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Corrosion protection properties of silica coatings formed by sol–gel method on Al: The effects of acidity, withdrawal speed, and annealing temperature

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ABSTRACT

In this research, silica films were coated onto aluminum sheets using the sol–gel dip-coating method from acidic and basic solutions containing $(C_2H_5O)_4Si$, C_2H_5OH, H_2O, and catalysts. NH_3 and HNO_3 were used as catalysts in the acidic and basic solutions, respectively. The characteristics of the films were investigated as a function of the sol catalyst, withdrawal rate, and heat treatment temperature. Morphology of the coatings was studied by scanning electron microscopy (SEM). Corrosion behavior of coated and uncoated aluminum sheets was measured in 0.1 M NaCl. Findings indicated that SiO_2 coatings can offer proper protective properties against corrosive environments. Results also showed that conditions used to prepare the coatings significantly affect the morphology and thus, the corrosion protection of the silica films.

1. Introduction

One of the most effective ways to improve the corrosion resistance of a metal is to coat it with a protective film. A sol–gel coating can be used for this propose. The sol–gel is a simple, low-cost process for preparing materials such as film, powder, and bulk form. In this process, the corrosion protective films can be prepared at low temperatures on a large-area substrate. The silica films derived by the sol–gel method were used as corrosion protection on a variety of metals and alloys, including stainless steel, magnesium alloy, carbon steel, and aluminum. The silica coatings have shown notable chemical stability, thereby enhancing the corrosion resistance of metals [1–9].

The precursors used in sol–gel processing consist of metal alkoxides (such as tetraethoxysilane, TEOS), water, alcohol, and an acid or base (as catalyst). The sol–gel process includes hydrolysis and condensation reactions of the alkoxide to produce the silica network. Eqs. (1) and (2) show the hydrolysis and condensation reactions of this study, respectively [10,11].

$$\equiv Si{-}OR + H_2O \rightarrow \equiv Si{-}OH + ROH \quad (1)$$

$$\equiv Si{-}OH + \equiv Si{-}OH \rightarrow \equiv Si{-}O{-}Si\equiv + H_2O \quad (2a)$$

$$\equiv Si{-}OR + \equiv Si{-}OH \rightarrow \equiv Si{-}O{-}Si\equiv + ROH \quad (2b)$$

The sol (dispersion of colloidal particles in a solution) is produced by hydrolysis of the metal alkoxide (Eq. (1)). The condensation eliminates either water (Eq. (2a)) or alcohol (Eq. (2b)) to produce the gel (silica network). The hydrolysis and condensation reactions are influenced by the type of catalyst (acid or base). The sol–gel dip coating process is an important method for preparing films, which are used in the corrosion protection. In this process, a substrate is withdrawn at a constant rate (typically 5–20 cm/min) from the sol. In this step, the semi-solid network (gel) is deposited on the substrate by gravitational draining, solvent evaporation, and condensation reactions. The final coating is obtained after being treated with heat at various temperatures. In the sol–gel coatings the nano-structure and, therefore, the properties of the film strongly depend on precursors (especially the type of catalyst), the withdrawal rate, and the heat treatment temperature [10,11].

In this study, the silica film was deposited on aluminum (Al) substrate using the sol–gel process. The corrosion resistance of the film was investigated as a function of the type of catalyst, withdrawal rate, and heat treatment temperature. The morphology of the films was studied.

2. Experiment

Substrate size was 30 mm × 90 mm × 5 mm. The substrates were selected from commercial cold-rolled aluminum (with a

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Table 1
Chemical composition of aluminum sheet (wt.%).

Al (%)	Si (%)	Fe (%)	Cu (%)	Mg (ppm)	P (ppm)
99	0.4	0.3	0.1	750	500

chemical composition as presented in Table 1). They were degreased in trichloroethylene for 1 min, then placed in a solution of 25% (Vol) HF–75% (Vol) HNO_3 for one min. This solution removed the oxide layer from the surface and neutralized the alkaline film left by the degreasing process. After each step, the substrates were rinsed with deionized water.

The substrates were electropolished with a solution contain phosphoric acid (58 wt.%), chromic acid (8 wt.%), sulphuric acid (14 wt.%), and water (20 wt.%). The electropolishing process was carried out at a constant current (2.5 A/cm^2) and temperature of 95 °C for 10 min [12].

The sol (basic and acidic) comprised 5 ml tetraethoxysilane (TEOS) and 48.8 ml ethanol. $NH_3{\cdot}H_2O$ (1.6 ml, 25 wt.%) was used to prepare the basic sol (pH = 9). HNO_3 (3.43 ml, 65 wt.%) was used to prepare the acidic sol (pH = 1). NH_3 and HNO_3 served as catalysts. The solution was stirred continuously for 1 h. The sols were kept for 24 h at room temperature to complete hydrolysis [12]. The acidity of sols was measured and pH fixed at 9 and 1 for the basic and acidic sols, respectively.

