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Corrosion performance of hydroxyapatite and hydroxyapatite/titania bond coating for biomedical applications

Tejpreet Singh Bedi¹, Santosh Kumar¹² and Rakesh Kumar¹³

¹ Assistant Professor, Department of Mechanical Engineering, Chandigarh Group of College, Landran, Mohali, Punjab India
² PhD Research Scholar, Department of Mechanical Engineering, IKG Punjab Technical University, Kapurthala, Punjab, India
³ PhD Research Scholar, Department of Mechanical Engineering, Chandigarh University, Gharuan, Mohali, Punjab, India

E-mail: santosh.3267@cgc.edu.in and santoshdgc@gmail.com

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Abstract

The aim of current investigation is to access in-vitro corrosion performance of flame sprayed titania (TiO₂) coated 316L stainless steel, hydroxyapatite (HAp) coated, hydroxyapatite/titania bond coated (HAp/TiO₂) 316L stainless steel and plasma sprayed zirconia (ZrO₂) coated 316L stainless steel. In HAp/TiO₂ bond coatings, TiO₂ was utilize as a bond coat between the 316L stainless steel substrate and HAp top coat. The different characterization methods such as SEM, EDS, XRD and electrochemical methods were used to analyse the electrochemical characteristics as well as microstructural morphology phases of the coatings. In addition the corrosion behavior of the coated and uncoated samples was performed in simulated body fluid. The tests were carried out for potentiodynamic polarization and open circuit potential. The experimental results reveal that after the deposition of bond coatings (HAp, TiO₂, ZrO₂ and HAp/TiO₂) the corrosion resistance of the steel was observed to increase.

1. Introduction

A bio-implant is a medical tool used to replace or to assist a damaged biological structure. Its major applications are in orthopedic implants (joint replacement of hip, knee, elbow, shoulder, etc.). Since, the use of bio implants improves the lives of patients and brings the patients to normal activity in personal as well as professional life [1]. Currently, in India, about 70 million people are suffered from joint related issues and this incidence is going to increase day by day [2]. Also the world-wide sale of orthopedic implants before 16 years ago was $ 8.7 billion and projected to enhance yearly at a growth rate of 12.5% [3]. In addition, dental implants are also increasing at higher rate [4]. Hence, a huge number of implants are required now a days and their demand will significantly grow in the near future. Hence there is a need to boost or develop better materials for orthopedic application [5–10]. The materials to be used for any biomedical applications must be, corrosion and wear resistant. Since, the corrosion and wear are the root causes of deterioration of the biomedical implant devices. To overcome this, distinct surface modification techniques are used. Among these, thermal spraying especially plasma spraying process has been successfully used for the same.

The important bioactive material used in the surface modification process is hydroxyapatite (HAp) which decrease the release of metal ions by forming it more resistant to wear/corrosion, and building the surface more bioactive and triggering bone growth [11–21]. Still, owing to high temperature involved in the plasma, harmful effects (residual stress, evaporation, phase alteration and gas release etc.), are generally take place in these coatings. Due to these undesirable characteristics of plasma spraying there is a requirement to investigate a new methods working at lower temperatures for coating biomaterials. Keeping in mind the above harmful effect of plasma spraying, high velocity oxy-fuel spray (HVOF) and flame spray techniques have been used successfully by some researchers for depositing biomaterials in the recent past.

Simon et al [22] studied various materials (metals, polymers and ceramics) used in orthopedic implants. Metals used in orthopedic implants comprises Ti and Ti alloys Co–Cr alloys and surgical grade stainless steel.
However, most widely used polymers used in orthopedic implants is Polyethylene and ceramics is alumina (Al₂O₃) and calcium phosphate [Ca₃(PO₄)₂]. These calcium phosphate implant coatings result in strong implant fixation.

Kutty et al. investigated the effects of grain size on sintered properties of commercially available HAp powder. It was found that hardness and relative density of the material decreased as the grain size exceeded a certain lower and upper limit respectively.

Saju et al. worked on thin film coating of crystalline hydroxyapatite on to a titanium substrate using sputter coating and an x-ray diffraction was performed on the coated sample before and after sintering. The results compared with the standard x-ray diffraction of hydroxyapatite and titanium and the coating was found to be successful having crystalline characteristics.

