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The role of excess hydroxyl ions in the crystallization behaviour of an Al_2O_3–ZrO_2–SiO_2–Na_2O glass-ceramic system

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The crystallization behaviour of a gel-derived Al_2O_3–ZrO_2–SiO_2–Na_2O glass ceramic system under different heat-treatment atmospheres has been studied. The excess hydroxyl ions retained in the treated gel were found to play a crucial role during the crystallization of various phases. The evolution of phase transformations from gels to crystalline phases was monitored with infrared spectroscopy, X-ray diffraction and differential thermal analysis.

1. Introduction

Most glasses prepared by conventional melting contain small quantities of dissolved water (0.01 to 0.03 wt %) [1, 2]. Such water has been found to cause significant changes in the properties of these glasses. Besides affecting the density, refractive index, thermal expansion, electrical conductivity and viscosity, it also affects the behaviour of phase transformations in glass-forming systems by enhancing the kinetics of phase separation and increasing the crystal growth rates [3].

Recent developments in the gel technology have produced glasses which contain considerably more water than those prepared by the melting techniques. The number of non-bridging oxygens (OH and OR) remaining in the desiccated silica gels has been estimated to range from 1.48/Si [4] to 0.33/Si [5] compared with 0.003/Si for vitreous silica. Enhanced phase separation and crystallization kinetics observed in these gel-derived glasses compared with conventional glasses of similar compositions has been attributed to the presence of excess hydroxyl ions in the former which probably act as impurities or mineralizers to effectively reduce the viscosity of glass [6–9].

The structural and microstructural properties of the crystalline phases in an Al_2O_3–ZrO_2–SiO_2–Na_2O glass ceramic system in relation to the role played by excess hydroxyl ions are described in this paper. The chemical composition of the system being studied is very close to that of the well-known electromelted refractory material.

The glass matrix of composition 45 Al_2O_3–37 ZrO_2–17 SiO_2–1 Na_2O (wt %) was prepared according to the method previously published [10] by applying a gelling process to a solution of alkoxide compounds and mildly heating the material so that a homogeneous glass was formed. That method has been extensively elucidated by Gottardi *et al.* [11] and Fagherazzi and Enzo [12] by differential thermal, thermal gravimetric and X-ray diffraction analyses. However, none of the above workers has observed the unique crystallization behaviour when the gel was heat treated in argon (Figs 1 and 2) as described elsewhere [13]. This phenomenon is further investigated in this paper by the infrared spectroscopy in an attempt to elucidate the role of excess hydroxyl ions in relation to the crystallization characteristics of the gel under different heat-treatment atmospheres.

2. Experimental procedure

Commercial purity silicon tetraethoxide, sodium acetate and laboratory prepared zirconium tetraethoxide and aluminium isopropoxide were used as starting raw materials for the preparation of gels. The latter were prepared according to the experimental recipes of Bradley *et al.* [14] and Whitaker [15], respectively.

Preparation of the gel involved mixing the metal alkoxides in a plastic cup containing carbon tetrachloride as the common solvent. The resultant solution was then diluted with some dry ethanol and subsequently hydrolysed dropwise with water under vigorous stirring. Upon completion of hydrolysis, a plastic film with several holes was used to seal the cup and the solution was allowed to gel over a period of several days in a constant humidity oven in which the temperature was increased in steps from 40 to 80° C.

Differential thermal (DTA) and thermogravimetric (TGA) analyses were performed with a Rigaku Micro-DTA apparatus. A heating rate of $10° C min^{-1}$ was used. A Philips X-ray Diffractometer (PW 1050/25 wide-angle goniometer) was used to identify the crystalline phases present in the heat-treated gel. Nickel-filtered Cu$K\alpha$ radiation was employed. Finely ground gel powder was placed on an aluminium disc as a substrate.

The carbon content present in the argon and air-treated gels was analysed at the Melbourne Research Laboratory of BHP, using a Leco CSO44 carbon analyser.

