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Corrosion behaviour of hydroxyapatite coatings on borate and phosphate passivated 316L stainless steel in Ringer's solution

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ABSTRACT

Corrosion resistance property of 316L Stainless Steel sample was studied in Ringer's solution after passsivating them with phosphoric acid (H_3PO_4) and sodium tetraborate. A few freshly phosphate and borate passivated samples were electrophoretically coated with Hydroxyapatite. These coated samples were tested for corrosion resistance in Ringer's solution.

Keywords: *Corrosion rate, prepassivation, Coating, Ringer's solution*

Introduction

MATERIAL used for implantation is known as implant material or biomaterial. Metallic implants are widely used in many treatments and are fairly successful. However, the main inconvenience of metallic biomaterials is their degradation upon interaction with body fluids, which necessitates a second surgery to remove the metallic implant after healing, and it increases the risk of the operation and increases the expenses of the patient.

Austenitic stainless steel enjoys the advantages of availability at low cost, similar mechanical properties related to bone mineral and ease of fabrication [1]. In the case of Stainless Steel, the metal surface is unable to tolerate the environment inside the human body and leads to the release of Fe, Cr and Ni ions in the human body [2]. The Cr and Ni are powerful allergens and are demonstrated to be carcinogenic [3]. Therefore, it would be better to reduce the metal ion release to avoid the deleterious effect caused by the corrosion products in the normal bone formation. Hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$], the biocompatible ceramic is used as a coating on the metallic substrates to resist the metal ion release and have neutral interaction with the new tissue [4]. However, due to the continuous interaction with the harsh environment, the HAP on the metallic surface also degrades as the time progresses and results in the corrosion of underlying metallic alloy. Hence, passivation of the alloy prior to the HAP coating is essential in the prevention of metallic corrosion of the metallic substrate and thus improve the long-term implant performance conditions. This is in line with the concept of double or multilayer coating on biomaterial surface reported by Silva et. al [5].

In this work the 316L Stainless Steel was prepassivated either in H_3PO_4 or in sodium tetraborate by applying instantaneous polarized potential in the respective passive regions followed by Hy-

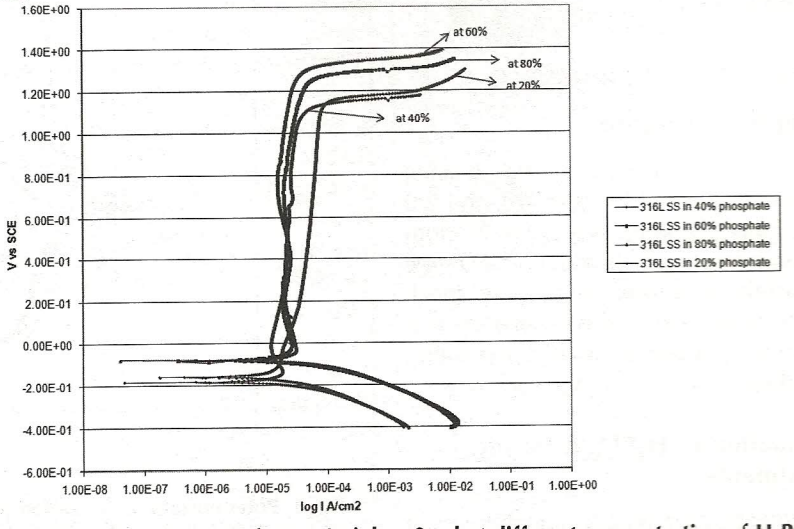

Fig. 1: Polarization diagram of 316L Stainless Steel at different concentration of H_3PO_4

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Table 1: Ecorr & Icorr values of 316L Stainless Steel in Ringer solution

Sample	Ecorr(V)	Icorr(A)
As received	$1.06*10^{-2}$	$8*10^{-6}$
Passsivated in H_3PO_4 at 0.242 V	$-2.03*10^{-2}$	$1*10^{-6}$
Passsivated in H_3PO_4 at 0.525 V	$-9.32*10^{-3}$	$1.5*10^{-6}$
Passsivated in H_3PO_4 at 0.881 V	$-2.13*10^{-2}$	$1.5*10^{-5}$
As received with HAP coated	$-9.46*10^{-2}$	$2*10^{-7}$
Passsivated in H_3PO_4 at 0.242 V & HAP coated	$3.00*10^{-2}$	$2*10^{-6}$
Passsivated in sodium tetraborate at 1.090 V	$-1.8*10^{-2}$	$1.5*10^{-6}$
Passsivated in sodium tetraborate at 0.995 V	$-2.15*10^{-2}$	$1.5*10^{-6}$
Passsivated in sodium tetraborate at 0.909 V	$-9.96*10^{-2}$	$1.5*10^{-7}$
Passsivated in sodium tetraborate at 0.909 V& HAP coated	$-9.02*10^{-2}$	$8*10^{-8}$

