



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis, characterization and performance of hydroxyapatite coated 316L stainless steel

Meenachi P. and Subashini R.*

Department of Biomedical Engineering, SSN College of Engineering, Kalavakkam, Tamil Nadu, Chennai 603 110, India

ABSTRACT

Hydroxyapatite, a major component and an essential ingredient of normal bone and teeth were synthesized by wet precipitation method. 316L Stainless steel (SS) are widely used for implantation in orthopedic surgery owing to corrosion resistance, mechanical property and low cost. Even though 316L SS are continuously being developed to replace implant materials used in the past, clinical studies show that these materials are also prone to corrosion to a certain extent. The localized corrosion attacks and discharge of metallic ions from implants demand improvement in the corrosion resistance of the currently used type 316L SS by modifying the surface. HAP coating was proposed to decrease the corrosion rate and improve the bioactivity of 316L SS. The surface morphology and elemental analysis of coated HAP powder on 316L SS substrate was investigated using Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-ray Spectroscopy (EDAX). From the results of X-Ray Diffraction (XRD) study, the peaks correspond to crystallographic structure of HAP in the coated surface. The presence of functional group bands of HAP coating was studied using Fourier Transform Infrared Spectroscopy (FTIR). The surface roughness, film stress and coating thickness were determined by stylus Profilometer Dektak XT. The electrochemical potentiodynamic polarization tests were performed in physiological solutions at $37\pm 1^\circ\text{C}$ to investigate the corrosion behavior of uncoated and HAP coated 316L SS. Thus, it was observed from the experimental data that the developed HAP coating on 316L SS substrate would be ideal for orthopedic applications.

Keywords: Hydroxyapatite, Stainless steel, film stress, electrophoretic deposition, surface roughness.

INTRODUCTION

Biocompatibility of metallic biomaterial is now a fundamental requirement of successful clinical behavior in orthopedic applications. Metallic biomaterials have a long history of use as implants and the type of metals used in biomedical applications depends on specific implants. The three commonly available materials used for implants are stainless steel (SS), cobalt chromium and titanium alloys. Among these medical grade 316L SS is generally used as implant material in India for orthopedic applications due to its excellent mechanical properties, ease of fabrication and low cost [1]. But it has been reported that 316L SS undergoes corrosion in vivo and causes the release of metal ions like Fe, Cr and Ni [2]. The wear and corrosion rate of metals change the chemical environment around the implant inducing the acidic pH and damage the surrounding tissues. These degradation products of corrosion result in inflammatory response locally and systematically [3]. For instance, the previous investigations reported that 90% of 316L SS implant devices failed due to localized corrosion such as pitting and crevice [4]. This revealed the importance of controlling the corrosion rate of the alloy in the human body and it can be achieved by using different surface modifications methods such as alloying, different chemical treatments, bioactive coatings etc. [5]. Among them, Hydroxyapatite (HAP) coating are well recognized because of their excellent biocompatibility and bioactivity properties.

HAP is an important material for bone and dental implants and it provides better osseointegration between bone and implants and surface protection against body fluids [6]. The potent of using HAP coating on metal implants is due to the similarity of chemical composition with hard tissues where metals provide the advantage of necessary mechanical features while HAP supplies needful biological properties [1]. Various methods of HAP coating developed to improve the wear and corrosion resistance of metallic implants. These include plasma spraying, sputtering, electrophoretic deposition [7] and sol-gel. Among all the above methods electrophoretic deposition plays a vital role due to many advantages such as: (a) possibility to deposit stoichiometric (b) ease of obtaining the desired thickness and high layer adhesion to the substrate (c) easy control on film thickness (d) excellent homogeneity (e) ability to coat complex shape (f) equipments can be assembled at low cost (g) low temperature in processing [8]. Hence, in the present study electrophoretic deposition was attempted to develop HAP coating on 316L SS.