The specimen for the infrared analysis was prepared by the pellet method. The gel powder was mixed with

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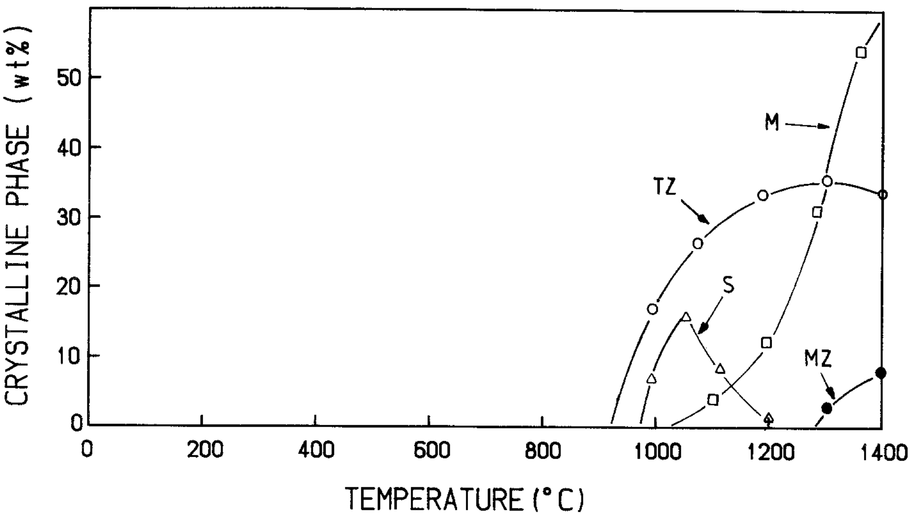

Figure 1 Crystallization of the gel treated in air. (M = mullite; S = Al–Si spinel; TZ = tetragonal ZrO_2; MZ = monoclinic ZrO_2.)

KBr and pressed into a thin disc ($\simeq 0.2$ mm). A sample of KBr : gel ratio of 1 : 40 was used. A pellet of pure KBr was used as a reference. The infrared spectrum of the gel was recorded on a Pye-Unicam SP3-200 spectrometer.

Absorption bands of hydroxyl groups present in the gel were recorded in the range 1400 to 4000 cm^{-1}. The hydroxyl ion concentration was computed from the corrected measured peak heights by using the Beer–Lambert law:

$$\log_{10}(I^0/I) = \varepsilon c d$$

where I^0 and I are the incident and transmitted light intensities, c is the hydroxyl ion concentration ($mol\, l^{-1}$), d is the sample thickness (cm) and ε is the extinction coefficient for the appropriate wave number range (181 litre mol^{-1} cm^{-1} at 3200 to 3500 cm^{-1}) [16].

All the heat treatments were done in a DTA furnace at a heating rate of 10° C min^{-1} and four different atmospheres (air, nitrogen, argon and argon–hydrogen) and atmospheric flow rates of 0.1 litre min^{-1} were employed. Crystallization of the gel was studied under the following heat treatment conditions: (a) air up to 1400° C; (b) nitrogen up to 1400° C; (c) argon up to 1300° C; (d) air at 800° C for 3 h and then in argon up to 1250° C; (e) argon at 800° C for 3 h and then continued to 1250° C; (f) air at 600° C for 1 h and then in argon + H_2 to 1250° C; (g) argon at 600° C for 1 h and then in argon + H_2 to 1250° C; (h) air at 800° C for 4 h and then in argon + steam to 1250° C; (i) air at 800° C for 4 h, followed by deposition of evaporated carbon under vacuum, the mixture was then heated in argon to 1250° C.

3. Results

XRD results indicate that the gel heat treated in air up to 950° C was non-crystalline. At about 970° C, a considerable amount of tetragonal zirconia and Al–Si (spinel) phases crystallized, to be followed by a small amount of tetragonal mullite at ~1000° C, and orthorhombic mullite was fully formed at ~1250° C. Traces of zircon formed at higher temperatures (Fig. 1). On the other hand, the gel heated in argon crystallized at ~835 and ~870° C resulting in the formation of tetragonal zirconia and tetragonal mullite, respectively, with no apparent formation of the spinel phase (Fig. 2). The tetragonal mullite formed in extensive quantities which rapidly attained its maximum amount at ~1200° C. Surprisingly, this metastable form of mullite persisted even at 1400° C.

