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Characterization and corrosion resistance of plasma sprayed HA and HA–SiO_2 coatings on Ti–6Al–4V

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ABSTRACT

The objective of this study is to evaluate corrosion resistance of plasma sprayed hydroxyapatite (HA) and hydroxyapatite–silicon oxide (SiO_2) coated Ti–6Al–4V substrate. In HA–SiO_2 coatings, 10 wt.% SiO_2 was mixed with HA. The feedstock and coatings were characterized by X-ray diffraction and scanning electron microscopy/energy dispersive X-ray spectroscopy. The corrosion resistance was determined for the uncoated and two coatings. The corrosion resistance of the Ti–6Al–4V was found more after the deposition of the HA + 10 wt.% SiO_2 rather than after HA coating and uncoated. Both HA, as well as, HA + 10 wt.% SiO_2 coatings were crack free after 24 h dipping in Ringer's solution for electrochemical corrosion.

1. Introduction

Surgical implants are usually fabricated from light metal or alloys such as Ti and Ti alloys which exhibit superior mechanical properties such as tensile strength, toughness and fatigue resistance [1,2]. The surfaces of metallic implants are usually coated with bioactive material to improve the biocompatibility of the metallic implant while preserving the useful mechanical properties of the implant materials [3–6]. Since their introduction in the 1980s, hydroxyapatite [($Ca_{10}(PO_4)_6(OH)_2$), HA] coatings on orthopedic implants have gained wide acceptance in metallic implants because of its excellent biocompatibility and chemical composition close to that of natural bone [7,8]. Bioactive and osteoconductive properties of HA, stimulate faster development of bone cells between the human tissue and metallic implant that results in the rapid biological fixation of implants [9]. The adhesive strength between HA and metallic implants is important to ensure long term fixation in artificial joints and dental implants, but HA has poor mechanical properties such as fretting fatigue, toughness, abrasive wear and adhesive strength [9,10].

The importance of silicon in bioactive materials for the bonding of bone and muscle as well as crosslinking agent in connective tissue has been reported [10]. One of the main functions of silicon is to partake in cellular development and gene expression. The silica content has a chemical function as the nature of bonding to bone of bioglasses relates to the in vivo solubility of these glasses [11]. The formation of apatite (bone-like tissues) was found to be enhanced when plasma sprayed silicon substituted hydroxyapatite coated bioimplants were immersed in simulated body fluid [12]. The mechanical function of silica particle is to improve the strength of a hydroxyapatite coating by enhancing the crack arrest or crack deflection [11].

There are numerous experimental deposition process such as thermal spraying [8,12–16], sputter coating [17–19], pulsed laser ablation [20–23], dynamic mixing [24], dip coating [12,25,26], sol–gel [27–30], electrophoretic deposition [31–37], biomimetic coating [38,39], and hot isostatic pressing [40]. Plasma spray process is the most commercially, well established preferred technique to deposit HA on metallic implants [14,16,41,42].

In this study, atmospheric plasma spray technique was employed to spray HA and HA–SiO_2 coatings on Ti–6Al–4V substrate. The as-sprayed coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) techniques. Subsequently corrosion behavior of HA-coated, and HA–SiO_2-coated Ti–6Al–4V has been investigated by the Tafel extrapolation method in simulated body fluid (Ringer's solution). After the electrochemical corrosion testing the crystallinity and morphology of the exposed specimens were investigated by XRD, SEM and EDX.

2. Experimental procedure

2.1. Materials

Medical grade HA powder (IFGL Bio Ceramics Limited, Kolkata, India) with particle distribution of 57–200 μm and silicon oxide (SiO_2) powder (Metroblue Industries, Madurai, India) with particle size 15–150 μm were used in this study. HA and SiO_2 powders were

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Table 1
Spraying parameters for HA and HA + 10 wt.% SiO_2 coatings.

Spraying parameter	Value
Arc current	500 A
Arc voltage	50 V
Primary gas (argon) flow rate	57 slpm
Secondary gas (hydrogen) flow rate	8 slpm
Spraying distance	75 mm
Powder gas pressure	11 slpm

mechanically stirred and mixtures of HA + 10 wt.% SiO_2 were prepared by stirring the powders in a ceramic pot for 20 min. Commercially available Ti–6Al–4V was used as substrate in this study. The pure HA and HA + 10 wt.% SiO_2 powders were plasma sprayed on substrate of dimensions 20 mm × 15 mm × 5 mm. Before spraying, the substrate surface was grit blasted with alumina of particle size 50–60 μm at a pressure of 5 bars for 2 min to roughen the surface and then subsequently air blasted to remove any residual grit.

2.2. Development of coatings

Pure HA and HA–SiO_2 powders were plasma sprayed (Miller Spray System) at Anod Plasma, Kanpur, India. The spraying parameters for both powders were identical and are listed in Table 1.

