

Improved stability of plasma-sprayed dicalcium silicate/zirconia composite coating

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Abstract

Dicalcium silicate/zirconia composite coatings were produced on Ti–6Al–4V substrates using atmospheric plasma spraying. Different weight ratios of zirconia (50 wt.%, 70 wt.%, 90 wt.%) were mechanically blended with dicalcium silicate (C₂S) powders as feedstocks. The composite coatings were immersed in a simulated body fluid (SBF) and a Tris–HCl solution for the *in vitro* appraisal of stability and long-term performance in a biological environment. The ion concentration changes of Ca, Si, and P in SBF and Tris–HCl solution were monitored using inductively-coupled plasma atomic emission spectroscopy (ICP–AES). Compared to the pure C₂S coating, our results show that the dissolution rate of the composite coatings is effectively reduced and the stability is improved by the addition of zirconia. The high content of zirconia in the coatings ensures the long-term performance in biological environment, while dissolution of C₂S in the coatings results in a higher Ca ion concentration in SBF and rapid precipitation of bone-like apatite on the composite coating surfaces indicating good bioconductivity of the coatings.

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1. Introduction

Plasma-sprayed hydroxyapatite (HA) coatings on Ti–6Al–4V substrates are widely used in orthopedics and dentistry [1]. However, the low crystallinity and poor bonding strength of the HA coatings result in degradation, peeling, and fatigue-induced failure under tensile loading [2–5]. Plasma-sprayed dicalcium silicate (C₂S) coatings exhibit excellent bonding strength (38.9 ± 3.5 MP) and bioconductivity and are promising medical materials in artificial bones and dental roots [6]. A dense layer of carbonate-containing hydroxyapatite (CHA) has been observed to precipitate on the coating surface after immersion in a simulated body fluid (SBF) solution for 2 days [6]. This expedites the integration of the implant with the existing bone tissues thus giving rise to significant improvements in the healing time as well as quality of life of the patients. The formation of CHA originates from the high Ca ion concentration

at the coating/solution interface due to the dissolution of C₂S. However, a dissolution rate that is too high leads to deterioration of the mechanical properties of the coatings.

Yttria-stabilized zirconia (YSZ) is a widely used ceramic with favorable mechanical properties such as high bending strength and fracture toughness. These characteristics are considered to be comparable to those of natural bones [7–9]. Owing to the high strength and stress-induced phase transformation toughening, it is frequently used to reinforce other ceramics [10–12]. It has been demonstrated by *in vivo* experiments that strength degradation of bioglass incorporated with zirconia powders can be mitigated [13]. It is also widely used to reinforce HA coatings [14] due to the excellent stability and anti-corrosion properties in a physiological environment. The biocompatibility of YSZ is another crucial advantage [15]. Osteoblasts are found to proliferate on the zirconia surface and dense cell layers form in close contact with the ceramics with good spreading and attachment. Such adhesive properties are regarded to be important to cell proliferation and differentiation into bone forming cells [16].

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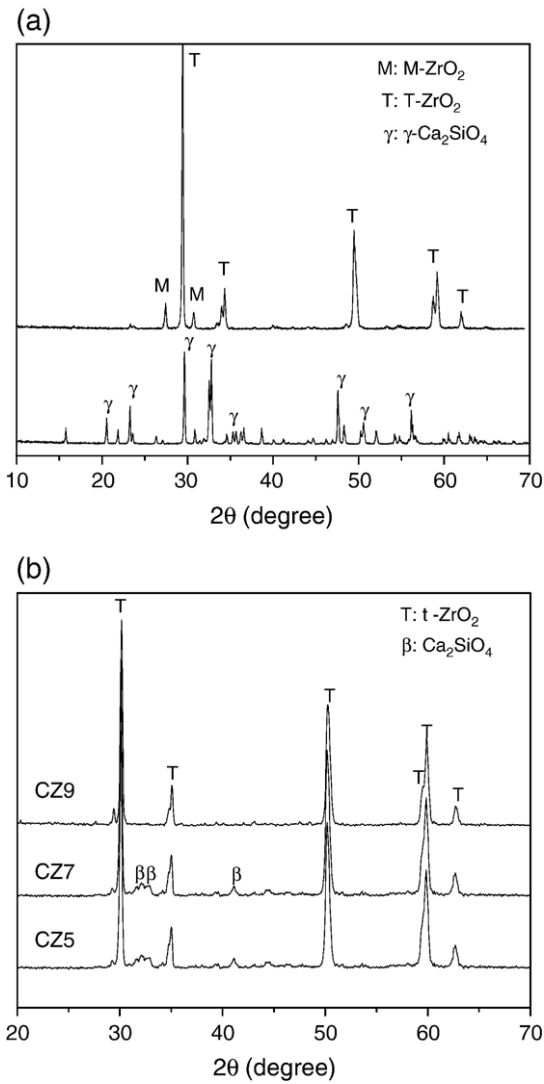


