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A new strategy based on thermodiffusion of ceramic nanopigments into metal surfaces and formation of anti-corrosion coatings

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ABSTRACT

The present paper is the first report about preparation of anti-corrosion coatings based on thermodiffusion of ceramic nanopigments into metal surfaces. At first, $Cr_{1.3}Fe_{0.7}O_3$ ceramic nanopigments have been synthesized by simple and environmentally benign sol–gel method. Annealing of the gels at different temperatures ranging from 600 to 1000 °C yielded the pure rhombohedral structure. The structural evolutions and microstructural characteristics of the synthesized nanoceramics were investigated through different methods containing X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Then $Cr_{1.3}Fe_{0.7}O_3$ ceramic nanopigments were coated on mild steel surface via thermodiffusion method. The surface morphology and the corrosion behavior of the $Cr_{1.3}Fe_{0.7}O_3$ coatings were evaluated using atomic force microscopy (AFM), field-emission scanning electron microscopy (FE-SEM), electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss measurements in a solution of 2.0 M HCl. It is found that morphology of diffusion coatings affects the protective properties of mild steel. On the other hand, in extra-corrosive HCl media $Cr_{1.3}Fe_{0.7}O_3$ nanoceramic coatings provide mild steel with high protective properties.

1. Introduction

Corrosion is a natural process that reduces the binding energy in metals. It occurs at the metal/environment interfaces, and causes a deterioration of the metals and their properties. During the corrosion process the metallic ions precipitate on the metal surface and by forming corrosion film separates the metal from the aggressive environment [1]. Iron and its alloys play key roles in our daily lives because of their excellent properties, such as high mechanical and structural strengths [2]. These materials are used in different industrial and have various engineering applications. Mild steel is now the most common form of steel because its price is relatively low while it presents material properties that are acceptable for many applications. Low-carbon steel contains approximately 0.05–0.15% carbon making it ductile and malleable. Mild steel has a relatively low tensile strength, but it is cheap and easy to form; surface hardness can be increased through carburizing [3]. Therefore, mild steel due to its excellent mechanical properties is the constructional material of choice in numerous chemical and petrochemical industries as well as daily life applications. The main drawback of mild steel is its low corrosion resistance. On the other hand, it is easily attacked and solubilized in acidic media which are widely used to remove of undesirable rusts and scales in several industrial sectors [4]. Oil-well acidizing, acid-pickling, acid-cleaning and acid-descaling, are usual industrial processes for cleaning the metals surfaces. Also it is necessary to apply acid solutions to eliminate undesirable scale and corrosion products from metals. Sulfuric acid and hydrochloric acid are generally used for this purpose; but, these acids attack the metal surface and begin corrosion process. Corrosion can cause drastic damage to the metal surface and degrade its properties, thus limiting its applications [5,6].

The use of corrosion inhibitors is very important method for protecting metals from corrosion, and numerous scientists are conducting research on this area. In principle, inhibitors prevent the corrosion process of metal by interacting with the metal surface

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by adsorption through the π-orbitals, donor atoms, electron density and the electronic structure of the molecule [7–10]. Hard coatings with carbide, nitride, boride, or carbonitride of transition metals are widely used in order to increase corrosion resistance [10]. The coatings are employed in order to isolate the metal and steel surfaces from the corrosive environment and prevent the diffusion of water vapor, oxygen, or ions, which act as a source that begins the corrosion [11]. Moreover, these ceramic coatings demonstrate high dielectric strength, which generates the formation of a more noble surface [12,13]. Conventional methods for making these coatings are thermal welding, spraying, chemical vapor deposition (CVD), electroplating and physical vapor deposition (PVD) [14,15]. All of the methods are high energy consumption techniques. Additionally, sometimes toxic elements such as cadmium are used as alloy coating but now require to be replaced with more environmental friendly materials [16,17]. Coating by composites or polymers is usually not suitable for high temperature applications because of their polymeric nature. However, oxide ceramics are suitable candidates as anti-corrosion coatings to be used under harsh environmental conditions [18,19].

In this study, the surface treatment of mild steel was carried out by the thermodiffusion of $Cr_{1.3}Fe_{0.7}O_3$ ceramic nanopigments for the first time. The theory of thermodiffusion for preparation of anti-corrosive coatings was discussed. Various properties such as phase composition and particle size distribution of the ceramic nanopigments have been evaluated. The effect of $Cr_{1.3}Fe_{0.7}O_3$ thermodiffusion on the corrosion inhibition of mild steel in hydrochloric acid media was investigated.

2. Experimental

2.1. Chemicals

Iron (III) nitrate decahydrate [$Fe(NO_3)_3{\cdot}10H_2O$], ammonium dichromate [$(NH_4)_2Cr_2O_7$], stearic acid, nitric acid and hydrochloric acid were obtained from Merck company (Darmstadt, Germany). All reagents were of analytical grade and used as received without further purification. Deionized water was used throughout this study.

