



Fabrication of nanoporous Sr incorporated TiO₂ coating on 316L SS: Evaluation of bioactivity and corrosion protection



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HIGHLIGHTS

- Nanoporous Sr-incorporated TiO₂ coatings were successfully fabricated on 316L SS.
- The coatings have excellent adhesion to the substrate and appreciable Vickers micro hardness value.
- Sr-incorporated TiO₂ coated specimens exhibited excellent hydroxyapatite growth due to slow release of Sr from the coating.
- Sr incorporation enhances the corrosion resistance of TiO₂ coating.

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ABSTRACT

In this paper, nanoporous TiO₂ and Sr-incorporated TiO₂ coated 316L SS were prepared by sol–gel methodology. The effect of Sr incorporation into TiO₂ coating on bioactivity and corrosion resistance was investigated. Attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy, X-ray diffraction analysis (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) results obtained after *in vitro* bioactivity test confirm the excellent growth of crystalline hydroxyapatite (HAp) over nanoporous Sr-incorporated TiO₂ coated 316L SS which may be attributed to the slow and steady release of Sr ions from the coatings. The electrochemical evaluation of the coatings confirms that Sr-incorporated TiO₂ coating offer excellent protection to 316L SS by acting as a barrier layer. The results showed that the incorporation of Sr enhanced both bioactivity and corrosion resistance of 316L SS. Hence Sr-incorporated TiO₂ coated 316L SS is a promising material for orthopaedic implant applications.

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1. Introduction

Metallic implants such as Ti and its alloys, Co–Cr alloys, austenitic 316L SS are being widely used to reconstruct degraded human tissue in dental and orthopaedic fields. These materials are employed in load bearing applications such as bone fixation and partial/total joint replacement due to their high mechanical strength, ductility and appreciable corrosion resistance [1,2]. It has been reported that in long term applications, 316L SS is susceptible to localized attack due to aggressive biological fluids such as blood and interstitial fluid. The release of metallic ions such as Cr and Ni *in vivo* lead not only to toxicity and allergy when combined with biomolecules such as proteins and enzymes but also affect the immune response as assessed by lymphocyte proliferation [3].

It has been reported that the formation of bone like apatite is an essential prerequisite for an implant material to make direct bond to living bone when implanted in the living body [4]. This process known as osseointegration is essential to stabilize an implant *in situ*, to minimize damage and to increase overall implant efficiency. When the implants surface properties does not support new bone growth, it results in insufficient bonding of the implant with the surrounding tissue [5]. Thus, the material used as an implant should be bioacceptable, resistant to the influence of tissue environment and bioactive.

In this regard, modifying the implant surface is quite essential to develop bioactive and corrosion resistant implants. Various surface modification techniques such as plasma spray, magnetron sputtering, chemical vapour deposition, electrophoretic deposition, thermal spray etc., have been employed for developing bioactive coatings [6–8]. All these techniques have complex operating procedures. In addition, the coatings developed by these methods have poor adhesion to the substrate. An effective method, which

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surpasses these drawbacks, is sol–gel methodology as it has the efficiency to produce both one component and multicomponent coatings with controlled microstructure and high purity at relatively low temperatures [9]. Besides, it is an excellent method to either incorporate metal atoms into the crystal lattice or deposit them on the crystal boundary.

The bioactivity of various ceramic oxide coatings synthesized by sol–gel methodology such as TiO₂, ZrO₂, Na₂Ti₃O₇, etc., have been well documented [10–12]. However, there is an ever increasing need for bone implant formulations that has better bioactivity. It has been reported that Sr is a trace metal in the human bone and is very effective in the treatment of osteoporosis due to its anabolic as well as antiresorptive activity [13]. *In vitro* and *in vivo* studies have indicated that Sr in low doses increases bone formation and reduces osteoporosis, enhances the replica of pre-osteoblastic cells leading to a gain in bone mass and improved bone mechanical properties in normal animals and humans [14]. Further, it has been reported that nanoscaled morphology can guide enhanced cellular migration on the surface, promote production of bone cells and enhance both short and long term osseointegration [15].

The effect of Sr incorporation into bioactive ceramics such as Ca₃(PO₄)₂ and bioglass has been reported [13,15]. The effect of Zn incorporated TiO₂ coating is studied for its antibacterial activity and bone formability [16]. However there is no report on the effect of Sr incorporation into TiO₂ coating. Hence, in the present investigation, nanoporous TiO₂ and Sr incorporated TiO₂ coatings were developed by sol–gel technique over 316L SS and the effect of Sr incorporation in increasing the corrosion resistance and biocompatibility of the specimen was studied. The nanoporous coatings were evaluated by various surface characterization techniques and biocompatibility was evaluated by *in vitro* bioactivity test. The corrosion resistance of the coatings was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopic techniques.

