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Mechanical performances and microstructural characteristics of plasma-sprayed bio-functionally gradient HA–ZrO_2–Ti coatings

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Abstract

Bio-functionally gradient HA–ZrO_2–Ti coatings on Ti_6Al_4V were fabricated through the plasma spraying process. The characteristics of gradient variations in physical performances, microstructure, chemical compositions, and fracture surface were investigated by means of nanoindentation, scanning electron microscopy with an energy dispersive spectroscopy and X-ray diffraction. The results showed that: (1) hardness and Young's modulus increased gradually from the Ti_6Al_4V substrate to the coating along the line vertical to the coating/Ti_6Al_4V interface; (2) microstructure and compositions changed gradually in the coatings, no distinct interface between adjacent layer of different compositions was observed by scanning electron microscopy; (3) the characteristic of the fracture surface demonstrated that the bio-functionally gradient coatings had the compositive mechanical properties such as intergranular cleavage and ductile tearing; and (4) as revealed by the X-ray diffraction results, the surface of the heat-treated coating was composed of crystal hydroxyapatite. According to ASTM C633-79 standard, the bonding strength of the two kinds of coatings were obtained and the value of heat-treated bio-functionally gradient coatings was 53.6 MPa, much higher than that of single HA coatings.

Keywords: Bio-functionally gradient coating; Nanoindentation; Plasma spraying; Bioactive; Biomaterials

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been extensively studied and used for bone-substitute materials in both orthopaedics and dentistry due to its excellent osteoconductive and chemical composition similar to that of the inorganic part of bone in comparison with other implant materials [1–4].

Plasma-sprayed HA coatings on metallic substrates can keep the mechanical properties of metallic substrate and, at the same time, take advantage of the HA ceramic biological performances [5–10]. However, due to a significant difference in thermal expansion coefficients and Young's modulus between the HA coating and the metallic substrates, large residual stress arises at the ceramic/metal interface. This residual stress often causes cracks and reduces the bond strength of ceramic coatings. For practical applications such as artificial joints and dental implants, there is a strong demand for HA coatings with excellent adhesion to the substrate to ensure long-term fixation. The approach to meet the clinical demands is to develop the composite such as bio-functionally gradient coating (FGC) with bioactivity.

FGC is a new breed of composite with a gradient compositional or structural variation. The gradient structures allow the integration of dissimilar materials such as ceramics, oxide and metals without severe internal stress and combine diverse properties into a single material system. Therefore, compared with single HA coating, FGC can effectively improve the microstructure of the coating, reduce the discontinuity in thermal expansion coefficients and Young's modulus between the intermediate

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layer and metallic substrate, and minimize the residual stress in the coating [11,12]. As a result, the properties of the FGC can be improved. For FGC, since the surface layer is HA, it appears to have excellent biocompatibility and is osteoconductive. Furthermore, since HA/zirconia or HA/titanium can be combined to form good composite coatings [9,10], FGC incorporated with the compositions of zirconia or titanium holds a potential to increase the mechanical strength.

Bearing this in mind, in the present work, the biofunctionally gradient HA–ZrO_2–Ti coatings were prepared by net-energy controlled plasma spraying process. The microstructure, chemical compositions and phases of the coatings were examined using scanning electron microscopy (SEM) with an energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The interfacial hardness and elastic modulus of the FGC/substrate were determined by nanoindentation. The bonding strengths of FGC were tested according to ASTM C633-79 standard.

2. Experiment procedures

The HA powders for spraying were produced by reacting calcium nitrate and $(NH_4)_2HPO_4$ in our lab according to the following formula:

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 6H_2O$$

The spray-dried HA powders were calcined at 1100 °C for 1 h to increase the degree of crystallinity. The heat-treated HA powders were sieved and the particles with size range from 20 to 60 μm were used for the depositing FGC. Commercial powders with size range from 40 to 70 μm of CaO-stabilized zirconia and titanium were employed as the main additional components of FGC. The substrate metal was titanium alloy (Ti_6Al_4V) with two different shapes: Ti_6Al_4V cylindrical stubs 25.4 mm in diameter and 25.4 mm in length for bonding strength and Ti_6Al_4V plate specimens $10 \times 10 \times 5$ mm for coating characterization.

The preparation of FGC was based on the precise control of the starting compositions by means of an advanced computerized closed loop powder feed system and a robot-controlled, fully computer-controlled plasma gun (Praxair4500 Thermal Inc, USA), which allowed to feed the HA, ZrO_2 and Ti powders at an accurate ratio. The feed system possesses three microfeeder for three different kinds of powders. The starting compositions were regulated so as to change gradually from Ti-rich at the bottom layer, ZrO_2-rich at the middle layer, and to HA-rich at the top layer. The FGC had 120 μm in thickness, including single-HA-component layer with 20 μm thickness. The plasma spraying processing parameters were summarized in Table 1. In order to further study FGC, single HA coatings (SHA) with 120 μm thickness for comparison were prepared by the same plasma spraying process. The two kinds of coatings were heat-treated at 750 °C for 2 h in atmosphere.

Table 1
Plasma spraying parameters for FGC

Primary gas	Argon 100 scfh
Auxiliary gas	Hydrogen 8 scfh
Carrier gas	Argon 30 scfh
Net energy	15 kw
Standoff distance	150 mm
Coating thickness	120 μm

The cross-sections of FGC for the microstructure characteristic examinations were mechanically polished with a solution of 10 g Cr_2O_3 in 100 ml water. Some samples were broken in liquid nitrogen for the observation of the fractured surfaces. The microstructures and chemical compositions were studied using a Cambridge Stereo Scan 360 (SEM) equipped with an energy dispersive spectroscopy (EDS, OXFORD detector) system. The phase composition was analyzed by an X-ray diffractometer (XRD, D8GADDS, Brucker Corp) with CuKα radiation at 40 Kv and 30 mA.

The bond strengths of the two kinds of coatings were measured by means of MTS 810 according to ASTM C633-79 standard. Both sides of identical cylindrical Ti_6Al_4V stubs with 25.4 mm in diameter were used as a set, one with the coating on the surface and the other without. A high-performance E-7 Epoxy glue was applied to join the two stubs. The surface of the uncoated stubs was sandblasted to enhance the adhesive strength. The two stubs were aligned and solidified at 100 °C for 24 h. In the measurement, a tensile load was employed normally to the samples at a crosshead speed of 0.5 mm/min. Each six samples were measured to obtain the average bond strength and standard deviation.

Nanoindentation was applied as an effective method for the determination of physical properties of the FGC/Ti_6Al_4V interface due to its extremely small test scale. The Young's modulus and hardness of the present samples were determined using a calibrated Berkovich diamond tip. The nanoindentation response was determined with a Nano Indentor™ II instrument on polished cross-sections of the coating and Ti_6Al_4V substrate. For each specimen, 20 indentations were performed, situated along a line parallel to the FGC/substrate interface. The load used for the present nanoindentation evaluation was 30 mN and the load/unload rate was 60 mN/min.

3. Results

3.1. Phase structure

The changes in phase compositions at FGC surface before and after heat treatment were shown in Fig. 1. The results showed a significant influence of heat treatment on