A, 1975]. Before compressive test, the diameter of the specimens was measured using micrometer (of 1µm accuracy). The tested specimens was aged for (one and seven days) from the end of trituration. The specimen loading speed was 0.5 mm/min. The compressive strength is calculated using the following equation [ASM, 1992]:-

$$\text{Compressive strength (N/mm}^2\text{)} = \frac{Max.force(N)}{cross\,\sec tional.area(mm^2)} \qquad (2)$$

6- Diametral Tensile Strength

The universal testing machine was used to measure the diametral tensile strength. The test carried out according to(A.D.A.) specification No.1 [A.D.A, 1975]. The specimen was placed in its lateral side between the flat jaws of the machine. The dimensions of the specimens have been measured with the mentioned micrometer. The test carried out at one and seven days 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]:-

$$\sigma_t = \frac{2P}{\pi DL} \qquad (3)$$

where
P = load at fracture (N).
D = diameter of specimen (mm).
L = length of the specimen (mm).
σ_t = tensile strength MPa.

8- Dimensional Change

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

9- Vickers Hardness test

Vickers hardness of (Cu - Ga and Ag − Ga) specimens were obtained using hardness test devise type (Digital Display Microhardness Tester HVs-1000) at one week after the end of trituration, the applied load is 0.1 Kg for 10 seconds. Vickers hardness value obtained directly from the devise.

Result and Discussion

Figure (1) illustrates the diffractogram of Ag-Ga alloy. Two different phases were existed in this alloy ($Ag_{0.72}Ga_{0.28}$ and Ag). The predominate phase is $Ag_{0.72}Ga_{0.28}$ which was the matrix of the alloy, and appears in different orientation as mentioned in **Figure1**, where the highest intensity peak was for (300) orientation (2θ of 40.189° and 100% intensity), this result agrees with the binary equilibrium diagram of Ag − Ga system, with percentage of 72 wt% Ag and 28 wt% Ga [ASM, 1992]. The presence of silver in the Ag-Ga alloy with low intensity means that there are unreacted silver particles in the alloy in small amount.

Figure (2) shows the diffractogram of Cu-Ga alloy. It can be seen two different phases in this alloy ($CuGa_2$ and Cu). The predominate phase here is $CuGa_2$ (alloy matrix) where appears in different orientation showed in figure (2). The highest intensity peak was for (102) orientation (2θ of 44.576° and 100% intensity), which agree with the binary equilibrium diagram of Cu − Ga system, according to the triturated percentage (33 wt% Cu and 67 wt% Ga)[ASM, 1992]. There are small amount of unreacted copper particles in the alloy, which in low intensity peaks with different orientations.

Figure (3) illustrates the microstructure of (Ag − Ga) restorative alloy phase, the matrix of the structure was the white regions of $Ag_{0.72}Ga_{0.28}$ phase, and unreacted silver particles as dark spheroidal regions distributed in the microstructure, where approved by the diffractogram of Ag-Ga alloy **Figure (1)**.

Figure (4) shows the microstructure of (Cu –Ga) restorative alloy phase, the light bright regions was the microstructure matrix of $CuGa_2$ phase, and the unreacted copper particles as light dark regions, which indicated by the diffractogram of Cu-Ga alloy **Figure (2)**.

Figure (5) shows the OCP- time curve for (Ag − Ga) in synthetic saliva solution. The OCP started with (-153.6 mV), then drops gradually due to increasing of anodic reaction (dissolution) of the alloy in the solution until reach approximately constant value of (-390 mV) after (75 mins) and remain within (-390 – -399 mV) range for (50 mins). OCP reachs the constant value when the anodic reaction (dissolution) equals to cathodic reaction (deposition) at the surface of specimen, and the final constant value of OCP for (Ag − Ga) is (-399 mV).