Fig. 1. XRD patterns: (a) original powders of zirconia and dicalcium silicate and (b) as-sprayed coatings.

In this work, C₂S coatings with various contents of YSZ (with 8 wt.% Y₂O₃) are deposited by atmospheric plasma spraying. The rapidly dissolved products of C₂S are believed to stimulate bone formation and promote faster initial bone fixation. The effects of YSZ on the bioconductivity and dissolution properties of the coatings are studied. The dissolution and mineralization behavior of the dicalcium silicate/zirconia composite coatings is studied by immersion in a SBF and Tris–HCl buffer solution. Our objective is to improve the stability of the coatings and prolong the lifetime by adding zirconia.

2. Experimental details

YSZ powders (typical sizes ranging from 50 to 106 μm) and C₂S powders (particle sizes 20–50 μm) were mixed in a polyethylene bottle with ethanol as the media to obtain the following compositions: 50 wt.% C₂S/50 wt.% YSZ (denoted as CZ5), 30 wt.% C₂S/70 wt.% YSZ (denoted as CZ7) and 10 wt.% C₂S/90 wt.% YSZ (denoted as CZ9) composite

powders. An atmospheric plasma spraying system (Sulzer Metco, Switzerland) was employed to fabricate the coatings. The composite coatings were deposited on Ti–6Al–4V coupons with dimensions of 10 mm × 7 mm × 2 mm to determine the microstructure, phase composition, as well as bioconductivity and dissolution behavior. Phase composition of the coatings was determined by X-ray diffraction (XRD, D/max 2550 v, Japan).

The specimens were immersed in 50 ml of Tris–HCl solution for the dissolution behavior evaluation. The Tris–HCl solution

