

Corrosion Resistance Nano-hybrid Sol–Gel Coating on Steel Sheet

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Titania-containing organic–inorganic hybrid sol–gel film was developed to improve the corrosion resistance property of steel. Titania precursor was prepared from titanium-isopropoxide and methyl hydrogen silicone was used as a coupling agent to enhance the adhesion and hydrophobic nature of coating. The kinetics, thermal resistance and morphology of films were analyzed by, fourier transformed infrared spectroscopy, thermo-gravimetric and differential thermal analysis and scanning electron microscopy. The anticorrosion performance of the sol–gel coated sample was investigated by electrochemical impedance spectroscopy. The results demonstrated that coatings were dense, uniform and provided excellent corrosion resistance properties.

KEY WORDS: sol–gel; corrosion; coatings; polymer; EIS.

1. Introduction

In recent years, organic–inorganic hybrid materials, due to their enhanced coating properties, such as; resistance to scratching and abrasion, thermal stability, corrosion resistance, *etc.*, have attracted considerable attention for research. The sol–gel route is the most commonly employed method for the preparation of organic–inorganic hybrids at macro/micro-scale. Various organo metal precursors based on silicone, titanium, aluminium, and zirconium have been used in sol–gel process for synthesis of the inorganic part.^{1–6)}

The hybrid materials combine some advantages of organic polymers (easy processing with conventional techniques, elasticity and organic functionalities) with properties of inorganic oxides (hardness, thermal and chemical stability, and transparency.⁷⁾ Most of the organic–inorganic hybrid materials reported in literature is thermally cured.^{8,9)} Alternatively, hybrid network materials can be prepared by the use of radiation curing an UV-curable binder system.^{10,11)}

Nanostructure sol–gel coatings have been shown to present a promising alternative to the chromate-based surface pretreatments.^{12–16)} Among them, organic–inorganic hybrid coatings are of special interest because they combine properties of organic polymers and inorganic ceramics.^{10,17–20)} Whereas the organic components allow tailoring of hydrophobicity, flexibility, and functional compatibility with organic paint systems; the inorganic components provide an increase of scratch resistance, durability, and adhesion to the metal substrate due to the formation of covalent Me–O-metal bonds. Moreover, incorporated inorganic nanoparticles can play the role of nano reservoirs for storage and

controllable release of the inhibitor species.^{11,21,22)}

Performance of sol–gel coating, specifically adhesion and barrier properties can be enhanced by incorporating different silane groups. It has been extensively demonstrated that organosilane offers effective corrosion protection on metal.^{23–25)}

In the present work, we focus on the preparation of stable titania precursor from titania iso-propoxide and sol–gel coatings using titania precursor and methyl hydrogen silicone. We analyse the different performance like flexibility, thermal behaviour, and corrosion resistance properties *etc.*

2. Experiment

2.1. Preparation of Sol–Gel Solution

Titanium alkoxide, due to the presence of electronegative alkoxy groups is very reactive toward water and make possible for a nucleophilic attack. Therefore titanium alkoxide needs to be complexed with a chelating agent such as acetyl acetone (AcAc), methacrylic acid (MA) *etc.* to control the rate of hydrolysis.²⁶⁾ The titania sol was prepared from ethylene glycol monomethyl ether (EGME, Merck Specialities Pvt. Ltd.), titanium(IV) isopropoxide (Ti, 97% Aldrich) and acetyl acetone (AA, Merck Specialities Pvt. Ltd.). Five milliliters of titanium(IV) isopropoxide was mixed with 65 mL of EGME. The mixture was vigorously stirred (600–800 rpm) at 60°C. Then 30 mL of AcAc was added slowly into the solution. After addition of all the chemicals the sol was stirred for next 60–90 mint for getting a complete homogeneous solution as outlined by Rout *et al.* and other.^{27–30)} After 24 h of aging methyl hydrogen silicone (Shin-Etsu Chemical Co. Ltd.) was added slowly into the titania precursor in a 1 : 1 volume/volume ratio at room temperature.

