Determination of optimum Al content in HA-Al₂O₃ nanocomposites coatings prepared by electrophoretic deposition on titanium substrate

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Abstract
In this research work, Hydroxyapatite (HA)-Al₂O₃ bio nanocomposite coatings were coated on titanium substrate by electrophoretic deposition (EPD) and reaction bonding process. The reaction bonding process densifies the coating and creates small uniform porosities. HA-Al₂O₃ bio nanocomposite coatings were analyzed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). For the coatings sintered for 2 hours at 850°C, XRD results demonstrated no significant HA decomposition. The adhesion strength increased from 10.2 MPa to 25 MPa. It was determined that 50 wt.% of Al is the optimum content for producing free-of-crack composite coatings on the titanium surface as shown by SEM examination.

KEYWORDS
Alumina, Apatite, Crack growth, HA-Al₂O₃ bio nanocomposite

1 | INTRODUCTION

The functions of diseased and broken calcified tissues, such as bone and teeth, can be restored by applying orthopedic and dental implants. The good fixation of these implants in the body depends on the presence of a stable and powerful interface between the bone and the implant.¹,² Bio inert metallic implants are used as high load bearing bones because of their superior strength, bio compatibility, and corrosion resistance.³,⁴ Metal implants have been applied in orthopedics due to their excellent toughness and mechanical strength against bioactive ceramics.⁵,⁶ The implants made by titanium and its alloys have better biocompatibility, corrosion resistance, and mechanical properties than other metallic implants.⁹,¹⁰ Hydroxyapatite (HA)-coated titanium implants are a favored option for biomedical applications due to its preferential biocompatibility and osteoconduction.¹¹-¹⁶ Among different methods utilized for HA-coated implants, electrophoretic deposition (EPD)¹⁷-²⁵ is a cost-effective method for generating a uniform HA coating on a metal substrate even with complex geometric shapes.²²,²⁶ However, the HA coatings still have some disadvantages such as the release of toxic elements from metal substrate, thermal expansion mismatch between metal substrate and HA coating, and decomposition of the HA coating at high temperature which is an inherent, inevitable part of production process.²⁷,²⁸ To solve these problems, several studies have been conducted, such as micro arc TiO₂ and anodic Al₂O₃ between bioactive HA coating and metal substrate, which led to some helpful results.²⁹-³¹ The problems caused by the shrinkage of ceramics during sintering can be solved by a reaction bonding process. When sintering process performs in an oxidizing air atmosphere, the metal phase changes to the metal oxide phase which is sintered and bonded to the substrate. Volume expansion created by the Al→Al₂O₃ reaction compensate the sintering shrinkage between coating and substrate. Therefore, low-shrinkage Al₂O₃ ceramics are produced.³²,³³ In this research project, the suspensions containing 20 g/L of HA nanoparticles and Al nanoparticles were prepared by different compositions. Isopropanol and acetone with the ratio of 50/50 and iodine (0.6 g/L) were used as a medium...
suspension and dispersant, respectively. HA-Al₂O₃ bio nanocomposite was coated on the titanium surface by EPD and reaction bonding process. Increasing the Al content in nanocomposite coatings decreased the cracks on the surface of coatings, as in HA-50 wt.% Al coatings, free-of-crack surface was obtained.

2 | EXPERIMENTAL

2.1 | Materials

For this study, HA nanopowder containing Ca(NO₃)₂·4H₂O and (NH₄)₂HPO₄ was produced by the chemical precipitation method. Figure 1 shows the detail of experimental procedure and the conditions of HA nanopowder produced by this technique. Then, the resulting powder was characterized after calcination by X-ray diffraction

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**TABLE 1** Suspensions used for the preparation of HA-Al₂O₃ coatings

<table>
<thead>
<tr>
<th>Suspension</th>
<th>HA powder (Wt. %)</th>
<th>Al powder (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>S2</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>S3</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>S4</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>S5</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

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**FIGURE 1** Modified chemical precipitation route for HA powder preparation

