

High temperature flow behaviour of SiC reinforced lithium aluminosilicate composites

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Abstract. The compressive flow behaviour of lithium aluminosilicate (LAS) glass, with and without SiC particulate reinforcements, was studied. The LAS glass crystallized to *b* spodumene during high-temperature testing. The flow behaviour of LAS glass changed from Newtonian to non-Newtonian due to the presence of crystalline phase. Further, with the addition of 40 vol.% SiC additions, the strain rate sensitivity of flow stress decreased. While the activation energy for flow in LAS was 300 kJ/mole, it increased to 995 kJ/mole with the addition of 40 vol.% SiC reinforcements.

Keywords. Lithium aluminosilicate (LAS); SiC particulates; flow behaviour; compression.

1. Introduction

Silicate glasses were proved to be promising matrix materials for the development of ceramic matrix composites (CMCs). Some of the advantages of silicate matrices are: availability in a wide range of compositions, thermal expansion to match with different types of reinforcements, easy fabrication, control over crystallization and formability. Easy densification of these composites could be achieved from the viscous flow of glass matrices at relatively lower temperature and on further densification, they offer superior thermal and mechanical properties. Keeping this in view, numerous glass and glass–ceramic composites have been developed by incorporating different types of reinforcements (Gadkaree and Chyung 1986; Prewo *et al* 1986).

At higher temperatures, glass exhibits Newtonian flow behaviour with strain rate sensitivity (*m*) of unity. But with the addition of extraneous reinforcements, the flow behaviour gradually changes from Newtonian to non-Newtonian and becomes sensitive to temperature, morphology, size and volume fractions of reinforcements (Murthy *et al* 1997; Das *et al* 1998, 1999). Rouxel and Verdier (1996) explored the effect of SiC particulate reinforcements in oxynitride glasses. Like in silicate composites, non-Newtonian behaviour was observed in oxynitride glasses but instead of shear thinning they observed shear thickening. This was attributed to change in composition of grain boundary glass coupled with agglomeration of SiC particulates in the glass. In these studies, the volume fraction of extraneous reinforcements was limited to 40% because the infiltration through reinforcements becomes

difficult at higher values. In glass–ceramics, by *in situ* crystallization, the solid volume fraction could be increased in controlled fashion to study the flow behaviour. Wang and Raj (1984) explored the flow behaviour of lithium aluminosilicate (LAS) system by varying crystalline phases (quartz and *b* spodumene) and corresponding residual glass contents. It was found that the flow behaviour was sensitive to the crystalline phase as well as grain boundary glass that formed during devitrification. Also, the flow behaviour was dependent on the grain size of crystallizing phase. Although the lithium aluminosilicate glass–ceramic exhibited high *m* (= 1) values in compression, the tensile elongations were dictated by the amount of residual glass phase and its properties and resistance to cavitation (Wang and Raj 1984). Further, the observed flow behaviour was explained based on solution creep with rapid diffusion through the interconnected liquid channels (Raj and Chyung 1981). However, the flow behaviour was not studied in the presence of extraneous reinforcements. The present study is taken up to investigate the flow behaviour of LAS glass ceramic in the presence of SiC particulate reinforcements.

2. Experimental

The composition of LAS glass used in this investigation was similar to that employed in an earlier investigation (Wang and Raj 1984). It was originally a Corning glass (code 9608) having the following composition (wt%) SiO₂: 69.93, Al₂O₃: 17.9, Na₂O: 0.4, Li₂O: 2.7, MgO: 2.6, ZnO: 1.0, TiO₂: 4.7, As₂O₃: 0.6, K₂O: 0.1, Fe₂O₃: 0.07. Titanium and arsenic oxides were added for refinement of grains whereas MgO partly substituted lithium oxide in the crystallizing phase (*b* spodumene)

