Microstructure and Mechanical Properties of HA/ZrO_2 Coatings by Gas Tunnel Plasma Spraying †

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Abstract

The gas tunnel plasma spraying method was employed to deposit HA/ZrO_2 composite coatings on SUS 304 substrate in an atmospheric chamber. The design of the plasma torch allows for the external and internal feeding of the sprayed powder. Pure HA powder was fed externally and ZrO_2 powder was fed internally. The feeding rate was controlled to deposit HA/ZrO_2 coatings with different zirconia contents. Two sprayed coatings with different zirconia contents were obtained. The influence of ZrO_2 and its volume fraction on the microstructure and mechanical properties of HA/ZrO_2 composite coatings was investigated. A comparison between the microstructure and mechanical properties of pure HA and HA/ZrO_2 composite coatings was made. Scanning electron micrographs of the coatings cross-sections showed good adhesion between the coatings and the substrate and also the dense structure of the coatings. The presence of ZrO_2 improved the hardness and abrasive wear resistance of the composite coatings compared with the pure HA coatings.

KEYWORDS: (Gas Tunnel Plasma) (HA/ZrO_2) (Microstructure) (Hardness) (Abrasive Wear) (Adhesion)

1. Introduction

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is an ideal material for bone implants because its chemical structure is close to the composition of the osseous tissue; it is highly biocompatible with body fluids and possesses a high osteoconductive capacity [1-4]. Hydroxyapatite is currently used as a coating on bio-inert metallic implants such as Ti and Ti-alloys and stainless steel for improvement of the compatibility properties and the growth of natural apatite on the metallic implants. The mechanical properties of HA coatings such as adhesive strength and bonding strength are important to keep the coatings stable for long times without damage, especially for permanent implants. Plasma spraying of HA coatings on metallic implants is an established technology for producing HA layers with a thickness range of 50-200 μm in short times. Controlling the spraying parameters is required to keep the crystallinity of HA at a high level (90%) and prevent the decomposition of the HA into soluble phases such as α-, β- calcium phosphates and oxy-phosphates. Gas tunnel plasma spraying (GTPS) was developed in Osaka University [5-7] and was employed for deposition high quality ceramic coatings [8-10]. In previous works [11, 12] the authors studied the effects of spraying distance, plasma power and gas flow rate on the microstructure and mechanical properties of HA coatings fabricated by GTPS. The results indicated that the external feeding of HA powders resulted in the deposition of crystalline HA coatings.

On the other hand, the crystallinity of HA was increased as the power and gas flow rate was increased at short spraying distances. Moreover, a dense structure with lower porosity was obtained. The phase structure and coating porosity affect the hardness and abrasion resistance of plasma spayed HA coatings as discussed by M. F. Morks et. al [13]. Bonding strength and adhesion properties of HA coatings affect the life duration of the coated implants. The qualified coatings should have a high adhesive strength for load bearing applications as in case of using the implants as joints or roots for teeth. For improving the mechanical properties of HA coatings, incorporation of hard ceramic materials are candidates for this task. Zirconia (ZrO_2) is one promised material which can form a high performance bio-gradient composite with HA.

In this paper, an attempt to improve the mechanical properties of HA coatings by incorporating ZrO_2 hard particles was investigated. A gas tunnel plasma spraying system was employed for the deposition process. In the spraying process, HA powder was fed externally to minimize the decomposition that occurs due to the particles overheating in the plasma jet. However, ZrO_2 powder was fed internally to reach the high melting point of zirconia particles. The carrier gas flow rate was controlled to spray HA-ZrO_2 composite coatings with

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different zirconia contents. The microstructure and mechanical properties of HA/ZrO_2 coatings were compared with the pure HA coatings.

