

Coating of strontium substituted hydroxyapatite on surface treated surgical grade stainless steel by electrodeposition for biomedical applications

D. Rajeswari, S. Ramya, D. Gopi* and L. Kavitha

Abstract— Surgical grade stainless steel (316L SS) is one of the widely used implant material in orthopedic surgeries. But often the release of metal ions is evidenced from the implants and subsequently a second surgery is required to remove the implant material. One way to control the release of metal ions is to coat the implant material with a biocompatible material like hydroxyapatite (HAp). Strontium (Sr) salts were found to stimulate bone formation and inhibit bone resorption both *in vitro* and *in vivo*. The present work deals with the electrodeposition (ED) of Sr substituted hydroxyapatite (Sr-HAp) on the HNO₃+H₂SO₄ treated 316L stainless steel (316L SS) at a current density of 2 mA/cm² for different durations like 15 min, 30 min and 45 min. The resultant coatings were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The SEM results revealed that the Sr-Hap coating obtained on the surface treated 316L SS by electrodeposition for 30 min consists of nano-rods of dimension ranging from 50 to 75 nm.

Keywords — 316L stainless steel, Surface treatment, Strontium substituted hydroxyapatite, Electrodeposition, SEM.

1 INTRODUCTION

Orthopedic implants are often prone to failures due to less resistive nature of the implant material inside the body. The need to reduce costs in public health services has compelled the use of stainless steel as the most economical alternative for orthopedic implants. For this reason, it is important to develop techniques to improve the corrosion resistance and bioactivity of this material. HAp (Ca₁₀(PO₄)₆OH₂) is considered as one of the potential candidates as a substitute for bone and bone related clinical applications [1]. Strontium is one of the metallic elements found in bones and teeth. Strontium appears to be one of the most effective substances for the treatment of osteoporosis and other bone-related conditions [2]. As calcium and strontium share the properties of group 2A elements, strontium can replace calcium in HAp and hence in bone, without much difficulty. It is reported that the stable strontium is non-toxic even when it is administered in large doses in our body for prolonged periods [3]. The strong chemical bonding of pure/substituted HAp makes its metal-implant coating to promote the new bone growth. However, due to the continuous interaction with the harsh environment, the HAp coating degrades during long-term implantation and results in the corrosion of underlying metallic alloy. Hence, surface treatment of a metal alloy prior to the development of coating is essential in the prevention of metallic corrosion and to withstand during long-term implant condition [4-6]. In the present study, the tendency of type 316L SS in a mixture of acids like HNO₃ and H₂SO₄ to form passive layer is explored and the Sr-HAp coatings on the acid treated 316L SS is obtained. The as-prepared

coating was characterised by FT-IR, XRD and SEM techniques.

2 EXPERIMENTAL DETAILS

The implant quality 316L stainless steel specimens having composition (wt.%) C— 0.0222, Si — 0.551, Mn — 1.67, P — 0.023, S — 0.0045, Cr — 17.05, Ni — 11.65, Mo — 2.53, Co — 0.136, Cu — 0.231, Ti — 0.0052, V — 0.0783, N — 0.0659 and rest Fe were cut into the dimensions of 10×10×3 mm. The specimens were mechanically wet ground with 120-1000 grit SiC paper until all visible scratches were removed and finally polished with diamond paste of 1.5 μm. After polishing, the specimens were degreased with acetone and ultrasonicated before surface treatment. The entire sample surface was subjected to surface treatment of complete immersion in a mixture of acids with 15% of sulphuric acid (H₂SO₄) and 40% of nitric acid (HNO₃) for 1h at room temperature. The surface modified samples were washed with distilled water and dried at 50°C for 30min. Further the Sr-HAp was deposited on the pristine and surface treated 316L SS specimens by electrodeposition method. The electrodeposition was performed in a standard three electrode cell in which 316L stainless steel specimens served as cathode while platinum acted as anode and the saturated calomel electrode (SCE) acted as the reference electrode. The electrolyte solution for deposition consisted of analytical grade 0.5 M of Ca(NO₃)₂, 0.5 M of Sr(NO₃)₂ and 0.3 M of (NH₄)₂HPO₄ at room temperature (28±1 °C) and the pH was maintained at 4.5. The coating process was carried out galvanostatically using an electrochemical workstation (CHI 760C, CH Instruments, USA) at constant current density of 2 mA/cm² for 15 min, 30 min and 45 min duration. The as-coated specimens were gently rinsed with deionized water and were subjected to different characterisation techniques such as FT-IR, XRD and SEM. Adhesion tests were carried out for the coated samples using a universal testing machine (Model 5569, Instron).