2.2. Synthesis of the nanopowder

$Cr_{1.3}Fe_{0.7}O_3$ ceramic nanopigments were synthesized via sol–gel method based on previous work [20]. Briefly, stearic acid was melted in a beaker at a temperature of 73 °C. Then, $Fe(NO_3)_3{\cdot}10H_2O$ and $(NH_4)_2Cr_2O_7$ were added in stoichiometric proportion to a mixture of water and nitric acid (1:1%v/v). The $Fe(NO_3)_3{\cdot}10H_2O$/$(NH_4)_2Cr_2O_7$ molar ratio was 0.7:1.3. This solution was added into the melted stearic acid. The beaker was kept in an oven at 90 °C for 48 h until a homogenous light red-brown sol was obtained. The sol was cooled down to room temperature and subsequently dried in an oven for 12 h. Finally the nanopowder was calcined at 600, 800, 900 and 1000 °C for 2 h.

2.3. Electrochemical cell

Corrosion experiments were performed in a three-electrode cell opened to air under stagnant conditions at a thermostated temperature of 25 °C. An Ag/AgCl/KCl (sat.) (Metrohm, Switzerland) and a platinum sheet (Metrohm, Switzerland) were used as the reference and counter electrodes, respectively. Corrosion inhibition tests were performed using specimens prepared from mild steel as working electrode, having the composition (wt%): C:0.027; Si:0.0027; Mn:0.34; P:0.009; S:0.003; Cr:0.008; Ni:0.03; Cu:0.007; Al:0.068; Nb 0.003, Ti 0.003, V 0.003 and Fe balance. The test specimens with dimension of 1 cm × 1 cm × 0.1 cm were used as substrate. The surface of mild steel electrodes mechanically abraded prior to use with different emery papers up to 1200 grade. The mild steel specimens were cleaned with analytical ethanol and then immersed in analytical acetone and finally washed with deionized water before coating. Then $Cr_{1.3}Fe_{0.7}O_3$ nanoceramic coatings were deposited onto mild steel specimen (working electrode) using thermodiffusion process. The process was performed by diffusion of $Cr_{1.3}Fe_{0.7}O_3$ nanopowder into the working electrode at 900 °C for 4 h. The mechanism of thermodiffusion process is discussed in Result and discussion section.

In this study, hydrochloric acid (2.0 M) was selected as corrosive solution and was prepared by dilution of analytical grade 37% HCl with deionized water.

2.4. Microstructural and electrochemical characterization

The crystal structures of the nanopigments were studied by X-ray diffraction (XRD) analysis. The diffraction patterns of the samples were obtained with a Seifert diffractometer (Model PTS 3003). The data were collected within 2θ angle from 10° to 80° using Cu K_α line ($\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) micrographs were obtained by an LEO 1455 UP analyzer (Oxford, UK). The morphology and crystallite size of the nanoceramics were investigated by transmission electron microscopy (TEM) using a Philips EM 208 electron microscope operated at an acceleration voltage of 100 kV.

The surface morphology of each specimen was studied using a 0201/A of ARA atomic force microscopy (AFM) and field-emission scanning electron microscopy (FE-SEM) (Mira 3 XMU) before and after immersion in 2.0 M HCl in the absence and presence of $Cr_{1.3}Fe_{0.7}O_3$ thermodiffusion.

Corrosion inhibition electrochemical tests of the $Cr_{1.3}Fe_{0.7}O_3$ nanoceramic coatings containing electrochemical impedance spectroscopy (EIS) and Tafel polarization were performed using an AUTOLAB model PGSTAT30. EIS studies were performed at corrosion potentials (E_{corr}) over a frequency range of 10 kHz–0.1 Hz with a signal amplitude perturbation of 5.0 mV. Then impedance data were analyzed using a Pentium IV computer and FRA software. The Tafel polarization experiments were carried out with a scan rate of 0.5 mV s^{-1} and the data were analyzed using GPES electrochemical software.

3. Results and discussion

3.1. Characterization of the $Cr_{1.3}Fe_{0.7}O_3$ nanopowder

3.1.1. X-ray diffraction

Fig. 1 represents XRD patterns for $Cr_{1.3}Fe_{0.7}O_3$ nanoceramics at different temperatures [20]. As can be observed the crystallinity of the as-prepared products was continuously improved with the increase of the calcination temperature from 600 °C to 1000 °C. Based on Fig. 1a, calcination in 1000 °C leads to formation of pure rhombohedral structure (JCPDS, Card No. 35-1112). There is no peak that could be attributed to Cr_2O_3 or Fe_2O_3.

3.1.2. Energy dispersive X-ray analysis

The chemical analysis for determination of the ceramic nanopigments composition was performed via energy dispersive X-ray spectroscopy (EDX). Fig. 2 demonstrates the EDX results of the ceramic nanopigments [20]. The spectrum shows prominent peaks of Cr and Fe. From the peaks, it is confirmed that the nanoceramics synthesized by sol–gel method. The atomic ratio of Cr/Fe detected by EDX analyzer was near stoichiometric value in $Cr_{1.3}Fe_{0.7}O_3$, confirming the expected high purity of the nanopigments.