Plasma Spray Deposition of HA-TiO_2 composite coating on Ti-alloy for Orthopedic Applications

Chander Prakash[1*]

[1]School of Mechanical Engineering, Lovely Professional University, Phagwara, Jalandhar, India.

Abstract. A biomimetic nano-porous 50HA-50TiO2 composite surface has been put on a plasma deposition process with the orthopedic use of Ti-6Al-4V alloy in the present research paper. Scanning electron microscope (SEM) fitted out of energy-dispersive spectroscopy (EDS) and X-ray (XRD) was used for analysis of the coated morphology, elementary, and phase composition of the test. The results show that Ti-6Al-4V's HA / TiO2-coated surface shows the natural bone-like nanoporous morphology that was favorable for bone growth in the host body around the implant. The study of EDS and XRD revealed that the deposited layer includes Ca, P, O materials, as well as the essential parent product components (Ti, Al, V), and bioactive phase oxides (TTCP, TCP, rutile) formed on the substrate surface. These corrosion resistance and bioactivity of the Ti-5Al-4V was increased significantly. The composite coating tests of nano-porous material have shown that the hardness and ruggedness values of the HA / TiO2 coating on the surface of the Ti-6Al-4V substratum are 977 HV and 3.59μm. Overall, the HA-TiO2 coating can be concluded that the Ti-6Al-4V alloy surface has been tailored to the requirements of orthopedic implants.

Keywords: Titanium; Biomedical implant; Hydroxyapatite Coating; Orthopaedic; Plasma Spraying.

1. Introduction

Titanium and its alloys have been used in medical implants for replace or repair of organs of the human body in the last few decades, as one of the most common metal biomaterials [1]. Among all the titanium alloys mainly the alpha-beta alloys were widely used in the orthopedics and dental applications. This was mainly due to their identical characteristics to human bones such as good fatigue strength, excellent biocompatibility, corrosion resistance, and low specific mass [2]. Although Ti alloys were highly reactive metal and which form an oxide (TiO_2) layer on the surface, which has extremely stable and it preventing the material from corrosion [3]. This layer protects Ti alloys against pitting corrosion, interangular corrosion and crevice corrosion, causing Ti alloys to be extremely biocompatible and biomimetic [4]. But, it was observed that with the passage of time, the TiO_2 oxide layer was degraded and unable to prevent the materials from corrosion in the host body [5]. So, the researchers were actively engaged in developing a suitable coating and their technique to improve the stability of implants in the human body [6]. In recent studies, the development/deposition of a composite on the surface of Ti-based implants to improve the mechanical, wear, corrosion and bioactivity were found the best solution [7].

The human body, with temperature 37° C and have an acidic oxygenated saline solution of 7.4 pH, which was a highly corrosive environment and Ti-6Al-4V start corroded in this environment [8]. To overcome this problem materials surface need to be modified by deposition of the biocompatible layer on the surface of the material that will standby for longer life span in the human body [9]. The coating or surface modification has been done by various types of deposition process such as sol-gel [10], biomimetic [11], electrolytic [12], sputtering ion coating [13], physical vapor deposition [14], plasma thermal spray [15], etc. Among them plasma spray deposition process was found potential because of their coating characteristics can be easily controlled like as coating thickness, roughness, chemical composition, and surface porosities. Moreover, the deposited surface has excellent fatigue, wear and corrosion resistance [16].

A number of coating materials were deposited by plasma spray deposition to improving the chemical, mechanical and biological properties of Ti-6Al-4V substrate, was used as composite coatings. Titania (TiO_2), Alumina (Al_2O_3), and Zirconia (ZrO_2) were used as a composite coating with Hydroxyapatite (HA-$Ca_{10}(PO_4)_6OH_2$) in various ratio to boost the mechanical and biological properties of HA coating [17]. But, HA was the bioactive ceramic material which has suitable for surface coating. HA was the main inorganic component of bone. However, it was brittle and has poor mechanical properties [18]. To avoid this, Titania (TiO_2) was preferred as a composite coat with HA due to its corrosion resistance, biological properties and capable of enhancing the cell growth [19]. The coating layer protects against the release of a metallic ion from the substrate. So, coating particles size has a significant effect on the properties of the coating in the substrate [20]. Properties get improve with decreasing the size of the particles. In a recent, advancement in nanotechnology have led to the development of nanocomposite coating [21].In order to avoid the above said drawback, owing to its corrosion resistance and biological properties, Titania (TiO2) was alloyed with HA to deposit composite coat to promote growth of the cell [19]. The surface film prevents the metal ion from being expelled from the substratum. Therefore, the size of the covering of particles influences the properties of the paint in the substrate[20] significantly. Through increasing the particle size, the properties boost. In recent developments in nanotechnology, nano-composite coatings were developed [21].