Thamaraiselvi et al. studied the effect of alkali treatment on SS 316 LVM alloy using sodium hydroxide and evaluated electrochemically through cyclic polarization experiments performed in Ringer’s solution. The SS 316 LVM alloy was evaluated with different amount of NaOH and coated electro-phoretically with (HAp). The performance of HAp coating on SS 316 LVM alloy was evaluated in-vitro through polarization tests. The Fourier Transform Infra-red Spectrometry (FT-IR) and XRD characterization techniques were used to study the performance of HAp coating. From the experimental result it was observed that the alkali treatment and HAp coating increased its corrosion resistance.

Singh et al. deposited a dense HAp and HAp reinforced with 10 wt% (80Al₂O₃–20TiO₂) coating on Ti-6Al-4V material using plasma spray techniques. The distinct characterization techniques (SEM + EDS analysis and by corrosion resistance testing with the aid of FT-IR spectroscopy and XRD) were used. Corrosion investigations were done in simulated body fluid. This investigation concluded that there was slight enhancement in surface roughness with reinforcement, micro-hardness and improved corrosion resistance.

From the overview of the research studies in the area of biomedical implants, it has been concluded that the identification and development of high corrosion resistant materials are the areas of prime interest in this field. Much of the work has been done on Co–Cr alloys whereas the researches in case of stainless steel are in incipient stage. Commercially available HAp has remained focal point of many biomedical implant studies. Among distinct coating techniques, thermal spraying especially plasma spraying process has been successfully used for the same due to its several advantages. However, due to high temperature occurred in the plasma spraying, some harmful effects (evaporation, residual stress phase alteration, residual stress, gas release and debonding etc) generally take place in these coatings. Thus there is need to research new method running at lower temperatures for coating biomaterials. Keeping in mind the harmful effects of plasma spraying, flame spray process has been considered under this research work for depositing novel coating compositions on the existing biomaterials.

Hence the focus of the present study is to deposit HAp, TiO₂ and HAp/TiO₂ bond coatings on 316L SS specimens by flame spray process and also to develop coating of ZrO₂ powder on 316L SS specimens by plasma spray process. Therefore, to provide better bio-compatible orthopedic implants, the performance evaluation of the coatings is to be carried out by SEM/EDAX analysis and by corrosion resistance testing with the aid of potentiodynamic polarization studies.

The various objectives of this research work are:

1. To investigate the possibility of use of flame spray process to deposit various coatings on 316L SS.
2. To prepare the novel coatings of HAp, TiO₂ and ZrO₂ powders on 316L SS.
3. To determine the metallurgical properties of the as-sprayed coatings using distinct characterization techniques.
4. Evaluation of the biological response of bare and coated specimens by in-vitro testing in simulated body fluids so as to evaluate their usefulness to prevent degradation of the base materials.

2. Experimental detail

In the present research work, in-vitro corrosion performance of bare, TiO₂, ZrO₂ and HAp/TiO₂ coated 316L SS specimens have been tested by the tafel extrapolation technique in simulated body fluids (Ringer’s Solution and Hank’s Balanced Salt Solution).

2.1. Substrate and feedstock powder

Commercially available biomedical stainless steel (316L SS) was utilized as base metal in this research work. The chemical composition of 316L SS in terms of wt% age: Carbon: 0.0240%, Chromium: 16.850%, Nickel:
10.735%, Molybdenum: 2.269%, Silicon: 0.468%, Manganese: 1.156%, Phosphorous: 0.032%, Sulphur: 0.017% and Iron- Bal was utilized as substrate material. The substrate material 316L SS was purchased from True Metals, Industrial Area, Phase II, Chandigarh. Then each samples having dimensions (15 mm × 10 mm × 2 mm) were prepared from the sheet of size 1500 mm × 3500 mm and of thickness 2 mm with the help of a mechanical press. Then cloth wheel polishing m/c were used for surface finishing of samples. The samples were then grit blasted prior to coating using grit blasting equipment. After polishing the samples were air blasted to free from residual grit.

The feedstock powders used for the development of coatings are:

- **Hydroxyapatite (HAp) powder** of 30 μm average particle size was obtained from Captal 30, Plasma Biotal Ltd, UK.

- **Titania (TiO₂) powder** of 35 μm mean particle size was obtained from Amperit 782.0, H C Starck GmbH & Co. KG, Goslar, Germany. The feedstock TiO₂ powder was agglomerated & sintered and exhibited a nominal particle size distribution from 20 μm to 50 μm according to the powder manufacturer.

