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Nanostructured coatings for corrosion protection in reprocessing plants*

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Abstract: The main process medium in the reprocessing industry is highly oxidizing nitric acid ranging from dilute to concentrated solutions containing fission products and from room temperature to boiling conditions. Corrosion resistance of materials chosen for reprocessing plants is of prime importance for uninterrupted operation. Surface modification and coatings can significantly improve the corrosion resistance of materials. A number of surface modification and coating development works such as double oxide coating on Ti for reconditioning (DOCTOR); mixed oxide coated Ti anodes (MOCTAs); nanostructured Ti, TiO_2, TiN, and ZrN; bulk metallic glasses (BMGs); and superhydrophobic (SHB) coatings for corrosion protection are being pursued in our laboratory. Nanostructured coatings developed on Ti-like DOCTOR and MOCTAs showed improved corrosion resistance and longer life. Nanostructured Ti, TiO_2, and ZrN coatings deposited on type 304L stainless steel (SS) by magnetron sputtering technique and Zr-based bulk metallic $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ alloy deposited on type 304L SS by pulsed laser deposition (PLD) technique showed improved corrosion resistance in nitric acid. SHB coating on 9Cr-1Mo and Ti lead to improved corrosion resistance and biofouling resistance of Ti. The surface modification and coating development carried out in our laboratory for corrosion protection in reprocessing plants are briefly highlighted.

Keywords: coatings; corrosion; electrochemistry; morphology; nanostructured materials; scanning electron microscopy (SEM).

INTRODUCTION

The availability of nuclear fuel reprocessing plants with uninterrupted operation depends on the use of high-performance and reliable corrosion-resistant materials, as the failure of the component leads to leakage of radioactivity. Metals and alloys undergo some form of corrosion and surface degradation depending on the severity of the environment. The majority of engineering components fail, as a direct consequence of a surface-initiated failure due to corrosion or wear. In the nuclear industry, various environments like high temperature, liquid sodium, process water, sea water, steam, etc. are encountered, while the associated spent nuclear fuel reprocessing plant employs nitric acid as the process medium under different concentrations and temperature and molten chloride for future pyrochemical reprocessing plants. Hence, the critical components need to be surface-modified, coated, and characterized for enhancing mechanical, tribological, and corrosion properties as well as to understand the science behind

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such improvements. Surface engineering today plays a vital role in the materials used in fast breeder reactors (FBRs) and nuclear fuel cycle technologies [1,2]. Numerous coatings and surface treatments have been developed and applied to delay failure and enhance the service life of engineering components. New approaches utilizing nanoscale effects can be used to create coatings with significantly optimized or enhanced corrosion properties. One manner in which nanomaterials could impact the quality and function of nuclear component is through the use of such nanocrystalline coating. The potential of nanostructured coating for corrosion protection is immense, and surface coating technology to achieve corrosion-resistant nanostructured coatings plays an important role in protecting the structural metals. Surface engineering plays a major role in preserving precious materials and enhancing the performance of components by suitably modifying the properties of the surface while retaining the bulk intact without any degradation. The modification of surfaces with corrosion-resistant coatings can be made from micron to nano grain structures and from monolayers to millimeter thickness using conventional and advanced processes for a variety of applications. A protective nanostructured coating provides long-term protection under a broad range of corrosive conditions, extending from atmospheric exposure to full immersion in strongly corrosive solutions. Bulk metallic glass (BMG) alloys [3,4] and superhydrophobic (SHB) coatings have attracted great interest in recent years due to their potential as new engineering materials and also possess good corrosion resistance. The corrosion resistance of various components in hostile corrosive and radioactive environments determines the availability and trouble-free operation of nuclear power plants and spent fuel reprocessing plants. A few important nanostructured coating development programs for application in spent fuel reprocessing plants are mentioned in this paper.

