To Investigate the Role of Thermal Spray Coating in Biomaterials for Combating the Rate of Corrosion In-Vitro

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***Abstract*—A bio-implant is a medical device made to replace and act as a missing biological structure These implants are broadly used in various biomedical applications such as surgical implants, including joints, total hips, knees and dentures. The aim of the present study is to evaluate in-vitro corrosion behavior of uncoated as well as thermal sprayed hydroxyapatite (HAP) coated 316LStainless steel. The economical technique for reducing the rate of corrosion and improves the bioactivity of these existing materials is considered to be Surface modification. Hydroxyapatite (HAP) coatings are used on these alloys to improve the characteristics such as biocompatibility, bone bonding ability and also reduces the toxic effect of bioimplants on living organism. The coating was characterized by electrochemical techniques and SEM/EDS. The results show that after the deposition of the HAP coating, the corrosion resistance of the steel increases. This property of enhanced corrosion resistance is used as a promising technology in biomaterial research and for many clinical applications.**

Keywords: 316L SS, HAP, in-vitro, corrosion, biocompatibility.

I. INTRODUCTION

Biomaterials are used to make devices to implant a part or a function of the body in safe, reliably economically, and physiologically acceptable manner. A huge variety of such devices and materials are used in the treatment of disease or injury including oral and dental implants.

Material of medical instrument, coating, and implant must be corrosion resistant and should tolerate the aggressiveness of biological fluids (blood, urine, lymph, gastric juice, etc.). Long-term exposure of implant material to living tissue should not exert toxic impact. No toxic effect should be observed during even short-term contact of medical instrument with living tissues. Medical instruments should not induce carcinogenesis, mutagenesis, or cytotoxicity during prolonged exposure. The metals or their alloys are not viable to be directly implanted in human body due to corrosion. Due to secretion of some metallic ions (like Fe^{+2}) in vicinity of these organs, it may lead to fibrosis, which is not suitable for body. So the base metal should be coated with materials whose composition be quite similar to that of bones and are biocompatible which may lead to the further growth and development of bones [1]. The coating material should be bioactive and bioresorable. Hydroxyapatite or Calcium phosphate are frequently used for coating. HAP is commonly used as the coating material because it shows bioactivity, bioresorbility, biocompatibility and also the ossoinduction [2].

HAP coating on metallic alloys enhances the bone bonding ability and also improves the biocompatibility and reduces the toxic effect of bioimplants on living organism. The implanted material is accepted to withstand applied physiological forces without any major change. In addition these coatings leads to biocompatibility, provides local source of calcium and phosphate ions required for bone cell to grow [3,4]. Plasma spray technique is generally used for deposition of HAP as a bioceramic but due to the inherent high temperature in the plasma, detrimental effects such as evaporation, phase altercation, residual stress, debonding etc., commonly occur in these coatings. Present study presents a novel approach to deposit HAP at a temperature below its melting point using thermal spray technique. The phase composition of the HAP deposited by the thermal process is identical to that of the powder has been been analysed by SEM/EDS. The HAP Coatings deposited using this process hold enormous potential for improving ossoinduction of bones in wide range of dental and orthopedic implants with technological basis. Hydroxyapatite ($Ca_{10}(PO4)_6(OH)_2$, has been widely used in dental and orthopedic implants, due to its structural and chemical similarity with bone minerals [5-7]. Nowadays, in order to increase the biocompatibility and to improve the performance, surface modification of implants has been carried out successfully. Biological response of the host depends on the primary interactions of biomaterials implanted at biological molecular surfaces. Therefore, the surface morphology influence the compatibility as well as the optimal performance of the implant in body [8].

II. EXPERIMENTAL SET UP

2.1 Feedstock Powder and Substrate

Metals like 316LSS, Ti-6V-4Al are most commonly used alloys as biomaterial. Due to low cost and high corrosion resistance 316LSS is mostly used .It has a very low Carbon content as compared to normal steel. The composition of 316LSS is as follows:

Table I: Chemical composition specification values in % according to ASTM A276 grade

Elements	Percentage
C	≤ 0.03
Mn	≤ 2.0
Si	≤ 1.00
P	0.045
S	≤ 0.030
Cr	16.0-18.0
Mo	2.0-3.0
Ni	10.0-14.0

2.2 Development of Coatings

The Captal 30, HAP powder (Plasma-Biotal, Tides well, UK) of 30µm average particle size was used in this study. The air blasted 316L SS specimens were then coated with the HAP powder using a flame spray system (CERAJET) at Metalizing Equipment Company Private Limited (MECPL), Jodhpur, India**.** CERAJET is a technique of MECPL, chiefly designed for ceramic coatings. In conventional flame spraying systems, the particle velocity is less than 100m/s, however the particle velocity of CERAJET is ≈300m/s and the temperature of oxyacetylene flames is ≈ 2700°C, while in case of plasma spray technique, the temperature is ≈12000^0C, so working temperature is much lower than the plasma spraying technique. The spraying parameters used in coatings are given in Table II.