Nonetheless, thermal plasma sprays have several drawbacks, such as mechanical properties modification, peeling and surface degradation, which further reduce the metallurgical bond strength between the coating and the substrate [22]. As a consequence, surface and subsurface defects in the coated substratum surface developed due to these various types. Researchers have made considerable strides in solving the problem of plasma deposition [23]. Among the different process investigated, the recent advance in nano-technology have to lead to the development of composite coating knows as nano-porous composite coating. The application of micro-size powder particle the performance of the layer and effectively reduces surface defects by depositing biocompatible composite coating on the substrate's surface [24]. Several studies have shown the wide use of Ti and its alloys due to its good mechanical and biological characteristics based on current literature [25]. In contrast, to date no reports have been reported focusing on biomaterial Ti-6Al-4V surface modifications in 50-50 wt of HA / TiO2 nano-porous composite bioceramics. Through incorporating TiO2, the crystalline of the polymer surface is effectively strengthened. In the human body implant, the biomaterial was in direct contact with muscle tissues so, the initial response of these tissues to the implant depends on its surface properties of implants. Longevity was must for orthopedic implants. Although medical orthopedic implants have excellent properties such as strength, elasticity, and biocompatibility [9]. Surface modification of the surface was one of the best solutions for the longevity of the orthopedic implants. The needs of alternative medical solution have not only demanded better biomedical devices but also more diverse functionality and bioactivity [17].

The success of the implantation depends on the biocompatibility, mechnaical properties, and surface intergrity and also the response of the living tissues around the implant during the healing process [26]. There are many other factors that depend on the biocompatibility of implant biomaterials such as material composition, surface wettability, and surface roughness. Therefore, the present investigation attempts have been used to produce bioactive and biomimetic ceramics coating layer that boost biocompatibility, micro-hardness, stiffness and wear resistance of the Ti-6Al-4V alloy by means of nano-porous HA-TiO2 composite coating using a plasma spray technology. A study was conducted to evaluate the effect of the plasma deposition as a technique of surface modification on biomaterials preparation for biomedical applications on micro-structure, morphological studies, coating thickness, microhardness and surface roughness of the modified surface.

2. Materials and Method

Ti-6Al-4V grade-V well known biomedical alloy was used as a substrate/workpice in this research. Ti-6Al-4V alloy having the composition with weight percentage was 0.02% N, 0.05% C, 0.01% H, 0.20% Fe, 0.16% O, 6.10% Al, 3.95% V and Ti was balance. Triangular shaped Ti-6Al-4V specimen was prepared for the investigation. High purity (99.9%) powders such as hydroxyapatite (HA) and titania (TiO_2) were used for the coating on the Ti-6Al-4V. The HA and TiO_2 powders of size 10-20 µm irregular in shape was used as coating materials in this study. Both the powder was mixed in the 50-50 wt%. The plasma spray deposition technique was used for the coating of HA-TiO2 on the Ti-6Al-4V substrate. The spraying parameter used in HA/TiO_2 composite coating is given in Table 1.

Table 1 Plasma Spray Process Parameters

Spraying Parameters	Value
Primary Gas Flow (Argon)	38.5 NLPM
Secondary Gas Flow (Hydrogen)	2.0 NLPM
Carrier Gas Flow (Argon)	5.0 NLPM
Voltage	64 volt
Current	500Amp