The DTA and TGA curves of these two systems are depicted in Fig. 3. The results clearly indicate a sharp contrast in the exotherms under various heat-treatment atmospheres. The TGA curve of the gel heated in air

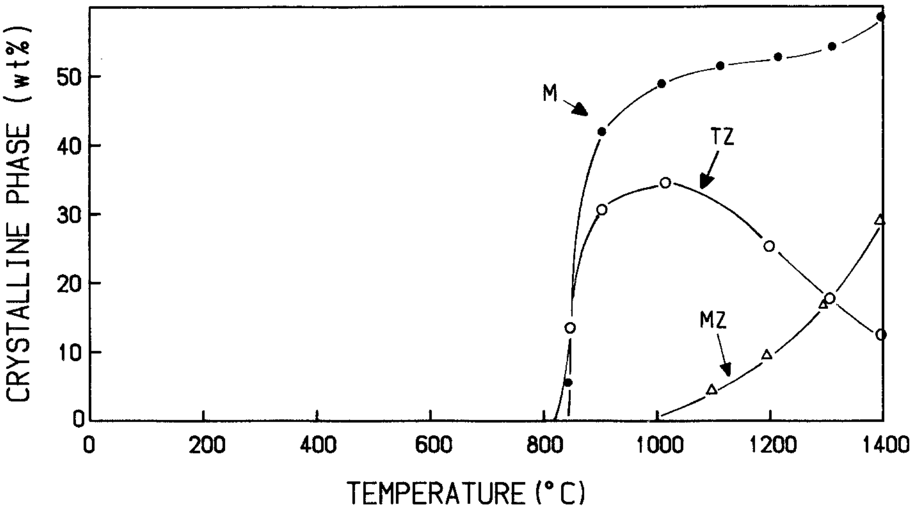

Figure 2 Crystallization of the gel treated in argon. (M = mullite; TZ = tetragonal zirconia; MZ = monoclinic zirconia.)

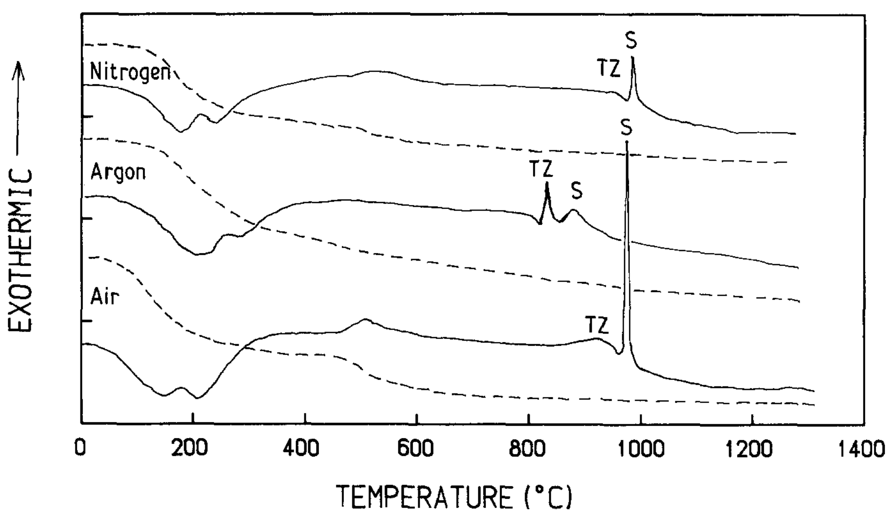

Figure 3 DTA and TGA curves of the gel treated in various atmospheres. (TZ = tetragonal zirconia; S = Al–Si spinel.)

showed a pronounced loss in weight at about 100° C which corresponded to the physical desorption of water. Another less pronounced loss in weight could also be detected at about 450° C which was probably due to combustion of carbon. Thereafter the loss in weight was very gradual and stopped slightly above about 800° C. On the contrary, the TGA curve of the gel heated in argon exhibited only a single pronounced loss in weight at about 100° C and the loss thereafter was gradual but continuous up to 1300° C (Fig. 3). The effect of nitrogen on the crystallization of the gel was intermediate between those of air and argon.