DOUBLE OXIDE COATING ON TITANIUM FOR RECONDITIONING

The high corrosion rates obtained with commercial grades of Ti (with high Fe content, 0.05–0.1 %), especially in the weld, suggested the need for a suitable surface modification procedure for improving the corrosion resistance of the materials in both welded and wrought conditions in boiling nitric acid medium. A process known as “double oxide coating on Ti for reconditioning” (DOCTOR), which consists of anodizing for 24 h in nitric acid containing Ru, Cr, and HF, and subsequent anodic treatment in a solution of 10 % ammonium per sulfate, lead to about a threefold reduction in corrosion rates of Ti in the Huey test [5]. The main focus of this method has been on dissolution of iron segregated at the surface, formation of a stable oxide film, and conditioning of the surface film. The presence of nanocrystalline oxide particles of Ti on DOCTOR coating exhibited superior corrosion resistance (Fig. 1).

Platinized Ta and Ti electrodes were used in the reprocessing plants of other countries. Mixed oxide coated Ti anodes (MOCTAs) were developed [1,5] for application as electrodes in the electrochemical processes employed for the dissolution and the purification of the spent (U, Pu)C fuel of a fast breeder test reactor (FBTR) in India. The MOCTA electrodes developed basically consist of Ti substrate coated with $RuO_2 + TiO_2$, with or without an overlay of PtO_2. These electrodes were prepared by thermal decomposition method by which the salt solutions of Ru and Ti were applied over a pretreated Ti surface and thermally oxidized to get an adherent, conductive, and electrocatalytic coating. The MOCTA samples exhibited typical cracked-mud morphology while the application of PtO_2 layer resulted in the formation of smooth and fine-grained surface. The MOCTA coating thus prepared worked satisfactorily up to 215 h at an operating current density of 6.5 mA/cm^2 in a simulated U-containing dissolver solution; beyond this, the cell current decreased to negligible values, indicating the electrode failure [2]. Another approach to increase the lifetime of the coating was made to develop metallic coatings over Ti substrate. Pt and Pt–Ir coatings were prepared by the “thermochemical glazing” process on Ti substrates with intermittent RuO_2 and TiO_2 layers, called MOCTAG electrodes, which also showed better electrochemical performance.

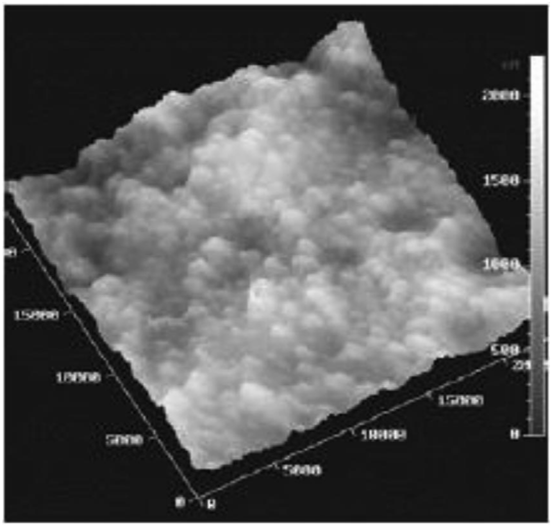

Fig. 1 AFM image of the DOCTOR-coated Ti showing the presence of fine oxide particles on the surface.

NANOCRYSTALLINE TiO_2-COATED TYPE 304L STAINLESS STEEL

Coatings such as TiO_2, SiO_2, and Al_2O_3 with very low electronic conductance or insulating properties are known to effectively protect metals and alloys from corrosive environment. Titanium dioxide (TiO_2) exhibits a wide bandgap and possesses good passivating surface with low anodic dissolution rate, making it one of the promising materials for corrosion protection [6–8]. There are a number of methods for preparing nanostructured TiO_2 coating; among which, magnetron sputtering is one of the preferred techniques for optimization of coating conditions in order to obtain the best coating properties [9,10]. The potentiodynamic polarization study of TiO_2-coated specimens showed decrease in passive current density, corrosion current density and increase in transpassive potential in 1 and 8 M nitric acid solution as compared to the uncoated condition (Fig. 2). Electrochemical impedance study of TiO_2-coated specimens revealed an increase in the magnitude of total impedance and phase angle as compared to uncoated specimens [11]. Figure 3a shows the atomic force microscopy (AFM) surface morphology of nanostructured TiO_2-coated 304L SS. The surface morphology of the polarized specimens examined using AFM after potentiodynamic polarization of TiO_2-coated stainless steel (SS) and uncoated SS in 1 M HNO_3 nitric acid is shown in Figs. 3b,c, respectively [11].

