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Biomaterials 23 (2002) 85–91

Biomaterials

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Titanium dioxide reinforced hydroxyapatite coatings deposited by high velocity oxy-fuel (HVOF) spray

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Received 21 July 2000; accepted 19 February 2001

Abstract

Hydroxyapatite (HA) coatings with titania addition were produced by the high velocity oxy-fuel (HVOF) spray process. Mechanical properties of the as-sprayed coatings in terms of adhesive strength, shear strength and fracture toughness were investigated to reveal the effect of the titania reinforcement on HA. Qualitative phase analysis with X-ray diffraction (XRD) showed that mutual chemical reaction between TiO_2 and HA, that formed $CaTiO_3$ occurred during coating formation. Differential scanning calorimetry (DSC) analysis of the starting powders showed that the mutual chemical reaction temperature was $\sim 1410°C$ and the existence of TiO_2 can effectively inhibit the decomposition of HA at elevated temperatures. The positive influence of TiO_2 addition on the shear strength was revealed. The incorporation of 10 vol% TiO_2 significantly improved the Young's modulus of HA coatings from 24.82 ($\pm$2.44) GPa to 43.23 ($\pm$3.20) GPa. It decreased to 38.51 ($\pm$3.65) GPa as the amount of TiO_2 increased to 20 vol%. However, the addition of TiO_2 has a negative bias on the adhesive strength of HA coatings especially when the content of TiO_2 reached 20 vol%. This is attributed to the weak chemical bonding and brittle phases existing at the splats' interface that resulted from mutual chemical reactions. The fracture toughness exhibited values of 0.48 ($\pm$0.08) MPa $m^{0.5}$, 0.60 ($\pm$0.07) MPa $m^{0.5}$ and 0.67 ($\pm$0.06) MPa $m^{0.5}$ for the HA coating, 10 vol% TiO_2 blended HA coating and 20 vol% TiO_2 blended HA coating respectively. The addition of TiO_2 in HA coating with the amount of less than 20 vol% is suggested for satisfactory toughening effect in HVOF HA coating. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxyapatite coating; HVOF; Mechanical properties; Mutual reaction; Toughening effect; Titania

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1. Introduction

Hydroxyapatite (HA) is widely used as implant material in clinical applications owing to its identified biocompatibility. Previous studies have shown that when thermally sprayed, mostly by direct currect (dc) plasma, HA coatings on titanium alloy substrate were capable of forming bioactive fixation with surrounding bony tissues [1–3]. However, it is severely limited by the intrinsic poor mechanical properties of HA material, which can lead to instability and unsatisfactory duration of the implant in the presence of body fluids and local loading. In osseous tissues, the mechanical strength of HA is further reduced, considerably, by fatigue [4]. Therefore, HA needs to be strengthened. The incorporation of bioinert ceramics is believed to be a method to improve the mechanical reliability of the HA matrix and, hence this investigation is reported [5–7]. It was found that the addition of biocompatible glass into HA had a major effect on HA structure [8] and could effectively improve the fracture toughness of bulk HA materials [9]. In addition, the crystallinity of HA needs to be increased and the phase transformation of HA to tricalcium phosphate (TCP), tetracalcium phosphate (TTCP) and CaO, etc., which usually occurs in plasma spraying [10–12], should to be minimized. The high velocity oxy-fuel (HVOF) process is an important manufacturing process for HA coating production with suitable crystallinity and improved mechanical properties [13,14].

Influence of an addition of titanium dioxide on thermal properties of sintered HA has attracted significant attention [15,16] because titania ceramics are potentially useful as porous cell carrier material whose properties, such as good permeability and high

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PII: S0142-9612(01)00082-5

biocompatability, serve to enhance cell vitality. The efficacy of different titanium dioxide materials on cell growth and distribution has been studied [17]. However, to-date, the reports focus solely on bulk HA composite materials. Investigation on composite HA coatings is rare. The effect of TiO_2 on the structure and mechanical properties of thermally sprayed HA coatings is still unknown.

