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# Development of conversion coating on mild steel prior to sol gel nanostructured $Al_2O_3$ coating for enhancement of corrosion resistance

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ABSTRACT

A conversion coating was formulated and applied on mild steel prior to sol–gel $Al_2O_3$ coating to improve the corrosion resistance of mild steel. The comparison was made between conversion coated and conversion followed by sol–gel $Al_2O_3$ coated mild steel. The modified surfaces, produced by conversion coating and conversion followed by sol–gel $Al_2O_3$ coating were characterized by X-ray diffraction, Raman and X-ray photoelectron spectroscopy, SEM, and AFM. The corrosion resistance of the sol–gel coating was evaluated in 3.5 wt.% NaCl solution by open-circuit potential measurement, DC polarization, and electrochemical impedance spectroscopy. The sol–gel coating reduced the corrosion current density of the substrate by 5 orders of magnitude and showed barrier type protection of the substrate up to more than 1.0 $V_{SCE}$.



## 1. Introduction

Mild steel is inexpensive and widely used structural material in several engineering applications. It has, however, limited service life unless effective measures are taken to improve its corrosion and wear resistance properties [1–5]. Ceramic based coatings are increasingly used for range of industrial applications to provide wear and erosion resistance, corrosion protection, and thermal insulation [6–8]. Among ceramics, $Al_2O_3$ is quite attractive as it has very low electron conductance, which is ideal for protective coatings. Alumina coatings may be prepared by various techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD), plasma spray, ion assisted deposition and sol–gel [9]. The sol–gel method appears to be promising as it is low cost, offers good adhesion to metallic surface via chemical bonding, and easy adaptability in industries due to its simple application procedure. One of the main advantages of sol–gel method is its capacity to yield coatings with a wide range of compositions on different substrates without limitation of size or geometry of the work piece [10].

Alumina based coatings by sol–gel method have been studied extensively for corrosion protection of stainless steel and other metals that form passive layer on their surfaces [11]. The improvement in pitting resistance of stainless steel was observed with the application of alumina sol–gel coatings. Masalski et al. [12] have varied the number of alumina layers on AISI 316L stainless steel and found breakdown potential and cathodic current to decrease with increase in sintering temperature in the range 500–850 °C. This was attributed to the conversion of less resistant γ-$Al_2O_3$ to the more resistant α-$Al_2O_3$ at increasing temperature; it though increased number of defects in the coating at higher temperature [11]. In case of actively corroding metals such as iron/mild steel, loosely bound and non-protective oxide is formed at the metal/coating interface during sol–gel coating and subsequent heat treatment at higher temperatures results into poor coating properties [13]. Efforts have been made to overcome such problem by introducing iron/zinc phosphate interlayer prior to sol–gel deposition [14–17]. The phosphate interlayer has been shown to provide better adherence to sol–gel coating through mechanical interlocking. However, it did not improve the corrosion resistance of coating to a significant extent. Potentiodynamic polarization on alumina coated pre-phosphated steel showed [15,17] gradual increase in corrosion current with potential. The gradual increase of current with potential indicates the penetration of $Cl^-$ ion to the substrate through pores/defects in the coating. A barrier coating generally leads to constant current region with increase in potential during potentiodynamic polarization.

In view of above, an attempt has been made to increase the corrosion resistance of mild steel (MS) by depositing alumina coating. An important goal of this study was to formulate a suitable conversion coating to provide adherent and protective layer on MS substrate for subsequent sol–gel coating. The coatings were characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), energy dispersive X-ray analysis (EDAX) and scanning electron microscope (SEM). The performance of the coating against wet corrosion was evaluated in 3.5 wt.% NaCl solution. Open-circuit potential (OCP), potentiodynamic

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polarization, and electrochemical impedance methods were employed to investigate the corrosion resistance of the coating.

## 2. Experimental

### 2.1. Preparation of substrate

Coupons of 30 mm × 20 mm × 2 mm size were cut from mild steel plate of nominal composition (in wt.%) C-0.06, Si-0.04, Mn-1.46, S-0.01, P-0.02, and Fe-balance. The coupons were abraded successively on emery paper from 120 to 500 grit followed by degreasing with acetone and finally cleaned with ethanol.

### 2.2. Conversion coating on MS

#### 2.2.1. Preparation of silica sol

The silica sol was prepared by mixing tetraethylorthosilicate (TEOS), obtained from Aldrich, Germany, with ethanol and distilled water. The ratio of TEOS:$C_2H_5OH$:$H_2O$ was kept at 4:5.5:90.5 (v/v). The solution was stirred for 10 min and was kept for 4 days for stabilization before use [18].

#### 2.2.2. Preparation of aluminum oxy-hydroxide sol

12.5 wt.% of aqueous $NH_3$ was added drop-wise to aluminum nitrate hexahydrate solution. The resulting precipitate was filtered and washed with distilled water. The precipitate was then dispersed in distilled water to obtain 0.4 M concentration of the resultant sol.

#### 2.2.3. Formation of conversion coating

The MS coupons were dip-coated in silica sol, prepared as above. The silica coated coupons were dried at ambient conditions, followed by dip-coating with aluminum oxy-hydroxide sol. Coupons were then dried in air and subsequently heated at 500 °C for 2 h followed by furnace cooling. After cooling, the coupons were cleaned in ethyl alcohol. The conversion coating thus obtained on mild steel surface will be referred as CcMS in the forthcoming text. A few such CcMS plates were subjected to corrosion evaluation and rests were kept for sol–gel $Al_2O_3$ coating.