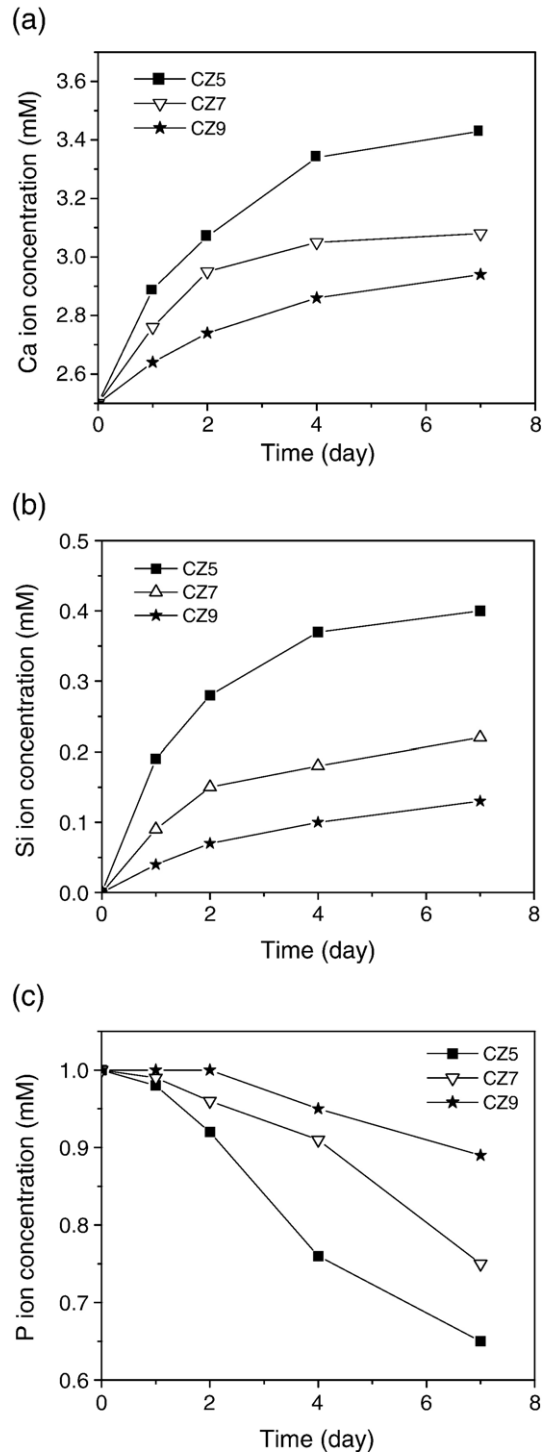


Fig. 2. Ca (a), Si (b), and P (c) ion concentration changes in the SBF.

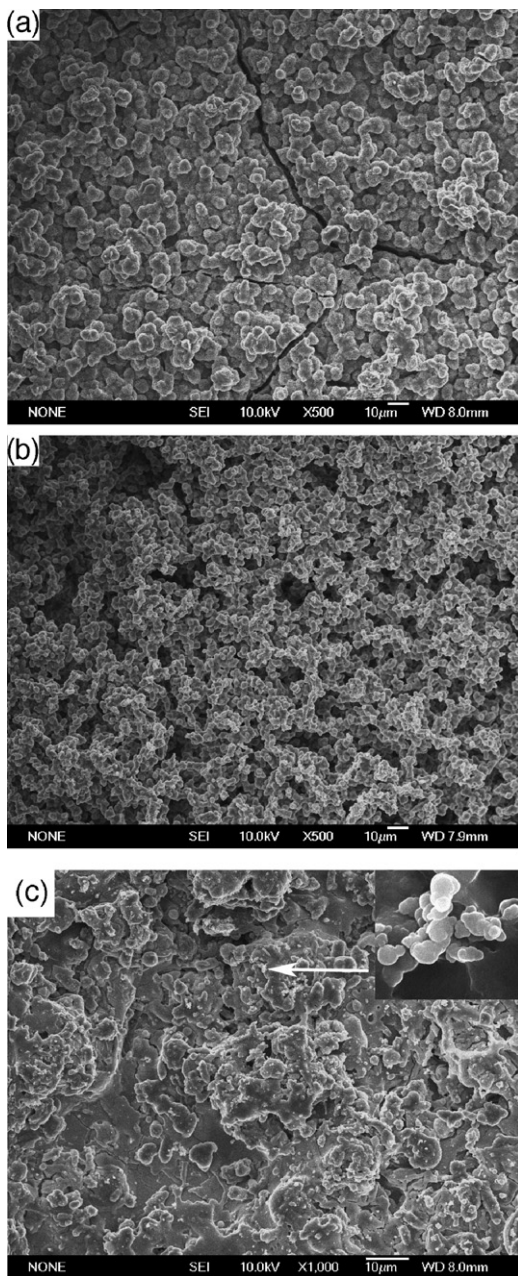


Fig. 3. SEM micrographs showing the surface morphology of the coatings after immersion in SBF for 7 days: (a) CZ5, (b) CZ7 and (c) CZ9.

was prepared by dissolving 50 mM Tris–hydroxymethyl–aminomethane ((CH_2OH) $_3\text{CNH}_2$) in double distilled deionized water and then buffered at pH 7.40 with hydrochloric acid (HCl) at 37 °C. The mass losses after immersion for 1, 2, 4, 7 days were measured. The average of five test data was reported to represent the dissolution rate.

A same size specimen was immersed in 50 ml SBF for *in vitro* bioconductivity evaluation. SEM and energy dispersive X-ray (EDS) analyses (INCA ENERGY, UK) were performed to observe the formation of bone-like apatite. The Ca, Si and P ion concentration changes in the SBF and Tris–HCl buffer were determined by inductively-coupled plasma atomic emission spectroscopy (ICP–AES) to assess the stability of the composite coatings.