In the present study, experimental investigation on HVOF sprayed HA/TiO_2 composite coating was conducted. The mechanical properties of the composite coating were evaluated in terms of adhesive strength, shear strength and fracture toughness. The influence of the titania content on the microstructure and phase composition of HA coating was also studied.

2. Materials and testing methods

2.1. Materials and spraying equipment

The spray-dried HA powders made by wet chemical method were used in the present study. Fully crystallized HA structure, $Ca_{10}(PO_4)_6(OH)_2$ (as the chemical formula) was prepared by heat-treating the spray-dried HA powders in furnace at 900°C for 1.5 h. The XRD pattern of the starting HA powders is shown in Fig. 1. The anatase form of titanium dioxide (TiO_2) was used and the mean powder size was around 1 μm. Fig. 2 shows the size distribution of the starting powders. The mean particle size of HA feedstock is 40 μm. The composite powders were prepared through mechanical blending process till fully mixed. Fully computerized HV2000 HVOF system (Praxair, IN, USA) with the nozzle diameter of 19 mm was employed for the coating production on sandblasted Ti6Al4 V substrate surface. The fuel gas was hydrogen and the powder carrier gas was argon. The flow rate of oxygen, hydrogen and argon was 283, 566 and 19 l/min, respectively. The spray distance was 250 mm, and the powder feed rate was 6 g/min.

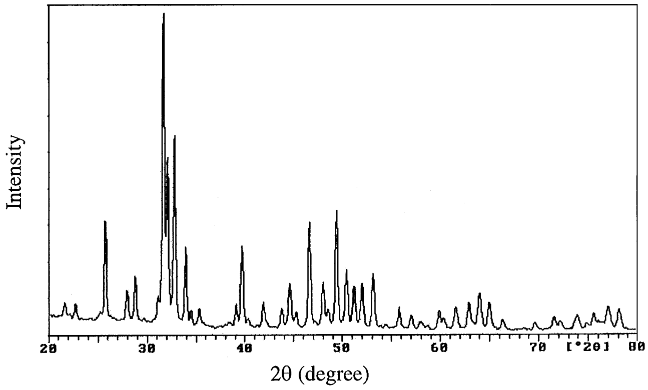
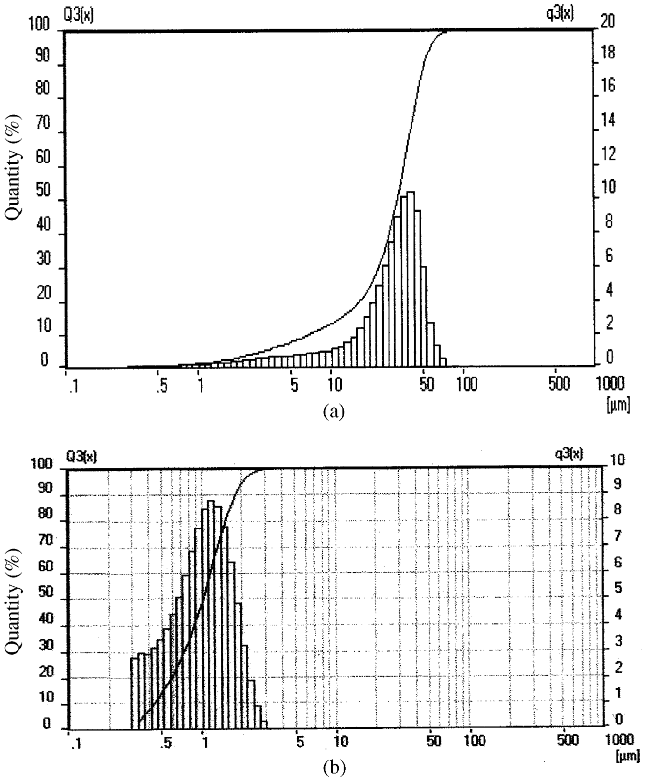


Fig. 1. XRD pattern of the hydroxyapatite feedstock powder.

