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In Vitro Bioactivity, Corrosion Resistance and Mechanical Properties of Nano Composite Coated 316L SS for Orthopaedic Applications

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ABSTRACT: Currently, the medical applications of hydroxyapatite coatings are limited due to the lack of anti-infection and poor mechanical properties. In this regard, new attempt has been made to fabricate nano composite coatings on 316L stainless steel (316L SS) using nano hydroxyapatite/ nano TiO_2 to increase the mechanical property, corrosion resistance and biocompatibility. Nano composite coating was carried out with different ratio of nano hydroxyapatite/ nano TiO_2 . The uniform distribution of coating was obtained at a ratio of 6:4. The coated surface was characterized by X-ray diffraction analysis, field emission scanning electron microscope with energy dispersive X-ray spectroscopy, optical microscopy and atomic force microscopy studies. Mechanical strength of the coating was analysed by tape adhesion test and vickers microhardness studies. Cyclic potentiodynamic polarization study was evaluated in Hank's solution at room temperature. Cell viability and proliferation studies were carried out using MC3T3-E1 osteoblast cell exhibited non-toxicity and higher level of cell proliferation of nano composite coated samples at the ratio of 6:4 by controlling the release of metal ion into surrounding body tissues.

KEYWORDS: Composite, Sintering, Corrosion resistance, Stainless steel, Proliferation.

I. INTRODUCTION

Metallic implants such as 316L Stainless Steel, titanium and its alloys, magnesium alloys and Co–Cr alloys have been widely used in load bearing applications due to they offer various properties like corrosion resistance, stability, strength and biocompatibility. Among the metallic materials 316L Stainless Steel (316L SS) implant is most commonly used for orthopedic properties in the medical field due to biocompatibility, high corrosion resistance, broader availability, excellent fabrication properties and low cost. The corrosion and wear of these implants result in the release of metallic ions into the surrounding body tissue. This problem leads to poor bonding between the implant and the bone and sometimes avoids the formation of bone tissue [1][4]. Many of the researchers have proved that there is a chance of pitting corrosion occurred in 316L SS implants material[2]. Many researchers have been performed to modify the metallic surface through protective coating and chemical treatment. Protective coatings carried out using HAP, TiO_2 , Al_2O_3 and ZrO_2 to improve the corrosion resistance and wear resistance of the 316L SS [3].

Nano Hydroxyapatite (HAP) is one of these bioceramics and is widely used in biomedical due to the fact that they possess similar chemical, structural and biological properties to that of the human bone, which in turn promotes osseointegration [4]. Bioactive bioceramic coatings using nano HAP alone is not suitable for the artificial hard tissue applications because of inadequate mechanical performances, low tribological features, and insufficient bonding strength under load-bearing circumstances [5]. Thus, to improve the mechanical properties of nano HAP materials the reinforcement of nano TiO_2 has been attempted. The reinforcing phase in the form of nano TiO_2 particles was selected due to the suitable biocompatibility, mechanical and adhesion properties [6]. However, the addition of nano TiO_2 into nano HAP as a composite coating on metallic implants causes an increase in the mechanical and adhesion properties of the implants.

II. RELATED WORK

Koike et al. have reported the composite coatings using TiO_2 /HAP on Ti–6Al–4V produced by plasma spraying technique led to increased corrosion resistance [7]. Webster et al. have proved TiO_2 nano phase promotes osteoblastic adhesion compared to conventional powders [8]. Durgalakshmi et al. have reported adhesion strength of composite coated titanium alloy was increased by TiO_2 and HAP using EPD process after sintering [9]. Amaravathy et al. have reported improving adhesion strength of the implant using HAP/ TiO_2 composite coating on

titanium alloy by sol gel method [10]. Many of the researchers have reported increase the adhesion strength and corrosion resistance of the coated implants using HAP/TiO₂ composite.

So far, there are no reports on suitable ratio of the composite mixture to provide suitable coating for implants. The present work investigates the electrophoretic deposition of nano HAP/nano TiO₂ composite coating on 316L SS and its corrosion resistance, mechanical stability, biocompatibility and cell proliferation. EPD was carried out at different ratio of nano HAP/nano TiO₂ in composite mixture and optimized the suitable ratio using electrochemical corrosion studies.

