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Bioactive titanium-particle-containing dicalcium silicate coating

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Abstract

Titanium particles with typical size ranging from 80 to 140 μm were used as scaffolds in the synthesis of bioactive dicalcium silicate (finer than 20 μm) coating by atmospheric plasma spraying to improve the physiological chemical bonding between the coating and bone. A bonding strength as high as 49.0 MPa was achieved between the coating and substrate as a result of the high titanium content in the coating and the similar thermal expansion coefficients of the coating and substrate. The favorable bioactivity was also accomplished as revealed by the formation of bone-like hydroxyapatite after immersion in simulated body fluids (SBF) for 7 days. The good biological properties were further demonstrated by adhesion and differentiation of human osteogenetic cells seeded directly on the coating surface. After dissolution experiments conducted in a Tris–HCl solution, very little changes in the mechanical properties were observed demonstrating the good durability of the coating. Our results thus show that the composite coating possesses not only good bioactivity but also long-term durability.

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Keywords: Bioactivity; Dicalcium silicate; Coating

1. Introduction

Titanium and its alloys are considered to be one of the best metallic materials for orthopedic and dental implants. Surface layers produced by plasma spraying have also drawn interests in the past decades because of their potential to induce osteoconduction and osseointegration [1–3]. A macro-porous layer of titanium coating fabricated by plasma spraying is in fact used in medical practice. The morphological fixation of an implant to bone through the porous titanium surface layer is, however, essentially a mechanical fixation which requires a long immobilization time and may cause mechanical loosening at the bone–implant interface [4]. Fabrication of a bioactive hydroxyapatite coating on the implant is a good way to improve the physiological chemical bond between the implant and bone [5]. However, the low bonding strength between the coating and substrate and dissolution of hydroxyapatite often cause failure in long-term in vivo conditions. Recently, in vitro experiments indicated that wollastonite and dicalcium silicate could induce the formation of hydroxyapatite in simulated body fluids (SBF) [6–8]. The bonding strength between this type of silicate ceramics and titanium alloy substrates is also much higher than that between hydroxyapatite and Ti. However, dissolution and degradation of the coatings still hamper long-term clinical uses.

Several methods have been developed to improve the durability and mechanical properties of these coatings. Among the various methods, the addition of insoluble particles as second phase is potentially useful. Titanium and zirconia are the preferred materials as reinforcing additives because of their high strength and toughness, good biocompatibility, and corrosion resistance [9–11]. Moreover, the titanium oxide formed during atmospheric plasma spraying can induce cell growth and enhance osteoblast adhesion [12,13]. In our previous works, the bioactivity of the composite coatings containing various titanium contents was evaluated in vitro [14]. It was found that the composite coatings with less than 70 wt.% titanium possessed good bioactivity and bone-like hydroxyapatite could form on the coating surface after 7 days immersion in SBF.

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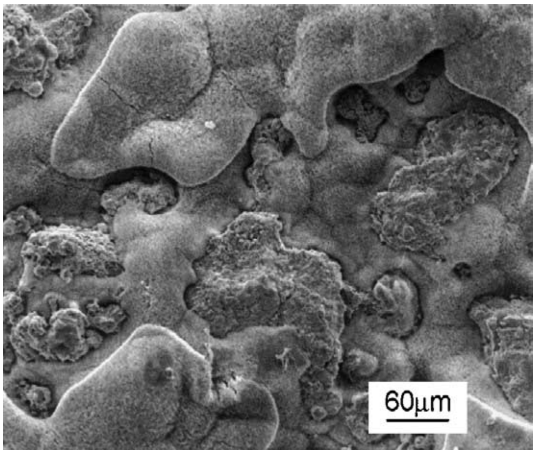

Fig. 1. Surface morphology of CT7 coating.

