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Transformation of alkoxy-derived SiO_2 gels without catalysts to glasses

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The evolution of the periodic structure, the strengthening of the Si–O bond and the formation of the 3-fold and 4-fold rings of Si–O were observed in SiO_2 gels, which were prepared from alkoxide solutions, with heating but without catalysts. The content of water in the alkoxide solution related to the content of residual organic species, the behaviour of the Si–O bond with heating, and the range of the periodic structure in the gel.

1. Introduction

We have studied the preparation of coatings by the sol–gel method using metal alkoxides on the surfaces of metals, e.g. aluminium, for the purpose of improving their properties, especially corrosion resistance, and the development of a fundamental technique for the metal–ceramic composites. Our previous paper [1] reported that it was necessary to use the alkoxide solution without acid as a catalyst to prepare SiO_2 coatings on aluminium; thin SiO_2 films showing good corrosion resistance could be prepared from an alkoxide solution, which had a controlled composition without any acids. It was also reported that the morphology of the film depended on the composition of the alkoxide solution.

Many papers [2–10] described the gel-to-glass conversion of the SiO_2 gels which were prepared from the solution in the $Si(OR)_4$–ROH–H_2O-catalyst systems. However, there was no information for the gel-to-glass conversion of the gel from pure alkoxide solutions with controlled compositions and without catalysts. It is important to obtain information for the gel without catalysts to determine the optimum conditions for the reaction between the SiO_2 film prepared from pure alkoxide solution, and various gases, for the improvement of such properties as anti-abrasion and the development of metal–ceramic composites by depositing ceramic materials on the SiO_2 film as a buffer coat.

In this paper, we discuss the gel-to-glass conversion, in which the gel is transformed into a dense glass, of SiO_2 gels from alkoxide solutions without catalysts prepared for SiO_2 coatings. We investigate the changes in structure of the gels during conversion by heating, and the effect of the composition of the alkoxide solution on the structure. Differential thermal analysis and thermogravimetry (DTA–TG), X-ray diffraction (XRD), Fourier transform infrared spectrometry (FT–IR) and Raman spectroscopy were employed to determine the structures.

2. Experimental procedure

Silicon tetraethoxide, $Si(OC_2H_5)_4$, 25 g, was poured into a 100-ml beaker and half volume of absolute ethanol (C_2H_5OH) was added to dissolve it. A mixed solution of distilled and deionized water and residual ethanol was dropped into the solution. During the above process, the solutions were stirred in air at room temperature. The compositions of the solutions are shown in Table I. After stirring for more than 1 h, the solutions were settled to the gels. The gels were heated at various temperatures for 30 min in air.

The weight loss of the gel during combustion of the organic species contained in the gel was examined by DTA–TG. The amount of each gels used for DTA–TG measurements was 0.024 g. XRD measurements were carried out in the range of 2θ angle from 10 to 40° with an accelerated voltage of 40 kV and an applied current of 80 mA. For FT–IR, the scan number was determined to be 64, to detect ambiguous peaks. Raman experiments were performed using the 514.5-nm excitation line of an Ar^+ laser.

3. Results and discussion

3.1. DTA–TG

Fig. 1 shows DTA and TG curves of the gels prepared from the solutions A and B. Both DTA curves had endothermic peaks below 200 °C, which indicated the elimination of the water and the solvent contained in the gel. 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 completed perfectly. The weight loss of the gel during decomposition after the elimination of the water and solvent was about 6.9% from the TG curve. On the other hand, two exothermic peaks at about 280 and 550 °C and an exothermic band around from 300 to 510 °C were observed in the curve of the gel from the solution B. These exothermic peaks and band were due to the decomposition of the residual organic species. The difference in these exothermic peaks originated from the organic species under different chemical surroundings in each gel. For the gel from solution B, the

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TABLE I Composition of the solutions