Feed rate	32 gm/min
Spray Distance	120 mm

The coated surface morphology and surface integrity was investigated by scanning electron microscope (SEM; JEOL JSM-6500) and elemental composition was investigated by Energy-dispersive Spectroscope (EDS). The coating thickness was measured at cross-section of the specimen and mounted in mould analyses. The mounted sample substrate was polished with emery paper with the different grade and etched with kroll's reagent. X-ray diffractometer (XRD) with Cu Kα radiation analyzed the phase composition of the substratum coating. The XRD angle 2θ was was used for scanning from 10° to 90°. The microhardness, surface topology, surface roughness and chemical composition of coating in the substrate was an important parameter for implant biomaterial interaction with living tissue and affect the biocompatibility of orthopedic application. Vickers hardness tester with a dent load of 0.2N was utilized to measure the microhardness of the HA/TiO_2 coated substrate. The surface roughness of a plasma sprayed HA/TiO_2 nano-porous composite coating was measured by Talysurf CCI lite, this is noncontact 3D surface profile.

3. Results and Discussions

3.1. Microstructural and elemental composition Analysis

Fig 1(a) shows the SEM morphology and EDS spectrum of biomimetic nano-porous composite coating of HA/TiO_2 on coated Ti-6Al-4V alloy by plasma spray deposition technique. Fig. 2 (a) shows the SEM micrograph and it can be seen that the deposited surface contains splat like morphology, globules, and cracters at a magnification of 500×. This may be because of the impact of molten material on the substrate during the PSD process occurs. During the PSD process, the large amount of thermal energy, produced from plasma jet and melt the mixture of nano-porous composite powder HA/TiO_2. The mixture of 50-50% HA/TiO_2 was in a molten state. Deposition of HA was presented by yellow color and TiO_2 presented by red color. The rutile TiO_2 was deposited in the form of splats and globules, whereas, HA was deposited in the form of brittle agglomerated structure. The HA deposited layer has a porous structure which enhances the bioactivity of the surface and accelerates the tissue growth or osseointegration in the host body. At higher magnification (500×), porous microstructure and small void on the surface of coated Ti-6Al-4V was observed.