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and helped in uniform nucleation (Raj and Chyung 1981). Glass samples for compression were obtained by conventional melting and quenching techniques. SiC particulates used in this study exhibited an uneven morphology with ragged edges. For preparation of composites, the glass powder was mixed with 20 vol.% as well as 40 vol.% of SiC particulates (32–45 μm) and hot pressed using a BN coated graphite die assembly at 1200°C with > 10 MPa pressure. Microstructural details were studied using X-ray (Seifert & Co, Iso-Debyeflex 2002, Cu K α), SEM (JEOL 840A) and TEM (JEOL 2000FX). For TEM studies, electron transparent samples were prepared by dimpling (Gatan 656) followed by ion beam milling (Gatan 600). All the compression tests were carried out in air on 6 × 6 × 10 mm samples at temperatures ranging

from 1100–1300°C. All the compression tests were carried out in the strain range of 10⁻⁵ to 10⁻² s⁻¹ using an MTS machine (model 810-12).

3. Results and discussion

During hot pressing, the LAS glass gradually crystallized to fine equiaxed *b* spodumene grains and the grain size was found to be around 2 μm (figure 1a). Besides spodumene phase, uniformly distributed rod shaped crystallites of aluminotitanite were also observed. These fine precipitates are believed to act as nucleating sites for *b* spodumene grains and also restrict the spodumene growth to some extent at higher temperatures (Chyung 1969; Bold and Groves 1978; Dalal and Raj 1981). In addition to these two phases, 10–12 vol.% residual glass was also observed. Most of this residual glass was concentrated at the triple junctions. In composites, a similar crystallization behaviour was seen but a marginal difference in the spodumene grain was observed due to heterogeneous nucleation sites of SiC. Interfacial reaction, in particular, carbon rich layer formation that was reported in SiC fibre reinforced silicate composites (Prewo *et al* 1986; Cooper and Chyung 1987; Lewis and Murthy 1991) was not detected (figure 1b). However, it could be present in nanometer scale.

The double logarithmic plots of base LAS glass, glass–ceramic and its composites are presented in figures 2 and 3. The rate sensitive flow behaviour was analysed in terms of a power law

$$s = K\dot{\epsilon}^m, \quad (1)$$

where *K* is a parameter that depends on structure of the material and temperature and, *m* the strain rate sensitivity index.

A glass in the vicinity of softening point exhibits Newtonian viscous flow behaviour with *m* = 1. LAS glass during heating cycle underwent crystallization and the flow behaviour drastically got affected due to the

