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Effect of Al_2O_3 Reinforcement and Al_2O_3–13 wt% TiO_2 Bond Coat on Plasma Sprayed Hydroxyapatite Coating

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ABSTRACT

In present work an attempt has been made to enhance mechanical properties of plasma sprayed hydroxyapatite coating by addition of 10 wt% aluminum oxide. A bond coat of Al_2O_3-13TiO_2 has been applied to improve strength of hydroxyapatite composite coating. Mechanical properties of coatings with addition of alumina and with incorporation of bond coat have been investigated in accordance with the ASTM C 633-79. Results indicate that the tensile bond strength of hydroxyapatite coating increased by 13 per cent by alumina reinforcement and 25 per cent by both reinforcement and application of bond layer respectively. The area of adhesive failure was found to decrease for hydroxyapatite-alumina composite coating and hydroxyapatite composite coating with bond coat as compared to pure hydroxyapatite coating. The microharness of specimens was found to increase with reinforcement, however the highest hardness was recorded for bond coat. The microhardness was found to decrease with distance from substrate coating interface.

Keywords: Bond coat, AISI 316 L stainless steel, microhardness, bond strength

1. INTRODUCTION

Hydroxyapatite (HA: $Ca_{10}(PO_4)_6\,(OH)_2$) is being used as substitute material for damaged bone and teeth over the past several decades because of its crystallographic and chemical similarity with various calcified tissues of vertebrates[1-2]. However, its intrinsic low strength generally leads to instability and lower service life in the presence of body fluid and local loading[3-4]. To employ HA in load bearing areas of human body, it is necessary to strengthen it. Bioinert materials with better mechanical properties are reinforced to HA to overcome the mechanical limitations[5-6]. The incorporation of bioinert materials, such as yttria stabilized zirconia (YSZ), titania, carbon nano tubes (CNT) and alumina into a hydroxyapatite matrix has demonstrated a significant improvement in mechanical properties[7-9]. Alumina, which is classified as bioinert material, has been investigated as reinforcement agent for HA[10]. Furthermore, in vitro study has shown that nano-sized ceramics posses significant capability of enhancing osteoblast adhesion on them[11].

Plasma spraying has advantage of high thermal efficiency, easy operation and relative economy[12]**.** It is the only thermal spray technique approved by Food and Drug Administration (FDA) of US for hydroxyapatite coating[13]. The mechanism of coating substrate adhesion in plasma spraying is mechanical interlocking[14]. The irregularities of surface are filled with spreading molten materials due to impact pressure and subsequent cooling leads to mechanical interlocking[15].

Thermal sprayed graded coatings[16-18], composite coatings[19-21] and bond coats[22-24] are adopted with incorporation of titanium, titanium oxide, aluminum oxide and zirconium oxide as reinforcing agents. A composite coating or a bond coat covered with HA main coat is technically feasible and economically rational[25].

Increase in fracture toughness by 56 per cent via addition of 4 wt% multi-walled carbon nano tubes (CNTs) to HA has been reported[26]. The increase in fracture toughness by reinforcing up to 20 wt% titanium oxide to HA as compared to pure HA coating deposited by HVOF process has reported. Entrapment of titanium oxide particles around HA splat boundaries during spraying may be responsible for increase in mechanical properties[20].

Evis and Doremus investigated 10, 25 and 40 wt% alumina – HA with 5 wt% CaF_2 prepared by cold pressing and sintering process onto *Ti*-6Al-4V. They reported an improvement in bonding of coating to substrate due to matching of thermal expansion coefficient of coating and substrate via addition of alumina[27]. Plasma sprayed HA composite coatings with 50 wt% *Ti*-6Al-4V showed superior mechanical stability than the pure HA coatings by signifying much better long term stability of composite coatings in physiological environment[28]. It has been reported that the mean bonding strength increased from 12.9 MPa to 14.5 MPa and 17.3 MPa by reinforcing the plasma sprayed HA coating with 20 wt% *Ti* and 60 wt% *Ti* respectively. The enhancement of adhesion of the coating to substrate was reported by increasing the contents of *Ti* in HA[29]. Significant improvement in bending strength by addition of 15 wt% ZrO_2-Al_2O_3 to HA have been reported[30].

Bond coating are already widely used in industrial plasma spray applications. Bond coat layers are used to provide a good thermal expansion match between substrate and top coating[31-33]. Moreover, bond coat is considered to act as a diffusion barrier, which reduces ion migration from metallic substrate into the HA top coat[34]. Several studies have focused on introduction of intermediate layer between substrate and main coating such as

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micro arc titania and anodic alumina. By incorporating bond coat some helpful results have been obtained[35-36].

