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Corrosion Behavior of Amalgam/Cockles Shells Composites in Artificial Saliva

Assistant Prof. Dr. Rana Afif Anaee*, Assistant Prof. Dr. Aseel Basim Al-Zubaidi,
Assistant Prof. Dr. Ahmed Abdulrahman Al-Tabbakh
*Materials Engineering Department, University of Technology, Iraq
Department of Physics, Al-Nahrain University, Jadiriya, Iraq

Abstract

Metal matrix composites have been prepared by adding cockles' shells CS powder to dental amalgam with three weight percents 14.2, 28.5 and 42.8 wt% as an attempt to improve the corrosion behavior of the final product. The corrosion behavior of the doped amalgam samples investigated using polarization measurements. The results indicate that addition of small amount of cockles shell CS powder improves the corrosion behavior due to a homogeneous distribution of the powder particles with metallic powders.

Keywords: Dental amalgam; Cockles shell powder; Artificial saliva; Corrosion.

Introduction

The impact of corrosion on industrial applications and personal security is well-recognized and subject to constant investigations. Corrosion can be a source of serious environmental contamination by heavy metals and different undesirable materials. Contaminations in pharmaceutical and food industries are some examples threatening personal security and health [1]. Corrosion has been recognized in a wide range of materials like composites, ceramics and different types of metallic alloys. Corrosion of dental amalgam is one such source of hazardous contamination with mercury in human body [1]. Research has been devoted to enhancement of the mechanical and aesthetic properties of the dental amalgam through doping with nanoparticles and other body-compatible materials [2].

However, corrosion of such material is an important aspect to be addressed especially in the case of reinforced dental amalgam. Previous studies on corrosion of undoped dental amalgam are available [3-6].

In this work, commercial dental amalgam doped with $CaCO_3$ powder from mechanically and thermally treated cockles' shells. The corrosion behavior of the doped amalgam investigated at different weight percent of cockle shells 14.2, 28.5 and 42.8wt% in saliva at 37ºC.

Experimental work

Cockles' shells powder produced from crushed shells after washing with water to remove dust and undesired foreign contaminants. The clean shells were primarily crushed to small pieces using JFSD – 100 crusher. The crushed shells were then subjected to a dry ball milling at 200 rpm for 24 hours to produce a fine powder. The obtained powder sieved for 15 minutes to discard large particles and to obtain a relatively fine powder of finite size distribution. Cockles' shells powder then treated thermally at 400 ˚C for 12 hours to obtain a relatively clean powder. The treated powder investigated by Inductively Coupled Plasma (ICP) spectroscopy measurements to obtain its compositional structure.

Commercial dental amalgam, composed of 56.7 wt. % of Ag, 28.6 wt. % of Sn and 14.7 wt. % of Cu, was used in this work. All specimens were prepared inside a conventional amalgamator. Cockles' shells powder added at three different weight ratios substituting equal amount of the amalgam powder prior to operation of the amalgamator. The percents of the cockles' shells powder in amalgam were 14.2, 28.5 and 42.8 wt%.

The composite specimens mounted using pyrex-polymer for corrosion test to isolate all side but one and then a hole made in mounted specimens for electrical connection. The composites surface polished carefully to a shine appearance due to reduce the surface asperities and protrusions at a micro-scale.

Modified Fusayama artificial saliva was used in the present investigation as a corrosion medium [7, 8]. Each liter of this saliva is composed of 0.4g KCl, 0.4g NaCl, 0.906 g $CaCl_2.2H_2O$, 0.69 g $NaH_2PO_4.2H_2O$, 0.005g $Na_2S.9H_2O$ and 1g urea. The pH value of this electrolyte is 6.2.