The main objective of this paper is to obtain HAP powder by wet precipitation method and coating on 316L SS by electrophoretic deposition method. The structural and morphological properties of HAP coated substrate were characterized by XRD, FESEM with EDAX. The chemical bonding present in the coated substrate was investigated by FTIR spectrometer. The corrosion behavior was measured in Ringer solution for coated and uncoated specimen by potentiodynamic polarization technique. The surface roughness, coating thickness, film stress was determined by stylus Profilometer Dektak XT. Hence, the present work is to achieve the HAP coating on 316L SS for improving the corrosion protection properties of the coatings.

EXPERIMENTAL SECTION

Preparation method of hydroxyapatite

HAP powders were prepared using wet precipitation method. The starting materials used in the synthesis of HAP were analytical grade reagents, the calcium nitrate tetra hydrate and diammonium hydrogen phosphate. The stoichiometric HAP was prepared based on the following modified wet chemical method [9]. The electrolyte used for the deposition of HAP on 316L SS was prepared by taking 1M solution of calcium nitrate tetra hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and 0.6M solution of diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) to attain Ca/P ratio of 1.67. The pH of the above solutions was retained by ammonia (NH_4OH). After balancing the pH, solution of diammonium hydrogen phosphate was added drop-wise into calcium nitrate tetra-hydrate on to a magnetic stirring maintained at 700 rpm and left undisturbed for 2 hrs. The particle size of the formed hydroxyapatite was dependent on the stirring time, if stirring time is more, the particle size gets smaller. Then, the synthesized HAP was filtered with the help of Whatman No: 1 filter paper. The precipitate obtained was washed with ethanol to remove the suspended impurities and followed by drying in hot air oven for 1hr at 80°C. After dehydrating, the HAP was crushed into powder using pestle motor. The crushed powder of HAP was sintered at 800°C in muffle furnace for 1hr.

Electrophoretic deposition

Electrophoretic deposition is a two-step process. In the first step, particles suspended in a liquid medium are forced to migrate towards an electrode under the influence of electric field applied to the suspension. In the second step, the particles are collected at one of the electrodes and formed a relatively dense and homogeneous compact film [10]. Several organic solvents are used for electrophoretic deposition, while in the current study deposition of hydroxyapatite on 316L SS was carried out by stirring 1gm hydroxyapatite powder in 50 ml of isopropyl alcohol for 30mins [11]. The sample 316L SS acts as cathode and 314L SS as anode. Both were immersed in suspension containing beaker. Coatings were carried out at a constant voltage of 40V for 5-10 mins at room temperature. The distance between the electrodes was 1-2 cm. The coatings were obtained on cathodized substrates and sintered in vacuum furnace at 800°C for 2 hrs. Since, the substrate surface induces decomposition above 900°C the above temperature was maintained [12].

Characterization technique

The phase purity of the HAP coated substrate was determined by X-ray diffraction (XRD) analysis (Rigaku) with $\text{Cu K}\alpha$ radiation with scan step 0.02° and scan speed 3°/min from diffraction angle of 20 to 80° at 40 kV and 100mA. The functional groups of HAP coated 316L SS substrates were characterized by FTIR spectrometer (Perkin Elmer Spect Two with a wave length range from 400 – 4000 cm^{-1} with precision of 4 cm^{-1} and resolution software). The surface morphology was observed with Carl Zeiss SUPRA-55 Field emission scanning electron microscope (FESEM). The elemental composition of the HAP coated 316L SS substrate was identified using Energy Dispersive X-ray spectroscopy (EDAX). The surface roughness, coating thickness and film stress was determined by stylus Profilometer Dektak XT.