Solution	Molar ratio		
	$Si(OC_2H_5)_4$	C_2H_5OH	H_2O
A	1	4	4
B	1	4	3

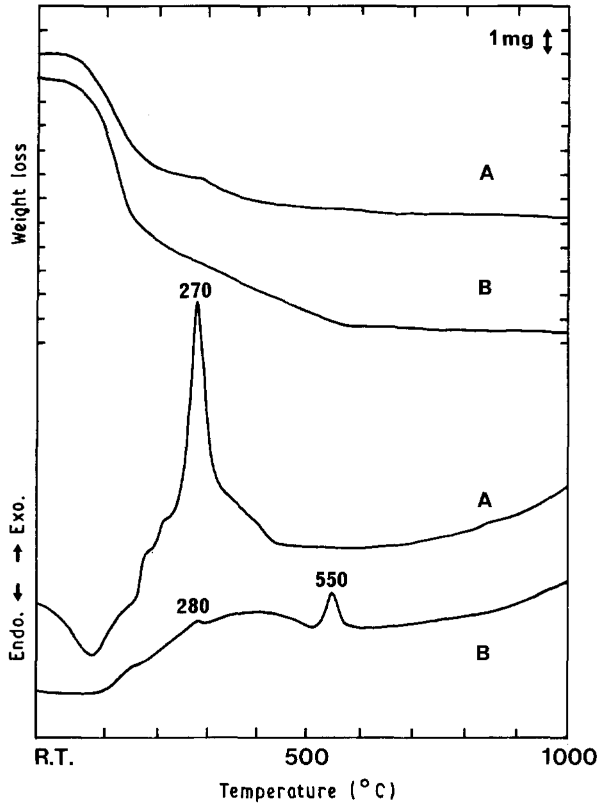

Figure 1 DTA–TG curves of gels prepared from solutions A and B.

weight loss during decomposition was 19.4% of the gel after the elimination. More organic species were found to reside in the gel from solution B than in that from solution A.

3.2. XRD

Fig. 2 shows XRD profiles of the gels which were prepared from the solution A and heated at various temperatures up to 1000 °C. There were no peaks which indicated crystalline phases, but there were broad bands around the 2θ angle of 21–24°. The 2θ angle of the centre of the band in the profile of the gel heated at 200 °C was about 23.7°. The band did not shift for gels heated at temperatures up to 400 °C. Increasing the temperature above 400 °C, the band shifted to a lower angle. The 2θ angles of the centres of the bands were about 21.4° in the profiles of the gels heated at 900 °C or higher temperature as 1000 °C. It was found that the range of the periodic structure in the gel from solution A became longer at temperatures above 400 °C. The long-range periodic structure was formed at temperatures below 900 °C.

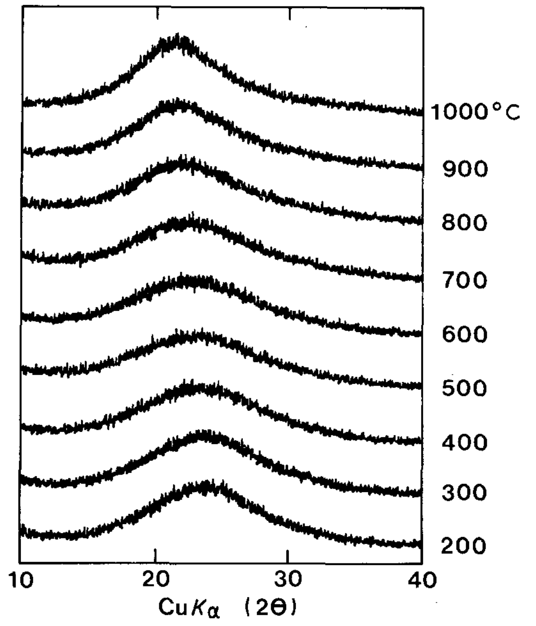

Figure 2 XRD profiles of gels prepared from solution A with heating.

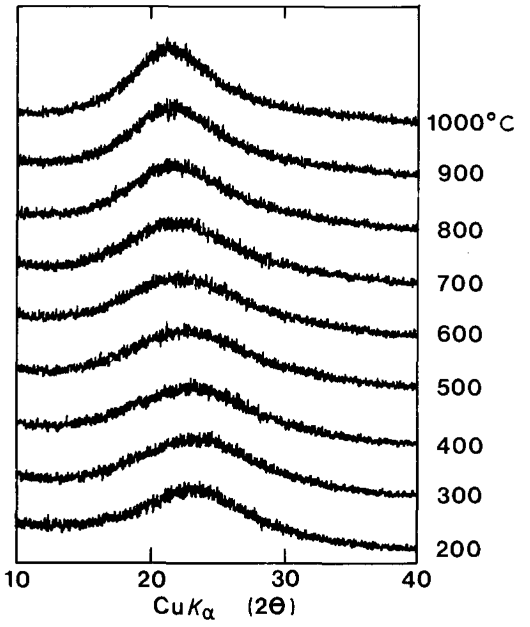

Figure 3 XRD profiles of gels prepared from solution B with heating.

