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Original Article

Preparation and corrosion behavior evaluation of amalgam/titania nano composite

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ABSTRACT

Background: Many attempts have been performed and continued for improvement of dental amalgam properties during last decades. The aim of present research was fabrication and characterization of amalgam/titania nano composite and evaluation of its corrosion behavior.
Materials and Methods: In this experimental research, nano particles of titania were added to initial amalgam alloy powder and then, dental amalgam was prepared. In order to investigate the effect of nano particle amounts on properties of dental amalgam, proper amount of 0, 0.5, 1, 2 and 3 wt% of titania nano particles were added to amalgam alloy powder and the prepared composite powder was triturated by a given percent of mercury. X-ray Diffraction, Scanning Electron Microscopy and Energy-Dispersive Spectroscopy techniques were use to characterize the prepared nano composites. Potentiodynamic polarization corrosion tests were performed in the Normal Saline (0.9 wt% NaCl) and Ringer's solutions as electrolytes at 37°C. Immersion corrosion tests were also performed immediately 2 h after preparation of cylindrical samples (4 mm in diameter and 8 mm height) via immersion into a 100 ml volumetric flask consisting of artificial saliva.
Results: The results indicated that the current corrosion density of amalgam/titania nano composite changes a bit with adding 1% of nano particles of titania. Also, during the 1st h after preparation, initial released mercury from prepared nano composite dental amalgam decreased.
Conclusion: By adding nano particles of titania and preparing amalgam/titania nano composite as a dental amalgam, corrosion behavior and mercury release during the 2st h after preparation could be improved.

Key Words: Corrosion behavior, dental amalgam, mercury release, nano particles, titania

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INTRODUCTION

Dental amalgam has been used as a restorative material for replacement of the decayed tooth structure for more than 150 years.[1,2] Hence, modified and improvement of its properties has been followed.[3,4] 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.[1,5,6] Up to now, several materials such as Au, In, Pa and organic materials were added to dental amalgam in order to improve its properties.[6-9] Palladium is one of the newest additive materials.[10,11] Pierre *et al*. evaluated the influence of palladium addition and particles morphology on corrosion behavior of dental amalgam. They showed that, adding 0.5 wt% palladium to a high copper amalgam powder improves the corrosion behavior of amalgam up to a period of 10 years.[9] Another new additive material which was used, is Ag-Cu nano powder. Chung *et al*. investigated morphology and electrochemical behavior of Ag–Cu nano particle-doped amalgams. The obtained results indicated that the significant increase in the corrosion resistance of

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Ag–Cu nano particle-doped amalgams indicate the potential of nanoparticle amalgam development.[3]

Titania have good antibacterial properties and is not toxic.[12-14] Also, the antibacterial properties depend on the surface of a material and increases with decreasing the size of particles. Nano particles of titania have more antibacterial properties than micro powder of titania.[14,15] So, it was selected as an additive for dental amalgam. It is expected that by adding the nano particles of titania to amalgam alloy powder in some different amounts, antibacterial properties may be improved. On the other hand, it is thus of interest to investigate the corrosion and electrochemical behavior of prepared nano composites, in comparison with dental amalgam.

The aim of present research was fabrication and characterization of amalgam/titania nano composite and evaluation of its corrosion behavior.

MATERIALS AND METHODS

Sample preparation

In order to prepare the dental amalgam/titania nano composite, Tytin dental amalgam (KerrDental, USA) in plastic capsules and titania nano particle [21 nanometer particle size and surface area >50 m^2/g (Evonike corporation, Germany)] were used. The composition of commercial Tytin powder alloy was 59 wt% silver, 28 wt% tin and 13 wt% copper with a recommended mercury to alloy ratio of 42.5%. Figure 1 shows the morphology and size of the comercial amalgam alloy powder. The amounts of 0.5, 1, 2 and, 3 weight percent of titania nano particles were added to amalgam alloy powder. Weighting was done by a digital balance by 0.0001 g accuracy. Also, a sample was fabricated without the addition of titania nano particles as Tytin dental amalgam. Then, the prepared mixed powder was triturated according to the manufacturer's instructions in a mechanical triturator (digital capsule amalgamator, Farazmehr corporation, Iran) and hand-condensed into a Plexiglass mold with 10 mm×10 mm×3 mm size using a condenser (Φ3 mm, Aesculap, Germany) by one oparator person. One h after condensing, specimens were taken out from the mold and were held for 24 h in the room temperature. Then, they were maintained in the water bath (Eyela Thermistor Temppt T-80) at 37±1°C for one week. Surface preparation consisted of polishing with 2400 and 4000-grit SiC papers with water coolant was done. Then, with Alumina suspension, a smooth mirror-like finish was obtained. The polished samples were washed by distilled water and were cleaned by acetone.