2. Experimental Procedure

2.1 Materials and spraying process

Pure HA and YSZ (5%wt%Y_2O_3 stabilized ZrO_2) powders with size ranges from 10-45 μm were used as spray materials. The HA particles are spherical in shape while the ZrO_2 particles are angular. The powders were sprayed on a roughened 304 SUS substrate with dimensions 50 x 50 x 2.5 mm. Spraying was carried out by using gas tunnel type plasma spraying (GTPS). A systematic diagram of the GTPS is depicted in **Fig.1**. The torch is composed of two copper anodes of diameter 8 mm (internal) and 20 mm (external) and one tungsten cathode. The external anode (vortex) is composed of a circular copper tube and the working gas (Ar) moves inside it in a rotational flow with high velocity. HA powder was fed externally to avoid the overheating and decomposition of the moving HA particles. However, ZrO_2 powder was fed internally to increase the dwell time of ZrO_2 particles inside the plasma jet and reach their high melting point. Before spraying, the substrate was preheated by the plasma jet (600K) to sustain the adhesion of the HA coatings. Details of the spraying parameters are listed in **Table 1**.

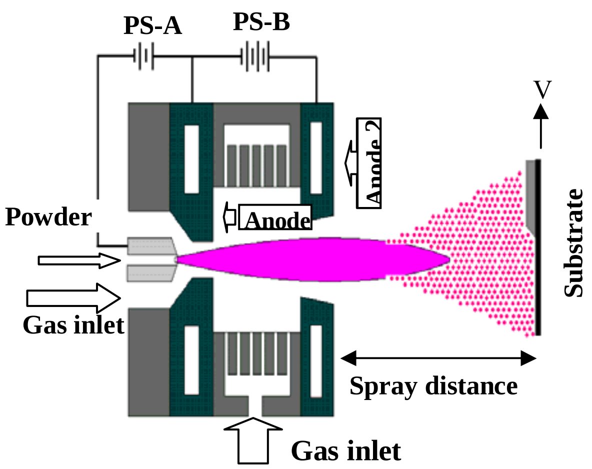

Fig. 1 Gas tunnel type plasma spraying torch.

Table 1 Spraying parameters for HA/ZrO_2 coatings.

Arc gun current (A)	50
Arc vortex current (A)	450
Gas flow rate (l/min)	150
Carrier gas flow rate (l/min)	10
Powder size (μm)	+10-45
Spraying distance (mm)	60
Substrate traverse speed (mm/s)	40

2.2 Characterization techniques

Microstructural investigation was carried out on the surface of the coatings and polished cross-sections. As-sprayed coatings were cut and mounted in hot-resin, followed by grinding and polishing by emery papers and finally mirror finished by buffing using an alumina slurry solution. The morphology of the coatings was observed using ERA-8800FE scanning electron microscope equipment. Elemental analysis of coatings was carried out using an electron dispersive spectrometer unit attached to the ERA-8800FE SEM. EDX analysis was used to search for evidence of the presence of zirconia particles inside the coatings.

The phase analysis of the composite coatings was carried out using a JEOL JDX-3530M X-ray diffractometer with Cu-K_α radiation source at 40 kV and 40 mA.

2.3 Mechanical Properties

Hardness was measured on polished and buffed cross-sections of coated samples using an Akashi AAV-500 series hardness tester. The load used was 490.3 mN and the loading time was 20 s. Each hardness value is the average of 10 readings.

Abrasive wear tests were carried out using a SUGA ABRASION TESTER which follows the NUS-ISO-3 standard. The tested samples were cut from the coated samples with surface area 25 x 25 mm^2. The samples were moved horizontally (oscillation mode) a distance of 1cm under load of 25 g on a slightly moved wheel (25 mm/min) covered with SiC emery paper. The width of the wheel is 1 cm and the contacted area with the test sample is 1cm^2. A schematic diagram of the abrasion tester and its components is illustrated in previous work [13]. The starting thickness of tested HA coatings was 120 μm. The test sample was exposed to movement against the abrasive wheel at different stroke numbers (5-180) and the weight loss was measured using a 6 digit electronic balance. The abrasive wear test was performed in dry conditions in an air atmosphere at room temperature.

The adhesive strengths of pure HA and HA/ZrO_2 composite coatings were measured. The coated samples of 1cm^2 area were cut and fixed from both sides (coat and substrate) between two copper rods (2 cm^2 cross-section) using adhesive material (Araldite). All the chosen coated samples have equal coating thickness of about 150 μm. A load was applied on the samples using a movable rod connected to a motor and weight scales. The load (kg) at which the coating is separated from the substrate was recorded by using the weight scale. Each adhesive strength value (MPa) is the average of three tested samples at different spraying distances (three readings for each spraying distance). The measured load is the load at which the whole coating is separated from the substrate. For the accuracy of the adhesive strength test, after adhesion test the substrate surface was examined by optical microscope and samples with fully separated coatings were considered.

