

Effect of the powders' melting state on the properties of HVOF sprayed hydroxyapatite coatings

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Abstract

High velocity oxy-fuel (HVOF) spray technique is being used for the deposition of hydroxyapatite (HA) coatings in recent years. The effect of melting state of HA powders on the coating microstructure and performance is investigated in this paper. Tensile adhesion test, X-ray diffraction (XRD) analysis and differential scanning calorimeter (DSC) analysis are used for the evaluation of the coatings. The coating microstructure is analyzed by scanning electronic microscopy (SEM). The results show that the tensile bond strength of the HVOF sprayed HA coatings can be up to 31 MPa and is largely dependent on the spray parameters. XRD result shows that the as-sprayed HA coating using powders with the size around 50 μm is composed of crystalline HA and very small amount of tricalcium phosphate (α -TCP). The coatings deposited using fine powders around 30 μm contained a lot of amorphous phase, crystalline HA and very small amount of α -TCP. Result from the DSC indicates that the crystallization temperature of the amorphous phase in the coatings is around 703°C. Amorphous phases in the as-sprayed coating significantly improved bond strength. The structure crystallized totally in heat-treated coatings below 750°C. SEM analyses of the tensile fractured HA coatings show that fracture occurs within the partially melted powders. The interface between the melted and unmelted parts of the powders is the weakest zone for crack propagation. This suggests that the fully melted state of the feedstock can result in the formation of amorphous phase and simultaneously decrease the bond strength. It also suggests that the fraction of the powders melted is the most critical factor influencing the bond strength and phase composition of the coatings. The partial melting state of HA powders is beneficial in terms of bond strength and crystallinity. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Among the biomaterials explored recently, hydroxyapatite (HA) attracts the most attention and resulted in extensive investigations. The stability and the mechanical performances of the prosthesis are considered to be the most significant factor pertaining to the failure of the implant, apart from infection. Therefore, studies on the microstructure and mechanical properties of HA materials have received considerable attention. Much effort has been diverted in recent years towards the development of optimum processing methods to deposit HA onto metallic substrates while minimizing its inherent mechanical

property limitations. In general, the methods for the production of HA prosthesis can be classified into two categories — thin coating and thick coating techniques [1]. Among the coating techniques, plasma spraying is by far the most widely adopted process [2–4]. This is due to advantages that include high deposition efficiency, low substrate temperature, and improved technology and equipments. However, this potency is limited by the poor cohesion strength and adhesion to the metallic substrate and, most importantly, large quantities of phase transformations [5–7]. In recent years, many new methods have been employed to produce HA coatings [8–11]. Among these methods, the high velocity oxy-fuel (HVOF) spray technique is thought to be the most promising method because it can deposit HA with similar set of advantages that plasma spraying can without the debilitating phase transformations following thermal decomposition

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of HA. The high particle velocities in HVOF are also believed to enhance the adhesion strength of the HA coating on the Ti substrate.

Available literature on the fabrication of HA coatings by the HVOF method is limited. Previous studies show that HVOF can produce a lower amount of amorphous phase in HA coatings [12,13]. However, there still lacks systematic investigations. Even though the *in vitro* and *in vivo* tests are important and useful methods for the evaluation of the HA coatings, the inherent mechanical properties of the HA coatings are important factors in determining the duration and behavior of HA coatings in clinical applications. Therefore, the improvement of the properties of as-sprayed HA coatings is of significant importance. The investigation of the coatings can lead its future applications, which may include medium to even high loading regions of the human skeleton. So far, there is still literature that focuses on the study of the melting state of HA powders on the coating properties. Owing to the extreme high temperature, the widely adopted plasma spraying results in fully melted HA powders that deposit coating composing of predominantly amorphous phases. The present study focuses on the unmelted state of the sprayed powders, which can be beneficial in the prevention of formation of amorphous phase during HVOF spraying. The bond strength of the HA coating to the metallic substrate is believed to be an important factor because the loosening of the implantation is the most common failure in use [14,15]. In the present paper, HVOF method is used for the production of HA coatings. The spray parameters and the powder size are altered to achieve different melting fraction of feedstock. The influence of melting state of the powders on the coating properties is analyzed in terms of bond strength and the phase composition. Furthermore, the crystallization of the amorphous coatings is investigated.

2. Materials and experimental procedures

Hydroxyapatite powders used for the deposition of HVOF coatings on titanium alloy (Ti–6Al–4V) substrates are manufactured by spray drying a HA slurry previously prepared by a wet chemical method. The production of this type of HA precursors for thermal spray processes has been reported in a previous publication [16]. Spray-dried HA powders are found to have suitable morphology conducive to consistent powder feed rates into the combustion chambers of thermal spray processes. For the purpose of investigating the melting state of the sprayed powders on the coating properties, two size ranges of HA powders are adopted; $50 \pm 5 \mu\text{m}$ (powder A) and $30 \pm 5 \mu\text{m}$ (powder B), respectively. The particle size analysis, which was performed by a laser particle size analyzer (Analysette 22, Fritsch GmbH, Germany), is shown in Fig. 1c. Heat-treatment is per-

formed in order to obtain a fully crystallized HA feedstock. The spray-dried HA powders are heated in an electrical resistance furnace at 900°C for 1.5 h and then cooled inside the furnace. Fig. 2 shows the XRD pattern of the heat-treated HA powders, which revealed 100% crystalline HA. This pattern represents powders A and B.