The increase in bond strength from 28.6 MPa to 36.2 MPa has been reported by introducing ZrO_2 bond coat between *Ti*-6Al-4V substrate and HA coating[23]. Goller reported an increase in bond strength of bioglass from 8.56 MPa to 27.18 MPa via incorporation of bond coat of alumina–40 wt% titania. The adhesive bonding characteristic turned to cohesive bonding characteristic by incorporation of bond coat[37].

The present study aims to elucidate strengthening the dominant mechanical weakness of plasma sprayed hydroxyapatite coating. Efforts were made to enhance cohesive and adhesive bonding strength of coatings.

2. MATERIALS AND METHODS

2.1 Development of the Coatings

2.1.1 Substrate Material and Coating Formulation

The AISI 316L stainless steel, being bio-inert, was selected as substrate material in rolled sheet form. Specimens with approximate dimensions 20 mm x 10 mm x 5 mm were cut from metallic sheet. The cylindrical specimens with dimensions 25.4 mm in diameter and 25.4 mm in length were machined from rod. The specimens were grit blasted with alumina powder (Grit 45). The HA powder having 100 per cent crystallinity with average particle size of 45 µm, a blend of finer and coarse particles (Captal 60–1') was commercially obtained from Plasma Biotal Limited, UK. It is observed from Fig. 1(a) that the HA powder particles have spherical and angular morphology with wide particle size range of 30 – 80 µm consistent with nominal range provided by the manufacturer. Alumina powder [Fig. 1(c)] with average particle size about 80 µm was obtained commercially from S.D. Fine Ltd., India and Al_2O_3-13TiO_2 was obtained commercially from Sulzer Metco, USA. Al_2O_3-13TiO_2 powder having angular morphology with wide particle size range of 10–50 µm is shown in Fig. 1(d). The feedstock for plasma spraying is shown in Fig. 1(e).

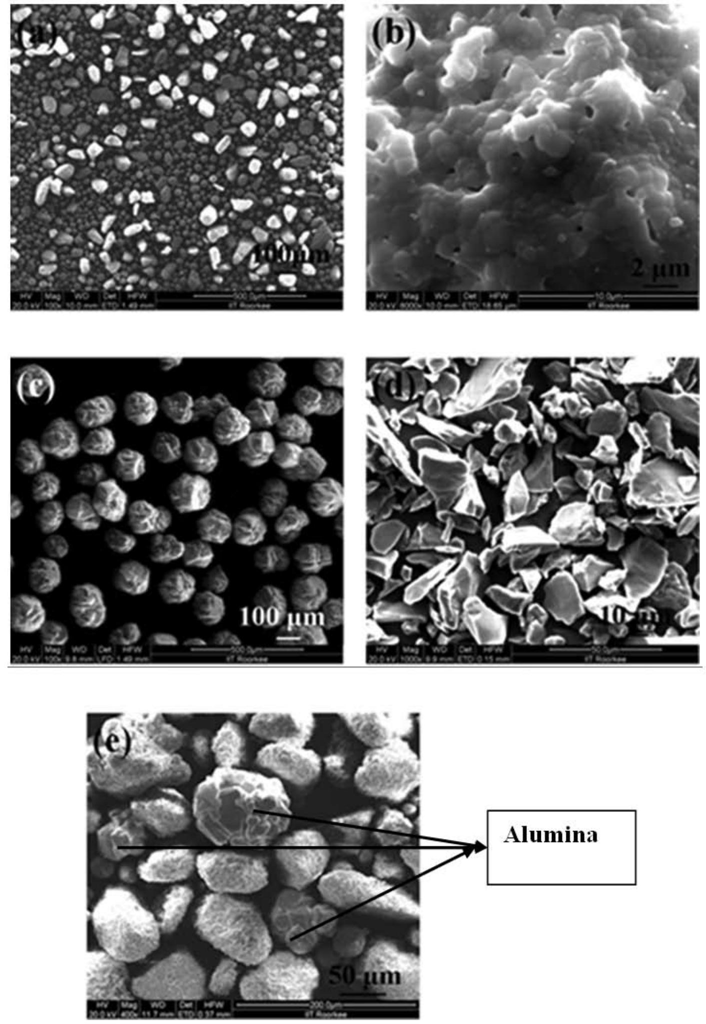

Figure 1. Low and high magnification FE-SEM image showing particle morphology of feedstock: (a, b) hydroxyapatite; (c) alumina; (d) alumina-13% titania and (e) HA-10 wt% Al_2O_3 feedstock.

