JOURNAL OF MATERIALS SCIENCE 5 (1970) 369–373

Hot Stage Transmission Electron Microscopy of Crystallisation in a Lithia-Silica Glass

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Hot stage transmission electron microscopy has allowed the nucleation sequence in a 30 mole % Li_2O-70 mole % SiO_2 glass to be monitored *in situ*. This result agrees with previous work, in that the sequence of phases observed is identical but small temperature changes give rise to pronounced morphology changes. Hot stage electron microscopy has been proven to be a very useful technique for observing glass crystallisation processes, but the results must be carefully interpreted because of possible surface effects.

1. Introduction

Transmission electron microscopy (TEM) has been employed by Charles [1], Seward *et al* [2], and James and McMillan [3] in the *post facto* examination of phase separation in glasses. The TEM technique has also been used extensively in metallurgical systems to study similar phenomena. The metallurgical applications have been greatly enhanced by the use of hot stage TEM to allow *in situ* observations of precipitation phenomena (for example, precipitation in Al-Ag, Hren [4]). The present authors are reporting the application of the hot stage TEM to the study of crystal nucleation in a glassy system.

The objective of this investigation was to examine the nucleation sequence in the 30 mole % Li_2O-70 mole % SiO_2 glass in order to confirm previous X-ray analysis and AC dielectric measurement results [5]. The previous measurements indicated the formation of a lithium metasilicate precipitate which disappears as the equilibrium lithium disilicate forms. The TEM allows one to distinguish between the lithium metasilicate and the lithium disilicate by the use of selected area diffraction techniques. The *in situ* observation also allows the rate of reaction to be examined and compared with previous observations of bulk crystallisation rates [6].

2. Experimental Procedure

Samples for examination by TEM were prepared as previously described [5, 7] and thinned to approximately 0.2 mm by mechanical techniques. After mechanical thinning, the samples were cut into 3 mm discs with a core drill. Chemical thinning to the final thickness was accomplished in two steps. The initial thinning or "dimpling" was effected by masking the outer edge of the sample with Microstop*. This sample was then immersed in a 10HF-4HCl-14HAc solution until a dimple developed. After the mask was removed, final thinning was accomplished by dipping the sample in a 5% HF-H_2O solution for short periods. When a visible hole developed, the sample was washed and inserted in the Philips EM-200 Microscope with an RTS stage and heating holder PW-5600.

The sample was then examined as a function of the time at temperature, utilising standard TEM techniques [8].

3. Experimental Results

A series of electron diffraction patterns taken in the microscope at 480° C are shown in figs. 1, 2, and 3. These patterns show the amorphous initial glass structure followed by the appearance of the crystalline ring patterns. The lattice

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* Commercial masking lacquer.

spacings for the diffraction patterns observed are compared in table I with the ASTM lattice spacings reported for lithium metasilicate and lithium disilicate crystals. Examination of this table* shows that lithium metasilicate crystals are present after 14 min. After 2.5 h both metasilicate and disilicate are detectable in what appears to be approximately equal quantities. After 3.75 h the disilicate is the dominant phase with only very weak metasilicate lines being observed, and with longer heat-treatments the metasilicate is not observed at all.

A bright and dark field electron micrograph taken while the metasilicate and disilicate crystals were both present is shown in fig. 4. The observable features in the dark field image are interpreted to be lithium disilicate crystals due to the predominant intensity of disilicate lines in selected area diffraction patterns taken from these features. It was not possible to obtain a dark field image of the metasilicate crystals because of the small quantity and small size of the crystals present.

An appreciable change in the reaction sequence occurs when the sample temperature is maintained at 500° C in the microscope. The appearance and disappearance sequence of the metasilicate phase is so rapid that it is often missed in the photographic process. The accelerated reaction process also results in a morphology change of the equilibrium crystals grown in the microscope.

Fig. 5, a dark field micrograph taken from the spot circled on the diffraction pattern in fig. 6, shows the morphology of the lithium disilicate crystals grown for one hour in the microscope at 500° C. This pronounced difference in morphology, compared to that of the 480° C results, reflects the large temperature sensitivity of the lithium disilicate growth process [6].