The HVOF system, model HV 280 (Praxair, IN, USA), with a nozzle diameter of 19 mm is used for thermal spraying of the HA powders. Hydrogen is employed as fuel gas and the powder carrier gas is argon. The coating deposition is well controlled by a robot-controlled, computerized spray system so that uniform coating thickness can be obtained. The classification of the coatings depending on the spray parameters and powder choice is listed in Table 1.

The bond strength testing of the coatings was performed according to ASTM C633 standard. The tensile speed was 1 mm min^{-1} and the coating thickness was $180 \mu\text{m}$. Nitrogen gas was used in DSC measurement, model D-240 (Netsch GmbH, Germany) with a flow rate of 150 ml min^{-1} , and a heating rate of 5°C min^{-1} .

3. Results and discussion

3.1. Phase composition of the as-sprayed coatings

The XRD plots of as-sprayed HA coatings investigated are shown in Fig. 3. It is revealed that the as-sprayed HVOF HA coatings deposited with powder A contained nearly no amorphous phase. Moreover, the phase composition of the coating is similar to that of the initial spray-dried powders. However, the coating made from powder B reveals evidence of amorphous phase, which is reflected by the large broad peak around $2\theta = 30^\circ$, and a corresponding decrease in the peak intensity of the crystalline HA peaks, shown in Fig. 3f. Besides the existence of crystalline HA, it is found that α -TCP appears in all the coatings, even though in small quantity.

In order to determine the possible reason for the phase composition of the coatings, the sprayed HA powders were collected in distilled water. Some powders were mounted in a resin and metallographically polished to reveal the cross-sectional features within each particle. Others were placed on a scanning electronic microscopy (SEM) sample holder for observation of the topographical features of the powders. SEM images of the powders, registered from exterior and cross-section views, are shown in Fig. 4. The melt-state of the powders can be verified through observing the cross-section morphologies in a SEM. For the sprayed powders (powder A) corresponding to C-5 coatings, partially melted features were observed. The resolidified layers within the powders (Fig. 4a and b) can affirm

this. Due to the detachment of the unmelted core of the powder that occurred during specimen preparation, only the melted shell of the powder remained for obser-

vation (Fig. 4c). The fraction of the melted part in the whole powder augments with the increase of flow of hydrogen and oxygen during the deposition process.

