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Comparative Study of Enhancement of Corrosion Resistance of Stainless Steel Alloy by Plasma Spray Technique and Biomimetic Deposition

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In this study, hydroxyapatite (HAP) coating was deposited on substrate of stainless steel alloy by biomimetic deposition and plasma spray technique. The corrosion resistance of plasma sprayed and biomimetic coating was compared with the help of electrochemical corrosion testing with respect to uncoated samples. The surface morphologies of the coatings were studied through scanning electron microscopy and energy-dispersive X-ray spectroscopy techniques. Analysis of the microstructure/composition and phase formation has also been done before and after corrosion testing respectively. The deposition of hydroxyapatite using both the techniques, *i.e.* plasma spray technique and biomimetic deposition lead to enhancement in corrosion resistance. From electrochemical corrosion testing, it was confirmed that biomimetic coated hydroxyapatite samples are more corrosion resistant in comparison to as-sprayed plasma spray coated samples and hence found to be better technique as compared to plasma spray technique.

Keywords: Corrosion resistance, Stainless steel, Plasma spray, Biomimetic deposition.

INTRODUCTION

The degradation of AISI 316L stainless steel in body fluids results in the formation of toxic substances [1]. The rate of agitation and destruction due to these toxic substances depends on the concentration of corrosion products formed during incubation period. Mudali *et al.* [2] in their study observed that the stainless steel implants gets corroded due to pitting and crevice corrosion that caused the permanent damage of these implants. The primary cause for exhaustion of stainless steel implants is corrosion forces [3]. The development of surface treatments for the enhancement of corrosion resistance property on stainless steel alloy is an important part of study in medical field. The aim of these coatings is the protection of metal surface by rigid attachment on their surface by any bioactive material, which is also compatible with human bone. Coated material must be helpful in growth of bone without producing any toxic substances. The surface modification is addition of bioactive material by varying thickness apparently on the surface of material. Hydroxyapatite (HAP) coatings have been applied on metallic surfaces as a physiologically active material by applying different coating techniques. This comprises plasma sprayed hydroxyapatite coating and physio-chemical process *i.e.* biomimetic, carried out under ordinary physiological conditions as the coating procedures [4].

The most commonly used technique for depositing hydroxyapatite coatings on bioimplants is plasma spraying, which has been effectively used for various years. The spraying process involves injecting hydroxyapatite powder into a plasma flame at high temperature. Due to this elevated heating requirement, it is a diverse and costlier process than any other procedure; it also results in the alteration of hydroxyapatite phases. Owing to these hydroxyapatite alterations, fixed implants gets loosen, hence collapse of the implant occurs. As a result, new surface coatings have been discovered and developed to get better implantation such as biomimetic [5].

These biomimetic obtained hydroxyapatite layers are thick and stable, which are not possible to achieve with plasma techniques. The ongoing improvement of biomimetic technique is due to its capacity to deposit hydroxyapatite coatings on all type of surfaces having different forms and arrangements [6]. Abe *et al*. [7] examined that hydroxyapatite layer could be obtained on dissimilar substances like glass, ceramics, metals and natural polymers. The thickness of this layer can be varied by varying the immersion time. Therefore, the type of coatings on the metallic surface affects both the compatibility and the encouraging performance of the implant in human body [8].

In the present study, surface coating of hydroxyapatite has been done on the surface of stainless steel by these two methods *i.e.* plasma spray method and biomimetic method and corrosion resistance property of hydroxyapatite coated stainless steel alloy is compared with the help of electrochemical corrosion testing. Biomimetic obtained coatings were found to be more corrosion resistant than that of plasma spray technique. But the biomimetic process required more time for coating hydroxyapatite as compared to plasma spray technique.

EXPERIMENTAL

The chemical composition of stainless steel alloy used as the substrate in this study has been shown in Table-1.

