Interfacial study of magnesium-containing fluoridated hydroxyapatite coatings

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A B S T R A C T
Magnesium-containing fluoridated hydroxyapatite (Mg,FHA) coatings have been developed to improve the biological performances of fluoridated hydroxyapatite (FHA) coatings. The coatings are deposited on Ti6Al4V substrates via a sol–gel process. The interface between the coating and substrate is characterized by scanning electron microscopy, glow discharge optical emission spectroscopy and X-ray photoelectron spectroscopy for coating thickness, elemental distribution and chemical states. Pull-off test is used to evaluate the adhesion strength. The results show that the interdiffusion of elements happens at the coating/substrate interface. The incorporation of Mg ions into FHA coatings enhances the pull-off adhesion strength between the coating and the substrate, but no significant difference is observed with different Mg concentrations.

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1. Introduction

Hydroxyapatite (HA) coated dental and orthopedic implants were developed to combine into one both the superior mechanical properties of metal substrate (titanium and its alloys) and the excellent biological performances of HA [1–4]. However, significant differences still exist in between synthetic HA and biological apatite. For example, the bioactivity, in vivo resorption and degradation of both synthetic bulk HA and HA coatings were all inferior to the bone mineral [5]. Trace elements have been added to HA for biological improvement: substitution of some Ca2+ with Mg2+ [6,7], Zn2+ [8,9], Sr2+ [10,11], Pb2+ [12], etc., replacement of some PO4 3− by HPO4 2− [13], CO3 2− [14–16] or SiO4 4− [17–19], and some OH− by F− [20–22] or Cl− [23]. Although the substitution does not change the crystallographic properties of HA very much, it affects the biological and mechanical properties.

In our previous studies, Mg and F ions were incorporated into HA coating simultaneously by the sol–gel dip-coating method [24,25]. The preliminary investigation showed that the in vitro bioactivity, cell proliferation and cell differentiation were significantly improved, especially at higher Mg concentration. Therefore, simultaneous incorporation of Mg and F ions into HA coating could benefit faster growth of new bone on hard tissue implant. For biomedical application, the long-term stability especially the adhesion strength between the coating and substrate is of great importance, as poor adhesion leads to loosening and ultimately failure of the implant.

In this work, the pull-off test is employed to evaluate the adhesion strength of coatings from the metal substrates. The interfacial elemental distribution and chemical states, etc. are characterized to elucidate the bonding structure.

2. Experimental procedures

2.1. Coating preparation and characterization

The preparation of sols and deposition of Mg-containing fluoridated hydroxyapatite coatings (Mg,FHA) were described in details in our previous work [24,25]. In brief, calcium nitrate tetrahydrate (Ca(NO3)2·4H2O, Merck, AR), phosphorous pentoxide (P2O5, Merck, GR), magnesium nitrate hexahydrate (Mg(NO3)2·6H2O, Merck, AR) and hexafluorophosphoric acid (HPF6 Sigma-Aldrich, GR) were dissolved in ethanol respectively to prepare the sols. The designed degree of substitution of Ca2+ by Mg2+ was indicated by the x value in the general formula of Cx(10−x)Mg x(PO4)6F(OH) (Mg,FHA), where x = 0/2, 1/2, 2/3 and 4/3, and the corresponding coatings were labeled as FMA0, FMA1, FMA2, FMA3 and FMA4, respectively. Fine polished Ti6Al4V (20 × 30 × 2 mm3) was used as substrate. The dipping-drawing-drying-firing process was performed 5 times for a final coating thickness of 1.5–2 μm.

As-deposited sample was cut into small pieces (10 × 10 × 2 mm3) followed by cold mounting. The mounted sample was polished for cross-sectional view by scanning electron microscopy (SEM, JEOL, JSM5600LV). The depth profiling was conducted in an analyzed area by glow discharge optical emission spectroscopy (GDOES, GD Profiler 2, HORIBA JOBIN YVON). To examine the chemical states around the interface of the coating and the substrate, the coatings were polished with SiC
sandpapers until the substrate was seen. The interface was examined by X-ray photoelectron spectroscopy (XPS, Kratos-Axis Ultra System) with monochromatic Al Kα X-ray source (1486.7 eV). The measured binding energy was calibrated using C 1s (BE = 284.8 eV).