In this work, a comprehensive study on the dicalcium silicate composite coating with 70 wt.% titanium content (denoted as CT7) was conducted. The biocompatibility was appraised by monitoring the adhesion and differentiation behavior of human osteogenetic cells seeded on the coating surfaces. The dissolution behavior in Tris–HCl solution, Young's modulus and bending strength changes in SBF were studied to assess the coating durability systematically.

2. Experimental details

30 wt.% dicalcium silicate powders (finer than 20 μm) synthesized in our laboratory were mechanically blended with 70 wt.% commercially available Ti powders (typical size ranging from 80 to 140 μm) in ethanol as the feedstock (denoted as CT7) for fabrication of the composite coatings. An atmospheric plasma spraying (APS) system (Sulzer Metco, Switzerland) was utilized to deposit the CT7 coatings on Ti–6Al–4V substrates with dimensions of 10 mm × 10 mm × 2 mm. After deposition, the specimens were immersed in 50 ml of Tris–HCl solution composed of 50 mM tris-hydroxymethyl-aminomethane ($(CH_2OH)_3CNH_2$) in doubly-distilled water buffered at pH 7.40 with hydrochloric acid (HCl) at 37 °C and the mass changes were measured after the immersion test.

Another set of 1.5 mm thick coatings was deposited on steel substrate (150 mm × 100 mm × 2 mm). After plasma spraying, the substrates were removed and the coating was polished carefully and cut into 25 mm (length) × 4 mm (width) × 1 mm (thickness) pieces. The changes of the standard three-point bending strength of the coating after immersion in SBF solution were measured using a material testing instrument (Instron-5566, UK) by ASTM standard test [15]. The Young's modulus was obtained by the relationship: $E = PL/4bh^3\delta$, where E is the Young's modulus, P is the load, L is the span length between support, b is the specimen width, h is the specimen thickness, and δ is the deflection at mid-span.

Human osteogenetic cells were cultured on the coating surfaces to evaluate the cytotoxicity and biocompatibility. About 10^5 cells were cultured on 1 cm^2 autoclaved titanium coupons. The cells were maintained at 37 °C under an atmosphere of 5% CO_2 and 95% air. The culture medium was changed every other day. After culturing for 4 days, the samples were fixed in 2.5% glutaradehyde in a 0.1 M sodium cacodylate buffer (pH = 7.4) for 1 h. After rinsing with PBS (phosphate-buffered saline) (3 × 10 min) and dehydrating in ethanol, the degree of cell spreading and propagation was determined employing scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows the surface morphology of the composite coating. The melted or half-melted titanium particles formed in the plasma spraying process are interconnected to form a net-like structure with dicalcium silicate particles dispersed in the mesh. This kind of structure is advantageous to the fixation of implants to bones. The bioactive dicalcium silicate particles are helpful to the physiological immobilization of the implant at the initial stage while the net-like titanium ensures long-term performance of the coating. The cavities remaining after dissolution of dicalcium silicate are useful for the morphological fixation of the implant to bone at the later stage.

The bonding strength of the coating was determined to be 49.0 MPa based on the ASTM standard method and it is much higher than that of plasma-sprayed HA coatings [16,17]. The high bonding strength of the composite coating may be attributed to the similarity of the thermal expansion coefficients between the titanium alloy substrate and CT7 coating. The thermal expansion coefficients of CT7 are compared to those of titanium alloy and HA as shown in Fig. 2. The abundance of titanium particles in the coating

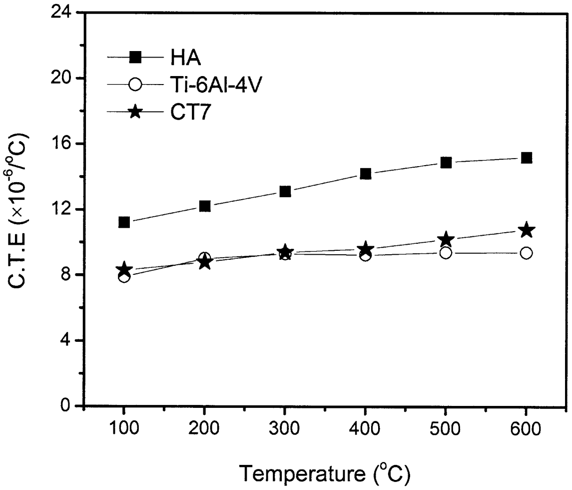

Fig. 2. Thermal expansion coefficients of CT7 coating compared with those of Ti–6Al–4V alloy and HA.