The DTA and TGA curves of heat treatments (d) and (e) are shown in Fig. 4. A depression in the crystallization temperature, T_c, of up to ~30° C was noted in treatment (e). All the other treatments (f) to (i) showed similar DTA and TGA curves to that of experiment (d). In short, neither hydrogen, steam nor carbon had any effect in depressing the crystallization temperatures of the heat-treated gel.

The carbon content of the gel heat treated in air and argon is shown in Table I.

Figs 5 and 6 depict the infrared transmission spectra of the gel heat treated at various temperatures in air and argon, respectively. The absorption band at around 3200 to 3500 cm^{-1} is the result of hydroxyl stretching vibration, and molecular water is apparently responsible for the absorption at ~ 1600 cm^{-1}. Broad, reduced intensity and poorly resolved absorption bands were observed for wave numbers less than 1200 cm^{-1}. Si–O stretching vibrations are reported to occur at 1172, 1100, 778, 647 and 608 cm^{-1}. Si–O–Si ring structures occur at around 800 cm^{-1} while Si–O–Al bands have vibrations of 1008, 753, 694 cm^{-1}. For comparison, the spectrum of a pure fused silica is also shown (Fig. 6). The results clearly indicate a large proportion of hydroxyl groups and relatively few Si–O, Si–O–Si or Si–O–Al bands or other glass forming networks are present in the gel at low temperatures, irrespective of heat-treatment atmospheres. The concentrations of the latter appeared to increase with increasing temperature. The hydroxyl groups were very readily driven off when heated in air at temperatures greater than 700° C whereas a considerable proportion of these groups were retained in the gel when heated in argon at the same temperatures. The hydroxyl concentrations present in the gel under various temperatures in both air and argon are given in Table II. Although there may be some uncertainty in the absolute values of the concentration of hydroxyl ions in Table II, the results are sufficiently accurate for comparison purposes. It is interesting to note that the hydroxyl contents of argon-treated gel were significantly greater than the similar gel heated in air. More than 180% excess hydroxyl ions were retained in argon-treated gel at about 800° C. At 900° C the excess was more than 500%. Thereafter, the excess decreased very sharply and at 1000° C it has dropped to about 160%.

TABLE I Carbon of heat-treated gel

Temperature (°C)	Atmosphere	Carbon content (wt %)
600	Air	0.60
600	Argon	1.00

4. Discussion

The results clearly indicate that the non-crystalline nature of the gel could be maintained to rather high temperatures if the heat treatment was carried out in air. This amorphous state was lost at comparatively low temperatures when argon was used (Fig. 2). In the former, the first crystallization temperature was about 970° C which agreed rather well with the work of Fagherazzi and Enzo [12] and they ascribed the sharp exothermic peak to the crystallization of tetragonal zirconia. Unfortunately, their claim cannot be fully justified for a number of reasons.

TABLE II Concentration of hydroxyl groups at various temperatures

Temperature (°C)	Air		Argon		$(C^* - C)/C$ (%)
	I^0/I	C (mol l^{-1})	I^0/I	C^* (mol l^{-1})	
500	72/28	0.1025	35/13	0.1034	1
700	52/45	0.0157	30/20	0.0440	180
800	28/25	0.0145	51/35	0.0409	182
900	23/22	0.0048	41/31	0.0304	533
1000	46/45	0.0024	36/34	0.0062	158