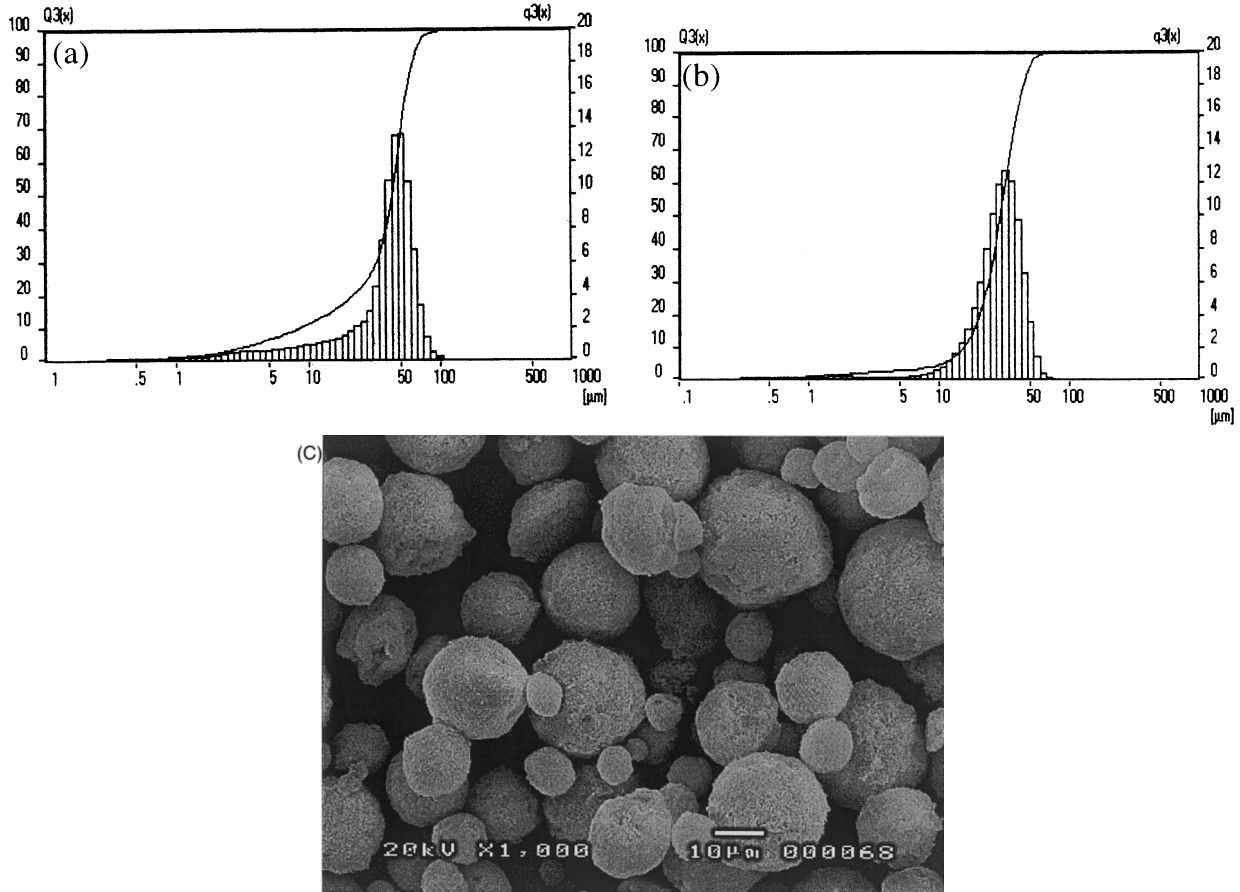


Fig. 1. HA particle size analysis (a) powder A; (b) powder B; and (c) typical HA powder surface morphology.

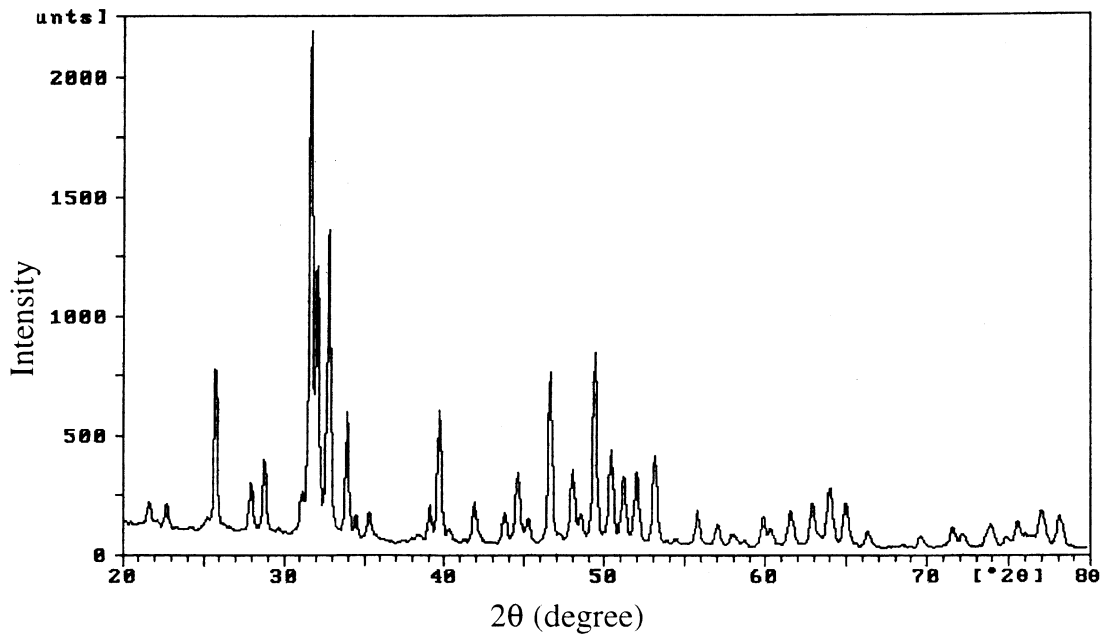


Fig. 2. XRD pattern of the HA powder.

Table 1
Classification of the coatings investigated

Coating type	Flow of oxygen (scfh)	Flow of hydrogen (scfh)	Spray distance (mm)	Powder
C-1	700	1200	250	A
C-2	600	1200	250	A
C-3	600	1100	250	A
C-4	500	1100	250	A
C-5	500	1100	210	A
C-6	600	1200	250	B

