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A comparative study of eco-friendly hybrid thin films: With and without organic coating application

H. Eivaz Mohammadloo[a], A.A. Sarabi[b,*], H.R. Asemani[c], P. Ahmadi[b]

[a] Colour, Resin & Surface Coatings Dept., Iran Polymer and Petrochemical Institute, Tehran, Iran
[b] Faculty of Polymer Engineering & Color Technology, Amirkabir University of Technology, Tehran, Iran
[c] Coatings Research Institute, Eastern Michigan University, MI, USA

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ABSTRACT

Effect of various eco-friendly surface treatments based on Titanium conversion coatings (in the presence of molybdenum, nickel, phytic and hexaflourozirconic acid compounds) on electrochemical and surface properties of steel substrates was studied comprehensively. Moreover, chromate and tri-cationic phosphate conversion coatings were used as references. Tungsten micro-electrode was used to study the film formation mechanism of conversion coatings and obtained results indicated that an increase in local pH (about 4 units) is responsible for the precipitation of coatings. FE-SEM and AFM images revealed that modification by Ni ions results in formation of uniform and pack layer structure which improves barrier properties of conversion coating. Moreover, the interaction of conversion coatings with epoxy coating was evaluated with respect to anti-corrosion and adhesion performance. Obtained results indicated that Ti-based surface treatments modified by nickel ions and phytic acid, have better adhesion strength to epoxy coating (4.2 and 4 MPa respectively) and indicated better anti-corrosion performance (according to EIS and salt-spray tests) compared to traditional chromate and phosphate conversion coatings.

1. Introduction

Cold rolled steel (CRC) substrates should be protected from different types of corrosion by application of various coatings (organic, inorganic and hybrid of them) [1]. Some organic and conversion coatings could retard corrosion rate by creation of physical barriers, insulation and increasing the adhesion forces at the interface of substrate/coating [2]. Numerous conversion coatings have been developed with the main purpose of not only being the protection of metallic substrates from corrosion but also as a pretreatment to enhance the adhesion of paints and adhesives [3]. Two kinds of traditional surface treatments for steel substrates are phosphating and chromating processes [4].

The chromate conversion coating (CrCC) provides effective corrosion protection. However, the chromating solutions include hexavalent chromium Cr(VI) which is responsible for carcinogenic effect and safety problems of CrCCs [5]. Phosphating is also a widely used process in industrial usages. Several limitations were highlighted for phosphate conversion coatings such as additional pore sealing step requirement (due to porous nature of phosphate conversion coatings), application at higher temperatures, sludge generation and eutrophication [6,7].

Accordingly, it is necessary to develop chrome-free surface treatments with the possibility of room temperature application, appropriate anti-corrosion resistance, and considerable cost savings. There have been researches in the past years over optimization of different factors affecting the performance of alternative eco-friendly conversion coatings frequently based on zirconium [8–10], titanium [11,12], cerium [13,14], lanthanum [15] and vanadium [16].

Among mentioned conversion coatings, those have based on zirconium and titanium has gained huge attention as a result of good anti-corrosion performance and wear resistance [17]. In our previous works, the morphological and electrochemical properties of H_2ZrF_6 based conversion coating on steel substrate along with optimization of solution parameters have been studied [18–20]. Besides, the effect of Ni and Mn ions addition on the performance of zirconium conversion coating has been investigated on galvanized steel and steel substrates, respectively [21,22]. The effect of this zirconium based pretreatment has also been studied when an organic coating containing anti-corrosion pigments was applied on steel substrate [23]. Furthermore, titanium-based surface treatments (H_2TiF_6 and $TiCl_4$) were prepared for steel substrate and effect of different parameters such as immersion time, pH and Ti concentration on electrochemical properties were evaluated [24,25].

There are researches regarding the improvements in the

* Corresponding authors.
E-mail addresses: h.mohammadloo@aut.ac.ir (H. Eivaz Mohammadloo), sarabi@aut.ac.ir (A.A. Sarabi).

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Table 1
Composition and details for different conversion coatings.

SampleComponents	H_2TiF_6 (g/lit)	Phytic Acid (g/lit)	Nickel Sulphate	Sodium Molybdate	H_2ZrF_6 (g/lit)
TiCC	1	–	–	–	–
TiPhACC	1	0.1	–	–	–
TiNiCC	1	–	1	–	–
TiZrCC	1	–	–	–	1
Tri-Cationic phosphate CC	Commercial				
TiMoCC	1	–	–	1	–
CrCC	Commercial				
Bare (un-treated)	–	–	–	–	–

performance of both phosphate and new generations of Cr(VI)-free conversion coatings by using different compositions of chemical solution and incorporation of additives [26–29], but something that is still insufficient in the study of such new generation of conversion coatings, is a comprehensive comparison between conventional chromium or phosphate based pretreatments and recently developed chemical conversion coatings to figure out whether or not these alternatives could exhibit appropriate anti-corrosion properties in respect to conventional ones as they solve environmental and energy consumption issues.

The main goal of this research was to investigate the performance of a titanium based conversion coating and its modified pretreatments by addition of Mo, Ni, phytic and hexaflourozirconic acid and compare their performance with tri-cationic (Tri-Cat) phosphate and chromate conversion coatings. Electrochemical and anti-corrosion properties of samples with different kinds of pretreatments were studied using DC polarization and electrochemical impedance spectroscopy (EIS). Various techniques such as Field Emission Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (FE-SEM/EDS), Atomic Force Microscopy (AFM) and contact angle were also utilized for surface characterization and morphology analysis. Also, tungsten micro-electrode was served for study the precipitation mechanism of Ti conversion coating (TiCC). Moreover, effect of all different conversion coatings used in this article on adhesion and anti-corrosion performance of a subsequently applied epoxy organic coating was evaluated comprehensively.