3.2. Particle Size Analysis

The formulated sol gel solution is kept for 30 d to observe any precipitation or gelling, but no gelling has been noticed even after 30 d of aging. Particle size distribution of 30 d aged sol-gel solution has been measured. It is found that particle size is in the range of 2–5 nm as shown in Fig. 3. This close size range is due to the controlled growth of the particles in the sol during hydrolysis and the condensation reaction of titania precursor in the presence of water and acetyl acetone (AcAc).³²⁾ The addition of AcAc might have inhibited both hydrolysis and condensation reaction of titanium precursor.

3.3. Thermal Analysis Study

The TG-DTA curve of the cured sample as shown in Fig. 4 demonstrates very small weight loss in the temperature range of 150–200°C which are characteristic of the desorption of physically adsorbed water molecules. There is a steady weight loss between 150 and 450°C and one exothermic peak is observed at 360°C, (Fig. 4), which can be attributed to the release of chemically bounded water (around 200°C) and the decomposition of the organic components (around 300°C). DTA curve demonstrates an exothermic peak near 400°C, which can be associated with the crystallization process of an amorphous oxide.³³⁾

After 700°C only 27.80% weight loss has observed which implies about rigid and integrated polymer network formed by titania and coupling agents. One of the important observations from TGA-DTA analysis is the slow and gradual degradation of polymer hybrid and there is no sud-

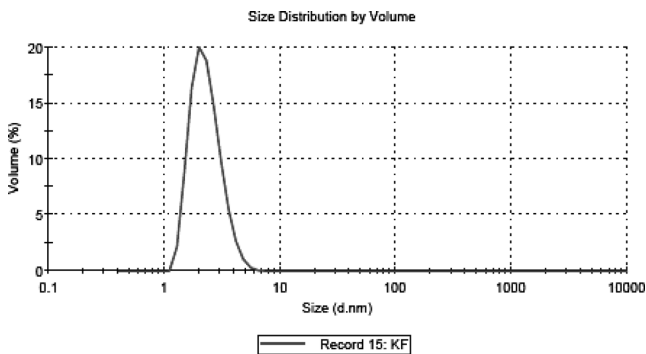


Fig. 3. Particle size distribution curve of sol-gel solution.

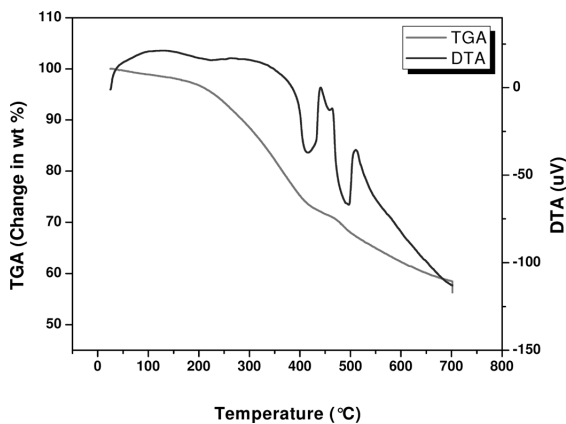


Fig. 4. TGA-DTA analysis of coated sample.

den decomposition of coating which could provide crack free surface to the applied coating even at higher temperature. This is not the case in general organic paints and coatings.

The glass transition temperature determined from the second heating cycle is found to be 72.61°C. This high glass transition temperature of cured coating, as shown in Fig. 5 indicates about high rigidity and integral cross linking network formed by titania and silane group. This integral cross linking network may create an environment for moisture and other aggressive anions which can not easily penetrate through coating and subsequently enhance the corrosion resistance of coated metal surface.

3.4. Contact Angle Measurement

The evaluation of the wetting properties, estimation of free surface energy, and hydrophobicity of the non coated and coated sample have been assessed by contact angle measurement. By applying following concept we can measured the surface energy of coated sample from the calculated contact angle.

The calculation of solid surface tension, γ_{sv} , from the contact angle, θ , of a liquid of surface tension γ_{Lv} state with Young's equation

$$\gamma_{SL} = \gamma_{sv} - \gamma_{Lv} \cos \theta \dots\dots\dots(1)$$

Where γ_{SL} is the solid liquid interfacial tension.