Fig. 3 shows XRD profiles of the gels which were prepared from solution B and heated. The 2θ angle of the centre of the band in the profile of the gel heated at 200 °C was about 23.4°, somewhat lower than that of the gel from solution A (Fig. 2). The band shifted to a lower angle in almost the same temperature range as for the gel from solution A. The 2θ angle of the centre of the band in the profile of the gel heated at 1000 °C was about 21.3°. The composition of the alkoxide solution was found to affect the range of the periodic structure formed in the gel.

3.3. FT–IR

Fig. 4 shows FT–IR spectra in the range 1500–400 cm^{-1} of gels prepared from solution A

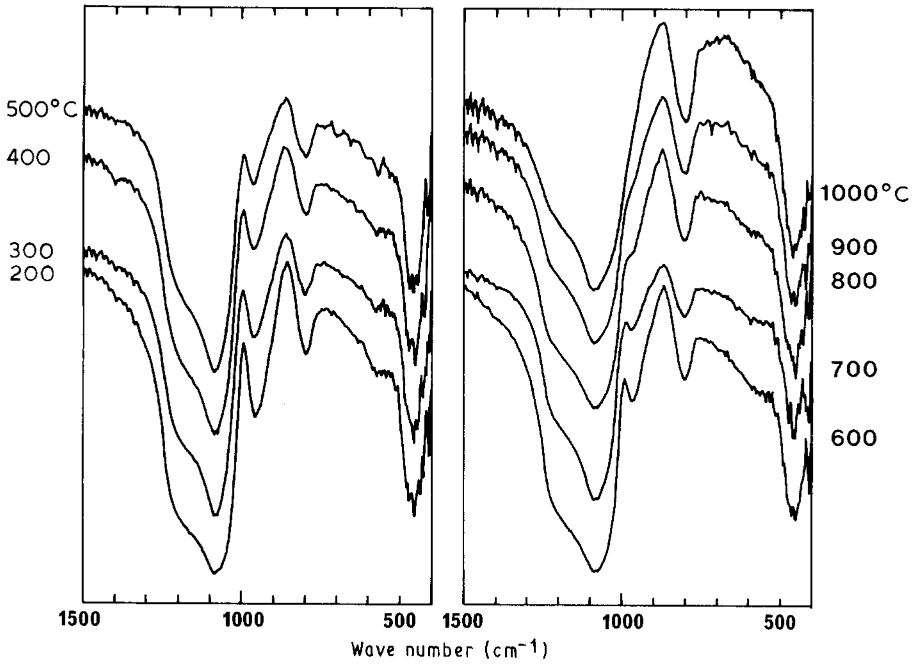

Figure 4 FT–IR spectra of gels prepared from solution A with heating.

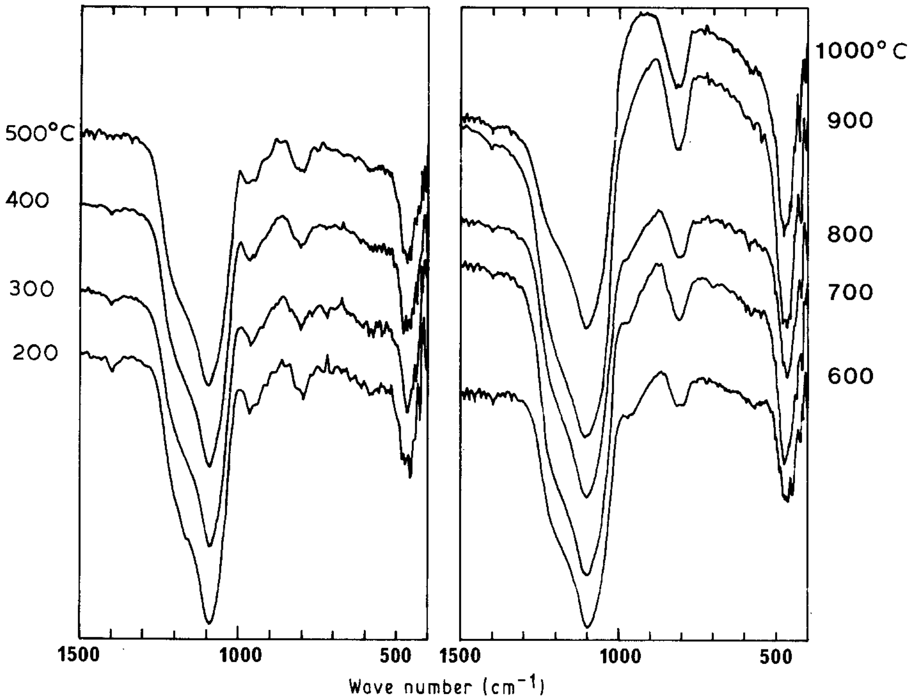

Figure 5 FT–IR spectra of gels prepared from solution B with heating.

