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Anisotropic Grain Growth in Boria-doped Diphasic Mullite Gels

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Abstract

Densification and anisotropic grain growth were investigated in sol-gel derived, boria-doped diphasic mullite. Boria enhanced viscous flow densification by reducing the viscosity and also produced a fine grain microstructure. Whisker-like mullite grains evolved from the dense, equiaxed microstructure. The onset temperature was ~1500°C. Chemical leaching was employed to characterize the anisotropic grains. Growth kinetics showed that anisotropic grains followed the empirical equation $G^n - G_o^n = Kt$ with $n = 3$ and $n = 4$ for the length and thickness directions, respectively. The activation energies for grain growth were 660 kJ mol^{-1} for elongation and 800 kJ mol^{-1} for thickening. © 1999 Elsevier Science Limited. All rights reserved

Keywords: mullite, sol-gel process, grain growth, microstructure-final, densification.

1 Introduction

Boria is known to enhance the transformation kinetics in mullite,[1–6] and it has been shown that the mullite transformation temperature decreases by 150°C in 5 wt% B_2O_3 doped diphasic gels.[1] The enhanced transformation kinetics in boria-doped samples was attributed to faster diffusion in the lower viscosity boria-containing glasses,[2,3] or due to enhanced nucleation as a result of the *in situ* formation of aluminum borate before mullite formation.[4–6] In addition, boria has been reported to reduce the grain size and to produce a fine grain microstructure in mullite.[2,3,6]

An earlier study showed that boria enhances anisotropic grain growth in diphasic mullite gels and results in a three-dimensional, interpenetrating microstructure.[1] However, microstructural characterization was incomplete because of the difficulty in measuring the actual 3-D grain size of rod-shaped grains from the 2-D polished section. The 95th percentile in the distribution of aspect ratios has been proposed as a better measure of grain shape anisotropy in rod-shaped microstructures.[7] The area weighted aspect ratio has been introduced also to overcome the underestimation of a small number of large grains.[8] These proposed methods appear to give reasonable values, but they have been shown to inadequately represent the true grain shape anisotropy.

One method to accurately characterize the rod-shaped grain microstructure is to fully disassemble the entire sample by chemical dissolution.[9,10] This process is applicable to silicate-based liquid phase systems because aqueous solutions of HF can dissolve the glassy phase. By separating individual grains, one can directly measure the grain size. This method has been effectively applied to analyze anisotropic grain growth in Si_3N_4[10] and mullite.[11]

In the present study, anisotropic grain growth kinetics in boria-doped diphasic mullite gels have been investigated. The grain growth kinetics are compared to anisotropic growth kinetics in the titania-doped diphasic mullite gels reported earlier.[11]

2 Experimental Procedure

The diphasic mullite gels were prepared from commercially available boehmite (Catapal D, Vista Chemical Co., Houston, TX) and silica (Ludox AS-40, Dupont Co., Wilmington, DE). Boria was introduced to the aqueous dispersion as boric acid. Additional processing details are described in an earlier paper.[1] After cold isostatic pressing the pure diphasic and 3 wt% boria-doped diphasic gel powders, the pellets were calcined at 500°C for 1 h to remove the water.

For phase development studies by XRD, boria-doped diphasic gels were calcined at 1100 and

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1350°C for 10 min in a Pt crucible. Densification was continuously monitored in 500°C calcined pellets using a thermomechanical analyzer (TMA) (TMA-50, Shimadzu, Kyoto, Japan). After dry and cold isostatic pressing, pure diphasic and 3 wt% boria-doped diphasic gel pellets were calcined at 500°C for 1 h to remove the water before TMA analysis.

For microstructural characterization, mullite grains were separated from the pellets by immersing the specimens into an ~30% aqueous HF solution. Leached grains were washed several times with distilled water and dilute NH_4OH to remove the adsorbed HF at the surface of the grains. Grain size was determined by measuring 200 grains per sample from SEM (SX40A, Akashi Beam Technology, Tokyo, Japan) micrographs. TEM (Philips 420T, Netherlands) was used to determine the orientation of the anisotropic mullite grains and chemical composition was analyzed by EDS. TEM sample preparation followed the standard procedures of polishing, disk cutting, dimpling, and ion milling.