On the other hand, contact angle data clearly support the Equation of state (EOS) approach; where by the solid liquid interfacial tension is thought to be a function only of the total solid and liquid surface tension irrespective of the types and relative magnitudes of the intermolecular forces present within each phase.

$$\gamma_{SL} = f(\gamma_{Lv}, \gamma_{sv}) \dots\dots\dots(2)$$

If the commonly used assumption of negligible liquid vapor adsorption is applied, then Eqs. (1) and (2) may be written in term of γ_L and γ_S

An old equation of state for solid-liquid interfacial tension is that

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S \gamma_L)^{1/2} \dots\dots\dots(3)$$

Combining Eqs. (1) and (3) gives

$$\gamma_S = 1/4 \gamma_L (1 + \cos \theta)^2$$

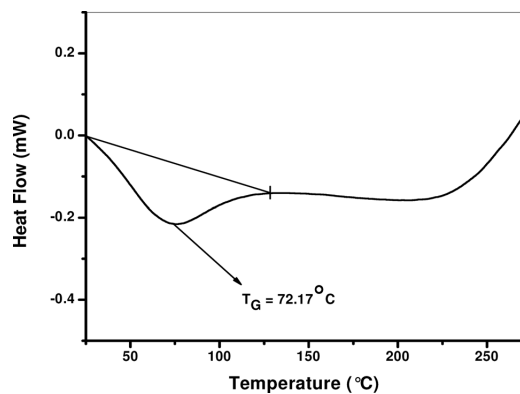


Fig. 5. Measurement of glass transition temperature (T_g) by DSC.

Contact angle of the coatings on phosphated sheet is found to be 100.96° and corresponding surface free energy measured by EOS method is found to be 22.45 mN/m (Table 1). Similarly contact angle of coating applied on CRCA sheet is found to be 98.9° and corresponding free surface energy is 23.73, which means, both the coated samples (phosphated and CRCA) impart hydrophobicity on the metal surface. As the water molecules do not retain on the surface due to this hydrophobicity, corrosion is also inhibited on coated metal surfaces.

3.5. Coating Morphology Study

The surface composition and morphology of the coating was determined with SEM/EDX using a Leo Scanning Electron Microscope (SEM) with an EDAX EDX-system for chemical analysis. Au was sputtered to suppress charging. The basic coating contains C, O, Si, and Ti along with Fe peaks. Although the EDX spectra don't supply information about chemical state of these elements we can expect that Si and Ti are present as oxides and the C is from the organic system. Oxygen is usually also present in organic polymers as hydroxyl (-OH) groups or oxides from metals. We can detect C peaks in our current EDX system at higher voltage.

It can be observed from SEM images (Fig. 6) that coating is uniform without any visible crack and there is no agglomeration of nano Ti and Si-particles in the polymer matrix films. EDX analysis of the coated sample shows that Ti

Table 1. Contact angle (C.A.) and surface free energy measurement.

Coating applied on	C.A. (Left) [Deg]	C.A. (Middle) [Deg]	C.A. (Right) [Deg]	Surface Free Energy [mN/m], by equation of state(EOS) Method
Phosphated sheet	101.0	101.0	100.9	-22.45
CRCA Sheet	98.8	98.9	99.0	-23.73
Uncoated CRCA sheet	21.5	21	21.5	-42.5

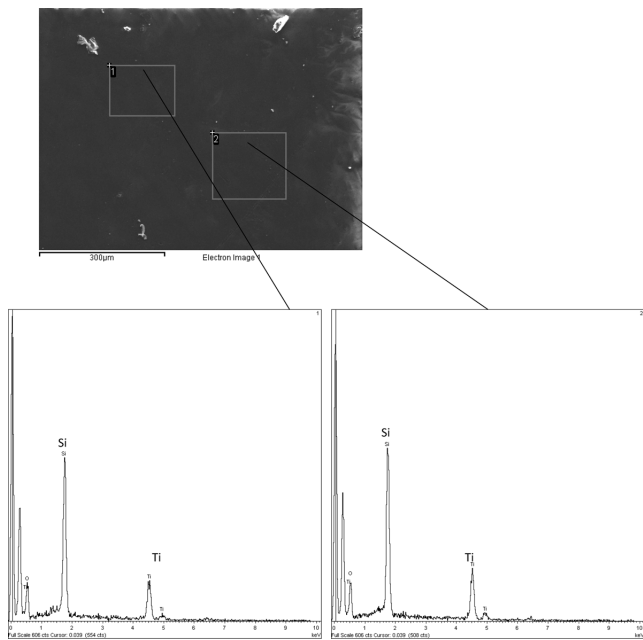


Fig. 6. SEM and EDX study of coated sample.

and Si and their Oxide completely covered the metal surface. These types of compact arrangement of particles resist nucleation and extension of micro cracks, resulting in better surface coverage, strength and toughness. The thickness of the films was estimated by the cross-section analysis (Fig. 7) and is about 5–6 µm.