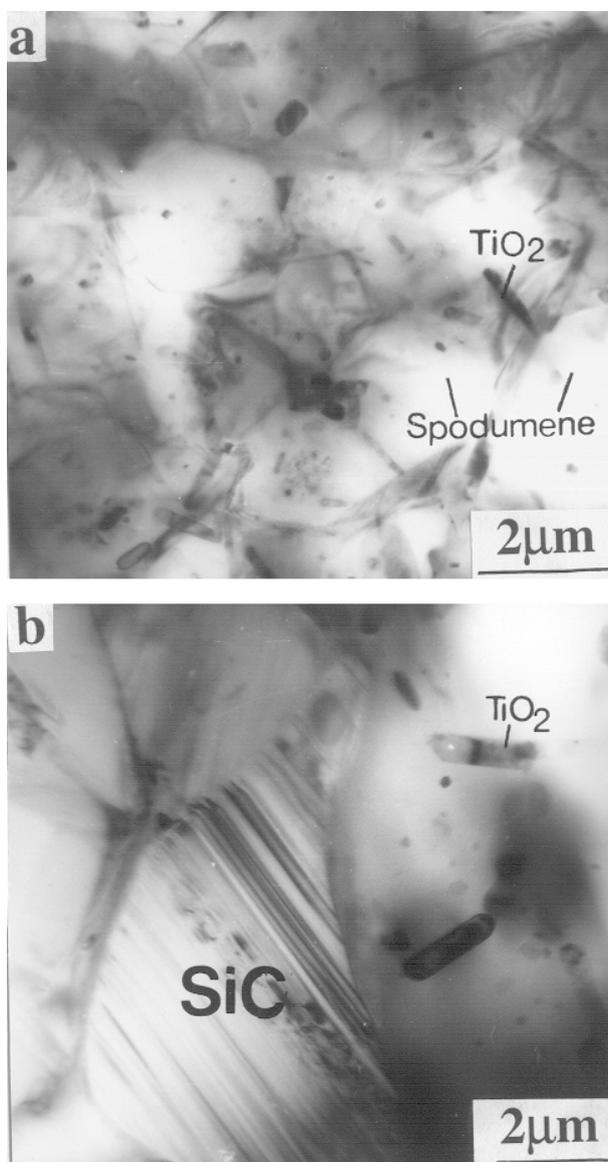


Figure 1. a. Microstructure of lithium aluminosilicate glass after testing at 1200°C and b. microstructure of hot-pressed SiC (40 vol%)–LAS composite.

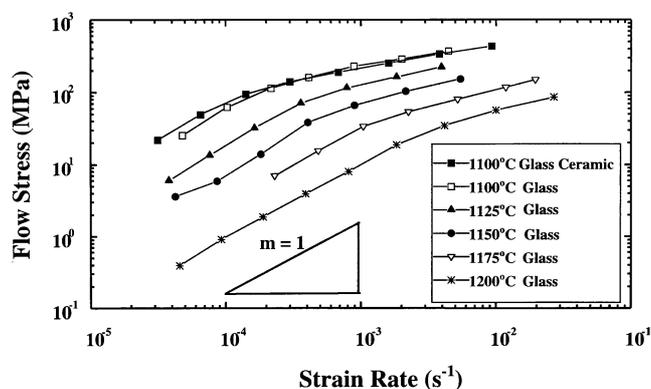


Figure 2. Flow stress vs strain rate plots for base LAS glass and glass–ceramic.

presence of *b* spodumene. To isolate the effect of residual glass on the flow behaviour, LAS glass was crystallized at 1100°C for 30 min prior to testing and then tested at a similar temperature. The difference in the flow behaviour between the glass–ceramic (crystallized one) and glass

samples was evident only at lower strain rates which could be attributed to the change in residual glass content and its flow behaviour. Further, the flow behaviour of LAS system is examined at different temperatures. In the lower strain rate regime, flow behaviour remained Newtonian, while at the higher strain rates it gradually became non-Newtonian at all temperatures (table 1, figure 2). The strain rate sensitivity in the non-Newtonian regime increased from 0.34 to 0.48 with increases in temperature, whereas the flow stress decreased due to softening of the glass phase at the grain boundaries. Addition of SiC particulates naturally affected the flow of LAS system. At any given test temperature, composites are expected to be stronger due to SiC reinforcements. Moreover, with the addition of SiC particulates grain boundary glass layer thickness is expected to decrease and the apparent viscosity (*h*) of the total system increases. Further, the strain rate sensitivity depends on volume fraction of reinforcement and it is observed to decrease with increasing volume fraction of reinforcements (table 1). In 20 vol.% SiC, *m* value varied from 0.2–0.5 as the temperature increased from 1100–1225°C whereas in 40 vol.% SiC composites it was nearly independent of temperature within the temperature range 1225–1300°C. On the other hand, during high temperature testing, impurities and silica (formed due to oxidation of SiC) get dissolved in the grain boundary glass. As silica gets dissolved in the grain boundary glass, the overall composition of the glass shifts more towards silica side in the binary phase diagram of *b* spodumene–silica (Dalal and Raj 1981). The accumulation of impurities further contributes for low temperature softening of the glass (Vincenzini and Babini 1984). As a result the glass softens at a lower temperature and flow stress decreases (figures 2 and 3). At still higher tempera-