The morphology of uncoated 304L SS specimens revealed grain boundary structures after polarization, which is due to intergranular corrosion (IGC) in nitric acid medium, while the improvement in corrosion resistance of TiO_2-coated 304L SS is attributed to its inertness in an electrochemical environment, mainly owing to its dielectric property and high lattice and bond energy, which inhibit the anodic dissolution process and provide a stable and protective surface [12,13].

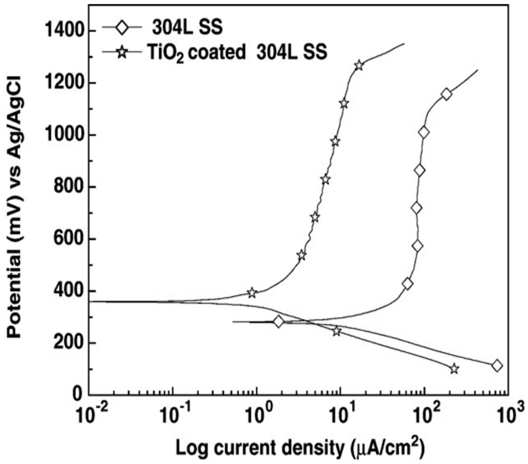

Fig. 2 Potentiodynamic polarization plot for uncoated and TiO_2-coated 304L SS in 1 M HNO_3.

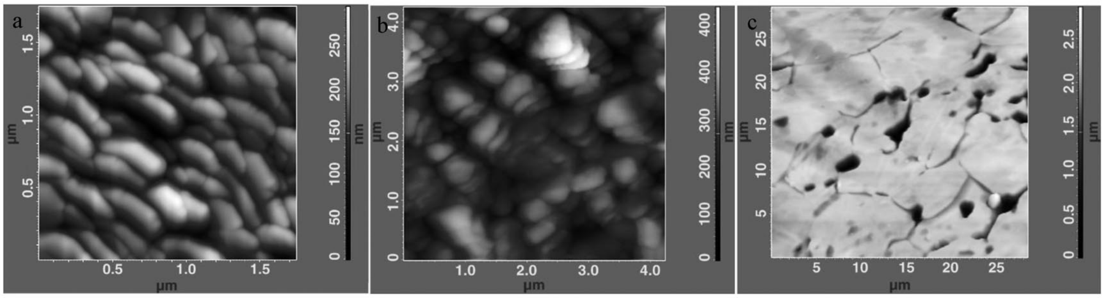

Fig. 3 AFM surface morphology of TiO_2-coated 304L SS (a) as coated (b) 1 M HNO_3 and (c) uncoated 304L SS (1 M HNO_3).

NANOCRYSTALLINE ZrN-COATED TYPE 304L STAINLESS STEEL

ZrN is a refractory compound and is attracting special attention owing to its high chemical and thermal stability, high hardness, low electrical resistivity, and gold-like color [14–18]. The corrosion behavior of five different ZrN-coated 304L SS considered for application in spent fuel fast reactor reprocessing plants prepared by magnetron sputtering at different substrate temperatures and sputtering pressure in nitric acid has been investigated. Figure 4 depicts ZrN coating deposited at room temperature with sputtering pressure of 15 mTorr (ZrN-1). The surface topography examined using AFM revealed the orientation in both 2D and 3D which are similar with densely compacted ZrN and oxide layer with negligible pores surmounted by small protrusions.