2.2. Pull-off test

The adhesion strength of the MgₓFHA coatings on Ti6Al4V substrate was measured by a universal instron mechanical testing system (Instron 5569). A clamping fixture was designed to avoid the misalignment during the uniaxial tensile test. An Al rod (8 mm diameter) was glued onto the coating surface with epoxy resin (Epoxy Adhesives DP460, 3M, Scotch-Weld™, USA) and cured at room temperature for 24 h. This rod-sample system was then put into a steel holder and the rod was ready for clamping by the Instron fixture (Fig. 1). In testing, the rod was pulled at a cross-head speed of 1 mm/min until coating failure. SEM was used to evaluate the failure mode at the fracture surface. Statistical analysis was carried out using one-way analysis of variance (ANOVA) at an average of ten replicates. Differences were considered statistically significant at \( p < 0.05 \).

3. Results and discussion

3.1. Interfacial analysis of the MgₓFHA coatings

All the MgₓFHA coatings have similar cross-sectional view after mounting and polishing, as shown in Fig. 2 (taking Mg₀FHA and Mg₂FHA as examples). The coatings are dense and uniform with a thickness of about 1.5–2.0 μm. No delamination is seen at the interface even after repeated abrading and polishing, suggesting good bonding between the coating and the substrate.

Glow discharge optical emission spectroscopy (GDOES) provides elemental information and was used to acquire elemental distribution from coating to substrate through depth profiling. GDOES depth profile of Mg₂FHA is plotted in Fig. 3. It shows the distribution of main elements of the coating and substrate along the depth direction, including Ca, P, O, Mg, F, Ti and Al. Along the depth direction, the elemental distribution at cross-section can be divided into three regions: the coating region \( R_c \), the transitional region \( R_t \), and the substrate region \( R_s \). The masses of Ca, P, O, and F in the coating are very stable in the coating region. The mass of Mg decreases from the coating to the substrate, in agreement with our previous study that Mg could only be partially incorporated into HA lattice, whereas extraneous ions were abundant on the surface of the coating [25]. At the boundary between \( R_c \) and \( R_t \), the concentration of Ca, P, Mg and F begins decreasing, whereas there is a slight increase of O concentration followed by a sharp decrease. The increase of O might owe to the presence of F ions, because nc-CaF₂ formed in the dipping sol could be easily absorbed on the substrate surface through hydrogen bond.
which could attract more O near the interface [26]. As can be seen in Fig. 2, as the coating thickness of Mg2FHA is about 2 μm, or $R_c \approx 2 \mu m$, the GDOES profile, thus the transitional region $R_t$ should be about 1 μm. As all the elements of the coating and substrate are seen in $R_t$, diffusion of coating elements into the substrate and substrate elements into the coating occur at the interface. At the boundary between $R_t$ and $R_s$, all the elements in the coating disappear and the elements of the substrate, Ti and Al, begin to stabilize.

Fig. 4 presents results of XPS narrow scan near the interface of the Mg2FHA coating and the substrate. Ti 2p spectrum is shown in Fig. 4a. Only Ti$^{4+}$ is detected, Ti 2p$_{3/2}$ at 458.3 eV and Ti 2p$_{1/2}$ at 464 eV, which can be attributed to TiO$_2$/TiO$_3^2^-$ [27,28]. Ca 2p (Fig. 4b) contains two different states: Ca 2p$_{3/2}$ at 347.2 eV is the typical binding energy of Ca$^{2+}$ in HA or FHA, and Ca 2p$_{3/2}$ at 346.4 eV corresponds to that in CaTiO$_3$ [27,29]. In consideration of the elements diffusion during the firing stage, it is reasonable that CaTiO$_3$ forms at the coating/substrate interface. Fig. 4c shows O 1s spectrum. The main component at the binding energy of 529.7 eV is attributable to O$^{2-}$ species in TiO$_2$/TiO$_3^2^-$, while that at 531.3 eV can be assigned to O$^{2-}$ in HA or FHA [27,29]. Correspondingly, the binding energy of P 2p of PO$_4^{3-}$ in HA or FHA is located at 133.2 eV (not shown here) [29]. Mg 2p spectrum in Fig. 4d presents only one peak at 50.4 eV, which is the typical binding energy of Mg$^{2+}$. As reported in the literature [30], MgTiO$_3$ could be formed around 400 °C. Also, Mg is detected in the transitional region ($R_t$) (Fig. 3). Therefore, it is speculated that MgTiO$_3$ also forms during firing at 600 °C. From above GDOES and XPS analysis, it can be concluded that chemical