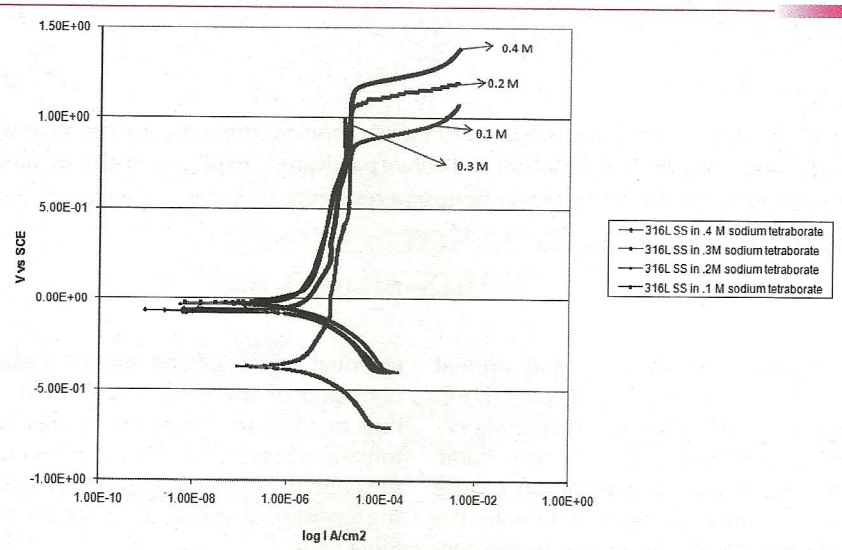

Fig. 2: Current Transient plots of 316L Stainless Steel in 60% H_3PO_4 solution during potentiostatic passivation at three passivating potentials

droxyapatite coating. The corrosion resistance property of the differently treated samples was evaluated by corrosion rate measurement.

Materials and methods

Sample preparation

316L SS samples were polished using emery papers of 120, 180, 1/0, and 2/0 grit. Final polishing was done in cloth polisher in order to produce scratch-free mirror-finish surface. The polished specimens were degreased with acetone and thoroughly washed with distilled water, dried and used for further studies.

Evaluation of H_3PO_4 & borate treatments

Potentiostatic polarization diagram of 316L in phosphoric acid (H_3PO_4) and sodium tetraborate solution of different strengths were experimentally obtained and passive regions were identified from *Fig 1 & 4*. The 316L SS samples were passivated at three potentials each in 60% phosphoric acid (H_3PO_4) and 0.4M sodium tetraborate solution *(Fig 2 & 5)*. The passivated samples were washed with distilled water and dried at 50°C for 30 minutes.

HAP coating

HAP Coating was done by electrophoresis. Electrolyte used for this was prepared by mixing 0.042 mol/l $Ca(NO_3)_2$ and 0.025 mol/l $NH_4H_2PO_4$ solution[7][8]. The 316L SS sample to be coated was made cathode and a copper plate was used as anode [9]. Both were immersed into the solution and the solution temperature was maintained at 40°C. After 30 min the sample was removed from the solution. The obtained coating, termed as initial coating, was then baked at 100°C for 1 hr [10]. The finally obtained coating was termed as treated coating. HAP coating was given to as received and prepassivated 316L samples.

Corrosion t esting

Standard Corrosion Cell was used to measure Icorr and Ecorr of flat metal specimens in Ringers solution (NaCl 8.6g/l, $CaCl_2.2H_2O$ 0.66g/l and KCl 0.6g/l). Polarization experiments were carried out using Gamry Potentiostat. The Icorr and Ecorr values were obtained by Tafel's