2.2.2 Characterisation of the Coatings

The as-coated samples were subjected to scanning electron microscopy/energy dispersive X-ray analysis (FE-SEM/EDX) to characterize the surface and cross-sectional morphology of the coatings. A Quanta 200 F field emission scanning electron microscope fitted with EDAX Genesis software attachment (Czech Republic) was used for scanning electron microscopy/ energy dispersive X-ray analysis. To identify the cross-section details, the samples were cut in cross-section, mounted and subjected to mirror polishing using 1µm alumina powder suspension.

2.3 Mechanical Properties of Coatings

Tensile bond strength of coatings was evaluated as per ASTM C633-79 standard. The tensile bond testing was conducted on Material Testing Machine (Model: H 25, K-S, Hounsfield Equipment Ltd., England) equipped with Hounsfield S-Series Testing software. The transverse speed of jaws of machine was kept at 0.1 mm/min for tensile bond strength evaluation.

The microhardness of the coatings along polished cross-section was determined using a digital Vickers hardness tester (Model: SHV-1000, Chennai Metco, India). A load of 2.942 N for dwell time of 10 s was applied on a square pyramidal diamond indenter to make indentations on the specimen and the hardness values were directly taken in Hv. The porosity was measured with an image analyzer using Dewinter Material Plus 1.01 software based on ASTM B276. A PME3 inverted metallurgical microscope (Olympus, Japan) was used to obtain the images. The surface roughness (Ra) was measured with non-contact optical profilometer (Wyco NT1100, Veecco Instruments Inc., USA) using software Vision-32.

Table 1. Spray parameters employed for plasma spraying

Arc current (A)	750
Arc voltage (V)	40
Powder flow rate (rev/min)	5.5
Spraying distance (mm)	100
Plasma arc gas (Argon) (psi)	60
Carrier gas (Argon) (psi)	40
Nozzle internal diameter (mm)	8

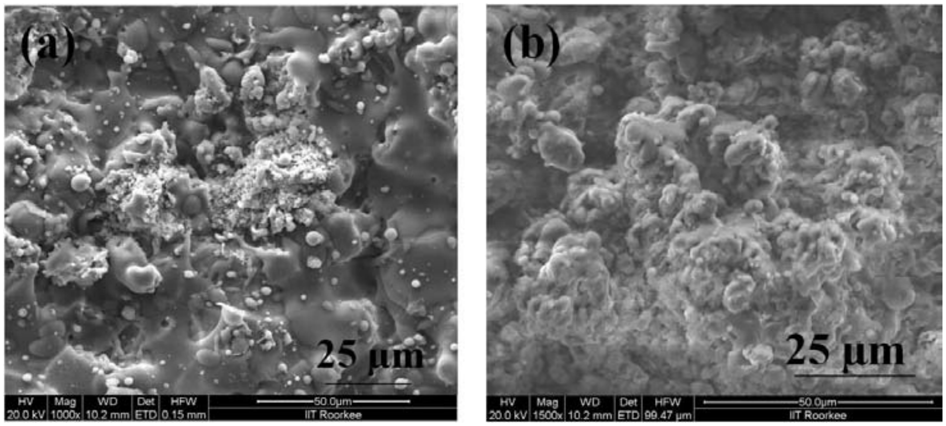

Figure 2. FE-SEM image of plasma sprayed HA–10 wt% Al_2O_3 coatings on: (a) SS 316L substrate, and (b) with bond coat of Al_2O_3–13 wt% TiO_2.

3. RESULTS AND DISCUSSION

3.1 Coating Thickness Measurement and Microstructural Analysis

The scanning electron microscopy of surface of as-coated specimen (Fig. 2) show irregular nature of coating. Surface consists of some glassy region [Fig. 2(a)] attribute to amorphous phase and rest of the area is composed of residual crystallites of hydroxyapatite powder. Some unmelted/partially melted particles are visible on the surface of completely molten splats. Very fine Microcracks can be seen on the surface of splats. Figure 2(b) show the micrograph of coating with bond coat. Partially melted particles are present on the surface of coating but cracks are absent on the coating surface. The overall coating in both the cases is massive with very low porosity. The unmelted/partially melted hydroxyapatite (HA) particles have spherical morphology.