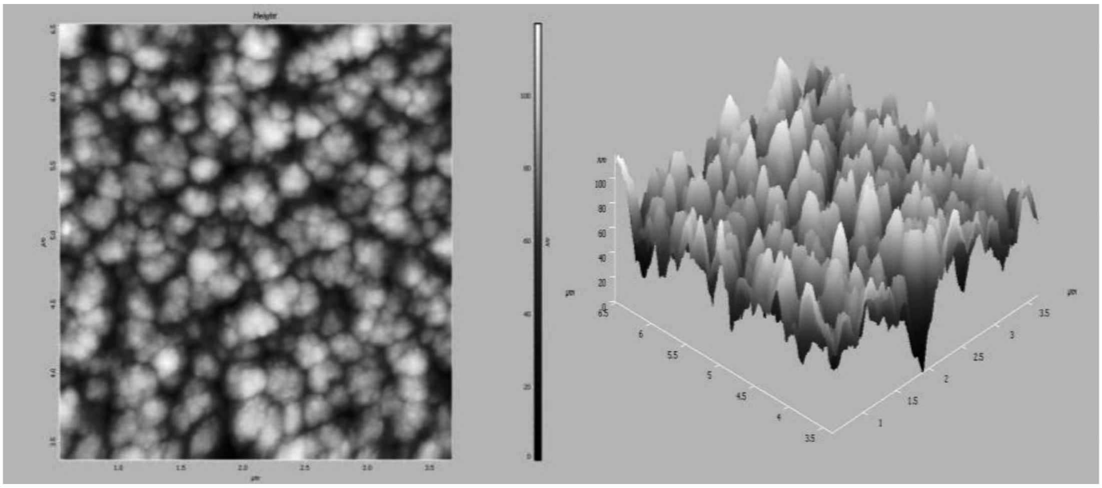

Fig. 4 Atomic force micrograph of ZrN-coated 304L SS.

The electrochemical corrosion results revealed that the corrosion performances of ZrN-coated 304L SS perform much better then the uncoated 304L SS substrate in 8 M HNO_3. The potentiodynamic polarization studies of five different ZrN-coated type 304L SS designated as ZrN-1, ZrN-2, ZrN-3, ZrN-4, and ZrN-5 and uncoated 304L SS specimen measured in 8 M HNO_3 are shown in Fig 5a. The potentiodynamic polarization test revealed that the corrosion resistance of the coated alloy is improved significantly except for ZrN-1 and ZrN-2 specimen. The Nyquist plot behavior of the impedance spectra, recorded under open-circuit conditions in 8 M HNO_3, is shown in Fig 5b. As can be observed, between the five different ZrN-coated type 304L SS, all the Nyquist diagrams showed a semi-circle arc.

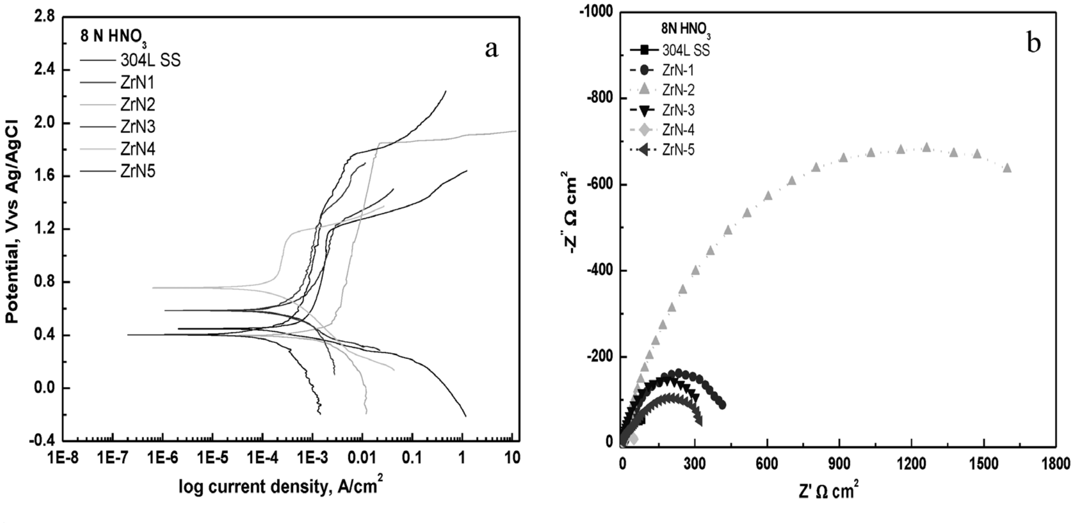

Fig. 5 (a) Potentiodynamic polarization plot, (b) Nyquist plot of ZrN-coated type 304L SS measured in 8 M HNO_3.

