

Enhancement of the corrosion resistance of substrates by thin SiO₂ coatings prepared from alkoxide solutions without catalysts

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The corrosion resistance of aluminium coated with SiO₂ films, prepared by the sol–gel method using alkoxide solutions without catalysts, was extremely enhanced. The corrosion resistance depended on the coating conditions. Only 0.02–0.05% of the surface of aluminium with the SiO₂ film, of which the thickness was submicrometre, was corroded after the corrosion test. Small etch pits were observed in surfaces of aluminium with the SiO₂ films, which showed good corrosion resistance, after the corrosion test.

1. Introduction

The sol–gel technique starting from metal alkoxides has been extensively studied for the preparation of thin films. The technique is very attractive, because it is applicable to various substrates such as metals, glasses and semiconductors with large surface areas. In particular, the technique which uses the polycondensation reaction during the hydrolysis of silicon alkoxides has previously been studied in detail [1–5]. An acid such as HCl was generally used as a catalyst to promote the reactions; however, the acid should not be used in the precursor solution in order to prevent attacks on metal substrates. It should be noted that the coating conditions, such as the composition of the precursor solution and temperature of the heat treatment, were restricted by the substrates.

We have studied the preparation of SiO₂ coatings on the surface of a metal by the sol–gel method using silicon alkoxide [6, 7]. It was necessary to use Si(OC₂H₅)₄–C₂H₅OH–H₂O solutions without acids to prepare SiO₂ coatings which showed good corrosion resistance on aluminium. In the Si(OC₂H₅)₄–C₂H₅OH–H₂O system without catalysts, homogeneous solutions as the precursor solutions for films were prepared in a limited range of composition [6]. The gel-to-glass conversion of SiO₂ gels from the precursor solutions without catalysts was also described, to compare with that of gels from the normally used solutions with acids [7]. It was found that the amount of water contained in the alkoxide solutions affected the morphology of the coatings and the process of gel-to-glass conversion [6, 7].

In this paper we discuss the effects of the coating conditions, such as the composition of the solution, the number of cycles from withdrawal to heat treatment and the temperature of the heat treatment, on the corrosion resistance of aluminium as the substrate. We also investigate the relationships between the

coating conditions and the morphologies of etch pits appearing on the surface of aluminium after the corrosion test.

2. Experimental procedure

2.1. Preparation

25g Si(OC₂H₅)₄ (TEOS) was poured into a 100 ml breaker and half of an adequate volume of absolute C₂H₅OH (EtOH) was added to dissolve it. Distilled and deionized H₂O and the residual EtOH were dropped into the solution. The composition of the solutions is shown in Table I. During the above process, the solutions were stirred at room temperature. After stirring for 1 h, the solution was allowed to settle to gel in the air.

Aluminium plates (40 mm × 20 mm × 2 mm) were used as substrates. The substrates were cleaned with ethanol and washed with water, and then dried before coating.

The films were prepared by a dip-coating method. The withdrawal speed was 0.7 mm s⁻¹. The as-prepared films were heated at various temperatures for 10 min after drying for a few minutes in air. The thickness of the films increased on repeating the cycle from withdrawal to heating.

2.2. Characterization

The thickness of films was measured by a stylus instrument.

The corrosion resistance of aluminium with coatings was determined by the copper-accelerated acetic acid salt spray test (CASS test). Aluminium samples with and without coatings were exposed to the atomization of a mixed solution containing NaCl and CuCl₂ · 2H₂O in concentrations of 40 and 0.205 g l⁻¹, respectively, and adjusted to pH 3 with acetic acid, at 50 °C for 24 h. After the exposure, the corroded areas

TABLE I Composition of solutions

Solution	Molar ratio		
	Si(OC ₂ H ₅) ₄	C ₂ H ₅ OH	H ₂ O
A	1	4	4
B	1	4	3

were determined by using a rating number which was normalized by Japan Industrial Standard JIS H 8502.

