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Microstructure and grain growth in $Li_2O-Al_2O_3-SiO_2$ glass ceramics

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Microstructure and grain growth were studied in two glass ceramics of the $Li_2O-Al_2O_3-SiO_2$ system, one an experimental material of basic composition $Li_2O-Al_2O_3-4SiO_2$ and the second a commercial material of approximately $0.7Li_2O-Al_2O_3-6SiO_2$ composition with small amounts of other oxides. There was evidence from transmission electron microscopy that the commercial material contained residual glass at grain-boundary triple points and glass layers at some but not all grain boundaries. No definite evidence was found for residual glass in the experimental material. The composition of second-phase regions in the commercial material was studied by STEM microanalysis. Al-rich regions of irregular morphology were found but there was no evidence that residual glass was SiO_2-rich, as has been previously suggested for this type of glass-ceramic. Grain growth showed a fairly similar time dependence in the two materials with growth more rapid in the commercial material at a given temperature. It is suggested that grain growth is controlled by precipitate particles rather than by residual glass phase.

1. Introduction

The properties of glass ceramics depend strongly on their microstructure. Of particular importance are the grain size and the existence of a residual glass-phase [1–4]. Chyung [5] suggested that there was a relationship between the glass phase and grain growth in an $Li_2O-Al_2O_3-SiO_2$ glass ceramic. He considered grain growth as the coarsening of particles surrounded by a glass matrix and used the model of Greenwood [6] for the growth of precipitates in solutions to account for a cube-root-of-time growth law. Chyung proposed that the residual glass phase inhibited grain growth [5]. However, Barry *et al.* [2] suggested that, on the contrary, grain growth would be accelerated rather than inhibited by a grain-boundary glassy layer. Raj and Chyung [7] have recently proposed a theory for creep in glass ceramics in which transport of material through a residual glass phase plays a key role. The model assumed for the grain-boundary structure in this theory was that of islands of good fit separated by a thin layer of glass phase – a postulate not yet supported by direct experimental evidence. Further investigation of these questions requires a more detailed study of the microstructure, especially in the region of grain boundaries as well as studies of grain growth. In this paper, grain growth in two $Li_2O-Al_2O_3-SiO_2$ glass ceramics of different compositions are studied, and a combination of techniques includ-

TABLE I

Material	Mol ratios relative to Al_2O_3								
	SiO_2	Al_2O_3	Li_2O	ZnO	CaO	Na_2O	K_2O	TiO_2	ZrO_2
A	4.0	1	1	–	0.03	–	–	0.18	–
D	6.1	1	0.68	0.13	–	0.03	0.01	0.11	0.07

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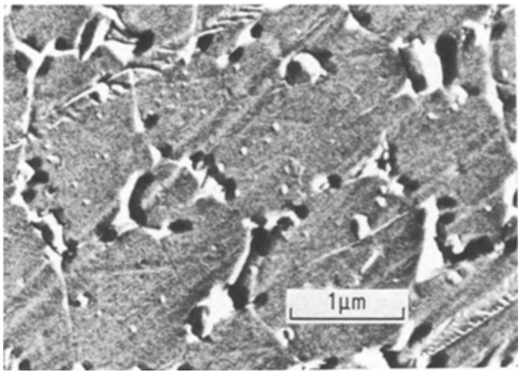


Figure 1 Replica of EDTA-etched surface of material D.

ing high-resolution electron microscopy and X-ray analysis is used to give as detailed a picture as possible of the microstructure of the materials.

2. Experimental procedure

The compositions of the two materials are listed in Table I. Material A is an experimental one and Material D is a commercial material (a cooker-top material made by Pittsburgh Plate Glass Company).

Specimens were prepared for replication electron microscopy by mechanically polishing to 1 μm finish and etching in EDTA solution as described by Chyung [5]. Au/Pd shadowed two-stage replicas were made by standard techniques [8].

