Improvement of corrosion resistance and dimensional change of the high copper dental amalgam by Al$_2$O$_3$ additions.

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Abstract. The main goal of this present investigation is to study the effect of the (Al$_2$O$_3$) addition on corrosion resistance and dimensional change of the high copper dental amalgam. One alloy has been prepared via casting composed of silver (47%), tin (30%), copper (22%), and zinc (1%). (Al$_2$O$_3$) addition is added in distinct percentages of the (0.5, 1, 1.5, 2) wt.%. Specimens were prepared according to ADA specification No. 1. The specimens have been stored at 37±1 Cº using a chamber prepared for this purpose. Corrosion resistance improved with addition from 0.5% to 2% (Al$_2$O$_3$) and observed that dimensional change of amalgam improved after (Al$_2$O$_3$) additions.

1. Introduction

Word amalgam is derived from the Greek name 'Emoliet' which means paste [1]. Dental amalgam restorations containing mercury have a long history starting with Chinese in 659 A.D. They were the first users of silver-mercury paste [2]. It has been in use since the 1800s, generally with limited known detrimental effects on humans [3]. The estimations show that a percentage of 75% of all a single restoration of the tooth is a restoration of amalgam. Furthermore, this percentage remained steady for diverse years. Easiness of placement and manipulation, a relatively low cost, a familiar history of the performance in an oral cavity have made the amalgams of dental extremely as the material of popular restorative [4]. The amalgam of dental is an alloy made from liquid mercury. Also, it is made from other alloys of solid metal particulate which are made from silver, copper, tin, and so on. At first with the amalgams of silver–mercury. Then later, it modified via the additions of tin to dominate an amount of the expansion. The amalgams manufactured a weak, corrodible intermetallic γ2 phase (Sn7Hg). Hence, a modern amalgam of a dental now also contains copper (>12%) to suppress this stage. A solid alloy is mixed within the liquid mercury via a mixer of mechanical vibrating (an amalgamator). Then, a producing material is packed up into a prepared cavity [5,6]. A reaction between the mercury and an alloy that follows up the mixing is nominated as the reaction of amalgamation. This reaction results in the formation of the hard material of restorative of a silver-grey shape. Generally, the color limits its utility for those cavities where the appearance is not the essential concern. A setting reaction for the amalgam involves the dimensional change. An overall effect can cause the slight final expansion or the slight final contraction [7]. An excessive contraction will lead to a big marginal gap between a material and a cavity. The expansion leads to the extrusion of material out of a cavity [8]. Amalgam may expand or contract. Ideally, the change of dimensional should be small. Also, excessive constriction can lead to microleakage and secondary caries. In contra, excessive expansion can lead
the pressure on a pulp and the sensitivity of postoperative. Also, the protrusion of restoration can occur. American association of dental (ADA) specification No. 1 requires that an amalgam must not extend or should not contracts further more than the 20μm/cm at 37 °C between 5 minutes-24 hours from the end of the trituration [9]. Amalgam filling generally tarnishes and shows discoloration but occasionally corrode too. Tarnished amalgam restoration is unaesthetic and if unattended it may lead to corrosion. The tarnished layer is mainly made up of tin sulfide, sulfur coming from a sulfur-rich diet. Products of corrosion may penetrate the dentinal tubules in the dentin and cause discoloration of the whole tooth. The corrosion products can also seal the small marginal gap thus preventing marginal breakdown and leakage. To prevent tarnish, and discoloration, cavity varnish should be applied to the cavity floor and walls before insertion of restorative materials. And also all amalgam fillings should be highly polished and made self-cleaning [10]. Nemours of the factors that can impact the rate of corrosion. Those factors involve the acidity of a contacting medium, the temperature that both can subject the variations of sharpness in a little period of the time in a cavity of oral. Further, an efficient potential of an amalgam [11].The present work aims to investigate the effect of (Al2O3) addition on the corrosion resistance and dimensional change of the dental amalgam of a high copper.