**FIGURE 2** The X-ray diffraction pattern of nano-HA particles
2.2 | Suspension preparation and the deposition

The suspensions containing 20 g/L of HA nanoparticles and Al nanoparticles were prepared by different compositions (listed in Table 1) in isopropanol (99.9%; Merck, Darmstadt, Germany) and acetone (99%; Merck) with the ratio of 50/50. PEG (0.2 g/L; Merck, reagent grade) and iodine (0.6 g/L; Merck) were used as dispersant and binder, respectively. Then, the mixture was magnetically stirred for 24 hours. Finally, the suspensions were dispersed by an ultrasonic device (Bandelin Sonorex Digitec, Berlin, Germany) for 30 minutes. Titanium plates (grade 2, ASTM B265 pure Ti) were cut with a size of $30 \times 10 \times 0.8$ mm and used as substrate materials. The titanium plates were sandblasted and cleaned by acetone, using an ultrasonic device. They were used as cathode for EPD and the anode was a stainless steel plate. The distance between the electrodes was 2 cm. EPD process was carried out at a constant voltage of 30 V for 40 seconds. Then, coated specimens were dried at room temperature. Then specimens were placed in a furnace in air and heated to 660°C with a rate of 2°C/min and kept at this temperature for 2 hours for the oxidation of Al to Al$_2$O$_3$. Thereafter, the specimens were placed in a tube furnace and the temperature increased with the same rate up to 850°C and held for 2 hours in an argon atmosphere for sintering. Finally, the specimens were cooled to room temperature in the furnace with a rate of 1°C/min.

2.3 | Characterization

Surface and cross-section morphologies of coatings were examined by Mira3 Tescan FESEM (Czech Republic). Chemical composition was analyzed by EDX (Oxford, UK) connected to the FESEM. Phase composition of the coatings was analyzed by XRD (APD 2000 GNR, Italy) using a Cu Kα radiation, with a scan step size of 0.02. The bonding strength of the coated specimens was tested in accordance with ASTM-C633. The value of bond strength was measured using a Universal Testing Machine (Zwick/Roell Z010, Ulm, Germany) with a crosshead rate of 1 mm/min. The failure force (F) was determined when the coating was isolated. The bonding strength ($\sigma_f$) was calculated by Equation 1:

$$\sigma_f = \frac{F}{A}$$

FIGURE 3 FE-SEM of hydroxyapatite nano powder

FIGURE 4 XRD patterns of the composite coatings result than HA/Al suspensions before heating
where $F$ is the failure force and $S$ is the surface of isolated coating.

MG-63 osteoblast cells (NCBI C555 Pasteur Institute of Iran) were used for cell culture test. To determine the toxicity of samples and their effects on cell growth and proliferation, the direct contact method was used. The specimens were sterilized in an autoclave. For MTT (3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyl tetrazolium bromide) test, $2 \times 10^4$ cells were placed in a volume of 100 mL culture medium on each of the sterilized samples in 12-well plates. Then, the samples were placed in an incubator at 37°C for 4 hours until the cells attached to the surface of specimens. After ensuring cell adherence, 2 ml of culture medium was added to each well. The culture medium on cells was discharged as much as possible after 2 and 4 days, and 400 µL MTT (Sigma, St. Louis, MO) with a concentration of 5.0 mg/ml was poured in each well in the incubator for 4 hours. After 4 hours, the solution on the cells was removed and isopropanol was added to them to dissolve the created purple crystals. The plates were placed on a shaker device for 15 minutes to dissolve the precipitated MTT completely. Then, 100 µL of purple solution from each well was transferred to a 96-well plate. Thereafter, the amount of material dissolved in isopropanol was measured, using a micro plate reader (STAT FAX 2100, USA) with a wavelength of 570 nm. The wells with a large number of cells showed optical density (OD) higher than the wells...
with a lower number of cells. Therefore, wells with higher cells were determined by the following equation (Equation 3) and compared with the control sample (blank). It should be noted that each sample was repeated 3 times.