ZIRCONIUM-BASED METALLIC GLASS COATED TYPE 304L STAINLESS STEEL

Among bulk glass-forming systems, Zr-based multicomponent alloys possess great potential for application in nitric acid environments [19–21], in comparison with conventional materials such as AISI 304L SS which undergoes severe general and IGC attack in concentrated nitric acid media [2]. Pulsed laser deposition (PLD) technique has been widely used for depositing thin film materials of technological interest [22]. A great advantage of PLD is the retention of the stoichiometry of virtually any target material during the deposition, and PLD is one of a few deposition techniques that can deposit coatings at room temperature (to retain the glassy structure) and with moderate energy (ranging from 10 to 100 eV of the ablation species) that is sufficient to densify the coating and provide enhanced adhesion [22]. Zr-based bulk metallic $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ alloy was successfully deposited on type 304L SS using PLD technique as shown in Fig. 6a.

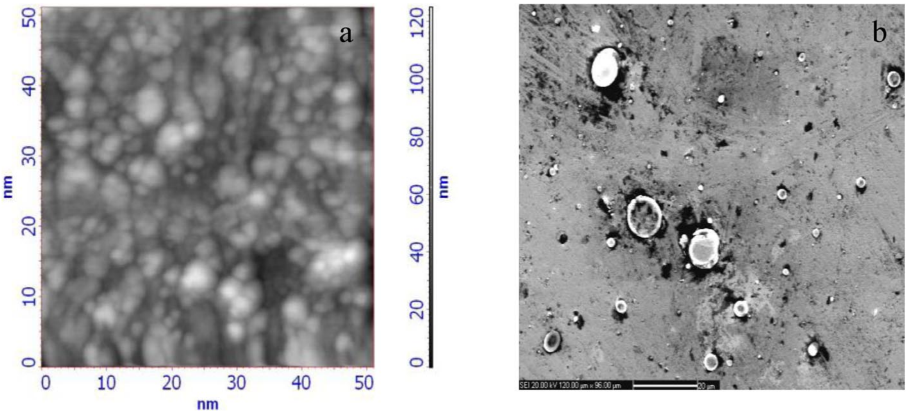

Fig 6 (a) Surface morphology of BMG $Zr_{59}Ti_3Al_{10}Cu_{20}Ni_8$ alloy coated 304L SS (b) after corrosion test in 11.5 M HNO_3.

The surface topography measurement using AFM revealed the formation of granular clusters with negligible pores in metallic glass-coated sample. The corrosion resistance of BMG-coated 304L SS was compared in different nitric acid concentrations. The potentiodynamic polarization results clearly revealed the effects of nitric acid concentration in BMG-coated 304L SS. The enhanced dissolution was observed in highly aggressive 11.5 M HNO_3. As shown in Fig. 7a, a similar trend could be observed for BMG-coated 304L SS with much higher I_{Pass} in 11.5 M HNO_3. However, at lower concentration below 6 M HNO_3, lower I_{Pass} can be observed for BMG-coated 304L SS, thereby revealing lower metal dissolution. A distinct difference was observed in the Nyquist plot for $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ alloy in 1, 6, and 11.5 M HNO_3, indicating the strong dependence on the nitric acid concentrations (Fig. 7b), which is due to the differences in the stability of passive film [21]. The marginally lower corrosion resistance observed in BMG-coated 304L SS can be attributed to corrosion attack observed around secondary-phase particles distributed in the amorphous matrix (Fig. 6b).