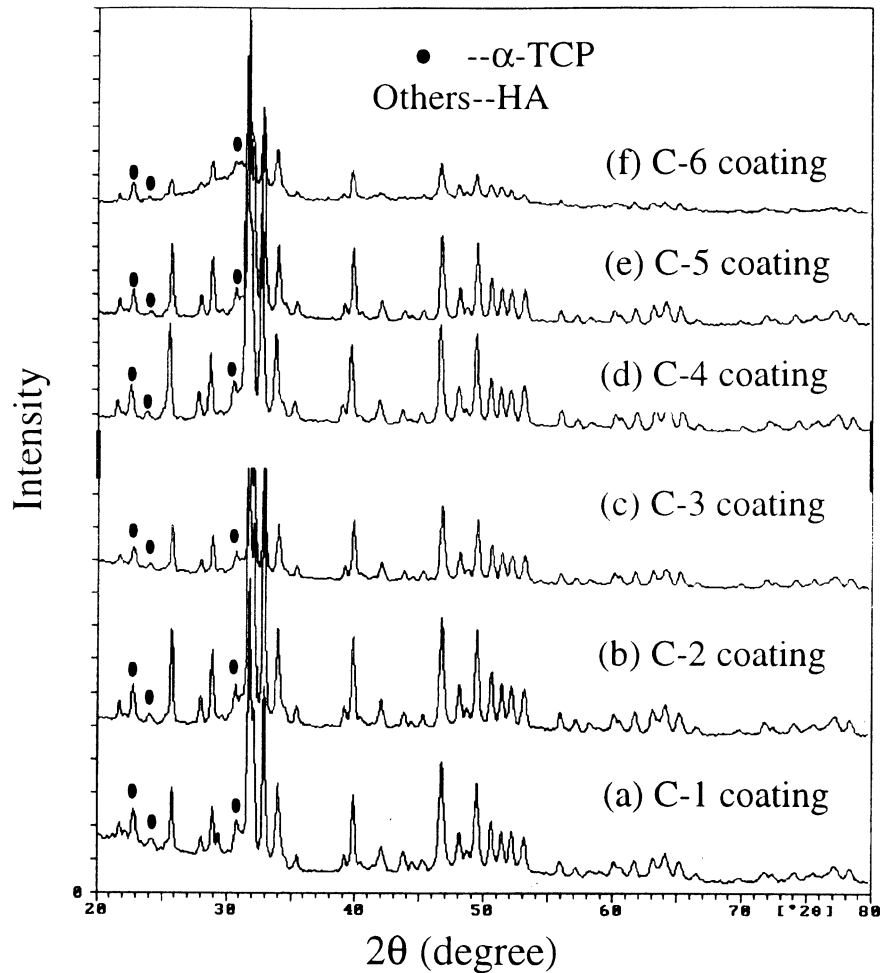
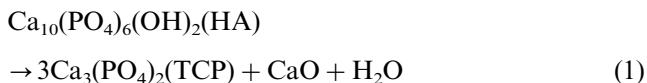


Fig. 3. XRD patterns of as-sprayed HA coatings.

While in powder B, fully melted state can be found through SEM images (Fig. 4d). It is believed that the fully melted part of the powder is responsible for the formation of the amorphous phase. The crystalline HA is the retained HA phase from the raw feed powders that were not affected by the HVOF process. The α -TCP comes from the decomposition of the melted part of the powders: [17–19]



The decomposition can release some CaO simultaneously, but because of the small content, it can not be detected by XRD. The reason why the chemical reaction occurs seems to lie in the melted state and the high cooling rate of the splat [20].

There is still debate on the benefits of amorphous calcium phosphates in the plasma-sprayed HA coatings [18,19]. Nevertheless, it is believed that the high crystallinity levels of the hydroxyapatite coatings is beneficial for the long-term survivability of the coatings in application and mechanical performances considering

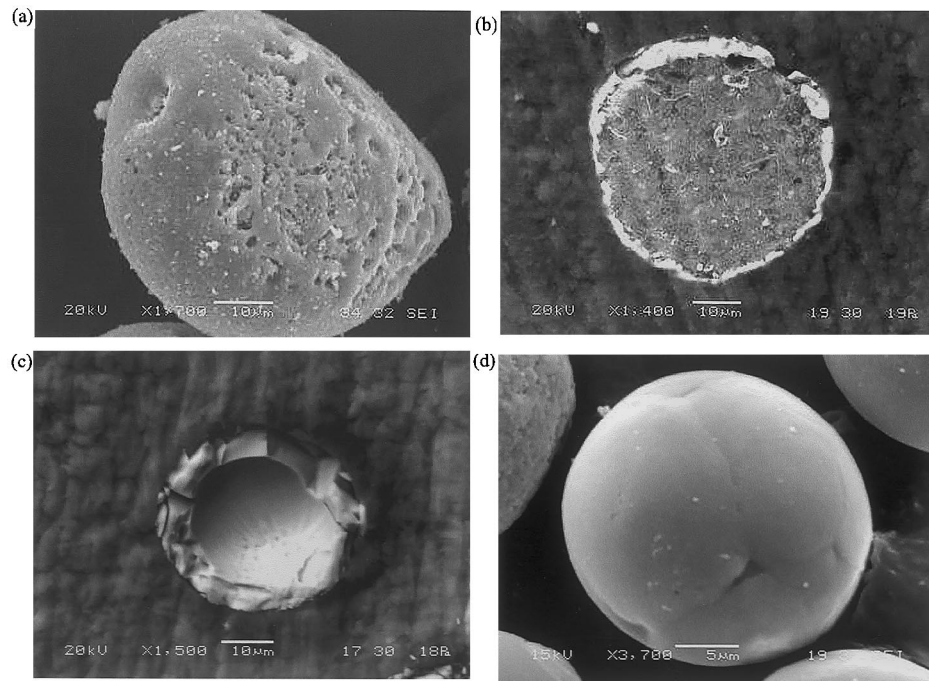


Fig. 4. SEM images of the sprayed HA powders: (a) made by parameter C-5; (b) made by parameter C-5; (c) made by parameter C-1; (d) made by C-6.

the resorbability in the bony tissues because the amorphous phase has a far greater resorbability in the bony tissues than crystalline hydroxyapatite. On the other hand, the high resorbability of the amorphous phase is valuable for accelerated fixation of the implant and it is also believed that amorphous calcium phosphate is good for facilitating mechanical mismatch, improving fatigue behavior and promoting faster bone remodeling and hard tissue attachment [21]. In consideration of the above discussion, HA coatings with a small amorphous content are hence preferred. The formation mechanism of the amorphous phase can be illustrated in terms of kinetic and thermodynamic principles [22]. The Gibbs free energy needed by the formation of the amorphous phase is smaller than that of HA and hence, the driving force of nucleation of HA is higher. Thus, under rapid cooling conditions, the amorphous phase forms readily.