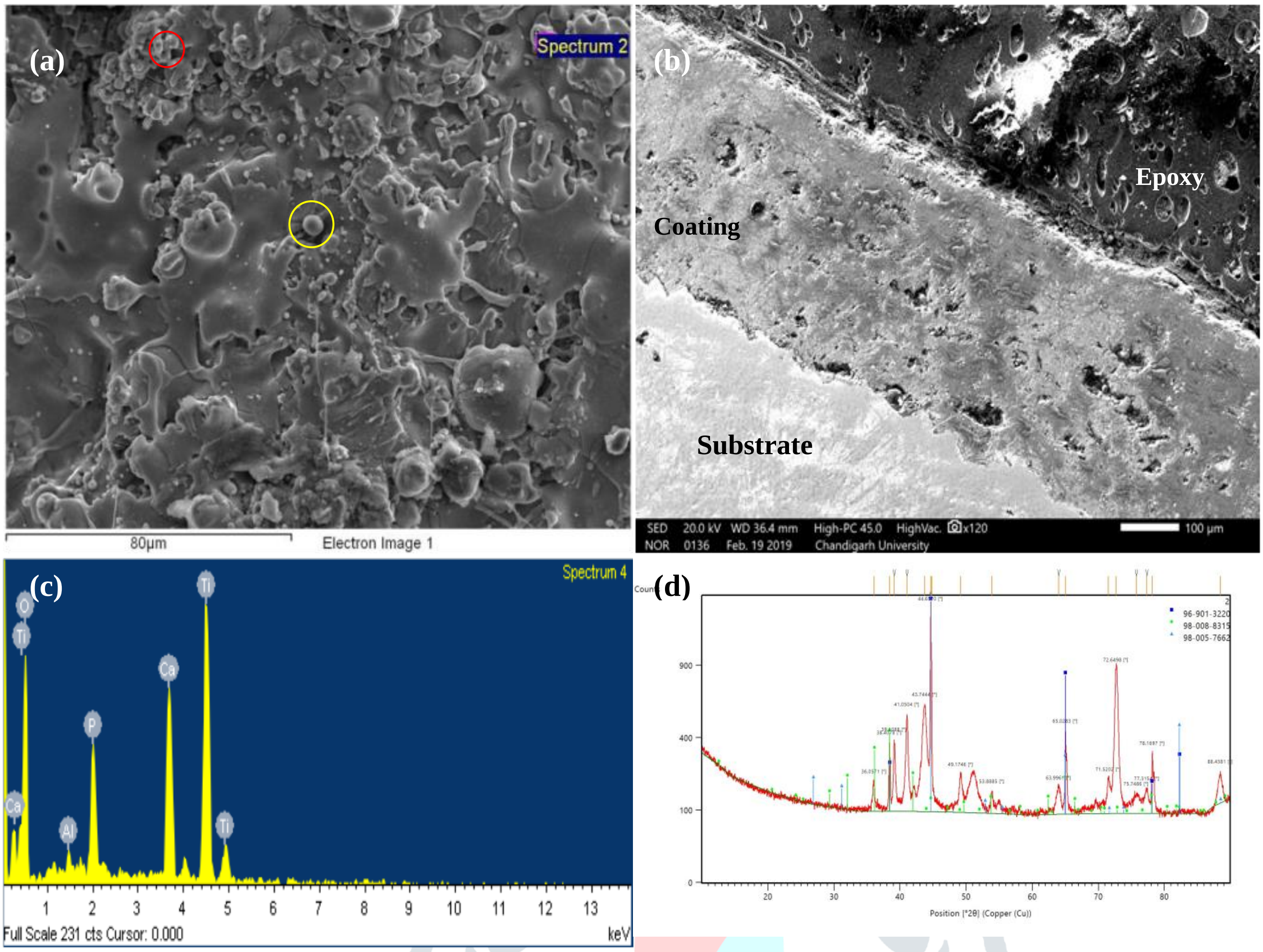

Fig. 1 (a) SEM morphology (b) Crosssectional SEM morphology (c) EDS spectrum of HA/TiO_2 coating (d) XRD patterns of Ti-6Al-4V coated surface.

The cross-section morphology of plasma sprayed HA/TiO_2 nano-porous composite coating on the Ti-6Al-4Vsubstrate is shown in Fig 1(b). From the cross-section, a micrograph was measured the average value of coating thickness was 250µm. HA/TiO_2 nano-porous composite coating appears to be well adhered and metallurgically bonded with the Ti-6Al-4V substrate. The coated surface has high adhesion strength (~25 Mpa) which resist the delamination of the coating. The EDS spectrum shows the elemental composition of HA/TiO_2 composite coating and confirmed the presence of rich content of Titanium (Ti), calcium (Ca), phosphorus (P) and oxygen (O) elements in the coating, which further conferred the deposition of HA and TiO_2 layer, as can be seen in Fig. 1(c). The presence of element revealed the development of biomimetic phases on the coated surface which enhances the corrosion resistance and bioactivity of the surface. The Ca/P ratio of the nano-porous composite coating observed the presences of other additional phases rather than HA in the coating. The ratio of Ca/P was calculated from the EDS spectrum for the HA/TiO_2 nano-porous composite coating ratio 1.68. If the Ca/P ratio was in the range between 1.5 to 2.2, which indicates the presence of Tricalcium phosphate (TCP), Tetracalcium phosphate (TTCP), and HA compounds on the coating form during decomposition of nano-porous composite powder [27].

The XRD analysis of the sprayed HA/TiO_2 nano-porous composite coating on the Ti-6Al-4V substrate is shown in Fig.1(d). The sharp peaks in the XRD pattern clearly show the nano-porous coating of HA/TiO_2 was in crystalline in nature. The major hump around 40-45° range of 2θ. The peaks were fitted within JCPDS reference for Ti-6Al-4V coated surface were 9-169 (β-TCP), 25-1137 (TTCP) and 9-432 (HA). By these result, it confirms the formation of $Ca_3(PO_4)_2$, $Ca_4(PO_4)_2O$, and rutile on the surface of the substrate. These phases indicate that the coated surface of Ti-6Al-4V was enhanced the bio-mechanical properties, biocompatibility and bioactive, which has potential application in orthopedics [28].