with heating at various temperatures up to 1000 °C. The characteristic bands appeared at about 1090, 960 and 800 cm^{-1} in the specimen heated at 200 °C. Changes with heating were as follows. The band at 1090 cm^{-1} due to the stretching vibration of the Si–O bond shifted to lower frequency at temperatures up to 400 °C and shifted to higher frequency in the temperature range above 400 and below 900 °C. The temperature range agreed with that related to the band shift observed in the XRD profile. The Si–O band appeared at 1090 cm^{-1} in the specimen heated at 900 or 1000 °C. The bands at 960 and 800 cm^{-1} due to the Si–OH bond and the symmetric stretching vibration of the Si–O–Si bond, respectively, shifted to higher frequency in the same temperature range. The Si–OH band at 960 cm^{-1} became a shoulder of the band at 1090 cm^{-1} and disappeared in the specimens heated at 900 or 1000 °C. These changes with heating were different from those reported for the gels prepared from alkoxide solutions containing acids [2, 10–13].

Fig. 5 shows FT–IR spectra of the gels prepared from solution B with heating. As with the gels from solution A, the characteristic bands appeared at about 1090, 960 and 800 cm^{-1}. The change of the band at 1090 cm^{-1} with heating was different from that of the gel from solution A. The band shifted to higher frequency as the bands at 960 and 800 cm^{-1} in the temperature range above 400 and below 900 °C without shifting to lower frequency at temperatures up to 400 °C. The Si–OH band disappeared in the specimen heated at 900 °C. The Si–O–Si asymmetric stretching vibration band and the symmetric stretching vibration band appeared at 1110 and 810 cm^{-1}, respectively, in the specimen heated at 900 °C.

These results indicated that the Si–O bond was strengthened after being softened temporarily in the gel prepared from the solution containing as much water as solution A with heating; however, the softening of the Si–O bond did not occur in the gel which was prepared from the solution containing comparatively less water than the solution B, including more residual organic species. The strengthening of the Si–O bond coincided with the evolution of the periodic structure in the gel during heating, and completed at the temperature at which the elimination of the OH groups finished.

3.4. Raman spectrometry

Fig. 6 shows Raman spectra of the gels prepared from solution A with heating at various temperatures. The broad band at about 800 cm^{-1} and two peaks at about 970 and 480 cm^{-1} appeared in the spectrum of the specimen heated at 200 °C. The band at about 800 cm^{-1} and the peak at about 970 cm^{-1} are assigned to the SiO_2 network vibration and the bulk Si–OH vibration, respectively. The peak at about 480 cm^{-1} is one of the 'Raman defect peaks', of which the origins have been discussed in many articles [3–9, 14–17]. The peak in the spectra of SiO_2 gels prepared from alkoxide solutions is assigned to the breathing vibration of a 4-fold ring of Si–O [4, 6]. With increasing temperatures higher than 500 °C, the Si–OH peak decreased the intensity and the 4-fold ring peak shifted to higher frequency. The Si–OH band disappeared perfectly and SiO_2 network bands at 1200, 1065 and 430 cm^{-1} were observed in the spectrum of the specimen heated at 1000 °C. The other 'Raman defect peak', which is assigned to a 3-fold ring of Si–O [4, 6], appeared in the specimens heated at temperatures higher than 500 °C. Compared with the gels from the solutions containing acids, the temperature was comparatively high.