Figure (6) reveals the OCP- time curve for (Cu − Ga) in synthetic saliva solution. The OCP for this alloy started with (-525 mV), then increases gradually in positive direction due to deposition of corrosion product on the surface of specimen, which is more noble than (Cu − Ga) alloy, until the potential reachs value of (-484.2 mV) at (60 mins) where the potential increases suddenly to (-388.5 mV) value at (65mins) because of passive film formation on the specimen surface and then increases gradually in a small amounts due increase passive film thickness until reach a constant value of (-340 mV) at (120 mins) because of balance between dissolution and deposition.

Polarization curve of (Ag − Ga) alloy is shown in **Figure (7)**. The corrosion parameters (E_{corr}, I_{corr}, and corrosion rate) of this alloy, which extracted from **Figure (7)**, are -572.5mV, 0.7287μA/cm^2 and 2.44 mpy respectively. $Ag_{0.72}Ga_{0.28}$ phase is the predominant phase, therefore, the polarization and corrosion parameters were of this phase. In cathodic polarization, the current

density decreases with increasing potential until reach value of -572.5mV, which is the corrosion potential E_{corr}, with increasing potential, anodic polarization starts. The behavior of anodic polarization was active, where the current density increases with increasing potential giving an indication of Ag0.72Ga0.28 phase dissolution, until reaches approximately constant value of current density indicating the presence of barrier film formation.

Figure (8) shows polarization curve of $CuGa_2$ phase. The corrosion parameters of this phase (E_{corr}, I_{corr}, and corrosion rate) are -438.4mV, $0.71939\mu A/cm^2$ and 2.178mpy respectively. When cathodic polarization, the current density decreases with increasing potential until reach E_{corr}, then anodic polarization starts with increasing potential, which was active anodic polarization, where current density increase with increasing potential indicating dissolution of $CuGa_2$ phase, until reaches approximately constant value of current density indicating the presence of barrier film formation. It can be seen from **Figure (7 and 8)** that the nobility of both phases are low, but have small corrosion rate due to absence of galvanic effect comes from presence of different phases in the same alloy which occur in gallium based restorative alloys [Horasawa, *et al*, 1999, Chitambar, 2010, Dingfei, 2011]

Table (4) reveals corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate (C.R.) for tested alloys. E_{corr} for $Ag_{0.72}Ga_{0.28}$ phase is less noble than $CuGa_2$ phase, where (E_{corr}) for $Ag_{0.72}Ga_{0.28}$ is more negative than that of the $CuGa_2$. Corrosion rate of $CuGa_2$ is slightly less than that of $Ag_{0.72}Ga_{0.28}$ due to the passive film formed on $CuGa_2$ phase is thicker than that on $Ag_{0.72}Ga_{0.28}$ phase as approved by OCP – time curve.

Table (4) shows the compressive strength, diametral tensile strength, dimensional change and hardness of Ag – Ga and Cu – Ga alloys.

Compressive strength reported after one and seven days from the end of trituration for both alloys. It can be seen from **Table (4)**, that the compressive strength of Ag – Ga alloy after one and seven days is (84 and 276) N/mm^2 respectively, which is of $Ag_{0.72}Ga_{0.28}$ phase. The compressive strength reaches about 30% after one day from its final value after one week, this is due to the reaction speed of silver with gallium not high enough to deplete gallium with considerable amounts after one day, where liquid gallium considers weak phase in the alloy and there is small amount of $Ag_{0.72}Ga_{0.28}$ phase. The compressive strength of Cu – Ga after one day is 67 N/mm^2 and after seven days is 234 N/mm^2, which is attributable to $CuGa_2$ phase. The compressive strength of $Ag_{0.72}Ga_{0.28}$ phase superior to that of $CuGa_2$ phase.

Diametral tensile strength for both alloys (Ag – Ga and Cu – Ga) has been reported after one and seven days from the end of trituration. From **Table (4)**, the diametral tensile strength for $Ag_{0.72}Ga_{0.28}$ phase (the predominant phase in the Ag – Ga alloy) after one day is 26 N/mm^2 and after seven days is 53 N/mm^2. It can be noted that the diametral tensile strength reaches 49% from its final value after one day from the end of trituration due to presence of liquid gallium phase and $Ag_{0.72}Ga_{0.28}$ phase formation not complete yet. The diametral tensile strength for Cu – Ga alloy after one day is 18 N/mm^2 and after seven days is 37 N/mm^2, which is of $CuGa_2$ phase. About 48% of the final value of the diametral tensile strength for Cu – Ga alloy was reached after one day from the end of trituration for same reason mentioned above.