TABLE-1
CHEMICAL COMPOSITION OF STAINLESS STEEL ALLOY

Elements	Wt (%)	Elements	Wt (%)
C	0.024	Mn	1.156
Cr	16.850	P	0.032
Ni	10.735	S	0.017
Mo	2.269	Fe	68.449
Si	0.468	–	–

Coating development

Substrate preparation: Stainless steel specimens, each measuring 20 mm × 15 mm × 2 mm were prepared. For plasma spray technique, the samples were refined by silicon carbide papers down to 180 grit. The samples were then grit blasted using grit blasting equipment. Al_2O_3 grits of 16 mesh sizes were employed in the abrasive grit blasting process at a pressure of 2-5.5 Kg/cm^2. The specimens were subsequently air blasted to eliminate the remaining grit.

For biomimetic technique this alloy of size 20 mm × 15 mm × 2 mm was used which was roughened mechanically using emery paper, followed by refining with silicon carbide of different grade papers (200-1000 grit). Then samples were cleaned in acetone, ethanol and distilled water and then dried in air. These substrates were kept in 5 % concentrated HNO_3 solution for 0.5 h. After dipping in acid, the substrates were washed with distilled water and acetone. Then, samples were dried at 40 °C for 1 h.

Feedstock powder

Plasma spray technique: The hydroxyapatite powder of particle size were (Medipure hydroxyapatite -150/+45 microns) applied in this study. The polished steel samples were coated among pure hydroxyapatite coating using a plasma spray process (pressure blasting model: MEC 9182) at Metalizing Equipment Company Private Limited (MECPL), Jodhpur, India. The plasma spraying parameters used for pure hydroxyapatite coating has been shown in Table-2.

TABLE-2
PLASMA SPRAYING PARAMETERS USED FOR PURE HYDROXYAPATITE COATING

Coating parameters	Units
Voltage	63.5 (volts)
Power	31.6 (kW)
Argon gas flow	38.5 (L/min)
Hydrogen gas flow	5.2 (L /min)
Carrier gas flow N_2	4.7 (L /min)
Working distance	5-6 (inch)

Biomimetic coating technique: In this technique, after acid etching, the samples were treated with alkaline treatment by using 5 M sodium hydroxide at 80 °C for 72 h in an electric oven followed by heat treatment at 600 °C as this was appropriate temperature to deposit the biological apatite [9-11]. After heating for 1 h in muffle furnace the specimens were then cooled to room temperature. By this process surface of substrates could be activated with hydroxyl groups from alkaline solutions.

The biomimetic coating process was performed in the simulated body fluid (SBF) solution having similar composition; pH and temperature are similar to that of human blood plasma. It was prepared by dissolving appropriate quantities of reagent grade NaCl, $NaHCO_3$, KCl, Na_2HPO_3, $MgSO_4$ $CaCl_2.2H_2O$, KH_2PO_4 and D-glucose into distilled water and then buffer solution was used to maintain pH of the solution at 7.4 at 37 °C. The solution (SBF) having ion concentrations (Table-3) was prepared from reagent-grade NaCl, KCl, $CaCl_2{\cdot}2H_2O$, Na_2HPO_3, $MgSO_4$, KH_2PO_4, $NaHCO_3$ and D-glucose into distilled water [12]. Buffer solution was used to maintain pH of the solution at 7.4 having temperature 37 °C. The deposition of coating of samples of stainless steel alloy was done by immersing in SBF solutions for four weeks at 37 °C. A thick layer of apatite was formed on its surface [9]. After drying, the samples were kept in desiccator to avoid absorption of moisture.

TABLE-3
INORGANIC COMPOSITION OF HANK'S BALANCED SALT SOLUTION (HBSS) AS SIMULATED BODY FLUID (g/L) [Ref. 12]

Component	Simulated body fluid (g/L)
NaCl	8.00
KCl	0.40
$CaCl_2{\cdot}2H_2O$	0.19
Na_2HPO_3	0.05
$MgSO_4$	0.10
KH_2PO_4	0.06
$NaHCO_3$	0.35
D- Glucose	1.00
Buffer solution	pH = 7.5

Electrochemical corrosion testing: To determine the electrochemical decay of the uncovered, plasma sprayed and biomimetic layered surfaces of steel alloy, potentiodynamic polarization tests were performed by using a Potentiostat/ Galvanostat (Series G-750; Gamry Instruments, Inc. USA), attached with a computer and assembled with Gamry electrochemical software DC105. The electrolyte used for replicate the human body fluid conditions was Ringer's solution having chemical ratio in g/L (Table-4) as 9 NaCl, 0.24 $CaCl_2$, 0.43 KCl

TABLE-4
CHEMICAL COMPOSITION OF RINGER'S SOLUTION (g/L)

Component	Strength (g/L)
NaCl	9.00
$CaCl_2$	0.24
KCl	0.43
$NaHCO_3$	0.20

and 0.2 $NaHCO_3$ at pH 7.2. The entire samples were dipped in Ringer's solution for 24 h prior to perform the corrosion studies.