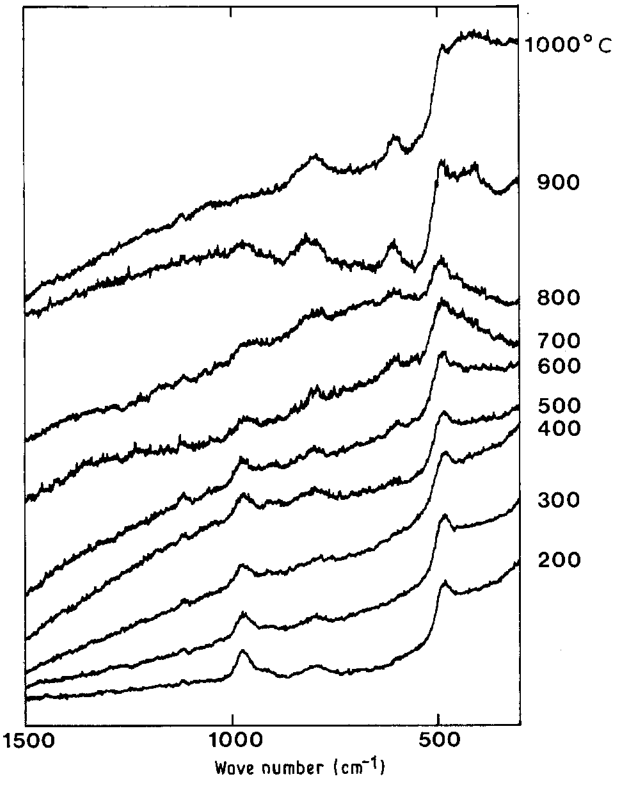

Figure 6 Raman spectra of gels prepared from solution A with heating.

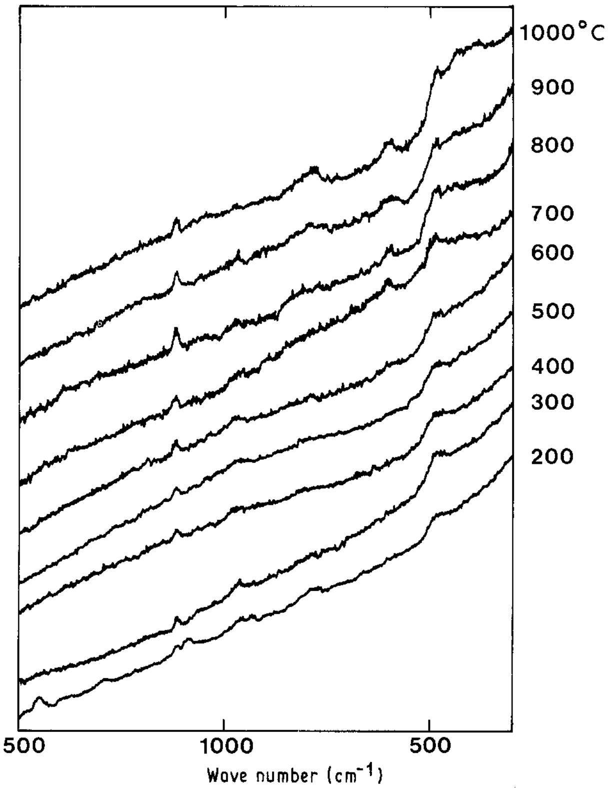

Figure 7 Raman spectra of gels prepared from solution B with heating.

Fig. 7 shows Raman spectra of the gels prepared from solution B with heating. The characteristic features were almost same as those of the gels from solution A; however, the band and peaks were not so clear as those which appeared in the spectra of the gel from solution A. The intensity of the Si–OH band was comparatively low. The 3-fold ring peak at about 605 cm^{-1} became distinct in the spectrum of the specimen heated at 600 °C.

It was found that the 3-fold rings were formed with the diminution of the Si–OH bonds during the evolution of the long-range periodic structure.

4. Conclusion

The long-range periodic structures were found to be evolved with the strengthening of the Si–O bond in the temperature range above 400 and below 900 °C, and the formation of the 3-fold ring by the condensation of OH groups at temperatures higher than 500 °C for the SiO_2 gels from alkoxide solutions without acids. The formation of the glass structure was completed when the elimination of OH groups finished.

The composition of the alkoxide solution affected the content of the residual organic species, the behaviour of the Si–O bond during heating, and the range of the periodic structure. A relatively large amount of the organic species resided in the gel prepared from the alkoxide solution: $Si(OC_2H_5)_4:C_2H_5OH:H_2O = 1:4:3$. The softening of the Si–O bond before strengthening occurred in the gel prepared not from this alkoxide solution, but from the alkoxide solution $Si(OC_2H_5)_4:C_2H_5OH:H_2O = 1:4:4$. The range of the periodic structure in the gel prepared from the alkoxide solution $Si(OC_2H_5)_4:C_2H_5OH:H_2O = 1:4:3$ was longer.

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