### 2.3. Preparation of $Al_2O_3$ sol and coatings

The $Al_2O_3$ sol was prepared by hydrolysis and polycondensation of aluminum isopropoxide (ACROS) and catalyzed by $HNO_3$ as reported elsewhere [12]. The sol thus prepared was kept for 72 h with intermittent stirring to obtain clear sol before coating. Coating was obtained on CcMS by dip-coating process in alumina sol using dip-coater (SDC 2007C, Apex instruments co., India) at a constant withdrawal speed of 30 mm/min. The coated plates were dried at ambient atmosphere for 30 min followed by heating at 250 °C for 15 min to remove the residual solvents. After repeating the process of dipping and drying for five times, coupons were then heated at 500 °C for 1 h. For comparison, sol–gel $Al_2O_3$ coating was also obtained on pre-phosphated MS as described elsewhere [14].

### 2.4. Characterization of the coatings

The phase identification of the film formed on CcMS was performed with X-ray diffractometer (Seifert, PTS 3003) using Co-Kα radiation. Almega dispersive Raman Spectroscope was used for analysis of surface film on CcMS by exciting the laser beam of He–Ne of 532 nm on the surface. The X-ray photoelectron spectroscopy measurements were carried out at room temperature using SPECS spectrometer, Germany for analyzing the film composition on CcMS surface. Ion etching to clean the specimen was carried out at 1 keV energy for 10 min; the charging effect, if any, was checked through the flood gun. The measurements were performed using Mg Kα X-ray source ($h\nu = 1253.6$ eV) in an ultrahigh vacuum of ~$5 \times 10^{-9}$ Torr with spot size of 100 μm and pass energy 20 eV. The topography of CcMS surface before and after sol gel coating was investigated by SEM at an accelerating voltage of 20 kV (JEOL 840A, Japan) and by AFM (SPA-400, SIEKO, Japan). The compositional uniformity of sol–gel $Al_2O_3$ coating was determined by point analysis through EDAX.

### 2.5. Electrochemical characterization

The electrochemical behavior of $Al_2O_3$ coating was studied in 3.5 wt.% NaCl solution at room temperature (25 °C). A conventional three electrode cell, consisting of saturated calomel (SCE), graphite, and coated MS as reference, auxiliary, and working electrode respectively, was used to study the electrochemical behavior. 1.0 $cm^2$ area of working electrode was exposed to the solution and the remaining area was covered with epoxy resin. After OCP stabilization, the AC (alternating-current) impedance measurements were made at open circuit potential with 10 mV amplitude of the sinusoidal voltage signal at applied frequencies in the range of $10^5$ to $10^{-2}$ Hz using ten points per decade. The polarization curves were recorded by sweeping the potential from −100 mV to ≥1.0 V (with respect to OCP) in the noble direction at a constant scan rate of 0.5 mV/s. All electrochemical experiments were carried out using computer controlled Potentiostat/Galvanostat/ZRA (PC4/750, Gamry Instruments, USA), DC105 Corrosion software, EIS300 Electrochemical Impedance Spectroscopy software, and Echem Analyst 5.30 for data fitting and calculation of results. The impedance and Tafel parameters were extracted by curve fitting procedure available in the software.

## 3. Results and discussion

### 3.1. Surface characterization

#### 3.1.1. Surface topography

Fig. 1 shows the surface morphology of CcMS and CcMS/$Al_2O_3$ coatings heat treated at 500 °C. The CcMS surface is fully covered with dense vermicular structure (Fig. 1a). After sol–gel $Al_2O_3$ coating ($0.36 \pm 0.03$ μm thickness), the surface appears smooth with featureless topography (Fig. 1b). The sol–gel $Al_2O_3$ coating is homogeneous and free from any defect. No change in the coating morphology is seen after prolonged immersion (240 h) in 3.5 wt.% NaCl solution and repeated anodic polarization (Fig. 1c). The EDAX at various spots on the surface of CcMS/$Al_2O_3$ coating shows uniform composition throughout the surface. The representative EDAX spectrum, shown in Fig. 2, indicates the presence of Al and O along with Fe on the surface. The Fe peak observed in the spectrum might have originated from the substrate due to higher penetration depth of X-rays.

The topography and roughness of CcMS and CcMS/$Al_2O_3$ coatings, investigated by AFM in non contact mode of operation, are depicted in Fig. 3. Different coating areas from 100 μm × 100 μm to 1.5 μm × 1.5 μm were scanned and the representative micrographs are shown in Fig. 3. The average roughness (Ra), measured diagonally, from 40 μm × 40 μm area scan are nearly 110 nm and 25 nm for CcMS and CcMS/$Al_2O_3$, respectively. Further, the AFM investigation reveals that the CcMS surface is grown as layered structure containing circular nano particles of less than 20 nm diameters (Fig. 3a); the layers being oriented in different directions. The three dimensional image (Fig. 3b) shows cluster of particles (nearly 1 μm size cluster) on the coated surface which indicates continuous growth from all possible directions. On the other hand, AFM image of sol–gel coating recorded in 100 μm × 100 μm area shows uniform $Al_2O_3$ coating on CcMS surface. At higher magnification (1.5 μm × 1.5 μm), small dots like features can be seen in agglomerates of approximately 300–350 nm diameter (Fig. 3c). The agglomerates appear like cauliflower grown in a random fashion. The particle of 10–30 nm sizes are grown and aligned one over the other. A three dimensional micrograph (Fig. 3d)