III. METHODOLOGY

Electrophoretic Deposition of Nano Composite

316L SS was obtained from Steel Authority of India Limited (SAIL) (ASTM F138- 13a). The sample dimension chosen was 10 mm × 10 mm × 2 mm. The samples were mechanically polished with grit SiC paper starting from the sheet 200 to 1200 grit. Then, the samples thoroughly washed with soap solution and then ultrasonically cleaned with acetone and dried at room temperature. 2% suspension of nano composite (nano HAP + nano TiO₂) was prepared in different ratio using Isopropyl alcohol (IPA) and 0.1 g of iodine in a 100 ml beaker. Iodine acts as a dispersant to stabilize the suspension. The different nano composite ratios are 5:5, 6:4, 7:3 and 8:2 respectively. Deposition of nano composite on 316L SS was achieved by EPD process at room temperature. The samples 314 SS (11 mm × 8 mm × 0.5 mm) acted as anode and 316L SS acted as cathode. These two electrodes were immersed in a nano composite suspension. Distance between these two electrodes was less than 1 cm in order to achieve optimum particle deposition on the exposed electrode surface area. One side of the sample masked with tape Teflon and deposition was carried out on other side of 1cm² surface areas. The optimized coating voltage and deposition time was set at 30 V and 60 seconds. After the coating process, the coated samples were subjected to sintering process at 700°C temperatures in air furnace at a heating rate of 10°C/min for one hour. The samples were removed after cooling from the furnace and were stored in vacuum desiccators.

Surface Characterizations

Nano composite coated samples after sintering were characterized by x-ray diffraction (XRD), Field emission scanning electron microscope with energy dispersive x-ray analysis (FESEM with EDS), optical microscopy study and Atomic Force Microscopy (AFM) techniques. The X-ray diffraction (Bruker model D8, Germany) analysis was carried out using Cu K α radiation, and λ of 1.5406Å. The micrographs of the coated sample were taken using (Leica, model DM 2700M) optical microscope. The surface morphology and elemental composition of the coated samples was observed using FESEM (Model CARL ZEIS SUPRA 55, Germany) equipped with EDS. Surface topography and the average surface roughness (Ra) for nano composite coated sample at different ratio were measured using AFM imaging technique (model MFP-3D with AC240TS-R3 cantilevers).

The adhesion strength of the nano composite coated samples at different ratios was evaluated using a tape-test method (American Society for Testing and Materials (ASTM D3359)). The cross-cut was developed on both direction using cross-hatch cutter and adhesive tape was applied on the cross-cut area and pulled back and then evaluation was made according to the ASTM standard (0% - 5B, <5% - 4B, 6-15% - 3B, 16-35% - 2B and 36-65% - 1B). The microhardness properties (ASTM E92-17) of the nano composite coated samples at different ratio were measured using Vickers Microhardness Tester (Ever One Enterprises Limited, India). A loading force of 100 gram Force (gF) was applied for the duration of 5 seconds to record the measurements.

Electrochemical corrosion behaviour of uncoated and nano composite coated sample at different ratio were tested in Hanks' solution at room temperature. Cyclic potentiodynamic polarization (CPP) studies were performed using a Biologic-SP 240 (EC- lab Version 10.37). A conventional three-electrode cell was used for electrochemical measurements according to ASTM guidelines (G61-86). A graphite electrode, saturated calomel electrode (SCE) and the nano composite coated 316L SS sample was used as a counter electrode, reference electrode and working electrode respectively. The composition of Hank's solution (8 g L⁻¹ NaCl, 0.40 g L⁻¹ KCl, 0.14 g L⁻¹ CaCl₂, 0.35 g L⁻¹ NaHCO₃, 1 g L⁻¹ Glucose, 0.10 g L⁻¹ MgCl₂·6H₂O, 0.10 g L⁻¹ NaH₂PO₄, 0.06 g L⁻¹ Na₂HPO₄·2H₂O, 0.06 g L⁻¹ MgSO₄·7H₂O respectively) which is very similar to our human physiological fluids, was prepared up to 1 liter with pH of 7.4.

The osteoblast cells MC3T3-E1 were obtained from National Centre for Cell Sciences, Pune (NCCS). Cell viability and proliferation was carried out on uncoated and nano composite coated 316L SS samples using osteoblast cells. In vitro cytotoxicity study was carried out using MTT assay [11].

