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Preparation of SiO_2 films from $Si(OC_2H_5)_4$–C_2H_5OH–H_2O solutions without catalysts

K. KATO
Toyama Industrial Technology Center, Futagami-machi 150, Takaoka-shi, Toyama 933, Japan

Thin and homogeneous SiO_2 films were prepared on aluminium plates from $Si(OC_2H_5)_4$–C_2H_5OH–H_2O solutions which had controlled compositions and did not contain any acid as a catalyst. Aluminium with the coatings showed good corrosion resistance. However, SiO_2 films prepared from alkoxide solutions with HCl contained Cl^- ions. Aluminium with coatings including Cl^- ions corroded in a corrosion test. Alkoxide solutions without acids were necessary for use in the coating of aluminium. The transformation of gels prepared from solutions without acids to amorphous SiO_2 was investigated.

1. Introduction

Preparations of ceramic coatings on the surface of metals are very important, because the coatings can not only give corrosion resistance but are also the first step to obtaining composite materials of ceramics and metals. The sol–gel technique has been developed for various coatings. In particular, the technique which uses the poly-condensation reaction during the hydrolysis of silicon alkoxides has previously been studied in detail [1–3]. The speeds of the hydrolysis reactions of silicon alkoxides were so slow that acids such as HCl and CH_3COOH were generally used as catalysts to promote the reactions [4–9]. In the case of preparations of coatings on the surfaces of metals, acids should not be used in the precursor solution in order to prevent attack on the metal.

In this paper, the formation of SiO_2 films on aluminium metal from $Si(OC_2H_5)_4$–C_2H_5OH–H_2O solutions without acids is discussed. We investigated the appropriate composition of the solution for the preparation of homogeneous films. To understand the process of the transformation from gel to amorphous SiO_2 films we followed the changes of the structure of bulk gels, prepared from the solutions, during subsequent heat treament. We also examined the corrosion resistance of SiO_2-coated aluminium.

2. Experimental procedure

$Si(OC_2H_5)_4$ (TEOS, 25 g) was poured into a 100 ml beaker and half of an aliquot volume of absolute C_2H_5OH (EtOH) was added to dissolve it. Distilled and deionized H_2O and the residual EtOH was dropped into the solution. To compare the effects of acids on the gelation of the solution, the morphologies of films and the reaction with metal, a solution containing HCl (HCl/TEOS = 0.02 in molar ratio) was also prepared. 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. Solutions with various viscosities before gelation were used for coating. 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 400 °C for 10 min after drying for a few minutes in air. The thickness of films increased on repeating the cycle from withdrawal to heating.

The viscosity of the solution was measured by a rotational viscometer at room temperature. The morphologies of films were observed by scanning electron microscopy (SEM). Trace elements contained in the films were analysed by fluorescent X-ray analysis (FXA). The corrosion resistance of the coated metals was measured by the copper-accelerated acetic acid salt spray test (CASS test). The changes of the structures of the gels with heating were investigated by differential thermal analysis (DTA-TG), X-ray diffraction (XRD) and Fourier transform infrared spectrometry (FT–IR).

3. Results and discussion

3.1. Compositions of coating solutions

Fig. 1 shows the compositions in the TEOS–EtOH–H_2O system without acids for coating. The miscible region of the system was narrower than for the TEOS–EtOH–H_2O system with HCl, which had been well defined by Sakka *et al.* [2]. The gels from the solutions with immiscible compositions consisted of two parts. One was more dense than the other. To prepare homogeneous and dense films, it was necessary to select miscible compositions rich in TEOS and H_2O. Typical compositions and viscosities of the solutions for coating are shown in Table I.