The TEM technique has the inherent problem of electron beam heating which leads to some uncertainty as to the actual sample temperature. This problem is at least part of the reason for the apparent increase in kinetics over those of the bulk materials [5, 6]. However, by comparing the lineal size of the disilicate crystals grown in the microscope with the size of crystals predicted by an extrapolation of the temperature-dependence-of-growth data reported by Morley [9], it is possible to estimate the sample temperature rise from beam heating. In this manner it was concluded that beam heating should not

Figure 1 Electron diffraction pattern of as-cast 30 mole % lithia-silica glass taken at room temperature.

Figure 2 Electron diffraction pattern of 30 mole % lithia-silica glass at 480° C.

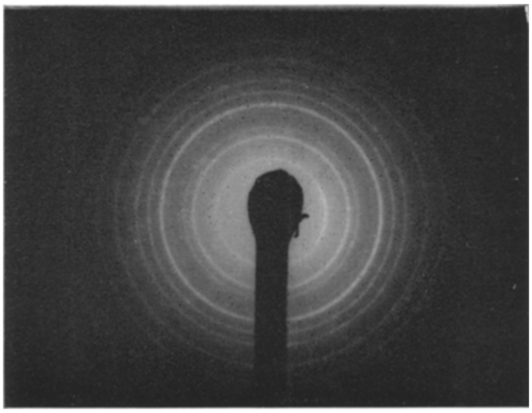

Figure 3 Electron diffraction pattern of 30 mole % lithia-silica glass at 480° C after 3.75 h at 480° C.

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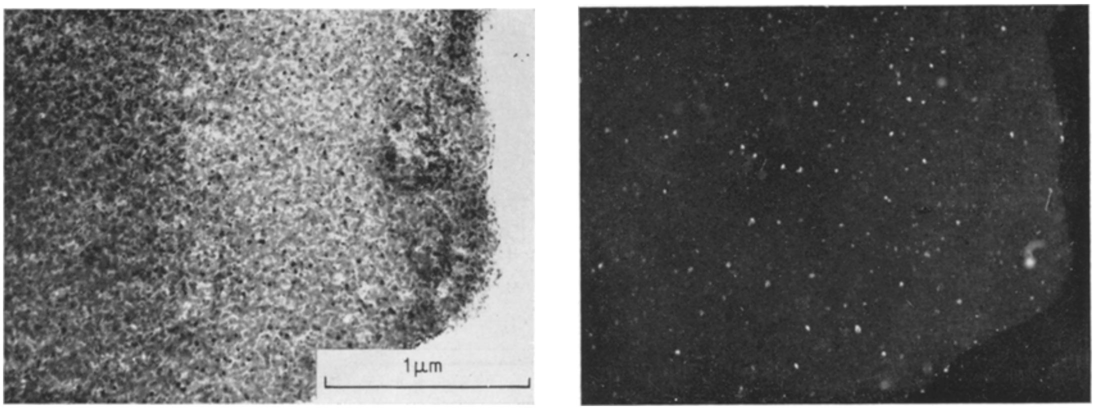
*See also discussion in Appendix.

TABLE I Summary of lattice spacings obtained from electron diffraction patterns of 30 mole % lithia glass at 480° C*

Standard crystal Li_2O-$2SiO_2$ disilicate		Standard crystal Li_2O-SiO_2 metasilicate		14 min at 480° C			2.5 h at 480° C			3.75 h at 480° C		
*d*Å	Intensity *I*	*d*Å	*I*	*d*Å	*I*	crystal	*d*Å	*I*	crystal	*d*Å	*I*	crystal
7.31	W	5.32	VW	2.72	VW	MS	3.74	S	DS	3.81	W	DS
5.41	W	4.70	S	1.915	W	MS	2.635	W	MS	2.650	VW	MS
4.02	VW	4.02	W	1.738	W	MS	2.345	W	DS	2.362	W	DS
3.75	S	3.32	S	1.560	VW	MS	1.855	W	DS	2.010	W	DS
3.66	S	3.20	VW	1.350	VW	MS	1.643	W	MS	1.855	W	DS
3.61	S	2.72	S	1.213	VW	MS	1.510	W	DS	1.662	VW	MS
2.91	VW	2.66	W				1.300	W	MS	1.509	W	DS
2.39	VW	2.59	VW				1.165	W	MS	1.460	W	DS
2.35	VW	2.35	W							1.391	W	DS
2.295	VW	2.10	VW							1.309	VW	MS
2.054	VW	1.78	VW							1.169	VW	MS
2.012	VW	1.66	VW							1.101	VW	—
1.966	S	1.57	W							1.009	VW	—
1.847	VW	1.53	VW							0.980	VW	—
1.833	VW	1.40	VW							0.921	VW	—
1.796	VW	1.36	VW									
1.533	VW	1.30	W									
1.521	VW	1.26	VW									
1.473	VW	1.18	VW									
1.468	W	1.14	VW									
1.442	VW											
1.423	VW											
1.376	VW											
1.251	VW											
1.224	VW											