3 Results and Discussion

Phase development in 3 wt% boria-doped diphasic mullite gel was determined by XRD (Fig. 1) The mullite transformation temperature in the 3 wt% boria-doped sample, as determined by DTA at 10°C/min, was 1260°C compared to the transformation of 1345°C in the undoped gels.[1] Before mullite formation (1100°C, 10 min), the major phases were δ (or θ) alumina and an amorphous phase. Aluminum borate was not detected by XRD in any sample prior to mullite formation. In the sample calcined at 1350° for 10 min, only orthorhombic mullite was detected indicating complete transformation.
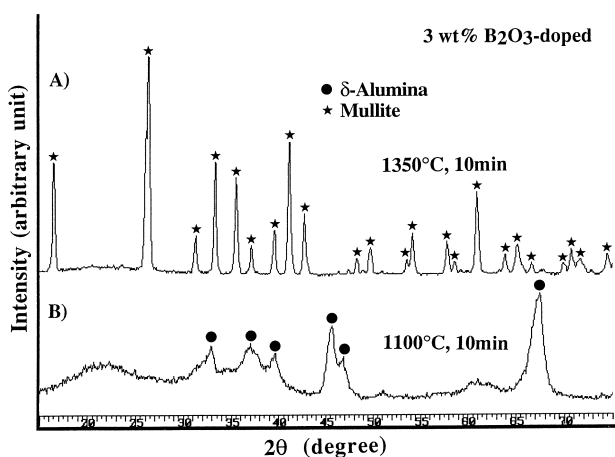
To determine the influence of boria on the densification of diphasic mullite gels, axial shrinkage, $\Delta L/L_o$, was measured by TMA (L_o = initial sample length and L = instantaneous sample length). The TMA results show that pure diphasic mullite gels densified between 1100 and 1300°C and the 3 wt% boria-doped gels densified between 1000 and 1200°C (Fig. 2)

As mentioned above, the mullite transformation temperatures determined by DTA were 1345 and 1260°C for pure and 3 wt% boria-doped diphasic mullite gels, respectively.[1] Thus, because most of the densification occurred before mullite crystallization, densification is assumed to occur by viscous flow. At the shrinkage plateau, samples reached ~93% theoretical density as measured by the Archimedes method (Fig. 2).

In the initial stage of viscous sintering, the linear shrinkage can be expressed by Frenkel's equation[12]

$$\frac{L(t)}{L_o} = 1 - \frac{3\gamma t}{8\eta r} \qquad (1)$$

where $L(t)/L_o$ is the shrinkage at time t, γ is the surface tension, η is the viscosity, and r is the particle radius. The rate of shrinkage is dependent on the surface tension, particle radius, and viscosity. The surface tension is weakly dependent on temperature and composition.[13] Thus, the temperature dependence of the sintering rate is mainly due to the change in viscosity.