2. Experimental work

2.1. Preparation of the Powder Alloy

The base alloy (silver, copper, tin, and zinc) is melted via utilizing the electrical furnace and an operation was completely done beneath the inert atmosphere by utilizing the argon gas. The alloy prepared via casting composed of silver (47%), tin (30%), copper (22%), and zinc (1%). An electrical furnace with a controlled inert atmosphere of the argon gas is utilized to melt an amalgam alloy to get the specimens of an alloy, which heat-treated at 400 °C for 4 hours to homogenize constituents and the phases of the ingot. Subsequently, a prepared cast alloy is transformed into the powder via turning and the ball milling and then heat-treated at the100 ºC for 3 hours under the atmosphere of vacuum for stress relief. A chemical analysis of the composition of the base alloy, ardent is shown in Tables (1).

| The Alloy   | Ag wt.% | Sn wt.% | Cu wt.% | Zn wt.% |
|------------|---------|---------|---------|---------|
| base alloy | 51.3    | 28.8    | 19      | 0.67    |
| Ardent     | 44.5    | 30      | 25.5    | --------|

2.2. Specimens Preparation

Specimens have been made depending on specification No.1 of ADA [12] via the trituration of an equal amount of the powder of an alloy and the mercury for 25 sec via the mechanical amalgamator with the type of (ling chen). Dimensions for specimens is1:2 (4 mm in diameter and 8 mm in the height). The specimens kept at a degree of 37±1 °C.

2.3. Characterization of Microstructure

2.3.1. X-Ray Diffraction Analysis

A (base alloy, M amalgam, and its amalgam together within 2% from Al2O3) have separately been analyzed via utilizing the diffraction techniques of X-Ray to determining existing phases in an alloy of an amalgam. A machine of X-Ray utilized was the SHIMADZU Lab Xe XRD - 6000o, Japan, the generator of X-Ray together within the copper radiation of Kα (λ =1.5406 A°), the filter of nickel. A domain of an angle of a diffraction 2θ° is (20°-80°).
2.3.2. The Observation of Microstructure

Specimens have been taken from each one of them (base alloy before & after the treatment of heat of homogenization and the amalgam together within all the additions) were ground via utilizing the different grades of emery papers of (400, 600, 800, 1200, 1500, 2000, 2500), then it polished via 3μm diamond paste. Specimens have been then thoroughly washed by using the distilled water and dried via the blast of air before the etching. Specimens of fills that polished have been etched via the chemical etchant (30 vol. % nitric acid) [13]. After that, it was examined under 400x magnification via utilizing optical microscopy and scanning electron microscopy. The distribution of the elements on every one of the surfaces of fill has been analyzed quantitatively and qualitatively.

2.4. Corrosion Test

The tests of polarization have been performed via utilizing the standard cell of electrochemical that containing the worked electrode (the amalgam), an electrode of the auxiliary (the Pt.electrode), and a reference electrode(SCE) which achieved in the synthetic saliva depending on an American Society to the Testing and the Materials (the ASTM)[14]. The experiments of polarization have been conducted in the type of a potentiodynamic (a Winking M Labf200o). Then, the potentiodynamic polarization has been started from the initial potential for the 250 mV which is beneath an open circuit potential when a specimen reaches a constant potential and a scan has been continued to move up until to the 250 mV in above an open circuit potential. Specimens have been scanned in a positive direction in the rate of the sweep of 0.4mV/s and a current has been reported together with the respect to a potential. The potentials of corrosion (Ecorr) and the existing density of corrosion (icorr) are acquired as the result of a test. Then, a measurement of the rate of corrosion is acquired via utilizing the following formula of equation [14]:

$$\text{Corrosion Rate (mpy)} = \frac{0.15 \text{icorr} \cdot (E.W.)}{A \cdot \rho}$$

(1)

Whereas:

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

A= the area (cm²).

ρ = the density (g/cm³).

icorr = the current density (µA/cm²).

2.5. Dimensional change

The first record has been immediately taken after the specimen has been formed (after trituration by 30 minutes), a specimen has been positioned in the measuring instrument (the micrometer) that has an accuracy of a 0.1µm. Specimens have been stetted free without any kind of restraint through the test. The second length of specimens has been measured after passing 24 hours after the end of the trituration. Moreover, specimens have been kept at a steady temperature which is 37±1°C at a chamber of glass. According to ADA specification No.1 a dimensional change should be together with the range of a ± 20 µm/cm.
3. Result and Discussion