Aluminum substrates were coated by dip-coating using the sol–gel solution. The samples were immersed in the sol solution for 1 min and then withdrawn at 5 cm/min and 20 cm/min speeds. The coated samples were heat-treated at 100 °C and 300 °C to determine the effects of annealing temperatures on their morphology and protective properties. Temperatures were increased at a constant rate of 1 °C/min. The samples were heated for 1 h and then cooled slowly to the desired temperature. The sample coating conditions and notations are listed in Table 2.

Scanning electron microscopy (SEM), Philips model XL30, was used to study the morphology of the samples. Potentiodynamic polarization curves were recorded with the aid of a Potentiostat/Galvanostat (Kimiastate model 210) instrument in 0.1 M NaCl electrolyte at room temperature. A three-electrode system was employed. The working electrode was formed by a sample masking to leave only 1 cm^2 area exposed to the electrolyte. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. A Sloan DekTak autoleveling profilemeter was used to determine the thickness of the films.

3. Results and discussion

The surface morphology of the silica films prepared from silica sols under different preparation conditions (acidic or basic catalyst, withdrawal rate, and heat treatment temperature) are shown in Fig. 1. It is obvious that the morphology of the films is greatly influenced by the type of catalyst, withdrawal rate, heat treatment temperature and film thickness.

The surface of the 5a100 sample was uniform (Fig. 1(a)). As seen in Fig. 1(c), the 20a100 sample had the same structure as the 5a100 sample (Fig. 1(a)). In other words, increasing the withdrawal rate in the acidic sol from 5 to 20 cm/min had an insignificant effect on the morphology of silica film. Conversely, increasing the withdrawal rate under basic conditions had noticeable effects on morphology. There were many cracks in the nano-metric scale (average width: ~13 nm and average length: ~113 nm) in the 5b100 sample (Fig. 1(b)). The cracks were more expanded and distinguished in 20b100 (Fig. 1(d)) with an average crack width and length of 22 and 188 nm, respectively. Comparison of the 5b100 (Fig. 1(b)) and the 20b100 (Fig. 1(d)) confirmed that in the base catalysis sol, a film with bigger cracks is obtained when the withdrawal rate is increased from 5 to 20 cm/min.

Fig. 1(e) shows the uniform structure for the silica film got at 300 °C from acidic sol (the 5a300 sample). Comparison of the 5a100 (Fig. 1(a)) and the 5a300 (Fig. 1(e)) confirmed that, in the acidic catalysis sol, a film with higher uniformity was obtained when the heat treatment was increased from 100 °C to 300 °C. Furthermore, as shown in Fig. 1(f), annealing at 300 °C in the base catalysis condition had a dramatic effect on the structure of the silica film obtained by 5 cm/min (5b300 sample). The surface of the 5b300 (Fig. 1(f)) was considerably non-uniform with a large quantity of holes with an approximate diameter of 130–570 nm (average diameter: 320 nm). In other words, the nanostructure of the film in the base catalysis condition was highly affected by withdrawal rate and annealing temperature. This effect agreed with other results. As a general rule, sol–gel derived silica film, under base-catalyzed conditions, yields more highly branched clusters which behave as discrete clusters, but the silica film derived by acid-catalyzed sol yielded mainly linear or randomly branched polymers [10,12,13]. It can influence the corrosion resistance properties of the film, as will be discussed in the next section.

Fig. 2 shows the polarization curves for the bare aluminum sample and the aluminum coated with silica film. The corrosion potential (E_{corr}) and corrosion current (I_{corr}) of the samples were obtained from the polarization curves and are listed in Table 3. As a result, the silica films have the corrosion protective effect. The effects of coating conditions (type of catalyst, heat treatment

Table 3
Potential of corrosion (E_{corr}) and corrosion current (I_{corr}) of the samples.

Sample	E_{corr} (mV *vs.* SCE)	I_{corr} (mA/cm^2)
Bare	−1111	6.8×10^{-4}
5b100	−1139	1.5×10^{-4}
5a100	−1199	4.5×10^{-5}
5b300	−1276	1.7×10^{-4}
5a300	−1215	4.2×10^{-5}
20b100	−1257	4.5×10^{-5}
20a100	−1245	3×10^{-5}
20b300	−1260	2×10^{-4}
20a300	−1256	2.5×10^{-5}

Table 2
The silica coating conditions.

Sample	Withdrawal rate (cm/min)	Catalyst	Heat treatment temperature (°C)	Film thickness (μm) ±5%
Bare	–	–	–	–
5a100	5	Acidic	100	0.157
20a100	20	Acidic	100	0.392
5b100	5	Basic	100	0.179
20b100	20	Basic	100	0.445
5a300	5	Acidic	300	0.085
20a300	20	Acidic	300	0.196
5b300	5	Basic	300	0.111
20b300	20	Basic	300	0.290