Boria-silica glasses have a much lower viscosity relative to pure vitreous silica (e.g. $10^{5.1}$ Pa.s for 28 wt% boria-72 wt% silica versus $10^{10.2}$ Pa.s for silica at 1300°C).[14] Based on the above arguments and assumptions of constant particle size and surface tension during viscous sintering, we conclude that the enhanced densification in the boria-doped samples is mainly due to the decreased viscosity.
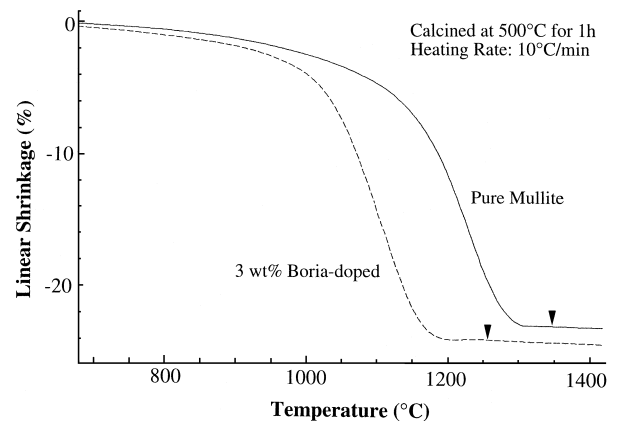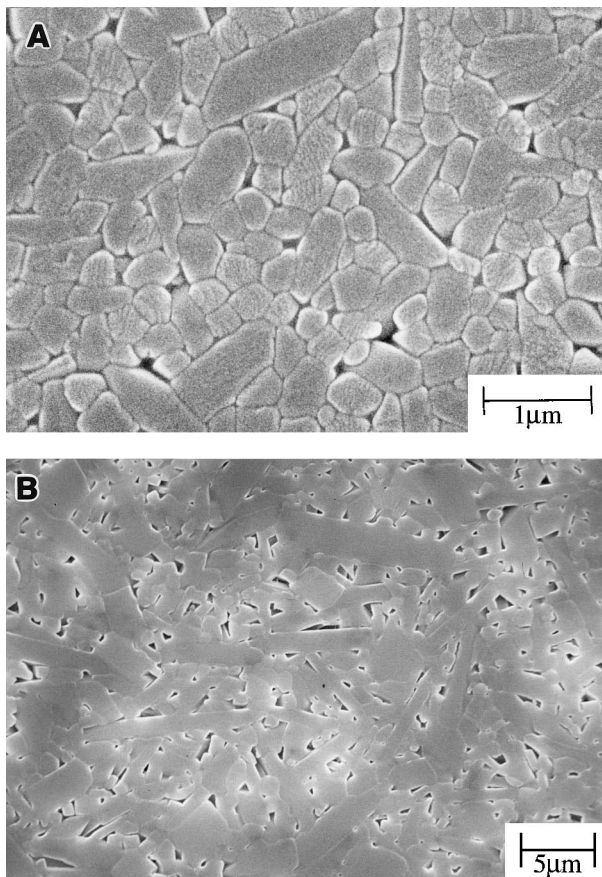

Fig. 1. X-ray diffraction patterns of 3 wt% boria-doped diphasic mullite calcined at (A) 1350°C for 10 min and (B) 1100°C for 10 min.

Fig. 2. Thermomechanical analysis (TMA) of pure and 3 wt% boria-doped diphasic mullite. Samples were pre-calcined at 500°C for 1 h and the heating rate was 10°C min^{-1} in air.

Compared to the fine TiO_2-doped case, boria promoted densification more with the same amount of doping and reached the shrinkage plateau at a lower temperature by $\sim 30°C$. This might be due to the lower viscosity in the boria-silica system than in the titania-silica system.

Figure 3 shows SEM micrographs of 3 wt% boria-doped diphasic mullite gels sintered at 1500 and 1650°C for 5 h. At low temperature, the microstructure consisted of fine, equiaxed grains of $< 0.5 \mu m$ and several elongated grains with straight grain boundaries. For the same conditions, undoped mullite consisted of equiaxed grains of $\sim 1 \mu m$.[1] These results agree with earlier observations that boria reduces the grain size of mullite.[2,3,6] It appears that anisotropic grain growth already started at 1500°C. After prolonged sintering or sintering at higher temperature, anisotropic grains continue to grow at the expense of the surrounding smaller grains. After 5 h at 1650°C, most grains are elongated with straight grain boundaries, and a three-dimensional, interpenetrating microstructure is developed. From SEM and TEM micrographs, the elongated grains are whisker-like and have square or rectangular cross-sections. The morphology of the anisotropic mullite grains in boria-doped samples is the same as in the titania-doped case.

