TRIBOLOGICAL CHARACTERIZATION OF PLASMA SPRAYED PURE HYDROXYAPATITE COATINGS

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ABSTRACT *In this manuscript tribological properties of hydroxyapatite (HAp) coating has been reported. Techniques like Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX) and X-ray diffraction analysis (XRD) has been used to study the microstructure and phase analysis of obtained coatings. The wear studies have been performed on coatings and the wear rate of HAp coatings was found to be 8.4 ×10^{-3} mm^{3} N^{-1}m^{-1}.*

Keywords: *database Hydroxyapatite; Wear; Plasma Spraying; SEM, XRD*

1 Introduction

The metallic implants suffer from some of the problems like corrosion, metallic ion release and buildup of wear debris, which leads to the improper fixation of implants. These problems can be overcome by using the implants coated with hydroxyapatite. The various surface modification techniques like plasma spraying, pulsed laser deposition, sol-gel, plasma electrolytic oxidation, have been used by the researchers to coat hydroxyapatite onto the metallic implants [1-7]. FDA, USA has approved plasma spraying technique to be used as a coating process for biomedical implants. The HAp coating improves the biocompatibility and fixation of the implants to the bone [8]. HAp[$Ca_{10}(PO_4)_6(OH)_2$], is an encouraging material for biomedical applications because its Ca/P ratio is very close to the human bone (1.67). However, its poor mechanical properties limit its usage for orthopedic applications like hip and knee joints [9, 10-13]. It is clear from from the tribological studies of the hydroxyapatite, that it is prone to wear which can affect the lifespan of the implant. So while performing the studies on the hydroxyapatite coatings wear resistance should be taken into consideration [14, 15]. In this article, HAp coatings were deposited on commercially pure titanium (cp-Ti) substrates using plasma-spraying process. Characterization techniques like SEM/EDX and XRD has been used to study the morphology and phase analysis of the coatings. The wear studies were conducted on coatings using Ball on disc tribometer under dry conditions.

2 Experimental Methods

2.1 Substrate material and specimen preparation

Hydroxyapatite powder (Captal 60-1) was used as the feedstock powder to develop HAp coatings on the commercially pure titanium. The samples (20mm x 15mm x 5mm) of pure titanium were used as substrates. Thick coatings were developed using Miller thermal spray apparatus at Anod Plasma Limited, Kanpur, India.

2.2 Material characterization

The surface morphologies of HAp coatings were investigated using SEM (Make: JEOL) attached to EDX attachment (Oxford-instruments). The phase structure of both feedstock powder and the coatings were identified with the help of PANalytical, XPERT-PRO diffractometer using Cu Kα radiation. The feedstock powder and coatings were scanned with a scan range of angle 2θ =10-80° and 2θ =20-90° using step size = 0.0170^{o}

2.6 Wear test of coatings

The wear testing of coatings was performed by using Ball on disc configuration using a tribometer and alumina ball of diameter 3mm was used as a counterpart. The coefficient of friction or friction coefficient was recorded for 2000 cycles at 1 N load with a sliding speed of 100 rev min^{-1}.

3 Results and discussion

3.1 SEM/EDX and Phase analysis of coatings

The SEM micrographs of the HAp coatings is shown in Fig. 1. The coating microstructure has some unmelted, partially melted and fully melted particles along with smooth splats on their surfaces.

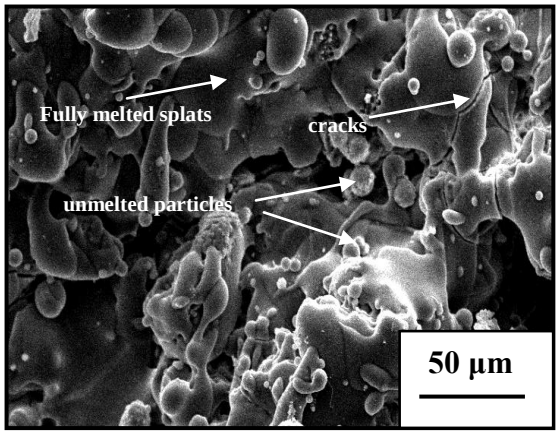

Fig. 1. SEM micrograph of the HAp coatings

The smooth splats are formed due to the excessive melting and flattening of the HAp particles when impacted upon the substrate [16]. A few cracks are also visible on the surface of the coatings, which possibly arise from residual stresses upon rapid cooling and solidification [17]. The XRD pattern of pure HAp powder is shown in Fig. 2. It shows the sharp peaks corresponding to HAp indicating crystallinity of the powder with no trace of the amorphous phase. All the major peaks of HAp powder and Al_2O_3 powder matches the Joint Committee on Powder Diffraction Standards (JCPDS) cards 73-0293 and 42-1468 respectively.