2.2. Coating analysis methods

The coating microstructure was analyzed on a polished coating cross-section by using scanning electron microscopy (SEM). Differential scanning calorimetry (DSC) (Netzsch Thermal Analysis, DSC 404C, Germany) was utilized for the determination of the chemical reaction temperature between HA and TiO_2. DSC test used nitrogen gas as the atmosphere with the flow rate of 150 ml/min and the heating rate was 10°C/min. The phase composition of the starting powders and as-sprayed coatings was analyzed by means of X-ray diffraction method (XRD) (MPD 1880, Philips, the Netherlands). The operating conditions were 40 kV and 30 mA by using Cu K_α. The goniometer was set at a scan rate of 0.015°/s over a 2θ range of 20–80°. The adhesive strength of as-sprayed coating was measured according to ASTM C633-79 standard and five samples were used for each type of coatings. The coating thickness for adhesive strength measurement was 180 ± 15 μm. The shear strength was determined by using double-face sprayed specimens, which is schematically depicted in Fig. 3, to ensure the symmetry of samples during shear test. Six samples were tested for each type of coatings. The double coated specimen with a coating thickness of 80 ± 10 μm was bonded with two coupled specimens together for tensile testing. The maximum tensile load at the point of failure is used to determine the shear



(a)

(b)

Fig. 2. Size distribution of the (a) HA powder and (b) TiO_2 powder.

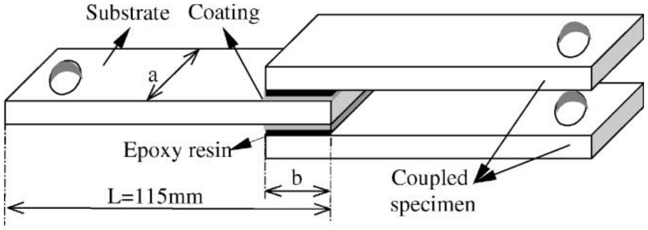


Fig. 3. Schematic depiction of shear strength testing.

strength. The epoxy resin used for adhesive strength test and shear strength test is DP-460 Epoxy Adhesive (3 M Scotch-Weld^{TM}, USA). The 3-point bending test was carried out for the determination of Young's modulus of the coatings, which was first proposed for the use in thick coating field by Fawcett [18] by using double-side coatings. The Young's modulus of 113 GPa for Ti6Al4 V was used and the coating thickness was 150 μm. The dimension of the substrate was 120 mm × 20 mm × 2 mm in length, width and thickness, respectively. Three samples were prepared for the bending test for each type of coatings and for every sample three bending curves were obtained by choosing different positions. A universal testing machine was used for the measurement of adhesive strength, shear strength and Young's modulus. The tensile crosshead speed was 1 mm/min for adhesive strength test and 0.2 mm/min for shear strength test and Young's modulus test. The fracture toughness of the as-sprayed coatings was studied by using indentation method. The following formula was utilized for the determination of the fracture toughness [19]

$$K_{Ic} = 0.016(E/H)^{1/2}(P/C^{3/2}), \quad (1)$$

where E is the Young's modulus of the coating, which was obtained from the three-point bending test in the present study, H is the hardness of the coating, C is the crack length caused by indentation and measured quickly following the unloading, P is the indenter load, which is 0.5 N in the present study with a load application time of 15 s. In total, 15 points were tested for each type of coatings.

3. Results

3.1. Phase composition

The XRD patterns of the as-sprayed coatings investigated are shown in Fig. 4. It reveals that the as-sprayed pure HA coating is mainly composed of crystalline HA and α-TCP. The crystalline HA, anatase TiO_2, α-TCP, amorphous calcium phosphate as well as some rutile TiO_2, $CaTiO_3$ and CaO are detected simultaneously in both the composite coatings. Comparing with the XRD pattern of the coating manufactured with hydroxyapatite depicted in Fig. 4(a), the composite coatings with TiO_2 exhibit more α-TCP with increasing amounts of TiO_2.