\[
\text{Toxicity\%} = \left(1 - \frac{\text{mean OD of sample}}{\text{mean OD of control}}\right) \times 100 \quad (2)
\]

\[
\text{Viability\%} = 100 - \text{Toxicity\%}
\]

### RESULTS AND DISCUSSION

Figure 2 shows the XRD result of HA nanopowders synthesized by the precipitation method. It shows that there are no other phases except HA that has hexagonal crystallographic structure with a space group P63/m. The mean crystallite size \(d\) of the synthesized particles was calculated by Scherrer Equation:

\[
d = \frac{0.94\lambda}{b\cos\theta} \quad (3)
\]

where \(\lambda\) is the wavelength (Cu K\(\alpha\)), \(b\) is the full width at half maximum of the HA lines, and \(\theta\) is the diffraction angle. The size of crystallites is about 50 nm. Figure 3 shows the FE-SEM images of HA nanopowders synthesized by the precipitation method. The particles have nearly spherical morphology with a size of
approximately 60 nm. X-ray diffraction results of the coatings, before and after heating at 650°C, and after sintering at 850°C in argon, are presented in Figures 4-6. As can be seen, before sintering, in addition to the hydroxyapatite peaks ($\theta = 31.717, 32.155, 32.8, 39.72, 46.62$), aluminum ($\theta = 38.488^\circ, 44.74^\circ, 65.12^\circ$ and $78.26^\circ$) alumina and titanium peaks are also observed. It shows that a small amount of aluminum powder changes alumina during milling, and titanium peaks are related to the Ti-substrate. In the spectra, as can be seen, the amount of hydroxyapatite decreases, and the amount of Al increases, which is logical. Moreover, as can be seen in Figure 5, after heating at 650°C, the aluminum peak at $\theta = 38.2$ is invisible, which could be related to the changing of Al phase to $\text{Al}_2\text{O}_3$. Furthermore, the presence of a peak at $\theta = 37.9$ in the XRD pattern of the heated sample at 650°C is due to the presence of alumina phase, showing that $\text{Al}_2\text{O}_3$ has been produced when Al particles are converted into $\text{Al}_2\text{O}_3$. The appearance of peaks of cubic-$\text{Al}_2\text{O}_3$ in the patterns confirm the occurrence of oxidation of Al to $\text{Al}_2\text{O}_3$ during sintering and that most of the Al particles were oxidized into $\text{Al}_2\text{O}_3$. In order to work of E. Karimi and J.-C. Huang.\textsuperscript{25,33} In addition, Ti atoms in the substrate have been oxidized and converted into $\text{TiO}_2$ during sintering at 850°C. As shown in Figure 6, after sintering of the green HA/Al coating at 850°C, no tri-calcium phosphate (TCP) phase is observed. Figure 7 shows the FESEM images of HA coating and HA-$\text{Al}_2\text{O}_3$ composite coatings after sintering at 850°C. The HA grains are brighter and the alumina grains are the dark ones. As it can be observed for HA-50 wt.% Al nanocomposite coating, a uniform microstructure without any cracks and agglomeration formations has been produced. As can be seen,
cracks are observed on the surface of other HA coatings. The results confirmed that HA coating has a tendency to crack, which is due to the mismatch shrinkage during the sintering process between the coat and substrate.\textsuperscript{39,40} Increasing the Al content in coatings decreased the cracks on the surface of coatings, as in HA-50\% Al coatings, no cracks were observed. Thermal expansion coefficients (CTE) of HA-Al\textsubscript{2}O\textsubscript{3} decreased as the amount of Al\textsubscript{2}O\textsubscript{3} increased. The CTE of the metal and the ceramic coatings are presented in Figure 8. The CTE of Ti is close to that of the composite containing 40\% Al\textsubscript{2}O\textsubscript{3}. With increasing Al\textsubscript{2}O\textsubscript{3} to 50\% Al, CTE of HA decreases from 9.36 \times 10^{-6} \degree\textsuperscript{C} to 8.17 \times 10^{-6} \degree\textsuperscript{C}, which is less than that of Ti substrate (CTE of Ti

