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Effects of surface treatment of aluminium alloy 1050 on the adhesion and anticorrosion properties of the epoxy coating

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ABSTRACT

The objective of this work is to investigate the effects of zirconium-based (Zr) conversion coating on the adhesion properties and corrosion resistance of an epoxy/polyamide coating applied on the aluminium alloy 1050 (AA1050). Field emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectrum (EDS), atomic force microscope (AFM) and contact angle measuring device were employed in order to characterize the surface characteristics of the Zr treated AA1050 samples. The epoxy/polyamide coating was applied on the untreated and Zr treated samples. The epoxy coating adhesion to the aluminium substrate was evaluated by pull-off test before and after 30 days immersion in 3.5% w/w NaCl solution. In addition, the electrochemical impedance spectroscopy (EIS) and salt spray tests were employed to characterize the corrosion protection properties of the epoxy coating applied on the AA1050 samples. Results revealed that the surface treatment of AA1050 by zirconium conversion coating resulted in the increase of surface free energy and surface roughness. The dry and recovery (adhesion strength after 30 days immersion in the 3.5 wt% NaCl solution) adhesion strengths of the coatings applied on the Zr treated aluminium samples were greater than untreated sample. In addition, the adhesion loss of the coating applied on the Zr treated aluminium substrate was lower than other samples. Also, the results obtained from EIS and salt spray test clearly revealed that the Zr conversion coating could enhance the corrosion protective performance of the epoxy coating significantly.

1. Introduction

Aluminium and its alloys have been widely used for different applications due to the combination of low density and fairly good mechanical properties. However, they show poor resistance to localized corrosion such as pitting corrosion in aqueous solutions containing complexing agents such as chloride ions (Cl^-) [1–5].

Attempts have been carried out to find proper methods in order to enhance the corrosion resistance of the aluminium and its alloys against aggressive environments. In this regard, the organic coatings are introduced as common method for protection of aluminium against chloride containing solutions. The organic coating acts as a physical barrier between corrosive electrolyte and aluminium substrate. However, the poor adhesion of the organic coatings on the aluminium surface has been become a big challenge for the researchers [6–14]. Lunder et al. [12] studied the effect of different surface pre-treatment methods on the durability of epoxy-bonded AA6016 aluminium joint by wedge adhesion measurement and filiform corrosion testing of the coated panels. They showed that surface treatment of the alloy by chromate-free pre-treatments could increase its resistance against filiform corrosion. Aluminium has very low electrochemical potential and therefore highly tends to react with the oxygen and humidity of the surrounding environments. As a result, the aluminium oxide layer composed of Al_2O_3 can be formed on the surface of aluminum immediately after exposure to the outdoor environment. The presence of such natural oxide layer on the surface of aluminium can result in poor adhesion of the organic coatings to the aluminium surface [1,2,14]. This is because of the low surface free energy and also low roughness of the aluminium surface in the presence of oxide layer, preventing the coating from good wetting leading to poor physical/mechanical bonds [15]. Therefore, when the corrosive electrolyte reaches the coating/metal interface, the hydroxyl ions (OH^-) creation on the cathodic sites (as a result of oxygen reduction reaction) would be responsible for the increase in local pH beneath the coating. This causes the adhesion bonds breakdown and the coating delamination from the aluminium surface [16]. In order to achieve reliable adhesion properties of the organic

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coatings on the aluminium surface, the naturally formed oxide layer on the aluminium surface should be removed and replaced with a new and corrosion resistant oxide layer. The most successful and widely used method of removing the oxide layer is alkaline cleaning followed by the immersion in acidic solution. These are efficient procedure to remove oxide layer, the insoluble oxides formed during the alkaline cleaning process and also intermetallic materials [14,17]. Hughes et al. [17] studied the surface treatment of the aluminium alloy 2024-T3 by various acid combinations. They found that changing the chemistry of the processing solutions could considerable affect the aluminium properties. Next step is the surface treatment of aluminium surface via suitable conversion coatings. It has been reported that conversion coating could enhance the corrosion resistance of the metal substrate and promote the paint adhesion [14,17,18]. Surface treatment of the aluminium via conversion coatings has been found as successful method to improve the organic coating adhesion properties. Chromate and phosphate based conversion coatings are the most popular kinds of chemical treatments which have been widely used for the surface treatment of aluminium and its alloys. However, the use of such conversion coatings has been gradually decreased in recent years due to theirs toxicity and carcinogenic nature [19]. Consequently, it has been tried to find non-toxic alternative processes such as rare earth [20,21], titanium or zirconium containing oxide/hydroxide coatings [22–30]. Andreatta et al. [27] studied the formation and properties of Zr and Ti conversion coatings on the surface of AA6016. It was found that surface treatment of the aluminium with these conversion coatings caused the improvement of the corrosion behavior and adhesion properties of the acrylic paint on the surface of alloy.