- **Zirconia (ZrO₂) powder** of 35 μm average particle was obtained from Metallizing Equipment Company Private Ltd, Jodhpur, India.

### Table 1. Parameters of Flame spray for HAp, TiO₂ and HAp/TiO₂ coatings.

| Parameters       | C₂H₂ flow rate | O₂ flow rate | Feed rate of powder | S O D | Particles velocity | Pressure of air |
|------------------|----------------|--------------|---------------------|-------|--------------------|-----------------|
| Value            | 73 L min⁻¹     | 44 L min⁻¹   | 25 g min⁻¹          | 10 cm | ≈300 m s⁻¹          | 4.5 kgf cm⁻²    |

2.2. Development of coatings

The deposition of flame sprayed HAp and TiO₂ coating on 316L SS samples were done at Metallizing Equipment Company Private Ltd, Jodhpur, India. The parameters employed during deposition of HAp, TiO₂ and HAp/TiO₂ bond coatings is depicted in table 1.

Zirconia (ZrO₂) powder was coated on air blasted 316L SS samples with plasma spray system using Praxair SG-100 torch fixed on the 5-axis ABB IRB-6 industrial robot at MECPL. Argon was applied as primary gas and hydrogen was applied as secondary gas. The spraying parameters have been represented in table 2.

2.3. Coatings characterization

The phase composition and surface morphology of the as-sprayed coatings was analyzed by an XRD, SEM and EDS machine at IIT Ropar. However, the EDS point analysis was done to determine the Ca/P ratios of the HAp coatings.

2.4. Electrochemical corrosion investigations

To examine the electrochemical corrosion performance of the coated and bare 316L SS samples, potentiodynamic polarization tests were performed using a Potentiostat –Galvanostat, linked with a mini computer and weighted with Gamry electrochemical software. The electrolytes used in electrochemical set-up for simulating human body fluid environment was Ringer’s sol⁶ and Hank’s balanced salt solution. The chemical contents of Ringer’s solution in terms of weight (mg/l) were: Sodium Chloride: 8900, Calcium Chloride: 240, Potassium Chloride: 430 and Sodium Bicarbonate: 200. However, the chemical contents for Hank’s balanced salt solution in terms of weight (mg/l) were: NaCl: 8000, CaCl₂ · 2H₂O: 19000, Na₂HPO₃: 50, MgSO₄: 100, KH₂PO₄: 60 and KCl: 400, NaHCO₃: 350 and D-Glucose: 1000.

Before performing the corrosion investigations, all the samples (having 1 cm² exposed area) were immersed in the sol⁶, for one day for stabilization at 37 ± 1 °C. The heating mantle was used to keep the temperature during test. During test the substrate material worked as electrode and each potential were determined w.r.t. saturated calomel electrode known as reference electrode. However, a graphite rod worked as the counter electrode. Each tests were analysed at a scan rate of 1 mV s⁻¹. and fresh sol⁶ was applied during each test. The Tafel plots having potential from –250 mV to +250 mV relative to open circuit potential was utilized to calculate the corrosion rate. The experiments were performed on aforementioned samples until three similar results were not obtained. Further, the exposed samples were studied using SEM analysis.
Table 2. Parameters for ZrO₂ coatings using plasma spray.

| Parameters          | Argon gas pressure | H₂ gas pressure | Ar gas flow | Hydrogen gas flow | Torch velocity | Electric current | Arc voltage | Carrier gas pressure | Carrier gas flow | Feed rate of powder | S.O.D. |
|---------------------|--------------------|-----------------|-------------|-------------------|----------------|------------------|-------------|---------------------|------------------|-------------------|--------|
| Value               | 100 psi            | 50 psi          | 70 slpm     | 10 slpm           | 400 mm s⁻¹     | 600 A            | 40 V        | 50 psi              | 40 slpm          | 25 g min⁻¹       | 10 cm  |
3. Results and discussion

In this chapter, the results of the phase composition and the surface morphology of the as-sprayed specimens have been summarized. The electrochemical characteristics and micro-structural phases of the coatings were studied.