IV. EXPERIMENTAL RESULTS

Fig. 1. shows that the XRD spectra for nano composite coated 316L SS at the ratio 6:4 after sintering. The peaks with maximum intensity were found at (210), (211), (300), (202), (310) and (213). The obtained result was compared with the JCPDS#09-0432, which confirmed the presence of the hydroxyapatite. Generally, TiO₂ crystallites exist in three forms; brookite, anatase, and rutile. At room temperature brookite and anatase phases are stable and they are changed to rutile phase on sintering. The maximum intensity peaks were observed at (101), (004) and (211). This result was compared with JCPDS#21-1276, which confirmed presence of nano TiO₂ [12]. No other peaks were detected indicating that formation uniform coating with strong adhesion on metal surface.

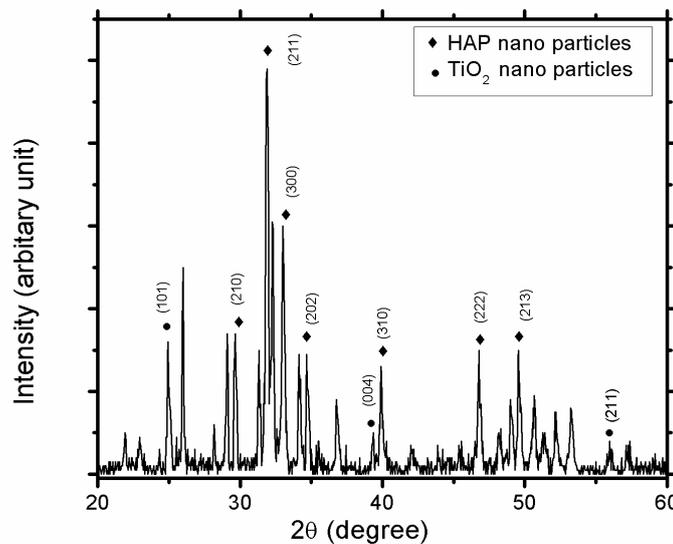


Fig. 1. XRD spectra of nano composite coated 316L SS at the ratio 6:4 after sintering

After sintering process nano composite coated 316L SS samples were visualized using optical microscope to study the morphological characterization and the images of nano composite coatings obtained at different ratios after sintering at 700°C for 1 hour is given in Fig. 2(a-c). No coating was observed at the ratio of 8:2 and very mild coating with hair line cracks was obtained at the ratio of 5:5. A uniform and crack free coating was observed at the ratio of 6:4. Dense coating was obtained at the ratio of 7:3. Thus, nano composite uniform coating without any crack was observed on 316L SS at the ratio of 6:4 than the other ratios coated samples.

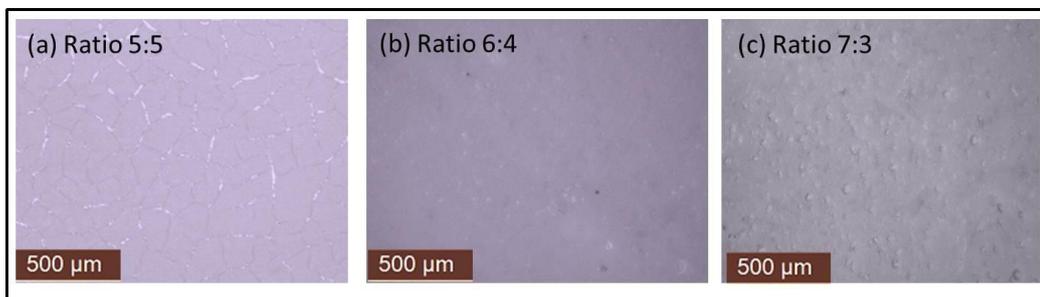


Fig. 2 Optical images of nano composite coated 316L SS at different ratio

Fig. 3a, b shows that the FESEM micrograph and EDS spectrum of nano composite coated 316L SS at the ratio of 6:4 after sintering. The surface morphology confirms that the nano particles are uniformly distributed without any crack on the coated surface with microporous coatings. The cells attachment, proliferation and bone-bonding ability improved by microporous coatings. Nano composite coating at the ratio of 6:4 were tightly packed on coated 316L SS surface because of nano HAP and nano TiO₂ with the dissimilar structure in crystal get expanded on sintering. EDS spectrum confirms the presence of Ca, P, O and Ti as a main element peak of coatings, which confirmed the presence of nano HAP and nano TiO₂ coating on 316L SS sample.

