Original Article

Enhanced corrosion properties of biological NiTi alloy by hydroxyapatite and bioglass based biocomposite coatings

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ABSTRACT

Enhanced corrosion resistance is always an obligatory property in biomedical applications. For this purpose, the surfaces of NiTi alloy were duplex coated both by Hydroxyapatite (HA)/Silver (Ag) and BioGlass (BG)/Silver (Ag) using the sol-gel method. The surface morphologies, and corrosion behaviours of the coatings were examined via SEM, EDS, XRD, and mechanically, by means of hardness as well as adhesion and corrosion tests. SEM analyses showed that the homogenous and crack-free structures were obtained in the biocomposite coatings. Spherical-like structures in the coatings were observed and pitting type of corrosion was formed in the biocomposite coated NiTi surfaces. After the corrosion tests, enhanced corrosion resistance was observed in both HA- and BG-based coatings. However, HA-based HA/Ag coatings on NiTi alloys were obtained to have higher adhesion strength as well as higher corrosion resistance compared to the BG-based biocomposite coatings. The findings in the present study can help the design of future implants with higher corrosion resistance.

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1. Introduction

Biological NiTi alloys have the potential of being commonly used to determine or fix parts such as short bone parts, fractured jawbones and skulls due to its reversible deformation properties. The biological NiTi alloys are also commonly used in the maxillofacial surgery, living tissue prosthesis, removal of stenotic vessels or urinary tract systems [1]. However, the major drawbacks of NiTi shape memory alloys, especially in long-term implantations that limit their usage are biological corrosion [2] and potential migration of toxic nickel ions [3] into human body, which can be detrimental and may even cause cancer.

Some unwanted biological and mechanical damages may occur due to insufficient corrosion resistance of metallic implants. In this context, studies are conducted to ensure the functionality of the biomaterials enabling the long-term use of these materials after the implantation [1,4]. The metallic biomaterials were coated with hydroxyapatite (HA) having...
a bone-like structure especially for hard tissue applications [5–12]. Similarly, the BG having high bioactivity, are used and such material was reported to show no toxic effect via in vivo studies [13–15]. However, the use of BG was restricted in the medical practices because of their lower fracture toughness compared to the high density bones [15].

Enhancing the tissue-implant interaction is another objective of the metallic implant coatings and various contributions have been made to improve the mechanical, corrosion and biocompatibility properties of the coatings [16–20]. In that context, different techniques to modify NiTi surface were used such as Sputtering, electrophoretic deposition, sol-gel and thermal spray [21–24]. However, sol-gel method has some advantages such as, better homogeneity, high purity, less energy consumption and low temperatures. In addition, there is no need for special or expensive equipment. Sol-gel is also associated with better control of the structure, extended composition ranges allowing the fabrication of any oxide composition as well as the production of new hybrid materials [20,22]. Protective coatings of metallic implants, such as by HA and BG with various surface dopants are being studied worldwide in functionalizing and improvement their biocompatibility and corrosion properties [21–25]. It is well known that some dopant like silver (Ag) significantly help biocompatibility and was also reported that it did not cause the microorganisms to lose their proliferation properties [26]. In the present work, as the first time in the literature, both HA/Ag and BG/Ag, multifunctional biocomposite protective coatings were achieved on the biological shape memory NiTi implants by using the sol-gel method. The surface morphology, structural characteristics and adhesion strength of the coatings as well as in vitro corrosion tests of the coated NiTi implants were examined in a comparative manner.

2. Materials and methods

2.1. Materials

NiTi plates ((Allotech Ind, ASTM F2063-05) with chemical compositions of 45 (wt%) Ti and 55 (wt%) Ni were used as the substrate. The samples having different dimensions at 20 x 10 mm and 60 x 10 mm were prepared for both coatings and adhesion tests, respectively. The preliminary surface cleaning operations (sand blast and ultrasonic cleaning) were carried out on the samples before proceeding to the coating process. After the preliminary surface operations were completed, the samples were kept in 25% HNO3 (Sigma–Aldrich) for 2 h for passivation.

