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Surface free energy characterization and adhesion performance of mild steel treated based on zirconium conversion coating: A comparative study

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The influence of zirconium based conversion coating on the surface free energy and adhesion performance of an epoxy coated mild steel substrate was evaluated before and after post heating. Surface free energy components (γ^{LW}, γ^{+} and γ) of the mild steel were measured before and after surface treatment using van Oss–Good method. The obtained data revealed that after formation of the conversion layer, γ^{-}component of the surface increased leading to increment of work of adhesion. This may be attributed to the formation of zirconium compounds and adsorbed fluoride ion on the steel surface, which are evident in the Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray spectroscopy (EDX) results, respectively. Pull-off adhesion test was performed for variety of the surface treatments including zirconium conversion coating (ZCC) and traditional phosphate and chromate layers. The results indicate that ZCC increased adhesion strength of mild steel to the organic coating and the zirconium treated mild steel adhesion performance is better than that of the three-cationic phosphate layer.

1. Introduction

There are different ways to control corrosion occurrence including using inhibitors, coatings, applying anodic/cathodic protection and proper design [1]. Organic coatings are frequently utilized in many industries in order to protect metal surface from aggressive environments [2]. Conversion coatings are extensively used as a surface treatment prior to organic coating application in order to increase adhesion strength between metal surfaces and organic coatings and also improving anticorrosion performance of a coating system [3–5]. Chromate and phosphate conversion coatings are frequently applied for this purpose as common industrial surface treatments. However, phosphate-base pretreatment is being increasingly replaced with various alternatives because of negative environmental impacts (eutrophication), energy and process standpoints, bath sludge and being a long-lasting process [5,6]. On the other hand, chromate conversion coatings, which have been wildly used for many years, consist of large amounts of carcinogenic materials [7–9]. Attempts have been made to introduce novel conversion coatings, which are environmentally safe for nature and are performed in ambient temperature. As replacement of traditional conversion coatings, those are based on zirconium [10–14], titanium [15–18], vanadium [19,20], cerium [21] and molybdenum [22] are the most probable replacements for industrial applications.

One of the most important requirements of a coating system is adhesion strength of the coating to the underlying substrate. Adhesion is defined as the state in which two surfaces are held together by interfacial forces, which may consist of chemical and physical forces or interlocking action or both, or even simply can be defined as the force that can resist separation of two surfaces in contact [23]. The wetting of a solid surface by a liquid, adhesion phenomenon and the concept of contact angle (θ) was first proposed by Young [24]. Fowkes [25,26] suggested that the surface energy of a liquid or a solid has two parts, namely, the dispersion and polar components. Hydrogen bonding has been suggested as the main attraction force at the interfaces according to recent theoretical developments of the surface energy of solids. Good et al. [27,28] described the total surface energy as the sum of the Lifshitz–van der Waals γ^{LW} and acid–base γ^{AB} components. The Lifshitz–van der Waals component includes London dispersion forces, Debye induction, and Keesom dipole–dipole forces. The acid–base component (or hydrogen bonding) includes electron acceptor γ^{+} and electron donor γ^{-} components, which are not additives and are expressed as:

$$\gamma^{AB} = 2\left(\gamma^{+}\gamma^{-}\right)^{0.5}. \quad (1)$$

The surface free energy components of a surface can be calculated from the contact angle data of three pure liquids with known surface

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Table 1
Surface tension components of the three liquids used for contact angle measurements [29].

	γ^{TOT} (dyn/cm)	Surface tension components		
		γ^{LW} (dyn/cm)	γ^{+} (dyn/cm)	γ^{-} (dyn/cm)
Water	72.8	21.8	25.5	25.5
Formamide	58	39	2.28	39.6
Diidomethane	50.8	50.8	0.1	0.0

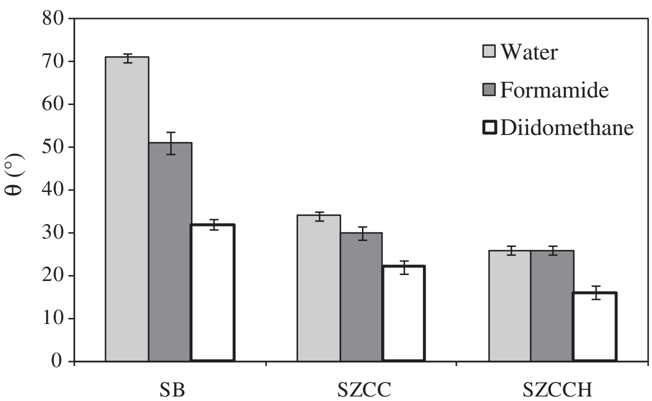

Fig. 1. Contact angles of the three liquids on the surface of three different substrates calculated from Wilhelmy plate technique at ambient temperature.

Table 2
Surface free energy components (calculated from Eq. (2)) and the work of adhesion (W_a) (calculated from Eq. (4)) of the polyamide epoxy resin on the three different substrates.