3.1. Microstructure Characterization

The base alloy which is used to prepare dental amalgam can be analyzed by determining the alloy phases present in Figure (1). Phases of the base alloy were determined via comparison together within the standard cards of XRD. The evaluation of a phase has shown that base alloy has three phases which are \( \gamma (\text{Ag}_3\text{Sn}) \), \( \varepsilon (\text{Cu}_3\text{Sn}) \), and phase \( \beta (\text{Ag}_4\text{Sn}) \). Where it can be noted the \( \gamma (\text{Ag}_3\text{Sn}) \) represents a matrix of the microstructure, while \( \varepsilon (\text{Cu}_3\text{Sn}) \) has secondary intensity and represents a coherent network in the matrix. The intensity peak of \( \beta (\text{Ag}_4\text{Sn}) \) phase is relatively small concerning other phase's peaks, which gives an indicator of its small amount.

![Figure (1) XRD patterns of base alloy.](image)

The XRD result of the master amalgam is illustrated in Figure (2). Phases of the amalgam have been determined via the comparison together within the standard cards of XRD. An analysis of a phase of these amalgam displays two phases; the \( \gamma_1 (\text{Ag}_2\text{Hg}_3) \), \( \eta (\text{Cu}_6\text{Sn}_5) \). The peaks of the intensity of the \( \gamma_1 \) phase have been representing a maximum intensity. This represents a matrix of the microstructure, a phase of \( \eta \) has a second peak of the intensity. This will leads to a conclusion that the phase of \( \eta \) represents the coherent network in a matrix.
The result of XRD of amalgam together within 2% from aluminum oxide is presented in Figure (3). Phases of an amalgam have been located via the comparison together within the standard cards of XRD. The analysis of a phase for those amalgams is displayed three phases which ($\gamma_1 (Ag_2Hg_3)$, unreacted ($Al_2O_3$), and ($\eta (Cu_6Sn_5)$). The peaks of the intensity of phase of $\gamma_1$ has been representing an extreme intensity that represents a matrix of the microstructure, and a phase of $Al_2O_3$ has a second peak of intensity. This will drive to a conclusion where the phase of the ($Al_2O_3$) represents an incoherent network in a matrix.
An observation of the microstructure of the amalgam of (M) and all the additions are presents in Figures (4 - 8) that consists of the white regions of the matrix of an amalgam of the ($\gamma_1$ (Ag$_2$Hg$_3$)) phase and Al$_2$O$_3$ phase, while the black regions in a second main phase of the $\eta$ (Cu$_6$Sn$_5$), and the regions of a dark gray of unreacted particles of ACS (Ag-Cu-Sn). The phases are confirmed via the results of the X-ray diffraction which are presented via Figures (2) (3). It can be noticed from the above figures that unreacted particles are surrounded by the phases of $\gamma_1$, and $\eta$. Different regions can be noted from an electron microscope of the scanning (SEM), whereas a first region represents the particles of gray color. That region have contains elements of (Ag, Cu, Sn) which from an EDS (the Dispersive Spectrometer of Energy). These regions within their results are unreacted particles. Also, a second region represents a light gray (a matrix). In this region, the highest content of an element is the Hg and the Ag that is $\gamma_1$ (Ag$_2$Hg$_3$) phase and the phase of Al$_2$O$_3$. In the same region, the higher content for the Cu and the Sn has been found, and it represents the phase of $\eta$. It can be noticed that the size of unreacted particles (ACS) will increases when the percentages of (Al$_2$O$_3$) are increasing because of the presence of the powder of (Al$_2$O$_3$). This powder decreases the diffusion of the mercury to particles of the powder alloy.

Figure (3) XRD patterns of amalgam with 2% from aluminum oxide.
Figure (4) The observation of microstructure of the amalgam alloy of (M).

a) Via the Optical Microscope at the magnification of (400X), b) Via the SEM where the ACS (Ag-Cu-Sn).

Figure (5) The observation of a microstructure of the (0.5% Al₂O₃) amalgam.

a) Via the Optical Microscope at the magnification of (400X), b) Via the SEM where ACS (Ag-Cu-Sn).
Figure (6) An observation of microstructure of the (1 % Al₂O₃) amalgam.
(a) Via the Optical Microscope at the magnification of (400X), (b) Via the SEM where the ACS (Ag-Cu-Sn).