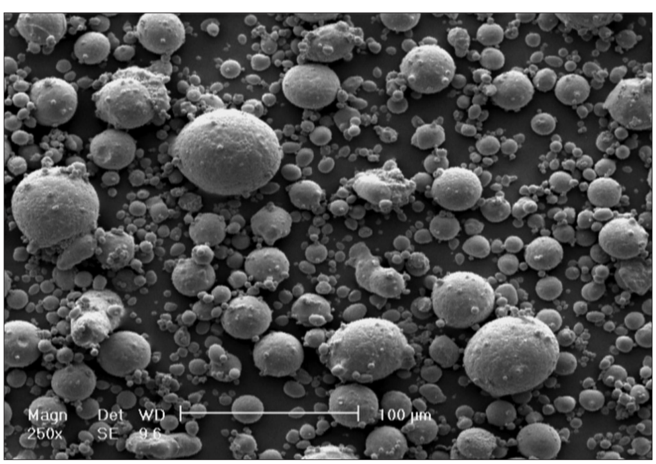

Figure 1: SEM micrograph of commercial Tytin amalgam alloy powder

Characterization of specimens

Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD; Xpert, Philips, Holland) with Cu target (λ=1.542A°) was used to determine the phases in the Tytin dental amalgam and amalgam/titania nano composites and scanning was done from 10° to 80° (2θ); a step size of 0.02° and 2 s step intervals were used. The microstructure, morphology and chemical composition of the prepared spcimens were investigated and characterized using SEM equipped with an X-ray Energy Dispersive Spectrometer (EDS, Seron, AIS 2100, Korea).

Potentiodynamic polarization test

The corrosion and electrochemical behavior of Tytin dental amalgam and amalgam/titania nano composites were examined in a three-electrode glass cell containing Normal Saline (0.9% NaCl) solution as electrolyte at 37±1°C. The reference electrode was a standard Saturated Calomel Electrode (SCE), the counter electrode was a Pt and the working electrode was an amalgam specimen. The used equipment was an electronic potentiostat/galvanosta (PARSTATE 2273, USA). After determining open circuit potential (OCP), dynamic polarization curves were recorded at a potential scanning rate of 0.5 mVs^{-1} begun from 250 mV more cathodic than the OCP. Three replicate tests of each group of specimens were performed. The anodic and cathodic polarization curves were obtained for each specimen. Tafel extrapolation polarization methods determined corrosion potential and corrosion current densities. The mean value and standard deviations of the results were calculated and reported.

Immersion test

For immersion corrosion test, the samples were prepared as mentioned above, but the mold was cylindical with 4 mm in diameter and 8 mm higth made of stainless steel. These samples removed from the mold about 2 h after preparation and immersed into a 100 ml volumetric flask consisting of artificial saliva. Table 1 shows the compositon of artificial saliva. Then, the volumetric flasks with the immersed samples, were placed into a water bath at 37±1°C for 2 h. After that, the samples were eliminated from the solutions and the each solution was evaluted in order to determine the concentration of released mercury ion from sample. Three replicate tests of each group of specimens were performed. The mean value and standard deviations of the obtained results were calculated. Inductively coupled plasma (ICP-OES) was used to determine the concentration of released mercury ion from dental amalgams.

RESULTS

As it could be seen in Figure 1, the particle morphology of Tytin amalgam alloy powder is spherical. The size of initial amalgam alloy particles was measured by Image Tools analysis software and it was obtained in the rang of 3 to 55 µm. The XRD pattern of commercial Tytin amalgam alloy powder is shown in Figure 2. The XRD patterns of Tytin dental amalgam and amalgam/titania nano composies can be observed in Figure 3.

SEM micrograph of Tytin dental amalgam is shown in Figure 4 and SEM micrographs of the prepared amalgam/titania nano composites are shown in Figure 5. Also, SEM micrographs in the back-scattered mode of Tytin dental amalgam and amalgam/titania nano composites are shown in Figure 6.

For evaluation of the different dental amalgam phases and the type of distribution of titania nano particle, EDS analysis technique was used for 2 types of nano composites [Figures 7 and 8]. Also, the EDS spectrum of the first area is shown for each specimen [Figures 7 and 8].