Compared to average particle size of HA powder (45 µm), the unmelted HA particles are smaller in size (5–8 µm), which suggests that these particles are unmelted cores. The degree of particle melt in plasma spray process depends upon many factors such as heat content of plasma to which they are exposed, location of particles in plasma, velocity and size of particles. Microcracks are result of reduction in volume of molten splats during solidification, presence of amorphous phases and difference in cooling rates of coating splats and substrate. The absence of microcracks in the coating with bond coat [Fig. 2(b)] may be due the partial matching of coefficient of thermal expansion.

The electron image of polished cross-section of hydroxyapatite–10 wt% Al_2O_3 (AHA) coating [Fig. 3(a)] shows that there is continuity in the interface between coating and substrate. Some craters are present which may be formed during grinding and polishing. The coating thickness was found to be in a range of 160–190 µm. The SEM image of polished cross-section of coating with bond coat [Fig. 3(b)] shows good contact of bond coat with the substrate and top coat. The thickness of bond coat is 40–50 µm.

The porosity provides chemical bonding between HA and bone. Moreover, an interconnecting pore network offers circulation of nutrients and facilitates deeper bone penetration.

Table 2. The porosity and roughness of coatings

Sample	Porosity [%]	Roughness (Ra) [µm]
HA coating	3.31 [0.25]	4.55 [0.41]
AHA coating	3.34 [0.29]	5.21 [0.87]
AHA/AT coating	--	5.51 [0.32]

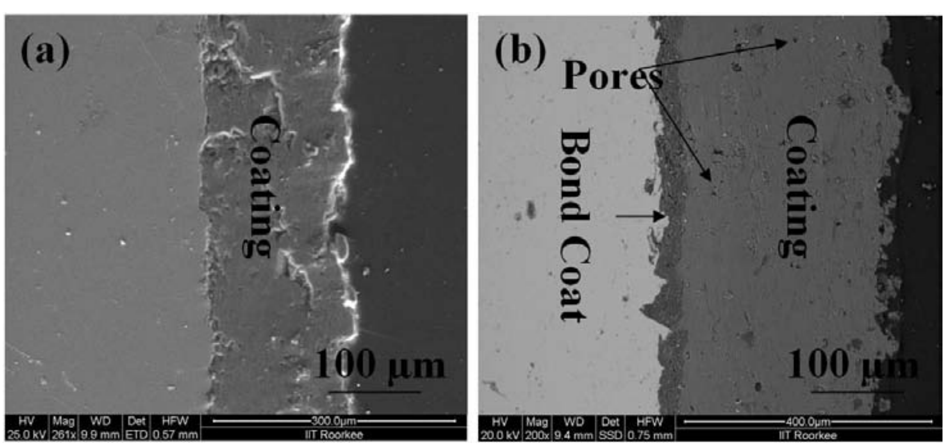

Figure 3. FE-SEM micrographs of the cross-section of: (a) HA-10 wt% Al_2O_3 coating, (b) with Al_2O_3-13 wt% TiO_2 bond coat.

Interconnections in pores are helpful for growth of tissues. The porosity and surface roughness (Ra) values are reported in Table 2. It has been reported that morphological roughness is beneficial for biocompatibility as it promotes the protein on the surface favoring cell attachment[26,38-39].

The tensile bond strength is found to increases from 32.7 MPa for AHA coating to 38.1 MPa for AHA coating with Al_2O_3-13TiO_2 bond coat (AHA/AT), whereas the bond strength for HA coating is 28.4 MPa. The morphology of fracture surface of the tensile bond strength specimens after ASTM C633-79 test is shown in Fig. 4. It has been reported that reinforcement of secondary bioinert phase to hydroxyapatite partially compensates the thermal expansion mismatch between hydroxyapatite and substrate[27,29-30].

3.2 Bond Strength and Microhardness of Coatings

The strengthening effect on the adhesion by incorporation of bond coat may be due to mechanical interlocking. The reduction in area for adhesive failure in AHA/AT coating as compared to AHA coating indicate that the adhesive strength of coating increased by introduction of bond coat. Furthermore, higher bond strength obtained for the (AHA/AT) than (AHA) coating indicates that the enhancement of adhesion between top coat and substrate is through bond coat. It has been reported that bond coat promotes the mechanical interlocking of the hydroxyapatite coating which turns adhesive bonding characteristic to cohesive bonding characteristic[23,37]. It should be accepted that both the cohesive strength of inter-lamella and intra-lamella of coating and the adhesive strength of the HA coating to the substrate influences the bond strength of the coating to the implant.