By keeping the temperature of Ringer's solution at 37 ± 1 °C, *i.e.* normal temperature of the human body which was maintained by using a heating coil. The depicted area of the samples in this solution was 1 cm^2. The substrate acts as a working electrode. All readings were determined with respect to a saturated calomel electrode (SCE) as the reference electrode. A graphite rod acts as a counter electrode. All the tests were carried out at a scan rate of 1 mV/s and new solution was used for each test. The corrosion rate was concluded using the tafel plots widely from -250 mV to +250 mV potential relative to open circuit potential. Before and subsequent to corrosion testing, substrates were further characterized by SEM/EDS techniques to analyse the microstructure/composition and phase formation respectively.

RESULTS AND DISCUSSION

SEM/EDS analysis: The coating of hydroxyapatite was successfully done by plasma spray technique on stainless steel alloy as shown in Fig. 1. The SEM microstructure of biomimetic coated stainless steel has been shown in Fig. 2. In the plasma spray process, coating surfaces have a characteristic surface morphology including thick and compress splats. Whereas in biomimetic coating the crystals developed round smaller particles gradually (Fig. 2), with extended dipping time, the spherical units build up continuously and no appreciable differences in morphology were observed [13]. The EDS spot analysis of pure hydroxyapatite coated specimens confirmed the significant occurrence of calcium, phosphorous and oxygen atoms; these are the major constituents of hydroxyapatite. The elemental ratio of these elements is shown with their atomic proportion in Fig. 1.

The EDS study (Fig. 2) of the biomimetic hydroxyapatite covering on alloy at different points indicates the presence of hydroxyapatite elements present in the coatings as well as their relative atomic % values. The identification of elements is useful to know the concerning Ca/P ratio in the coatings. The immersion of the substrate in NaOH solution followed by heating at 600 °C for 1 h augmented the vigorous hydroxyl sites on the surface of stainless steel. This leads to the formation of hydroxyapatite on its surface.

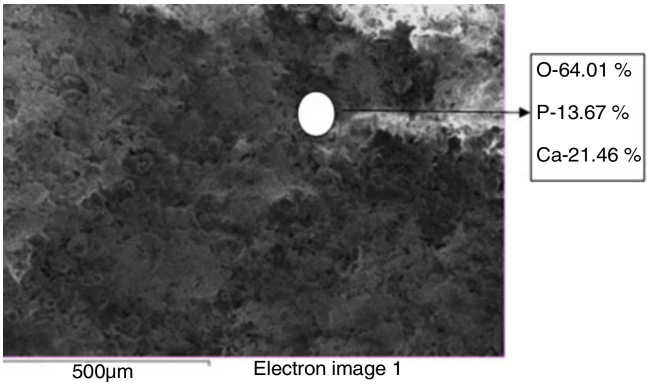

Fig. 1. SEM analysis along with EDS point analysis showing the elemental composition of plasma sprayed pure hydroxyapatite coating on stainless steel alloy

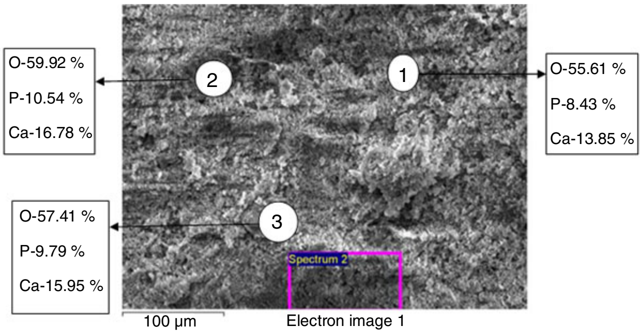

Fig. 2. SEM analysis along with EDS point analysis showing the elemental composition of biomimetic hydroxyapatite coated stainless steel alloy