Vickers hardness of Ag – Ga and Cu – Ga alloys are reported after one and seven days from the end of trituration. The hardness of Ag – Ga alloy after one day is 123 Kg/mm^2 and after seven days is 304 Kg/mm^2 and for Cu – Ga after one and seven days are (42 and 111 Kg/mm^2) respectively. The final hardness value is of ($Ag_{0.72}Ga_{0.28}$ and $CuGa_2$) phases. It can be seen from both values, hardness reaches about 40% from the final hardness value after one day from the end of triturated, as mentioned above, this is due to presence of liquid gallium phase and($Ag_{0.72}Ga_{0.28}$ and $CuGa_2$) phases formation are not complete yet.

Strength of both phases is approximately similar to that obtained by many researchers for gallium based restorative alloys [Dunne, *etal*, 2005, Miller, *etal*, 1999, Sarraj, *etal*, 2011, and McComb, 1998].

Dimensional change of Ag – Ga and Cu – Ga alloys are (+ 7.3 and + 12.6 μm/cm) respectively. The allowable limit for dimensional change According to A.D.A. specification No. 1 is (± 20

μm/cm) [A.D.A, 1975], therefor, the dimensional change of both alloys are within A.D.A. limit. The dimensional change occurs due to formation of new phases that have different crystal structure from that of the original materials that consist of. Gallium based restorative alloys have excessive poste placement expansion [Ballester, *et al*, 2001, Sarraj, *etal*, 2011], which is different from ($Ag_{0.72}Ga_{0.28}$ and $CuGa_2$) phases, and can be attributed to presence of unreacted gallium in the fillings

Conclusion

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

1- $Ag_{0.72}Ga_{0.28}$ phase dissolute in synthetic saliva until dissolution equals deposition when reaches constant value of OCP (-399 mV).
2- When immersion of $CuGa_2$ phase in synthetic saliva, passive film formation will start, with increasing time passive film increases too, until reaches constant value of OCP (-340 mV).
3- $Ag_{0.72}Ga_{0.28}$ and $CuGa_2$ phase have active anodic polarization with barrier film formation at the last part.
4- $CuGa_2$ phase is more noble than $Ag_{0.72}Ga_{0.28}$ phase, and both phases are corrosion prone.
5- Compressive strength, diametral tensile strength and hardness of ($Ag_{0.72}Ga_{0.28}$ and $CuGa_2$) phases reach about (30 – 49) % of the final value after one day from the end of trituration.
6- The final value of compressive strength, diametral tensile strength and hardness for both phases are of considerable amount.
7- The dimensional change of ($Ag_{0.72}Ga_{0.28}$ and $CuGa_2$) phases are (+7.3 and +12.6 μm/cm) respectively, and within A.D.A. limit.

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

alloy	Composition (wt%)		
	Ag	Cu	Ga
Ag - Ga	72	-	28
Cu – Ga	-	33	67

Table (2) Chemical composition of synthetic saliva. [8].