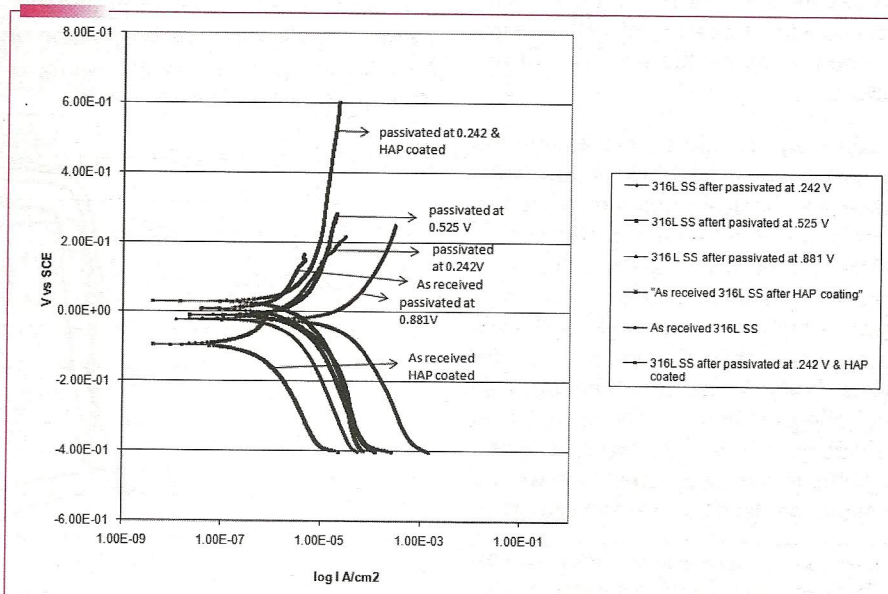

Fig. 3: Potentiostatic Polarization of as received, phosphate passivated & coated 316L Stainless Steel in Ringer's solution for estimation of Icorr & Ecorr

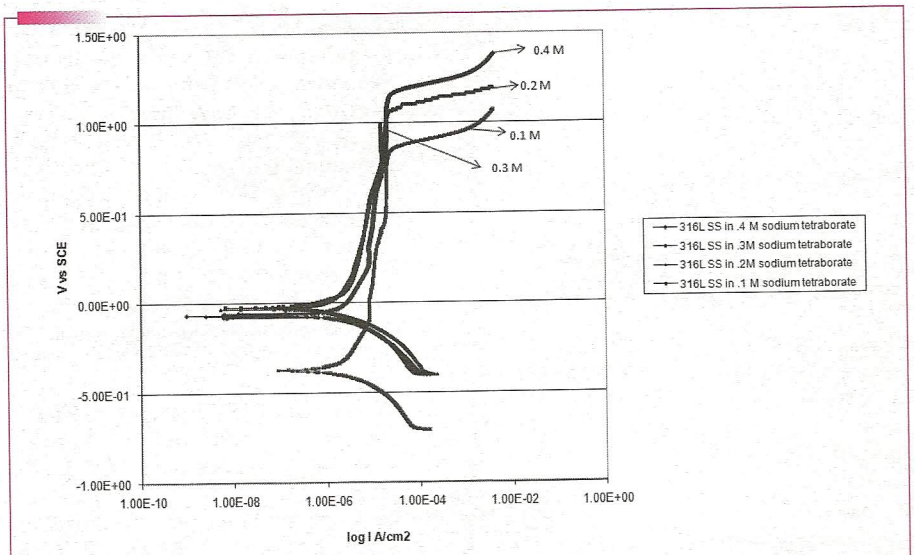

Fig. 4: Polarization diagram of 316L Stainless Steel at different concentration of sodium tetraborate

extrapolation method. The data is given in *Table 1*. The pH of the solution was maintained at 7.4 throughout the experiment.

Results and discussions

In one of the reported work [6][11][12] the efficiency of hydroxyapatite (HAP) coatings on H_3PO_4 treated 316L SS has been investigated through electrochemical studies. Here passivation was done by immersing in the H_3PO_4 solution. In a recent M.Tech (Master of Technology) project in the department of Metallurgical & Material Engineering Jadavpur University [13] it was observed that potentiostatic passivation of 304 stainless steel by application of polarized potential in the passivating range considerably improved its corrosion resistance properties in Ringer solution. So instead of complete immersion of the material in various concentrations of H_3PO_4, passivation of 316L Stainless Steel was carried out in H_3PO_4 solution. From the polarization diagram of 316L Stainless Steel *(Fig 1)* it is clear that in 60% phosphate the ZCP (zero current potential) is the noblest than in other phosphate solutions. Moreover compared to the polarization diagrams in 20%, 40% and 80% solutions the passive region in 60% is widest. So for passivation 60 % concentration of H_3PO_4 was chosen for further treatment and three different passivation potentials chosen from the polarization diagram *(Fig 1)* were 0.242 V, 0.525 V and 0.881 V vs SCE such that one point is near the beginning of passivation, one is close to the breakdown of passivation and the rest one is between them.

From the current transient plot *(Fig 2)* it is evident that at 0.242 V vs SCE the stabilization occurs at the minimum current. Electrochemical corrosion rate measurements of the passivated and passivated and coated were performed in Ringer's solution to assess the corrosion resistance after passivation of the stainless steel at the three passivation potentials *(Fig 3)*. The Ecorr & Icorr values are tabulated in *Table 1*. Among the passivated samples, the ones passivated at 0.242 V & 0.525 V show similar Icorr values whereas samples passivated at 0.881 V shows comparatively poor Icorr value. HAP was electrophoretically deposited onto the as received sample and samples passivated at 0.242V in phosphoric acid. Among the passivated and coated samples the passivated at 0.242 V and then HAP coated sample shows much nobler Ecorr though best Icorr was obtained for HAP coating on as received sample. Though K.Prabakaran et.al did not tabulate the Icorr and Ecorr values [6], from their polarization diagram Ecorr & Icorr could be read out and it was seen that the Icorr was nearly 400-500μA/cm^2 and Ecorr was around -.200 mV vs SCE. In this work even just the phosphate passivation yielded better corrosion resistance properties of 2 μA /cm^2 Icorr and 0 .03 Volts vs. SCE Ecorr.