3.6. Corrosion Performance Study

3.6.1. Salt Spray Study (ASTM B-117)

Salt spray result indicates about the good corrosion resistance of metal sample coated with titania sol-gel coating which may be due to the three dimensional network of polycondensation of Ti(OH)₄ and silane group and adherence to the metal substrate through hydrogen bond between functionalise titania and metal substrate immediately after application. These bonds can be transformed into stable covalent bond during the baking and curing process.¹³⁾ Even after 400 h exposure time in ASTM B117 salt spray chamber (saline environment) there is no trace of blister formation on phosphated steel sheet, (Fig 8, Table 2). After 168 h of exposure time CRCA panel has developed medium size blister which is converted to dense blister after 200 h. This

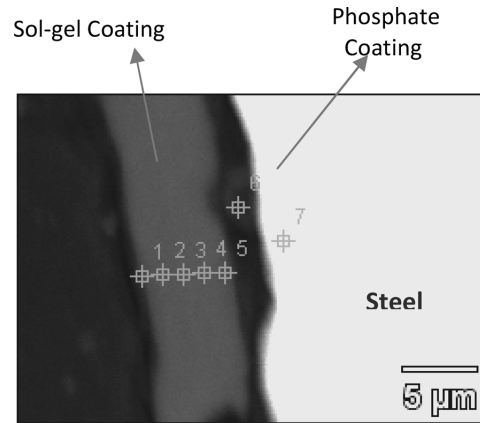


Fig. 7. Depth profile study of coated sample by SEM-EDX.

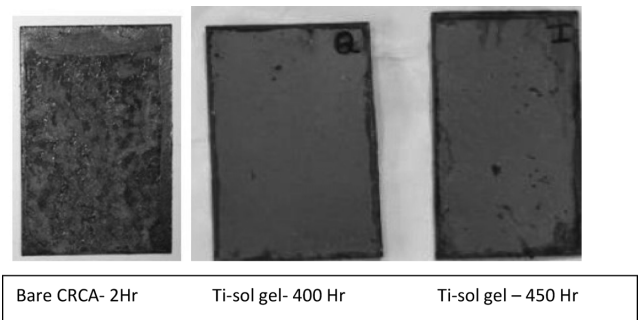


Fig. 8. Corrosion resistance study of coated samples in salt spray chamber.

Table 2. ASTM B117 salt spray test data (M-medium, D-Danced).

Surface	Exposed Time, hr							
	24	48	72	100	144	168	200	400
CRCA	Blister	10	10	10	10	10	8-M	8-D
	Red Rust	10	10	10	10	8-F	8-M	8-D
Phosphate	Blister	10	10	10	10	10	10	9-F
	Red Rust	10	10	10	10	10	10	8-M