2.3. Characterization of the coatings

XPERT-PRO X-ray diffractometer system was employed to analyze the phase structure of the feedstock and coatings. In the phase analysis, the radiation source was Cu Kα; the operating generator setting was 45 kV/40 mA. The coated samples were scanned over the 2θ range of 20°–60°. Microstructural investigation was carried out on the surfaces and polished cross-sections of the coatings by SEM (EVO MA 15 ZEISS) coupled with EDX. As-sprayed coatings were cut with a low-speed precision saw and mounted in hot resin using a hot mounting press, followed by polishing with emery papers of 220, 320, 400, 600, 800, 1000, and 2000 grades, and finally mirror finished by buffing using an alumina slurry solution on napped cloth. To achieve the desired conductivity for observation in SEM the gold sputter coating were applied to samples. Elemental analysis of the coatings was carried out using an EDX to provide evidence of the presence of silica particles and to display the distribution of elements in the coatings as well as to evaluate Ca/P ratios of the HA and HA–SiO_2 coatings.

2.4. Surface roughness

Surface roughness, surface topography, surface energy and chemical composition have been reported as very important factors for implant tissue interaction and to affect the biocompatibility in clinical use [43,44]. High surface roughness will increase the coating and body-fluid interface, and thus increase the dissolution rate and apatite precipitation [45]. The surface roughness values of uncoated Ti–6Al–4V, plasma sprayed HA and HA + 10 wt.% SiO_2 coatings on Ti–6Al–4V specimen were measured by a roughness tester (SJ-201 MITUTOYO), using a filter of Gaussian type for a cut-off wavelength of 0.8 mm. Roughness parameters such as R_a (the arithmetic mean of the departures of the roughness profile from the mean line), R_q (root mean square (RMS) of average roughness), and R_z (average of the highest peaks and the lowest valleys) were measured at four different positions on the surface of the samples. The average value of each parameter at various positions is reported here.

Table 2
Parameters for conducting the potentiodynamic scan.

Parameter	Value
Initial potential	0.25 V vs open circuit potential
Final potential	−0.25 V vs open circuit potential
Scan rate	1 mV/s
Sample area in Ringer's solution	1 cm^2
Initial delay	24 h

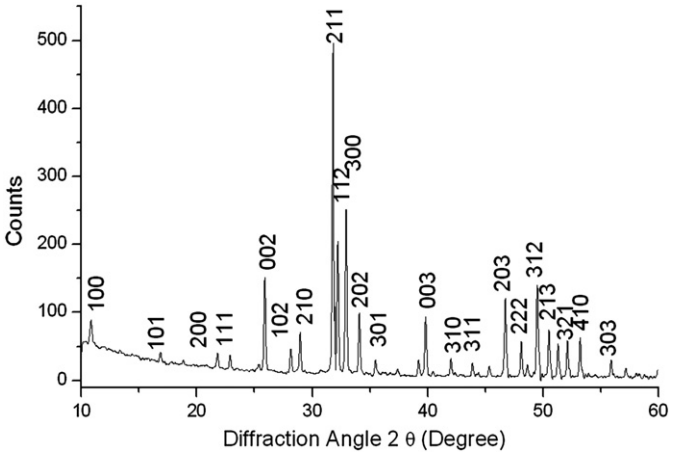

Fig. 1. XRD pattern of HA powder.

2.5. Electrochemical corrosion studies

Potentiodynamic polarization tests were conducted to investigate the electrochemical corrosion behavior of the uncoated Ti–6Al–4V, pure HA and HA + 10 wt.% SiO_2 coated Ti–6Al–4V specimens. Potentiostat/Galvanostat (Series G-750; Gamry Instruments, Inc. USA), interfaced with a computer and loaded with Gamry electrochemical software DC105 was used on to conduct the test. Ringer's solution with chemical composition (in g/L) as 9 NaCl, 0.24 $CaCl_2$, 0.43 KCl, and 0.2 $NaHCO_3$ at pH 7.2 was used as the electrolyte for simulating human body fluid conditions. The Ti–6Al–4V specimen forms the working electrode. The saturated calomel electrode (SCE) was the reference electrode. A graphite rod served as the counter electrode. The instrument measures and controls the potential difference between a non-current carrying reference electrode and one of the two current carrying electrodes (the working electrode). The parameters for conducting the potentiodynamic scan to calculate the corrosion rate by plotting the Tafel plot are listed in Table 2. The initial delay refers to the stabilization of immersed specimen in Ringer's

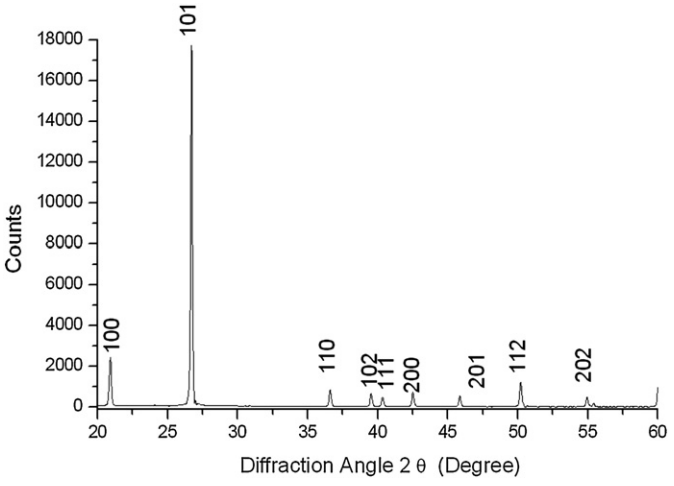

Fig. 2. XRD pattern of SiO_2 powder.