2.2. Coating

NiTi substrates were double coated with (HA/Ag) and (BG/Ag) as group $S_1$ and $S_2$ respectively by using the Sol-gel method. In the HA based first layer of the sample group, $S_1$, Ca$\text{PO}_4\cdot$OH$_2$ ($\text{Merck}$) were used as HA at particle size 25 mµ, the first layer of the sample group $S_1$, and in the BG based $S_2$ group, 45S5 (45% SiO$_2$, 24.5% Na$_2$O, 24.5% CaO and 6% P$_2$O$_5$) powders (10–20 µm) were used (Biomat-ww7-Erlangen). Firstly, the HA and BG based sols were prepared individually for both coating groups $S_1$ and $S_2$. In order to ease gelation and sinterability, P$_2$O$_5$, Na$_2$CO$_3$ and KH$_2$PO$_4$ (Sigma–Aldrich), were added at determined quantities into the sol at determined concentrations, respectively. The sol was ultrasonically homogenized (15 min) until a homogenous gel was obtained. Then, the substrates were dipped into the gel and dip-coated at ascending and descending rates of 10 mm/s. The coated samples were kept under room temperature and then were subjected to the pre-drying in the furnace (130 °C, 24 h) and finally subjected to sintering process at 700 °C temperature (3 °C/min).

Secondly, the HA and BG coated samples were HA/Ag and BG/Ag coated. For this, Sol–Ag was prepared for HA/Ag double-layered coatings (S2). The Sol–Ag (10% Ag (w/v)) was prepared by using AgNO$_3$ (Sigma–Aldrich, 0.5 M aqueous solution), P$_2$O$_5$ and distilled water (DW). In order to reduce Ag, the AgNO$_3$ solution was dropped into a clean beaker and 30% ammonia was then added until the initial precipitate just dissolved. HA powders were then mixed in DW and subsequently subjected to homogenisation treatment for 20 min. The Ag-ammonia solution was added dropwise into the HA solution. After completion of the reaction, the Ag-containing HA powders were collected through filtration, rinsed with DW and alcohol several times and finally oven-dried at 60 °C. Composites with different amounts of silver content were obtained by adjusting the amount of AgNO$_3$ solution. The obtained sol was stirred in a baker by using a magnetic stirrer for 30 min then was homogenized in an ultrasonic homogenizer (Cole Parmer, 750 W) for 10 min until gelation was achieved. Distilled water, Gelatine, P$_2$O$_5$ and AgNO$_3$ (Sigma–Aldrich) aqueous solution (0.5 M) were used for the second layer of Ag coating. Finally, HA/Ag and BG/Ag coated samples were dip-coated at immersion speed of 10 mm/sec and the final sintering operation was performed (500 °C) at the heating rate of 3 °C/min.

2.3. Mechanical tests

The adhesion strength of the coatings was measured by shear test. DP460 epoxy (3 M) glue was used for the shear tests. In order to adhere and execute shear test, the coated and uncoated surfaces (15 x 10 mm) were glued together by DP460 epoxy. Then, 500 g weights placed on those glued coated and uncoated surfaces were allowed to dry for 12 h under room conditions. The shear tests were carried out at 2 mm/min speed in a tensile machine with a tensile tester (Shimadzu-50kN-AG-X) in accordance with ASTM C 633 standards. Four tests were performed for each sample and the adhesion strength values of the coated samples were calculated by dividing the shear rupture force to glued area. In addition, the surface hardness of the samples was measured by micro-hardness tester (Emco-Test Durascan) by applying 300 gf load for 10 s. Six hardness measurements were carried out and the mean values were taken into consideration.

2.4. Corrosion

Corrosion test samples were joined by copper wires (1.7 mm in diameter) on the corrosion unit to ensure conductivity and taken to the cold bakeite in such a way that only coated surfaces were exposed. The corrosion tests were performed by
potentiodynamic polarization technique (PDP) using Ringer Solution (37 °C) in Gamry FC14/750 (USA) corrosion test unit. Saturated silver/silver chloride (Ag/AgCl), platinum wire (Pt), and the already prepared corrosion samples were used as reference electrode (RE), counter electrode (CE), and working electrode (WE), respectively, for the tests. A minimum of 2 tests were performed for each sample group until the steady state was determined. The open circuit potential (OCP) measurements and (PDP) were performed for the corrosion samples. Time dependant change of the mixed potential (de-t) was determined by OCP tests and the potential changes were measured to evaluate the localized interactions of the samples. In PDP tests, the characteristics of the corrosion were determined by plotting the polarization curves of the samples. The samples were kept in Ringer sol for 33 min until they reached the OCP and then all test samples were subjected to the PDP measurements at the scanning speed of 1 mV/sec. Finally, the corrosion properties were determined by the polarization curves.