The electrochemical potentiodynamic polarization curves of Tytin dental amalgam and amalgam/titania nano composites in the Normal Saline solution are shown in Figure 9. The respective corrosion current densities and corrosion potentials were listed in

Table 1: Artificial saliva's composition[16]

Components	Concentration (mg/l)
NaCl	125.6
KCl	963.9
KSCN	189.2
KH_2PO_4	654.5
Uréia	200.0
$Na_2SO_4.10H_2O$	763.2
NH_4Cl	178.0
$CaCl_2$, $2H_2O$	227.8
$NaHCO_3$	630.8

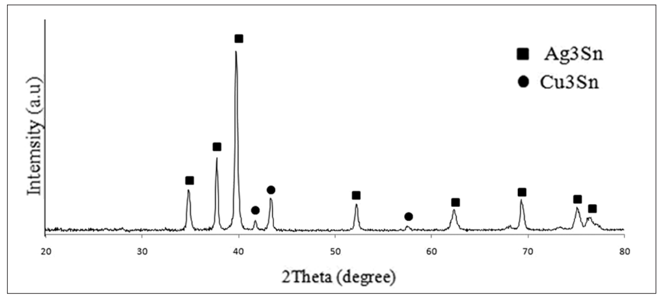

Figure 2: XRD pattern of Tytin amalgam alloy powder

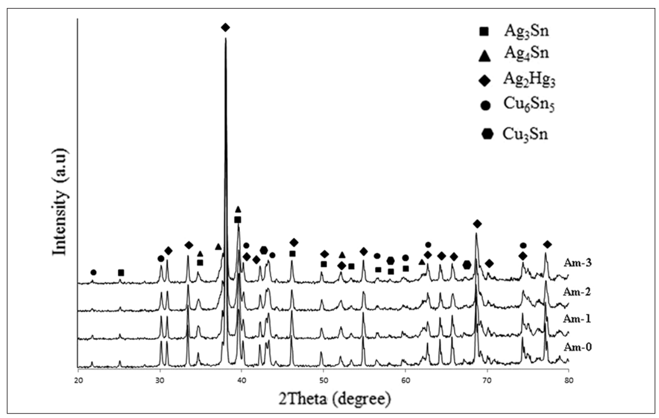

Figure 3: XRD patterns of Tytin dental amalgam as a reference dental amalgam (Am-0) and amalgam/titania nano composite prepared by adding 1, 2 and 3 wt% nano particles of titania (Am-1, Am-2 and, Am-3)

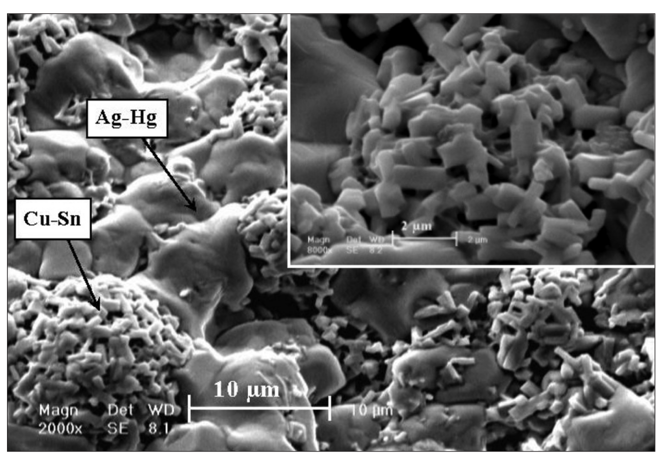

Figure 4: SEM micrographs of Tytin dental amalgam

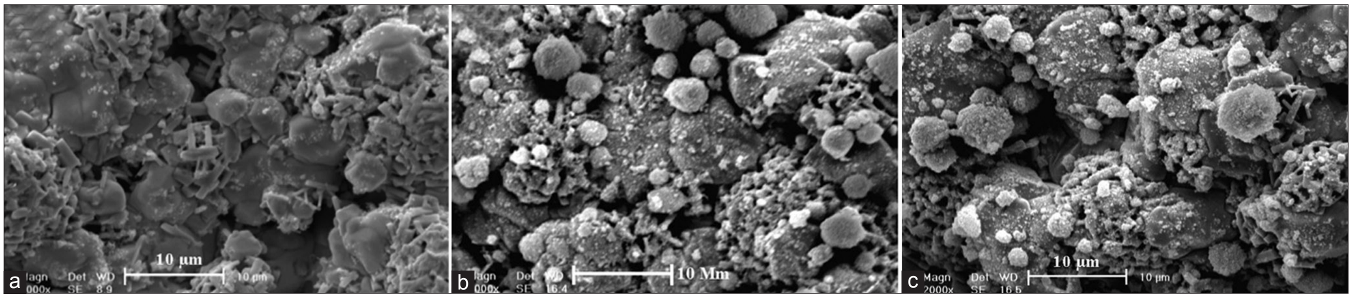

Figure 5: SEM micrographs of prepared amalgam/titania nano composites; (a) 1 wt%, (b) 2 wt%, (c) 3 wt% of titania nano particles