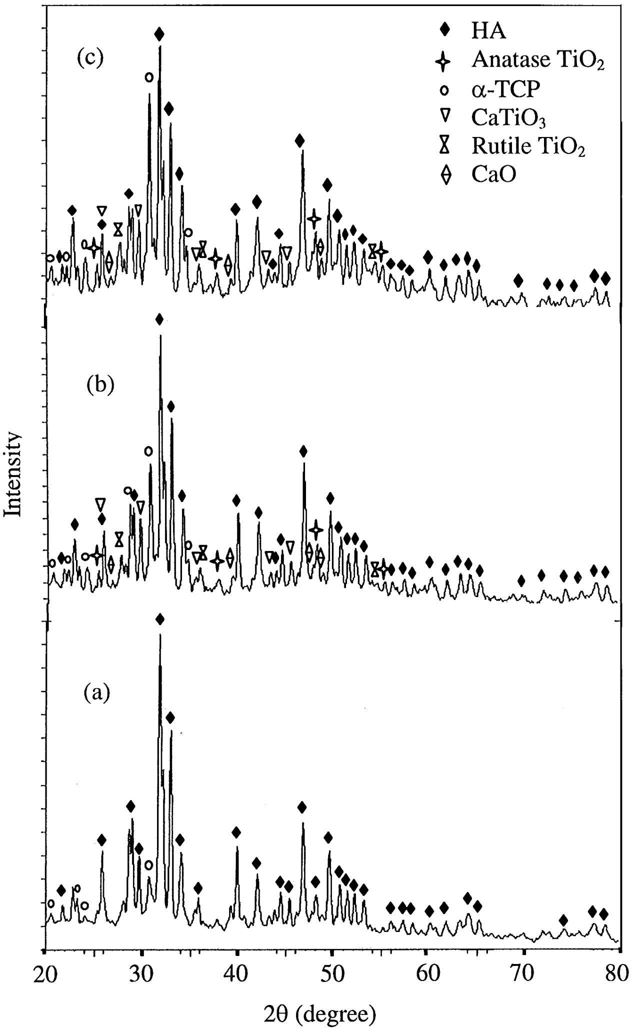


Fig. 4. XRD patterns of as-sprayed coatings, manufactured from (a) hydroxyapatite, (b) HA + 10 vol% TiO_2 and (c) HA + 20 vol% TiO_2.

3.2. Mechanical properties

The effect of TiO_2 incorporation on the shear strength and adhesive strength of HA coatings is shown in Fig. 5. It is found that the shear strength slightly increases with the increase of TiO_2 content in the coatings. However, it demonstrates that the addition of TiO_2 has a negative effect on the adhesive strength of the coatings. With the increase of TiO_2, adhesive strength decreases from 27.93 (± 1.51) MPa for pure HA coating to 26.82 (± 2.27) MPa for the composite coating composed of 10 vol% TiO_2 and down sharply to 17.19 (± 1.23) MPa as the content of TiO_2 increased to 20 vol%.

The Young's modulus of the as-sprayed coatings obtained from the three-point bending test is

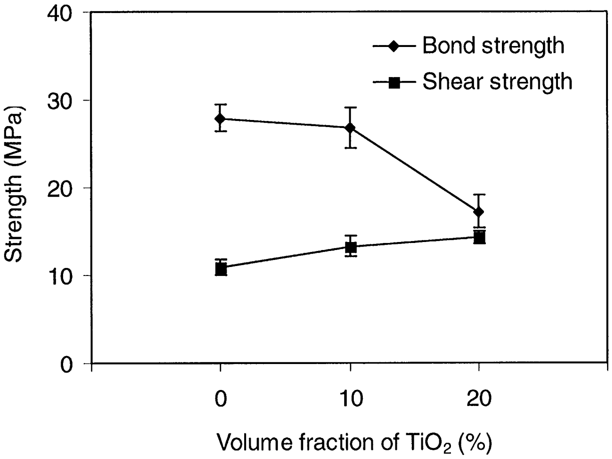


Fig. 5. Effect of TiO_2 addition on adhesive strength and shear strength of HA coatings.