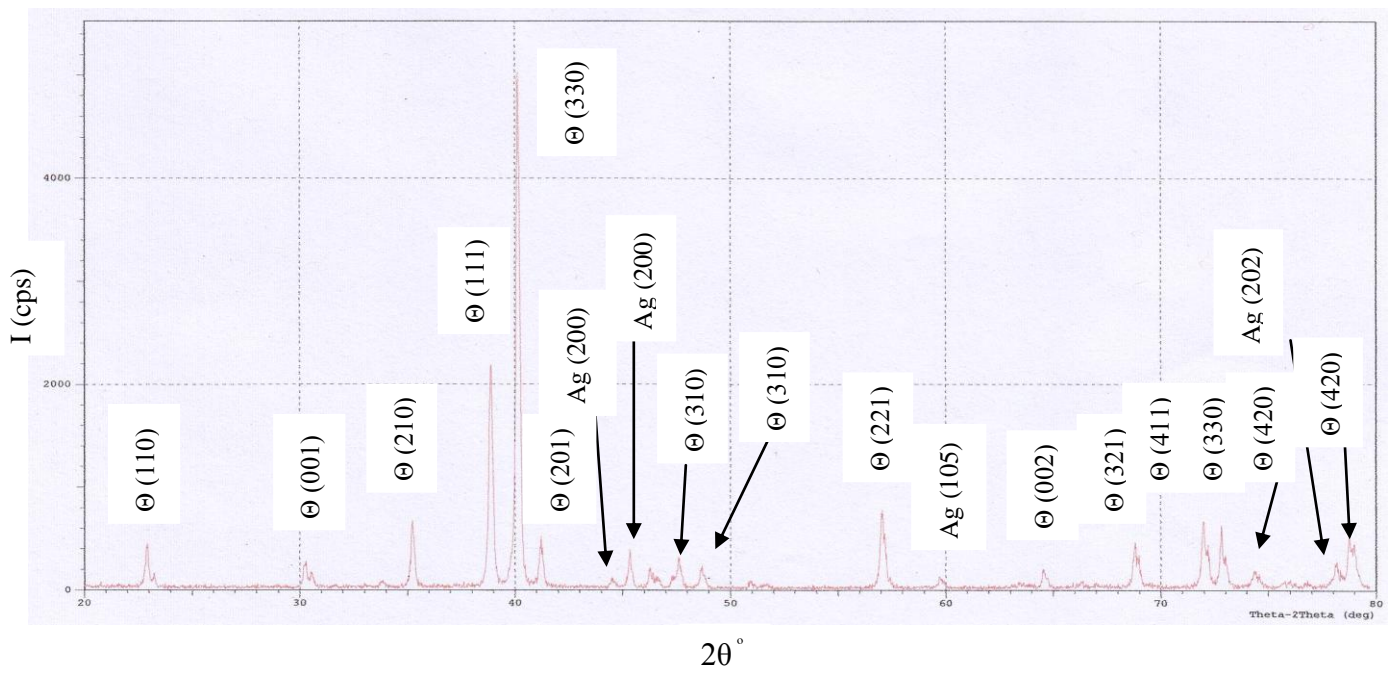| No.	Constituent	gm/l
1	KCl	1.5
2	$NaHCO_3$	1.5
3	$NaH_2PO_4.H_2O$	0.5
4	KSCN	0.5
5	Lactic acid	0.9