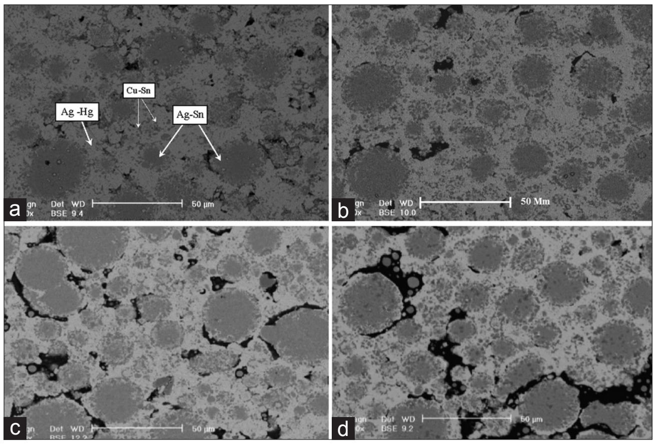

Figure 6: SEM micrographs in the back-scattered mode of; (a) Tytin dental amalgam, (b) amalgam/titania nano composite with 1 wt%, (c) amalgam/titania nano composite with 2 wt% and, (d) amalgam/titania nano composite with 3 wt% of titania nano particles

Table 2. These curves were selected because their extracted data was the most nearest to the mean values of the corrosion current densities of each group of specimens. The similar curves of Tytin dental amalgam and amalgam/titania nano composites in the Ringer's solution are plotted in Figure 10, too. The respective corrosion current densities and corrosion potentials in Ringer's solution were listed in Table 3. The corrosion current density was achieved for Tytin dental amalgam was in close data in other investigations.[17] The results showed statistically significant differences between the mean corrosion current densities values of 3 different groups of the samples ($P<0.05$).

Data from potentiodynamic polarization curve of Tytin dental amalgam in Normal Saline shows that it has a corrosion current density equivalent of 0.71 (0.11) µA/cm^2 [Figure 9], whereas the amalgam/titania nano composites samples with 2 and 3 wt% titania possessed more corrosion current density (i_{corr} = 11.3(0.721) µA/cm^2 and 16.6(0.812) µA/cm,^{2} respectively [Figure 10] in comparison with specimens of amalgam/titania nano composites with lower amounts than one percent of titania nano particles. This means that Tytin dental amalgam and nano composites with lower amounts than 1% of titania nano particles possessed more corrosion resistance in comparison with other nano composites.

Table 2: Mean values (standard deviation) of corrosion current densities and corrosion potentials of the samples in normal saline solution at 37±1°C

Sample code	Additive (wt%)	i_{Corr} (µA/Cm^2)	E_{Corr} (mV)
Am-0	0	0.71 (0.075)	−198
Am-0.5	0.5	0.78 (0.035)	−174
Am-1	1	0.92 (0.05)	−164
Am-2	2	11.3 (0.721)	−100
Am-3	3	16.6 (0.812)	−85

Table 3: Mean values (standard deviation) of corrosion current densities and corrosion potentials of the samples in Ringer's solution at 37±1°C

Sample code	Additive (wt%)	i_{Corr} (µA/Cm^2)	E_{Corr} (mV)
Am-0	0	0.72 (0.050)	−198
Am-0.5	0.5	0.77 (0.066)	−146
Am-1	1	0.92 (0.077)	−132
Am-2	2	11.2 (0.643)	−170
Am-3	3	16.3 (0.693)	−185

The concentrations of released mercury from Tytin dental amalgam and prepared amalgam/titania nano composites were determined, which are summarized in Table 4.

DISCUSSION

SEM micrographs in the back-scattered mode of Tytin dental amalgam and amalgam/titania nano composites reveal a homogeneous distribution of dental amalgam phases and did not have any change in phase distribution by adding nanoparticles of titania [Figure 6]. The dental amalgam phases were identified by lable in Figures 4 and 6. Both of Tytin dental amalgam and amalgam/titania nano composite contain Ag-Hg, Sn-Cu and Ag-Sn phases and it was in close

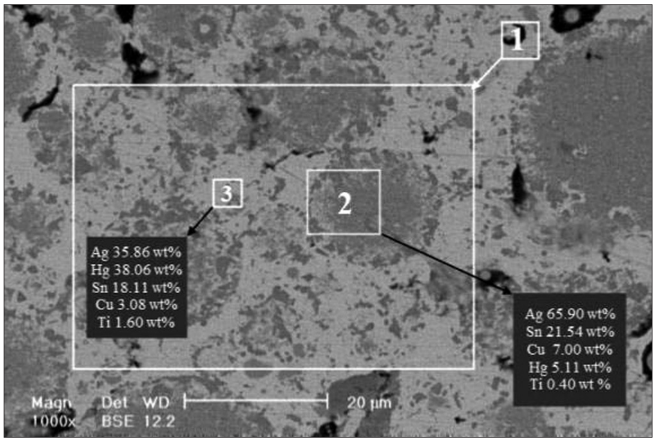

Figure 7a: EDS results of amalgam/titania nano composite prepared by 0.5 wt% of titania nano particles. SEM micrograph and EDS results for regions of 2 and 3,