Figure (7) the microstructure observation of (1.5% Al₂O₃) amalgam.
(a) Via the Optical Microscope at the magnification of (400X), (b) Via the SEM where the ACS (Ag-Cu-Sn).
3.2. Corrosion Test

The electrochemical corrosion by using two specimens of each (ardent, M amalgam, and amalgam with the additions) can conveniently be described via a schematic existing potential curves (curves of polarization) are display in Figure (9) which clarify the curves of cathodic and anodic polarization for each (ardent, M amalgam and amalgam with additions) in the solution of synthetic saliva. Furthermore, the current densities of corrosion, the potentials of corrosion, and calculated rate data of corrosion from that curves are clarified via Table (2). From table (2) it can be noticed that there is a most and significant improvement in the resistance of corrosion of the amalgams together within distinct additives of Al₂O₃ (0.5, 1, 1.5, and 2%) which is (50, 55, 71 and 84%) respectively and Icorr for specimens are graded from 6.8 (µA/cm²) for 0.5% (Al₂O₃) to 2.3 (µA/cm²) for 2% (Al₂O₃) which are lower than the Icorr for the M amalgam that is 13.7 (µA/cm²) and ardent 13 (µA/cm²). Despite that, the values of Ecorr are graded from -564 mV for 0.5% (Al₂O₃) to -385.5 mV for 2% (Al₂O₃) are lower than the Ecorr for the amalgam of M which is -655.5 mV and ardent -650.5 mV. It's noted from Figure (9), which represents the curve of the polarization for (ardent, the amalgam of (M) and an amalgam with the additions). Also, in the polarization of a cathodic, the voltage is increases with a current decreasing till it reaches a minimum possible value. While in the polarization of anodic, the voltage will increase with increasing current. In the reality, an increase of a voltage and flow together demonstrates an active behavior of the anodic polarization that displays a continuous dissolution for the metal. Through noticing from the curve of the anodic, it's evidenced which clarify there is an absence for a passive region of all (ardent, the M amalgam, and amalgam with additions).
Figure (9) The potentiodynamic polarization curves of each (ardent, M amalgam and amalgam with additions).

Table (2) Corrosion potential (Ecorr), the corrosion current (icorr), the rate of corrosion and the percentage of the improvement.

| The Alloys | Mean Ecorr (mV) | Icorr (µA/cm²) | Rate of Corrosion (mpy) | Improvement Percentage% |
|------------|----------------|---------------|-------------------------|-------------------------|
| Ardent     | -650.5         | 13            | 68                      | ------------------------|
| M          | -655.5         | 13.7          | 69                      | ------------------------|
| 0.5%       | -564           | 6.8           | 34                      | 50                      |
| 1%         | -446.5         | 6.2           | 31                      | 55                      |
| 1.5%       | -426           | 4             | 20                      | 71                      |
| 2%         | -385.5         | 2.3           | 11                      | 84                      |

3.3. Dimensional change

The mean value of the dimensional change which was obtained via the five specimens for each one of them (ardent, M amalgam, and amalgam with additions) are display in Table (3). ADA specification
No.1 determines the allowable dimensional change is ±20 μm/cm. A result for all amalgams together with an allowable limit set via ADA and the dimensional change of the amalgam which stabilized together within the increasing content amount of (Al₂O₃). From Table (3) it can be noticed that there is a most significant improvement in the dimensional change of amalgams together within distinct additives of Al₂O₃ (0.5, 1, 1.5, and 2%) which are (15, 31, 53, and 78%) respectively.

Table (3): the values of a mean and a percentage of improvement of a dimensional change of the amalgams.

| The Alloys | Mean Dimensional Changeμm/cm | Improvement Percentage% |
|------------|------------------------------|-------------------------|
| Ardent     | +14.35                       | ---                     |
| M          | +15.3                        | ---                     |
| 0.5%       | +13.05                       | 15                      |
| 1%         | +10.6                        | 31                      |
| 1.5%       | +7.3                         | 53                      |
| 2%         | +3.4                         | 78                      |

4- Conclusion

1-Alumina addition decreases the dimensional change of dental amalgam, dimensional change decreases with increasing alumina content, the maximum improvement of dimensional change was 78% at 2 wt.% Al₂O₃ which is (+3.4).

2-Alumina addition increases the corrosion resistance of dental amalgam, corrosion resistance increases with increasing alumina content, the maximum improvement of corrosion resistance was 84% at 2 wt.% Al₂O₃ where the corrosion rate was 11 mpy.

5. References

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