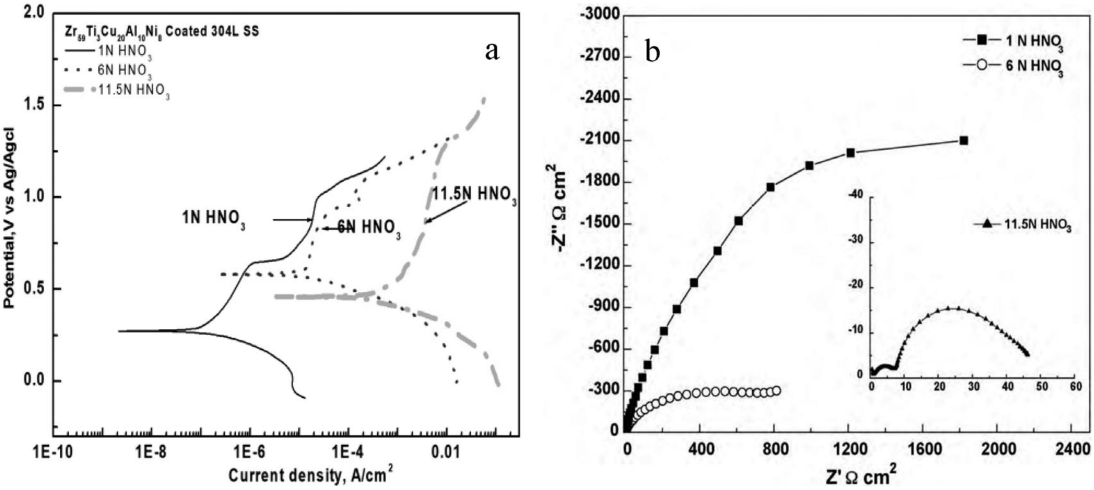

Fig. 7 (a) Potentiodynamic anodic polarization plot, (b) Nyquist plot of BMG $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ alloy coated 304L SS measured in 1, 6, and 11.5 M HNO_3.

NANOSTRUCTURED NITRIDE COATINGS FOR URANIUM MELTING APPLICATIONS

Cathode deposit consolidation operation after electrorefining of spent metallic fuels of FBRs involves melting of U and Pu at 1300 °C after distillation of occluded chloride salt and Cd, in graphite crucibles. Nitride coatings possess high hardness, melting point, and thermodynamic stability against reactive materials, and molten LiCl–KCl salts have greater potential for coating the graphite crucibles. Nitride coatings on high-density graphite crucibles deposited by PVD technique are considered for U melting applications in cathode processor. Toward this nanocrystalline TiN, ZrN and Ti–Si–N were deposited on high-density graphite crucibles by magnetron sputtering technique. Preliminary tests conducted on TiN, ZrN, and Ti–Si–N coated high-density graphite crucibles with U indicated that TiN and Ti–Si–N coating offers better stability and ease of ingot release. There is no major difference in the surface morphology of nanocrystalline TiN coating before and after U melting as shown in Figs. 8a,b [23].

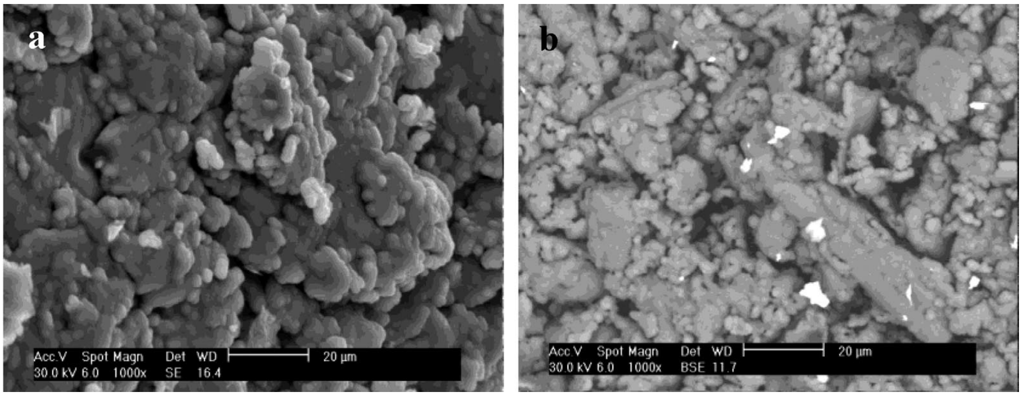

Fig. 8 (a) SEM micrograph of as-deposited nanocrystalline TiN, and (b) after U melting experiment.