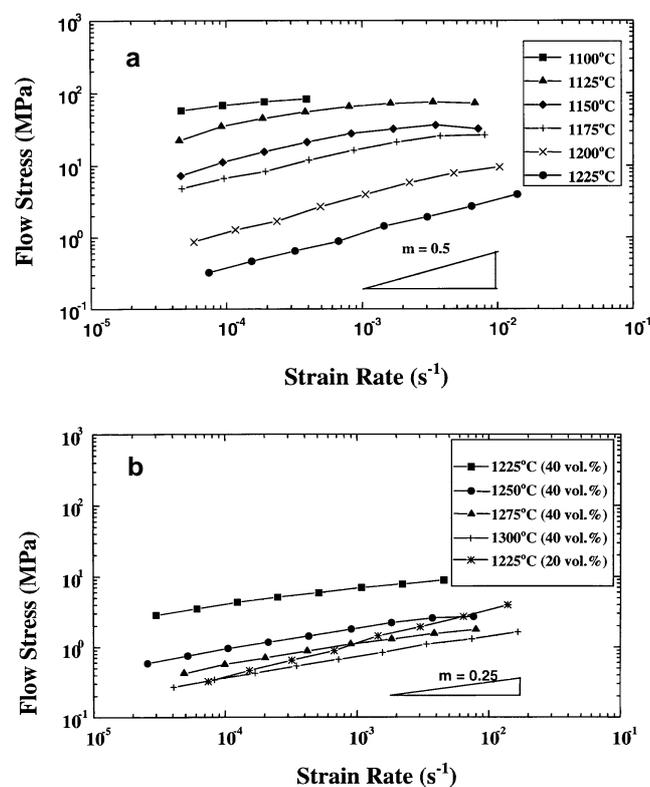


Figure 3. Flow stress of **a.** 20 vol% and **b.** 40 vol% SiC–LAS composites as a function of strain rate.

Table 1. Various *m* values for LAS glass and LAS–SiC composites.

Temperature (°C)	Material	Strain rate sensitivity index (<i>m</i>)	
		Linear regime	Non-linear regime
1100	Heat treated for 30 min at 1100°C	0.97	0.33
1100	Non-heat treated glass	0.99	0.34
1125		1.0	0.40
1150		1.0	0.46
1175		1.0	0.47
1200		1.0	0.48
1100	20 vol.% SiC–LAS composites		0.17
1125			0.23
1150			0.30
1175			0.35
1200			0.48
1225			0.48
1225	40 vol.% SiC–LAS composites		0.23
1250			0.28
1275			0.28
1300			0.30

tures, further softening of intergranular glass and grain growth of spodumene and oxidation of SiC pose problems. The activation energy (Q) for the flow was assessed making use of the following constitutive equation with Arrhenius temperature dependence

$$\dot{\epsilon} = AS^{(1/m)}e^{-(Q/RT)}, \quad (2)$$

where A is a constant and R the gas constant. The activation energy values were calculated making use of stress data corresponding to a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. The activation energy for the flow in LAS without reinforcements was 300 kJ/mole, whereas it was 995 kJ/mole for composites with 40% SiC reinforcements.

Although base LAS glass ceramic material exhibited Newtonian behaviour in compression (at test temperature above 1100°C), the tensile elongation was restricted to 135% because of cavitation problem (Wang and Raj 1984). In the case of SiC particulate composites, the m values in compression are very low and hence high tensile elongation may not be possible.

4. Conclusions

(I) LAS glass crystallized to b spodumene phase while hot-pressing. The flow behaviour of glass was affected due to presence of crystalline phase. In lower strain regime, flow behaviour was Newtonian but it changed to non-Newtonian at higher strain rates.

(II) With the addition of SiC particulates, the strain rate sensitivity decreased. In 20 vol.% SiC composites, the strain rate sensitivity increased from 0.2 to 0.5 as the temperature increased from 1100–1225°C, whereas in 40 vol.% composites, sensitivity values were nearly independent of temperature over the range 1225–1300°C. The activation energy for flow in composites with SiC reinforcements is higher than that of LAS without reinforcements.

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