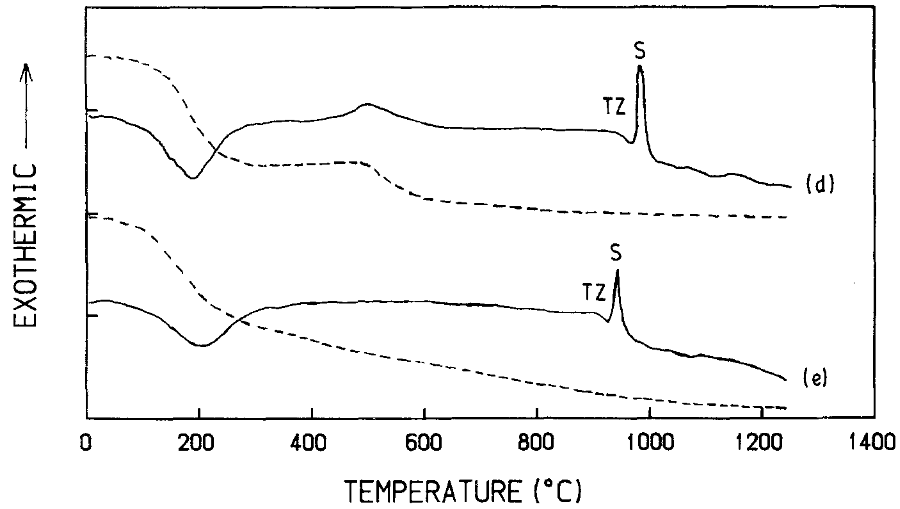

Figure 4 DTA and TGA curves of experiments (d) and (e). (TZ = tetragonal zirconia; S = Al–Si spinel.)

It is well established elsewhere [3, 17] that zirconia crystallized over a wide range of temperatures depending on the proportion of zirconia present in the gel and a broad or dilute exotherm, rather than a sharp peak was obtained. In addition, a perusal of the results of the above workers revealed that some tetragonal mullite crystallized together with tetragonal zirconia at 970° C. Therefore, the sharp peak at 970° C could also be due to the crystallization of mullite. A similar sharp exotherm at around 970° C has also been reported in the crystallization of clay minerals and alumino-silicate glasses. Although there is still much controversy over the origins of this peak, it has been generally accepted to be the result of crystallization of mullite. This phase would fully develop only after long heating times at temperatures much higher than 970° C. Hence, it is not surprising that only a small amount of metastable mullite was obtained by Fagherazzi and Enzo which led them to misinterpret the results. Further justification comes from the results shown in Fig. 1 where, in addition to tetragonal zirconia, a spinel and traces of tetragonal mullite were also formed immediately after the sharp exotherm, a phenomenon which prevails in clay minerals. Hence, the exotherm could not possibly have been due to the crystallization of tetragonal zirconia. It has been established by Low [13] that the 970° C exotherm was the result of the crystallization of an Al–Si spinel phase. The apparently broad and diluted exotherm just prior to the sharp peak is consequently ascribed to the crystallization of tetragonal zirconia.

The characteristic sharp peak of the gel treated in air was lost when argon was used, resulting in the formation of a much diluted peak associated with the crystallization of the spinel but a sharper exotherm for the tetragonal zirconia. Both exotherms were also observed to move to much lower temperatures and the treated gel was black. These intriguing features invite the following hypotheses to be suggested.

1. Carbon present in the gel acts as nucleating agents.

2. The reducing atmosphere due to the presence of carbon depresses the glass transition temperature, T_g, and/or decreases the viscosity of the glass which consequently enhances the rapid crystallization of the gel.

3. Molecular water and/or hydroxyl groups present in the gel act as effective mineralizers.

4. The presence of Na_2O acts as a mineralizer.

The heat-treatment experiments (d) to (i) were devised to test these hypotheses. Experiment (i) was designed to test hypothesis 1. The gel was heated to 800° C in air and held for 4 h to allow sufficient hydroxyl groups or water to be eliminated. Hence if deposited carbon causes a drop in the crystallization temperatures (T_c) of the gel, the hypothesis is proven.