- D. Rajeswari is currently pursuing Ph.D. in Physics in Periyar University, Salem 636 011, Tamilnadu, India. E-mail: rajihubli@gmail.com
- S. Ramya is currently pursuing Ph.D. in Chemistry in Periyar University, Salem 636 011, Tamilnadu, India.
- *D. Gopi is Professor in Chemistry and Additional Coordinator, Centre for Nanoscience and Nanotechnology, Periyar University, Salem 636 011, Tamilnadu, India. E-mail: dhanaraj_gopi@yahoo.com
- L. Kavitha is Assistant Professor in Physics, Department of Physics, Periyar University, Salem 636 011, Tamilnadu, India.

3 RESULTS AND DISCUSSION

Fig. 1 shows the FT-IR spectra of the Sr-HAp coating on mixed acid treated 316L SS at 2 mA/cm² for 15 min, 30 min and 45 min duration which confirms the functional groups of the as-prepared Sr-HAp coating. The characteristic peaks appeared at 1016 cm⁻¹ (ν₃), 592 cm⁻¹ (ν₄) and 472 cm⁻¹ (ν₂) as well as the bands observed at 1080 cm⁻¹ (ν₃) and 947 cm⁻¹ (ν₁) are assigned to the phosphate groups of Sr-HAp [7,8]. Apart from these, the broad stretching band at 3440 cm⁻¹ and a bending band at 1620 cm⁻¹ are attributed to the stretching and bending mode of water molecule, while the absorption bands at 3590 cm⁻¹ and 639 cm⁻¹ are assigned to the stretching and bending vibration of OH⁻ groups of Sr-HAp, respectively. Thus the FT-IR spectrum (**Fig. 1a**) strongly demonstrates the formation of Sr-HAp coating on the mixed acid treated 316L SS at 2 mA/cm² for 15 min duration. Also, the FT-IR spectra as shown in **Fig. 1b & 1c** confirm the formation Sr-HAp coating on mixed acid treated 316L SS at 2 mA/cm² for 30 min and 45 min.

Fig. 2 shows the typical XRD patterns of the Sr-HAp coating on the mixed acid treated 316L SS at 2 mA/cm² for 15 min, 30 min and 45 min. The main diffraction peaks of Sr-HAp are visible between 31° and 34°, and other secondary peaks are present in the 39–54° interval. All the patterns indicate the presence of a crystalline structure of the as-formed Sr-HAp coating.

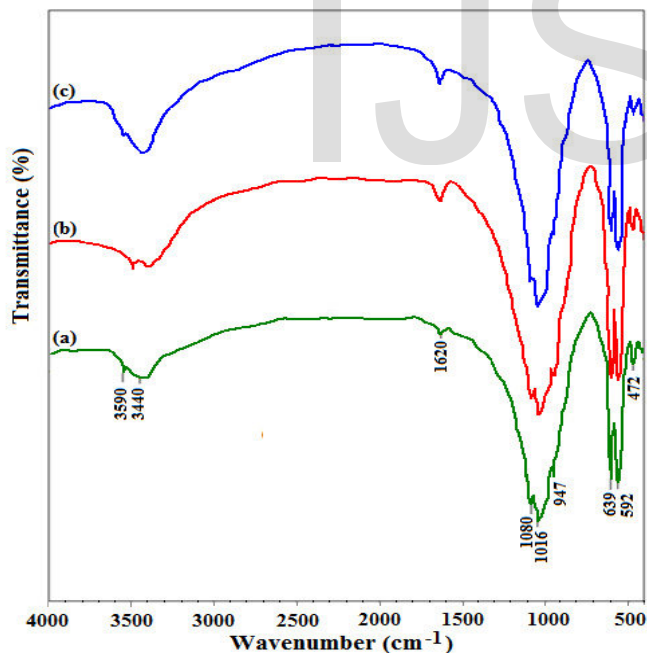


Fig. 1 FT-IR spectra obtained for the Sr-HAp Coating on surface treated 316L SS at 2 mA/cm² for (a) 15 min (b) 30 min and (c) 45 min.