The surfaces of the samples after the corrosion test were observed by scanning electron microscopy (SEM).

3. Results and discussion

The thickness of the SiO₂ film increased in proportion to the number of repetitions of the coating cycle. The thicknesses of SiO₂ films prepared from solution A by repeating the coating cycle from withdrawal to heating at 400 °C 10 and 20 times were about 0.5 and 1.0 μm, respectively. It appeared that a 50 nm thin film was deposited by one coating cycle.

Tables II and III show the coating conditions, such as the solution, number of repetitions of the coating cycle and temperature of heat treatment, and the corroded area of the surface of aluminium with and without the SiO₂ films after the CASS test. 30% of the surface of aluminium without SiO₂ films was corroded after the test. The corroded area decreased with the number of repetitions of the coating cycle, as shown in Table II. For solution A, the corrosion resistance of aluminium was extremely enhanced by repeating the coating cycle more than five times and three times at temperatures of heat treatment of 250 and 400 °C, respectively. In order to enhance the corrosion resistance of aluminium by using solution B, the coating cycle needed to be repeated more times than in the case of solution A. Only 0.02–0.05% of the surfaces of aluminium with the SiO₂ films, prepared from solution A by repeating the coating cycle from withdrawal to heating at 250 and 400 °C ten and five times, respectively, or from solution B by repeating the coating cycle from withdrawal to heating at 400 °C 20 times, were corroded after the test.

When the number of repetitions was constant as 10, the corroded area decreased with the temperature of heat treatment as shown in Table III. The corrosion resistance of aluminium with the SiO₂ film prepared from solution A and heated at as low a temperature as 250 °C was extremely enhanced. However, the corrosion resistance of aluminium with the SiO₂ film, prepared from solution B and heated even at 400 °C was not so good. 400 °C is considered to be the ultimate temperature, because the melting point of aluminium is 660 °C.

The difference of chemical properties such as the resistance against acid attack of the SiO₂ films could be explained by the changes of the structure of SiO₂ gels from the precursor solutions with heating, which depended on the composition of the precursor

TABLE II Coating conditions and corrosion resistance of aluminium with coatings

Solution	No. of cycles	Temperature (°C)	Corroded area (%)
–	0	–	30
A	1	250	25
	3	250	25
	5	250	0.10–0.25
	10	250	0.02–0.05
A	1	400	0.25–0.50
	3	400	0.10–0.05
	5	400	0.02–0.05
	10	400	0.02–0.05
	20	400	0.02–0.05
B	1	400	25
	5	400	0.10–0.25
	10	400	0.05–0.07
	20	400	0.02–0.05

TABLE III Coating conditions and corrosion resistance of aluminium with coatings

Solution	No. of cycles	Temperature (°C)	Corroded area (%)
–	0	–	30
A	10	200	0.25–0.50
		250	0.02–0.05
		300	0.02–0.05
		400	0.02–0.05
B	10	200	0.10–0.25
		300	0.10–0.25
		400	0.05–0.07

solutions. We have examined and discussed the change of the structure of the gels during heating by using differential thermal analysis (DTA) and thermogravimetry (TG), X-ray diffraction (XRD), Fourier transform infrared spectrometry (FT-IR) and Raman spectroscopy [7]. DTA curves of the gels from both solution A and solution B had endothermic peaks below 200 °C, which indicated the elimination of water and solvent contained in the gels. A remarkable exothermic peak, which resulted from the decomposition of residual organic species in the gel, appeared at about 270 °C in the curve of the gel from solution A. Most of the weight loss of the gel from solution A occurred up to the temperature at which the decomposition was perfectly complete. On the other hand, two exothermic peaks at about 280 and 550 °C and an exothermic band from around 300 to 510 °C, which were due to decomposition of the residual organic species, appeared in the curve of the gel from solution B.