RESULTS AND DISCUSSION

High bioactivity can be achieved by performing the coating in conditions that is near to the human internal environment. Bioceramics plays a dual role both in preventing the release of metal ions and also in making the metal surface bioactive. Hydroxyapatite (bioceramic) is the most stable calcium phosphate compound under physiological conditions such as temperature, pH and composition of the body fluids. Stoichiometric HAP is stable in vacuum at temperatures below 1000°C, sintering of HAP coatings in high temperature causes diffusion of phosphorus into the substrate and as a result HAP partially decomposes to form tetra-tricalcium phosphate (TTCP) with a higher Ca/P ratio [13]. Hence in the current study, HAP coatings were obtained on cathodized substrates and sintered in a vacuum furnace at 800°C for 2 hrs. The coated surface was characterized by various characterization techniques such as FTIR, XRD and FESEM with EDAX.

Surface morphological and elemental analysis

Figure.1. Shows the FESEM (Field Emission Scanning Microscope) images for the pure HAP coated 316L SS substrate sintered at 800°C for 2 hours. The microstructure coating of HAP was strongly influenced by the applied voltage. Deposit obtained at 40V exhibited homogenous microstructure with dense packing. Sintered HAP coating were dense and well adherent to the substrate [14]. The cross section examination of FESEM analysis reveals the crystalline structure with no visible cracks; it is therefore assumed that micro cracks perceived on coating surface are limited in electrophoretic deposition method.

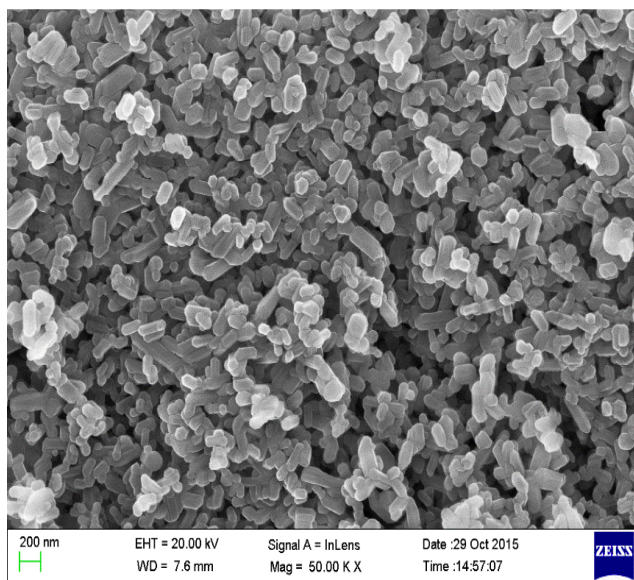


Fig.1. FESEM images of HAP coated 316L SS substrate

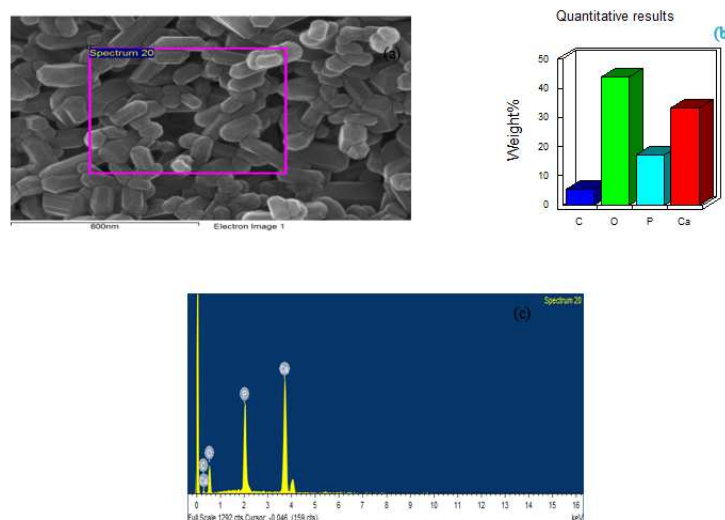


Fig.2. FESEM Image and EDAX analysis of (a, b, c) HAP coated 316L SS

Figure 2 (a, b, c), shows the quantitative EDAX (Energy Dispersive X-Ray Spectroscopy) analysis of pure HAP coated 316L SS substrate sintered at 800°C for 2 hours which confirm the presence of Ca, P, O introduced during synthesis step. Calcium and phosphorous were detected as the predominant element in the deposits. Also the weight percentage of various species is nearly equal to the weight percentages obtained in EDAX analysis. No other peaks are obtained that confirms the purity of the samples [15].