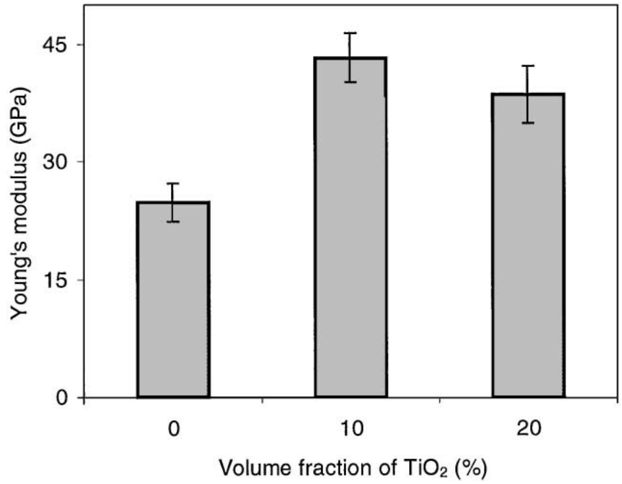


Fig. 6. Effect of TiO_2 addition on Young's modulus of HA coatings.

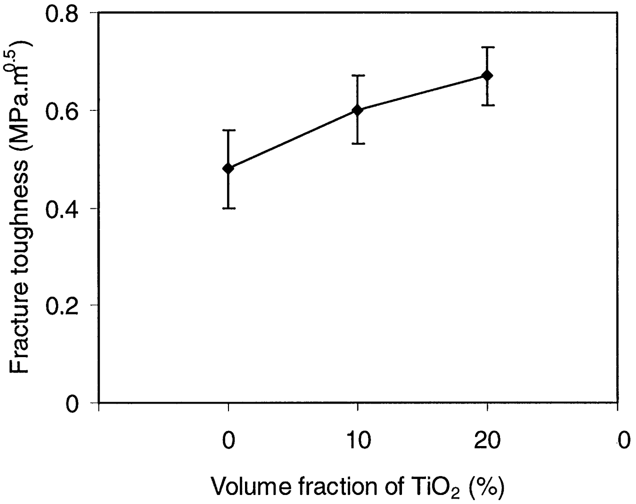


Fig. 7. Effect of TiO_2 addition on fracture toughness of HA coatings.

demonstrated in Fig. 6. The E value is increased by the addition of TiO_2 but starts decreasing as the content of the secondary phase reaches 20 vol%. Fig. 7 shows the effect of TiO_2 addition on the fracture toughness of HA coatings. It shows that the fracture toughness, K_{Ic}, increases with the increase of amount of TiO_2 in HA coatings, from 0.48 ($\pm$ 0.08) MPa $m^{0.5}$ to 0.60 ($\pm$ 0.07) MPa $m^{0.5}$ and 0.67 ($\pm$ 0.06) MPa $m^{0.5}$, respectively. It should be noted that only small increase of K_{Ic} value was revealed for the 20 vol% TiO_2 composite coating from the 10 vol% TiO_2 composite coating compared to that between pure HA coating and 10 vol% TiO_2 composite coating.

4. Discussion

The following decomposition formula has been proposed when HA is heated to elevated temperatures during coating formation [20–22]