3.1. XRD study of As-sprayed coatings

3.1.1. XRD analysis of HAp coating

The XRD pattern of the HAp coated 316L SS samples using flame-sprayed has been demonstrated in figure 1. The tetracalcium phosphate \([Ca_4(PO_4)_2O]\), TTCP has been shown by symbol (T) and b-tricalcium phosphate \([Ca_3(PO_4)_2]\), \(\beta\)-TCP has been shown by (\(\beta\)) and HAp by unmarked peaks. The peak broadening and low intensity of peaks in x-ray diffraction pattern symbolized the existence of amorphous phases. The existence of an amorphous background hump from 29° 2\(\theta\) to 32° 2\(\theta\) also represent the existence of an amorphous Ca-P phase in the aforementioned coating. The phase composition of the HAp coating revealed the existence of HAp, with small peaks for tetracalcium phosphate \([Ca_4(PO_4)_2O]\), TTCP and b-tricalcium phosphate \([Ca_3(PO_4)_2]\), \(\beta\)-TCP phases.

3.1.2. XRD analysis of TiO2 coating

The XRD profile of the flame-sprayed TiO2 coated 316L SS substrate has been shown in figure 2. Figure 2 indicates the presence of rutile (R) as a major phase and anatase (A) and Ti3O5 (X) as a minor phase [27]. The deoxidization of TiO2 is owing to the cooling rate of the semi molten or fully molten droplets. Since, rutile phase is a stable/balanced phase whereas the anatase phase is a meta-stable phase and it changes to rutile at 1100 K [28].

3.1.3. XRD analysis of HAp/TiO2 bond coating

Figure 3 indicates the XRD profile of HAp/TiO2 bond coating on 316L SS sample using flame spray. Here, tetracalcium phosphate \([Ca_4(PO_4)_2O]\), TTCP is indicated (T) and b-tricalcium phosphate \([Ca_3(PO_4)_2]\), \(\beta\)-TCP is indicated by (\(\beta\)) and HAp by unmarked peaks.

3.1.4. XRD analysis of ZrO2 coating

The XRD profile of the plasma-sprayed ZrO2 coated 316L SS substrate has been depicted in figure 4. The as-sprayed coating was mainly consist of the tetragonal (t-ZrO2) phase and minor amount of cubic (c-ZrO2) phase [29]. It was noted that there was absence of monoclinic (m-ZrO2) during the phase transformation in the plasma spraying process. The XRD analysis of the as-sprayed coating indicated that the tetragonal and cubic phases are retained during the coating deposition.
Figure 2. XRD profile of TiO$_2$ coated 316L SS using flame-spray.

Figure 3. XRD profile of HAp/TiO$_2$ bond coated 316L SS using flame-spray.

Figure 4. XRD profile of ZrO$_2$ coated 316L SS using flame-spray.
3.2. SEM/EDS examination of As-sprayed coatings

3.2.1. SEM/EDS examination of HAp coating

SEM micrograph of HAp coating (in figure 5) showed that the microstructure composed of absolutely molten splats with dense appearance. In addition, some small globular particles (un-melted particles) in the matrix were also seen.

From EDS study of HAp coated samples indicates the existence of Calcium, Phosphorous and Oxygen. The Ca/P proportion of HAp coated samples before corrosion testing at point 1, 2 and 3 were 1.46, 1.64 and 1.69 respectively.

3.2.2. SEM/EDS analysis of TiO2 coating

SEM micrograph of TiO2 coating (in figure 6) indicates a splat-like structure with entirely molten splats in most of the region. It can be seen from the SEM micrograph that the TiO2 powder used in the flame spray process was mostly in melted state. However, due to the quick cooling, the meta-stable anatase phase can be slightly retained.

Figure 6 indicates that coated TiO2 coated samples indicates the existence of remarkable amounts of titanium and oxygen elements, which are the major elements of TiO2.
3.2.3. SEM/EDS analysis of HAp/TiO2 coating
In most of the area, the HAp/TiO2 bond coating indicates a splat-like structure with entirely molten splats as shown in figure 7. However, the EDS investigation of HAp/TiO2 coated surface revealed the existence of calcium, phosphorous and oxygen elements. But, no Ti was seen on the surface of HAp/TiO2 coated samples. It indicates that the bond coating of TiO2 was totally shielded with a HAp top coat.

