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Near net-shape fabrication of alumina glass composites

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Abstract

The purpose of the present study is to fabricate alumina glass composites by melt infiltration with better dimensional control through reducing both the presintering and infiltration temperature. Main efforts were put to develop glasses that are chemically compatible with alumina. After extensive investigations, a glass of $21SiO_2$–$24B_2O_3$–$35Al_2O_3$–$15Li_2O$–5CaO wt.% was successfully developed. The glass shows good chemical compatibility with alumina at elevated temperatures and low viscosity above 900 °C. Dense alumina glass composites can be fabricated by the melt infiltration process at 950 °C, which is 150 °C lower than the current state-of-art. Investigations showed improved net-shape capability for the newly developed composites, where the total linear shrinkage for the sintering and infiltration at 950 °C is less than 0.1%, as compared with the shrinkage of 0.5% induced by the presintering and infiltration at 1100 °C. Preliminary mechanical tests showed that the fracture strength and toughness of the composites are 303 MPa and 3.4 MPa $m^{1/2}$, respectively. The lower processing temperature and the better dimensional control are the major advantages for the newly developed alumina glass composites.

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1. Introduction

Alumina–glass composites are attractive materials for many applications, including electronic,[1] mold[2] and biomedical applications.[3,4] Many of these applications require complex shapes with well controlled dimensions. For example, dimensional tolerances of less than 0.1% are normally demanded by these applications.[5] Near net-shape fabrication is crucial for a successful application as post-fire machining is quite expensive (up to 60% of the total production cost) and very difficult due to the required complex shapes and the brittle nature of ceramics.[5,6] Alumina–glass composites are usually fabricated by a melt infiltration process (e.g., the Vita In-Ceram process),[7,8] where alumina green bodies (e.g., from slip casting, uniaxially pressing, solid freeform processes, etc.) are first partially sintered at 1100–1400 °C, followed by infiltration using a lanthanum–aluminosilicate glass at 1100 °C. The dimensional change of the process is dependent on both the presintering and infiltration temperature. Investigations showed that when both the presintering and the infiltration were performed at 1100 °C, the total linear shrinkage is 0.4%, where 0.3% of the shrinkage comes from the presintering.[7] For further reduction of the shrinkage, it is essential to lower both the presintering and the infiltration temperature. Many studies on melt-infiltrated alumina glass composites have been reported in literature,[3,4,9–11] but all the glasses used in these investigations are based on the lanthanum–aluminosilicate glass,[7] where a minimum infiltration temperature of 1100 °C is required. Therefore, in order to reduce the fabrication temperature, it is necessary to develop new glasses that allow infiltrating alumina at lower temperature.

The purpose of the present study is to fabricate alumina glass composites by the melt infiltration process at lower temperatures. Efforts were put to develop new glasses,

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aiming at achieving spontaneous infiltration at 900–1000 °C. The shrinkage during the presintering and the infiltration processes was characterized. Mechanical properties for the newly developed composites were determined.

2. Experimental

2.1. Glass development

Three criteria were adopted for the glass development. Namely: (1) the glass should be chemically compatible with alumina at elevated temperatures; (2) the glass should have a low viscosity at 900–1000 °C; (3) the glass should have a good leaching resistance. The glass development starts from the composition design. To get a proper guess of a composition, information from various sources often needs to be considered. First literature data will be checked for a particular system. In most cases, not all the properties concerned can be found in literature, so theoretical models like the viscosity model[12] and the leaching model[13] were also employed to predict certain properties. Phase diagrams and thermodynamic simulations can also provide useful information in some cases. Upon obtaining the designed composition, glass formation was attempted. If the guessed composition forms a glass after quenching, two experiments are performed to verify the above three criteria. First, leaching tests are employed to check the leaching resistance of the glass. Then, infiltration tests are performed on alumina preforms below 1000 °C, from which the other two criteria can be verified, e.g., the check of glass melt shape during infiltration and infiltration distances after infiltration processes gives clear indications about whether the viscosity is sufficiently low; X-ray diffractometry (XRD) and scanning electron microscope (SEM) investigations on infiltrated samples provide information on the chemical compatibility of glasses with alumina at infiltration temperatures. If the above two experiments generate positive results, mechanical properties (mainly fracture strength and toughness) of the infiltrated composites are further characterized.

Glasses were melted on a 10–20 g scale. Borosilicate glasses are made through melting mixtures of reagent grade oxides and carbonates in right proportions using a Pt crucible at 1250–1400 °C in air for 2 h, followed by quenching glass melts in water. These reagents include SiO_2 (99% purity, Teco-Sol powder, CE-minerals, UK), B_2O_3 (99% purity, Merck, Darmstadt, Germany), Al_2O_3 (99.99% purity, TaiMei Chemicals Co. Ltd., Tokyo, Japan), Li_2CO_3 (99.9% purity, Rhone-Poulenc Chimie Fine, France), $BaCO_3$ (99% purity, Merck) and $CaCO_3$ (99% purity, Merck). In the case of phosphate glasses, the proper amount of ammonium dihydrogen phosphate (99% purity, Merck) was first heated up to 450 °C for 5–7 h in an Al_2O_3 crucible. Other oxides or carbonates were then mixed with the resultant P_2O_5 in the Al_2O_3 crucible in right proportions. The mixture was then heated to 900–1300 °C for 2 h depending on the glass, followed by casting the glass melts on a copper plate at room temperature.

