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Coatings of hydroxyapatite — nanosize alpha alumina composites on Ti-6Al-4V

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Abstract

Composites of hydroxyapatite (HA) and nanosize-alpha-(α)-Al_2O_3 with 5 wt.% CaF_2 were coated on Ti-6Al-4V rods by cold pressing and sintered in air or argon atmosphere at 1100 °C to improve the bonding between the metal and the ceramic. 25 and 40 wt.% α-Al_2O_3-5 wt.% CaF_2-HA composites gave the best results of strong bonding. 25 wt.% α-Al_2O_3-5 wt.% CaF_2-HA and Ti-6Al-4V showed the same thermal expansion coefficients. The thermal expansion coefficient of the 40 wt.% α-Al_2O_3-5 wt.% CaF_2-HA composite was slightly smaller than that of Ti-6Al-4V, which created a compressive stress on the coating, resulting in improved bonding between the metal and the ceramic.
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1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been widely used as a bulk implant in non-load bearing areas of the body and as coatings on implant metals. HA is a bioactive ceramic, which can bond to bone, because it is very similar to the mineral part of bone [1,2]. It has a fracture toughness of approximately 1 MPa√m [3].

HA-alumina composites can be made more resistant to high temperature sintering by substituting small amounts of impurities in the HA phase such as Na^+, Mg^{2+}, CO_3^{2-}, CaF_2 or increasing the Ca/P ratio in HA [4,5].

Coatings of HA have been used in orthopedic and dental implants. For the best bonding, the HA phase should be more than 95% of the coating [6]. HA coatings generally have a thickness of 50 to 200 μm [7]. The porosity of the HA coating should be minimized because highly porous coatings result in weak bonding [6].

HA is generally coated on metals by plasma spraying commercially [8]. In this technique, the spraying temperature of HA powders on metals exceeds HA's decomposition temperature to tri-calcium phosphate (TCP) (above 1300 °C) and tetracalcium phosphate (above 1400 °C) [9–11]. α or β-TCP, which is more degradable than HA, can form in addition to HA during plasma spraying. Some of the commonly used metals as coating substrates are commercially pure titanium, Ti-6Al-4V, 316L stainless steel, and CoCrMo alloys. Metals and HA have different thermal expansion coefficients (CTE) [12]. As a result of this difference, tensile forces result in cracks on HA coatings and poor adhesion of HA on the metal substrate. To overcome the difference between the CTE of HA and Ti-6Al-4V, HA-alumina composites were coated on Ti-6Al-4V.

2. Experimental procedures

The materials used in this research are pure HA, composites of HA and nanosize-α-alumina, and Ti-6Al-4V as substrate metal in coatings.

HA was synthesized by a precipitation method by mixing reagent grades of calcium nitrate and di-ammonium hydrogen phosphate in the alkaline pH region [13]. The powders

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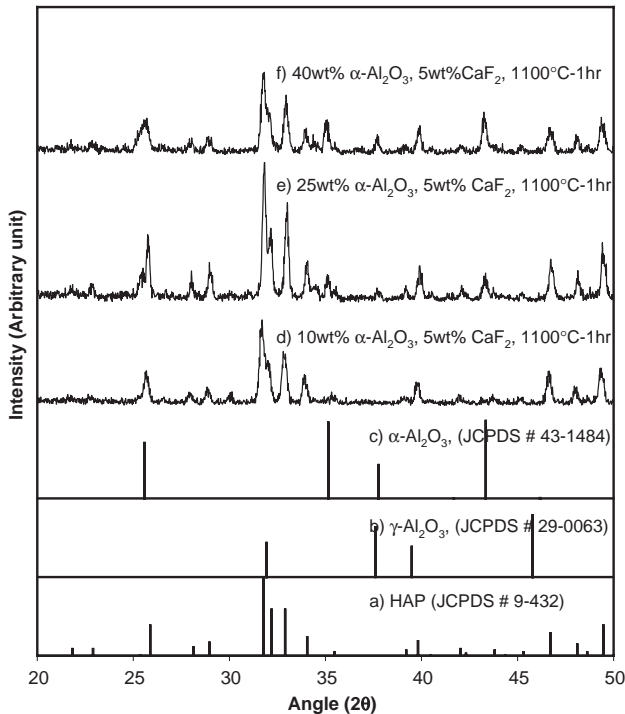Fig. 1. X-ray diffraction spectra of 10, 25, and 40 wt.% α-Al$_2$O$_3$ - HA composites with 5 wt.% CaF$_2$ sintered in sintered in argon at 1100 °C.

of nanosize Al$_2$O$_3$, (48 nm particle size, Nanophase Technologies Inc., Burr Ridge, IL) were mixed with HA powder. Nanosize γ-Al$_2$O$_3$ (as received) was transformed to nanosize α-Al$_2$O$_3$ by a heat treatment in a platinum crucible at 1300 °C for 10 min before mixing with HA.