2.5. Surface analysis

The surface morphologies and film thickness of the coated samples were analysed by scanning electron microscope (SEM, JEOL JSM 7001F) and electron dispersive spectroscopy (EDS, Oxford INCA). Additionally, the coatings were characterized by X-ray diffraction (XRD, Bruker D8) using CuKα. XRD analyses were performed at 1.5406 (λ) wavelength with step size of 0.02° from 10 to 90°.

3. Results and discussion

In biocomposite coatings, it is desirable that the coating have biocompatible and homogeneous surfaces with low crack insidence to improve osseointegration [27]. The crack-free-solid (Fig. 1a) and cracky-porous (Fig. 1b) surface structures were obtained after coatings and sintering in HA/Ag and BG/Ag coatings, respectively. SEM figures illustrate the typical appearance of the morphology of NiTi coatings. As seen from SEM morphologies in Fig. 1a and b, there were no severe cracks observed within the coatings. Morphological differences in between HA/Ag and BG/Ag coating surfaces can be clearly observed. HA/Ag coating shows more solid and well bonded structure (Fig. 1a) as some porous and cracky surface occurred in BG/Ag coating (Fig. 1b). This is probably due to different thermal expansions in between the metallic substrates and bioceramic coatings that caused such cracks [20]. The average film thicknesses for both HA/Ag and BG/Ag coatings on NiTi substrates and shown in Fig. 1c were evaluated by SEM to be 13 ± 0.3 micron (Fig. 1c). Although the effect of film thicknesses on morphology, mechanical properties and corrosion results was not investigated in this work, relevant studies [22] reported that increasing film thickness cause a decrease in corrosion resistance.

Fig. 2 shows SEM and EDS spectra of uncoated (a), HA/Ag coated and BG/Ag coated (c) specimens, where, the existence of NiTi (Fig. 2a) and Ag were confirmed in spectra of HA/Ag and BG/Ag biocomposite coatings (Fig. 2b and c). By comparing EDS spectra, before (Fig. 2a–c) and after corrosion (Fig. 3a–c), it was observed that the amount of oxygen increased in the uncoated sample after the corrosion. The content of Ca/P decreased in HA/Ag coated sample (S1) and the content of Si-Ca-P also decreased in BG/Ag coated sample (S2) after the corrosion. The SEM images in Fig. 3(a–c) show that severe damage and pitting occurred in metallic sample groups which were not coated by HA and BG (Fig. 3a). However, HA/Ag and BG/Ag coated samples showed some minor pittings (Fig. 3b and c), respectively. Such results had proved that the HA and BG coating with Ag doping was formed on the surface of the NiTi alloy.
Figs. 4 and 5 show XRD spectra before and after the corrosion, respectively. The results of XRD analyses before and after the corrosion were found to be similar with each other. XRD spectra revealed that the presence of the main phases in coated NiTi material and the corrosion did not cause any prominent change in the uncoated sample (S0). NiTi and Ti4O7 phases were observed to form on the uncoated surface and HA, NiTi, Ni3Ti, Rutile and Ag peaks were determined in the sample group S1. Also NiTi, Ni3Ti, Rutile, CaSiO3 and Ag peaks were determined in the sample group S2. Such results prove that HA/Ag and BG/Ag coatings have formed on the surfaces of the NiTi groups of S1 and S2.

Through the mechanical tests; microhardness and shear tests were performed in the coated surfaces of NiTi alloy. Hardness tests results of HA/Ag coatings and BG/Ag coatings were measured as 327 ± 1 HV and 124 ± 1 HV, respectively (Fig. 6a).
In literature, it was indicated that the sintered hardness of HA and BG to be 537.5 HV and 407.5 HV, respectively [29,30]. However, in this study, the reason for a lower hardness values obtained such as 327 and 124 HV after the coatings can be associated with the fact that the Ag doping and porous surfaces reduced the hardness values.