Figure 4(B) shows a TEM micrograph of an acicular grain seen in Fig. 4(A) in a sample of 3 wt% boria-doped diphasic mullite gel sintered for 5 h at 1650°C. From electron diffraction, the growth axis of the grain is $\langle 001 \rangle$ and the lateral planes are $\{110\}$ crystallographic planes. The elongated grains are surrounded by glass pockets of triangular shape. EDS analysis demonstrated that the glass pockets are mainly silica with a minor amount of alumina (Fig. 5) The low energy peaks at < 0.2 keV in the EDS spectrum are due to the instrument and carbon coating. Although boria solubility in mullite is not available, residual boria is likely to be in the glass and will modify the silica glass characteristics. Unfortunately, boria was not detectable by the EDS system available and thus could not be quantified.

Figure 6 shows chemically separated, 3 wt% boria-doped mullite grains after sintering at 1550°C for 10 min. Mullite grains are whisker-like with sharp ends. Grain thickness is about the same for all grains, but grain length and thus, the aspect ratio is widely distributed.

Microstructural characterization of boria-doped samples was performed using micrographs of

Fig. 3. SEM micrographs of 3 wt% boria-doped mullite sintered at (A) 1500°C for 5 h and (B) 1650°C for 5 h.
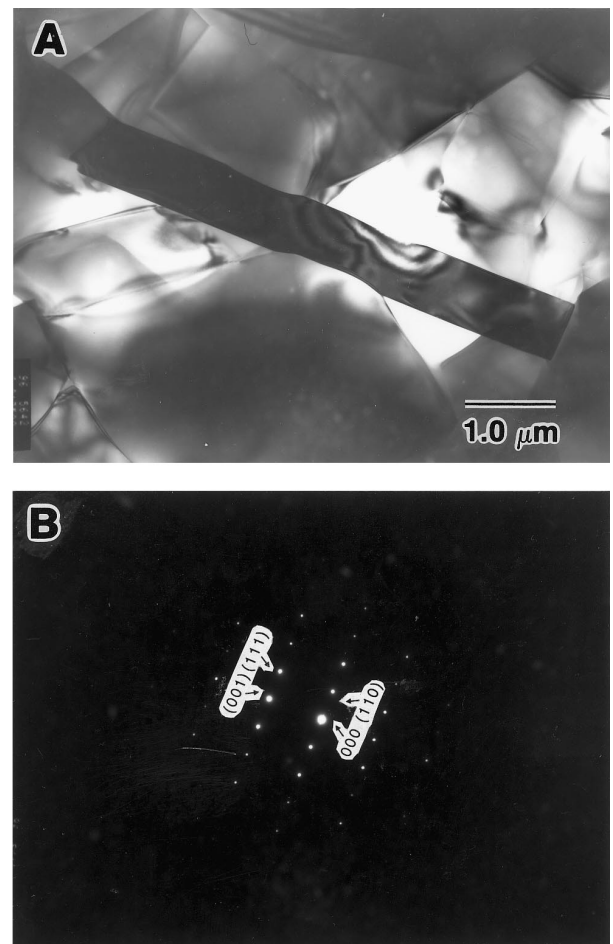
Fig. 4. TEM micrograph and electron diffraction pattern of an anisotropic mullite grain in 3 wt% boria-doped mullite sintered at 1650°C for 5 h.