3.2. Microhardness and Surface Roughness

Fig. 3(a) shows the micro-hardness measurement of plasma spray deposition of HA/TiO_2 nano-composite coating on Ti-6Al-4V substrate along the polished cross-section. The HA/TiO_2 nano-composite coating exhibited a hardness of 977 Hv. The value of micro-hardness shows the good crystallinity form in the nanocomposite coating. In comprarison with other research studies showed that coating hardness value has been a significant enhancement. From the indented image, it was clear that the coating has developed in the Ti-6Al-4V substrate was excellent metallurgical bonding. Also, the hard surface of the coating has to resist abrasive wear. The surface roughness of implanted surface beneficial for both the bone anchoring and biomechanical stability. The surface roughness was measured by 3D optical measurement system for coated surface of Ti-6Al-4V substrate and the average value was used as roughness value (Fig. 3(b). The average value for coated Ti-substrate was 3.59 µm. This roughness value due to the presences of TiO_2 in the nano-porous composite coating.

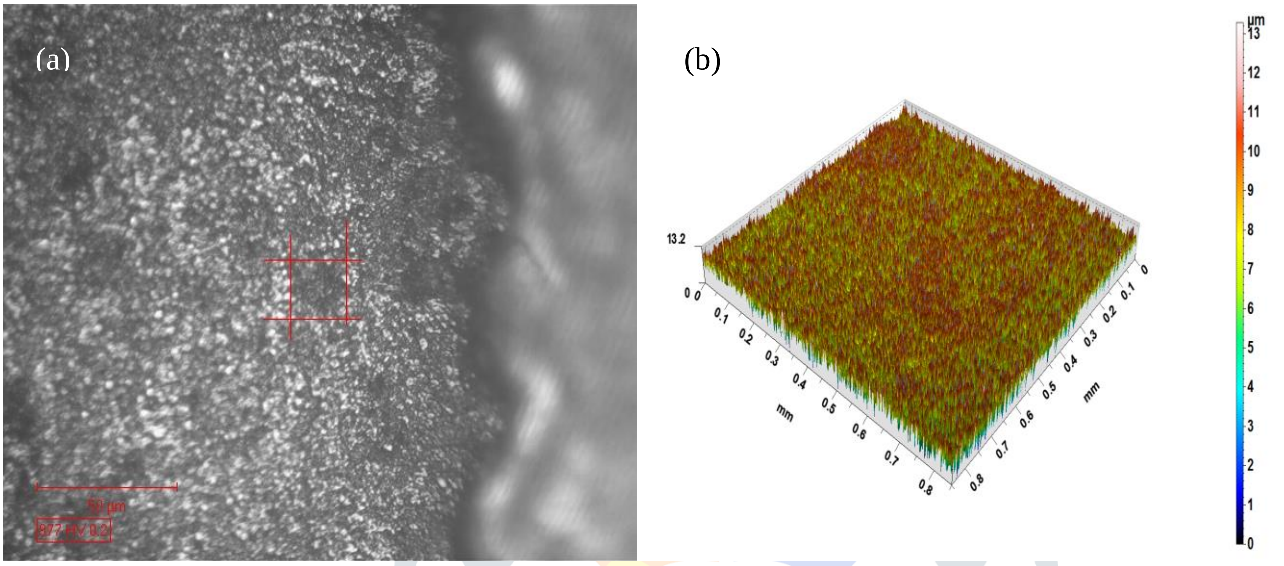

Fig. 3 (a) Micro-hardness of coating, (b) 3D plot of surface roughness.

4. Conclusions

In this research work, HA/TiO_2 nano-porous composite coating was successfully deposited by the plasma spray technique on Ti-6Al-4V substrate. The HA/TiO_2 composite powder was prepared by mixing HA and TiO_2 powder in 50:50 wt %. The salient conclusions from the present investigation were summarized as following:

- The composite coating of HA/TiO_2 layer and interface analysis confirmed that there was a strong metallurgical bonding of coating with Ti-6Al-4V substrate.
- The surface morphology analysis confirmed that nano-porous biomimetic coating has been deposited, which enhanced the bioactivity of the alloy. The thickness of coating was measured around 250 µm.
- The HA/TiO_2 coating exhibits good microhardness ~ 977 Hv which enhanced the wear resistance of Ti-6Al-4V alloy.
- The surface roughness was measured ~ 3.59 µm, which helped in cell adhesion and growth of tissues.
- The phase analysis shows the different phase such as TTCP, TCP etc. on the HA/TiO_2 coated surface Ti-6Al-4V, which increase corrosion resistance and biocompatibility of substrate.

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6. References

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