The compositions of the coatings used in this research were 10, 25, and 40 wt.% α-Al$_2$O$_3$ - HA with 5 wt.% CaF$_2$. The dried HA particles were ground to ≤ 75 im (-200 mesh) powder using a mortar and pestle, and calcined at 900 °C for 1 h. The calcined HA and nanosize α-Al$_2$O$_3$ powders were mixed by ball milling. The ball milled and dried powders were ground with a mortar and pestle.

The composites were coated on Ti-6Al-4V rods with a diameter of 4.75 mm. The composite powder was cold pressed at ~100 MPa around the metal to produce a total diameter of 12.7 mm. The coatings were sintered in air or argon at 1100 °C for 1hr.

The bond strength of the coatings on metal rods was determined by a push-out test. The ceramic coating and the metal substrate were pushed away from each other using an INSTRON Universal Testing Machine. A speed of 0.1 mm/min was applied during the push-out test. The following formula was used to calculate the push-out strengths of the coatings.

$$S = \frac{P}{\pi * d * L} \tag{1}$$

where P: applied load, d: metal rod diameter (4.75 mm), L: height of the ceramic coating along metal rod.

The CTE of the composite coatings and Ti-6Al-4V was measured with an Orton automatic dilatometer from RT to
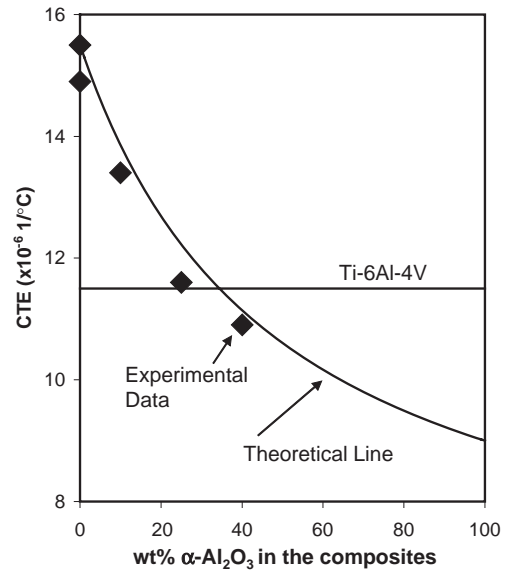

Fig. 2. Coefficients of thermal expansion of HA matrix composites with α-Al$_2$O$_3$.

1100 °C. Samples were cut to cylindrical shapes of 1″ length and 0.2″ diameter. Samples were heated in the dilatometer at a rate of 3 °C/min.

3. Results and discussion

X-ray diffraction results of HA- α-Al$_2$O$_3$ composites with 5 wt.% CaF$_2$, which were sintered in argon at 1100 °C, are presented in Fig. 1. The HA and α-Al$_2$O$_3$ were stable in the presence of CaF$_2$ after sintering at 1100 °C. CTE decreased as the amount of Al$_2$O$_3$
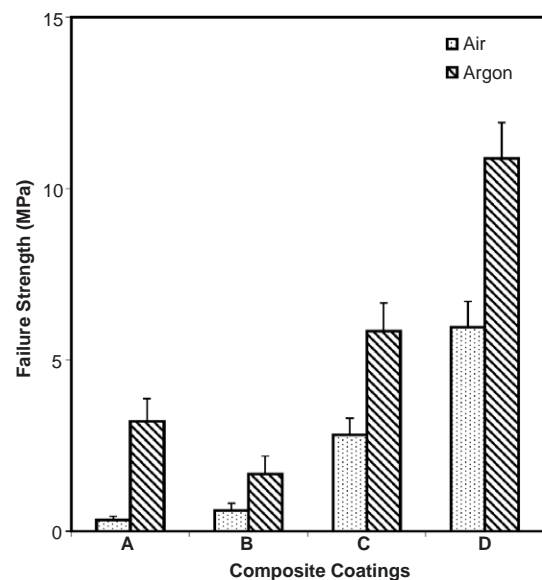