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chemically leached grains. In Fig. 7 the average aspect ratios are plotted as a function of boria concentration for samples sintered at 1600°C for 5 h. The aspect ratio increased rapidly with boria concentration and the range of aspect ratios increased as indicated by the larger standard deviation in the Fig. 7.
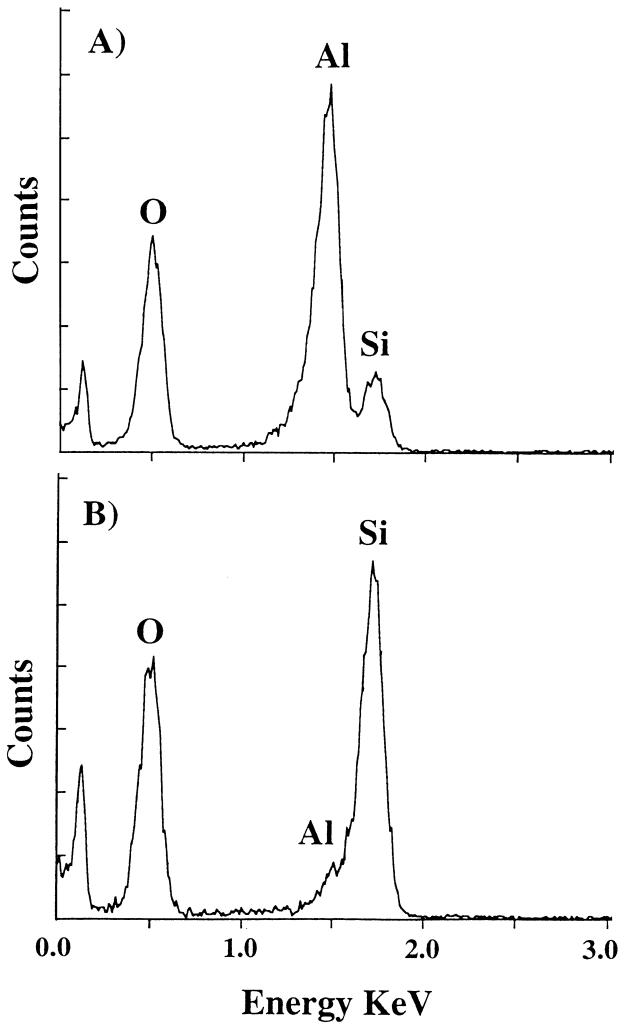

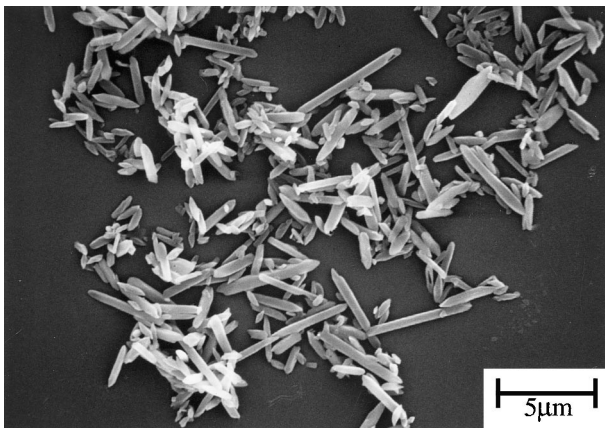Fig. 5. EDS spectra of (A) mullite grain and (B) glass pocket.

Fig. 6. SEM micrograph of chemically separated mullite grains from the 3 wt% boria-doped mullite sintered at 1550°C for 10 min.

To evaluate the anisotropic grain growth kinetics, the grain length, grain thickness, and aspect ratio were measured at several temperatures for different times in 3 wt% boria-doped samples (Fig. 8) Anisotropic grains grew more rapidly compared to titania-doped mullite gels such that the aspect ratios at 1650°C for 10 min were ~9·5 and ~5·5 in boria- and titania-doped samples, respectively. This is due to the finer grain size in boria-doped samples and the lower viscosity of the boria-containing glass. The aspect ratio continued to increase but leveled off after prolonged heating. At the same doping and heating conditions, the average aspect ratio in boria-doped samples is larger than that in titania-doped samples. For example, the average aspect ratio and standard deviations were 12·5 ± 3·9 in 3 wt% boria-doped and 9·8 ± 3·3 in 3 wt% coarse titania-doped samples after sintering 5 h at 1650°C.[11]

The grain growth kinetics can be expressed by the empirical equation.[15]
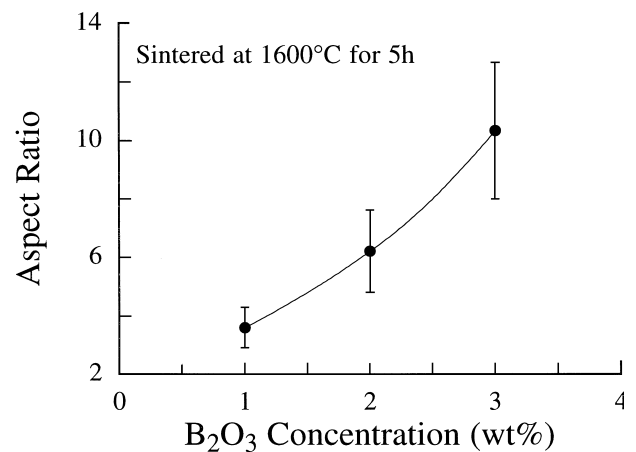
$$G^n - G_o^n = Kt \qquad (2)$$