3.2.4. SEM/EDS analysis of ZrO2 coating
SEM micrograph of ZrO2 coating (in figure 8) showed that it consists of tetragonal zirconia. During plasma spraying it was observed that the monoclinic zirconia occurring in the initial powders changed into tetragonal phase.

3.3. In-vitro corrosion study in simulated body fluids
All the test samples were assessed by distinct corrosion parameters as determined from potentiodynamic curves were immersed in Hank’s Balanced Salt and Ringer’s soln. The distinct corrosion variables were cathodic Tafel slope (βc), anodic Tafel slope (βa), corrosion current density (I_{corr}) and corrosion potential (E_{corr}). At a given potential, more is the I_{corr}, means higher prone is the material to corrode [30].

Figure 7. FE-SEM + EDS investigation of HAp/TiO2 coating.

Figure 8. FE-SEM + EDS investigation of ZrO2 coating.
3.3.1. Corrosion performance in ringer’s solution

The electrochemical corrosion performance of the coated and uncoated samples was determined in Ringer’s solution using standard procedure already given in section 2.4. The corrosion variables for uncoated and coated test samples were calculated from the potentiodynamic curves by the Tafel extrapolation technique have been given in table 3.

The comparison of \( I_{\text{Corr}} \) (\( \mu A/cm^2 \)) tafel slope value for bare and coated samples is shown in figure 9.

From figure 9, it is seen from the investigations of Tafel slope values that the corrosion current density (in \( \mu A/cm^2 \)) of the various coatings at a given potential varied in the following order:

\[
I_{\text{Corr}}(\text{uncoated}) > I_{\text{Corr}}(\text{ZrO}_2\text{coated}) > I_{\text{Corr}}(\text{HApcoated}) > I_{\text{Corr}}(\text{TiO}_2\text{coated})
\]

Since we know the material with the highest corrosion current density will corrode first [30]. Therefore, HAp/TiO\(_2\) bond coated specimen has the least corrosion rate in Ringer’s solution. Based upon the above corrosion resistant behavior of different coatings for in-vitro electrochemical testing in Ringer’s solution can be predicted as follows:

\[
(\text{HAp/TiO}_2\text{coated}) > (\text{TiO}_2\text{coated}) > (\text{HAp coated}) > (\text{ZrO}_2\text{coated}) > (\text{Uncoated})
\]

3.3.2. Corrosion performance in Hank’s stabilized salt soln

Similarly, electrochemical corrosion performance of the coated and uncoated samples was determined in Hank’s stabilized solution using standard procedure already given in section 2.4. The corrosion variables for test samples were calculated from the potentiodynamic curves by the Tafel extrapolation technique have been given in table 4.

The comparison of \( I_{\text{Corr}} \) (\( \mu A/cm^2 \)) tafel slope value for bare and coated samples is shown in figure 10.

It can be seen from the analysis of Tafel slope values that the \( I_{\text{Corr}} \) (in \( \mu A/cm^2 \)) of the various coatings (figure 10) at a given potential varied in the following order:

\[
I_{\text{Corr}}(\text{uncoated}) > I_{\text{Corr}}(\text{ZrO}_2\text{coated}) > I_{\text{Corr}}(\text{HApcoated}) > I_{\text{Corr}}(\text{TiO}_2\text{coated})
\]

Since the material with the highest corrosion current density will corrode first [30]. Therefore, HAp/TiO\(_2\) bond coated specimen has the least corrosion rate in Hank’s balanced salt solution. Based upon the above
results, the corrosion resistant behavior of different coatings for in-vitro electrochemical testing in HBSS can be predicted as follows:

\[
(H\text{Ap/TiO}_2\text{coated}) > (TiO_2\text{coated}) > (H\text{Ap coated})
\]

\[
> (ZrO_2\text{coated}) > (Uncoated)
\]

3.4. SEM/EDS analysis of coatings after electrochemical testing

The exposed samples were then analyzed by SEM with EDS techniques for the micro-structural investigation of their surfaces and to detect compositional changes, if any, after the electrochemical testing in Ringer’s and Hank’s balanced salt solution. A complete study of the SEM images of the exposed specimens was carried out to draw various conclusions.

3.4.1. SEM/EDS analysis in Ringer’s soln

The microstructure of the exposed (corroded) uncoated specimen after the electrochemical testing in Ringer’s solution was composed of large pits of irregular size as represented in figure 11.