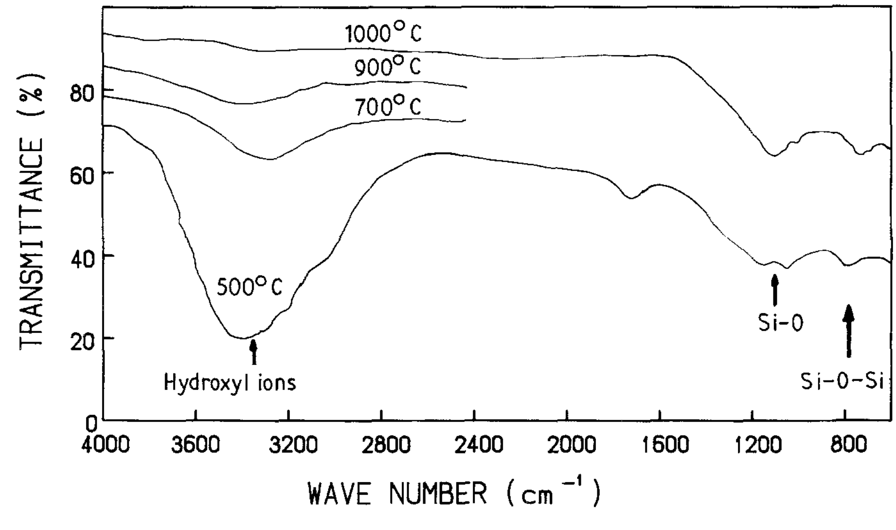

Figure 5 Infrared spectra of the gel heat treated in air.

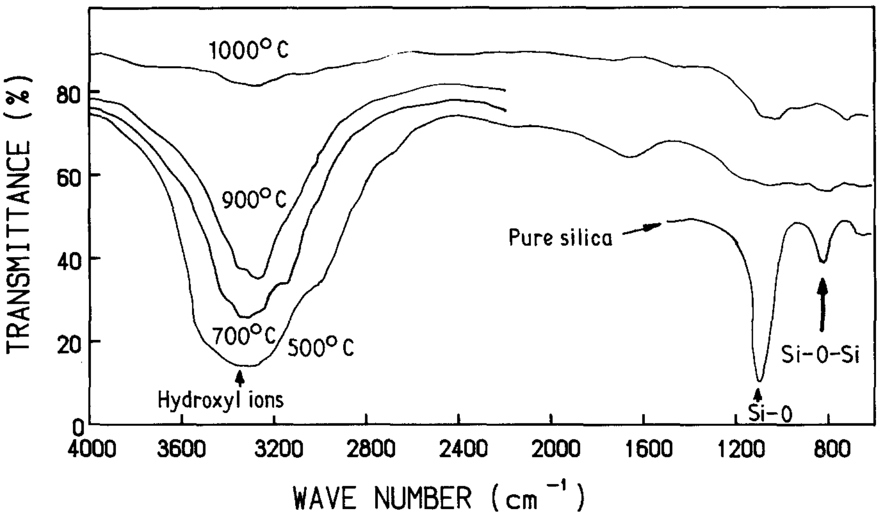

Figure 6 Infrared spectra of the gel heat treated in argon.

However, a negative result was obtained which indicates that graphitized carbon could not act as a nucleating agent. However, the result of this experiment is neither convincing nor conclusive, because all the deposited carbon was apparently burnt in argon (as evidenced by the formation of a white by-product), probably by the presence of partial oxygen pressure, a feature which was not observed in argon-treated gel. Apparently, graphitized carbon was a poor simulation of the carbon formed in the gel which was most probably polymeric, very heat resistant and did not form graphitic structures readily. This type of carbon is classified as "hard carbon" in contrast to the graphitized "soft carbon" of petroleum and coal-tar pitches. The former is readily formed from polyfurfuryl alcohol and phenol formaldehyde resins which tend to produce glassy or vitreous forms of carbon while the latter result in highly graphitic structures on heating to above 1000° C. These "hard carbons" have indeed been used by Chi [18] and Elmer and Meissner [19] to be incorporated into their glasses to reduce the tendency of devitrification. As polymeric carbon has been found to retard the devitrification of glasses, a feature which is in contradiction to the results obtained for the gel treated in argon, the presence of any form of carbon cannot possibly act as nucleating agent to enhance devitrification. Hypothesis 1 is, therefore, proved to be wrong. Hypothesis 2 was tested in experiments (f) and (g). Again sufficient water or hydroxyl ions were allowed to escape and any reduction in T_c must be due to the effect of a reducing atmosphere (experiment f). The results indicated no apparent depression of T_c and the end product was black which was unexpected, because the starting sample was white after pretreatment. This interesting feature might serve to indicate that the end product formed was probably non-stoichiometric. The results obtained for experiment (g) were unexpected because the residual hydroxyl ions present after the pretreatment should be sufficient to cause some depression of T_c. The negative results suggest that the hydrogen gas might have reacted with the hydroxyl ions to form water vapour ($\frac{1}{2}H_2 + OH \rightarrow H_2O$) which escaped, thus causing the T_c to remain unchanged. This behaviour is in contrast with that of glasses whose crystallization kinetics were effected by the partial oxygen pressure of the firing atmosphere [20].