Fig. 2 shows SEM photographs of the surfaces of

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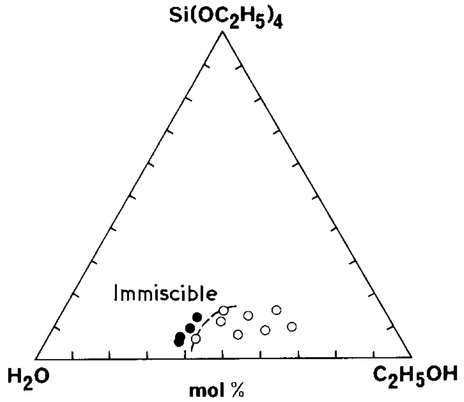
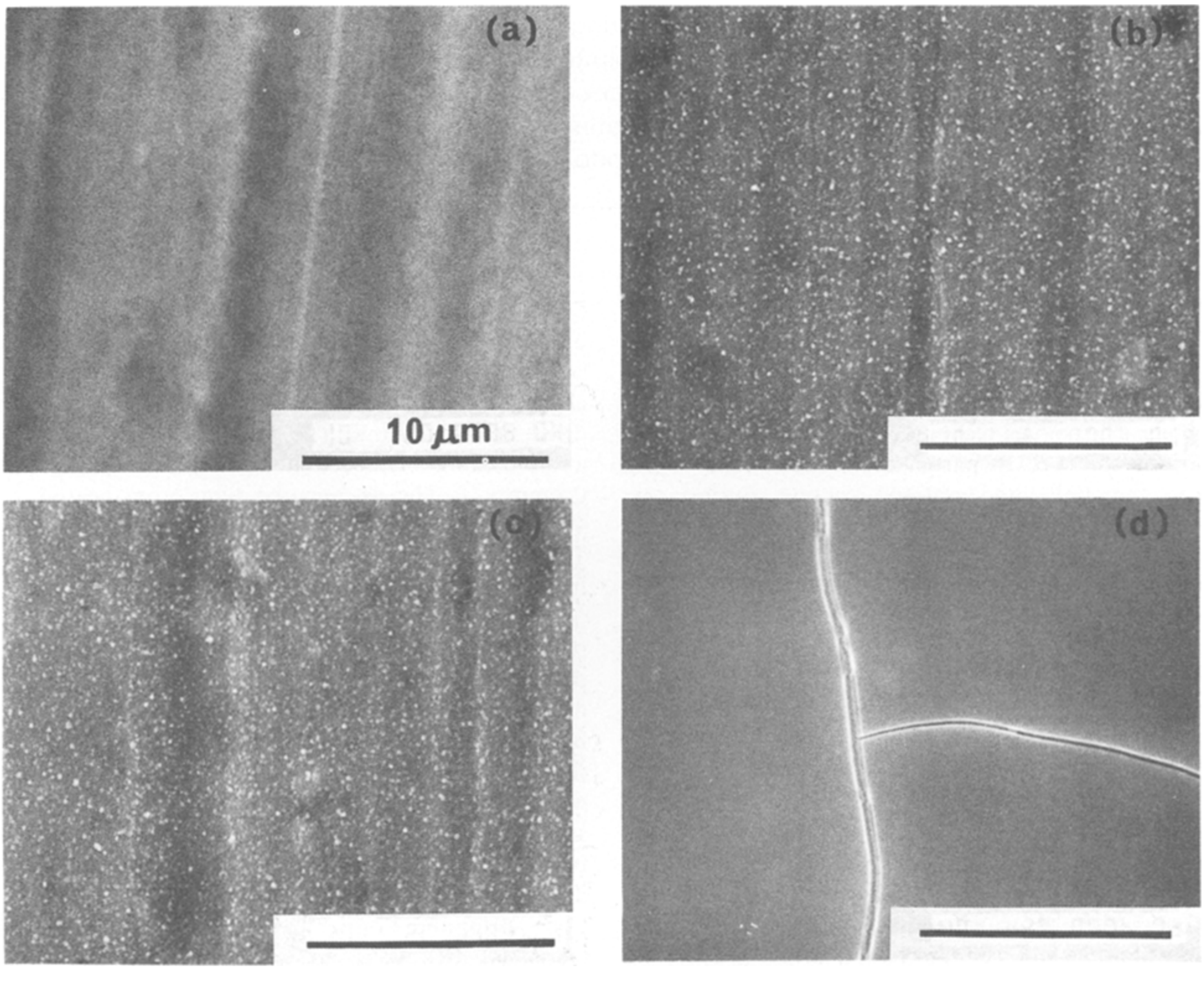


Figure 1 Compositions in the TEOS–EtOH–H_2O coating system without acids: (○) homogeneous solutions, (●) phase separation.

aluminium plates with and without coatings. The films coated with solution I (Fig. 2a) were homogeneous, dense and crack-free. In contrast, there were microparticles (diameter under 0.1 μm) in the films coated with solutions II and III (Fig. 2b and c, respectively). The amounts of water contained in solutions II and III were less than that in solution I. It seems that microparticles grew by heterogeneous and rapid hydrolysis and decomposition during the heat treatment, because of poor poly-condensation reaction in solutions II and III. The appropriate composition for the preparation of homogeneous films was that the molar proportions TEOS:EtOH:H_2O were equal to 1:4:4.