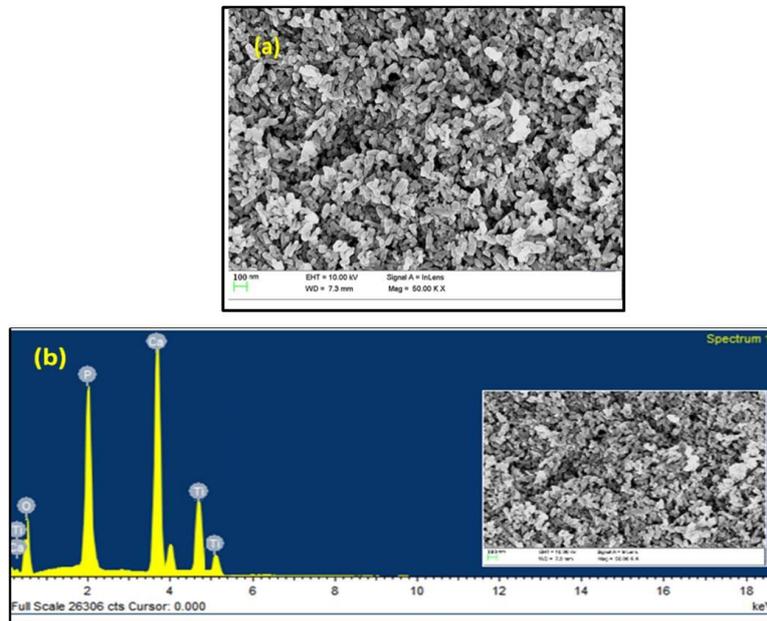


Fig. 3FESEM with EDS spectrum of nano composite coated 316L SS at the ratio 6:4

Atomic force microscopy topography of nano composite coated 316L SS at different ratios are shown in Fig. 4. The average surface roughness (R_a) of nano composite coated 316L SS at the ratio of 5:5, 6:4 and 7:3 were found to be 19.17 ± 0.02 nm, 41.10 ± 0.02 nm and 27.03 ± 0.02 nm respectively. Thus surface roughness was very high at the ratio of 6:4 when compared to other ratio coated samples. The increased surface roughness obtained at the ratio of 6:4 is due to interlocking of rough porous surface of nano HAP with nanoTiO₂ powder on uniform nano composite coated layer. Surface roughness is a one of the important characteristics for cell growth. Generally, the stability of the implant can be improved by increasing the surface roughness of the coatings. Many reports which revealed that osteoblast cell were attached more rapidly on the implants with high surface roughness. This can provide a suitable environment for the bone cells attach to the surface of the implant. Thus the nano composite coated layers at the ratio of 6:4 showed good osseointegration than other coated samples.

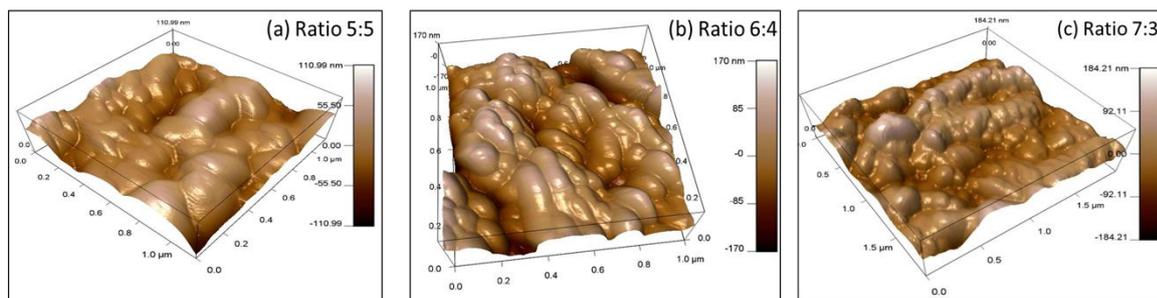


Fig.4 Atomic force microscopy of nano composite coated 316L SS at the ratio of (a) 5:5 (b) 6:4 (c) 7:3

Implants meet complex physiological environment not only have good biological properties but also obtain adequate mechanical strength for durable performance[13].The adhesive strength of the nano composite coated 316L SS samples at various ratio were tested by tape adhesion test (ASTM D3359). The nano composite coated sample at the ratio of 5:5 and 7:3 shows less adhesion property between metal and the coated layer. This results exposed delamination occurred after the adhesion test and it was categorized as 3B and 4B grade respectively. The improved adhesive strength was obtained at the ratio of 6:4 as a result of no delamination occurred after the test representing that the coating was stable and this could be categorized using the maximum grade of 5B. In this coating enhanced adhesion strength occurred due to the presence of nano TiO₂ then it forms a very strong chemical bonding with nano HAP particles along with metal surface, which was also enhanced by sintering. Enhanced adhesive strength is most important for biomedical applications [14].