Specimens for transmission electron microscopy were made by mechanically grinding and polishing slices to a thickness ~ 10 μm followed by ion beam thinning at 5 kV at an angle of incidence of 10–15°. High-resolution electron microscopy was carried out with a JEOL JEM 200CX microscope operating at 200 kV with an objective aperture out to 6 nm^{-1}. Low-beam currents were used as the specimens were extremely beam sensitive, making high-resolution work unusually difficult. For microanalysis, a JEOL JEM 100CX was used, the specimen being mounted on a carbon block to minimize spurious peaks. The ratio method was used for analysis [9, 10]. For example, the ratios of the atomic concentrations of Si and Al, C_{Si} and C_{Al} were assumed to be given by

$$\frac{C_{\text{Si}}}{C_{\text{Al}}} = K\frac{I_{\text{Si}}}{I_{\text{Al}}}$$

where I_{Si} and I_{Al} are the intensities of the Si and Al X-ray peaks and K is the constant for the relative detection efficiencies of Si and Al. The value of K was determined from a jadeite specimen of known composition.

3. Results and discussion

3.1. Microstructures

The replicas of EDTA-etched specimens partially revealed the grain boundaries in specimen D but not in specimen A (Figs 1 and 2). The appearance of replicas from D is similar to that found by Barry *et al.* [2] and Chyung [5] for similar material. It is assumed that the etchant attacks residual glass phase. If this is correct, then it is apparent that the residual glass in D is concen-

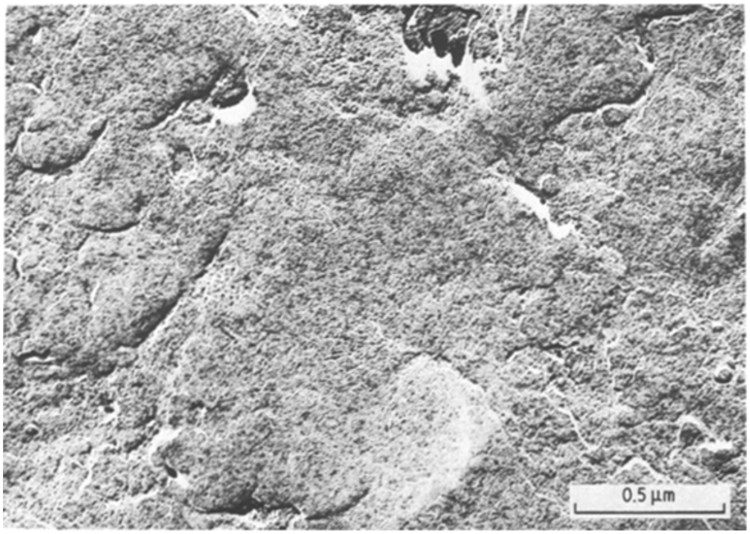


Figure 2 Replica of EDTA-etched surface of material A.

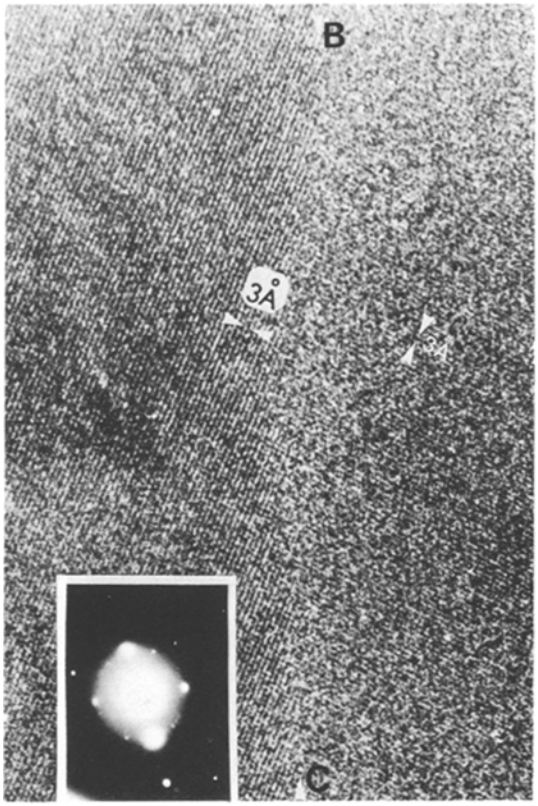


Figure 3 Grain boundary in material A.