Figure (1) Diffractogram of Ag-Ga restorative alloy $(\Theta = Ag_{0.72}Ga_{0.28})$
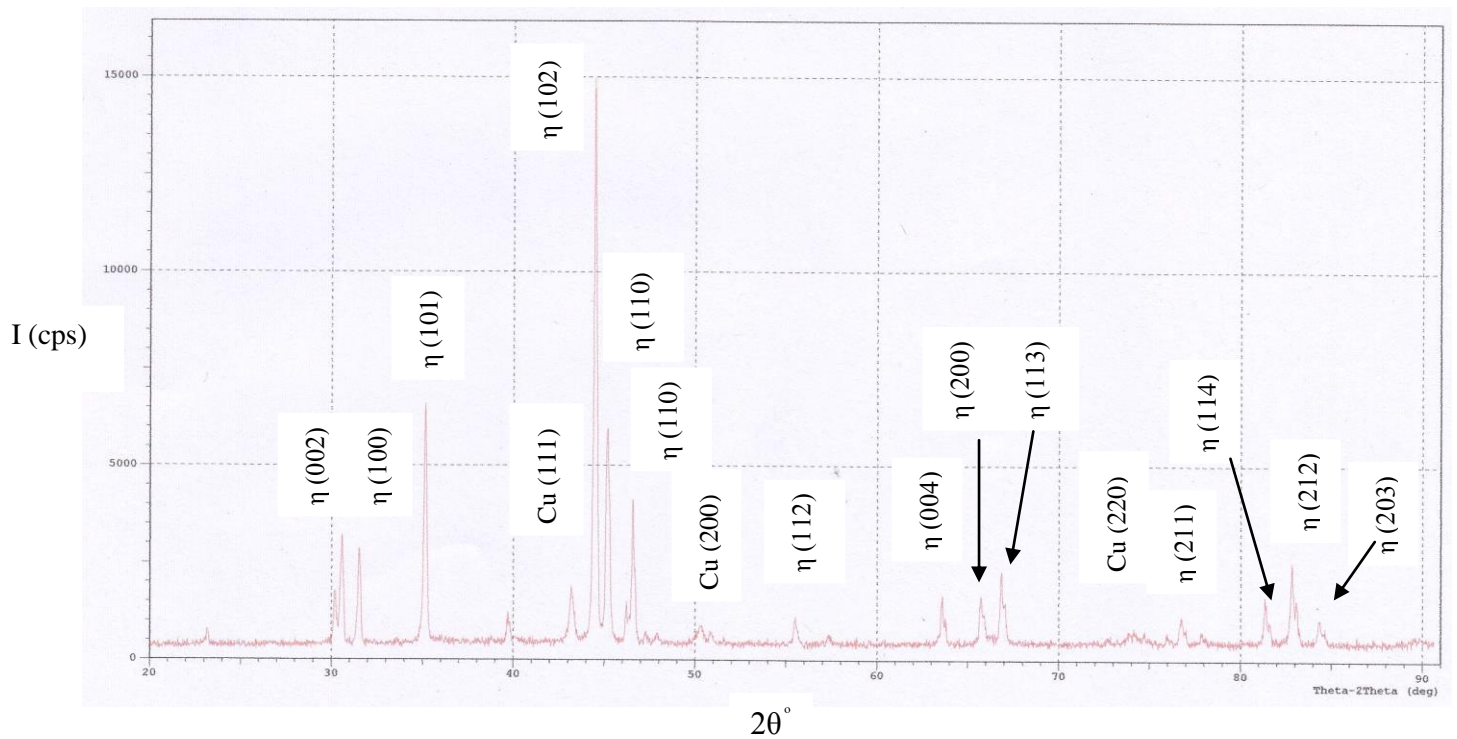
Figure (2) Diffractogram of Cu-Ga restorative alloy. $(\eta = CuGa_2)$
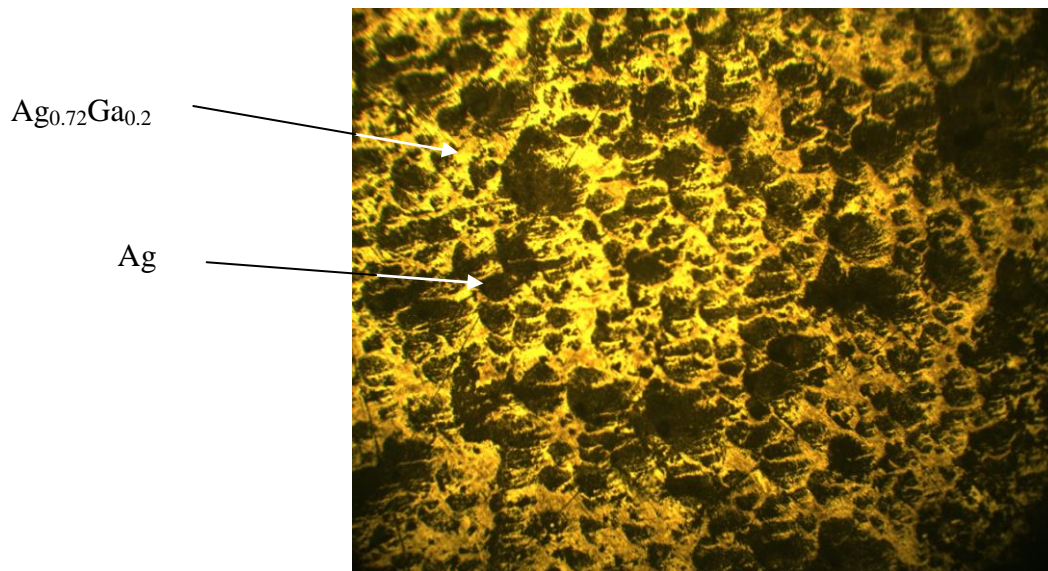
Ag$_{0.72}$Ga$_{0.2}$