Table II: Thermal spray process parameters for HAP coatings spraying parameters value.

Spraying parameter	Value
Acetylene flow rate (l/ min^1)	73
Oxygen flow rate (l/min)	44
Air pressure (kg/cm^2)	4.5
Powder feed rate (g/min)	15
Spray distance (cm)	10

2.3 Electrochemical corrosion studies

To analyze the electrochemical corrosion behavior of the uncoated and HAP coated 316LSS specimens, Potentiostat/Galvanostat (Series G-750; Gamry Instruments, Inc. USA), interfaced with a computer and loaded with Gamry electrochemical software DC105, potentiodynamic polarization tests were conducted. Ringer's solution has been used as electrolyte for simulating body fluid (SBF) with chemical composition (in g/l) as, and at pH 7.2.

Table III: Chemical composition of ringer solution

Component	Strength (in g/l)
NaCl	9
$CaCl_2$	0.24
KCl	0.43
$NaHCO_3$	0.2

Before conducting the corrosion studies, each sample was immersed in Ringer's solution (SBF)for 24 hours for stabilization at 37 ± 1˚C, as the normal temperature of the human body, maintained using a heating mantle. The exposed area of the samples in the Ringer's solution was $1cm^2$. A graphite rod served as the counter electrode and a saturated calomel electrode (SCE) as reference electrode, all the potentials were measured with respect to SCE. Fresh Ringer solution was used for each specimen and the scan rate was 1mv/s. The specimen forms the working electrode. Tafel/Elog plots sweeping potential from -250 mV to +250 mV relative to open circuit potential, all the electrochemical tests were carried out on various samples as at least three similar results were required to ensure the reproducibility of the result. Before and after corrosion testing, the specimens were further analyzed by SEM/EDS techniques to analyse the microstructure/ composition and phase formation respectively.

III. RESULTS AND DISCUSSION

3.1 Electrochemical Polarization Behavior

The electrochemical corrosion behaviour of the bare and HAP coated steel was carried out using the procedure discusses in Section 2.3. The potentio-dynamic curves of bare and flame-sprayed HAP coated 316LSS specimens in Ringer's solution (SBF) for 24 hours for stabilization at 37±1˚C temperature (body temperature) were obtained and are shown in Fig. 1 and 2, respectively.

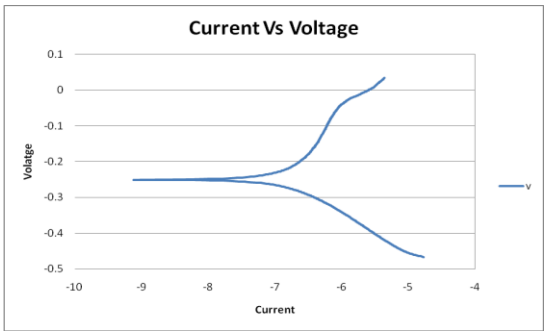

Fig.1 Potentio-dynamic curves of uncoated 316L SS specimens in Ringers solution at 37 ± 1˚C

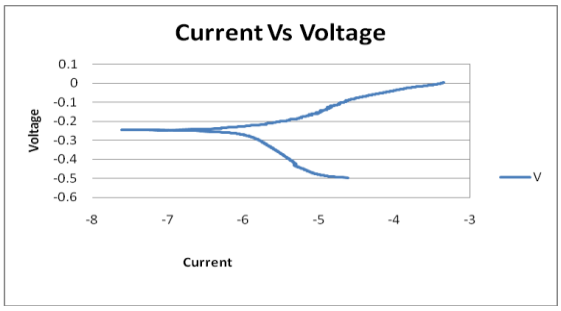

Fig.2 Potentio-dynamic curves of flame-spray HAP coated 316L SS specimens in Ringers solution at 37 ± 1˚C

Table IV: Corrosion parameters of coated and uncoated 316LSS in ringer solution at 37±1°C temperature.

Parametres	Uncoated 316 LSS	HAP coated 316 LSS
ECorr e^{-6} (mV)	-372.1	-245
ICorr (Acm-2)	3.460	1.002
CR e^{-3} (mpy)	1485	451.8

The results of Tafel slope values (Table IV), show that corrosion current density of un-coated 316LSS specimen in Ringer's solution (ICorr = 3.460Acm^{-2}, ECorr= -372.1e^{-6} mV) is higher than of the coated specimen. The polarization curve, for the un-coated 316L SS specimen got shifted towards the right in comparison to the other specimen. The shift of polarization curves of HAP coated 316L SS to lower ICorr values shows a lower tendency towards corrosion in comparison with the uncoated specimen. The higher the corrosion current density (ICorr) at a given potential, more prone is the material to corrode. HAP coatings have shown a minimum corrosion current density (ICorr = 1.002 Acm^{-2}, ECorr = -245e^{-6}mV) as compared to uncoated sample. Corrosion rate (C_R=451.8mpy) of coated sample is lower as compare to uncoated sample (C_R=1485mpy).