Conversion coatings can improve the organic coating adhesion to the metal surface by two main ways including changing the surface chemistry and topography. They can enhance the wettability of the aluminum surface by increasing its surface free energy. Changing the aluminium surface nature from hydrophobic to hydrophilic could help the organic coatings to produce strong adhesion bonds through their polar groups [16,29–32]. In fact, most of the conversion coatings include metal oxides which can produce strong chemical bonds with high polarity existing in the organic coating. For example, the epoxy coating includes hydroxyl groups which can produce strong chemical bonds with the active hydrogens of the conversion coating. Mirabedini et al. [15] studied the surface free energy of differently pretreated 1050 Al. Comparison of these results with adhesion strength measurements showed that good wettability is an essential factor in achieving relatively good dry adhesive joints, however; this cannot be considered to be a sufficient reason for the high bond strengths achieved in practice. Surface treatment of the metal surface also causes the increase of roughness. In this way, the organic coating can penetrate into the porosities of the surface making the adhesion bonds through mechanical interlocking [31].

The present study aims at studying the effects of zirconium (Zr) based conversion coating on the surface characterizes of the aluminium alloy 1050. Moreover, the adhesion and corrosion protection properties of the epoxy coating were evaluated on the AA1050 samples without and with Zr conversion coating. Field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy (EDS) and atomic force microscope (AFM) were employed in order to investigate the surface characteristics of the Zr treated samples. The surface free energy and work of adhesion were also obtained by measuring water contact angle on the untreated and Zr treated samples. The effects of Zr conversion coating on the adhesion and corrosion protection properties of the epoxy coating were also studied by pull-off, EIS and salt spray tests.

2. Experimental

2.1. Materials

Aluminium alloy 1050 (AA1050) specimens (having thickness of 2 mm) with the composition given in Table 1 were supplied by Arak Al Co.

Acetone, nitric acid (HNO_3) and sodium hydroxide (NaOH) (prepared from Mojallali Co. and Merck Co.) are the materials used to prepare the Zr conversion coating bath.

2.2. Surface preparation of AA1050

The surface of aluminum panels was degreased by acetone followed by chemical etching. The chemical etching was done by immersing the degreased aluminium samples in 5% w/w NaOH solution (alkaline etching) at 50 °C for 3 min [1]. In this process, the oxide and any deformed layers presented on the surface of aluminium can be carefully removed. Then, the etched samples were washed with distilled water and then were immersed in the acid etching (desmutting) solution composed of 50% v/v nitric acid solution for 1 min (at ambient temperature) [1]. Finally, the desmutted samples were washed with distilled water. All prepared samples were kept in a desiccator before coating application, for preventing the occurrence of further corrosion on these samples.

2.3. Surface treatment of AA1050 with Zr conversion coating

The surface prepared aluminium samples were dipped in hexafluorozirconic acid (H_2ZrF_6) based solution with Zr concentration of 100 mg/l in deionized water. The pH of the solution was adjusted to 4.5 using sodium hydroxide (NaOH 0.1 M). The surface treatment was done at ambient temperature for 3 min.

2.4. Epoxy coating application

The epoxy/polyamide coating was applied on the surface of aluminum panels before and after Zr treatment. The epoxy resin used was Araldite GZ7 7071X75 (based on bisphenol-A in a xylene solution). The solid content, epoxy value and density of the resin were 74–76%, 0.1492–0.1666 Eq/100 g, and 1.08 g/cm^3, respectively. The epoxy coating was prepared through mixing the epoxy resin with polyamide hardener (in which the ratio of epoxy resin to hardener was 70:40 w/w). Moreover, additives like leveling agent (BYK-306) and defoamer (Efka-2025) were added to the coating formulation to enhance its film formation performance. Finally, the coatings prepared were applied on the aluminium samples with and without Zr conversion coating. The epoxy coating was applied on the aluminium surface via film applicator. Samples were then cured in an oven at 120 °C for 30 min. A dry film thickness of 40 ± 5 μm was measured on the cured samples.

2.5. Methods

2.5.1. Surface characterization of Zr treated samples

The topography and chemical composition of the AA1050 samples with and without Zr conversion coatings were studied by FE-SEM (Mira) equipped with EDS model SAMx. An Ambios model AFM was used in order to investigate the topography of the Zr treated sample. Static contact angles were measured on different

Table 1
Chemical composition of AA1050 (% w/w).

Others	Zn	Mg	Mn	Cu	Fe	Si	Al
0.03	0.01	0.03	0.03	0.01	0.23	0.08	99.58