The microhardness of coatings was measured across the cross-section and microhardness values along the distance from interface are presented in Fig. 5. The highest microhardness values are 320 Hv and 400 Hv for HA coating and AHA coating respectively were measured near the interface. The average microhardness of bond coat is 590 Hv. In all the cases microhardness values are found to decrease with increase in distance from the interface.

The higher microhardness value near the interface is due to the reason that metallic substrate act as heat sink for the molten particles. The cooling or solidification time for molten HA particles is as short as 10^{-7}–10^{-6} s, which further depend on the thermal conductivity of substrate material and thickness of previously deposited lamellae. The solidification time increases with the thickness of lamellae, therefore hardness of coating decreases with increase in distance from interface or with increase in coating thickness.

4. CONCLUSIONS

The hydroxyapatite with 10 wt% aluminum oxide was successfully deposited on the AISI 316L SS via shrouded plasma spray process with and without incorporation of Al_2O_3-13 wt% TiO_2 bond coat. The bond strength is found to increase by 13 per cent via addition of alumina and by 25 per cent via both reinforcement of alumina and incorporation of bond coat as compared to hydroxyapatite coating. AHA composite coating possess 20 per cent higher hardness than HA coatings. This suggests that the fabrication of HA-Al_2O_3 composite coating is a useful way of improving bond strength and hardness of coatings without compromising biocompatibility of hydroxyapatite as alumina and titania are bioinert materials.

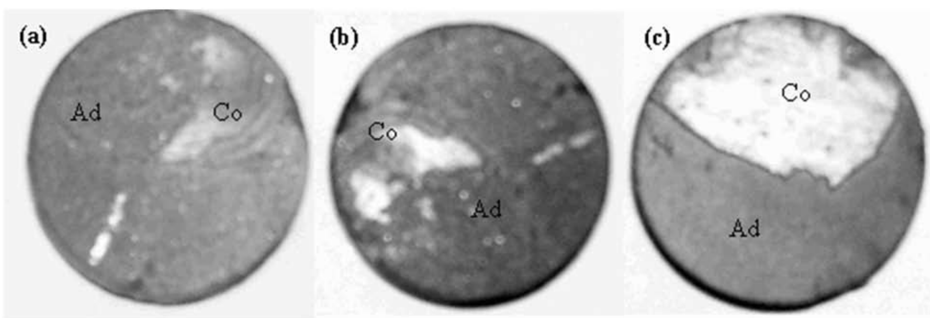

Figure 4. Macrographs of fractured surface after tensile strength test: (a) HA coating, (b) HA–10 wt% Al_2O_3, and (c) HA–10 wt% Al_2O_3 with Al_2O_3–13 wt% TiO_2 bond coat (Co: cohesive failure; Ad: adhesive failure)

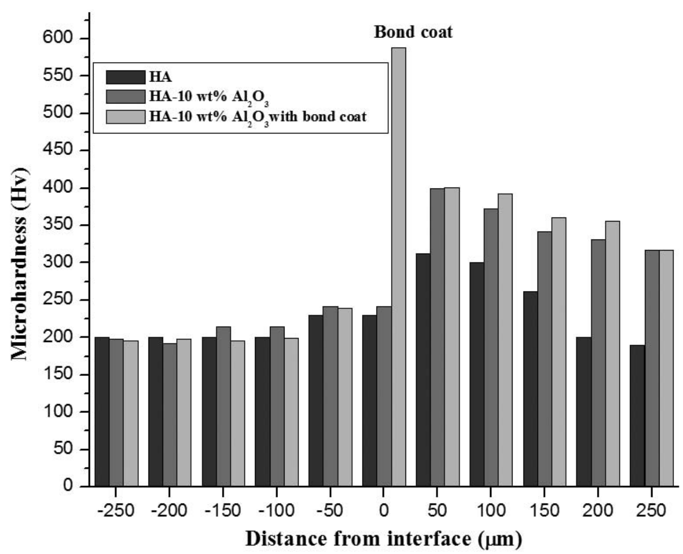

Figure 5. Microhardness profile of coatings along the cross-section : HA coating, HA–10 wt % Al_2O_3 coating, and HA–10 wt% Al_2O_3 coating with Al_2O_3–13 wt% TiO_2 bond coat.

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