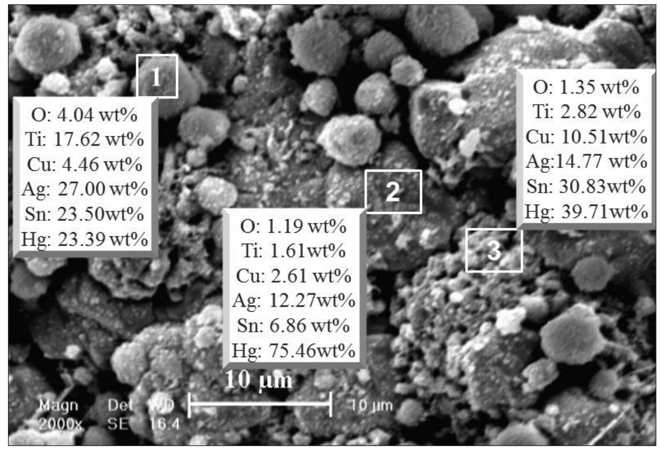

Figure 8a: EDS results of amalgam/titania nano composite prepared by 2 wt% of titania nano particles; SEM micrograph and EDS results of 1, 2 and 3 region

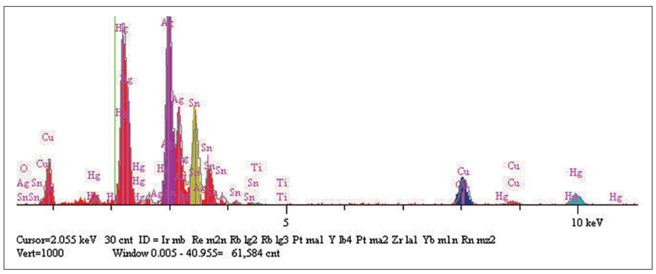

Figure 7b: EDS results of amalgam/titania nano composite prepared by 0.5 wt% of titania nano particles. Spectrum of EDS analysis of the region 1

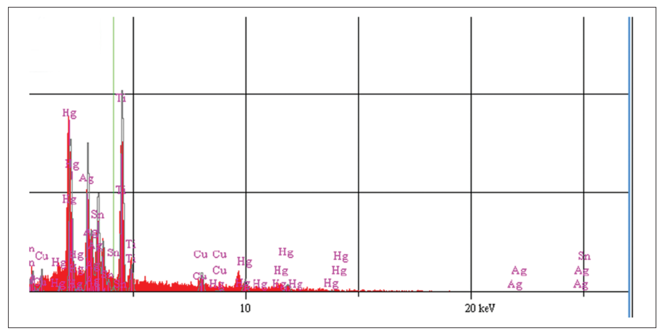

Figure 8b: EDS results of amalgam/titania nano composite prepared by 2 wt% of titania nano particles (b) spectrum of EDS analysis for the third region

Table 4: Mean values (standard deviation) of the concentration of released mercury from Tytin dental amalgam and amalgam/titania nano composites

Sample code	Mean value (standard deviation)
Mercury concentration (mg/ml)	
Am-0	0.124 (0.022)
Am-1	0.06 (0.012)
Am-2	0.064 (0.017)

agreement with the findings of previous studies.[1,4-6]

In order to appraising distrubtion of titania in the dental amalgam, EDS analysis was used for a prepared nano composite by 0.5 wt% nano particles of titania [Figure 7]. Three areas was selected; (1) First area contains of all present phases in the dental amalgam; (2) Second area includes mainly γ and, (3) Third area chiefly contains γ and ή. The results of total area was shown 45.63 wt% Ag, 20.03 wt% Sn, 6.05 wt% Cu, 26.25 wt% Hg and 1.43 wt% Ti, thus present of 1.5 wt% Ti in the nano composite is logical. The second area have more γ phase, which it is expectable to have more Ag and Sn in the EDS results: There are 21.5 wt% Sn and almost 65.9 wt% Ag. In addition, the amount of Ti was a little (about 0.4 wt%). The matrix of a dental amalgam mainly have γ_1, so it would be more mercury in the EDS analysis of this area. Also, there are approximately 1.6 wt% titanium and 3.2 wt% O in the matrix, therefore, it can be concluded that nanoparticles of titania was significantly existed in the matrix.