Fig. 2d shows an SEM photograph of the surface of an aluminium plate coated with solution IV which contained 0.02 mol % HCl. There were many cracks in the film. The viscosity of solution IV was higher than that of solution I, which had the same composition as solution IV. The thickness of the film prepared by one cycle of dip-coating from solution IV was so thick that many cracks grew due to the stress caused during the heat treatment. The viscosities of solutions to prepare homogeneous films were about 3 to 4 cP at room temperature. The viscosities of solutions without HCl



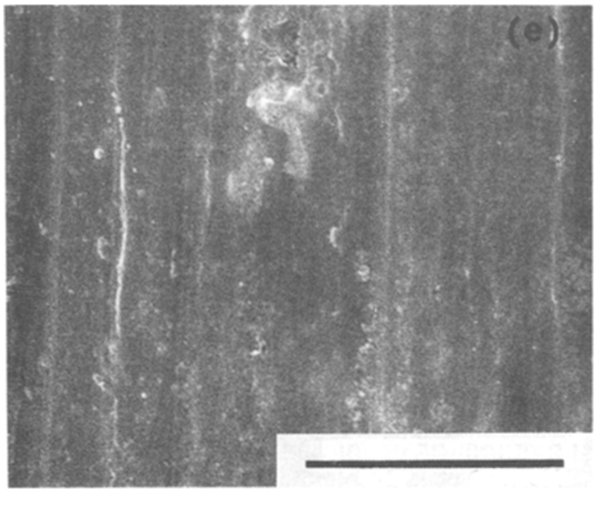


Figure 2 SEM photographs of the surfaces of aluminium plates coated with (a) solution I, (b) solution II, (c) solution III and (d) solution IV, (e) surface without coating.

TABLE I Compositions and viscosities of coating solutions

Solution	Mole ratio				Viscosity (cP)
	$Si(OC_2H_5)_4$	C_2H_5OH	H_2O	HCl	
Solution I	1	4	4	–	3.6
Solution II	1	4	3	–	3.7
Solution III	1	4	2	–	2.9
Solution IV	1	4	4	0.02	5.1

were constant for more than a month until the gelation. Homogeneous films could be prepared from the solutions at any time before gelation.

3.2. Changes of gel structure

The DTA–TG curves of gels prepared from solution I indicated that ethanol and water contained in them evaporated at temperatures up to 100 °C; combustion of the residual organic groups occurred at about 270 °C, and elimination of the products of combustion was completed at 400 °C.

Fig. 3 shows FT–IR spectra of as-prepared and heat-treated gels prepared from solution I in the range 1500 to 700 cm^{-1}. Bands were observed at about 1380, 1090, 960 and 800 cm^{-1} in the as-prepared specimen [4, 10, 11]. The band at 1380 cm^{-1} is assigned to the C–O bond, which corresponds to residual organic groups. The bands at 1090 and 800 cm^{-1} are assigned to the Si–O–Si bond. The band at 1090 cm^{-1} due to the stretching vibration of the Si–O bond was almost constant, while the band at 800 cm^{-1} shifted to higher frequency in the range of temperatures from 400 to 800 °C. This change is different from that observed before in the system containing HCl [4, 10]. The Si–OH band at 960 cm^{-1} disappeared in the specimens heated at 650 °C or higher temperatures. These results indicated that Si–O bonds had been formed in the as-prepared specimen, and the decomposition of water and the formation of a continuous SiO_4 network structure were completed by the heat treatment up to 800 °C.

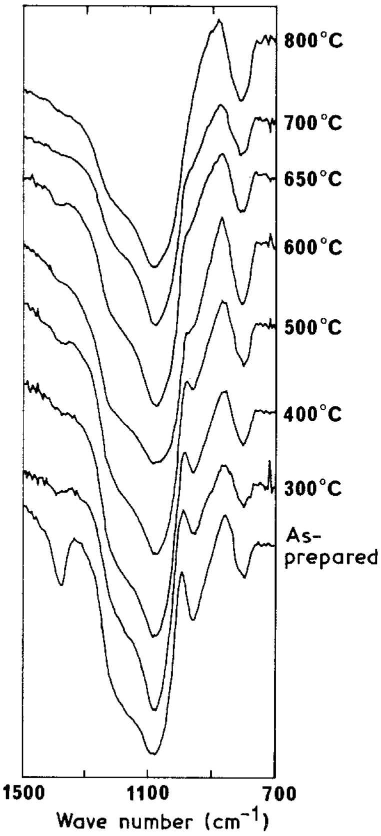


Figure 3 FT–IR spectra of as-prepared and heat-treated gels prepared from solution I.