The mechanical strength of uncoated and nano composite coated 316L SS samples at different ratio were measured by Vicker’s micro hardness test. A total of five microhardness measurements were carried out for each coated sample,

and the average hardness value was calculated. The hardness values for uncoated and nano composite coated 316L SS samples at different ratio are shown in Fig. 5. The obtained hardness values for uncoated 316L SS is 148 HV and the hardness value for nano composite coated samples at different ratio of 5:5, 6:4 and 7:3 were found to be 206 HV, 361 HV and 263 HV respectively. The nano composite coated samples showed considerably enhanced hardness value compared to uncoated 316L SS sample because of protective coating. The coated 316L SS sample at the ratio of 6:4 shows higher mechanical strength than other coated samples and the uncoated sample. The higher mechanical strength observed on nano composite coated samples at the ratio of 6:4 due to uniform and crack free protective coating with enhanced adhesion strength in the existence of nano TiO₂ in the composite mixture.

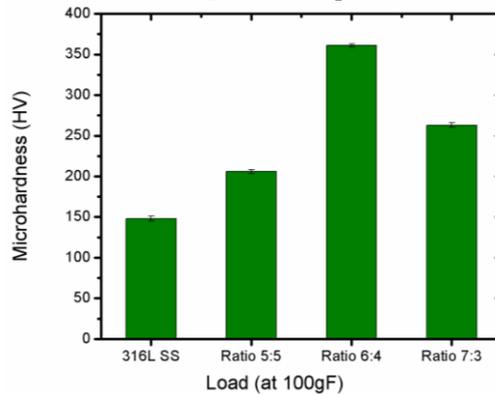


Fig. 5 Vicker's micro hardness of uncoated and nano composite coated 316L SS

Cyclic potentiodynamic polarization plots for uncoated and nano composite coated 316L SS at different ratio are shown in Fig. 6. From CPP curves, the polarization parameters such as corrosion potential (E_{corr}), breakdown potential (E_b) and repassivation potential (E_p) were measured. Table 1 shows the CPP results for uncoated and nano composite coated 316L SS sample. The corrosion potential for uncoated 316L SS was found to be -254 mV (vs. SCE) and E_{corr} value for nano composite coated 316L SS sample at the ratios of 5:5, 6:4 and 7:3 are -141 mV, 95 mV and 68 mV (vs. SCE) respectively. The E_{corr} value for nano composite coated sample at different ratio shifted to nobler direction when compared to uncoated sample and this result further confirms that the coated samples have superior passivation when compared to the uncoated sample. Among all the other coated samples at the ratio of 5:5 and 7:3, coating at 6:4 ratios shows the highest E_{corr} value because of maximum protection from the corrosion reaction. Nano composite coating at the ratio of 6:4 produced uniform layer with crack free coating, which is used to protect the metal surface from the corrosion reaction by controlling the release of the metal ion. At this ratio of 6:4, the coated layer strongly binds with the metal surface through strong adhesion strength after sintering.

Nano composite coated sample at different ratios shows the breakdown potential (E_b) in nobler direction than the uncoated sample. E_b values for uncoated 316L SS sample is 341 mV and for nano composite coated 316L SS at different ratio of 5:5, 6:4 and 7:3 were found to be 506 mV, 720 mV and 656 mV respectively. Significantly coated sample at the ratio of 6:4 has higher breakdown potential (720 mV) than the other coated and uncoated sample. This indicates that coating at 6:4 ratios provides the suitable passivity on the coated metal surface. Similarly, repassivation potential (E_p) values for uncoated and nano composite coated 316L SS sample at different ratio were found to be -239 mV, -95 mV, 314 mV and 85 mV respectively. This result shows that enhanced protection attained on nano composite coated 316L SS sample at the ratio of 6:4 due to the higher passivation of coated sample in this condition. Thus, nano composite coated sample at the ratio of 6:4 provides enhanced electrochemical properties. It shows that the superior corrosion resistances on the metal surface due to the formation of the uniform with crack free coating through the strong adhesion strength after sintering.

