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Wear studies on plasma sprayed Al_2O_3–40 wt% 8YSZ composite ceramic coating on Ti–6Al–4V alloy used for biomedical applications

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ABSTRACT

The relative wear resistance of three candidate coatings for titanium alloy-based orthopedic applications was compared using a reciprocating test method. Micrometer-sized powders of the following compositions were plasma sprayed onto Ti–6Al–4V (TAV) alloy: (i) Al_2O_3 (AO), (ii) 8 mol% yttria stabilized zirconia (8YSZ) and (iii) Al_2O_3–40 wt% 8YSZ (A4Z). Deposits were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and porosity measurements. In addition, microindentation hardness measurements and scratch-based adhesive/cohesive strength measurements were also performed. The composite coating (A4Z) had superior wear resistance. Wear track examination suggests two reasons for this improvement. First, the A4Z coating had improved cohesive strength between splats, and second, there was a phase transition toughening mechanism associated with tetragonal zirconia. Results of contact mechanics calculations support the experimental findings.

1. Introduction

Ti–6Al–4V alloys are found to be increasingly used in load bearing bio-implants due to their advantageous properties such as low density, high strength to weight ratio, greater corrosion resistance and excellent biocompatibility. The other added advantage of Ti alloy is its modulus of elasticity (113 GPa) which is closer to that of bone (30 GPa), compared to that of other conventional alloys such as 316 stainless steel and Co–Cr whose modulii of elasticity are 210 GPa and 240 GPa and it should be noted that the lower modulii results in the decrease of the stress shielding effect which in turn leads to enhanced service period. However, poor tribological properties of Ti alloys restrict their usage for articulating devices used in biomedical field. The alloy Ti–6Al–4V has been widely used despite concerns in the medical community that Al might be carcinogenic and that V might lead to Alzheimer disease. This eventually led to the usage of II/III generation alloys such as V free Ti–6Al–7Nb and further several low modulus beta titanium alloys with non-toxic alloying elements have been developed and extensively investigated by several researchers all over the world. The metallurgical aspects and biocompatibility issues of different Ti alloys have been discussed in detail in the review article written by two of the authors of the present paper [1]. Amongst different beta titanium alloys, TNZT and Ti–13Nb–13Zr alloys have received greater attention and cataloged under ASTM. In spite of the fact that certain issues related to Ti–6Al–4V implant are still relevant, several major manufacturers of implants continue to offer Ti–6Al–4V alloy to develop orthopedic implants. Hence, in this study we have attempted the coatings on the most widely used Ti–6Al–4V implant with the aim of choosing the best coating which has higher wear resistance.

Currently, ceramic materials are considered to be an alternative for metal–polyethylene based implants or metal–metal articulating devices due to their unique features of high hardness, superior tribological performance along with the excellent biocompatibility. Further, the recent works in this area reveals that, the wear rates are reduced significantly when ceramic femoral head is made to move either over polyethylene or ceramic cup [2–7]. Though many previous works have reported that Al_2O_3 and ZrO_2 ceramic materials have withstood the harsh environment in the human body, brittleness and low fracture toughness of pure alumina and hydrothermal instability of zirconia implants limit their usage for biomaterial implants [9,10] and therefore more recently alumina–zirconia toughened composites have been proposed for the fabrication of the acetabular cup and femoral heads, as they provide the superior combination of mechanical properties and wear resistance. The increase in the fracture toughness of these composites is attributed to the presence of zirconia as the fracture strength of zirconia ceramic is approximately double that of alumina and the enhanced tribological properties due to the addition of hard alumina [3,8]. Hip simulator experiments carried out on different compositions of alumina–zirconia (ranging from 0% to 80%) clearly demonstrated

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that alumina–zirconia ceramic cup and ball offer the highest wear resistance with enhanced mechanical properties than pure alumina [3]. However, susceptibility to slow crack growth, squeaking noises, stripe wear and head–neck taper mismatching are the major concerns in ceramic-on-ceramic articulating devices [9,10].

Ceramic coatings on implant materials using different surface modification techniques are considered to be alternative solutions to overcome failure of bulk ceramic materials. TiN, DLC and oxide coatings have been attempted using techniques such as ion implantation, PVD, CVD etc. [11–14]. However, thin layers formed using these techniques is one of the major disadvantages as they wear out with time.

Amongst the different surface modification techniques, plasma spraying which can deposit thick ceramic coating with faster deposition rate is considered to be the highly efficient technique by industries to develop different kinds of hard and soft coatings to prevent the substrate from various surface degradations. Especially in the field of aerospace, and navy, thermal sprayed coatings are very much utilized as they provide high wear resistance to the substrate material that possesses superior combination of mechanical properties like ductility and strength [15]. Plasma-spraying has also been advocated to develop bio-ceramic (Hydroxyapatite-HAp) coating on Ti based implants to enhance osseointegration [16,17] and has also been approved by Food and Drug Administration (FDA), USA, for coatings on joint prostheses [18]. However, it is also well known that HAp coating on TAV is not the right combination as the coating does not get adhere well with the substrate due to mismatch in thermal expansion coefficient and this has been studied in greater detail [26–28].