3. Results and Discussion

3.1 Phase structure

The X-ray diffraction patterns of the as-sprayed HA and HA/ZrO_2 composite coatings are presented in **Fig. 2**. The HA coating is mainly composed of crystalline HA phase as shown by sharp and high intensity peaks that match the JCPDS 9-432 card. The HA/ZrO_2 composite coating has 40% volume fraction zirconia and is mainly composed of crystalline HA and ZrO_2 phases. The peaks of ZrO_2 are strongly represented with high intensity beside the peaks of HA in the HA/ZrO_2 composite coatings. The crystal structure of ZrO_2 phase is tetragonal according to the JCPDS 50-1089 card of zirconia. The presence of Y_2O_3 (5 wt%) in the feeding zirconia powder slowed down or eliminated the phase transformation from tetragonal to monoclinic during cooling process of the moving particles.

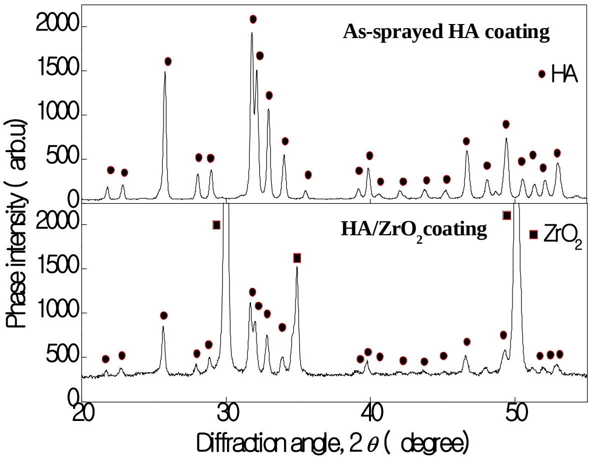

Fig.2 XRD patterns of HA and HA-40%ZrO_2 coatings.

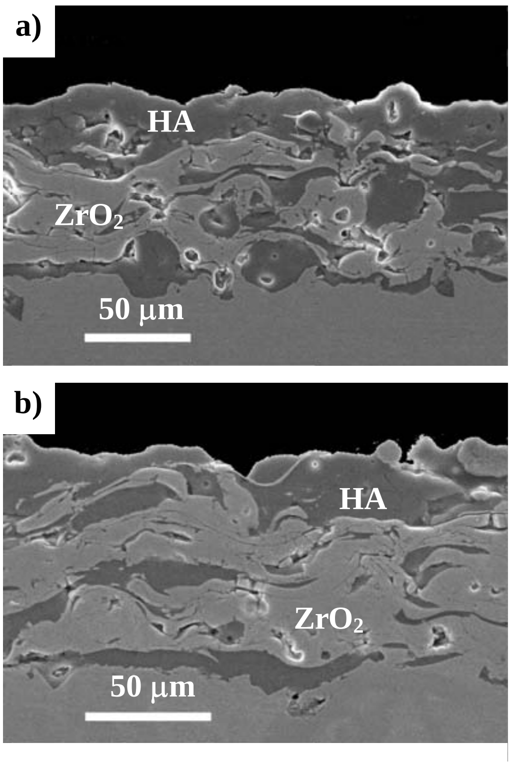

Fig. 3 SEM micrographs of HA/ZrO_2 coatings with different volume fractions of zirconia: a) 40% and b) 60%.

3.2 Cross-sectional microstructures

Scanning electron micrographs of plasma sprayed HA/ZrO_2 coatings are shown in **Fig. 3**. The thickness of the coatings is around 120 μm. The cross-sectional microstructures of the coatings show two micrographs for as-sprayed HA/ZrO_2 composite coatings with different volume fractions of zirconia (40% and 60%). The coatings are composed of a huge number of accumulated and flattened HA and ZrO_2 particles/droplets that strike the substrate. The lamellar structure is the main structure of the coatings. HA coating (dark grey area) is well adhered to the ZrO_2 (light grey area) coating. There are no significant cracks existing in the coatings which indicates that the residual and thermal stresses were decreased. Also, the micrographs show a good adhesive strength at the interface which is required for high quality biomedical coatings. The porosity is low and the coatings exhibit dense structures. The morphological features of the coatings agree with the XRD analysis results explained previously.