Structural analysis of coated HAP

Figure.3. Shows the XRD (X-Ray Diffraction) pattern of the pure HAP coated 316L SS substrate sintered at 800°C for 2 hours. The majority of the diffraction peaks matches with the HAP phase. The 2θ values of 26, 30, 32, 33, 34, 40, 48, 50 obtained correspond to HAP (002), (210), (211), (300), (202), (130), (222), (213) reflection plane respectively and it is in good accordance with American Society for Testing and Materials (ASTM) data (JCPDS) file (no. 9002214). The diffraction peaks particularly in the planes (002), (211) and (300) are high and narrow implying that HAP crystallizes well. In addition, preferential crystal orientation of HAP at the [002] direction is indicated by a sharp peak at 26°, as previously reported by others for HAP coatings [6]. No other characteristic peaks (calcium hydroxide and calcium phosphate) were observed, implying that single phase of HAP on coated 316L SS substrate [15, 16].

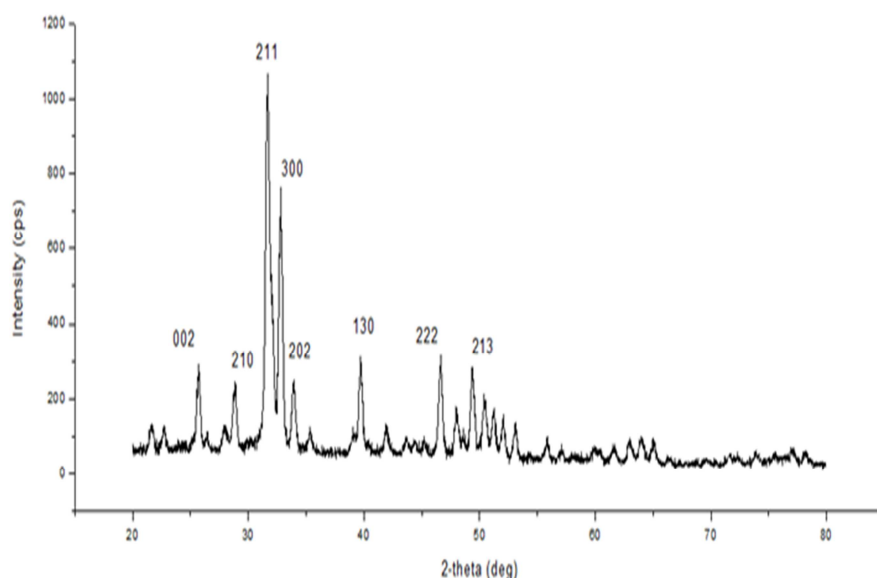


Fig.3. XRD pattern of HAP coated 316L SS substrate

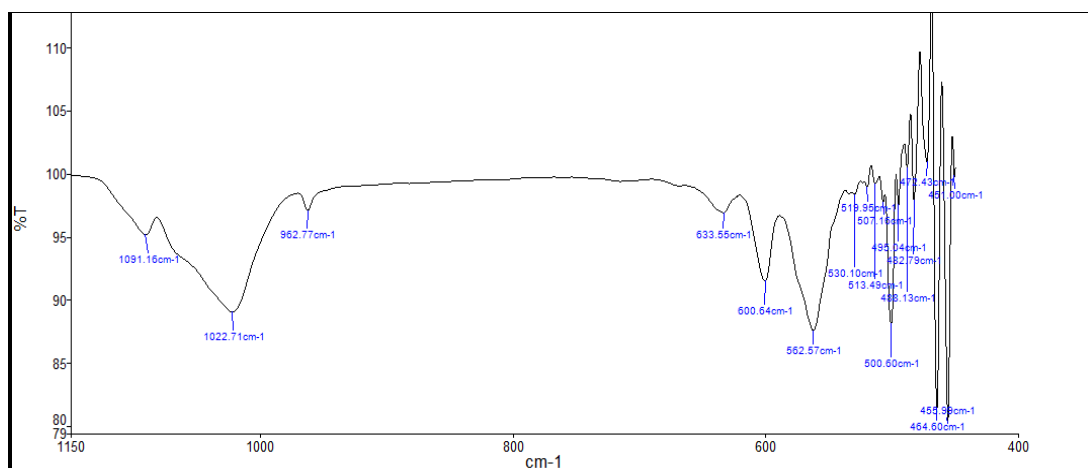


Fig.4. FTIR spectra of HAP coated 316L SS sintered at 800°C

Functional group analysis

Figure.4. Shows the FTIR (Fourier Transform Infrared Spectroscopy) of the pure HAP coated 316L SS substrate sintered at 800°C for 2 hours. The infrared spectra of HAP coated sample showed absorption in two regions i) The peaks for