trated at grain-boundary triple points and that only a limited number of boundaries show evidence of a continuous glass layer. This at once casts some doubt on the interpretation of grain growth in terms of a model of the coarsening of particles embedded in a continuous matrix. Further evidence on the presence of glass phase was sought by transmission electron microscopy. High-resolution techniques are very difficult because of the rapid loss of crystallinity of the major phase, β spodumene, in the electron beam so that there is, for example, no opportunity to tilt a grain boundary into exact parallelism with the electron beam. Fig. 3 shows a high-resolution image of a high-angle grain boundary in specimen A. Although there are some signs of beam damage there is clearly crystalline material within 1 nm of the boundary along BC, i.e. any disordered region can be no more than 1 nm in width. An alternative technique which has been used to reveal grain-boundary glass layers in ceramics is the displaced aperture dark-field technique [11]. The objective aperture is set in a position to select only diffuse scattering from amorphous material. Fig. 4 shows a region of specimen D in which part of a grain boundary shows strong diffuse scattering, indicating a local intergranular glassy layer. However, it should be emphasized that this technique gave no evidence of a *continuous* glassy layer, even in material D. This result is in agreement with the replica observations of EDTA-etched specimens and it confirms that the microstructure of these glass-ceramics cannot be envisaged as crystalline particles embedded in a continuous glassy matrix. A third method for detecting thin intergranular films which has been proposed is that of defocus imaging [11]. Out-of-focus fringes, qualitatively similar to Fresnel fringes formed at the edge of a specimen, arise due to a difference in potential between the grain and an intergranular layer. Fig. 5 shows that this technique again gives evidence of glassy layers at some grain boundaries but not all.

STEM microanalysis showed that the majority of precipitates in material D contained both Ti

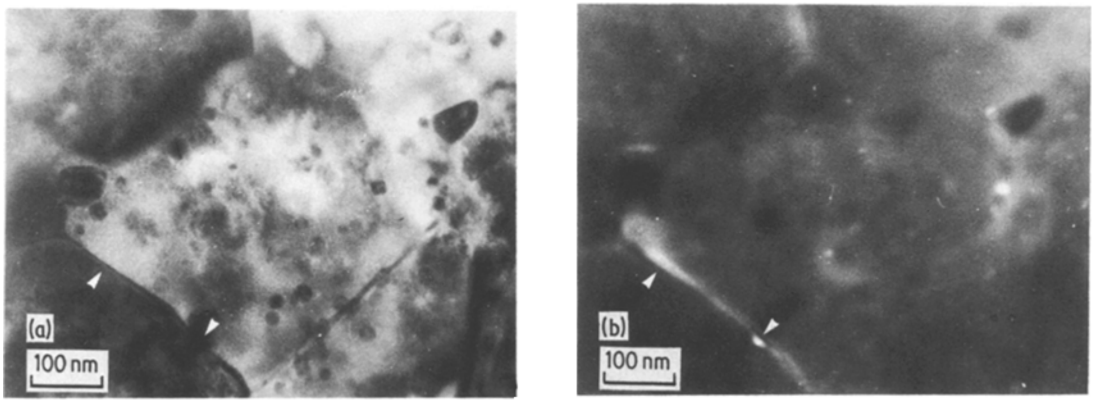


Figure 4 (a) Bright-field and (b) displaced aperture dark-field micrographs of grain boundaries in material D.