It has been observed, two phases in SEM micrograph of Tytin dental amalgam: The Ag-Hg crystals and Cu-Sn, so that they cover unreacted spherical alloy particles [Figure 4].[18] These phases were found out in all of amalgam/titania nano composites while they were covered by titania and by increasing titania, the phases were covered more and more [Figure 5]. Also, in the high amounts of titania nano particles, were made some changes: Some large porosities produceed in the near of unreacted alloy particles. Furthermore, it was seen some small spherical particles, individually [Figures 5 and 6]. To investigating this concept, EDS analysis was used [Figures 7 and 8]. The EDS results of amalgam/titania by 2 wt% additive indicated that

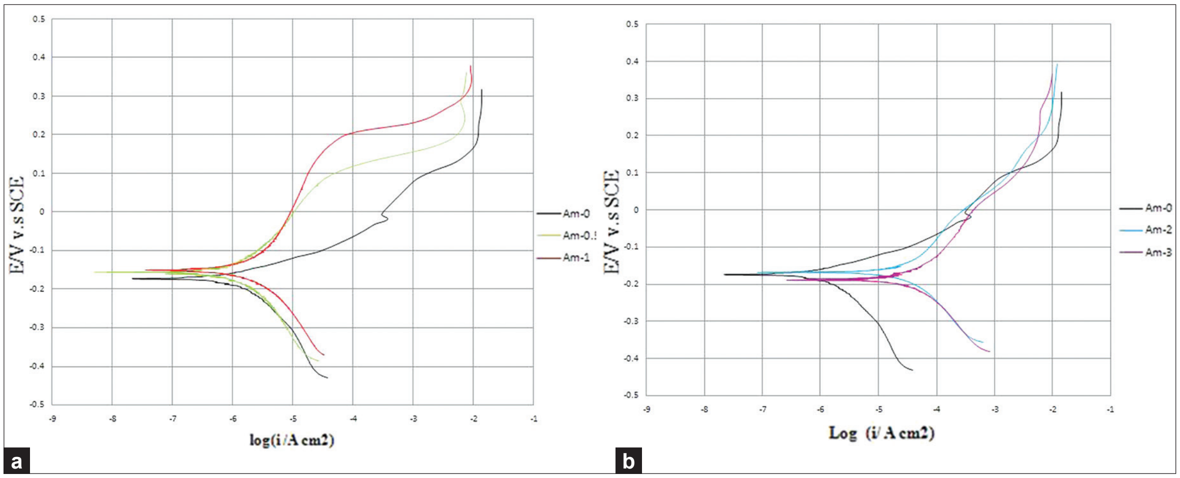

Figure 9: Potentiodynamic polarization curves of Tytin dental amalgam and nano composites with a scan rate at 0.5 mV s^{-1}. (a) Tytin dental amalgam and nano composites with 0.5 and 1 wt% and (b) Tytin dental amalgam and nano composites with 2 and 3 wt% of titania nano particles in the Normal Saline solution at 37±1°C

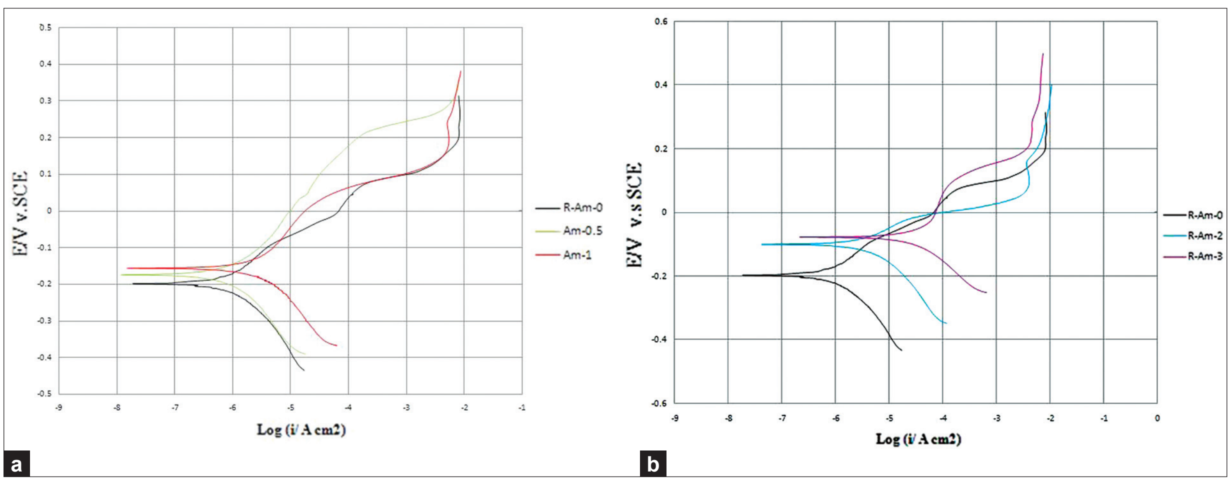

Figure 10: Electrochemical Potentiodynamic polarization curves of Tytin dental amalgam and nano composites with a scan rate at 0.5 mV s^{-1}. Tytin dental amalgam and nano composites with 0.5 and 1 wt% and (b) Tytin dental amalgam and nano composites with 2 and 3 wt% of titania nano particles in Ringer's solution at 37±1°C