3.3 Surface Morphology and EDX analysis

By means of an EDX unit attached to the EAR-8800Fe SEM, elemental analysis was carried out on the cross-sectional microstructure of as-sprayed HA-ZrO_2 of 60% volume fraction ZrO_2. By means of this method, it was easy to detect the HA and ZrO_2 regions as shown in **Fig. 4**.

The surface morphology of as-sprayed HA/ ZrO_2 composite coating of 60 % volume fraction ZrO_2 is shown in **Fig. 5**. It is clear from the surface morphology that the majority of HA and ZrO_2 particles were melted and completely flattened during the solidification stage. There are some unmelted particles appeared in the coating. Also, the splats of HA and ZrO_2 are mechanically adhered together.

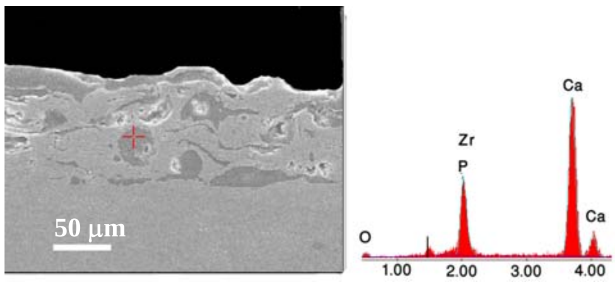

Fig. 4 EDX analysis on the cross-sectional microstructure of sprayed HA-60%ZrO_2.

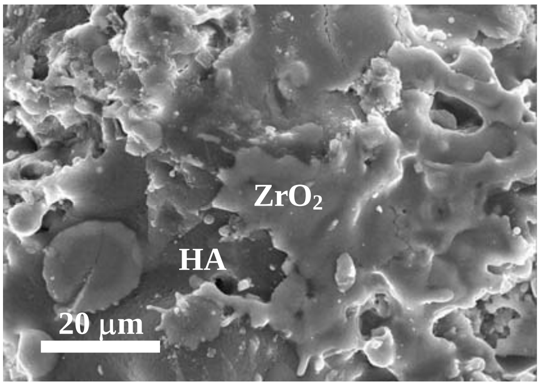

Fig. 5 SEM micrograph of the surface of HA- 60% ZrO_2 (vol. fraction) composite coating.

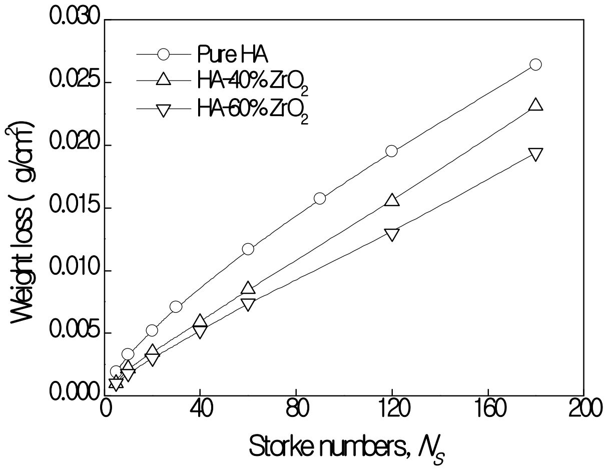

Fig. 7 Abrasive wear of pure and HA/ZrO_2 coatings.

3.4 Mechanical Properties

3.4.1 Hardness

Hardness of the composite coatings was measured on polished and buffed cross-sectioned samples. The hardness values of pure HA and HA/ZrO2 composite coatings are shown in **Figure 6**. The presence of zirconia increased the hardness of the coatings mainly due to the high hardness of zirconia particles and, as the volume fraction of zirconia was increased, the hardness increased. The measurements showed that, the mean value of the Vickers hardness of pure ZrO_2 coatings is 900 and of pure HA coating is 430. Pure HA coating is considered a soft ceramic material compared with the hard ZrO_2 coatings.