Electrochemical polarization behaviour: The electrochemical corrosion behaviour of the uncoated, plasma spray coated hydroxyapatite and biomimetic coated hydroxyapatite on stainless steel alloy was determined by using the process discussed as above. The potentio-dynamic curves of all the samples after placing in Ringer's solution (SBF) for 24 h at 37 ± 1 °C temperature (body temperature) were obtained and are shown in Figs. 3-5. The results of Tafel slope values (Table-5), shows the corrosion current density of uncoated alloy specimen in Ringer's solution ($I_{corr} = 1.696e^{-6}$ A cm^{-2}, $E_{corr} = -365e^{-6}$ mV). The corrosion rate (C_R) of uncoated stainless steel specimens is 764.9 mpy which is higher than both of the plasma spray and biomimetic coated specimens. The polarization curve, for the uncoated alloy specimen got shifted towards the right in comparison to the other specimen. The shift of polarization curves of plasma spray hydroxyapatite coated and biomimetic coated alloy to lower I_{corr} values shows a lower tendency towards corrosion in comparison with the uncoated specimen. The lower the corrosion current density (I_{corr}) at a given potential, more is the corrosion resistance property. The results of Tafel slope values show that the corrosion current

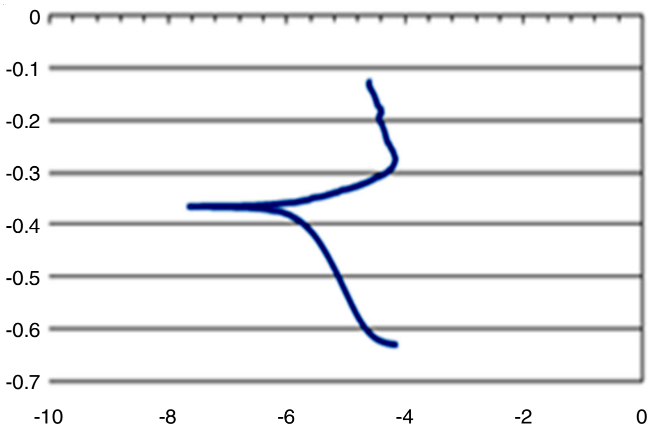

Fig. 3. Potentio-dynamic curves (current *vs.* voltage) of uncoated sample of stainless steel

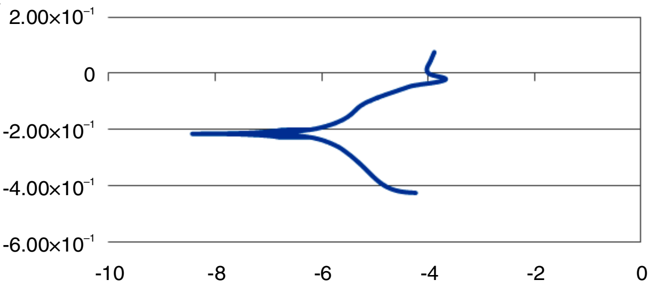

Fig. 4. Potentio-dynamic curves (current *vs*. voltage) of plasma spray coated hydroxyapatite sample of stainless steel

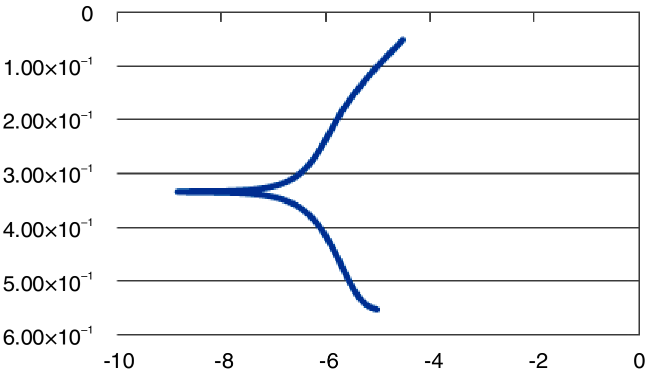

Fig. 5. Potentio-dynamic curves (current *vs*. voltage) of biomimetic obtained coated sample of stainless steel