area 1 (concluding individual spherical particles) have more Ag and Sn but have lower Cu than the other area. Therefore, this area is related to Ag-Sn(γ) phases. Besides, mentioned area have high amounts of titania (about 18wt %), whereas in the other region (2 and 3 that they consist of mostly Ag-Hg and Cu-Sn phases, respectively), this amount decrease to 6 times. So, it was indicated that by high amounts of additive, titania could act as a barrier for linking the unreacted alloy particles to the matrix phase. Hence, large porosities were made near this particles. These porosities weaken properties of dental amalgam, because porosity have the lowest corrosion resistance and led to decrease strength.[1,19]

Corrosion behavior of amalgam/titania nano composite was evaluated by the electrochemical corrosion test in 2 types of solution as electrolyte [Figures 9 and 10]. There was not a significant difference between Tytin dental amalgam and amalgam/titania nano composites consisting of 0.5 wt% or 1 wt% nano particles of titania, but by increasing the weight percent of titania nano particles, the corrosion current density increased and therefore, corrosion rate would be more. This occurrence can be related to changes in microstructure of nano composite by high level of additives. As mentioned above, it makes large porosities in near the alloy particles and these weaken properties of dental amalgam, because the porosity have the lowest corrosion resistance and led to decrease strength.[19] So, presence of large porosities near the alloy particles is responsible of decline in corrosion resistance.

The polarization curves of Tytin dental amalgam and nano composites were earned in Ringer's solution, too [Figure 10]. It could be seen that, the same trend in the Ringer's solution and it confirms the obtained results related to the Normal Saline solusion. Figure 11, shows SEM micrographs of Tytin dental amalgam and amalgam/titania nano composite consisting of 1 wt% titania nano particles, before and after potentiodynamic polarization test. In the both of them, dark regions could be observed around the unreacted alloy particles which demonstrated that Cu-Sn phases were corroded.[20] Additionally, pitting corrosion was observed in mentioned micrographs. This kind of corrosion leads to the creation of small holes in the metal. This driving power for pitting corrosion is the depassivation of a small area, which becomes anodic while an unknown but potentially vast area becomes cathodic, leading to very localized galvanic corrosion. These pits were specifed by white arrows. These are on the surface of unreacted alloy particles.

In recent decades, the biocompatibility of dental amalgam and effect of mercury on the human body was very challenging subject.[17,21,22] Investigations on the released mercury from dental amalgam were shown that the level of released mercury after placement in the dental cavity is very high, but by passing time it decreased.[17,21,22] Subsequently, it was decided to evaluation the level of released mercury from Tytin dental amalgam and nano composite. The concentrations of mercury are summarized in Table 4. Data from this test shows that present of nano particles of titania decreased level of released mercury from dental amalgam so that the mercury level from 0.124 mg/ml decline to about 0.06 mg/ml for nano composites. This changes can be related to covered phases of dental amalgam by titania nano particles. Indeed, nano particle of titania hinder releasing of mercury and it seems to have this behavior until nano particles of titania present on the dental amalgam phases surfaces.

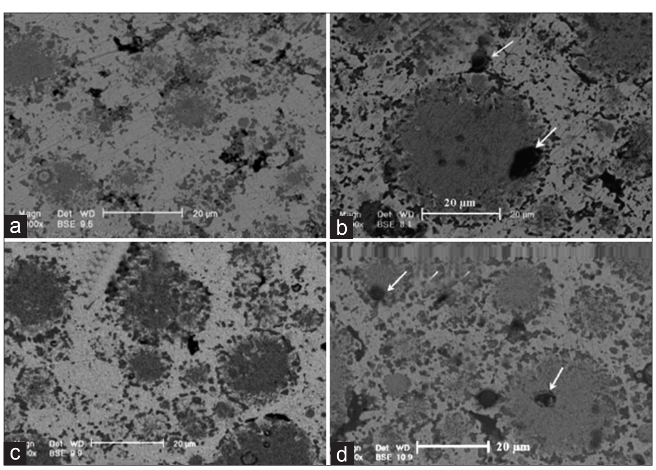

Figure 11: SEM micrographs of Tytin dental amalgam (a) before and, (b) after potentiodynamic polarization test and SEM micrographs of amalgam/titania nano composites consisting 1 wt% titnia (c) before and, (d) after potentiodynamic polarization test