It is also important to show whether the coatings had adequate adhesion between the metal and biocomposite coatings. In order to show the adhesion strengths of the HA/Ag and BG/Ag coatings of the NiTi substrates, a shear test was performed. The results of the tests shown in Fig. 6b that HA/Ag(S1) biocomposite coatings had higher adhesion strength (23 MPa) than the BG/Ag (S2) biocomposite coatings (13 MPa). Since the minimum required adhesion strength of HA coatings was reported in literature to be between 7 and 10 MPa for orthopedic applications [28], the achieved adhesion strengths (13–23 MPa) for both BG/Ag and HA/Ag coatings, respectively, are adequate enough for biomedical applications.

Some previous research confirmed that by deposition of HAp coatings onto metallic biomaterial an improvement performance occurred [20,22]. In the current work, the achieved biocomposite coating layers have demonstrated significantly better corrosion protection of NiTi implant. After implementing the corrosion tests, performed by PDP technique, OCP and PDP curves were plotted and presented in Figs. 7 and 8. Tables 1 and 2 show the corrosion parameters used in these curves (E_{ocp}, E_{corr}, I_{corr}, R_A, and R_C). Obtained OCP values showed that the applied NiTi coatings caused OCP values (E_{ocp}) to shift to noble values. Moreover, the corrosion potential was determined to prominently decrease in the HA/Ag coating (S1) in particular. These results exhibited that both of the coatings increased the corrosion resistance of the NiTi metallic surfaces, and HA/Ag coatings ensured higher corrosion resistance than BG/Ag coatings.

Fig. 7 shows the changes in comparative OCP curves obtained as a result of the corrosion tests. It has been shown that E_{ocp} values from OCP curves decrease with time in biocomposite coated samples in S1 and S2, whereas these curves increase with time in uncoated S0 samples. It has been found that the stabilization time of the coatings in the Ringer solution is much shorter than the uncoated state, and that the
obtained potential vibration amplitudes of the coated samples are lower than the uncoated samples. The presence of local corrosion on the surface showed that the coatings in the Ringer solution had more anodic potential than their potential with time-dependent changes in Eocp values. While the OCP value of the (HA/Ag coated) S1 samples in Ringer solution was approximately $-67 \text{ mV}$, however, this value was measured as $-157 \text{ mV}$ in the (BG/Ag coated) S2 samples. Compared to the uncoated sample ($-169 \text{ mV}$), the OCP values of the both coatings were found to be more noble. Therefore, it has been found that NiTi-based material loses its surface reactivity significantly with bio-composite coatings. Although the noise amplitudes of the time-dependent changes in OCP of the uncoated sample was highly variable, these changes in the coatings were observed to be very low. Such situation can be explained by the fact that the passive film of the localised corrosion in the uncoated samples became locally thick and the localisation was resulted from the accumulation of both compounds of Ni and Ti the same area at high concentrations.

Fig. 8 shows comparatively the PDP curves of the samples in Ringer solution at body temperature. The purpose of this process was to reveal corrosion differences by increasing the potential on the samples subjected to free corrosion for a while. The coatings have been excessively polarized by PDP method in the anodic direction. PDP curves exhibited that the potential of all the coatings increased in the cathodic area while the current decreased regularly. This situation have revealed that all of the coatings had an activation controlled corrosion mechanism. The passivity curves of the samples were seen to be the first point drawing attraction in the PDP curves. For a good corrosion protection of a coating, it is necessary to possess a noble potential as much as possible with low

<table>
<thead>
<tr>
<th>Specimen group</th>
<th>Eocp (mV)</th>
<th>Ecorr (mV)</th>
<th>Icorr ($\times 10^{-9}$ A/cm²)</th>
<th>$\beta_A$ ($\times 10^{-3}$ V/dec.)</th>
<th>$\beta_C$ ($\times 10^{-3}$ V/dec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>Uncoated</td>
<td>$-169$</td>
<td>$-173$</td>
<td>119</td>
<td>327</td>
</tr>
<tr>
<td>$S_1$</td>
<td>HA/Ag</td>
<td>$-67$</td>
<td>$-119$</td>
<td>45</td>
<td>298</td>
</tr>
<tr>
<td>$S_2$</td>
<td>BG/Ag</td>
<td>$-157$</td>
<td>$-175$</td>
<td>100</td>
<td>289</td>
</tr>
</tbody>
</table>
current density. When the obtained PDP curves were examined; the value of the current density flowing from the HA/Ag coating (S1) for any of the potential values in the anodic field was found to be lower than the current density flowing from the BG/Ag coating (S2). The S1 sample revealed better corrosion potential between all samples.