2. Experimental section

2.1. Preparation of Sr-incorporated TiO₂ sol

The preparation of TiO₂ and Sr incorporated TiO₂ sols were as follows: Titanium tetraisopropoxide (TIP) (Sigma Aldrich), Iso-propanol (iPrOH) (Merck, India), Acetylacetone (ACA) (Merck, India), Polyethylene glycol 400 (PEG) (Merck, India) were used as the starting materials without further purification. The molar ratio of each chemical in the sol was 1:0.1:15:0.05:0.02 (TIP:ACA:i-PrOH:SrEH:H₂O). Iso-propanol was mixed with stoichiometric amount of ACA and PEG. The solution was vigorously stirred at 80 °C for 15 min. In order to facilitate slow hydrolysis and condensation, ACA was added. Then, TIP–i-PrOH solution was added drop by drop and vigorously stirred for another 30 min. Strontium was added in the form of strontium ethylhexanoate (SrEH, Sigma Aldrich, India) to the reaction mixture and stirring was continued for 1 h. To enable hydrolysis at a controlled rate, H₂O was added as the catalyst and the mixture was continuously stirred vigorously at 80 °C for another 3 h. The resultant clear sol was aged for 24 h to facilitate gelation. To synthesis pure TiO₂ sol, synthesis was carried out without the addition of SrEH prior to the addition of H₂O and the rest of the procedure was the same as that of Sr-incorporated TiO₂ sol.

2.2. Substrate preparation and coating process

The 316L SS specimens of size 30 × 15 × 3 mm were abraded with 400-grit silicon carbide paper, washed thoroughly with double distilled water, degreased with acetone, etched with a mixture of 15% HNO₃ and 5% HF for 2 min to remove the surface oxides, washed thoroughly with double distilled water, ultrasonically

degreased with acetone and finally dried at 40 °C. The composition of 316L SS is given in Table 1.

The specimens were then spin coated with the as prepared sol at a rotation speed of 2000 rpm for 2 min. Thus obtained TiO₂ and Sr-incorporated TiO₂ coated specimens were dried in air at 60 °C to facilitate further gelation and condensation. The dried specimens were then sintered at 450 °C for 1 h at a slow heating rate of 2 °C min⁻¹. Calcination at slow heating rate enables oxide conversion and removal of solvent and residual organics. Moreover, the oxides could crystallize during the sintering process. The specimens were then allowed to cool to room temperature gradually.

2.3. Surface characterization of the coatings

The ATR-IR spectrum of TiO₂ and Sr-incorporated TiO₂ coatings on 316L SS before and after *in vitro* bioactivity test was recorded in the 4000–400 cm⁻¹ range on a Perkin Elmer FT-IR spectrometer Spectrum Two with UATR Two Accessory and KBr window. The X-ray diffraction patterns of TiO₂ and Sr-incorporated TiO₂ coatings on 316L SS before and after *in vitro* bioactivity test was recorded with a Pan Analytical X-pert pro diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm), with 40 kV and 30 mA, at a scan rate of (2 θ) 0.02° over the range of 10–80°. The average crystallite sizes of TiO₂ and Sr-incorporated TiO₂ were determined from the most intense X-ray peak by Scherrer's equation [17].

$$\text{Crystallite size} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where, k is a constant related to the crystallite shape (0.89), β is the full width of half maximum (FWHM) of the diffraction peak. λ and θ represent wavelength and diffraction angle of the X-rays, respectively.

The surface morphology of the coatings on 316L SS before and after *in vitro* bioactivity test was characterized by scanning electron microscope (SEM) on a Hitachi Model-S 3400 with an accelerating voltage of 10–30 kV. The surface morphology of the nanoporous coatings on 316L SS was characterized by Atomic Force Microscopy (AFM) on Agilent Technology's Pico LE SPM in contact mode. Silicon cantilevers with force constants 0.02–0.77 N m⁻¹ and tip height 10–15 nm was used. The microstructures of the coated films scratched off the substrates were examined using transmission electron microscopy (JEOL 2000FX).

Hydrophilicity of the uncoated, TiO₂ and Sr-incorporated TiO₂ coated 316L SS were studied using the contact angle meter (OCA 15 EC, Data physics instruments, Germany). Drops of ultrapure water were delivered onto the specimen surface by a syringe with a set drop volume of 10 μ L at a dosing rate of 1 μ L s⁻¹. An average of 10 readings was taken for each sample and duplicate measurements were made for each type of coating.

2.4. Mechanical characterization of the coatings

The thickness of the coated films on 316L SS were measured using Elcomaster thickness meter. Tape adhesion measurements were performed on TiO₂ and Sr-incorporated TiO₂ coated 316L SS according to ASTM D 3359. Six parallel score lines were made with a separation of 1.0 mm; further six score lines were scribed

Table 1
Composition of 316L stainless steel.

Element	Cr	Ni	Mo	Mn	N	C	Fe
Wt %	17.20	12.60	2.40	1.95	0.02	0.03	Balance

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