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Significance of in-situ dry-ice blasting on the microstructure, crystallinity and bonding strength of plasma-sprayed hydroxyapatite coatings

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ABSTRACT

To obtain hydroxyapatite (HA) coatings with high crystallinity which have long-term stability in clinical applications, coarse powders were usually injected to less energetic plasma. However, the HA coatings accumulated by partly melted particles usually have high porosity and poor mechanical properties, especially poor bonding strength. In this work, by profiting its quenching and mechanical impact, dry-ice blasting was in-situ employed during plasma spray process to improve the microstructure characterization and bonding strength of HA coatings. In addition, the influence of in-situ dry-ice blasting on the phase composition and crystallinity of plasma-sprayed HA coatings was investigated. The results show that a significant reduction of porosity and an apparent increase in bonding strength are revealed in plasma-sprayed HA coatings due to the cleaning effect of dry-ice blasting on the convex unmelted particles and splashing fragments. HA coatings prepared by the combination process of plasma spraying and dry-ice blasting have a compromise structure with minimum globular pores but with pronounced microcracks. The disappearance of CaO phase and the increase in crystallinity also derive from the application of dry-ice blasting.

1. Introduction

Considering hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) material could not be used in bulk form for load bearing applications due to its poor mechanical properties, such as, low strength and fracture toughness (Morks and Kobayashi, 2007; Zhao et al., 2009), HA-coated Ti alloys have attracted considerable attention because of their dominant role in orthopedics and dentistry (Inagaki and Kameyama, 2007; Yan et al., 2003; Zhang et al., 2001). They combine the biocompatible properties of HA and the superior mechanical properties of Ti alloy metals. Plasma spraying has been used as a widely adopted technique to deposit HA coatings, mainly due to its high deposition rate and relative economy (Li et al., 2004; Xue et al., 2004; Lu et al., 2003). However, the decomposition of HA coatings and the formation of amorphous HA are inevitable during spraying, which are related to the extremely high temperature of the plasma flame (Xue et al., 2004; Prevéy, 2000; Feng et al., 2000; Vilotijevic et al., 2011). It is deemed that amorphous HA tends to dissolve rapidly in the physiological environment so that HA coatings with low crystallinity could be a problem either during surgical operation or after implantation for a given time (Mohammadi et al., 2008; Lu et al., 2003).

Considerable efforts have been made to improve HA crystallinity, mainly by controlling the melt state of HA particles (to obtain only partly melted HA particles), such as, the use of coarse powder injected to less energetic plasma (Dyshlovenko et al., 2006; Khor et al., 2004; Tsui et al., 1998; Sun et al., 2003). However, the HA coatings accumulated by partly melted particles usually have high porosity and poor mechanical properties, especially poor bonding strength. As for the bonding strength, Zheng et al. Zheng et al., (2000) have enhanced the bonding strength of HA coating by forming a composite coating with Ti without the bioactivity reduction. Khor et al. Khor et al., (2000) have developed HA/YSZ(yttria partially stabilized zirconia) composite coatings to improve the bonding strength of HA coating systems. Moreover, graded coatings (Kumar and Maruno, 2002) and bond coats (Chou and Chang, 2001) were designed to overcome the low bonding strength between the HA coating and Ti alloy substrate. As for the porosity of HA coatings, it may play an important role in the physiological environment, for example, it is conductive to the initial fixation of bone, but the long-term stability of HA coatings having high porosity is questionable.

It is postulated that HA coatings having a compromise structure with minimum globular pores but with pronounced microcracks could be achieved by plasma spraying coupled with dry-ice blasting, owing to the high cooling rate and mechanical impact of dry-ice blasting

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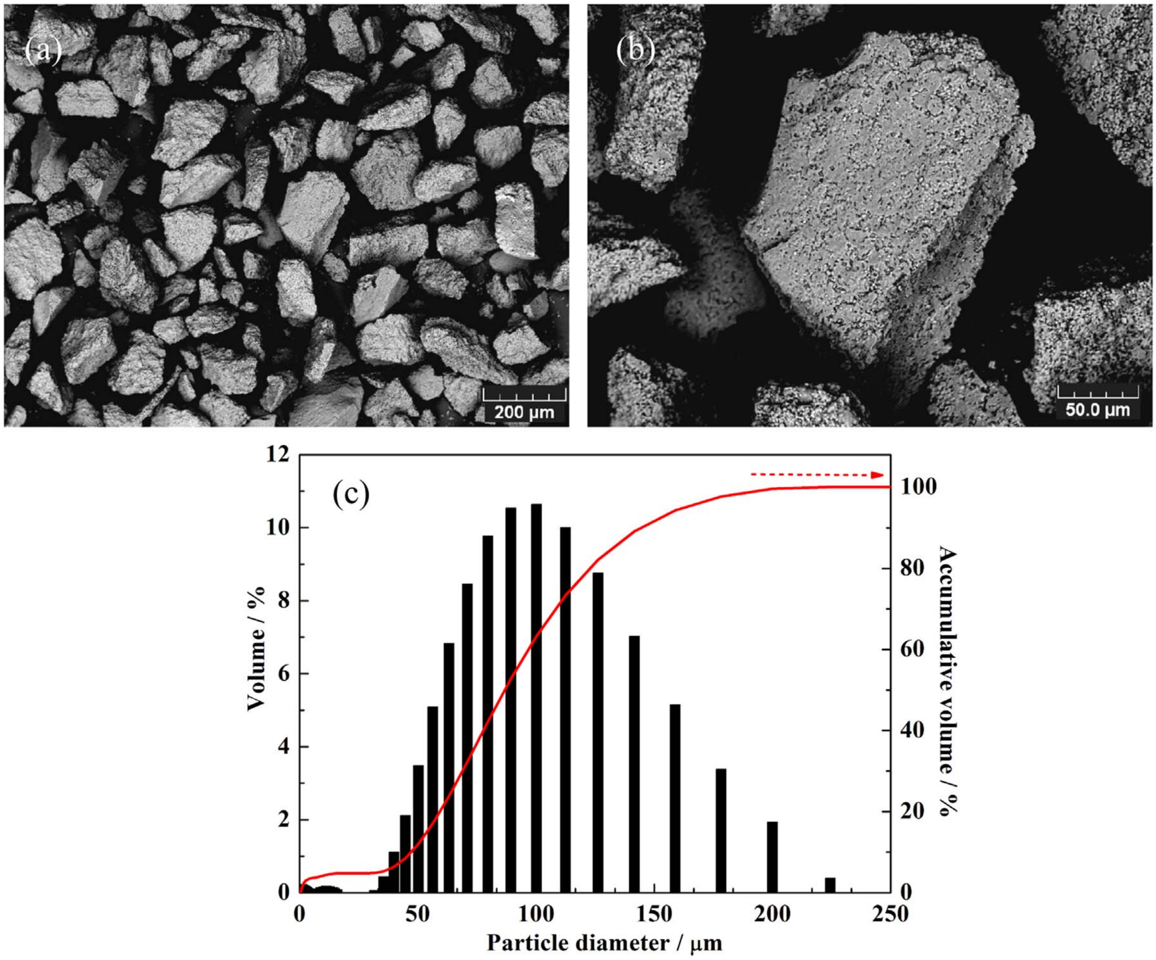