Ag

Figure (3) The microstructure of (Ag – Ga) restorative alloy phase. (X 150)
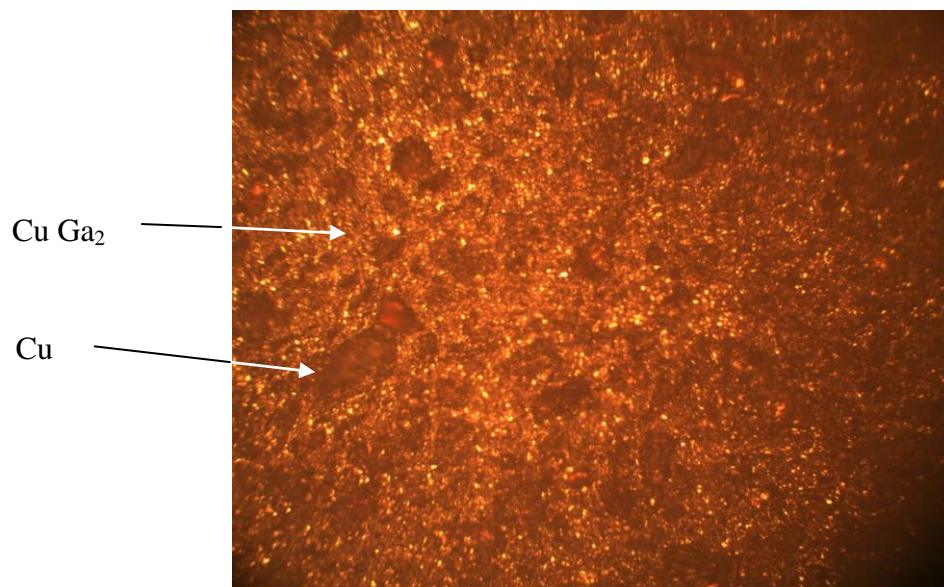

Cu Ga$_2$

Cu

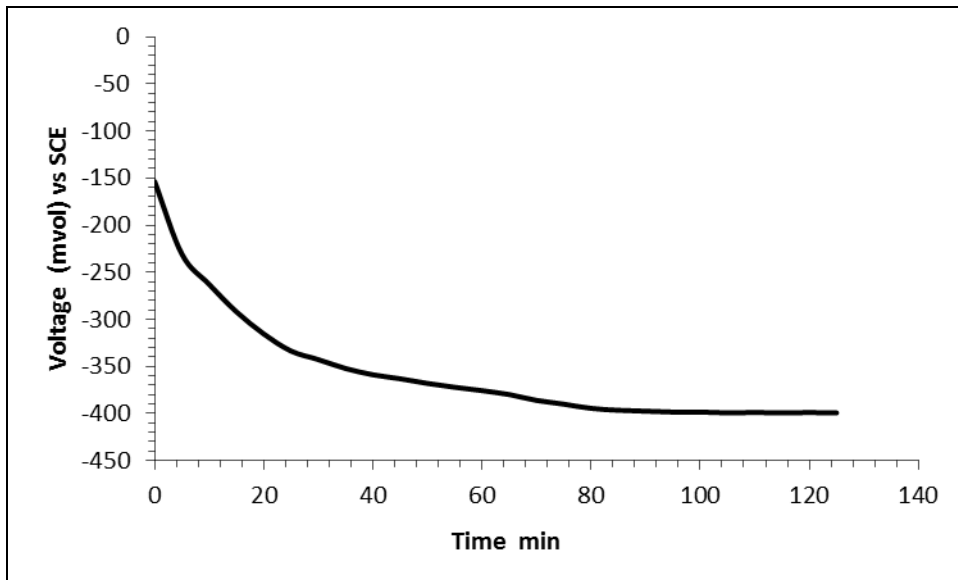**Figure (4)** The microstructure of Cu-Ga restorative alloy phase. (X 150)