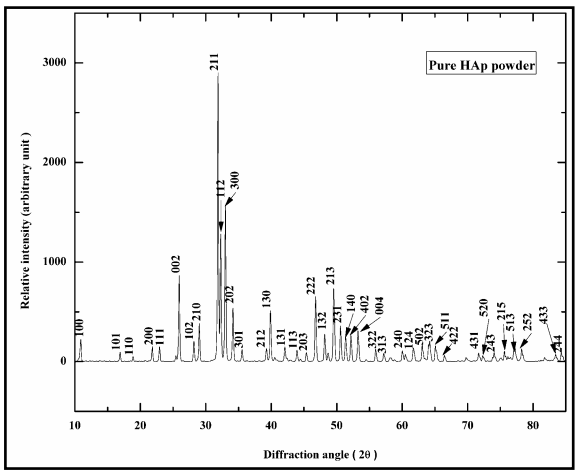

Fig. 2. X-ray diffraction patterns of Pure HAp powder.

The XRD pattern of the coatings is shown in Fig. 3. It clearly indicates that the peaks corresponding to HAp broaden after coating indicating the presence of amorphous phase at approximately 2θ = 30-33° along with some minor peaks.

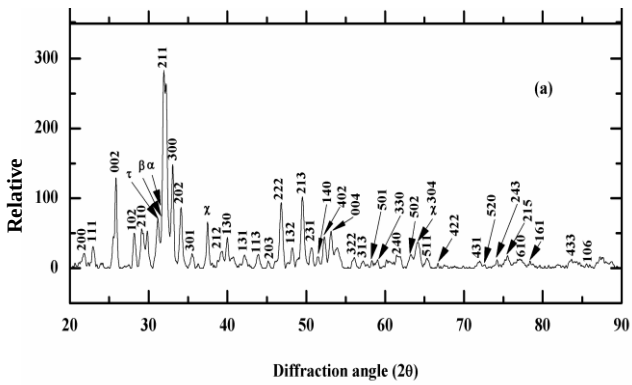

Fig. 3. X-ray diffraction patterns of (a) Pure HAp coatings
[α: α-TCP, β: β-TCP, τ: TTCP, χ: CaO].

These extra peaks probable relate to tricalcium phosphate (α-TCP and β-TCP) and tetra calcium phosphate (TetCP). Also, the traces of the CaO can be observed between 2θ = 37-39° and between 2θ = 64-66° for pure HAp coatings. The thermal decomposition and dehydroxylation of hydroxyapatite powder particles while subjected to a very high temperature of plasma jet are the main reason for the formation of these phases [18-22]. These phases are not desireable because of their amorphous nature and high solubility rate in the body fluids which makes the implants loose [18, 19, 22, 23].

3.5 Tribological study of coatings

The average coefficient of friction of the pure HAp coatings was found to be 0.21 ± 0.04. According to the reported literature [15] high friction coefficients facilitate the implant fixation, and provide stability for the bone growth. The wear rates of the pure HAp coatings are reported in Table.1.

Table.1. Wear rate of HAp coatings under dry sliding conditions

Parameter	HAp coatings
Coefficient of friction	0.21 ± 0.04
Wear volume (mm^3)	0.187 ± 0.08
Wear rate ($mm^3\ N^{-1}\ m^{-1}$)	8.4×10^{-3}

The wear rates of pure HAp coatings were found to be 8.4×10^{-3} $mm^3\ N^{-1}\ m^{-1}$. The wear volume for the pure HAp coatings was found to be 0.187 ± 0.08 mm^3. The functionality of the biomedical implants improves if the damage to the coatings during implantation is minimal. This can be achieved only if the wear volume of the coating is less [15]. It has been reported by Qi et al. [24] that poor wear resistance of the implant biomaterials is the major reason for the release of carcinogenic metal ions in the body environment and for this reason, the wear resistance of the implant material should be improved.

Conclusions

Pure HAp coatings were deposited on commercially pure titanium (Grade2) substrates by plasma spraying process. SEM micrographs showed that HAp coatings coatings contain some unmelted, partially melted and fully melted particles on their surfaces. The presence of unmelted and partially melted particles on the surface of the coatings contributed to the roughness of the coatings. Some unwanted phases like α-TCP, β-TCP, TTCP and CaO has been observed in the plasma sprayed pure hydroxyapatite coatings The wear studies shows that the wear resistance exhibited by HAp coatings may be attributed to the presence of dense microstructure.

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