The hypothesis that molecular water present in the gel might be responsible for the observed effect was tested in experiment (h) whereby a stream of argon and steam was passed through the gel which had been previously deprived of any water or hydroxyl groups. The T_c of the gel remained almost unchanged. Numerous investigators [9, 21] have observed enhanced phase separation as well as crystal growth rates in the crystallization kinetics of glasses containing a considerable quantity of water. Unfortunately, most of these investigators have not bothered to treat the molecular water and hydroxyl ions in their glasses as two separate entities. A few investigators [6, 9] have argued that hydroxyl ions rather than molecular water are responsible for the enhanced nucleation and crystallization of glasses. Indeed, results of experiments (d), (e) and (g) also suggest that hydroxyl ions rather than molecular water were responsible for the depression of T_c of the gel heat treated in argon. In experiment (d), no depression of T_c was recorded because of the negligible number of hydroxyl ions left after the pretreatment of 800° C for 3 h in air. However, a pretreatment at the same temperature and duration in argon was not expected to eliminate all hydroxyl groups and a sufficient proportion was retained to depress T_c by about 30° C (Fig. 4). Hence, there seems to exist a correlation between T_c and the concentration of hydroxyl ions retained in the gel.

Hypothesis 4 was tested by repeating experiments (a) and (c) on a gel of the same composition which was deprived of Na_2O. The crystallization behaviour of this gel was similar to that of sample (i) in that both gels were sensitive to the heat-treatment atmosphere and depression of T_c was observed in argon-treated gels. This and other evidence serve to suggest beyond any doubt that excess hydroxyl ions was the single most important parameter which dictates the crystallization characteristics of the gel sample thus investigated.

This hypothesis is further substantiated by the results of the infrared studies (Table II and Figs 5 and 6). The broad absorption band at around 3200 to 3500 cm^{-1} was probably the result of intermolecular hydrogen bonds among the hydroxyl groups which initiate the formation of a polymeric network. Similar results have also been recently observed by Wood *et al.* [22] in colloidal gel-derived high-silica glasses.

The origins of the excess hydroxyl ions retained in the argon-treated gel may be the result of the formation of polymeric carbon which effectively seal off pores in the gel network before the residual organic radicals and hydroxyl groups have the chance to burn off or escape. Consequently, the gel is coated with carbon and saturated with excess hydroxyl ions which tend to lower the viscosity of the treated gel and enhance its tendency to devitrify. The presence of polymeric carbon in concert with the reducing atmosphere is believed to be responsible for the "stabilization" of the metastable mullite at high temperatures. Indeed, this stabilization effect of carbon has been observed by Chi [18] and Elmer and Meissner [19]. They reported a considerable reduction in the tendency for glasses containing polymeric carbon to devitrify. The reducing atmosphere may contribute to the stabilizing effect by depriving the tetragonal-like mullite with the necessary oxygen atoms needed to form the equilibrium (3:2) mullite.

The interesting results of this investigation may serve to invite suggestions for utilizing them to the advantage of glasses and ceramics fabrication. Indeed, these effects have been well employed by Doi *et al.* [23] and Chi [18] in tailor-making their glass-ceramics and glasses, respectively. In the former, hydroxyl groups were deliberately introduced to shorten the crystal nucleation and growth times or lower the heat-treatment temperatures required while maintaining the same fine grain microstructure. In the latter, carbon-containing monolithic glasses were prepared via the sol–gel process by heating the glasses in an inert atmosphere. The black glasses obtained have mechanical and thermal properties comparable to those of fused glasses but with lower volume resistivity and a lower tendency towards devitrification. The cleansing effect of hydrogen as shown by experiment (g) suggests a possibility of utilizing this gas or other gases (e.g. HCl or Cl_2) to monitor the concentration of hydroxyl ions to the advantage of tailor-making glasses and glass-ceramics with specific properties.

