



# Effects of combined surface treatments of aluminium nanoparticle on its corrosion resistance before and after inclusion into an epoxy coating



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## ABSTRACT

Aluminium nanoparticles were modified by cerium oxides/hydroxides in order to enhance their corrosion resistance. Then, Ce-Al nanoparticles were functionalized with 3-aminopropyltriethoxy silane (APTES) to enhance their dispersion properties and interfacial interactions. Surface chemistry of the Ce-Al nanoparticles was characterized by energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). Field emission scanning electron microscopy (FE-SEM) was utilized to investigate the surface morphology of nanoparticles before and after modification by cerium nitrate. Furthermore, nanoparticles modified with APTES were characterized by Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA). The corrosion resistance of the Ce-Al, Si-Al and Si-Ce-Al samples was studied by measuring the volume of hydrogen gas evolved in an acidic solution. The effect of three types of modified nanoparticles (Ce-Al, Si-Al and Si-Ce-Al) on the corrosion protection properties of the epoxy coatings was studied by an electrochemical impedance spectroscopy (EIS). Results obtained from FE-SEM analysis revealed that the surface modified aluminium particles remained unchanged after modification with cerium nitrate in acidic solution. It was revealed that surface treatment of Ce-Al nanoparticles by APTES changed their surface nature to more hydrophobic and enhanced their dispersion properties in the epoxy coating. Deposition of Ce oxide/hydroxide layer on the nanoparticles surface was realized by XPS and EDS analyses. It was shown that surface modification by Ce film and functionalization of the nanoparticles by APTES significantly enhanced their corrosion resistance. It was shown that addition of Ce- and Si-modified nanoparticles significantly improved the corrosion protection properties of the epoxy coating. Better results were obtained when Si-Ce-Al nanoparticles were incorporated into the coating.

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## 1. Introduction

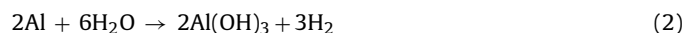
Organic coatings have been commonly used on the metal substrates to protect them against corrosion. In fact, the organic coating acts as a physical barrier between the metal surface and the corrosive environment. However, water and oxygen can penetrate through all polymeric coatings to some extent [1,2]. Features, such as light weight, bright appearance and barrier properties, have made the aluminum pigment as an attractive material for the researchers [3,4]. In recent years, corrosion inhibitive pigments of nanometric size are highly regarded due to their special properties

[5–7]. Aluminum nanoparticles, in particular, have attracted considerable attention and their application in the corrosion inhibitive coatings has become a research field of interest. Because of the high specific surface area and small particle size, aluminium nanoparticles can affect the barrier and mechanical properties of the organic coatings [6,8]. High electrochemical reactivity and tendency of aluminium nanoparticles for reaction with oxygen and moisture causes an oxide layer formation on their surface that prevents further corrosion. But this layer is unstable at low (<5) and high (>8) pHs resulting in passive layer decomposition which reduces its life span and protective behaviour in corrosive environments [9,10]. Therefore, surface modification of aluminium nanoparticles is an important issue due to their inherently high electrochemical and

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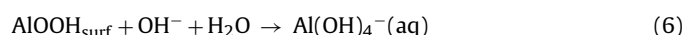
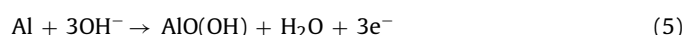
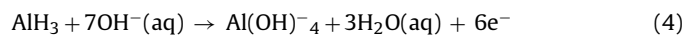
chemical reactivity. The corrosion reactions of Al nanoparticles in acidic and alkaline pHs are listed below [3,11–14]:



(under neutral media)



(under acidic media)



(under alkaline media)

Consistent effort has been made to find effective and environmental friendly methods of inhibiting the corrosive ions attack to the aluminium pigments. One of the most common ways is removing and replacing the unstable aluminium oxide layer by a more stable oxide layer [15]. Oxides of chromium are particularly effective in passivating the aluminium substrates against corrosion. Chromate has been performed as a conversion layer on the metal substrates; specially aluminium [16–18] and also used as an inhibitive pigment [19–21]. Both of these applications of chromate compounds provide strong corrosion inhibiting effects on the aluminium metal. However, due to its carcinogenic nature, attempts have been performed to find more suitable environmentally friendly alternatives for this traditional corrosion inhibitor.

Other organic and/or inorganic compounds including plant extracts [22,23], silane coupling agent [24–27],  $\text{TiO}_2$  [28–30] and cerium [31–34] have been the subject of many researches for passivation of aluminum.

Among various surface treatment methods the most promising environmentally friendly surface treatments for aluminium are based on cerium conversion coatings. The composition of cerium layer strongly depends on the pH and temperature of treatment procedure. The Ce can deposit on the metal surface in two states of Ce(III) and Ce(IV) [35–37]. Previous reports have showed that in the presence of  $\text{H}_2\text{O}_2$  the Ce salt precipitates mostly in the form of  $\text{CeO}_2$  on the metal surface.  $\text{H}_2\text{O}_2$  provides high alkalinity at the metal surface and act as an oxidizing agent transforming the Ce(III) into Ce(IV). The  $\text{CeO}_2$  is a stable layer that covers the metal surface providing efficient corrosion resistance through blocking the active sites from aggressive ions access. In addition, the self-healing role of  $\text{Ce}^{4+}$  is another parameter affecting its corrosion protective performance [35–39].