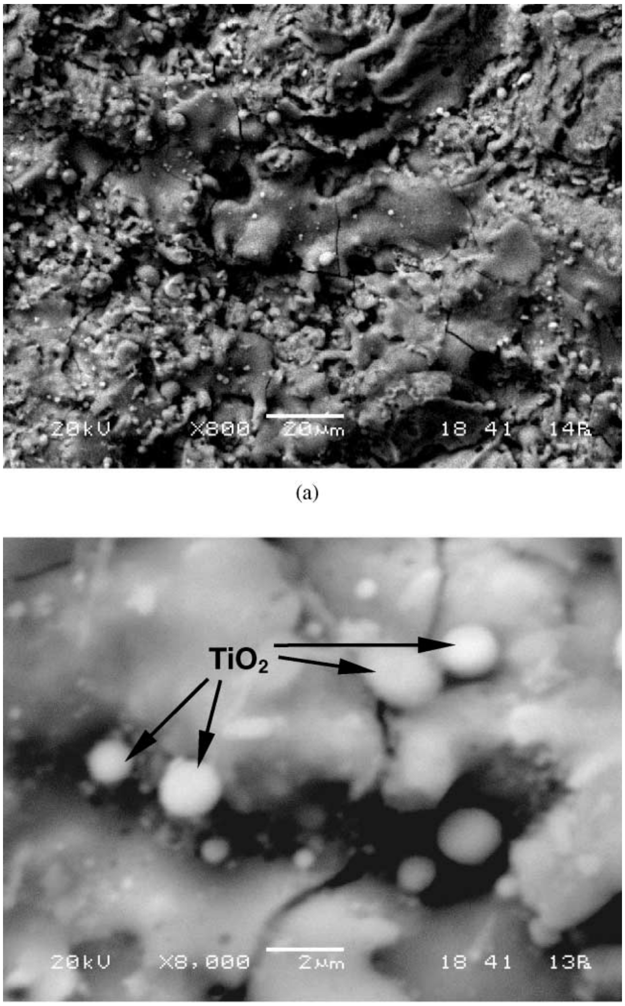
$$Ca_{10}(PO_4)6(OH)_2\ (HA) \rightarrow 3Ca_3(PO_4)_2\ (TCP) + CaO + H_2O \uparrow . \qquad (2)$$

It should be noted that the reason why CaO could not be detected in the present HA coating lies in the very small amount of this phase in the coating. The crystallinity of as-sprayed pure HA coating is 86% obtained by using the area-integration method [23] from XRD pattern. Basically, TiO_2 is a chemically stable material with transformation from anatase to rutile at 400–1000°C [T_m(rutile) = 1855°C] [24]. From the XRD patterns of the composite coatings illustrated in Fig. 4(b) and (c), the point that some rutile phase is detected suggests that transformation of part of anatase TiO_2 powder to rutile occurs and the core of the powder remains in the original form. Combining with the EDX analysis, the surface morphology of the composite coating shown in Fig. 8 indicates that the TiO_2 powders were totally unmelted during coating formation. The spherical particle on the coating surface is the unmelted TiO_2.

The formation of $CaTiO_3$ indicates that the mutual reaction between HA and TiO_2 took place during coating formation. The following chemical reaction is suggested:

$$Ca_{10}(PO_4)_6(OH)_2 + TiO_2 \rightarrow 3Ca_3(PO_4)_2\ (TCP) + CaTiO_3 + H_2O. \qquad (3)$$

It has been pointed out in a study where composites were heated in air higher than 900°C that HA prefers to chemically react with anatase rather than rutile [15]. For the purpose of further revealing reaction mechanism between TiO_2 and HA, the starting composite powders, HA + 20 vol%TiO_2, was investigated by DSC. The DSC curves are shown in Fig. 9. The comparison among the mixed powders (a) and pure HA (b) and TiO_2 (c) powders indicates that the mutual chemical reaction



(a)

(b)

Fig. 8. Surface morphology of an HA–20 vol% TiO_2 coating. TiO_2 areas are identified as bright spheres at (a) low magnification and (b) high magnification.

occurs at around 1410°C under the present DSC conditions, subsequently followed by further phase transformation of HA materials [25] remained in the mechanically blended powders. This phenomenon suggests a solid state reaction.