(a) (b)

Figure 4 Transmission electron micrograph of 30 mole % lithia-silica glass at 480° C after 35 min at 480° C, (a) bright field; (b) dark field (× 28 000).

have produced more than a 10° C uncertainty in sample temperature. Morley's growth rates were obtained using an optical microscope, and therefore were based on the sample having a free surface, as in the present experiment. Therefore, it is proposed that the major difference between the kinetics of the metastable reaction sequence and the growth of the equili-

*See Appendix for discussion.

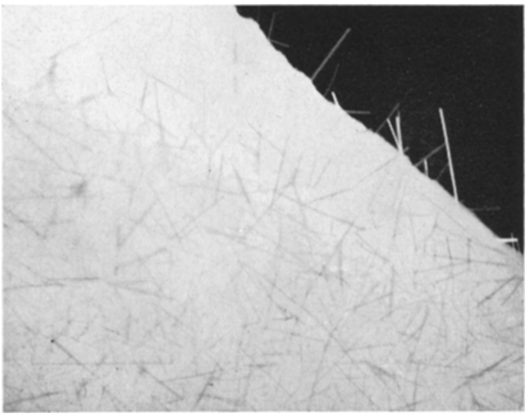


Figure 5 Dark field transmission electron micrograph of 30 mole % lithia-silica glass at 500° C after 1 h at 500° C (× 18 900).

Figure 6 Selected area electron diffraction pattern of sample shown in fig. 5.

brium crystals in the present experiment, and those obtained in bulk samples, is a result of volumetric constraints in the bulk processes.

4. Conclusions

It is concluded from this work that the nucleation sequence in a 30 mole % Li_2O-SiO_2 glass involves the precipitation of the metasilicate crystals followed by the appearance of disilicate crystals and the concurrent dissolution of the metasilicate. This reaction sequence agrees with that previously predicted from X-ray and dielectric analysis.

These results also demonstrate that *in situ* TEM observations of crystal precipitation processes in glass-ceramic systems can serve as a fundamental technique in describing the mechanisms of glass crystallisation.

Appendix

Differences between the reported values of the *in situ* TEM crystallite phases and ASTM lattice spacings are due to several sources. It is probable that solid solutions of SiO_2 occur in the MS and DS phases similar to that reported by Williamson and Glasser [10] and Glasser [11]. Lattice distortions accompanying the solid solution alter symmetry in the crystallites and thus serve to shift lattice spacings and eliminate diffraction from various planes. Such "transition phases" are also commonly observed to be precursors to the equilibrium phases in the heat-treatment of metallic solid solutions [4]. The gradual change in location of the MS and DS lines with heat-treatment is interpreted to be a result of alteration in the solid solution structure as the equilibrium DS phase nucleates and grows.

Line-broadening associated with the approximately 100 to 200 Å crystallites [12] also produces a potential 1% uncertainty in the assignment of specific lattice spacings. Thermal expansion variations in spacings, however, contribute only a maximum of 0.4% error based on dilatometric measurements of the glass-ceramics reported. Although the combination of these uncertainties produces a possible ambiguity in the assignment of individual lines, the combination of lines reported still results in a conclusive crystal identification.

Acknowledgement

The authors would like to acknowledge many helpful discussions with John Hren and the able laboratory assistance of E. J. Jenkins. The financial support of the Advanced Research Projects Agency of the Department of Defense monitored by the AFCRL under Contract No. F-19628-68-8-0058 is also acknowledged.

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Received 7 July and accepted 26 August 1969