3. Results and discussion

3.1. Phase composition of the coatings

The XRD patterns acquired from the original YSZ and C_2S powders are shown in Fig. 1a. The phase of the C_2S powder is $\gamma\text{-C}_2\text{S}$. The main phase of the zirconia is tetragonal and a trace of monoclinic ZrO_2 can also be seen in the XRD pattern. Compared to the XRD patterns of the original powders, the phases of the as-sprayed coatings are mainly composed of tetragonal zirconia and $\beta\text{-C}_2\text{S}$. This phase transformation phenomenon is believed to result from the rapid heating and cooling process during plasma spraying [6].

3.2. Coating dissolution and apatite precipitation in SBF

There are two reversible reactions occurring on the coating surfaces at the same time: Dissolution of dicalcium silicate and precipitation of bone-like apatite layer. Degradation of the coatings releases Ca ions to the solution benefiting the formation of a bioconductive bone-like apatite layer and subsequent bone fixation. Precipitation of apatite consumes some of the Ca ions in the solution further enhancing the dissolution of C_2S . On the other hand, the formation of dense apatite layer on the surface inhibits the diffusion of Ca and decreases the dissolution rate of C_2S .

The dissolution and mineralization behaviors of the coatings were studied by monitoring the ion concentration changes in the SBF. Ca, Si, and P ion concentration changes in the SBF were determined by ICP–AES and shown in Fig. 2. As shown in Fig. 2a, the Ca ion concentration increases with the immersion time and C_2S content. The solution immersing the CZ5 coating exhibits a faster increasing rate and higher Ca ion concentration than that of the other two composite coatings up to 7 days of immersion. In comparison, the CZ7 coating solution is nearly in the equilibrium state after 2 days of immersion. The slightly increased Si ion concentration in the CZ7 coating solution demonstrates that the dissolution of C_2S still occurs although the Ca ion concentration is quite stable after 2 days of immersion. The results indicate that the Ca ions released from the CZ7 coating are nearly equal to those consumed during the precipitation of apatite from the second to seventh day. The Ca ion concentration increases slightly in the CZ9 coating solution although less Ca ions dissolve in the solution due to the smaller C_2S content in the CZ9 coating. It can be explained by that less Ca ions are consumed as a result of the smaller number of nucleation sites on the coating surface and consequently, there is less apatite formation.

The Si ion concentration changes in the SBF reflect the dissolution rates of the three composite coatings to some extent. The higher the C_2S content, the more rapid the dissolution rate of the coating is, and the higher the Si ion concentration in the SBF. Changes in the P ion concentration are directly related to the precipitation of bone-like apatite, and the rate of the P ion concentration changes indicates increasing precipitation rate with increasing Ca contents in the coatings.

The top views of the coating surface after immersion in SBF for 7 days are depicted in Fig. 3. A new dense layer is found on