Fig. 7. Measured aspect ratio as a function of boria concentration. Samples were sintered at 1600°C for 5 h.
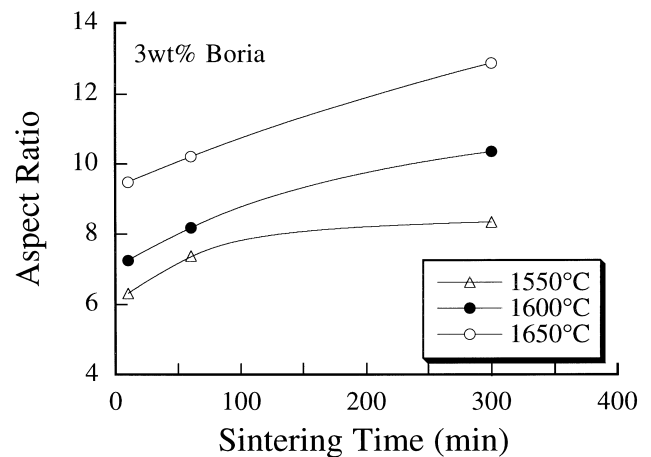

Fig. 8. Aspect ratio variation with sintering time at several temperatures. All the samples were doped with 3 wt% boria.
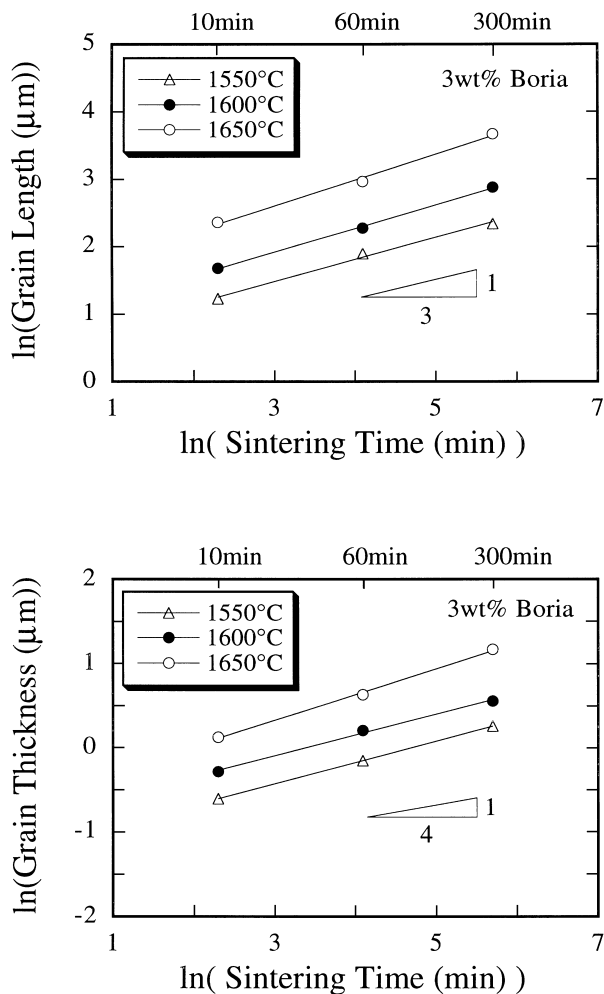
where G is the grain size, G_o is the initial grain size, K is the rate constant, and t is time. The rate constant K is temperature dependent and related to the diffusivity of the diffusing species, specific surface energy, and so forth. To compare the growth rates in the length and thickness directions, the above equation was applied as follows:

$$L_P - L_o p = K_L t \tag{3}$$

$$Dq - D_o q = K_D t \tag{4}$$

where L and D are the grain length and thickness. L_o and D_o are the initial grain length and thickness. Because the initial grain dimensions are relatively smaller than the anisotropic grains the initial dimensions can be ignored in the evaluation of the anisotropic growth kinetics. From the plot of ln (grain length or grain thickness) versus ln (t), the slope was determined to be 3 and 4 for the grain length and thickness, respectively (Fig. 9)