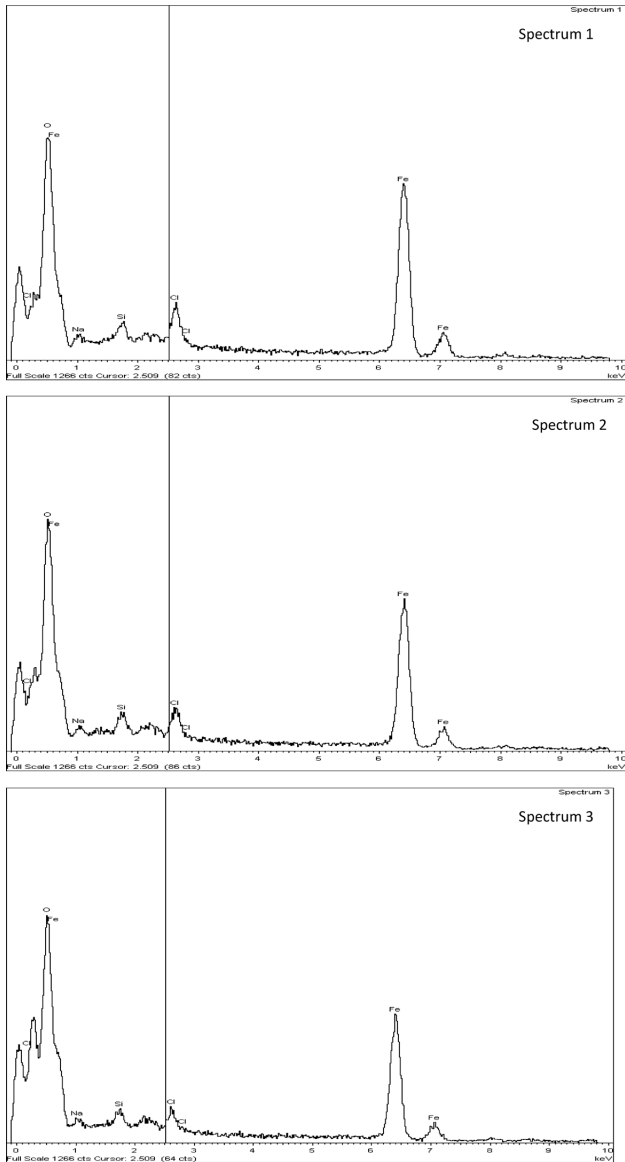
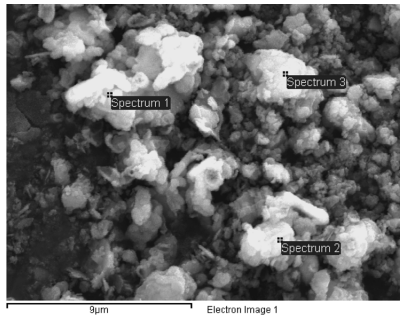


Fig. 9. SEM-EDX study of coated sample (after 400 h salt spray exposure).

coating shows good barrier and corrosion resistance properties (400 h for phosphated and 168 h for CRCA coated sample) as against bare CRCA sheet which corrodes after only 2 h of exposure. The higher salt spray resistance of the developed coating may be due to the formation of strong covalent bonds between polymer molecule and metallic surface.³⁴⁾ It is believed that well condensed net work will generate high cross linking density. Water molecule can not easily penetrate the highly cross linking network, and help to increase the corrosion resistance properties of the

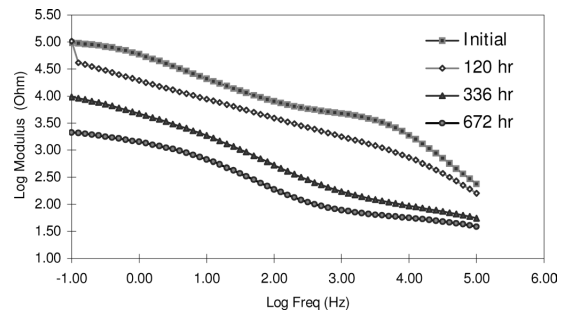


Fig. 10. EIS study of phosphated coated sample at different time interval.

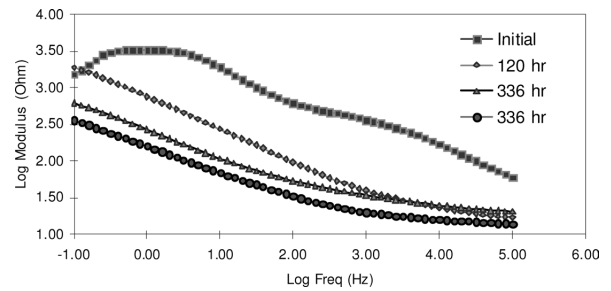


Fig. 11. EIS study of CRCA coated sample at different time interval.

coating.