PO_4^{3-} at 560, 600, 960 cm^{-1} and from 1000 to 1100 cm^{-1} corresponds to ν_2 bending, ν_4 bending, ν_1 stretching and ν_3 asymmetric stretching vibration modes respectively ii) the peak at 630 cm^{-1} indicate the bending

vibration of hydroxyl group. These bands are similar to those reported by Ivana Škugor and Liga Berzina Cimdina [5, 17]. All these obtained peaks confirmed the formation of HAP.

Mechanical properties

Coating thickness

Thickness (Figure.5) of the HAP coated 316L SS samples were examined using Stylus Profilometer Dektak XT. An increase in coating thickness increases the problem related to mechanical competence of the coating. The average value of the coating thickness is estimated to be 28 micrometers which lies within the range of 20 – 100 micrometers for the electrophoretic deposition method [18, 19].

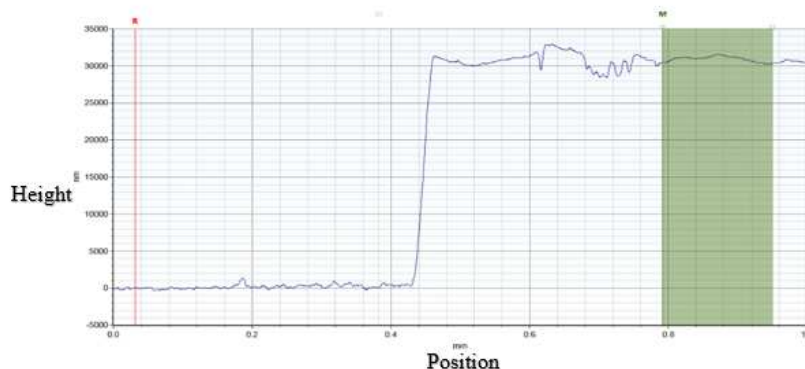


Fig.5.Coating thickness of HAP coated 316L SS

Stress analysis

The film stress (Figure.6) of HAP coated 316L SS is measured by Stylus Profilometer Dektak XT. The estimated value of the compressive stress of the film is 5.1GPa. The value reveals the uniform grains and improved densification achieved through the electrophoretic deposition method followed by sintering. Moreover, if the ceramics were sintered to nearly full density, the presence of HAP decreased the mechanical properties due to excessive grain boundary phase [19].