As expected from the SEM micrographs, the growth kinetics are different and faster in the

length direction. In the TiO$_2$-doped system,[11] the time exponents for grain length and thickness are 3 and 6, respectively. The growth exponent in the length direction was 3 which implies a diffusion-controlled growth mechanism. However, boria-doped samples showed a smaller growth exponent in the thickness direction than the titania-doped samples.

Grain growth is a thermally activated process and thus, the rate constant can be expressed as:

$$K_L = K_{Lo} \exp(-E_{aL}/RT) \tag{5}$$

$$K_D = K_{Do} \exp(-E_{aD}/RT) \tag{6}$$

where E_{aL} and E_{aD} are the activation energies, and K_{Lo} and K_{Do} are preexponential terms for axial and radial growth, respectively. From the plot of ln K versus $1/T$, the estimated activation energies are 660 and 800 kJ mol^{-1} for the length and thickness, respectively (Fig. 10) The estimated rate constants at 1600°C are ln $(K_{1600}) = 2\cdot40$ for the length direction and $\ln(K_{1600}) = -3\cdot40$ for the thickness direction.

Both titania and boria produced similar anisotropic grain microstructures and showed slightly different growth kinetics. As mentioned earlier, anisotropic mullite grains grew more rapidly in boria-doped than the titania-doped samples at the same conditions, and boria-doped system showed comparable growth exponents in the length and thickness directions. These differences have their origin in the smaller grain size prior to anisotropic grain growth and the lower viscosity of the glass phase in the boria-doped samples. Both factors will enhance the dissolution and reprecipitation processes, which are believed to be the processes required for anisotropic grain growth in this system.

Fig. 9. Grain growth in the length and thickness directions as a function of sintering time in 3 wt% boria-doped diphasic mullite.
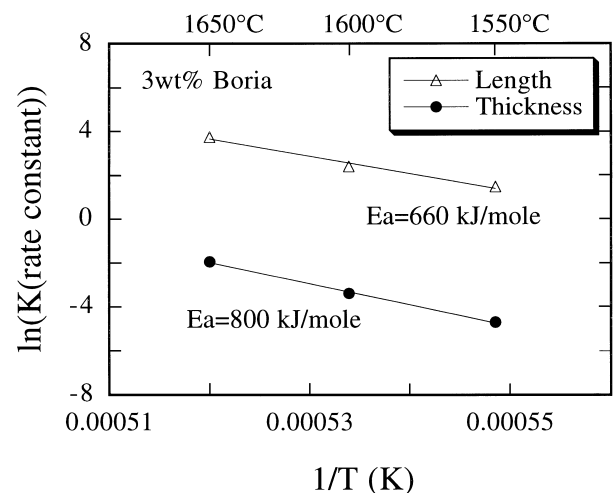
Fig. 10. Activation energies for the length and thickness directions from the plot of ln (rate constant) versus the reciprocal temperature.

4 Summary

Boria reduced the viscosity of silica glass and enhanced densification in diphasic mullite gels. In addition, boria reduced the grain size and resulted in a fine, equiaxed grain microstructure of $0.5\,\mu$m at 1500°C. Anisotropic grains started to grow from these dense equiaxed grain microstructure, and growth kinetics in the axial direction followed a cubic growth law. The growth exponent in the thickness direction was 4. The activation energies for growth were $660\,\mathrm{kJ\,mol^{-1}}$ in the length direction and $800\,\mathrm{kJ\,mol^{-1}}$ in the thickness direction which were similar to those in titania-doping case.

Acknowledgements

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