There were some dark regions seen in the microstructure of the exposed uncoated specimen. Cracks were also found on the surface of the specimen after the corrosion testing. The micrograph of the exposed uncoated specimen showed that the surface was corroded completely and the pitting corrosion had taken place after its immersion in the Ringer’s soln.

SEM micrographs of the exposed HAp coating (as shown in figure 12) after its immersion in the Ringer’s soln, indicates flattened splats (spherical-shaped particles) and keep their structure even after subjected to corrosion testing. In addition, no cracks were observed on the top surface of the coated samples after immersion in Ringer’s soln. However, some micro pores were observed in their microstructure.

The morphology of the corroded TiO_2 coating has been depicted in figure 13. The SEM micrograph of the exposed TiO_2 coating after its immersion in the Ringer’s solution indicated irregular splat-like morphology. No cracks were noticed on the surface of the TiO_2 coated specimen. Some voids in-between the splats were observed on the coating.

The morphology of the corroded HAp/TiO_2 bond coating has been depicted in figure 14. SEM micrograph of exposed HAp/TiO_2 bond coating exhibited that it has maintained its structure even the corrosion testing. No titanium was detected on the surface of HAp/TiO_2 bond coated 316L SS samples. From the analysis, it appeared that HAp/TiO_2 coating was better adhered than HAp coating to the 316L SS substrate.
after subjected to the corrosion testing. The HAp/TiO$_2$ bond coating was homogenous and dense in nature. TiO$_2$ bond layer showed good adhesion to the substrate material and top HAp coating even after immersion in Ringer’s soln. The interface of the coating–substrate was appeared to be defect free.

SEM micrograph of the ZrO$_2$ exposed coating after its immersion in the Ringer’s solution has been shown in figure 15. As it was clear from the micrograph, the coating was composed of splats having irregular morphology.
Some pits can be observed on the surface of exposed ZrO$_2$ coated 316L SS sample. No visible cracks were found on the surface of the ZrO$_2$ coated specimen.

### 3.4.2. SEM/EDS analysis in Hank’s balanced/stabilized salt soln

The microstructure of the corroded uncoated specimen after the electrochemical testing in HBSS has been represented in figure 16.

Similar to the specimen exposed to corrosion in Ringer’s solution, large cracks were also seen on the surface of the specimen in HBSS. The surface of the coating was mostly distorted after the its immersion in the solution.

The microstructure of the corroded HAp coated after the corrosion testing HBSS has been depicted in figure 17.

The microstructure was composed of minute spherical-shaped particles dispersed in the matrix. Some unmelted splats (dark regions) can also be observed even after subjected to the corrosion testing. No cracks were seen on the surface of the coating.

The corroded TiO$_2$ coating after subjected to the corrosion testing in HBSS showed (in figure 18) a crack free microstructure. Some splats can be seen irregularly dispersed on the surface of the coating. Some pits represented by dark regions are observed in the microstructure of the corroded TiO$_2$ specimen.

The SEM image of the exposed HAp/TiO$_2$ bond coating in HBSS has been depicted in figure 19.

The major portion of the coating was composed of micro-sized spherical particles separated by unmelted (dark) zones. No titanium was detected on the top surface of HAp/TiO$_2$ bond coated 316L SS samples. Results indicates that HAp/TiO$_2$ coating was better adhered than HAp coating to the 316L SS samples after subjected to the corrosion testing in HBSS.
The ZrO\(_2\) coating after subjected to the corrosion testing in HBSS showed (in figure 20) irregular sized splats throughout the exposed surface. The formation of minor cracks can be observed in the microstructure of the coating. Some small pits have been observed on the surface of the coated 316L SS specimen.

Figure 16. SEM image of bare sample after corrosion test in HBSS.

Figure 17. SEM image of HAp coating after corrosion testing in HBSS.

Figure 18. SEM image of TiO\(_2\) coating after corrosion test in HBSS.
3.5. Discussion
All the aforementioned coating were deposited on 316L stainless steel by flame-spray and plasma spray techniques. Further, all the coated samples were examined using SEM + EDS and XRD analysis.