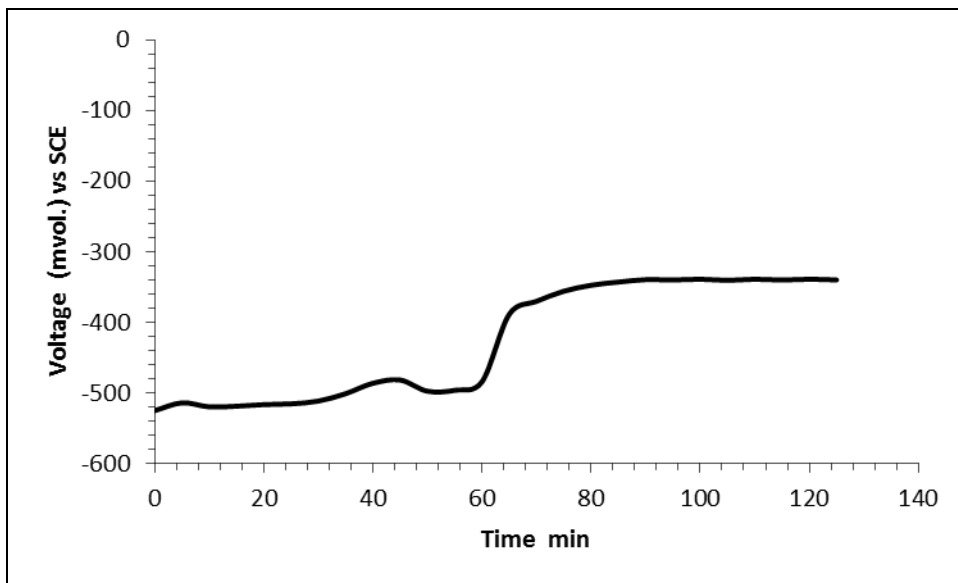**Figure (5)** OCP – time for Ag – Ga alloy in synthetic saliva solution.

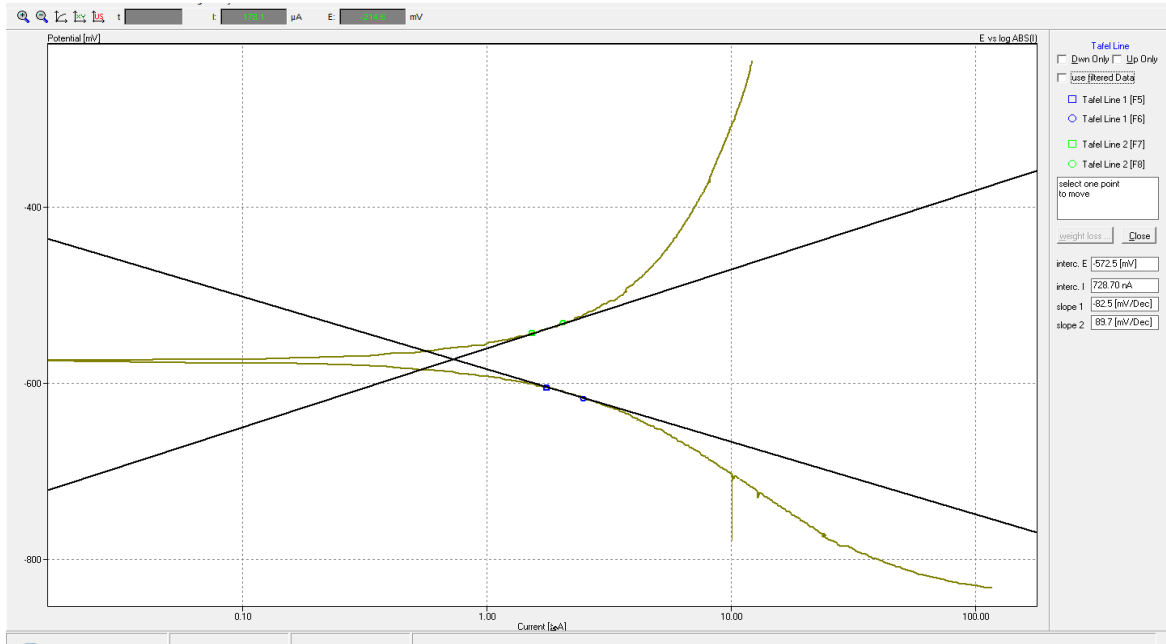**Figure (6)** OCP – time for Cu – Ga alloy in synthetic saliva solution.