2. Experimental

2.1. Material and surface treatments

Cold rolled steel (CRS) was used as substrate by following elemental composition: 0.03% Al, 0.009% P, 0.002% C, 0.006% S, 0.04% Mn (in wt.%) and balanced Fe. The samples were cut in size of 2 cm × 4 cm × 0.07 cm. Initially, all the samples were abraded with SiC polishing papers (400, 800 and 1200 grit respectively) to remove oxide layers and contaminants. After mechanical abrading, samples were cleaned using acetone. Afterwards, they were degreased with KOH solution for 10 min prior to conversion treatment. Samples were then immersed in a conversion solution for treatment. In case pH needed to be adjusted, diluted solutions of HCl/ NaOH were used. Samples were rinsed with deionized (DI) water between each step of preparation and also after treatment. Table 1 shows the constituents of the conversion coating solutions. To prepare phosphate conversion coatings, CRS samples immersed into conventional phosphate solution (Nasir Co.) for 5 min at 50 ± 2 °C. Also, chromate conversion coatings (Nasir Co.) have been prepared by dipping specimens in chromating solution for 2 min at room temperature according to the supplier suggestion. Epoxy/polyamide coatings (Khuzestan petrochemical) were applied on the un-treated and pre-treated CRS substrates with a dry film thickness of 30 ± 5 microns to investigate the interaction of epoxy coating with different conversion coatings.

2.2. Methods of characterization

Electrochemical experiments were conducted using AUTOLAB PGSTAT302 N instrument, with electrochemical workstation enabling three-electrode electrochemical cell measurements. A platinum rod and Ag/AgCl electrode selected as the counter and reference electrodes, respectively. Direct Current (DC) polarization and Electrochemical

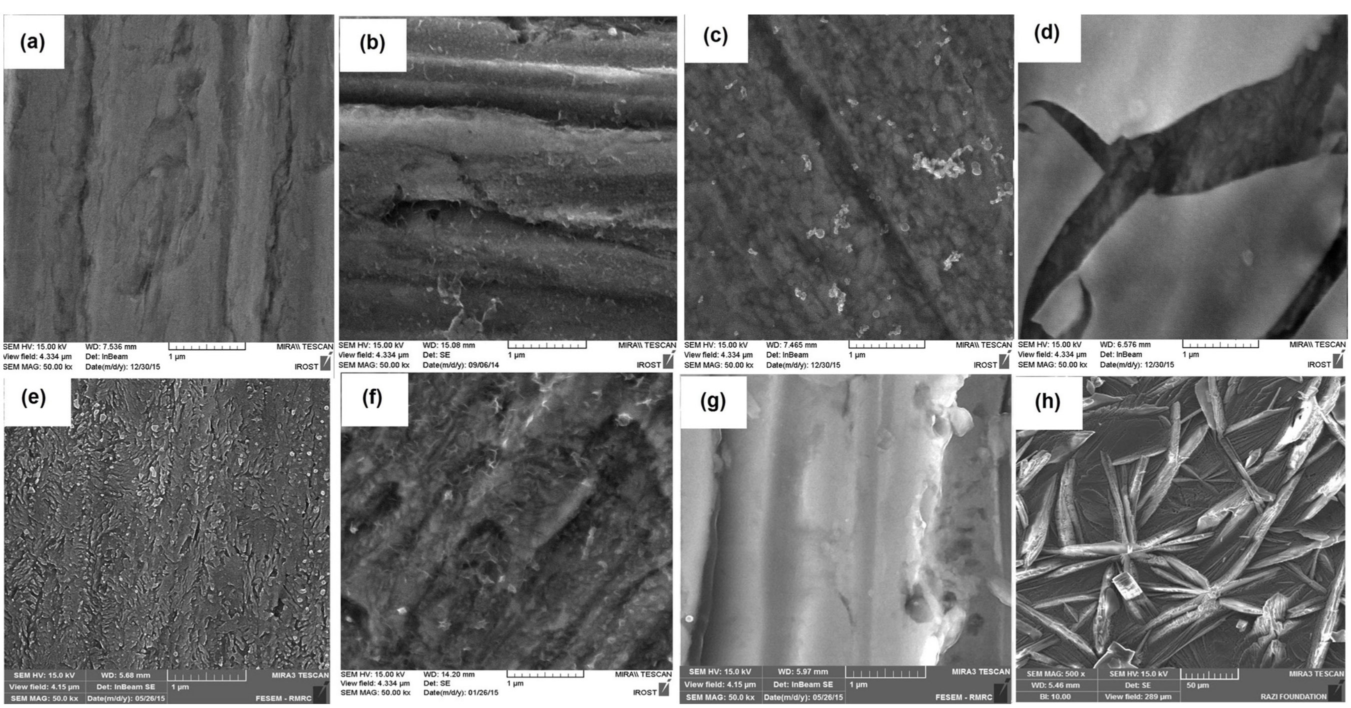

Fig. 1. FE-SEM images for bare CRS (a) and samples treated by TiCC (b), TiNiCC (c), TiMoCC (d), TiPhACC (e), TiZrCC (f), CrCC (g) and Tri-Cationic phosphate conversion coating (h).