CONCLUSION

This report presents a new investigation about the synthesis of amalgam/titania nano composite. The results showed that phases and distribution of dental amalgam phases do not change by adding nano particles of titania. Also, the results indicated that corrosion current density in nano composite consisting of 1 wt% and lower than it, changes a little while by increasing more than one present additive, corrosion current density changes significantly. Hence, it can be concluded that small amount of titania nano particles is suitable and seems to be a promising action to improve the properties of this dental material. Additionally, released mercury from dental decreases in due to present of titania nano particles on the dental amalgam phases surfaces. The results of present study suggest that amalgam/titania nano composite with 1% nanopaticles of titania provide a better characters for dental applications.

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REFERENCES

1. Craig RG. Restorative Dental Materials, 11th ed. St. Louis, Missouri: Mosby-Year Book, Inc.; 2004.
2. Acciari HA, Guastaldi AC, Brett CM. Corrosion of dental amalgams: Electrochemical study of Ag–Hg, Ag–Sn and Sn–Hg phases. Electrochimica Acta 2001;46:3887-93.
3. Chung KH, Hsiao LY, Lin YS, Duh JG. Morphology and electrochemical behavior of Ag–Cu nanoparticle-doped amalgams. Acta Biomaterialia 2008;4:717-24.
4. Chern Lin JH, Chen FYY, Chiang HJ, and Ju ChP. Effect of ball milling on structures and properties of dispersed-type dental amalgam. Dental Materials 2011; 27(4): 65–79.
5. Fathi MH, Mortazavi V. Effect of Surface Characteristics and Clinical Procedures on Corrosion Behavior of Dental Amalgams. Surface Engineering 2002;18:363-7.
6. Mortazavi V, Fathi MH. The effect of clinical operation on the corrosion resistance of dental amalgam. Dent Res J 2003;1:47-55.
7. Youdelis WV. Dental powder composite and amalgam, USA patent, patent number: 4039329, 1977.

8. Colon P, Pradelle-Plass N, Galland J. Evaluation of the long term corrosion behavior dental amalgams: Influence of palladium addition and particle morphology. Dent Mater 2003;19:232-9.
9. Oxman JD, Fundingsland JW. Adhesive amalgam system, USA Patent, patent number: 5662886, 1997.
10. Chern Lin JH, Chen KI, Ju CP. Particle size effect on structure and properties of dispersed Pd-containing dental amalgam. Biomaterials 2002;23:597-608.
11. Koikea M, Ferracaneb JL, Adeyb JD, Fujiia H, Okabec T. Initial mercury evaporation from experimental Ag–Sn–Cu amalgams containing Pd. Biomaterials 2004;25:3147-53.
12. Thompson TL, Yates JT. TiO2-based photocatalysis: Surface defects, oxygen and charge transfer. Topics in Catalyst 2003;35:197.
13. Amin SA, Pazouki M, Hosseinnian AT. Synthesis of TiO2–Ag nanocomposite with sol–gel method and investigation of its antibacterial activity against *E. coil*. Powder Technol 2009;196:241-5.
14. Skaa AZ, Kowalskaa E, Sobczakd JW, Ckab IL, Gazdac M, Ohtanie B, *et al*. Silver-doped TiO2 prepared by microemulsion method: Surface properties, Bio-and photoactivity. Sep Purif Technol 2010;72:309-18.
15. Beydoun D, Amal R, Low G, McEvoy S. Role of nanoparticles in photocatalysis. J Nanopart Res 1999;1:439-58.
16. GaL JY, About a synthetic saliva for *in vitro* studies. Talanta 2001; 53: 1103–1115.
17. Mortazavi V, Fathi MH. The effective parameters on the corrosion behavior of dental amalgam. Beheshti Univ Dent J 2005;22:65-71.
18. Anusavice KJ. Phillips' Science of Dental Materials. 10th ed. Chap. 17. Philadelphia: W.B. Saunders Company; 1996. p. 361-385.
19. Gjerdet NR, Egdahl TH. Porosity, strength, and mercury content of amalgam made by different dentists in their own practice. Dental Materials 1985;11:150-3.
20. Chern Lin JH, Marshall SJ, Marshall GW. Microstructures of high copper amalgams after corrosion in various solutions. Dent Mater 1987;3:176-81.
21. Fathi MH, Mortazavi V. A Review on Dental Amalgam Corrosion and its Consequences. J Res Med Sci 2004;9:42-51.
22. Spencer AJ. Dental amalgam and mercury in dentistry. Aust Dent J 2000;45:224-34.

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