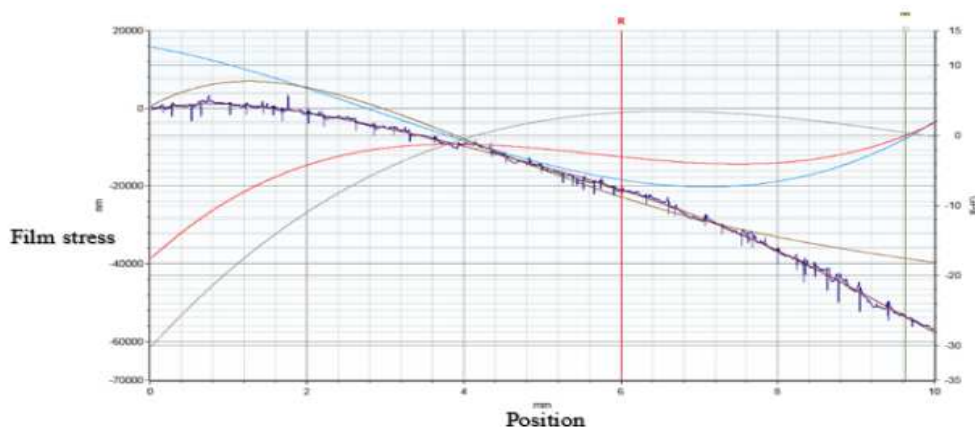


Fig.6.Film stress of HAP coated 316L SS

Roughness analysis

The Stylus Profilometer Dektak XT indicates the surface profile of HAP coated 316L SS. Figure.7. Indicates the average value of the roughness (P_q) $5\mu\text{m}$ (5980.90nm). This clearly shows the HAP coated 316L SS have higher surface roughness[19].

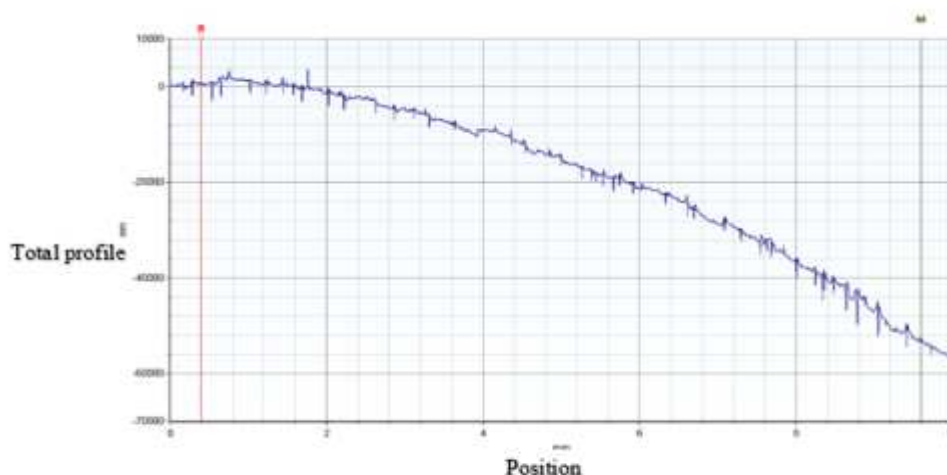


Fig.7.Surface profile of HAP coated 316L SS

In Vitro electrochemical analysis

Open circuit potential

Potentiodynamic polarization studies of the uncoated and HAP coated samples were carried out in simulated body fluid (Ringer solution, 9 g L^{-1} NaCl, 0.42 g L^{-1} KCl, 0.2 g L^{-1} NaHCO₃, 0.24 g L^{-1} CaCl₂) at acidic pH and a temperature of 37°C in order to establish a steady state between the electrolyte and the specimen. The 316L SS specimen forms the working electrode. All potentials were measured with respect to saturated calomel electrode as the reference electrode. A graphite rod served as the counter electrode. The change in potential with respect to time was monitored until the potential reaches a steady state. The potential of the working electrode with respect to reference electrode after stabilization period is termed as open circuit potential OCP or corrosion potential (E_{corr}) [20,21].

Figure.8 (a) shows the OCP curves for the uncoated substrates. A continuous decrease in OCP towards active potential with time was noticed for the uncoated sample, before it attained the steady state potential. The uncoated sample initially showed an OCP of -0.23V and constantly shifted towards active direction and then reached a potential of -0.35V after 35 minutes.