Moreover, sample S1 displayed higher pitting potential ($E_{p1}$) than the other two sample groups of S0 and S2. Additionally, the values given in Table 2 showed that both biocomposite coatings caused the decrease in the corrosion rate of the alloy and an increase in the polarization resistance. However, it was determined that the samples of S1, i.e. HA/Ag coatings, had lower corrosion rate and higher polarization resistance than the samples of S2 (BG/Ag). Overall, the results indicated that the S1 samples revealed the highest corrosion resistance compared to others. It was observed that there exist some fluctuations in the passive area of the uncoated sample (S0) on PDS curve, but these fluctuations were not formed on the anodic area of the biocomposite coated samples. It is thought that fluctuations in the current density values of uncoated samples may be caused by the deterioration of the oxide film owing to the increase in potential over passivity potential through conservation, repair and successive self-repetition. This view is confirmed by the time-dependent changes in the amplitude of the noise in the OCP curves of coated and uncoated samples shown in Fig. 8.

The similar trends were also obtained for the samples in S2 group which were coated with BG/Ag. From the EDS spectrum, the decrease in the Si-Ca-P rates and increase in the Ni and Ti rates were observed after the corrosion. Such results indicated that the corrosion damaged the coatings and reached to the surface of the substrate. Even though the BG-based bioactive coating, giving $E_{corr}$, $I_{corr}$ and $R_{p}$ values close to the values of the uncoated sample, this situation indicate that no significant improvement was achieved in the base material in terms of surface protection. This is probably due to porous coating surface that caused lower adhesion and so lower corrosion resistance in BG/Ag coatings on NiTi substrates. Nevertheless, it is clearly seen that, it managed to prevent such formations on the surface and contributed to the formation of a stable protective oxide film on the surface. As a result of the corrosion tests performed in Ringer Solution (37 °C), it was determined that the corrosion caused severe damage on uncoated samples (S0) and the content of oxygen (O) on the surface increased after the corrosion (Fig. 2b). The increase in the content of O after the corrosion can be explained by the oxides forming on the structure due to the effect of corrosion. Similarly, the corrosion has caused the formation of pitting in the samples S1 and S2. An increase in the content of NiTi-O was observed, while the prominent decrease in the rates of Ca and P was observed in the S1 sample group after the corrosion.

<table>
<thead>
<tr>
<th>Specimen group</th>
<th>Corrosion rate (mpy)</th>
<th>$R_{p}$ ($\times 10^2$ ohms.cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>635</td>
<td>286</td>
</tr>
<tr>
<td>S1</td>
<td>187</td>
<td>1214</td>
</tr>
<tr>
<td>S2</td>
<td>428</td>
<td>403</td>
</tr>
</tbody>
</table>

4. Conclusions

- The surface of a NiTi shape memory alloy was modified by executing multifunctional coating layers consisting of (HA/Ag) and (BG/Ag).
- Crack-free surface morphologies were achieved in HA/Ag compared to BG/Ag biocomposite coatings.
- The adhesion strength of the HA/Ag coatings was found to be statistically significant and measured as 79% higher than BG/Ag biocomposite coatings.
- The surface hardness (327 HV) of the HA/Ag biocomposite coatings was also measured much higher than BG/Ag (124 HV) coatings.
- Some deep pitting defects on the uncoated NiTi surfaces were formed with the effect of corrosion, however, BG/Ag coating have been seen to have little effect in the corrosion resistance compared to HA/Ag coatings. In addition, it was determined that the corrosion resistances of HA/Ag and BG/Ag coatings on NiTi substrates increased with respect to the adhesion strengths.
- Future works should be focused on studying the tendency of layers to corrosion in a simulated body fluid, with their in vitro biocompatibility and cytotoxicity antibacterial tests. Such future works will provide to constitute the basis of more specialized cell lines e.g. human osteoblast lines via in vivo tests.

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Ethical approval

No need any ethical approval.

Conflict of interest

All authors declare no conflict of interest.

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