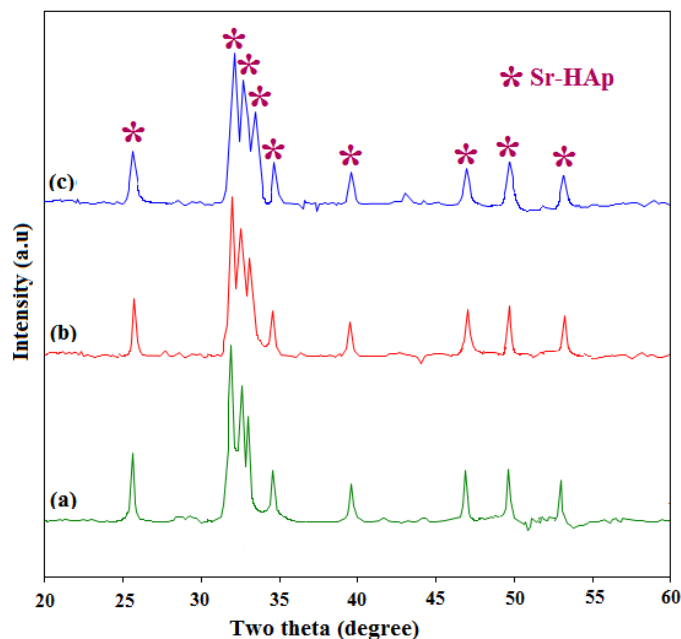


Fig. 2 XRD patterns of Sr-HAp coating on surface treated 316L SS at 2 mA/cm² for (a) 15 min (b) 30 min and (c) 45 min.

Fig. 3(a,b,c,d) presents the typical surface morphologies of the surface treated 316L SS and the Sr-HAp coatings on surface treated 316L SS specimens at 2 mA/cm² for 15 min, 30 min and 45 min duration, respectively. **Fig. 3(a)** shows the modified surface of the mixed acid (15% of H₂SO₄+40% of HNO₃) treated 316L SS. **Fig. 3(b)** reveals the agglomerated crystalline Sr-HAp coating on the surface treated 316L SS at 2 mA/cm² for 15 min duration. The SEM morphology as shown in **Fig. 3(c)** for the Sr-HAp coating on the surface treated 316L SS at 2 mA/cm² for the duration of 30 min consists of nanorods of size ranging between 50 and 75 nm. When the duration was increased to 45 min for the Sr-HAp coating on the surface treated 316L SS at 2 mA/cm², the coating morphology became very much agglomerated as shown in **Fig. 3(d)**. Hence the Sr-HAp coating obtained with nanorod formation on the surface treated 316L SS at 2 mA/cm² for 30 min duration is considered as optimum. Such a nanostructured coating can possess great biological efficacy due to its enhanced bioactivity and biocompatibility.

The adhesion test results revealed an enhanced adhesion strength (11.4±0.6 MPa) for the Sr-HAp coating on the mixed acid treated surface when compared to that of the Sr-HAp coating on pristine 316L SS (9±0.6 MPa).

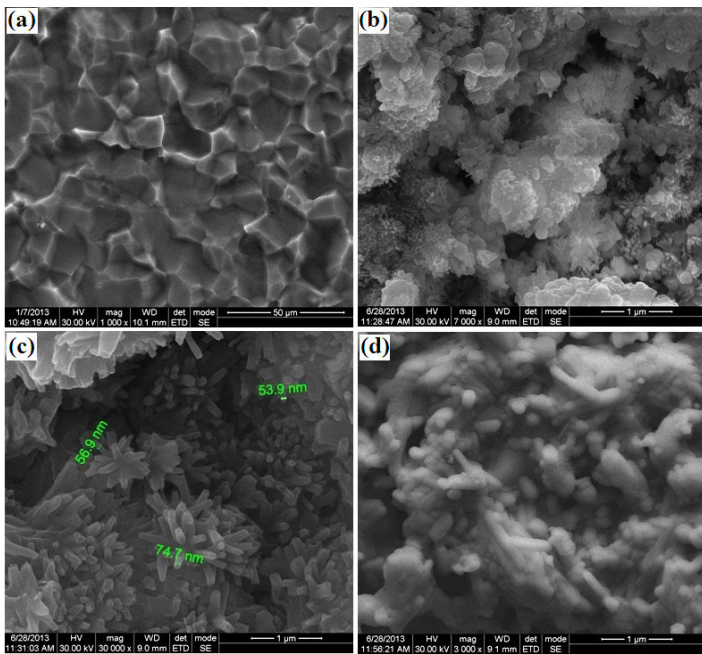


Fig. 3 SEM images of (a) mixed acid treated 316L SS; Sr-HAp coating on mixed acid treated 316L SS at 2 mA/cm² for the duration of (b) 15 min (c) 30 min

4 CONCLUSION

The 316L SS was surface treated with mixture of 15% H₂SO₄ and 40% of HNO₃ for 1h at room temperature and subsequently electrodeposited with Sr-HAp at 2 mA/cm². The FT-IR and XRD results confirmed the functional groups and the crystallinity of the as-formed Sr-HAp coating, respectively. The Sr-HAp coating obtained on the surface treated 316L SS at 2 mA/cm² for 30 min duration exhibited nanorod formation and thus considered as optimum. The size of the nanorods ranged between 50 and 75 nm. The as-formed Sr-HAp coating on the mixed acid treated surface of 316L SS showed enhanced adhesion strength of 11.4±0.6 MPa. The as-prepared coating can be promising for biomedical applications.

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