The corrosion behaviors of the pure and the doped specimen investigated WINKING M Lab 200 potentiostat from BANK-ELEKTRONIK instruments. Pure amalgam and three composites used as a working electrode, platinum (Pt) as an auxiliary electrode and saturated calomel electrode (SCE) as reference electrode. A Luggin capillary used to define a clear sensing point for the reference electrode near the working electrode [9]. The electrochemical measurements were performed at a scan rate of 3mV/sec. Results were obtained in terms of corrosion potential ($E_{corr.}$) and corrosion current density ($i_{corr.}$) using Tafel extrapolation method [10].

Microhardness of samples measured by HVS-1000 micro hardness tester from LARYEE according to micro-indentation hardness principle ASTM E384 and ISO 6507. Vickers indenter used in the measurement, which has a diamond shape and is known to produce similar indentations at all testing forces, with a load of 1 kg (9.8N) for 15 seconds in the micro hardness tester. Averages then obtained from these measurements.

Results and discussion

ICP measurement showed that the predominant elements composing the powder are calcium, carbon and fewer quantities of Al, Si and Sr. The estimation of these elements are presented in table 1. These compositions are in agreement with other results from the literature [11].

Table 1. Chemical composition of cockles shell powder obtained from ICP measurement.

Element	CaC	Al	Si	Sr	Mg	Na	Others
% ratio	97.23	1.02	0.63	0.34	0.54	-	0.24

Figure 1 shows evolution of open circuit potential (E_{oc}) over 600 seconds for the four prepared specimens after immersion in artificial saliva at 37°C. The results of E_{oc}, corrosion potentials E_{corr} and corrosion current densities i_{corr} are shown in table 2. Reaching steady state potentials were found to take place within few minutes after immersion of samples in the artificial saliva. The presence of 14.2 and 28.5 wt% of cockle shell CS in amalgam shift the open circuit potential to more active direction. While adding 42.8wt% shifts to more noble.

Table 2: Corrosion parameters for amalgam and amalgam/cockle shell composites with three wt% in artificial saliva at 37°C.

Sample	E_{oc} (mV)	E_{corr} (mV)	i_{corr} (μA.cm^{-2})
Pure amalgam	-302	-811.8	13.52
Amalgam/14.2wt%CS	-640	-610.7	0.0265
Amalgam/28.5wt%CS	-781	-807.3	61.88
Amalgam/42.8wt%CS	-82.0	-512.1	8.30

Figure 2 show Tafel plots for amalgam and composites in artificial saliva at 37 ˚C. Tafel plots emphasize the presence of both anodic and cathodic sites on the surfaces of the samples. At cathodic sites, reduction of hydrogen can occurs due to acidity of saliva according to the following reaction:

$$2H^+ + 2e \rightarrow H_2 \quad ....(1)$$

In addition to reduction of oxygen to water molecules:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \quad ....(2)$$

While at anodic sites dissolution of metals in amalgam can occur such as Ag, Sn and Cu. Mercury diffuses into the alloy particles and reacts with silver, tin and copper, forming various compounds. The exact compounds formed depend on the chemical composition of the powder and on particle shape (which can be spherical or irregular) but are mainly phases of the systems Sn–Hg, Ag–Hg, with Ag–Cu and Ag–Sn phases remaining from the reactants. For the currently used, high copper amalgams, the main reaction is:

$$\gamma\text{-}Ag_3Sn + Ag\text{–}Cu + Hg \rightarrow \gamma_1\text{-}Ag_2Hg_3 + \gamma_2\text{-}Sn_7Hg + \gamma\text{-}Ag_3Sn + Ag\text{–}Cu \quad .....(3)$$

The Sn–Hg phase, which has a relatively low corrosion resistance, then undergoes further reaction, according to

$$\gamma_2\text{-}Sn_7Hg + Ag\text{–}Cu \rightarrow \acute{\eta}\text{-}Cu_6Sn_5 + \gamma_1\text{-}Ag_2Hg_3 \quad .....(4)$$

The microstructure of the dental amalgam is complex, consisting of new microphases, as produced in the reactions above, and the remains of the powder alloy particles, within the γ_1-Ag_2Hg_3 matrix phase. For this reason, and in order to understand better the role of the various phases, individual phases have electrochemical measurements can lead to an improved understanding of the processes that take place at the amalgam electrode surface as well as the influence of surface oxide [12].

