Progress in Organic Coatings 77 (2014) 322–330

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

A comprehensive study of the green hexafluorozirconic acid-based conversion coating

H. Eivaz Mohammadloo[a,b,**], A.A. Sarabi[a,*], R. Mohammad Hosseini[a], M. Sarayloo[a], H. Sameie[b], R. Salimi[b]

[a] Faculty of Polymer Engineering & Color Technology, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran
[b] Color and Polymer Research Center, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran

ARTICLE INFO

Article history:
Received 30 July 2013
Received in revised form 13 October 2013
Accepted 22 October 2013
Available online 20 November 2013

Keywords:
Conversion coating
Hexafluorozirconic acid
Corrosion
Polarization
EIS
AFM

ABSTRACT

The effect of four practical parameters (deposition temperature, time, bath pH and concentration of Zr) on electrochemical and morphological properties of zirconium based conversion coating (ZrCC) on cold rolled steel (CRS) substrates was investigated. DC polarization and electrochemical impedance spectroscopy (EIS) measurements were used for electrochemical studies. Micro structural characterization was carried out by FE-SEM, AFM and EDS. The optimal conditions were determined as follows: solution temperature 20–30 °C, immersion time 60–120 s, pH = 4 and acid concentration of 4% vol. In such condition, corrosion resistance values were maximum and uniformity was improved. Microscopical observations revealed that ZrCC comprises a two-layered structure. The film formation mechanism of ZrCC was discussed in detail. After achieving the optimum conditions, epoxy nanocomposites were applied on ZrCC treated CRS samples and corrosion performance of fully painted system was investigated. Finally the adhesion strength of subsequently applied organic coating on ZrCC treated substrates was measured by pull-off technique which exhibited considerable high values.

1. Introduction

Most metals are inherently unstable and that is why corrosion occurs. This natural phenomenon has an enormous economic impact; however, it can be controlled, but at a cost [1]. In order to improve corrosion protection and adhesion to the next layer (organic paints and finishes), surface pretreatments are used on metal surfaces. One of these pretreatments is the application of chemical conversion coatings. Phosphate conversion coating has been widely used in various industries, for instance, automotive, agriculture and appliance. In particular, tri-cationic phosphate conversion coating on steel and galvanized steel substrates has shown good results, but phosphates are not ecologically the best option. This process has several limitations, i.e. eutrophication, requiring frequent desludging, additional sealing step to reduce porosity and expensive energy input [2–6].

Chromate conversion coatings are produced on various metals by chemical or electrochemical treatment with mixtures of hexavalent chromium and certain other compounds [3]. Although Cr (VI) conversion coatings have high corrosion resistance, good paint adhesion, and are cost-effective [4], due to the hazards associated with them (recent EU directive (2000/53/EC) on "End-of-Life Vehicles" sets stringent requirements on manufacturers to ensure that the use of environmentally hazardous heavy metals is phased out. In particular, the use of lead, mercury, cadmium and hexavalent chromium should be prohibited) there is an intensive worldwide research effort in identifying possible eco-friendly conversion coating replacements.

In the last decade, one promising new pretreatment was the application of zirconium oxide (ZrO_2) on metal surfaces by sol–gel method [7–10] or by immersion in or rinsing with hexafluorozirconic acid solution [11–16]. The nanoceramic reinforced H_2ZrF_6 conversion process is a novel study [17], but the study does not address the correlation between practical immersion parameters and the microstructure and anticorrosive performance of conversion coatings. Effective immersion parameters such as immersion time, pH value, acid concentration and treating temperature have direct influence on the coating's microstructure and corrosion performance. The use of electrochemical techniques, in particular electrochemical impedance spectroscopy was proved to be very useful. EIS not only provides results in a short time, but also the obtained data can give indications on the actual corrosion mechanisms. In addition, corrosion and coating damage may be determined prior to its visual manifestation [18–20]. As suggested

* Corresponding author at: Faculty of Polymer Engineering & Color Technology, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran. Tel.: +98 21 664542427; fax: +98 21 66418601.
** Co-Corresponding author. Tel.: +98 21 66418600; fax: +98 21 66418601.
E-mail addresses: h.mohammadloo@aut.ac.ir (H. Eivaz Mohammadloo), Sarabi@aut.ac.ir (A.A. Sarabi).

0300-9440/$ – see front matter. Crown Copyright © 2013 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.porgcoat.2013.10.006

in other literatures, combination of EIS data with other electrochemical tests such as DC polarization may lead to more authentic inferences [21].

In our previous work [22], the effects of solution pH and temperature and also immersion time on electrochemical and morphological properties of zirconium based conversion coating (ZrCC) were studied in detail. In this paper, first we reviewed previous works briefly and then investigate the effect of acid concentration on corrosion performance and morphology of ZrCC. Furthermore, practical parameters (pH, temperature, acid concentration and immersion time) were optimized during film formation. After drawing an overall conclusion from the effects of practical parameters, adhesion, corrosion performance, composition and morphological structure were studied in more details at optimized point. Finally epoxy nanocomposites were applied on ZrCC treated CRS samples and corrosion and adhesion performance of fully painted system was investigated.