Substrate	Surface free energy components (erg/cm^2)			W_a (erg/cm^2)
	γ^{LW}	γ^{+}	γ^{-}	
S_B	42.1	0.1	10.2	83.2
S_{ZCC}	44.3	0.15	43.8	91.4
S_{ZCCH}	45.5	0.12	50.5	92.8

tension components by using the van Oss–Good methodology [29]:

$$(1+\cos\theta)\gamma_l^{TOT} = 2\left[\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{0.5} + \left(\gamma_S^{+}\gamma_L^{-}\right)^{0.5} + \left(\gamma_S^{-}\gamma_L^{+}\right)^{0.5}\right] \quad (2)$$

where the superscript l refers to liquid and s for solid and γ_l^{TOT} is the total surface free energy. Assuming a geometric mean for the interaction, the total interfacial energy between solid and liquid (γ_{SL}) is [28]:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left[\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{0.5} + \left(\gamma_S^{+}\gamma_L^{-}\right)^{0.5} + \left(\gamma_S^{-}\gamma_L^{+}\right)^{0.5}\right]. \quad (3)$$

As a result, the Young–Dupre equation [29] of the work of adhesion (W_a), the amount of energy needed to separate two surfaces, is given as:

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} = 2\left[\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{0.5} + \left(\gamma_S^{+}\gamma_L^{-}\right)^{0.5} + \left(\gamma_S^{-}\gamma_L^{+}\right)^{0.5}\right]. \quad (4)$$

Although different surface analytical techniques including X-ray Photoelectron Spectroscopy (XPS), FE-SEM, Atomic Force Microscopy (AFM) and Auger Election Spectroscopy (AES) were extensively used to surface characterization of the zirconium treated metals [3,10–12,30], there is a lack of scientific reports on the fundamental and practical adhesion performance of organic coatings to the zirconium conversion layer.

In this study, three different liquids, namely water, formamide and Diidomethane, were chosen to determine the contact angle data using dynamic contact angle measurement (Wilhelmy plate technique) and afterwards, the work of adhesion was calculated using Eq. (4). In the next step, adhesion strength of mild steel treated in different ways including traditional three cationic phosphating, chromating and ZCCs (with and without post heating) was evaluated using pull-off adhesion test.

2. Material and methods

2.1. Materials

Mild steel sheets (ST37 type) were obtained from Mobarake Steel Company. Samples were polished with a magnetic polisher to remove mill scale from the surface and followed by an acetone degreasing to remove organic contaminants. The treatment baths were prepared from hexafluorozirconic acid (Sigma Aldrich Chemical Co.) with Zr ion

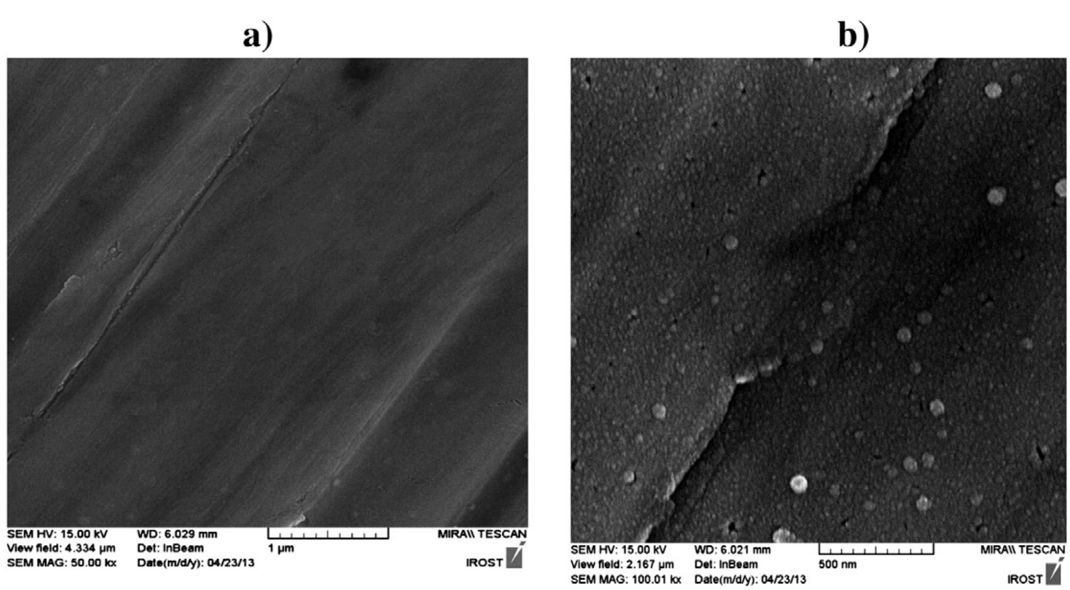

Fig. 2. The FE-SEM micrographs of the mild steel surface: (a): bare mild steel and (b): zirconium treated steel.