TABLE-5
CORROSION PARAMETERS OF UNCOATED, PLASMA SPRAY HYDROXYAPATITE COATED AND BIOMIMETIC HYDROXYAPATITE COATED STAINLESS STEEL SAMPLES IN RINGER SOLUTION AT 37 ± 1 °C TEMPERATURE

Samples	Parameters		
	E_{corr} e^{-6} (mV)	I_{corr} e^{-6} (Acm^{-2})	C_R e^{-3} (mpy)
Uncoated stainless steel	-365	1.696	764.9
Plasma spray HAP coated sample	-215	1.289	581.9
Biomimetic coated HAP sample	-334	0.408	184

density (I_{corr}) of plasma spray hydroxyapatite coated and biomimetic hydroxyapatite coated alloy specimen in SBF solution is 1.289e^{-6} A cm^{-2} and 0.408e^{-6} A cm^{-2} respectively. Corrosion rate (C_R) of uncoated, plasma spray coated and biomimetic coated specimens is 764.9 mpy, 581.9 mpy and 184 mpy respectively. All the coatings have shown better corrosion resistance in comparison to their uncoated counterparts. The biomimetic coated hydroxyapatite sample of stainless steel alloy has shown lower corrosion rate (C_R) than plasma spray coated hydroxyapatite.

SEM/EDS analysis after corrosion testing: The SEM micrograph for the uncoated stainless steel alloy after corrosion testing has been shown in Fig. 6. In uncoated sample, there is formation of uniform oxide layer over the surface which covers the whole surface.

The SEM/EDS analysis has shown elemental composition of plasma spray hydroxyapatite coated alloy as depicted in Fig. 7. The SEM analysis indicates the microstructure of oxide layer (presence of oxygen as shown in EDS ratio) on the surface of alloy due to corrosive environment and the surface seems to be non-uniform. The EDS point analysis of plasma spray hydroxyapatite coated alloy after corrosion testing at different points indicates the presence of various elements present in the coatings as well as SBF solution. EDS verify the presence of calcium, oxygen and phosphorus elements with their atomic percentage in the coated sample of alloy.

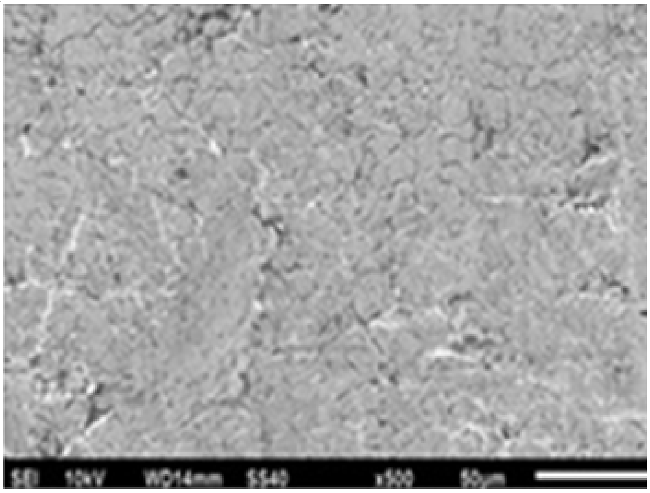

Fig. 6. SEM analysis showing microstructure of uncoated stainless steel alloy after electrochemical corrosion testing

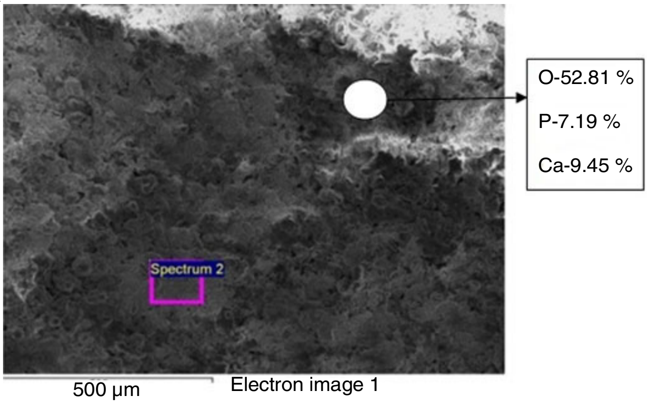

Fig. 7. SEM/EDS analysis showing the microstructure of plasma spray hydroxyapatite coated Stainless steel alloy after electrochemical corrosion testing