After 450 h of exposure in ASTM B 117 sample shows red rust particle accumulated in some areas of the titania coated surface with the creep diameter less than 2 mm and the peripheral coated area had good intact with metal substrate, composition of this red rust particles were analysed by SEM-EDX., from the EDX spectrum, as shown in Fig. 9, it has been observed that these red rust particles are composed of Fe, Si, O, Cl and Na. This confirms that nano titania coating provides a good barrier property and even after 400 h of expose in salt spray chamber there is no free Ti-particle found in blister and rusted area (no breaking of Ti–O–Metal bond)

3.6.2. EIS Study

To assess the anticorrosive properties of the sol–gel films, immersion tests in 3.5% (w/v%) NaCl solution were performed. The corrosion behaviour of the coated substrates was studied by the EIS method. The typical impedance spectra of the samples coated with titania-containing hybrid films after different interval of time are presented in Fig. 10. One well defined time constants can be observed on the bode plots after 1-d immersion. The high frequency time constant is resulted from the capacitance of the sol–gel layer. After several days of immersion an additional time constant appears on the impedance spectrum in the low frequency region due to the started corrosion attack (Fig. 10 and Fig. 11).

The numerical fittings using the appropriate equivalent circuits were used in order to estimate the evolution of corrosion protection properties for different coatings under study. The Randal equivalent circuits were selected for fitting the experimental results basing on the physico-chemical model of the corrosion process. The hybrid coatings demonstrate the highest resistance, R_{coat} , at the beginning of

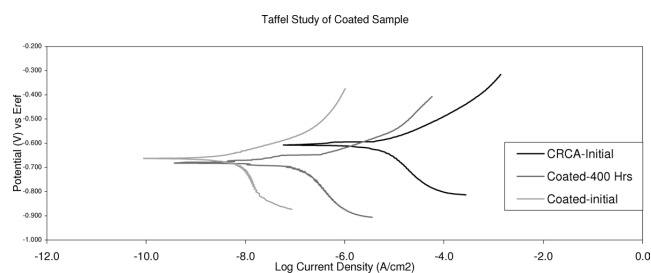


Fig. 12. Tafel polarisation study of coated sample.

immersion. However, this resistance decreases rapidly during the first 24 h of contact with chloride solution. Penetration of water molecules and chloride ions through the finest pores of the film is most probably responsible for this resistance drop. Characteristically, the initial coating resistance is significantly higher for coatings applied on phosphated sheet as compared with coating applied on CRCA sheet, and the following drop in R_{coat} is higher with coating applied on CRCA sheet. The appearance of second time constant in the initial plot for CRCA coated sheet can be ascribed to the presence of intermediate oxide film at the metal/coating interface. After several days of immersion (360 h), due to the onset of corrosion attack on CRCA coated sheet an additional time constant appears in the low frequency region on the impedance spectrum. Coatings applied on phosphated systems have almost two orders of magnitude difference in the initial R_{coat} . However, even after 672 h of immersion, the resistance in phosphated coated sample is higher than that of initial coating resistance of CRCA coated sample. It should be noted that after 120 h of immersion, CRCA coated sample demonstrates the separation of the high frequency time constant by two parts. This effect may be associated with the formation of two layers in the coating during the immersion: a more defective outer layer (first time constant) and a dense inner layer (second time constant). Taking into the account the presence of two layers, the fitting results show that the capacitance of the first layer is 30 times lower than the second one, which supports an assumption of the separation of sol-gel film this small change in impedance value is possible due to the high crosslinking density (high T_g) of the polymer net work formed by nano titania-hybrid coating and also due to the hydrophobic surface of the coating, therefore water molecules or any other corrosive ingredient do not penetrate through the surface of the coatings. This provides a good barrier property.^{35,36)}

Figure 12 shows the typical results of potentiodynamic polarisation curves of Ti-coated sample, Ti-coated sample after 400 h expose in 3.5% (w/v%) NaCl solution and bare CRCA sheet. All the measurements were carried out in 3.5% (w/v%) NaCl solution in air at room temperature. Even after 360 h of exposure in 3.5% (w/v%) NaCl solution, Ti-coated sample shows less corrosion current than bare substrate. This is due to very good barrier properties of the coating. This corrosion resistance property is supported by high contact angle, low free surface energy, and high T_g value.

4. Conclusion

As indicated by salt spray test, corrosion resistance enhanced from about 2 h to 168–400 h by nano structural sol-gel coating is due to the barrier developed between the substrate and corrosive medium. The surface coverage by the nano particles (2–5 nm) formed by controlling the growth during hydrolysis and condensation appears to be more or less uniform. The coating adhesion to the surface may be due to the formation of covalent bonds between the polymer molecules and metal surface.

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