5. Conclusions

The crystallization behaviour of a gel with the composition 17 wt % SiO_2–37 wt % ZrO_2–45 wt % Al_2O_3–1 wt % Na_2O was studied in great detail in different heat-treatment atmospheres by XRD, DTA, TGA and infrared spectroscopy. Immense contrast was recorded on the gel treated in air and argon in relation to the sharpness of exotherms and the variation of crystallization temperatures. The origin of this contrast was attributed to the excess concentration of hydroxyl ions retained in the argon-treated gel as the single most important parameter, although the role played by the concurrent presence of carbon and reducing atmosphere cannot be ruled out. They may contribute to exemplify the contrast synergistically. The latter is believed to be responsible for the "stabilization" of tetragonal-like mullite at high temperatures. The carbon formed in the argon-treated gel was most probably polymeric and very heat resistant. It was believed to seal pores of gel networks and cause excess hydroxyl ions to be trapped.

The results of this investigation also offer some unique ways of tailor-making glasses and ceramics with particular properties.

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References

1. E. N. BOULOS and N. J. KREIDL, *J. Can. Ceram. Soc.* **41** (1972) 83–90.
2. J. P. WILLIAMS, Y. S. SU, B. L. BUTLER, and D. E. CAMPBELL *Bull. Amer. Ceram. Soc.*, **55**, (1976) 524–527.
3. C. J. R. GONZALEZ-OLIVER, P. F. JAMES and H. RAWSON, *J. Mater. Sci.* **14** (1979) 1159.
4. M. YAMANE, S. ASO and T. SAKAINO, *ibid.* **14** (1975) 607.
5. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER and C. S. ASHLEY, *J. Non-Cryst. Solids* **48** (1982) 47.
6. S. P. MUKHERJEE, J. ZARZYCKI and J. P. TRAVERSE, *J. Mater. Sci.* **11** (1976) 341.
7. H. SCHMIDT, H. SCHOLZE and A. KAISER, *J. Non-Cryst. Solids* **48** (1982) 65.
8. M. C. WEINBERG and G. F. NEILSON, *J. Mater. Sci.* **13** (1978) 1206.
9. *Idem, J. Amer. Ceram. Soc.* **66** (1983) 132.
10. G. CARTURAN, V. GOTTARDI and M. GRAZIANI, *J. Non-Cryst. Solids* **29** (1978) 41.
11. V. GOTTARDI, M. GUGLIELMI and A. TIZIANI, *ibid.* **43** (1981) 105.
12. G. FAGHERAZZI and S. ENZO, *J. Mater. Sci.* **15** (1980) 2693.
13. I. M. LOW, PhD thesis, Monash University, Australia (1986).
14. D. C. BRADLEY, F. M. A. HALIM, E. A. SADEK and W. WARDLAW, *J. Chem. Soc.* April–June (1952) 2032.
15. G. C. WHITAKER, *Adv. Chem. Series* **23** (1957) 184.
16. J. E. SHELBY, J. VITKO and R. E. BENNER, *J. Amer. Ceram. Soc.* **65** (1982) C59.
17. I. M. LOW and R. McPHERSON, Proceedings 11th Australian Ceramics Society Congress, Sydney, 29–31 August, 1984 (Australian Ceramic Society, 1984) pp. 471–4.
18. F. K. CHI, *Proc. Ceram. Engng Sci.* **4** (1983) 704.
19. T. H. ELMER and H. E. MEISSNER, *J. Amer. Ceram. Soc.* **59** (1976) 206.
20. B. E. YOLDAS, *J. Non-Cryst. Solids* **51** (1982) 105.
21. P. W. McMILLAN, *ibid.* **52** (1982) 67.
22. D. L. WOOD, E. M. RABINOVICH, and E. M. JOHNSON *J. Amer. Ceram. Soc.* **66** (1983) 693.
23. H. DOI, T. KANDORI and O. KAMIGAITO, *Jpn J. Appl. Phys.* **12** (1973) 742.

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