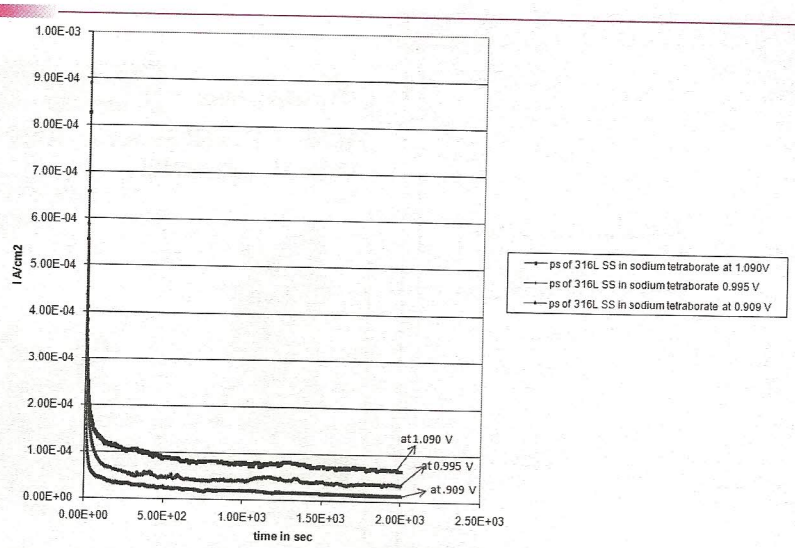

Fig. 5: Current Transient plots of 316L Stainless Steel in 0.4M sodium tetraborate solution during potentiostatic passivation at three passivating potentials

Passivation was also done in sodium tetraborate [14] in which 0.4M sodium tetraborate was taken. In the present study polarization diagrams were obtained for *(Fig 4)* of 0.1M, 0.2M, 0.3M & 0.4M tetraborate solutions respectively. From *Fig 4* it can be seen that the ZCP of the sample in 0.4M solution was nobler and passive region was also widest. From the polarization diagram the three passivation potentials in passivation region selected were 0.909V, 0.995V, 1.09V vs SCE respectively. Potentiostatic passivation of the sample at these potentials was carried out and the current transient plot is given in *Fig 5*. The curve at 0.909 V stabilized at lowest current. Consequently corrosion rates of the passivated samples were measured in Ringer solution by potentiostatic method *(Fig 6)*. The Ecorr & Icorr values obtained from the diagram are tabulated in *Table 1*. As the sample passivated at 0.909 V gave better Icorr value ($1.5*10^{-7}$ A/cm^2) for HAP coating this sample was chosen. The values of coated sample are tabulated in *Table 1*. The sample passivated at .909 V and then HAP coated shows the best Icorr ($8*10^{-8}$A/cm^2) which means best corrosion resistance property.

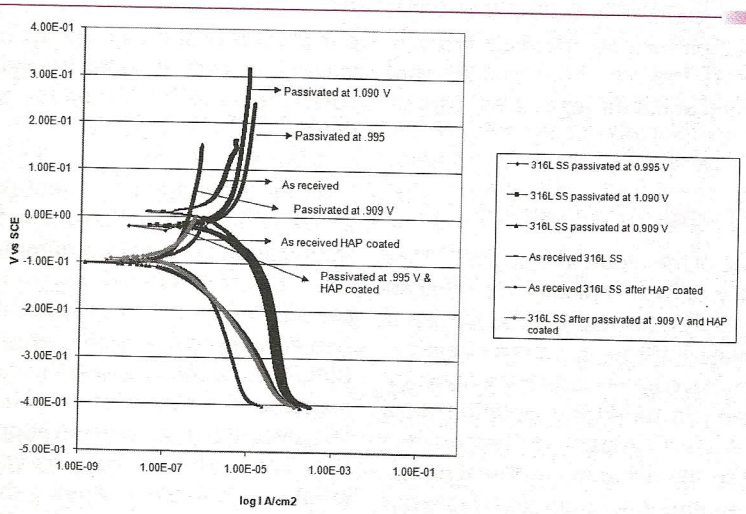

Fig. 6: Potentiostatic Polarization of as received, borate passivated & coated 316L Stainless Steel in Ringer's solution for estimation of Icorr & Ecorr

Conclusion

1. Both coating and passivation has a good effect on the corrosion resistance property of 316L Stainless Steel.
2. Borate passivated and coated sample shows better corrosion resistance property than phosphate passivated sample.
3. Phosphate passivated and coated sample shows much nobler value than other samples.

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