The difference in these exothermic peaks originated from the organic species arising in the different chemical surroundings in each gel. The weight loss during decomposition continued up to a higher temperature for the gel from solution B than for the gel from solution A. These results indicate that 250 °C is the

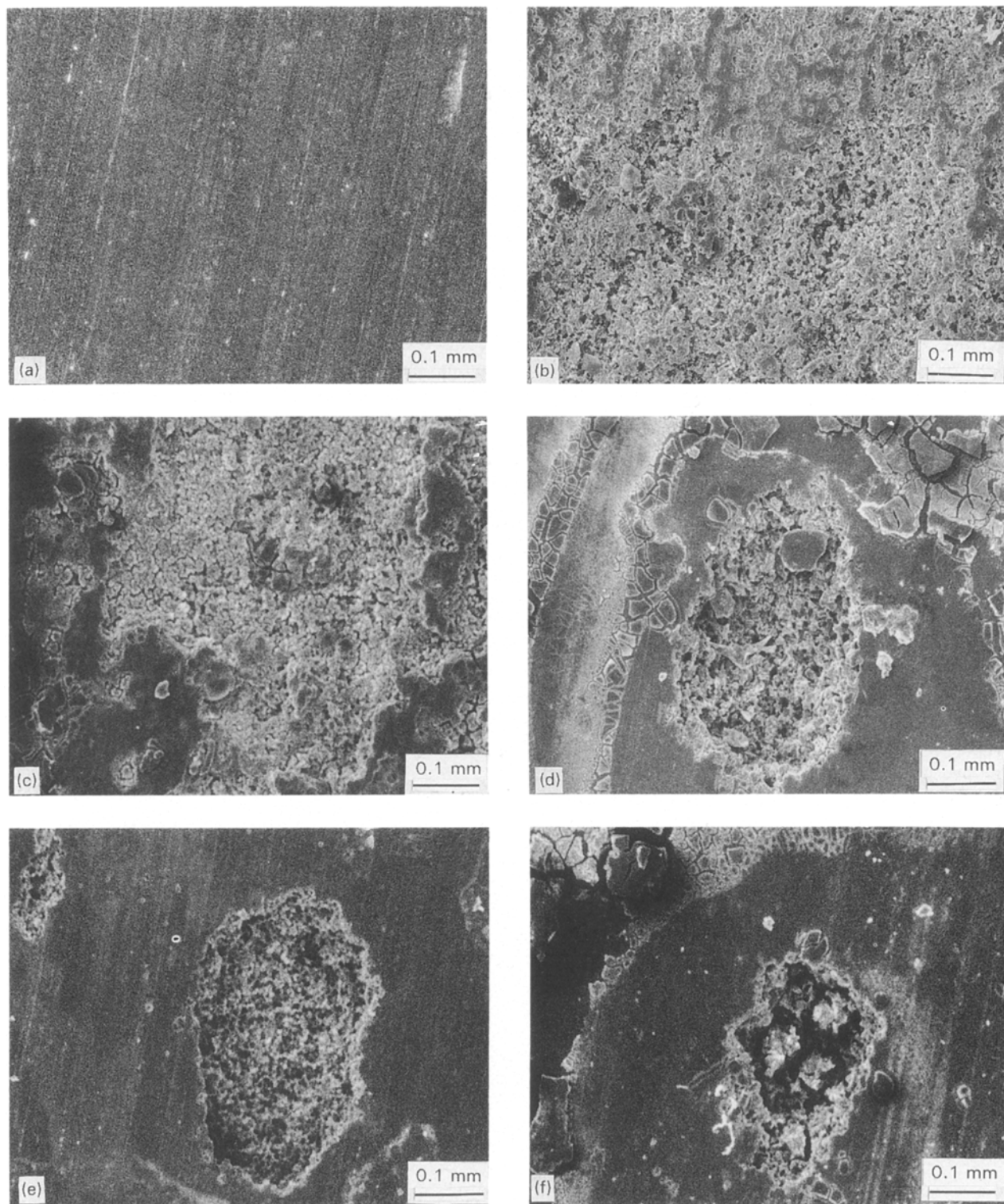


Figure 1 SEM photographs of the surface of aluminium (a) without SiO₂ films before the CASS test; (b) without SiO₂ films after the CASS test; (c) with SiO₂ film prepared from solution A by one coating cycle from withdrawal to heating at 400 °C, after the CASS test; (d) with SiO₂ film prepared from solution A by repeating the coating cycle from withdrawal to heating at 400 °C five times, after the CASS test; (e) with SiO₂ film prepared from solution A by repeating the coating cycle from withdrawal to heating at 250 °C ten times, after the CASS test; (f) with SiO₂ film prepared from solution B by repeating the coating cycle from withdrawal to heating at 400 °C 20 times, after the CASS test.

critical temperature at which an SiO₂ film containing less organic species can be prepared from solution A, and that 400 °C is not high enough to prepare organic species-free SiO₂ films from solution B.

There were no peaks, but there was a broad band, in the XRD profile of the gel prepared from the precursor solution and heated [7]. The 2θ angle of the centre of the band in the profile of the gel from solution B was

somewhat lower than that from solution A. The difference of the 2θ angle of the centre of the band meant that there was a difference in the range of the periodic structure in the gels. In a series of FT-IR spectra of the gels from solution A with heating, a band at 1090 cm⁻¹ due to the stretching vibration of the Si-O bond shifted to a lower frequency in the range of temperature from 200 to 400 °C. This shift, which indicated a

softening of the Si–O bond before the strengthening occurred at higher temperature, was not observed in FT-IR spectra of the gels from solution B.