3.2. Bond strength

The influence of spray parameters and the particle size on the bond strength of the HA coatings is illustrated in Fig. 5. The spray parameters obviously have an influence on the bond strength. It is revealed that higher the flow rates of oxygen and hydrogen, higher are the bond strengths of the coatings. The bond strength C-1 coating attained a value of 31 MPa, which is higher than the reported value for HA coatings by plasma spray method, 14 MPa [23]. The high bond strength can be attributed to the impingement of the

powders onto the substrate or pre-coated coatings with very high velocity, more than twice of plasma sprayed deposits. It is believed that the high flow of both oxygen and hydrogen results in high velocity of the powders, which is useful for the mechanical interlocking, the main bond mechanism, of the coating to the substrate. In C-5 coatings, the short spray distance results in pre-mature deposition of the droplets because the flame torch length is around 210 mm. The particles are not allowed sufficient time to attain their maximum velocities. Therefore, long spray distance brings about higher bond strength under the same conditions. Considering the melt-state of the HA powders illustrated in Fig. 4, it can be found that the partial melt-state of the powders is beneficial for the improvement of the bond

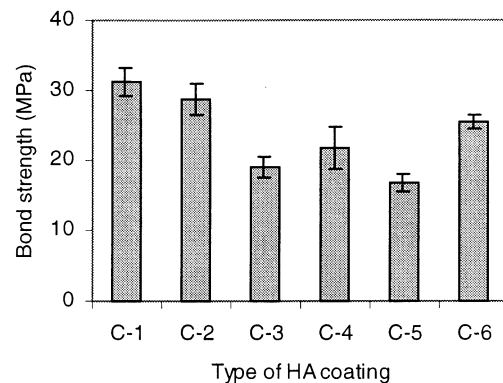


Fig. 5. Bond strength of as-sprayed HA coatings.

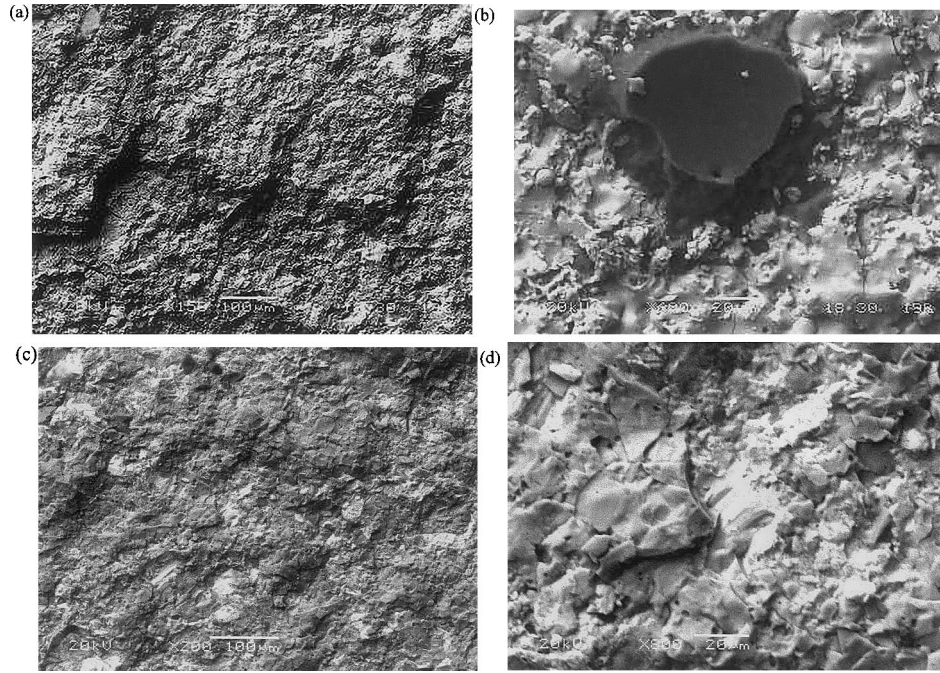


Fig. 6. Typical morphologies of tensile fractured surface of HA coatings. (a) Fractured surface of C-1 coating showing cohesive failure and corresponding large magnification (b) reveals the fracture behavior of HA splat; (c) fractured surface of C-6 coating and corresponding large magnification (d) clearly revealing the tensile fracture locates at the splats' interface.