Figure.8 (b) shows the open circuit potential for the coated substrate. The curve obtained for the coatings with deposition potential of 40V, showed variations in OCP. This may due to the existence of large diffusion path within HAP coatings, capable of causing large potential drops. The shift was observed for the coated samples when compared to the uncoated samples which indicate its better corrosion resistance.

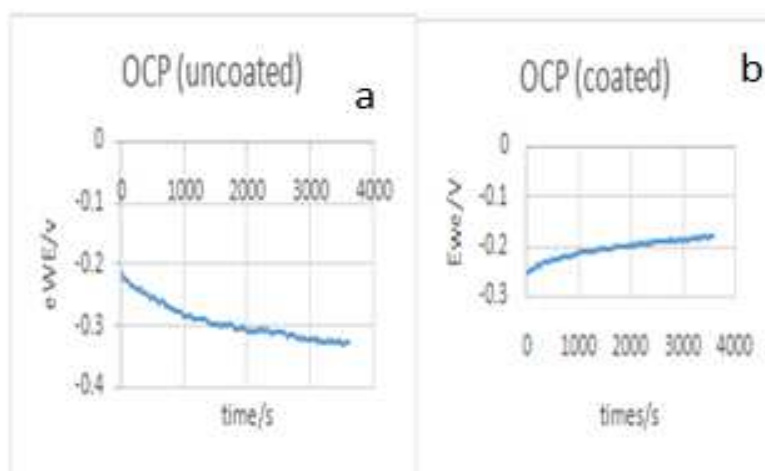


Fig.8. Polarization curves of a) bare and (b) HAP coated 316L SS substrate

Impedance analysis

Figure.9. shows the impedance spectra for HAP coated 316L SS in simulated body fluid solution. The coated sample indicates the passivity surface similar to capacitive behavior. The capacitive loop lies in the high frequency range touching the X-axis involving charge transfer reaction and the inductive loop lies in the low frequency range results in reduction process. There is no depression of semicircle in high frequency range it shows the homogeneity of the coated substrate. The oxidation reaction is greater than the reduction process it leads to decrease in inductive loop with increase in electrode impedance. Therefore, partial semicircle indicates the impedance response for the formation of thin oxide film on the coated substrate to oppose the charge transfer. This may represent the ohmic resistance of corrosion product film and solution enclosed between working and reference electrode [22].

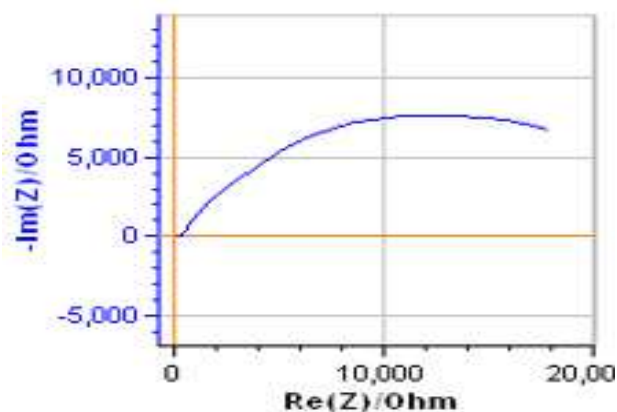


Fig.9.Impedance spectra of HAP coated 316L SS

CONCLUSION

Chemically precipitated hydroxyapatite powders were electrophoretically deposited on 316L SS substrates to increase the bioactivity and biocompatibility. XRD analysis confirmed the phase purity and stoichiometric characteristics of HAP coatings and a uniform distribution of deposits was observed in FESEM. The mechanical properties showed the increase in roughness and compressive stress of the HAP coated 316L SS. According to potentiodynamic polarization experiments, the HAP coating offered a better corrosion protection of 316L SS substrate, compared to bare substrate, because it provided better adhesion to the substrate and porosity was not connected to the substrate surface which blocked the electrochemical process that may occur at the metal surface. The above result concludes that HAP coating processes may be used to modify the surface of the currently used 316L SS orthopedic implant devices.