This study deals with using a combined surface treatment procedures including cerium and an amino functionalized-silane compound on the aluminium nanoparticles highlighting the role of these agents at mitigating aluminium corrosion reactions. In this study, the effect of modification conditions with cerium, e.g. pH, as well as the silane concentration is investigated. Deposition of Ce film on the Al nanoparticles was evaluated by XPS and EDS analyses. FTIR and TGA analyses were utilized to reveal the APTES grafting on the nanoparticles. Corrosion resistance of pure Al, Ce-Al and Ce-Si-Al nanoparticles was investigated by hydrogen evolution measurements. The effect of incorporation of these nanoparticles into the epoxy coating on its corrosion protection properties was studied by salt spray test and EIS analysis.

## 2. Experimental

### 2.1. Materials

Aluminum nanoparticles of 90–110 nm particle size, density of  $1\text{--}1.2\text{ g/cm}^3$  and BET (Brunauer–Emmett–Teller) surface area of  $15.5\text{ m}^2/\text{g}$  were acquired from Alex Co. St-37 steel substrates were obtained from Foulad Mobarakeh Isfahan Co. The chemical composition (wt.%) of the mild steel (MS) was as follows: C (0.19), Mn (1.39), S ( $>0.005$ ), Si (0.42), Cu (0.04), Cr (0.03), Mo (0.02), Co (0.06) and Fe (balance). Epoxy coating was prepared using an epoxy resin of Epiran-01 (obtained from Khozestan petrochemical (Iran)) (KZPC) and an amido polyamide, CRAYAMID 115, from Arkema Co. The solid content and density of the epoxy resin were 75% and  $1.09\text{ g/cm}^3$ , respectively. The cerium nitrate salt and diethanolamine (DEA) were prepared from Merck Co. Aminopropyltriethoxysilane (APTES) was purchased from Sigma-Aldrich Co.

### 2.2. Surface modification of nanoparticles

#### 2.2.1. Ce-Al nanoparticles preparation

Aluminum nanoparticles were modified with Ce solution, whose composition was optimized to 5 mmol/L  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Merck Co.); at pHs i.e. 3.0, 3.4, 3.8 and 4.2 (adjusted by diethanol amine) and 10 mL/L  $\text{H}_2\text{O}_2$  (30%). The temperature was kept at  $25^\circ\text{C}$  and after spontaneous deposition under magnetic stirrer (600 rpm) for 10 min, the nanoparticles were rinsed four times with deionized water and dried at  $40^\circ\text{C}$  for 24 h. The nanoparticle obtained is coded as Ce-Al.

#### 2.2.2. Si-Al nanoparticle preparation

The surface of aluminum nanoparticles was modified by APTES. The surface modification was done using various amounts of APTES. The stoichiometric amount of silane was calculated according to Eq. (7) [40].

$$M = \frac{Mp \times Ss}{MSC} \quad (7)$$

where M, Mp, Ss and MSC are the amount of silane (g), the amount of nanoparticles (1 g), the specific surface area of nanoparticles ( $15.5\text{ m}^2/\text{g}$ ) and the minimum surface coverage of particles ( $353\text{ m}^2/\text{g}$ ) [41], respectively. According to Eq. (7), the stoichiometric amount of silane requires for surface modification of 1 g nanoparticles is 0.043 g. Si-Al nanoparticles were prepared in a 3-neck reactor equipped with a reflux system and oil bath. The temperature was kept at  $60^\circ\text{C}$ . Homogenizer was used to disperse the suspension. Nitric acid was added to the suspension (the pH was adjusted at 1.5–2) to catalyse the silane hydrolysis rate. Then, the suspension was kept under reflux for 1 h. Thereafter, the pH of the suspension was adjusted in the pH range of 8–9 through drop wise addition of sodium hydroxide. The suspension was stirred for 2 h for the completion of the condensation process. Finally, the resultant mixture was centrifuged and washed with a mixture of ethanol and deionized water (1:1 w/w) for five times. Then, nanoparticles were dried in oven for 24 h at  $40^\circ\text{C}$ . Si-Al code was assigned to the particles obtained from this step.

#### 2.2.3. Si-Ce-Al nanoparticles preparation

After surface treatment with cerium nitrate salt, the obtained particles were subjected to silanization reaction. This reaction was done through the same sol-gel process explained in the previous section. After this step, particles were centrifuged and washed five times with water/ethanol mixture. These nanoparticles were called Si-Ce-Al. To obtain dried particles, Si-Ce-Al samples were placed in an oven at  $40^\circ\text{C}$  for 24 h.

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