The changes of structures of gels with temperatures were also confirmed by XRD. Specimens after heat treatment at temperatures up to 1000 °C showed broad-band features, which indicated that the specimens were amorphous. Fig. 4 shows typical XRD profiles of as-prepared and heat-treated gels in the range of $2\theta = 10$ to 40°. The band shifted to smaller values of 2θ with temperatures from 400 to 800 °C. In relation to the small-angle X-ray scattering, no scattering was seen for the specimens at 800 °C or higher temperatures as represented by Kamiya *et al.* [11]. It appeared that the average length of the periodic structure became longer with the transformation of the gel structure to a random SiO_4 network structure.

3.3. Trace elements in the films

No trace elements except main elements such as silicon and aluminium were detected by FXA in the films prepared on aluminium plates from solution I. Fig. 5 shows the FXA diffraction profiles of aluminium with and without coatings. The accelerating voltage and current were 50 kV and 30 mA, respectively. Germanium was used as a spectral crystal. The small peak at about 92.76° attributed to the Cl$K\alpha$ diffraction line was observed only in the film made with solution IV, as shown in Fig. 5c. It was found that Cl^- ions still remained in the films prepared from solutions containing HCl and heated at temperatures up to 400 °C.

3.4. Corrosion resistance of aluminium with coatings

Aluminium samples with coatings were exposed to the atomization of a mixed solution, containing NaCl and $CuCl_2 \cdot 2H_2O$ 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 were measured. The surface of the aluminium coated with solution IV was corroded over about 0.25% of its

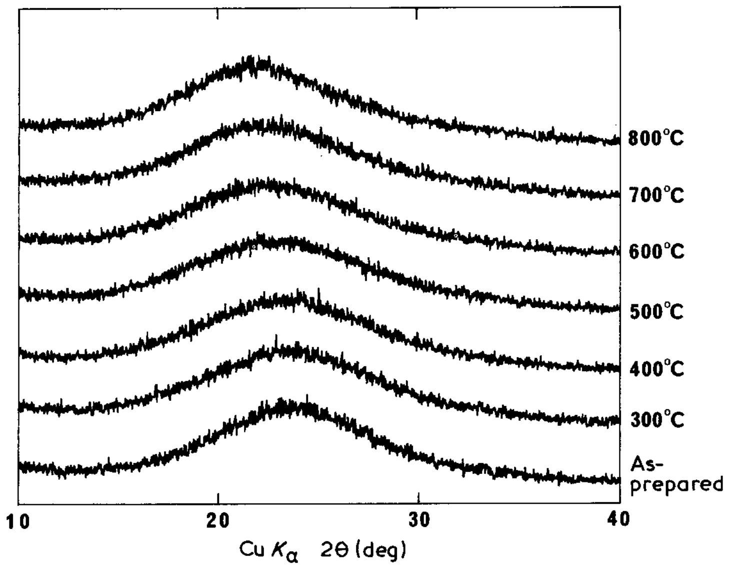


Figure 4 XRD profiles of as-prepared and heat-treated gels prepared from solution I.

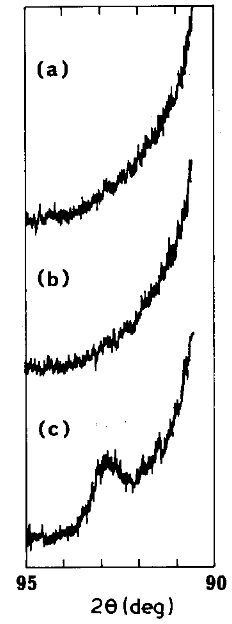


Figure 5 FXA diffraction profiles of aluminium (a) without coating, (b) coated with solution I and (c) coated with solution IV.

area, while the corroded area was less than 0.02% in the aluminium coated with solution I.

4. Conclusion

Aluminium plates could be coated with thin and homogeneous films of SiO_2, prepared from solutions of TEOS–EtOH–H_2O without acids with controlled compositions. The aluminium with the coatings showed good corrosion resistance. It was found that Cl^- ions remained in the coatings prepared from the alkoxide solution with HCl, and this affected the corrosion resistance. The gels from TEOS–EtOH–H_2O solutions transformed to amorphous SiO_2 with long-range periodic structure at temperatures up to 800 °C.

Coating the surface of aluminium with SiO_2 thin films by this method should be a fundamental technique for making metal–ceramic composites.

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