The SEM/EDS analysis of hydroxyapatite coated stainless steel alloy by biomimetic technique has been shown in Fig. 8. The SEM analysis indicates the microstructure of oxide layer on the surface of alloy due to corroding environment and the surface seems to be non-uniform. The EDS point analysis of the biomimetic coated hydroxyapatite coatings after corrosion testing at different points indicates the presence of various elements present in the coatings as well as SBF solution. EDS verify the presence of carbon, calcium, oxygen, sodium, phosphorus and titanium elements with their atomic %age in the hydroxyapatite coated alloy. The Ca/P ratio has shown reduction after electrochemical corrosion testing. Surface modifications have high prospective for the enhancement of the implant performances, such as to increase the rate of osseointegration, the shielding from chemical corrosion exerted by body fluids and the reduction of bacterial linkage. Biomimetic coated hydroxyapatite alloy was more corrosion resistant than that of plasma spray coated hydroxyapatite as shown from the results in Table-5. Singh *et al*. [14] examined the natural corrosion of exposed and plasma sprayed hydroxyapatite (HAP) coated

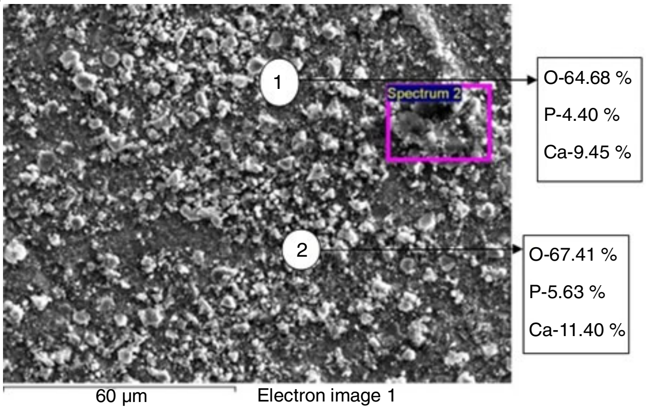

Fig. 8. SEM/EDS analysis showing the microstructure of biomimetic coated hydroxyapatite stainless steel alloy after electrochemical corrosion testing

316LSS and study of contents of calcium phosphate (Ca-P) on corrosion behaviour of hydroxyapatite (HAP) coatings in the simulated body fluid by varying ratio of hydroxyapatite. Plasma sprayed coated samples showed enhancement in corrosion resistance. In the current work there has been reduction in Ca/P ratio after dipping in Ringer's solution, but still it showed the presence of calcium phosphate compounds in different forms. Similar results were also observed after electrochemical corrosion testing by plasma spray coated hydroxyapatite (Fig. 5) which has shown the presence of black molten splats. However, the biomimetic coating technique confirmed better method by enhancing corrosion resistance properties, supported its use as a surface modifications [15]. The biomimetic coated samples have shown lesser corrosion rate than that of plasma sprayed samples and an uncoated sample, which was a encouraging aspect for biomimetic technique in clinical applications next to plasma spray technique. It can be summarized that on the basis of results obtained in this work, biomimetic coating technique provides a new approach for bioimplants coatings, although coating process takes a lot of time as compared to plasma spray technique. On other hand, plasma sprayed coating technique, is the most accepted method for the bioactive materials which can give an implant with reduced risk of contamination and improved bone implant stability [4,16].

Conclusion

- Plasma spray method produced thick and uniform hydroxyapatite coatings, which provide comparatively less corrosion resistance to stainless steel.
- Biomimetic methods generally produced compact and thin coatings which are more corrosion resistant than plasma spray. However, biomimetic technique requires more time *i.e.* 4 weeks for the deposition process.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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