The DSC curve of anatase powder indicated that the transformation to rutile occurs slowly while absorbing heat. It is found that the separate HA powder exhibits the absorbing-heat peaks, which spans approximately from 1180°C to 1340°C. These broad peaks refer to the phase transformation from HA to α-TCP or even $Ca_4O(PO_4)_2$ [21,26] together with the allotropic transformation from β-TCP, the impurity with very limited amount in the starting powder, to α-TCP. And beyond 1200°C HA would lose its OH groups gradually [25]. The present study suggests that the existence of TiO_2 powders can effectively inhibit HA phase transformation at the temperatures lower than that of mutual reaction point, which is indicated by the disappearance of correspondent peaks marked from 1180°C to around 1340°C. Even though Weng et al. [15] reported that the HA/titania composites sintered at 900°C with 60 min demonstrate the chemical reaction resultant, $CaTiO_3$, the long heating time seems to play an important role in determining the reaction rate and the temperature at which point the reaction can occur. And the particle size of titania and its content in the composites should also be considered. The peak labeled at around 1457°C would be the point where further transformation of HA occurs [25]. Since the solubility of TCP is higher than crystalline HA and the decomposition of HA decreases the biocompatibility [27], the inhibition of chemical decomposition of HA by the additives is useful.

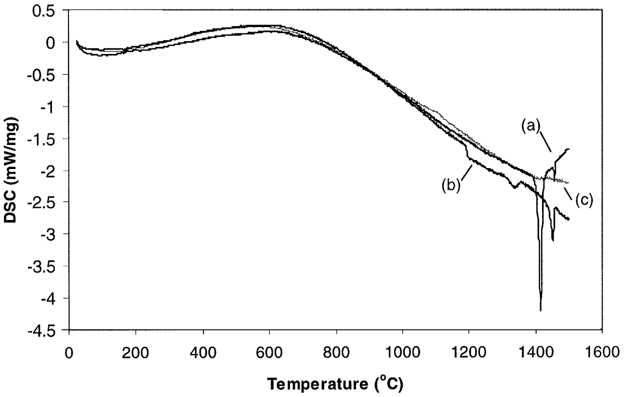


Fig. 9. DSC curves of (a) mechanically blended HA and titania powder, (b) HA powder and (c) TiO_2 powder.

It is noted that the Young's modulus of the composite coating composed of 10 vol% TiO_2 nearly satisfies the linear relationship [28] which describes the particulate reinforced composite materials without the consideration of the contribution of defects and chemical products in the coating

$$E_c = E_p V_p + E_m V_m, \tag{4}$$

where E_c is coating Young's modulus, V is volume fraction, subscripts p and m represent secondary particles and matrix, respectively. It is believed that while the TiO_2 content in HA coating is small, the influence of an added interface and a third phase, such as $CaTiO_3$, is small. The improvement of the Young's modulus is attributed to the mere existence of TiO_2. The decrease of the Young's modulus in the 20 vol% TiO_2 coating indicates the considerable influence of the multi-phases in the coatings that resulted from chemical decomposition and mutual reaction. Even though Metsger et al. [29] thought that the decomposition of HA was capable of increasing the modulus of bulk HA materials, the positive effect can not be assured in this study due to the appearance of $CaTiO_3$ from mutual reactions. Moreover, it is believed that the incorporation of TiO_2 in HA coating changes the residual stress that was believed as the major factor in determining the Young's modulus of HA materials [29].

In order to reveal the possible reason why the effect on shear strength and adhesive strength exhibited, tensile failure morphology of the composite coatings is analyzed. It is found that the shear failure is located exclusively at the coating/substrate interface. The improved shear strength value suggests a better coating/substrate interface of the composite coatings compared with pure HA coating. Given that the coefficient of thermal expansion (CTE) of anatase TiO_2 and HA are 10.2×10^{-6}/K and 16.0×10^{-6}/K [30], respectively, and, the CTE of the titanium alloy substrate is 8.9×10^{-6}/K, the incorporation of TiO_2 can effectively reduce the residual tensile stress near the coating/substrate interface caused possibly by the CTE mismatch during the cooling of coating. For both pure HA coating and composite coatings, the tensile failure demonstrated in Fig. 10 is located within the coatings rather than at the coating/substrate interface, which demonstrates the importance of the splats' interface. The resultant phase, $CaTiO_3$, distributed at the splats' interface is probably responsible for the reduced adhesive strength. In addition, it seems that the increased α-TCP content along the splats' interface is detrimental for coating cohesion. From the coating surface morphology demonstrated in Fig. 8, chemical bonding is suggested as the main bonding mechanism between HA and TiO_2 splats. The addition of a secondary phase is not capable of enhancing the adhesive strength of HA coatings. However, since calcium phosphate coatings dissolve after extended implantation periods [31], the chemical bonding between HA/titania splats resulted from mutual reaction may be beneficial for the prevention of releasing of titania particles into surrounding tissues or releasing of these particles as wear products that can lead to prosthesis rejection, or, infection.