For the as-sprayed HAp coatings, tetracalcium phosphate [(Ca₄(PO₄)₂)O], TTCP and b-tricalcium phosphate [Ca₃(PO₄)₂], β-TCP phases were observed. From the XRD analysis of as-sprayed TiO₂ coatings, rutile (R) and anatase (A) phases were the main phases noted. For the as-sprayed HAp/TiO₂ bond coatings, tetracalcium phosphate [(Ca₄(PO₄)₂)O], TTCP and b-tricalcium phosphate [Ca₃(PO₄)₂], β-TCP phases were observed. In the as-sprayed ZrO₂ coatings, tetragonal (t-ZrO₂) and cubic (c-ZrO₂) phases were recorded by the XRD analysis.

The SEM analysis of the as-sprayed coatings represented typical splat like microstructure for all the coatings. All the aforementioned coatings were found to be crack free and adherent. The existence of Ca, P and O elements in the as-sprayed HAp coatings and HAp/TiO₂ bond coatings were observed. Also there was the presence of Ti and O elements in the as-sprayed TiO₂ coatings and the presence of Zr and O elements in the ZrO₂ coatings as depicted from the EDS analysis.

The electrochemical corrosion studies of the bare and coated 316L SS samples were conducted using potentiodynamic polarization investigation. All the uncoated and coated steels were tested in two simulated body fluids (Ringer’s and Hank’s balanced salt solution). All 316L SS coated samples exhibited an improvement in the corrosion resistance after applying HAp, TiO₂ coatings and HAp/TiO₂ bond coatings in simulated human body fluid environment using flame-spray. Also plasma-sprayed ZrO₂ coatings exhibited enhanced corrosion resistance.
After corrosion investigation in Ringer’s solution, the following trend of corrosion rate was observed:

\[ \text{Corr (uncoated)} > \text{Corr (ZrO}_2\text{coated)} > \text{Corr (HAp coated)} \]
\[ > \text{Corr (TiO}_2\text{coated)} > \text{Corr (HAp/TiO}_2\text{coated)} \]

and for Hank’s balanced salt solution, following trend of corrosion rate was followed:

\[ \text{Corr (uncoated)} > \text{Corr (ZrO}_2\text{coated)} > \text{Corr (HAp coated)} \]
\[ > \text{Corr (TiO}_2\text{coated)} > \text{Corr (HAp/TiO}_2\text{coated)} \]

Hence, the performance evaluation study suggested that the HAp/TiO\(_2\) bond coating was the best amongst all the bare and coated 316L SS samples. The trend of the corrosion resistance observed for different specimens was as below:

\[ (\text{HAp/TiO}_2\text{coated)} > (\text{TiO}_2\text{coated)} > (\text{HAp coated)} > (\text{ZrO}_2\text{coated)} > (\text{Uncoated)} \]

4. Conclusions

1. The flame-sprayed HAp, TiO\(_2\) coating and HAp/TiO\(_2\) bond coatings were successfully deposited on 316L SS and ZrO\(_2\) coating was deposited by plasma spray process.
2. The existence of P, Ca and O elements in the as-sprayed HAp and HAp/TiO\(_2\) coating was revealed by the XRD investigation. Also there was the existence of titanium and oxygen elements in the as-sprayed TiO\(_2\) coating whereas Zr and O elements were observed for the ZrO\(_2\) coatings from the XRD analysis.
3. SEM analysis indicated the formation of splats in the flame-sprayed and plasma-sprayed coatings.
4. The EDS analysis further confirmed the presence of elements in the as-sprayed coatings as observed from the XRD analysis.
5. The electrochemical investigation exhibited an enhancement in the corrosion resistance of the 316L stainless steel samples after the deposition of flame-sprayed HAp, TiO\(_2\) coatings, HAp/TiO\(_2\) bond coatings and plasma-sprayed ZrO\(_2\) in simulated human body fluid environment.
6. Amongst all the coated and bare steels studied in Ringer’s solution, HAp/TiO\(_2\) bond coatings showed best corrosion resistance to the in-vitro electrochemical testing.
7. For the uncoated and coated specimens studied in HBBS, HAp/TiO\(_2\) bond coatings showed best corrosion resistance to the in-vitro electrochemical testing.
8. The uncoated specimens showed the development of cracks on the surface whereas no cracks were found on the surfaces of all the coated steels.

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ORCID iDs

Santosh Kumar @ https://orcid.org/0000-0003-4414-3305
Rakesh Kumar @ https://orcid.org/0000-0002-7806-6208

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