2. Experimental

2.1. Materials and specimen preparation

Cold rolled steel (CRS) with the size of 3 cm × 3 cm × 0.07 cm was used as substrate to investigate conversion coating properties. The CRS was obtained from Dongbu Company. The composition of the CRS in wt% was listed as following: 0.002% C, 0.009% P, 0.006% S, 0.04% Mn, 0.03% Al, and balanced Fe. All samples were abraded to 1200 grit with SiC polishing paper. Before immersion treatment, samples were cleaned with cold deionized (DI) water and then with 10 wt% KOH solution and acetone. The conversion solution contains: H_2ZrF_6, DI water, nanoceramic metal oxide particles and pH adjuster. The pH of all treatment solutions was adjusted by addition of Parco® Neutralizer 700 (5–15% of ammonium bicarbonate, Henkel Corporation). Bonderite NT-1 was used for each treatment solution. The specimens were rinsed with deionized water after the conversion process, dried in a cool air stream and stored in a desiccator for subsequent analyses. Solution temperature, immersion time and pH were constant and equal to 25 ± 2 °C, 90 s and 4 respectively for investigation of acid concentration effect. As it is very important to understand the behavior of fully coated system, epoxy resin (Epon 828), based on diglycidyl ether of bisphenol A (DGEBA) with solid content, epoxy value and density of 95–100%, 185–192 and 1.17 g cm^{-3} respectively and amine containing hardener (Epikure F205) were purchased from Shell Chemicals. Organo-montmorillonite clay, Closite 30B was purchased from Southern Clay Products, Inc. As it was reported by the supplier, the particle size in 80% is between 2 and 13 μm [27]. Nanoparticles were added to epoxy resin at weight ratio of 3 wt% and dispersed in epoxy resin. Nanocomposites were applied over the cleaned CRS untreated sheets and ZrCC coated CRS by a film applicator (with a wet film thickness of 60 ± 5 μm).

2.2. Surface examination

The morphology of treated and untreated CRS substrates was investigated using a Field Emission Scanning Electron Microscope (FE-SEM; Hitachi, Model S4161, Japan) and Atomic Force Microscope (AFM, Ambios Tech, USA). Energy dispersive X-ray spectrum (EDS) was also used to analyze the micro-zone composition of the surface. Prior to examination, the samples were sputter-coated with a layer of gold in order to enhance picture sharpness.

2.3. Electrochemical measurements

The electrochemical studies on bare and coated specimens were conducted using AUTOLAB PGSTAT 302N. Hot melt mixture of bees wax and colophony resin was used to seal a certain area of CRS treated panels for electrochemical tests. The test was carried out in deaerated 3.5 wt% (0.6 M) NaCl solution (200 ± 2 mL) using conventional three electrode cell equipped with specimen as working electrode (1 cm^2), platinum and Ag/AgCl as counter and reference electrodes, respectively. The reference electrode was placed closer to the surface of the working electrode to minimize IR drop. The samples were immersed in NaCl solution for 5 min in order to stabilize open circuit potential (E_{ocp}). EIS studies were carried out in the frequency range of 100 kHz–10 mHz. The amplitude of the applied alternating potential was 10 mV peak to zero on E_{ocp}. The acquired data were curve fitted and analyzed using Nova 1.6 software. The potentiodynamic polarization measurements were carried out with upper and lower potential limits of ±150 mV with respect to E_{ocp}. The corrosion current density (i_{corr}) values were obtained by extrapolation of cathodic and anodic regions. At least three samples were repeated in each experiment to get reproducible results.

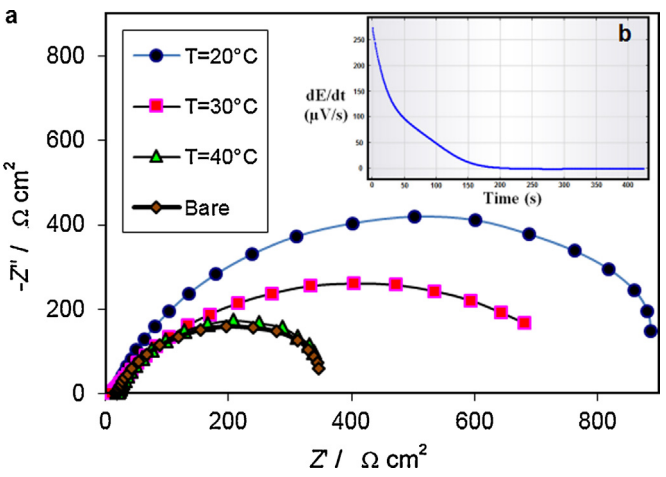

Fig. 1. Nyquist plots of CRS samples treated at different solution temperature (a) and sample of potential variation per second for conversion coated samples immersed in test solution before running DC and AC measurements.

2.4. Adhesion measurement

The adhesion strength of epoxy nanocomposites coatings to bare CRS and conversion coated CRS was determined by a direct pull-off standardized procedure via Posi test pull-off (DEFELSKO).

3. Results and discussion

3.1. Effect of practical parameters

3.1.1. Effect of solution temperature

The effect of solution temperature on electrochemical properties of ZrCC was investigated via AC (EIS) method. Fig. 1 indicates Nyquist plots of samples treated in different solution temperatures and variation of potential per second for conversion coated samples immersed in test solution before running DC and AC measurements for ensuring about OCP stabilization. In Nyquist plots, the diameter of the arc can be interpreted as polarization resistance (R_p) of the coating [25]. The electrical equivalent circuit for electrode–electrolyte interface is shown in Fig. 2. In this figure, R_s, R_p and *CPE* represent solution resistance, polarization resistance at metal–electrolyte interface and non-ideal double layer capacitance, respectively. Constant phase element (*CPE*) was used instead of capacitance in this work. For a bare metal, R_p value may be defined as the intercept of experimental impedance data with the real axis of a Nyquist plot as the frequency approaches zero, i.e.