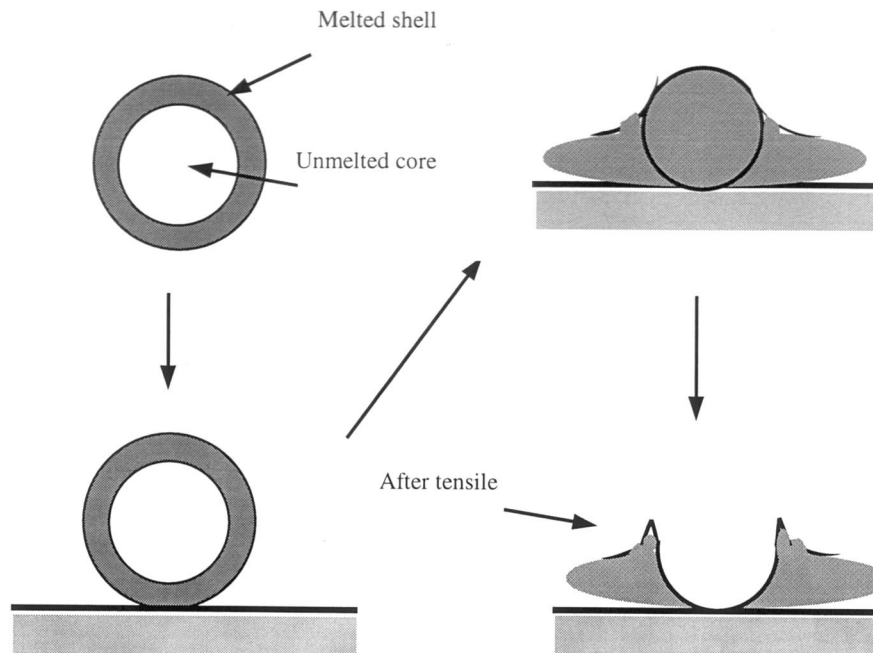


Fig. 7. Schematic illustration of the tensile fracture behavior of the splat.

strength, which is suggested by the comparison between C-2 and C-6 coatings.

The fractured surface of HA coatings after tensile test is shown in Fig. 6. It is found that the fracture totally occurs within the coating. This means that the value attained during the mechanical test represents the cohesion strength of the coatings and not adhesion.

Furthermore, the fractured surface suggests a brittle fracture regime. High magnification of the images reveals the crack propagation path. Fig. 6b shows that the fracture is located within the splats. As explained earlier, the interface between the unmelted and melted part of the powder is the weakest region. The tensile fracture occurs just at this smooth interface, which is

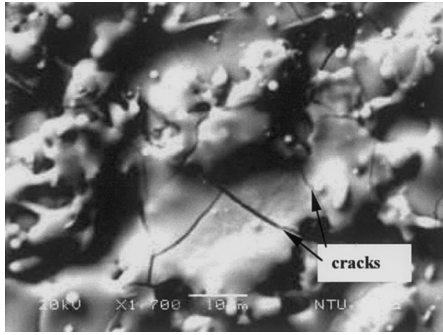


Fig. 8. Surface morphology of as-sprayed C-6 coating.

schematically shown in Fig. 7. From this viewpoint, the partial melt-state contributes to the improvement of cohesion of the coatings. The phenomenon that tensile

fracture occurs at the splat–splat interface for the C-6 coating, which is shown in Fig. 6c and d, suggests that totally molten powders are not necessarily beneficial for good cohesion. The surface of as-sprayed C-6 coating, which is shown in Fig. 8, reveals the possible reason. During the impingement of the entirely melted powder, the flattening procedure results in the net-shape-like microcracks. The cracks reduce the cohesion.

The typical microstructure of the HA coatings made from large powders and small powders is shown in Fig. 9. It is found that C-6 coating is denser than C-2 coating. Owing to the brittleness of HA coating, the smooth cross-sectional morphology can not be easily obtained under the present grinding and polishing conditions.

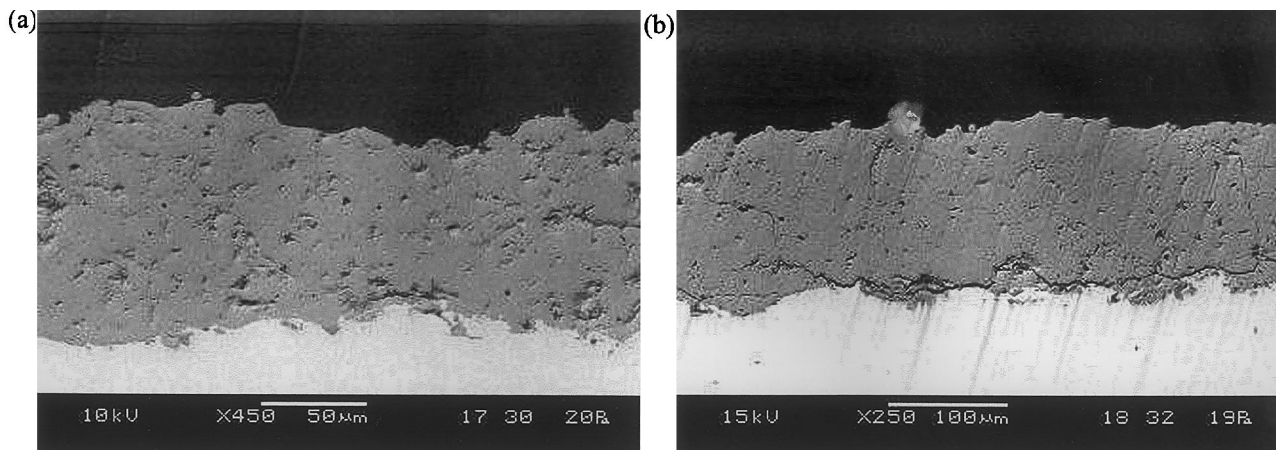


Fig. 9. Typical SEM images of (a) C-2 coating and (b) C-6 coating.