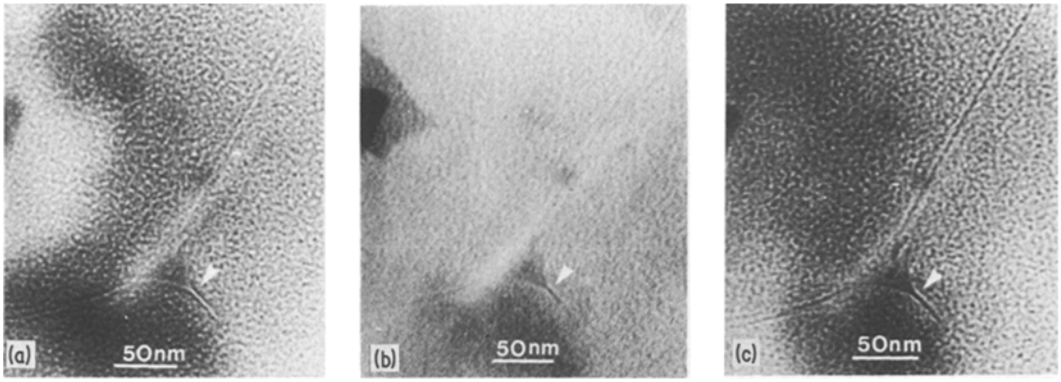
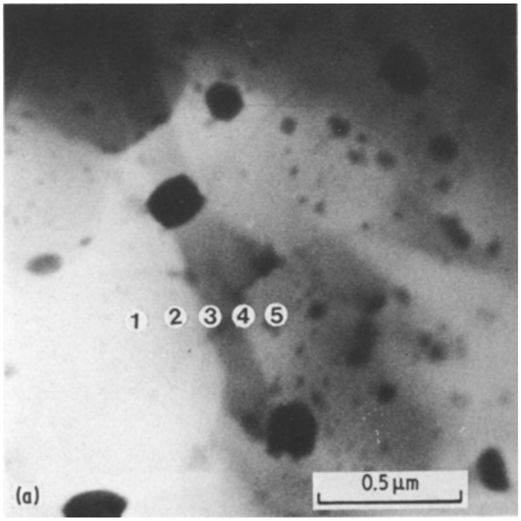
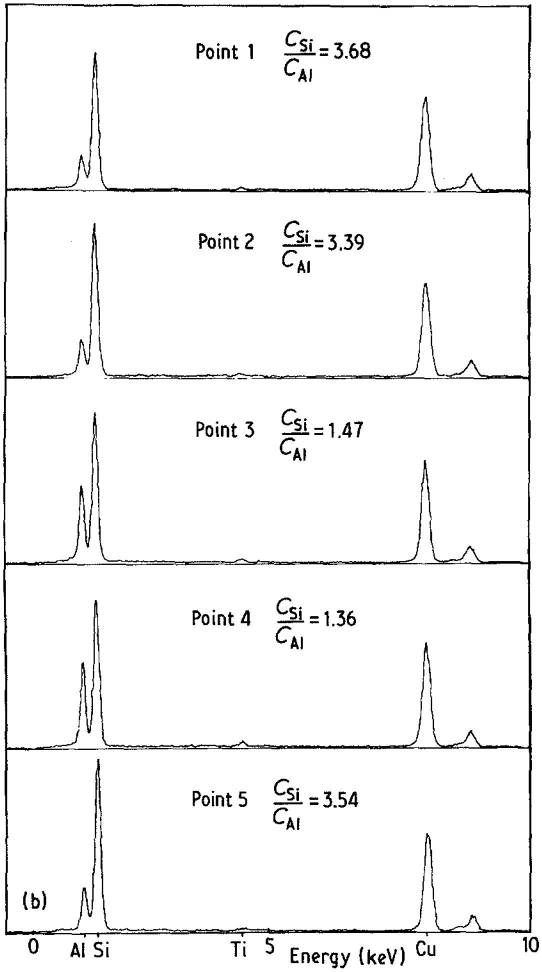


Figure 5 Through-focus series of micrographs of grain-boundary junction in material D. (a) Under focus, (b) near focus and (c) over focus.