makes the thermal expansion coefficient of the composite coating (10.5×10^{-6}/°C, 20–600 °C) similar to that of titanium alloy (9.40×10^{-6}/°C). In contrast, the higher thermal expansion coefficient of HA (15.20×10^{-6}/°C) compared to titanium results in tensile stress and micro-cracks at the interface between the coating and substrate and consequently, low bonding strength for the HA coating.

The dissolution behavior of the CT7 coating was measured by monitoring the mass loss in Tris–HCl solution. The results are shown in Fig. 3. Compared to the dicalcium silicate coating, the mass loss of the CT7 coating obviously diminishes and the dissolution rate is reduced with the addition of titanium particles.

It is well known that the Young's modulus and bending strength depend on structural characteristics such as porosity, crystallinity, and phase composition. Dissolution of dicalcium silicate in the physiological environment leads to increased porosity and weakened interlamellar microstructure in the coating as well as worse interfacial bonding between the coating and substrate. The degradation in the mechanical properties is illustrated in Fig. 4. In the CT7 coating, the melted or half-melted titanium particles constituting a net-like structure dispersed with finer dicalcium silicate. The mechanical properties are mainly contributed by the large titanium particles and so do not deteriorate after immersion in SBF for 4 weeks.

Fig. 5 shows the morphologies of the CT7 coating surface after seeding human osteogenetic cells for 4 days. The cells overlap and their density is quite large on the dicalcium silicate surface. A bridge-connection with a three-dimensional configuration is formed after 4 days of culturing. Fewer cells can be found on the titanium particles surface and the dicalcium silicate exhibits the characteristics of a typical bioactive material. The Ca^{2+} ions in the dicalcium silicate first dissolve in the culture media and $[Si-O]^-$ functional groups are then formed on the surface. This process increases the negative surface charge that is beneficial to the interactions with proteins leading to increased protein adsorption and/or biological activity. The surface functionality and charges are the main factors influencing cell attachment. A high density of the surface