Fig. 3. Failure strengths of the bond between the Ti-6Al-4V substrates and the ceramic coatings of A: HA; B: 10 wt.% α-Al$_2$O$_3$, 5 wt.% CaF$_2$,-HA; C: 25 wt.% α-Al$_2$O$_3$, 5 wt.% CaF$_2$,-HA, D: 40 wt.% α-Al$_2$O$_3$, 5 wt.% CaF$_2$,-HA after the push-out test.
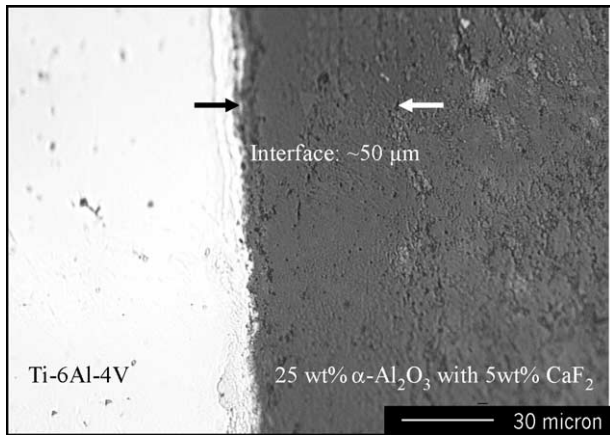
Fig. 4. Optical microscopy image 25 wt.% α-Al_2O_3-5 wt.% CaF_2 composite coated on Ti-6Al-4V, no crack formation by matching the CTE of the coating and the metal.

increased. The CTE of the metal and the ceramic coatings are presented in Fig. 2. CTE of Ti-6Al-4V is close to that of the composite containing 25 wt.% α-Al_2O_3 and 5 wt.% CaF_2.

Sintering of the coatings in air resulted in excessive oxidation of the metals. This oxide formation on the metal surfaces diminished the bonding between the metal and the coating. Bond strengths of HA and 5 wt.% CaF_2-α-Al_2O_3- HA coatings on Ti-6Al-4V by push out tests are presented in Fig. 3. Increasing the amount of nanosize-Al_2O_3 in the coatings improved the bonding strength because the CTE of Ti-6Al-4V and HA-alumina coatings were more closely matched. The composite containing 40 wt.% α-Al_2O_3 and 5 wt.% CaF_2 resulted in highest bond strength between the metal and ceramic because of the compressive stresses formed on ceramic. To make HA and nanosize-Al_2O_3 composites, α-Al_2O_3 powder was used because of its better sinterability than γ-Al_2O_3 [14].

Diffusion and mass transport affect the final densification by controlling the removal of pores and increasing the reactivity of the matrix and particles. We are hypothesizing that Ca^{2+} ions were transported from CaF_2 or HA to the contact surface of Al_2O_3 particles. At temperatures above about 1150 °C in ambient atmosphere, HA begins to decompose by the following reaction:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O. \tag{2}$$
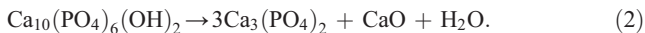
CaF_2 probably prevented reaction 2 so that water is not given off and fewer pores are formed. The addition of calcium fluoride to the powder mixtures of the composites strongly reduced the tendency of the HA to decompose during sintering. Presumably the fluoride substitutes for OH^- groups in the apatite structure; the reaction can be written as:

$$Ca_{10}(PO_4)_6(OH)_2 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2 + CaO + H_2O. \tag{3}$$
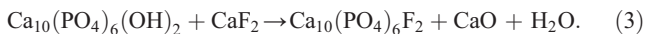
The reaction between HA and calcium fluoride can occur at temperatures (900 °C) lower than the sintering temperature of 1100 °C [15]. Therefore this reaction eventually improved the stability of the composites at 1100 °C.

Coating of HA on Ti-6Al-4V is difficult because of their different thermal expansion coefficients, which results in crack formation. When the CTE of the coating and the metal is matched, no crack formation can be observed, as seen in Fig. 4.

Otherwise, cracks generally start to form at the interface between the metal and ceramic and result in cracking of the ceramic coating. Measured CTE's of the composites agreed closely with CTE's from a simple mixture formula, as shown in Fig. 3. The formula is [16]:

$$\alpha_c = \frac{\alpha_m E_m V_m + \alpha_p E_p V_p}{E_m V_m + E_p V_p} \tag{4}$$

where E and V represent the Young's modulus and the volume fraction of the matrix (m), the particles (p), and α the CTE.

Pure HA or 10 wt.% α-Al_2O_3-HA with 5 wt.% CaF_2 composite resulted in poor bonding with the titanium alloy because their CTE was higher than that of the alloy, resulting in a tensile stress on the coating. The CTE of 25 and 40 wt.% α-Al_2O_3-HA with 5 wt.% CaF_2 composites matched with that of Ti-6Al-4V, giving better bonding of the coating on the metal by eliminating tensile stresses between them.

4. Conclusion

Composites of HA and nanosize-α-Al_2O_3 with 5 wt.% CaF_2 were coated on Ti-6Al-4V rods by cold pressing and sintering. Matching the thermal expansion coefficient of the ceramic coating and the metal substrate improves the bonding and minimizes the formation of cracks. Nanosize alumina-HA coatings showed better bonding than the pure HA coatings on Ti-6Al-4V. Addition of nanosize alumina into HA resulted in smaller thermal expansion coefficient, bringing it close to that of Ti-6Al-4V.

Acknowledgements

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