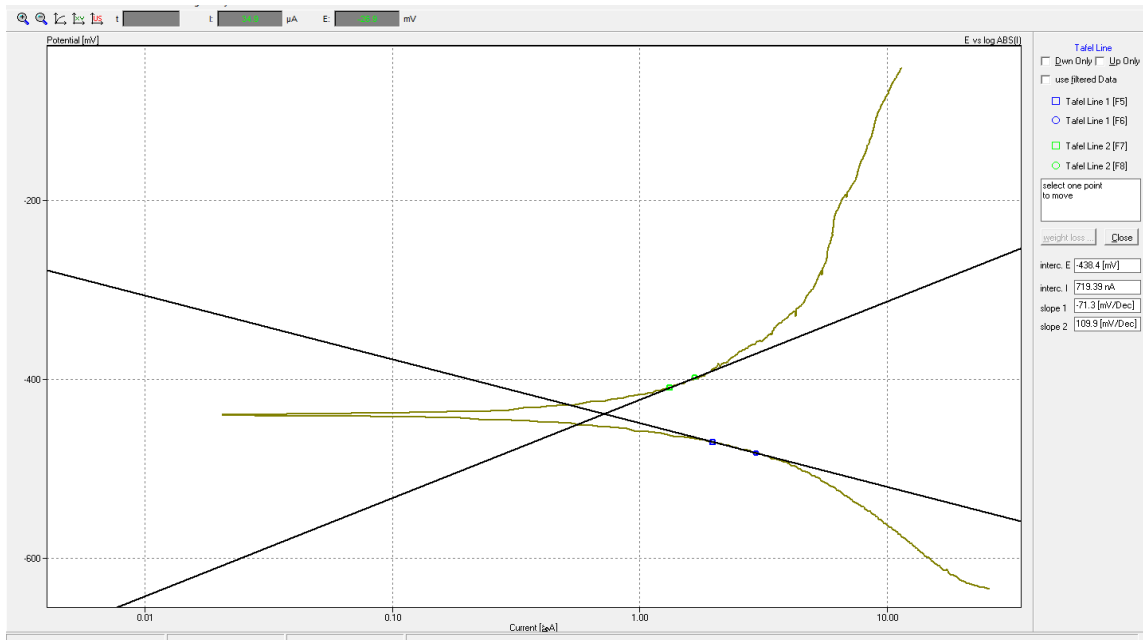**Figure (7)** polarization curve of Ag – Ga in synthetic saliva.

Figure (8) polarization curve of Cu – Ga restorative alloy in synthetic saliva.

Table (3) The corrosion potential (E_{corr}) , corrosion current density (I_{corr}), corrosion rate of the amalgam and Ag – Ga and Cu – Ga alloys.

Alloy	E_{corr} (mV)	I_{corr} (nA/cm^2)	Corrosion Rate (mpy)
Ag - Ga	-572.5	728.7	2.44
Cu – Ga	-438.4	719.39	2.178

Table (4) The compressive strength, diametral tensile strength, Dimensional Change and Hardness of   Ag – Ga and Cu – Ga.

Alloy	compressive strength (N/mm^2)		diametral tensile strength		Dimensional Change (μm/cm)	Hardness Hv (Kg/mm^2)	
	One day	Seven days	One day	Seven days		One day	Seven days
Ag – Ga	84	276	26	53	+7.3	123	304
Cu – Ga	67	234	18	37	+12.6	42	111