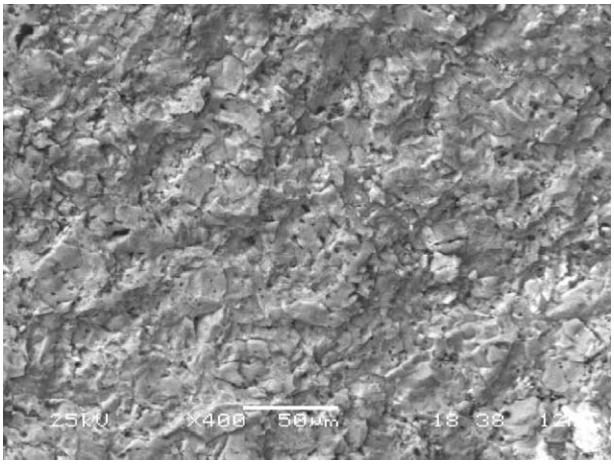


Fig. 10. Typical tensile failure surface morphology of the composite coating (HA + 10 vol% TiO_2).

The relatively high fracture toughness exhibited by the composite coating compared to pure HA coating indicates the improved bonding area of splats' interface. It deems that the mutual chemical reaction between the two components provides higher density, which was believed as one beneficial factor influencing fracture toughness [32]. The phases resulted from mutual reaction or chemical decomposition are likely to be located along the splats' interface and reduce the defects along splats' interface, thus improve the ability to inhibit crack propagation induced by an indenter.

The fracture toughness of pure HA coating in the present study shows a lower value than the reported values for bulk HA materials: 1.2 MPa $m^{0.5}$ by Champion et al. through single edge notched bend technique [33], 0.7 MPa $m^{0.5}$ by Gautier et al. [7] and 0.72 MPa $m^{0.5}$ through Vicker's indentation technique [9]. Moreover, a composite HA bulk material containing 20 vol% Al_2O_3 showed a fracture toughness of 2.0 MPa $m^{0.5}$ through single edge notched bend technique [33]. The relatively low K_{Ic} value in the present study can be attributed to the identified inhomogeneous layered structure of thermally sprayed coatings. The defects existing within the coating, such as pores, microcracks and poorly bonded interface between splats supply preferable propagation path for the cracks. It nevertheless affirms that HVOF process produces HA coatings with competitive fracture toughness.

5. Conclusions

1. The addition of TiO_2 is found to improve the Young's modulus, fracture toughness and shear strength of HVOF sprayed HA-based coatings. The increase of titania content from 10 to 20 vol% induces a small decrease in Young's modulus. Chemical reaction between HA and TiO2 is found to occur during coating deposition.
2. The incorporation of the secondary titania phase is found to have a negative effect on the adhesive strength of HVOF HA coatings. This consequence is attributed to the weak chemical bonding and brittle phases that exist at the splats' interface.
3. The titania is found to inhibit the decomposition of HA at elevated temperatures lower than 1410°C, at which point the mutual chemical reaction occurs.
4. Small amount of TiO_2 addition in HVOF HA coating with less than 20 vol% is therefore recommended for strengthening of HA-coatings.

Acknowledgements

The project was financially supported by Nanyang Technological University of Singapore through JT ARC 4/96.

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