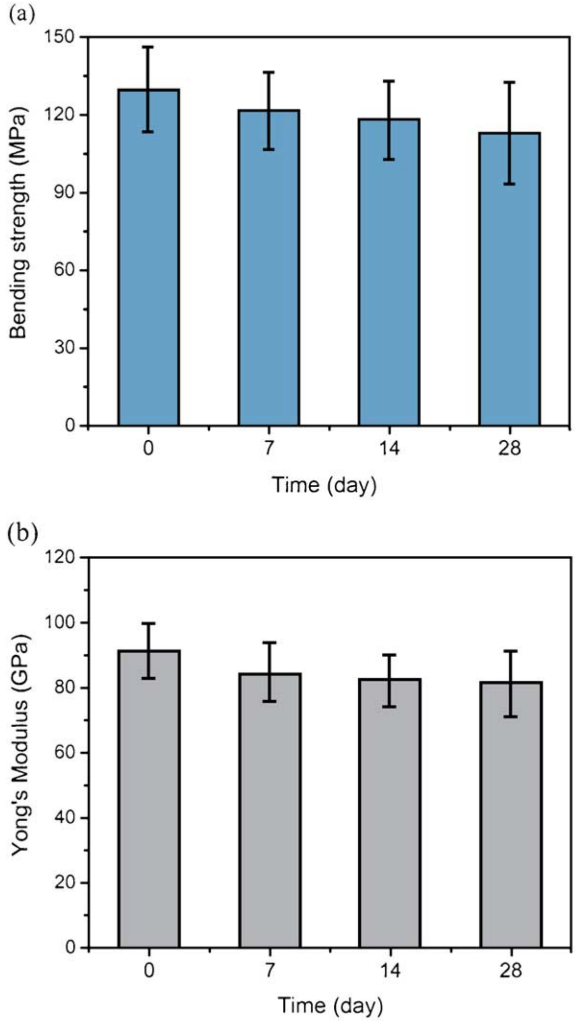

Fig. 4. (a) Bending strength and (b) Young's modulus changes of CT7 coating after immersion in SBF solution.

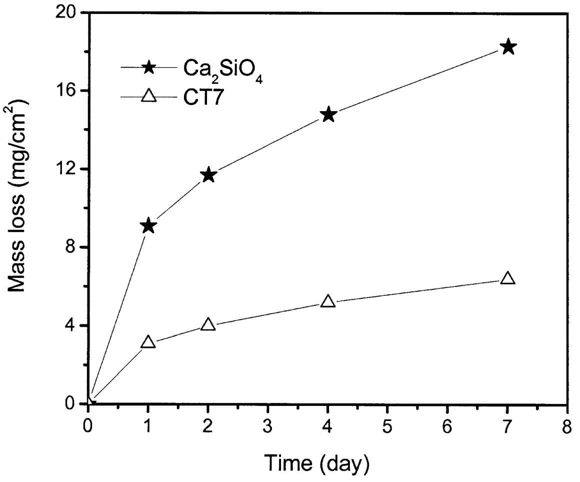

Fig. 3. Mass loss from CT7 after immersion in Tris–HCl solution.

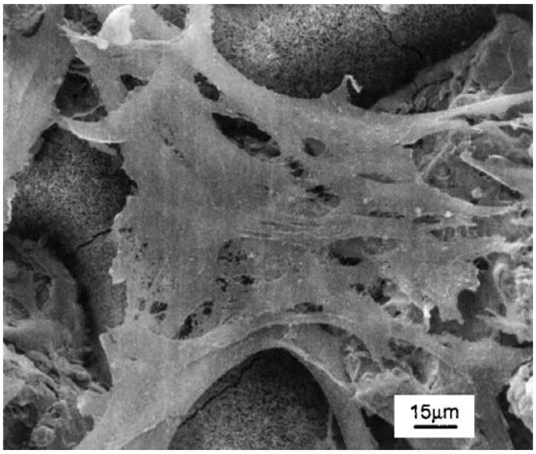

Fig. 5. SEM micrographs of the human osteogenetic cells after culturing on CT7 coating surface for 4 days.

charges gives rise to more attached cells. According to our results, slight dissolution of dicalcium silicate from the coating causes early fixation of the implant to bone while the mechanical properties of the coating are kept by the net-like titanium.

4. Conclusions

Large titanium particles were mechanically blended with small dicalcium silicate powders for the fabrication of composite coatings using atmospheric plasma spraying. A bonding strength as high as 49.0 MPa was achieved between the coating and substrate because of the high titanium content in the coating as well as similar thermal expansion coefficients of the coating and substrate. The large titanium particles melted or half-melted in the plasma spraying process are intertwined to form a net-like structure consisting of small dicalcium silicate localized in the mesh. Dissolution of dicalcium silicate and release of Ca^{2+} result in the formation of $[Si-O]^-$ groups that are beneficial to the precipitation of bone-like hydroxyapatite on the surface and adhesion and proliferation of human osteogenetic cells. Good bioactivity and biocompatibility are thus accomplished. Furthermore, the interconnected titanium particles enhance the durability of the coating, as shown by the Young's modulus and bending strength of the composite coating after immersion in SBF for 28 days. All in all, the composite CT7 coating not only possesses good long-term stability but also introduces suitable dissolution for faster initial bone fixation.

Acknowledgments

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