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Synergistic effect of silane modified nanocomposites for active corrosion protection

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Abstract

This work presents an effective anticorrosion behavior of a hydrophobic surface on stainless steel 304. The protective coating has been designed by dispersing nanocomposites (cloisite 15A, multiwalled carbon nanotubes and cerium chloride) which act as a corrosion inhibitor. The sol was prepared by using 3-glycidoxypropyltrimethoxysilane (GPTMS), octyltriethoxysilane (OTES) and zirconium (IV) butoxide as precursors. The corrosion resistance of coated stainless steel got improved when nanocomposites were homogeneously embedded in silica sol. The influence of nano-particles on the barrier coatings impedes corrosion. The coatings were analyzed by X-ray diffraction (XRD) to ensure the intercalation and distribution of nanocomposites in layered silicates. Fourier transform infrared spectroscopy (FTIR) was employed to characterize the nanocomposites modified silica sol. Scanning electron microscopy (SEM) was used to examine the morphology of the modified silane coating. The contact angle measurements ensured the hydrophobic behavior of the coatings. The corrosion behavior was investigated using Electrochemical Impedance Spectroscopy (EIS). This study has led to a better understanding of active anticorrosive coatings with embedded nanocomposites and the factors influencing the anticorrosion performance. $© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.$

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1. Introduction

The environment consists of different materials in contact with atmosphere. Many structural alloys corrode merely on exposure to moisture in air. Corrosion is the deterioration of a metal and is caused by the reaction of the metal with the environment especially moisture and impurities present in air. Stainless steel (SS) 304 is an important construction material widely used in the nuclear power plants (NPPs). However, it is susceptible to undesirable degradation in oxidizing environments. The oxide film formed on stainless steel plays a vital role in enhancing degradation resistance and buildup of radiation fields. Till now, some oxidation mechanisms have been proposed to elucidate the oxidation process [\[1\].](#page--1-0) There are many methods for rendering corrosion protection through surface engineering and one such is the use of sol–gel coatings.

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Sol–gel technique is a simple process that employs low temperature curable coatings which are used for decorative purposes and also for surface protection. The surface protection mechanism could be based on providing a simple barrier coating (Inorganic and organic–inorganic hybrid-based), Inhibitor coating, sacrificial coating or a coating with self-healing property. The sol–gel technique introduces multi-functionality in the protective coatings and has been identified as a viable process for inhibitor coatings [\[2\]](#page--1-0). The most effective metal corrosion control technique consists of the electrical isolation of anode from the cathode [\[3,4\]](#page--1-0). The use of chromium oxide $(Cr₂O₃)$ passivation layer formed on the surface of stainless steel in oxidizing environments has been reported and it guarantees a better durability and corrosion resistance of this particular alloy [\[5,6\].](#page--1-0) However, chromates are now heavily restricted in corrosion control procedures due to Cr (IV) toxicity and its carcinogenic nature. Due to this negative aspect a number of promising candidates, so called green inhibitors have been explored with the hope of replacing chromates. Among them, silane group of silicon based

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organic–inorganic chemicals has emerged as a very promising alternative [\[7\]](#page--1-0). The coating efficiency can be achieved by incorporation of some inhibitor like Ce^{3+} instead of the hazardous chromates. The Ce^{3+} inhibitor efficiency is a consequence of the redox couple Ce^{3+}/Ce^{4+} . The Ce^{4+} ions are converted into insoluble Ce (IV) hydroxide that precipitate at the cathodic sites of a corroding alloy and thus blocking the corrosion process [\[8\].](#page--1-0) Many researches are thus dealing with the combination of silanes with inhibitors (cerium) [\[9\]](#page--1-0) or inhibitor nanocontainers [\[10\]](#page--1-0). Cerium nitrate added into the electrolyte showed an effective corrosion inhibiting effect on sol–gel based silane coating for magnesium alloy [\[11\]](#page--1-0). Hybrid sol–gel coatings loaded with corrosion inhibitor – cerium molybdate and 2-Mercaptobenzothiazole (MBT) has been reported [\[12\].](#page--1-0) Cerium is chosen as an inhibitor in most of the protective anti-corrosion coatings [13–[19\].](#page--1-0)

Carbon material, especially the Multiwalled Carbon Nanotubes (MWCNTs) are used as ideal reinforces for coatings due to their high strength, light weight, good geometrical properties, and also for their outstanding mechanical properties. Fabrication of well dispersed poly (N-vinylcarbazole) (PVK)/ MWCNTs done via solution mixing process in different solvents have reported good anti-bacterial and anti-corrosive coating on metallic substrates [\[20,21\]](#page--1-0). Surface of nanotubes were modified by nitric acid [\[22\]](#page--1-0) and by Dielectric Barrier discharge Plasma (DBP) [\[23\]](#page--1-0). MWCNTs have been used in coating for anti-bacterial application but more rarely in silica sol modification for corrosion barrier coatings.