There were fluorescent bands due to residual organic species in the Raman spectra of the gels, not from solution A but from solution B with heating [7]. It was not until a relatively high temperature that the organic species were decomposed and eliminated from the gels prepared from solution B. The decomposition and elimination of the residual organic species during the structural evolution of alkoxy-derived gels in the early stage of conversion to glasses influenced chemical properties of the gel films such as the resistance against attacks of acids. It was thus found that a relatively thin SiO₂ film, prepared from solution A and heated at as low a temperature as 250 °C, did not contain organic species and could enhance the corrosion resistance of the substrate.

Fig. 1 shows SEM photographs of the surface of aluminium with and without SiO₂ films before and after the CASS test. A wide range of the surface of aluminium without SiO₂ films was corroded after the test (Fig. 1b). Etch pits were observed on the surface of aluminium with the SiO₂ films after the test. The size and the depth of the pits depended on the coating conditions. The pits on the surface of aluminium with SiO₂ films prepared by one coating cycle were relatively large, as shown in Fig. 1c. There were only a few pits on the surfaces of aluminium with SiO₂ films which showed good corrosion resistance. The size of the pits was about 0.2–0.4 mm in diameter (Fig. 1d, e and f). The pits on the surface of aluminium with the SiO₂ film prepared from solution B, by repeating the coating cycle from withdrawal to heating at 400 °C 20 times, were deep and lined up along stripes on the surface of the aluminium.

4. Conclusions

The corrosion resistance of aluminium was improved by being coated with thin SiO₂ films from alkoxy solutions without acids. The chemical property of resistance against acid attack of the SiO₂ films depended on the coating conditions, especially on the composition of the precursor solution. A 0.25 µm thin SiO₂ film, prepared from the solution TEOS:EtOH:H₂O = 1:4:4 and heated at 400 °C, extremely enhanced the corrosion resistance of aluminium. It was found that a relatively thin SiO₂ film (about 0.5 µm in thickness) prepared from the same solution, and heated at as low a temperature as 250 °C, could also enhance the corrosion resistance of aluminium. This method for the preparation of thin films with excellent chemical properties is expected to be applied to the field of semiconductor devices, in which impurity is the dominant problem.

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