and Zr, the nucleating agents. Precipitates appearing square in projection contained a high Zn concentration and were probably gahnite. Particular attention was paid to the microanalysis of intergranular regions. It has been proposed that residual glass phase is of a high SiO_2 composition [5] – probably 95% SiO_2 5% Al_2O_3. If this were so, intergranular regions of high Si concentration might be expected, but such regions were not in fact found. Indeed, intergranular regions of an irregular morphology which on micrographs were judged, intuitively, to be "glass-like" were found in fact to be enriched in Al_2O_3. An example is shown in Fig. 6 – other, similar examples were found. Unfortunately it was not possible to determine whether these regions, in fact, were glassy by microdiffraction, because of the rapid loss of crystallinity of the crystalline spodumene when examined by microdiffraction. However, the study casts serious doubt on the existence of very high

Figure 6 (a) STEM micrograph of material D. (b) X-ray microanalysis traces for the points indicated in (a). The Cu peaks arise from the specimen holder.





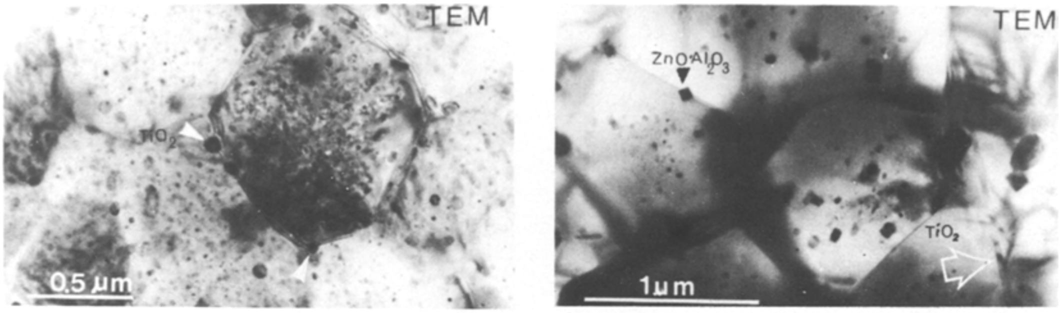
SiO_2-rich glass regions of any significant extent in material D. It is not obvious that crystallization from a glass at temperatures well below the solidus where the spodumene phase produced has a very wide composition range, accepting SiO_2 well in excess of the stoichiometric composition, should lead to a rejection of SiO_2 into residual glass. On the other hand, when the Li_2O content of the material is lower than the stoichiometric composition of β-spodumene requires, as shown for material D in Table I, the substitution of Si by Al in the crystalline phase may be limited by the supply of Li, leaving an excess of Al to be accommodated. An Al_2O_3 rich glass phase could reasonably be expected in such a case.

3.2. Grain growth

The measurement of grain sizes is not a simple matter since the etching technique does not show up a continuous grain-boundary network even in specimen D. The replication of the etched fracture surfaces was found to give a good result for some specimens of D but for specimen A only TEM or STEM observation of ion-beam thinned specimens was effective, the STEM technique giving somewhat higher grain contrast. For specimens of D the STEM technique was compared with measurements from replicas of etched surfaces and was found generally to give a somewhat smaller grain size, consistent with the difficulty of delineating all the boundaries in the replica technique. Fig. 7 shows TEM and STEM micrographs of materials A and D. The grain-growth results for A and D plotted as $\log d$ against $\log t$ are shown in Fig. 8. Assuming a relationship of the form $d = Kt^n$, the value of n is approximately 0.3 for material D and 0.2 for material A. The data, at least for specimen D, are not inconsistent with a $t^{1/3}$ law for grain growth. However, the Greenwood theory for the growth of dispersed precipitates in solution, predicting