Fig. 1. SEM images (a), (b) and size analysis (c) of the HA powder used to spray.

technique. The HA coating with such compromise structure is expected to possess both the long-term stability and the fast initial bone fixation (Xue et al., 2004). In this work, dry-ice blasting was thus in-situ applied during plasma spraying to deposit HA coatings. The quenching of dry-ice blasting could account for the formation of microcracks in the coatings while its mechanical impact could benefit for the cleaning of the unmelted particles and splashing fragments with poor bonding. Therefore, dry-ice blasting shows potential for the porosity reduction and the improvement in the bonding strength of HA coatings. In addition, the influence of in-situ dry-ice blasting on the phase composition and crystallinity of plasma-sprayed HA coatings was also investigated.

2. Experimental procedure

Commercial pure HA powder ($Ca_5(PO_4)_3OH$, MF/09-3862 20-15, MEDICOAT, France), conforming to ASTM designation F-1185, was used as the starting powder for the coating deposition. This powder was manufactured based on the sintering-crushing-milling-sieving ceramic technology. Fig. 1 shows the powder morphology and its size distribution. The starting feedstock is characterized by irregular angular particles. The mean particle size D50 is 97.39 µm with the D10 of 53.11 µm and D90 of 161.61 µm.

Atmospheric plasma spraying using a Sulzer-Metco F4 plasma gun was employed to deposit HA coatings. Argon was used as both plasma-operating and powder carrier gas. Spray parameters were set up as follows: arc current (600 A), arc voltage (59 V), primary plasma gas (Ar, 40 SLPM), secondary plasma gas (He, 20 SLPM and H_2, 4 SLPM), powder carrier gas (Ar, 3.0 SLPM). The plasma spray distance was fixed at 90 mm. During plasma spray process, in-situ dry-ice blasting was employed to treat the samples. Dry-ice blasting was carried out using a mobile blasting device (ic4000 system, HMRexpert, France), which comprises a similar-Laval nozzle with a rectangular outlet dimension of 9×40 mm, a mass flow controller with a pneumatic motor, a storage tank, and a compressed air supplier. In this work, cylindrical dry-ice pellets (−78.50 °C) with a diameter of 3 mm and a length of 3–10 mm were used for dry-ice blasting medium, the mass flow rate of dry-ice pellets was 42 kg. h^{-1} under a gas pressure of 0.6–0.8 MPa. The distance between the axis-exit of the dry-ice blasting nozzle and substrate is about 25 mm. The plasma torch and dry-ice blasting gun were mounted on the flange of a robot (ABB, Sweden) and vertically moved with a line speed of 12 mm/s for a uniform and reproducible deposition of coatings in front of cylindrical sample holder. The cylindrical holder with a diameter of 200 mm rotated with a speed of 120 rpm, where Ti-6Al-4V cylindrical substrates measuring 25 mm in diameter and 10 mm in thickness were installed. All the substrates were blasted prior to spraying using alumina grit. Two groups of HA coatings were prepared without dry-ice blasting using 25 and 40 deposition passes, named as HA-25 and HA-40, respectively. Moreover, two groups of HA coatings were prepared with in-situ dry-ice blasting using the blasting distances of 25 mm and 100 mm, named as HA with CO_2 d25 and HA with CO_2 d100, respectively.

By referring the literature (Yang, 2007), the index of crystallinity (IOC) of HA coatings advanced as the temperature went up to attain a maximum at 500–600 °C owing to a maximum nucleation rate. In this work, parts of HA coatings were post heat-treated at 600 oC for 3 h in a vacuum four in order to further improve the crystallinity. The heating rate of the four is 20 °C/min. The coating samples were held at 600 °C