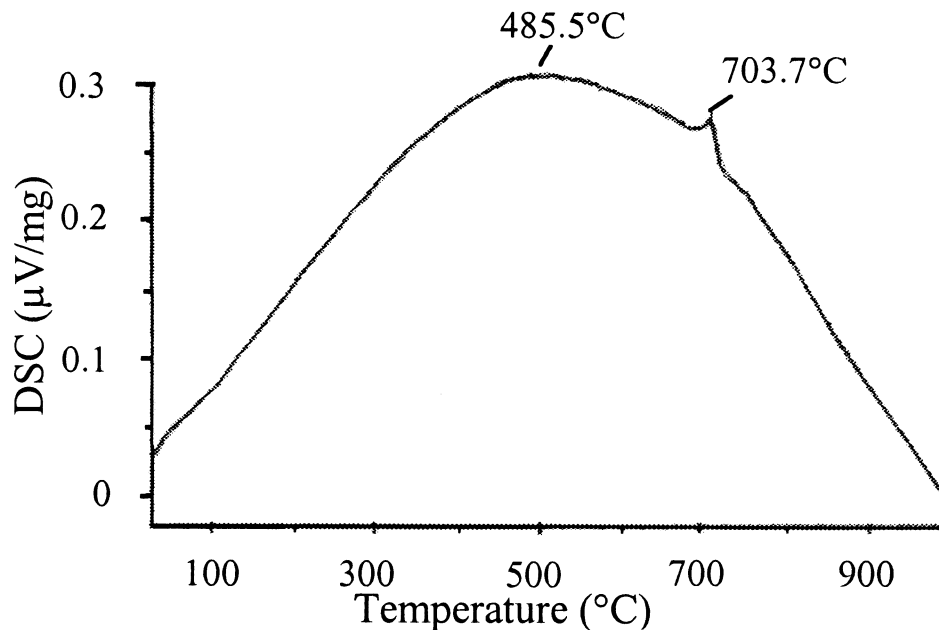


Fig. 10. DSC curve of C-6 coating.