3.2 SEM /EDS analysis

The HAP powder was successfully deposited by Flame spray technique on 316L SS. The SEM microstructure of HAP coating on 316LSS has been shown in Fig. 3. As clear from the micrograph the coating show the presence of spherical shaped particles along with well-flattened splats. EDS analysis confirms the presence of Ca, P and O elements in the HAP coated samples. The SEM/EDS micrograph after corrosion testing has been represented in Fig. 4. A comparison of the SEM micrographs of the as-sprayed and exposed HAP coatings showed that the coating has retained its morphology even after exposure to the corrosion testing, which is a positive attribute. Ca and P have been detected as the predominant elements in the coatings.

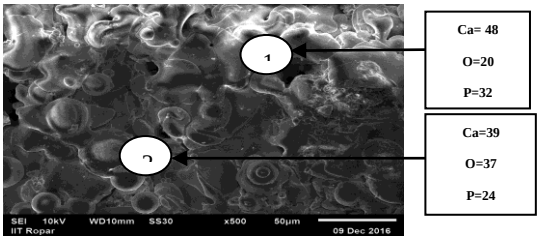

Fig.3 SEM analysis along with EDS point analysis showing the elemental composition of as-sprayed HAP coating on 316LSS.

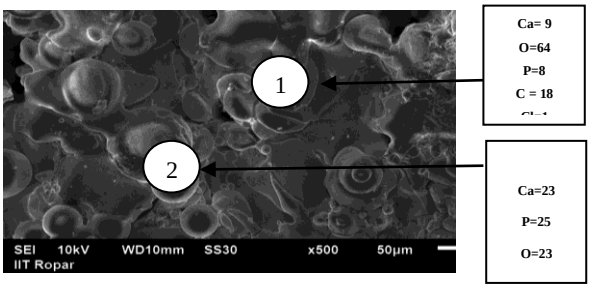

Fig.4. SEM analysis along with EDS point analysis showing the elemental composition of flame-sprayed HAP coating on 316LSS after corrosion testing.

Table V: Ca/P Ratio of flame sprayed HAP coating at selected points.

Fig no	HAP coating	Point 1	Point 2
Fig 3	Ca/P ratio	1.5	1.62
Fig 4	Ca/P ratio	1.12	0.92

The calculated Ca/P ratio from EDS spectra for the flame sprayed HAP coating before and after corrosion testing are tabulated in Table V. The observed different Ca/P ratios confirm the presence of different calcium phosphate compounds in both the HAP coating. The results indicate reduction in Ca/P ratios in the coated specimen after immersion testing. The Ca/P ratio is less in case of sample immersed in ringer solution as O is present in this case.

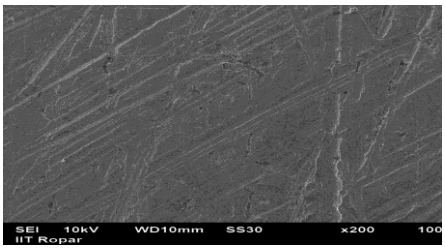

FIG 5. SEM Analysis Of Uncoated 316LSS After Corrosion Testing

In uncoated sample, there are formation of various ferrous oxides. Formation of uniform oxide layer over the surface covers whole the surface. The SEM micrograph for the uncoated 316LSS after corrosion testing has been shown in Fig. 5.

IV. CONCLUSION

In this present paper, a specially designed flame spraying equipment was used to carry out HAP coatings on 316LSS implant material. The following conclusions have been drawn from the study:

A. Using CERAJET flame spraying apparatus, HAP powder was deposited successfully on 316LSS.

B. The electrochemical study revealed an improvement in the corrosion resistance of the 316LSS by deposition of HAP by flame spray technique after immersion in simulated human body fluid.

C. EDS analysis confirmed the presence of the of Ca, P and O in the as-sprayed coating.

D. No cracks were found on the surface of HAP coated specimens even after immersion in Ringer's solution.

The supremacy of O in exposed coatings indicated the onset of oxidation which leads to corrosion. EDS mapping observations confirm that the coating was successful to retain their adherence even after corrosion testing. Future in-vivo studies of flame-spray HAP and 316LSS and further complete analysis of these results can help in assessing their use in clinical applications

V. ACKNOWLEDGMENT

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