![Fig. 4. XPS spectra of Ti 2p (a), Ca 2p (b), O 1s (c) and Mg 2p (d) near the interface of the Mg2FHA coating and the substrate.](image)

![Fig. 5. Schematic illustration of the failure modes ((a): adhesive failure; (b) cohesive failure; (c) combination of all the failures).](image)
bonds especially Ca–O–Ti and Mg–O–Ti bonds form at the coating/substrate interface.

3.2. Pull-off adhesion strength of the MgxFHA coatings

ASTM C633 standard governs the determination of the degree of adhesion of a coating to a substrate or the cohesion strength of the coating in a tension normal to the surface. According to the standard, two kinds of failure modes are defined: 1) adhesive failure happens at the coating-substrate interface, and is referred to as "the adhesion strength of the coating"; 2) cohesive failure occurs within the coating, and is referred to as "the cohesion strength". The failure between the epoxy and the coating is also regarded as the cohesive failure [31]. However, a combination of these failures is often observed in one specimen. Fig. 5 gives a schematic illustration of the failure modes for clear identification. Fig. 5(a) shows the typical adhesive failure, Fig. 5(b) for the typical cohesive failure, and a combination of both adhesive and cohesive failure in Fig. 5(c).

SEM is used to observe the morphology of rupture surfaces after pull-off test. The typical morphology of the Mg2FHA coating is shown in Fig. 6. It can be seen that both the adhesive and cohesive failure are present. Fig. 6(a) shows the typical adhesive failure: a piece of the coating is detached from the substrate and others still adhere to the substrate. Cohesive failure can be observed in Fig. 6(b). It happens within the coating, and is spot flaking around the surface of the coating.

Since both adhesive and cohesive failure is present, the “pull-off adhesion strength” is used not to distinguish adhesive and cohesive failure, calculated using: 

\[
X = \frac{4F}{\pi d^2},
\]

where \(X\) is the “pull-off adhesion strength”, \(F\) is the actual force applied to the test surface at rupture, and \(d\) is the equivalent diameter of the original surface area stressed [32]. Calculated pull-off adhesion strength is compared in Fig. 7. Without Mg incorporation (Mg0FHA), the pull-off adhesion strength is about 12 MPa. When Mg is incorporated, it increases significantly (\(p<0.05\)) to about 18 MPa. However, there is no significant difference between different Mg concentrations.

As both the mechanical interlocking and the chemical bonding contribute to the adhesion between the coating and substrate, in this work, all the substrates were polished to grade #1200 of SiC sandpapers to achieve the same finish. Moreover, Blackwood DJ, et al. proved that the adhesion became independent of surface finish at levels smoother than #600 [33]. Therefore, the mechanical interlocking is considered as identical among all the samples, thus the main contribution to adhesion strength is the chemical bonds at the interface of the coating and substrate formed during the coating deposition process, especially at the firing stage. During the firing process, the elements of the coating and substrate diffuse towards each other. As can be seen in Fig. 3, all the elements are present in the transitional region (\(R_t\)). Without Mg incorporation, chemical bonds between Ti–O–Ca–P–F formed at the interface, such as Ti–O–Ca bonds, which could contribute to higher adhesion strength [26]. When Mg ions are incorporated, Ti–O–Mg bonds form at the interface as well as Ti–O–Ca bonds, which would make the chemical bonds even stronger and result in much higher adhesion strength. Since more Mg ions are abundant on the surface the coating, Mg concentration near the interface might be not significantly different among MgxFHA coatings, thus there is no significant difference between different Mg concentrations.

4. Conclusions

At the interface of magnesium-containing fluoridated hydroxyapatite coating (MgxFHA coating) and Ti6Al4V substrate, mutual diffusion of the elements in the coating and the substrate take place in firing process and chemical bonds form at the interface. Mg incorporation into FHA coating improves the pull-off adhesion strength, but there is no significant difference between different Mg concentrations.

References