**FIGURE 10** Cross-sectional microstructure and the corresponding local EDS of HA-20 wt. % Al coating

**TABLE 2** Bonding strength test results for HA and HA-Al coatings after sintering at 850\degree\textsuperscript{C}

<table>
<thead>
<tr>
<th>Coatings</th>
<th>HA</th>
<th>HA-10 wt.% Al</th>
<th>HA-20 wt.% Al</th>
<th>HA-30 wt.% Al</th>
<th>HA-50 wt.% Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding strength (MPa)</td>
<td>10.2</td>
<td>12.5</td>
<td>13.2</td>
<td>14</td>
<td>25</td>
</tr>
</tbody>
</table>
is $8.4 \times 10^{-6}$ 1°C) in order to Zafer Evis et al.\textsuperscript{41} Figure 9 shows the surface morphologies of sintered HA and HA-50 wt.% Al composite coatings. As can be seen in Figure 9A, large pores remained in the HA coating which indicates relatively low densification. Moreover, in Figure 9B, the pores within the HA/Al\textsubscript{2}O\textsubscript{3} nanocomposite coating are lower and smaller than that of the HA coating. It can be concluded that the HA/Al\textsubscript{2}O\textsubscript{3} nanocomposite coating was better sintered with a higher densification than other HA coatings. Figure 10 shows the cross-sectional microstructure and the corresponding local EDS of HA-20 wt.% Al coating sintered at 850°C after the bonding strength test. Section A is the part of the coating that includes Al\textsubscript{2}O\textsubscript{3}, HA and TiO\textsubscript{2}, and section B is the titanium substrate. The bonding strength values of different coatings based on the Al wt.% in suspensions are presented in Table 2. As can be observed, the bonding strength of the HA 50 Wt. % Al is much higher than that of the pure HA coating. The relatively poor adhesion of HA coating mainly arises from the presence of cracks and residual stress after the heat treatment. It is higher than the reported value 23.54 MPa for HA/Al functionally gradient coating by Huang et al.\textsuperscript{33} Wu Zhenju et al\textsuperscript{42} reported the adhesive strength of the HA/Al\textsubscript{2}O\textsubscript{3} bio composite coating on titanium prepared by the multistep technique, including physical vapor deposition(PVD), anodization, electro deposition, and hydrothermal treatment is 21.3 MPa. Figure 11 shows the cell viability expressed by MTT assay 2 and 4 days in the incubator. Titanium plate was used as the control process (blank). As can be seen, most cell proliferation has occurred on the HA-Al\textsubscript{2}O\textsubscript{3} coating. The work of Sarama Bhattacharjee et al\textsuperscript{43}, cytotoxicity data of TiO\textsubscript{2}/HAp bi-layer, and HAp- coated Ti, TiO\textsubscript{2}-coated Ti measured after 48 hours did not show any significant differences compared to the control sample and Ti foil. The results thus testify the high biocompatibility of the implants.

4 | CONCLUSION

HA-Al\textsubscript{2}O\textsubscript{3} composite was coated on Ti plates by EPD and the reaction bonding process. The reaction bonding process increases the coating densification. Matching the thermal expansion coefficient of the ceramic coating with the metal substrate compensates the bonding and decreases the number of cracks created on the surface of the coating. Increasing the Al content in nanocomposite coatings decreased the cracks on the surface of coatings, as in HA-50 wt.% Al coatings, free-of-crack surface was fabricated, which also had the highest bonding strength than other coatings. Therefore, the optimum amount of Al to fabricate free-of-crack composite coatings is 50 weight percent.

ACKNOWLEDGMENTS

The authors thank Semnan University, Iran for the financial support provided for this research and Pasteur Institute of Iran for cellular tests.

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How to cite this article: Askari N, Yousefpour M, Rajabi M. Determination of optimum Al content in HA-Al2O3 nanocomposites coatings prepared by electrophoretic deposition on titanium substrate. *Int J Appl Ceram Technol*. 2017;00:1-10. [https://doi.org/10.1111/ijac.12826](https://doi.org/10.1111/ijac.12826)