Acknowledgements

This work was supported by SSN College of Engineering, Kalavakkam, India. We are grateful to Dr. T. M. Sridhar, professor, Department of Analytical Chemistry, University of Madras for the support and valuable guidance.

REFERENCES

- [1] S Kannan, A Balamurugan, S Rajeswari, *Artif. Organs*, **2002**, 16 (1), 8-11.
- [2] M Geetha, D Durgalakshmi and R Asokamani, *Recent Patents on Corrosion Science*, **2010**, 2, 40-54.
- [3] SP Patterson, RH Daffner R and RA Gallo, *American Roentgen Ray Society*, **2005**, 184, 1219-1222.
- [4] M Siva Kumar and S Rajeswari, *Journal of Materials Science Letters*, **1992**, 11, 1039-1042.
- [5] IS Rončević, Z Grubač, MM Huković, *Int. J. Electrochemical. Sci*, **2014**, 9, 5907 – 5923
- [6] OS Yildirim, B Aksakal, H Celik, Y Vangolu and A Okur, *J. Med. Eng. Phys*, **2005**, 27(3), 221–228.
- [7] M Wei, AJ Ruys, BK Milthorpe and CC Sorrell, *J Biomed Mater. Res*, **1999**, 45, 11-19.
- [8] L Besra and M Liu, *Progress in Materials Science*, **2007**, 52, 1-61.
- [9] Zhitomirsky and Gal-Or, *Materials in Medicine*, **1997**, 8, 213-219.
- [10] OO Van der Biest and LJ Vandeperre, *Annual Review of Materials Science*, **1999**, 29, 327-352.
- [11] F Zude and S Qishen, *J. Mater.Sci.Technol*, **2003**, 19: 1, 30-32.
- [12] AJ Ruys, KA Zeigler, BK Milthorpe, CC Sorrell, MJ. Bannister (Ed.), *Ceramics, Adding the Value*, CSIRO, Melbourne, **1992**, 591.
- [13] N Deepak and B Uma, *Journal of Chemical and Pharmaceutical Research*, **2015**, 7(4), 1018-1023
- [14] K Prabakaran, TV Thamaraiselvi and S Rajeswari, *Trends in Biomater. Artif. Organs*, **2006**, Vol 19(2), 84-87

-
- [15] K Prem Ananth, P J Sujin, AN Joseph, HO Tae, D Mangalaraj and AM Ballamurugan, *Advanced Materials Letter*, **2015**, 1-11.
- [16] K Azzaoui, A Lamhamdi, E Mejdoubi, M Berrabah, A ELidrissi, B Hammouti, S Zaoui and R Yahyaoui, *Journal of Chemical and Pharmaceutical Research*, **2013**, 5(12), 1209-1216.
- [17] BC Liga and B Natalija, *Materials Science, Engineering and Technology*, 123-149.
- [18] AR Boccaccini I, S Keim, R Ma, Y Li and I Zhitomirsky, *J. R. Soc. Interface*, **2010**, 7, 581–613
- [19] Dektak xt Stylus Profiler User manual ©**2011**, Bruker Corporation Printed in the United States of America. May 31, 2011 <http://mmrc.caltech.edu/DektakXT/Manuals/User%20Manual%20Dektak%202011-05-31.pdf> 59
- [20] TM Sridhar, UM Kamachi, M. Subbaiyan, *Corrosion Science*, **2003**, 45, 237–252.
- [21] Abdulsalam K.S and Eman A.O. <http://www.jeaconf.org/UploadedFiles/Document/1238cb30-7c7c-4149-9a90-e239976aef83>
- [22] HH Hamdy, A Essam, AA Mohammed, *Sciencedirect*, **2007**, 6359-6366.