Corrosion parameters were measured using Tafel extrapolation method [13]. These parameters indicate that adding CS to amalgam shift corrosion potential to more noble value. Corrosion potential is a thermodynamic parameter, which is a criterion of the extent of the corrosion likelihood under the equilibrium potential. At the same time, the corrosion current density is known as a kinetic parameter, which represents the rate of corrosion under specified equilibrium condition. Any factor that enhances the current value is expected to directly reflect on the corrosion rate on pure kinetic ground. The lowest corrosion current density ($i_{corr.}$) was obtained amalgam with lowest wt% of CS (14.2). This result is due to partial substitution of the metallic *powder* in the dental amalgam with cockles' shells powder. It is important to obtain homogeneity of the CS powder distribution in the amalgam. The lowest weight percent of ceramic materials gave the lowest corrosion rate; this may be due to the inhomogenous structure of an metal matrix composite which must be considered in designing a corrosion protection system. Surface treatments applied to metal matrix composites will encounter reinforcement particles that may disrupt any protective coatings and hinder effectiveness of passive coatings [14].

Optical microscope in Figure 3 shows microscopic images of the surfaces before and after corrosion measurements. Amalgam with lowest addition (14.2wt%) of CS gave more homogeneous compared with other additions 28.5 and 42.8wt%. This homogeneous reduce the anodic and cathodic sites which may be form on amalgam surface in addition to reduction in particles agglomeration. This result was good agreement with the results of corrosion test.

In order to evaluate the susceptibility of the samples to pitting corrosion in artificial saliva, a cyclic polarization curves obtained. Figure 4 shows cyclic polarization of amalgam and amalgam/CS composites, which indicate that best resistance to pitting show in amalgam/14.2wt%CS.

Conclusions

Study the corrosion behavior of metal matrix composites in biomaterials has been investigated by adding cockle shells to amalgam to improve corrosion resistance with three weight percent of cockle shells 14.2, 28.5 and 42.8 wt%. Corrosion behavior was carried out in artificial saliva at 37ºC, the results indicate that the lowest percent gave the highest corrosion resistance depending on corrosion current density values and optical microscopy test.

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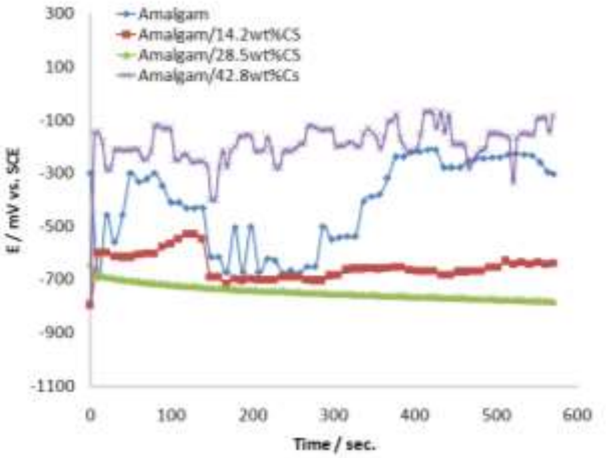

Fig. 1. Potential – time measurements for amalgam and its composites with cockle shells with three weight percents in artificial saliva at 37ºC.

