Available online at www.sciencedirect.com

SCIENCE DIRECT

Materials Letters 59 (2005) 3824 – 3827

materials letters

www.elsevier.com/locate/matlet

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

Zafer Evis [a,*], Robert H. Doremus [b]

[a] Middle East Technical University, Engineering Sciences, Ankara, 06531, Turkey
[b] Rensselaer Polytechnic Institute, Materials Science and Engineering, Troy, NY, 12180, United States

Received 3 May 2005; accepted 3 July 2005
Available online 25 July 2005

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.

Keywords: Hydroxyapatite; Nanosize alpha alumina; Coating; XRD

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

---

* Corresponding author.
E-mail address: evis@metu.edu.tr (Z. Evis).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.07.020

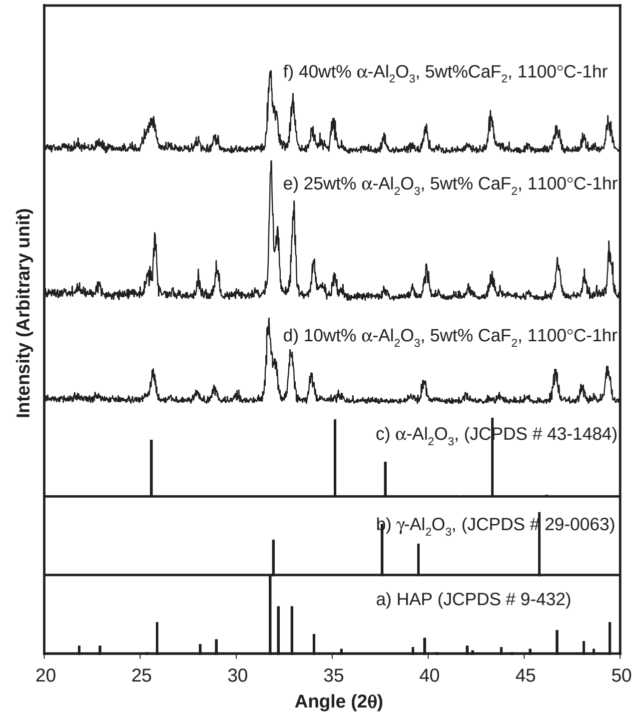

Fig. 1. X-ray diffraction spectra of 10, 25, and 40 wt.% α-Al_2O_3 - HA composites with 5 wt.% CaF_2 sintered in sintered in argon at 1100 °C.

of nanosize Al_2O_3, (48 nm particle size, Nanophase Technologies Inc., Burr Ridge, IL) were mixed with HA powder. Nanosize γ-Al_2O_3 (as received) was transformed to nanosize α-Al_2O_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_2O_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_2O_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 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.

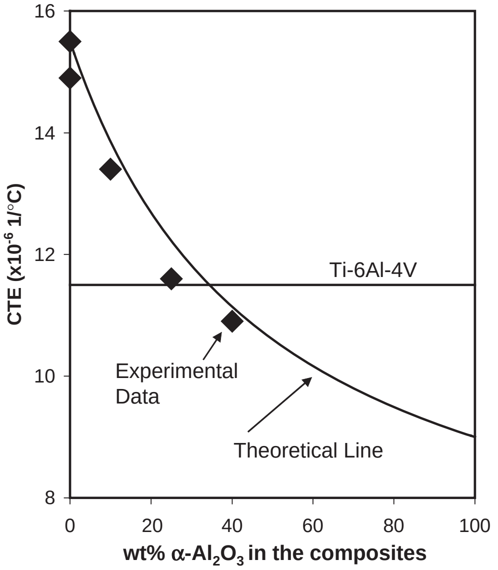

Fig. 2. Coefficients of thermal expansion of HA matrix composites with α-Al_2O_3.

3. Results and discussion

X-ray diffraction results of HA- α-Al_2O_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_2O_3 were stable in the presence of CaF_2 after sintering at 1100 °C. CTE decreased as the amount of Al_2O_3

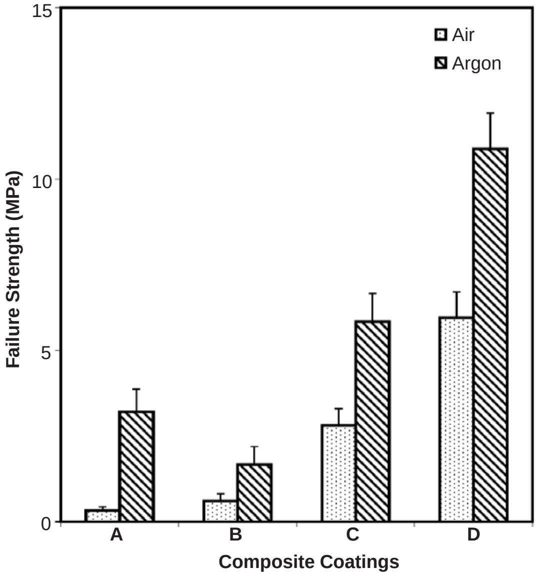

Fig. 3. Failure strengths of the bond between the Ti-6Al-4V substrates and the ceramic coatings of A: HA; B: 10 wt.% α-Al_2O_3, 5 wt.% CaF_2,-HA; C: 25 wt.% α-Al_2O_3, 5 wt.% CaF_2,-HA, D: 40 wt.% α-Al_2O_3, 5 wt.% CaF_2,-HA after the push-out test.