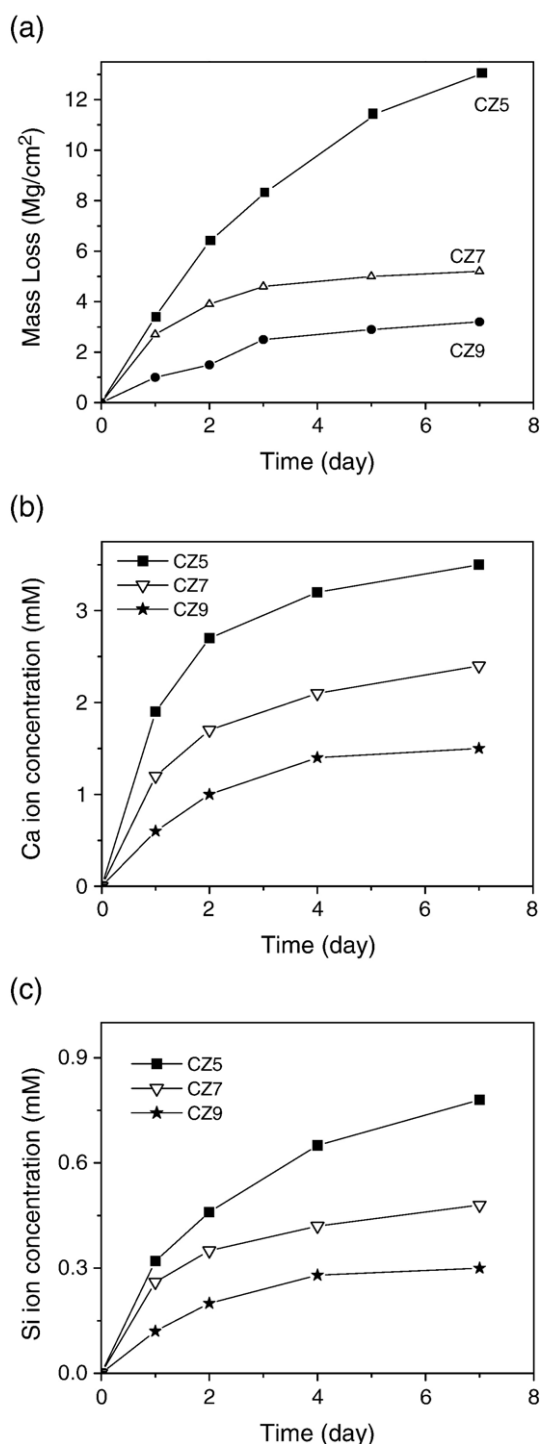


Fig. 4. (a) Mass losses, (b) Ca ion concentration changes, and (c) Si ion concentration changes in the Tris–HCl solution.

the CZ5 and CZ7 coating surfaces. Scattered particles can also be seen on the CZ9 coating surface (Fig. 3c). A higher magnification micrograph of the particles is shown at the right corner in the CZ9 picture. The corresponding EDS results reveal that either the new formed layers on CZ5 and CZ7 or the particles on CZ9 coating surface are mainly composed of calcium and phosphorus. Succeeding tests confirm that they are bone-like apatite.

3.3. Dissolution behavior in a Tris–HCl solution

The mass losses from the coatings due to the dissolution in the Tris–HCl solution were measured and are shown in Fig. 4a. At the same time, the Ca and Si ion concentration changes in the Tris–HCl solution were also determined by ICP–AES. It can be seen from Fig. 4 that the dissolution rates decrease with reduced C₂S contents like in the SBF. No Zr ions can be detected in both the SBF and the Tris–HCl solutions after 7 days of immersion because of its higher stability in an aqueous solution. It is also noticeable that the Ca ion concentration in the solution is much higher than that of the Si ion. The Ca/Si ratio is about 5 and much higher than the stoichiometric ratio of C₂S.

There is evidence that Ca²⁺ on the C₂S surface dissolves rapidly resulting in a Si-rich surface layer [6]. The surface structure will undergo reconstruction reactions that increase the connectivity of the network [17] and incorporate undissolved zirconia to reduce the release rate of Ca. On the other hand, surface pores may also be produced due to the stress on the coating surface and reconstruction of the network, thereby exposing additional surfaces to the solution. These cracks allow water molecules to penetrate through the surface layer to react with the inner layer of the coatings.

4. Conclusion

Dicalcium silicate (C₂S) and zirconia powders of different weight ratios were mechanically blended to fabricated composite coatings on Ti–6Al–4V substrates by atmospheric plasma spraying. The CZ5 and CZ7 composite coatings exhibit more substantial formation of bone-like apatite due to the higher C₂S contents. The rapid dissolution of C₂S results in higher Ca concentration in the SBF solution. It thus fosters rapid precipitation of bone-like apatite on the surfaces. The addition of zirconia with high mechanical strength and anti-corrosion properties effectively improves the stability of the composite coatings. The dissolution behavior in the Tris–HCl solution demonstrates that mass losses from the coatings mainly stem from the dissolution of C₂S and the dissolution is incongruous. The Ca ion release is much quicker than that of the Si ion. Further work is being conducted to further fathom the mechanism of the improved bioconductivity as well as the long-term stability of these composite coatings.

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