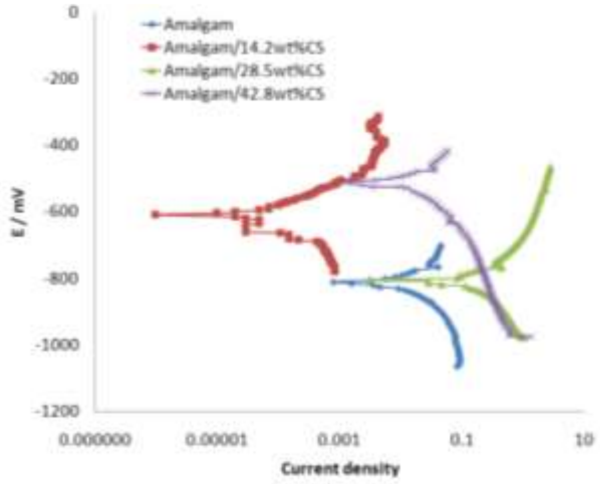

Fig. 2. Tafel plots for amalgam and its composites with cockle shells with three weight percents in artificial saliva at 37ºC.

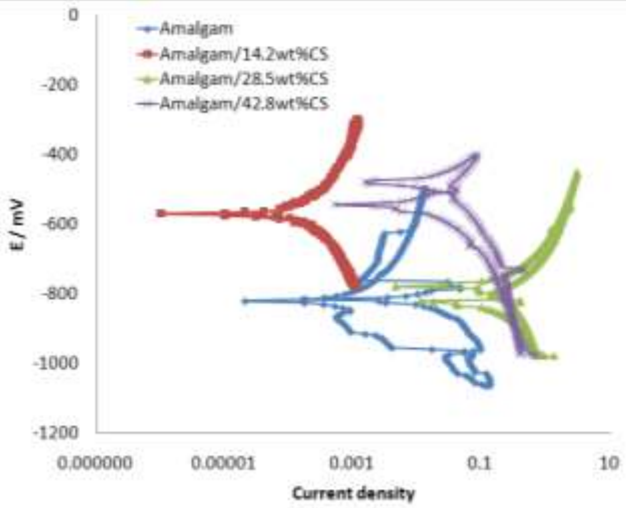

Fig. 3. Cyclic polarization for amalgam and its composites with cockle shells with three weight percents in artificial saliva at 37ºC.

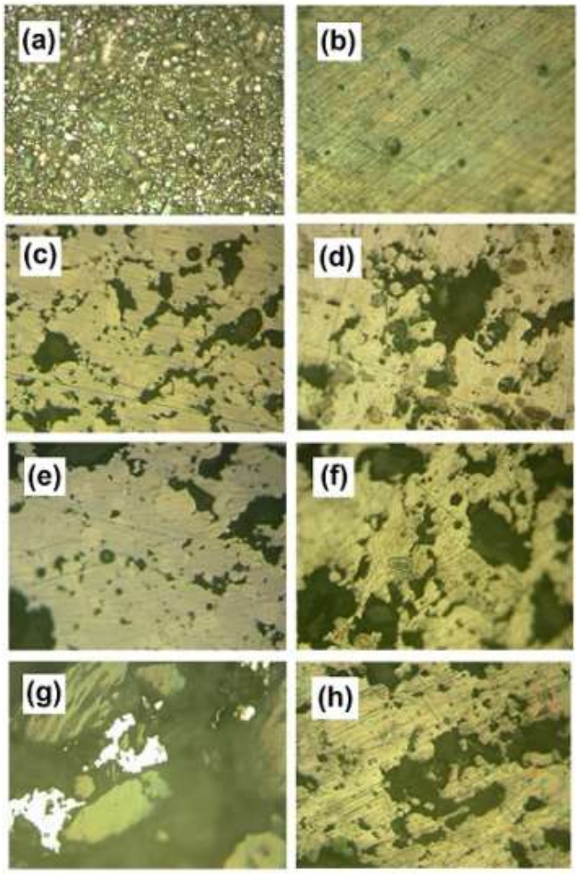

Fig. 4. Optical microscopies of amalgam (a-before corrosion, b-after corrosion), amalgam/14.2wt% CS (c & d), amalgam/28.5wt% CS (e & f) and amalgam/42.8wt% CS (g & h).