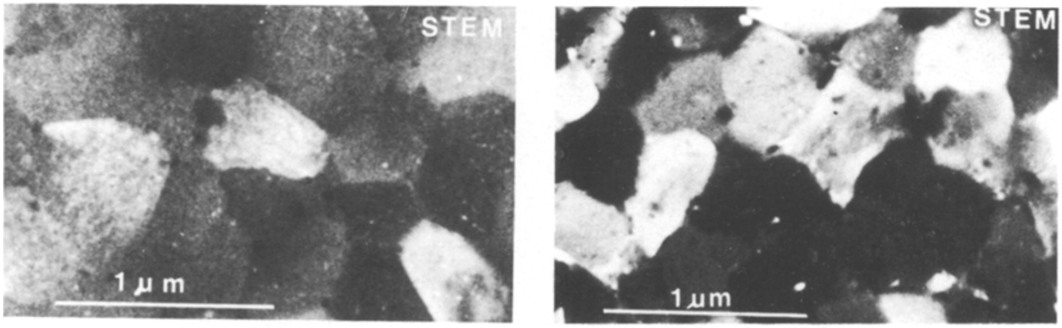
$$d^3 - d_0^3 = Kt$$

was developed for well-separated particles. Greenwood argued that his theory might be extended to closely spaced particles but it seems unlikely that it could be applied to the present systems, regarded as crystalline particles in a glass matrix when the glass phase is not even continuous, i.e. there is not a complete and continuous layer of glass separating the grains. It seems reasonable instead to consider the role of what is, in fact, a more prominent feature of the microstructure, namely the high density of precipitate particles,



Glass ceramic A.

Glass ceramic D after 10 h heat treatment at 1150° C.



Glass ceramic A.

Glass ceramic D.

Figure 7 TEM and STEM micrographs of materials A and D. The STEM technique gives stronger grain contrast.

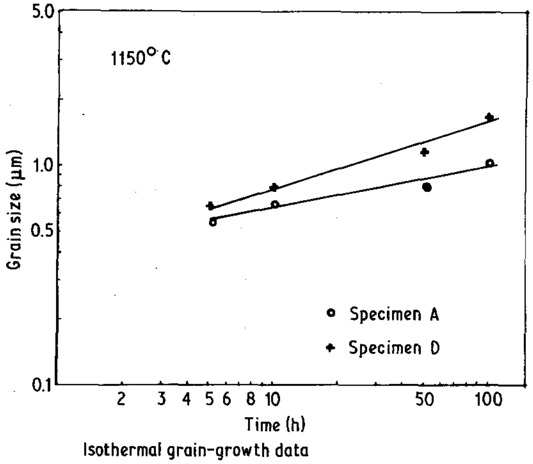


Figure 8 Grain growth in materials A and D at 1150° C.

some of which are located at grain boundaries. If the grain boundaries are held back by precipitates according to the Zener mechanism [12] then grain growth may be controlled by precipitate coarsening, i.e. Ostwald ripening. The kinetics of this depend on whether the coarsening is controlled by lattice or grain-boundary diffusion. In the former case the mean precipitate radius $r \propto t^{1/3}$ [13] and since according to the Zener mechanism the grain size $d \propto r$, a $t^{1/3}$ dependence for the grain size would be expected. If grain-boundary precipitates coarsen much more rapidly by grain-boundary diffusion than by lattice diffusion, their mean size should increase as $t^{1/4}$ [14]. The presence of rapid grain-boundary diffusion might lead to some departure from a $t^{1/3}$ grain-growth law.

4. Conclusion

High-resolution TEM studies of $Li_2O-Al_2O_3-SiO_2$ glass ceramics are very difficult, because of the rapid degradation of the β spodumene phase to an amorphous structure in the electron beam. Nevertheless, such studies combined with replica studies have given evidence of intergranular residual glass layers. However, even in a commercial material not all boundaries show evidence of such a layer, from which it is concluded that the glass does not form a continuous matrix. Grain-growth data may be explained on the basis that the grain size is controlled by precipitate particles. The compositions of second phases have been analysed by STEM microanalysis. Commercial material contains precipitates of mixed TiO_2/ZrO_2 and gahnite, and Al-rich regions of irregular morphology but there is no evidence of SiO_2-rich regions which have been proposed as a stable residual glass phase.

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