SUPERHYDROPHOBIC COATINGS OVER TITANIUM

The lotus leaf is a famous example of a naturally occurring SHB surface, where water droplets falling onto them bead up and roll off. Recently, a lot of attention has been attributed to SHB coating on material surfaces. Surfaces whose contact angles exceed above 150° are known as SHB surfaces. Attempts were made to develop SHB surfaces resistant to nitric acid environments over Ti by dip-coating method using myristic acid as the SHB coating material. SHB coatings of myristic acid were also made on 9Cr-1Mo surface, and the coatings were stabilized in chloride medium by baking at 110 °C for 1 h. The results showed that the SHB-coated 9Cr-1Mo steel showed increased corrosion resistance and good coating stability (Fig 9a). Electrochemical impedance spectroscopy (EIS) results (Figs. 9b,c) showed that SHB coating on 9Cr-1Mo and Ti has high R_p value and low capacitance value than uncoated, which infers the coatings on these surfaces were stable and there was a significant increase in the corrosion resistance. These results indicate SHB surface prepared by coating myristic acid on 9Cr-1Mo and Ti surfaces leads to increased corrosion resistance and biofouling resistance of Ti surfaces.

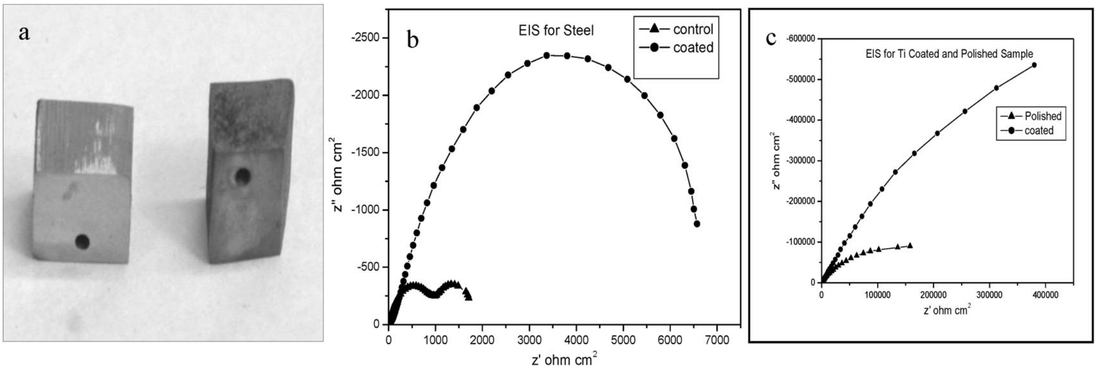

Fig. 9 (a) Photograph showing absence of corrosion on coated 9Cr-1Mo sample and corrosion on uncoated sample, (b and c) EIS analysis of SHB coated and uncoated 9Cr-1Mo and Ti surfaces, respectively.

CONCLUSIONS

Corrosion resistance of materials chosen for reprocessing plants is of prime importance as the process medium used is highly corrosive. As metals and alloys undergo severe corrosion and surface degradation depending on the severity of the environment, the challenge is to improve the corrosion resistance by suitable surface modification and coatings. Nanostructured coatings offer a great opportunity to improve corrosion resistance apart from unique combination of properties. The surface modification and coatings like Ti, TiO_2, TiN, ZrN, DOCTOR, and MOCTAs, developed in our laboratory, improved the corrosion resistance by achieving nanostructured coatings for the nuclear fuel reprocessing industry. BMGs also offer excellent corrosion resistance depending on the composition. The surface coating technique employed to deposit Zr-based bulk metallic $Zr_{59}Ti_3Cu_{20}Al_{10}Ni_8$ alloy on type 304L SS showed good corrosion resistance. Apart from increased corrosion resistance, biofouling resistance was improved by SHB coating.

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