Amongst the different ceramic powders that are considered for developing wear resistant coatings, several studies have revealed that the microhardness, toughness, and wear resistance of the Al_2O_3 coatings can be further improved by the addition of other oxides like ZrO_2 or TiO_2 [19–24]. Especially, there are many reports which indicate that Al_2O_3 coatings with 40 wt% ZrO_2 on steel and stainless steel substrate developed by plasma spray process yields better tribological results which has made us to choose such a coating in the present study [19,22,23]. Though, nanostructured coatings have become an emerging technique, the associated challenging problems such as (i) agglomeration of individual nanoparticles into micron sized particles, (ii) careful control of particle temperature in the plasma jet in order to develop bimodal microstructure [25] and (iii) variation in coefficient of thermal expansion of nanomaterials and micron sized materials have led us to choose micron sized powders for this present work. To the best of the authors' knowledge, even though alumina with ZrO_2 has been tried to develop ceramic balls, coating of this combination of ceramic powders on TAV alloy has not been carried out so far for biomedical load-bearing applications.

Hence, in the present work an attempt has been made to make use of the advantageous properties of Al_2O_3–40 wt% ZrO_2 ceramics and develop a composite coating on TAV alloy using atmospheric plasma spraying process for artificial hip prostheses and to investigate their tribological properties in simulated body fluid environment. In addition, the coating parameters optimized in this study for plasma spraying of ceramic powders is applicable for any Ti alloy. This work was carried out in order to understand the effects of the novel ceramic composite composition proposed in this study on the tribological behavior of Ti alloy.

2. Experimental methods

2.1. Materials and processing

Commercially available Al_2O_3 with particle size 5–45 μm and 8 mol% yttria stabilized ZrO_2 with the same particle size as that of Al_2O_3 were used to obtain the composite feed stock powders. The as-received Al_2O_3 powders (fused and crushed) are angular and with irregular shapes, whereas the 8YSZ powders (sintered and agglomerated) are of spherical morphology. Composite feed stock powder was obtained by blending 60% of Al_2O_3 and 40% of 8YSZ (by weight) powders using planetary ball mill at a speed of 200 rpm for the duration of 3 h. Metco 3MB plasma gun with 40 KW atmospheric plasma spray system was used to develop the coatings as was done in our earlier studies [30]. All the coatings were deposited on biomedical grade Ti–6Al–4V sample of size $30 \times 30 \times 3\ mm^3$ using the optimized parameters, which were obtained after conducting several experiments with different processing parameters. The parameters employed in the present study which led to thick, dense and adherent coatings are given in Table 1. Before the deposition, the substrate was sand blasted using corundum of size # 24 meshes at an air pressure of about 50 psi.

Table 1
Plasma spray parameters of the feedstock.

Parameters	Al_2O_3	8YSZ	A4Z (composite)
Current (A)	490	510	550
Voltage (V)	70	70	70
Primary (Ar) gas flow rate (l/min)	42	42	42
Secondary (H_2) gas flow rate (l/min)	7.2	7.2	6.5
Spray distance (mm)	100	100	100
Powder feed rate (g/min)	7	7	9
Carrier gas flow rate (l/min)	5	5	5

2.2. Characterization

Surface morphology of all the feed stock powders and as-sprayed coatings were investigated using scanning electron microscope (Hitachi, S-3400N). Surface morphology of the coated surfaces as well as cross section was investigated using both optical and scanning electron microscope. For the microstructural investigation, the samples were mounted using bakelite powder and then polished using SiC papers of grit sizes ranging from 120 μm to 1600 μm and followed by mirror polishing with diamond paste of size 1 μm.

Phase analysis of the feed stock powders and the as-sprayed coatings were performed using X-ray diffractometer (Brucker, D8 Advance) with Cu Kα radiation. The current and voltage were set at 40 kV and 20 mA and all the readings were collected in the 2θ ranges from 10° to 90° in a step scan mode with a step of 2°/min. Vickers microhardness tester was used to find the microindentation hardness of the coatings. Microindentation hardness values were was measured across the polished cross-section of the coated samples using a load of 200 g for 15 s and the hardness were measured at ten different points and its average value is reported. Porosity measurements were performed on the cross section of the coatings at seven different areas using the optical microscope (Carl Zeiss, Canada) attached with clemex image analyzer.

2.3. Scratch testing for evaluating adhesion/cohesion strength

The scratch test was performed on the surface of the coatings to determine the cohesion/adhesion strength using microscratch tester (DUCOM, India). Scratch test which is commonly used to determine the adhesion strength of thin coatings is used here to determine the cohesion strength of thick coatings. The load at which the coating fails usually determines the adhesion strength of the coating, while the cohesion strength is determined by observing the failure within the coating after the scratch test using optical microscope [31,32]. In the present study, Rockwell