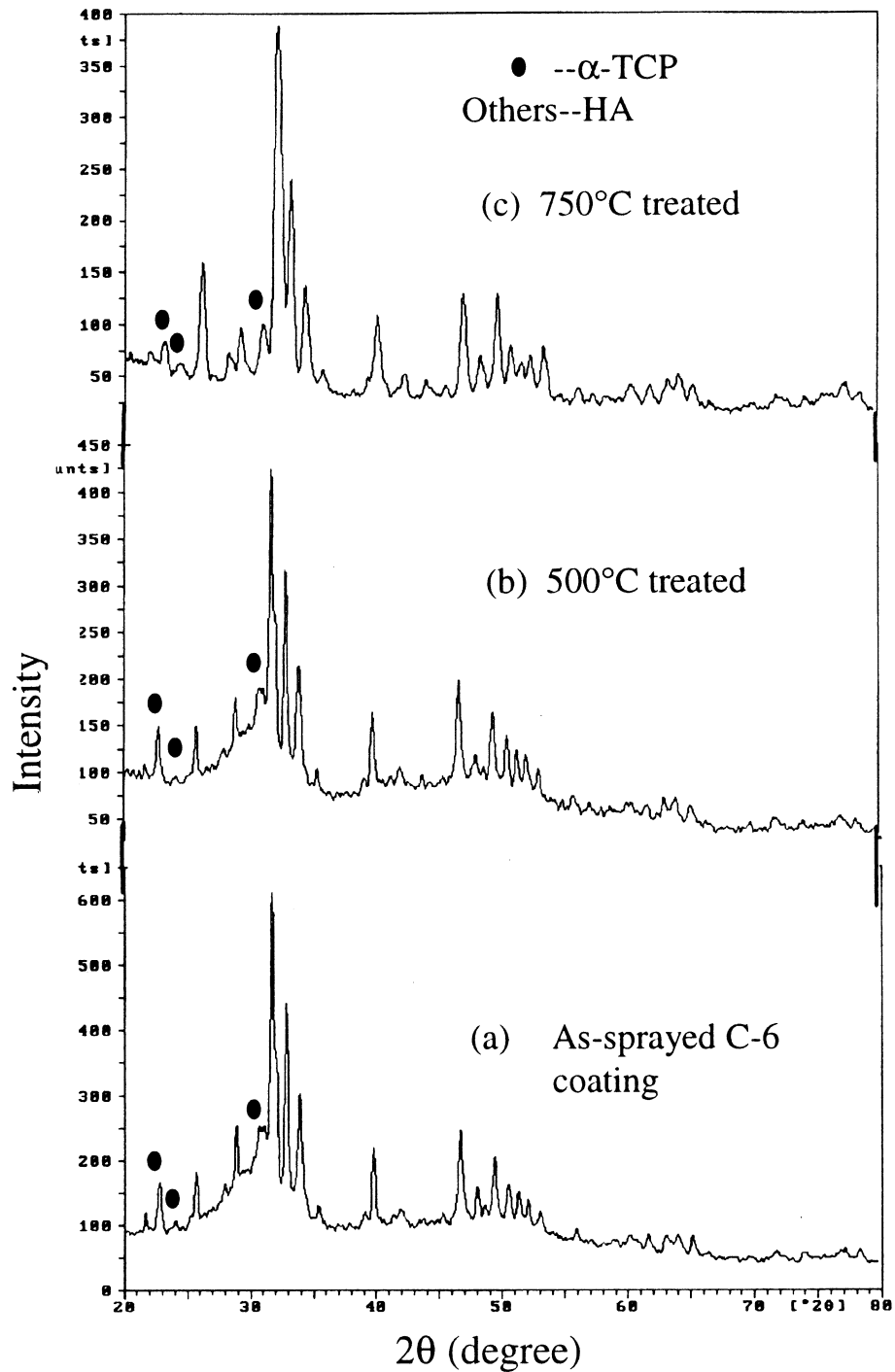


Fig. 11. Influence of heat treatment on phase composition of HA coatings.

3.3. Crystallization of amorphous coatings

Fig. 10 shows the DSC result of the amorphous C-6 coating. The curve reveals that the recrystallization of the amorphous phase occurs at around 703°C. The large exothermal peak at $\sim 495^\circ\text{C}$ represents the transition from the chaotic glassy state to the ordered crystalline state. In order to investigate the influence of the

crystallization of the coating on the properties, the post-spray heat-treated coatings are analyzed. The DSC result is confirmed by the XRD analysis of the heat-treated HA coatings after 500 and 750°C, respectively, and is shown in Fig. 11.

From Fig. 11, it can be found that complete crystallization does not result in other calcium phosphate phases apart from HA. The α -TCP content remained

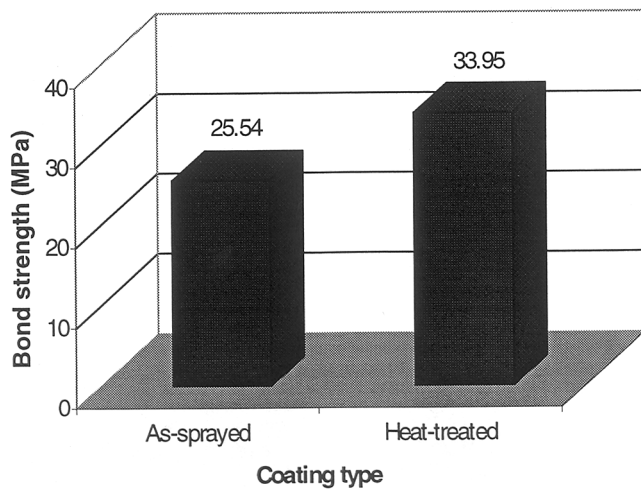


Fig. 12. Influence of crystallization heat treatment on the bond strength of HA coatings.

constant, which means that the amorphous to crystalline phase transformation did not bring about any by-products. The amorphous phase had transformed directly to crystalline HA.

The influence of heat treatment at 750°C on the bond strength of HA coatings is shown in Fig. 12. The bond strength of the C-6 coating improved from 25.54 to 33.95 MPa. The tensile fracture of heat-treated HA coating also occurred within the coatings. The reason for the improvement of bond strength seems to lie in the release of the residual stress formed during the formation of the coating. The strengthening mechanism still needs further investigation.

4. Conclusions

The maximum bond strength of HVOF sprayed HA coatings is found to be ~ 31 MPa and is dependent on the spray parameters. The high bond strength can be attributed to the impingement of the powders onto the substrate or pre-coated coatings with very high velocities, more than twice of plasma sprayed deposits. It is believed that the high flow of both oxygen and hydrogen results in high velocities of the powders, which contributed positively towards the mechanical interlocking among the splats and irregular substrate surface, the main bond mechanism, of the coating to the substrate.

The HA coatings made from partially melted powders show a nearly complete crystalline structure. Thermal decomposition occurs in the melted part of the particles and α -TCP is one of the products. The content of amorphous calcium phosphate in HVOF sprayed HA coating can be controlled through adjusting the melting state of the powders, which can be achieved through the alteration of spray parameters (oxygen and hydrogen flow rates) or powder size.

Tensile mode fracture occurs at the interface between the melted and unmelted parts of the powder. The partial melt-state of the HA powder is beneficial for improving the bond strength and the overall phase composition of the resultant coating.

The recrystallization temperature of the amorphous phase in the as-sprayed HA coatings was determined to be $\sim 703^\circ\text{C}$. The annealing treatment at 750°C is useful and contributed to the significant improvement of bond strength of the HA coatings.

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