3.4.2 Abrasive wear test

Abrasive wear tests were carried out on the surface of pure HA and HA/ZrO_2 composite coatings of surface area 25x25 mm^2. The weight loss of the coatings was measured at different stroke numbers as illustrated in **Fig. 7**. It was evident that the abrasive wear resistance of as-sprayed HA/ZrO_2 composite coatings is higher than that of pure HA coating. Note also that the abrasive wear resistance was increased as the volume fraction of ZrO_2 was increased from 40% to 60%.

It can be concluded that the presence of ZrO_2 improved the abrasion resistance due to the high hardness and dense structure of the composite coatings.

3.4.3 Adhesion

Adhesive strength of the biomaterial coatings is an important factor for the load application of the coated implants. Failure of the coatings is mainly related to the adhesive strength and bonding strength. The adhesive strength of pure HA was compared with the adhesive strength of HA/ZrO_2 composite with 40 and 60 % volume fraction ZrO_2 as shown in **Fig. 8**. The adhesive strength of pure HA coating sprayed at the same spraying conditions of the composite coatings is around 40 MPa. However, the average value of the adhesive strength of HA/ZrO_2 (40% and 60%-vol. fraction ZrO_2) is 55 and 62 MPa, respectively. The results indicate that the presence of ZrO_2 improved the adhesive strength of HA coatings and as the volume fraction of ZrO_2 was increased, the adhesive strength was increased.

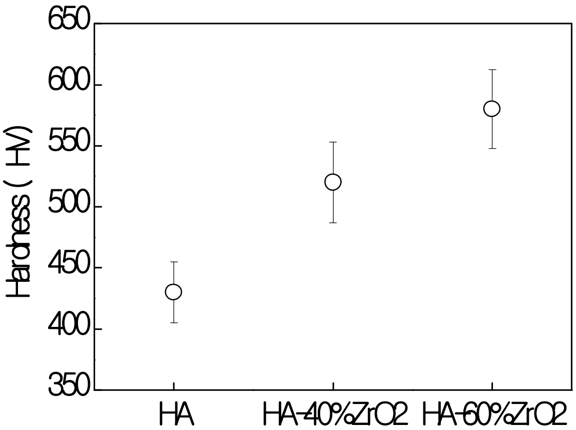

Fig. 6 Hardness of pure and HA/ZrO_2 coatings.

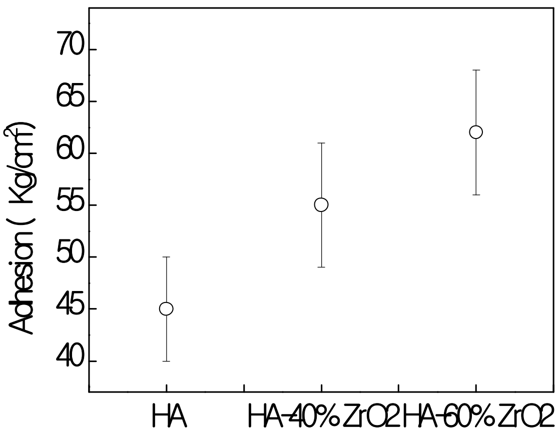

Fig. 8 Adhesion property of pure and HA/ZrO_2 composite coatings.

4. Conclusions

HA and HA/ZrO_2 composite coatings were plasma sprayed on 304 SUS substrates using a gas tunnel plasma spraying torch. The microstructure and mechanical properties of the coatings were investigated and the results can be summarized as follow:

(1) SEM micrographs showed that HA/ZrO_2 composite coatings are composed of lamellar structure of HA and ZrO_2 layers.

(2) Phase analysis by XRD diffraction showed that the coatings are composed of highly crystalline HA and ZrO_2 phases.

(3) The mean value of the Vickers hardness measured for HA/ZrO_2 coatings is higher than that of pure HA coatings because of the high hardness of zirconia particles.

(4) The abrasive wear resistance of HA/ZrO_2 composite coatings is higher than that of pure HA. The abrasion resistance was increased as the volume fraction of ZrO_2 was increased in the composite coatings.

(5) The presence of ZrO_2 improved the adhesive strength of HA coatings and as the volume fraction of ZrO_2 was increased, the adhesive strength was also increased.

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