Table 1 Cyclic potentiodynamic polarization parameter for uncoated and nano composite coated 316L SS at different ratio in Hank's solution at room temperature

Coating parameter	Corrosion potential E_{corr} (mV) Vs SCE	Breakdown potential E_b (mV)	Repassivation potential E_p (mV)
Uncoated 316L SS	-254	341	-239
Ratio 5:5	-141	506	-95
Ratio 6:4	95	720	314
Ratio 7:3	68	656	85

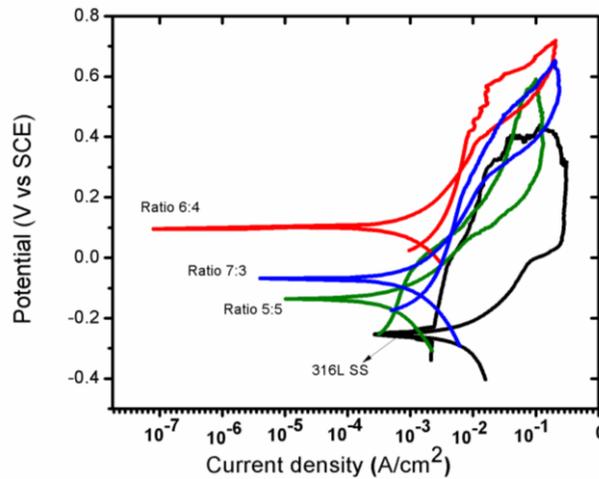


Fig. 6 Cyclic potentiodynamic polarization plots of uncoated and nano composite coated 316L SS sample at different ratio in Hank's solution

Cell viability with MC3T3-E1 osteoblast cell after 48 hours for uncoated and nano composite coated sample at the different ratios are shown in Fig. 7. Coated samples at different ratios show that more cell viability than uncoated sample. Very poor cell viability was observed for uncoated 316L SS sample due to non-protective layer on metal surface. Uncoated metal surface easily affected by corrosion reaction by release of metal ion from the metal surface. From Fig. 7, enhanced cell viability was observed on nano composite coated sample at the ratio of 6:4 than the other coated sample. Thus, the nano composite coated surfaces at the ratio of 6:4 act as a protective layer to prevent the release of the metal ion from metal surface. The improved protection is obtained at this ratio of 6:4 due to formation of uniform layer with crack free coating through the strong adhesion strength. All other coated samples at the ratios of 5:5 and 7:3 shows slightly less cell viability due to insufficient protection and less adhesion strength between coated layer and metal surface. The coated sample at the ratio 5:5 shows mild crack on the coated surface after sintering, it possible to release the metal ion from metal surface due to non-protective coating. Similarly, at the ratio 7:3 produce dense coating, it leads to less adhesion strength between coated layer and metal surface. So that coating at the ratio 5:5 and 7:3 shows less cell viability on the MC3T3-E1 osteoblast cell.

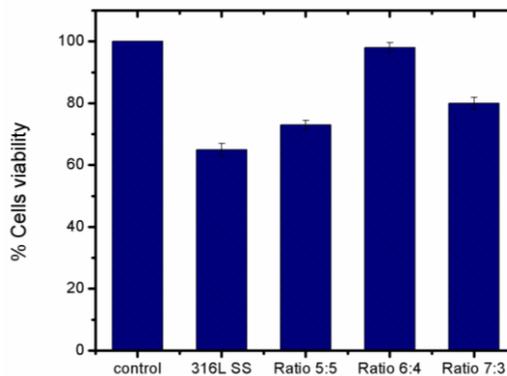


Fig. 7 Cell viability with MC3T3-E1 osteoblast for uncoated and nano composite coated 316L SS at different ratio after 48 h

V. CONCLUSION

Nano composite has been successfully deposited onto 316L SS sample at different ratios. The coating ratio for electrophoretic deposition was optimized at 6:4. XRD studies revealed the presence of nano HAP and nano TiO₂ on the nano composite coated 316L SS sample after sintering. No other peaks were detected. Optical microscopy and FESEM studies show the formation of uniform and crack free coating on metal surface at the ratio of 6:4. AFM studies proved that enhanced surface roughness was observed on the coated sample at the ratio of 6:4 when compared to other coated samples. Mechanical studies also confirm that the adhesion strength of nano composite coating is higher at the ratio 6:4 than the other coated samples. Cyclic potentiodynamic polarization study shows that nano composite coating at the

ration 6:4 act as protective coating which prevents the release of metal ion from metal surface. The cell viability was found to be higher on coated sample at the ratio of 6:4 than other coated and uncoated sample. It is mainly due to uniform with crack free coatings, improved corrosion resistance, high surface roughness and enhanced adhesion strength of nano composite coatings. Hence, it can be concluded that nano composite coated 316L SS in the ratio of 6:4 could improve the life time of implant and it can be used for orthopaedic applications.

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