GEL-FORMING REGION AND THE THERMAL STABILITY OF GELS IN THE Na2O-ZrO2-SiO2 SYSTEM

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1 INTRODUCTION

ZrO2 containing glasses are drawing considerable attention because of its chemical resistance, especially alkali resistance[1, 2]. The maximum ZrO2 content in commercially produced glasses is presently about 21wt%[3]. Kamiya et al[4] prepared gel glasses in the ZrO2-SiO2 and Na2O-ZrO2-SiO2 systems with ZrO2 content up to 60wt%. Hara et al[5] studied the possibility of applying the Na2O-ZrO2-SiO2 gels to repairing damaged glass lining. In this study, gel forming region and thermal stability of the gels were studied in the Na2O-ZrO2-SiO2 system.

2 EXPERIMENTAL

2.1 Gel-forming region

Silicon tetraethoxide, zirconium n-propoxide (70wt% in n-propanol), and sodium ethoxide were used as raw materials in the sol-gel process. Ethanol and n-propanol were used as solvent in such a quantity that metal alkoxides : solvent ratio equals 30 : 70 in wt%. Sol was prepared according to the scheme shown in Fig.1 with no water addition. Sodium ethoxide was not dissolved completely in compositions of Na2O>10, ZrO2<80 and SiO2<30mol% as shown by ( zdjęć) marks. Water was not added because water addition induces too fast hydrolysis of zirconium alkoxide. Sols were covered with a polyethylene film with pin holes. Hydrolysis of alkoxides proceeds with moisture in the air at room temperature. Gelation is defined as the state without fluidity.

2.2 Amorphous region after heat-treatments

Gels were dried at 50°C for 1 week and dried gels were heat-treated at 600, 800, and 1200°C for 1h. X-ray diffraction analysis determined amorphous regions.

2.3 Crystallization temperature

DTA measurement was performed on pre-treated gels (600°C, 1h) of 10Na2O-(x)ZrO2-(90-x)SiO2 composition, where x=0~70 mol%, with a heating rate of 5°C/min and crystallization temperature, Tc, was obtained.

3 RESULTS

3.1 Gel-forming region

The gel forming region of the Na2O-ZrO2-SiO2 system is shown in Fig.2 by (○) marks. Crystal region is shown by (●) marks. Gel was obtained all over the ZrO2-SiO2 binary system.

3.2 Amorphous regions

The change of amorphous region (or crystallized regions) on heating at fixed temperatures(600, 800, 1200°C) is shown in Fig.2 by (○) marks. Gel region is shown by (●) marks. Gel was obtained all over the ZrO2-SiO2 binary system.

Fig.1. Flow chart for gel preparation.

Fig.2. Gel region of the Na2O-ZrO2-SiO2 system.
1200°C for 1h) is shown in Fig. 3. Heated at 600°C for 1h, ZrO₂ rich compositions (>70 mol% ZrO₂) yielded ZrO₂ crystal, but ZrSiO₄ crystal did not precipitate from the 50ZrO₂-50SiO₂ composition. Heated at 800°C for 1h, compositions of fairly large area crystallized. Heated at 1200°C for 1h, most of the amorphous regions that had survived the 800°C for 1h heat-treatment crystallized (©). Only small area shown by (©) (2ONa₂O-10ZrO₂-70SiO₂) remained as amorphous after 1200°C-1h heat-treatment.

Fig. 3. Amorphous regions after heat treatments at various temperatures for 1h.

3.3 Crystallization temperature

Figure 4 shows the variation of crystallization temperature, Tₐ, on dried gels of 10Na₂O-(x)ZrO₂-(90-x)SiO₂ series where x=0~70mol%. It is found that Tₐ rises steeply with ZrO₂ addition from 740°C at x=0 mol% until a maximum (Tₐ=884°C) is reached at x=20mol%.

Fig. 4. Crystallization temperature of 10Na₂O-(x)ZrO₂-(100-x)SiO₂ gels after heat treatment at 600°C for 1h.

4 DISCUSSION

As mentioned in section 3.2, ZrO₂ precipitated in the ZrO₂-SiO₂ system. This suggests that ZrO₂ is not incorporated evenly in the SiO₂ network as ZrSiO₄ unit. ZrO₂ may be present as ZrO₂ clusters in SiO₂ network. Lee et al[6] reported the precipitations of ZrSiO₄ and ZrO₂ crystals in heat-treated (48h at 1100°C) ZrO₂-SiO₂ gels of 42.4 and 64.0 mol% ZrO₂ content. However, heating condition is different in the present study (1h at 1200°C).

Nogami[7] studied IR spectra of gel-derived glasses of the ZrO₂-SiO₂ system and concluded that Zr⁴⁺ ions take up interstitial positions in the silica network. Takahashi et al[8] studied the influence of tetravalent cations (M⁴⁺) such as Ge⁴⁺, Ti⁴⁺, Sn⁴⁺, Zr⁴⁺, Th⁴⁺ on thermal expansion coefficient of glasses of the 0.20Na₂O-(x)MO₂-(0.80-x)SiO₂ and 0.30Na₂O-(x)MO₂-(0.70-x)SiO₂ series. They showed that thermal expansion coefficient decreases with ZrO₂ addition. It was shown also that Tₐ increases with ZrO₂ addition in the Na₂O-ZrO₂-SiO₂ glasses. The suggestion by Nogami[7] and the result by Takahashi et al[8] are not inconsistent with the present idea of ZrO₂ cluster-formation.

Silica network is rather spacious. Introduction of ZrO₂ clusters into the interstitial position of the silica network fills up the free space. The increased packing density will increase viscosity. As a result, thermal stability of gels against crystallization will increase with ZrO₂ addition. The amorphous forming ability of ZrO₂ is small compared with that of SiO₂, and ZrO₂-SiO₂ gels should be unstable when ZrO₂ is introduced more than the interstitial accommodation limit. The maximum Tₐ (Fig.4) would be a result of increasing viscosity and increasing crystallization tendency with the increase of ZrO₂ content.

Figure 3 indicates that thermally stable gel region in the Na₂O-ZrO₂-SiO₂ system shifts to higher SiO₂ composition with the increase of Na₂O content. Forming non-bridging oxygens, silica network will become more fragile and amorphous forming ability of SiO₂-Na₂O network is reduced, and the accommodation limit for ZrO₂ must be reduced.

REFERENCES