A protective multilayer film formed by alternate layers of corrosion inhibitors poly cation bearing catechol group and nanoclay induces good barrier properties [\[24\].](#page--1-0) Meera et.al has reported that organically modified montmorillonite (MMT) sol–gel silica/nanoclay composites act as hydrophobic coating [\[25\]](#page--1-0). Nanocomposites membrane prepared using sulphonated poly (ether ether ketone) (SPEEK)/cloisite 15A shows good barrier properties [\[26\]](#page--1-0). In the comparative study of cloisite 15a and Cloisite $Na⁺$ for hydrophobic coatings using sol–gel method, cloisite 5A showed good result [\[27\].](#page--1-0)

The aim of this paper is to incorporate the nanoclay, MWCNTs and cerium chloride into the hybrid silica sol for the development of protective sol–gel films protects stainless steel 304 with the help of inhibitors. These acts as nanoreservoirs and inhibitors embedded in the hybrid silica network which releases the active species under an external trigger. The results show that, coatings based on silane hybrid solutions improve the corrosion resistance of the stainless steel 304 substrate by the addition of nanomaterials as inhibitors. Further, the method proposed in this work is simple to apply and compatible with actual environmental.

2. Experimental

2.1. Materials

The chemicals and reagents used for the preparation of silica sols using the precursors, such as 3-glycidoxypropyltrimethoxysilane (GPTMS), octyltriethoxysilane (OTES) and zirconium (IV) butoxide from Aldrich®, 2-butoxy ethanol $(C_6H_{14}O_2)$ and hydrochloric acid (HCl) from MERCK. Cerium (III) chloride $(CeCl₃)$ from Avra Synthesis, nanoclay (Cloisite 15A) from Southern Clay Products, Multiwalled Carbon Nanotubes (MWCNTs) from Sharda Enterprises and double distilled water were used throughout the experiments.

2.2. Preparation of sol

The sol was prepared by adding the chemicals such as GPTMS, OTES, 2-butoxy ethanol and zirconium (IV) butoxide in the ratio of 3:1:11:1respectively in 0.1 M HCl. The solution was stirred at room temperature for 24 h. The resultant sol was clear and homogeneous solution and is referred to be as GZ. To the three parts of above solution, 1% by weight each of cloisite 15A, MWCNTs and CeCl₃ were added and these sols are referred to as GZ-15A, GZ-CNT, and GZ-Ce, respectively. A pretreatment was carried out for cloisite 15A and MWCNTs and not for cerium chloride.

2.2.1. Pretreatment of MWCNTs

MWCNTs were functionalized by nitric acid [\[28\]](#page--1-0). MWCNTs were preheated to 100° C for 2 h. Then 4 M $HNO₃$ was added to the preheated MWCNTs in the ratio 3:1 by weight. The mixture was then boiled at 100 °C for 2 h and washed with distilled water to give neutral pH. The sample was then dried in oven for 2 h and sonicated in the ratio 1:36 of MWCNTs with acetone. It was dried and manually grinded in a mortar.

2.2.2. Pretreatment of cloisite 15A

Before the addition of cloisite 15A to the silica sol it was dried in an oven at 60 °C overnight and ultrasonicated with acetone for 20 min. Again it is dried in the oven and manually grinded in a mortar. With the help of an ultrasonicator the MWCNTs and cloisite 15A were dispersed to avoid agglomeration in the coatings.

2.3. Substrate and coating deposition

The substrate used for the present investigation is stainless steel 304. The chemical composition of stainless steel 304 alloy is given in the Table 1.

The substrates with dimensions of 20 mm×40 mm×1 mm were polished with emery papers of finer grit down to 1200. The polished substrates were washed with distilled water and acetone to remove all the dirt and grease. It was then dried in air. The cleaned substrates were dipped into the sol for duration of 10–15 s at a withdrawal speed of 170 mm/min. The films were dried at room temperature for 20 min, to

Table 1 Chemical composition of stainless steel 304 (wt%).

C		Mn PS Si Cr Ni Al		Fe
				0.08 2.00 0.045 0.030 0.750 20.0 10.5 0.1 Balance

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