2.2. Presintering and infiltration

Porous alumina preforms were prepared through uniaxially pressing alumina powder (A17 NE, Alcoa Industrial Chemical, USA) under ∼73 MPa for 2 min, followed by sintering at 900–1200 °C for 3 h. The infiltration process was investigated through putting a certain amount of glass on the top of the alumina preforms at 900–1200 °C for 2–6 h. The infiltrated composites were then subjected to various characterizations. In-Ceram alumina glass composites were also prepared according to the manufacturer's instructions using materials (porous alumina blocks and infiltration glass) bought from the manufacturer (Vita Zahnfabrik, Bad Sackingen, Germany). The In-Ceram alumina–glass composite served as the reference for mechanical property characterizations.

2.3. Characterization

The physical dimensions of samples were measured after the presintering and the infiltration using a micrometer with 10 μm resolution, from which the linear shrinkage was calculated.

The infiltrated samples were analyzed using X-ray diffractometry to identify phases formed. The microstructure of infiltrated specimens was investigated using a scanning electron microscope. For the SEM characterization, bars were cut from the infiltrated samples and ground to the nominal dimensions of 10 mm × 5 mm × 3 mm. The prospective observing surface was then polished in successive steps to 0.1 μm.

The fracture strength was measured by a three-point bending test with a span of 10 mm and a crosshead speed of 0.5 mm/min in air using specimens with nominal dimensions of 3 mm × 1 mm × 15 mm. The fracture toughness was determined by the indentation strength (IS) method[14] on beams of the same dimensions as the strength test. Prior to fracture, an indentation was made by a Vickers indenter using a dwell time of 30 s under a load of 153 N. Special care was taken to orient one set of the radial cracks parallel to the cross section of the specimen where the prospective rupture would occur. Indented beams were fractured using the same fixture and procedure as the strength test. Every specimen was checked to confirm that the fracture was initiated from the indent. The fractured specimens that did not fail from the indention were excluded from the data pool of toughness evaluation. The fracture toughness was then calculated according to the equations in reference.[14]

2.4. Leaching resistance

The leaching resistance of various glasses was tested through immersing a piece of glass of ∼0.5 g into 50 ml distilled water at 70 °C for up to 1 week. The leaching rate (L) was then determined using the following equation:

$$L = \frac{W_0 - W_t}{W_0} \times 100 \times \frac{1}{t}$$

where W_0 and W_t are the weight of a sample before and after the leaching test and t is the leaching time in minute. The leaching rate of a commercial glass (DURAN®, Schott Glass, Mainz, Germany) was also measured using the same procedure as above for comparison.

3. Results and discussion

The glass development was divided into two steps, where in the first step various glasses were screened in order to find a potential system to work with further. Then the screened glasses were further investigated and optimized in the second step. The criteria employed for the glass screening were good leaching resistance together with low viscosity at ∼1000 °C. Many glasses have been investigated. Some of them are listed in Table 1 for the sake of explanations. It was generally found that glasses of low viscosity normally also had bad leaching resistance. For example, the viscosity of $LiPO_3$ glass is low enough for spontaneous infiltration at 700 °C, but the leaching resistance is so poor that the glass totally dissolved after leaching at 70 °C for 63 h. The barium and magnesium phosphate glasses in Table 1 do have good leaching resistance comparable with that of durable DURAN® glass, but the viscosity of these glasses is quite high even at 1100 °C. After extensive searching, the $60P_2O_5$–15CaO–$10Li_2O$–$10B_2O_3$–$5Al_2O_3$ (mol%) and $55SiO_2$–$23B_2O_3$–$17Li_2O$–5CaO (wt.%) were found to meet the screening criteria, where they have good leaching resistance and low viscosity at ∼1000 °C. They were, therefore, subjected to further investigations.

For the $60P_2O_5$–15CaO–$10Li_2O$–$10B_2O_3$–$5Al_2O_3$ (mol%) glass, the glass melt has sufficiently low viscosity for achieving spontaneous infiltration and very good wetting to alumina at 900 °C. However, infiltration tests showed that the glass melt did not penetrate into the porous preform at 900 °C. Increasing infiltration temperature did not show any notable improvement for the infiltration. Various tests were performed to investigate the causes for the non-infiltration. It was found that the non-infiltration was mainly attributed to the interfacial reactions between the glass melt and alumina at elevated temperatures. Due to the reaction, aluminum phosphates are formed in the interface, which prevents the infiltration process. As shown by the XRD pattern in Fig. 1(B), only aluminum phosphates formed after the infiltration. Infiltration tests were also tried using other phosphate glasses in Table 1 at 700–1200 °C. These tests showed similar results as the $60P_2O_5$–15CaO–$10Li_2O$–$10B_2O_3$–$5Al_2O_3$ (mol%) glass. No infiltration was possible due to the severe reactions between the alumina preforms and the phosphate glasses at elevated temperatures, and aluminum phosphates were the main products after the infiltration tests as indicated by XRD patterns in Fig. 1(C) and (D). These investigations demonstrated that phosphate glasses are very reactive to alumina, and it seems difficult to find a chemically compatible glass for alumina in the phosphate system. Therefore, further glass development in the phosphate system was stopped.

For the $55SiO_2$–$23B_2O_3$–$17Li_2O$–5CaO (wt.%) glass, initial investigations showed similar results as the phosphate glasses. Despite the low viscosity and good wetting, only limited infiltration (within 1 mm) was achieved after several hours' infiltration at 900 °C. But unlike the phosphate glasses, increasing infiltration temperature promoted the infiltration process, where samples of ∼4 mm thickness could be fully infiltrated after 3 h infiltration at 1200 °C. Investigations revealed that the limited infiltration at 900 °C was

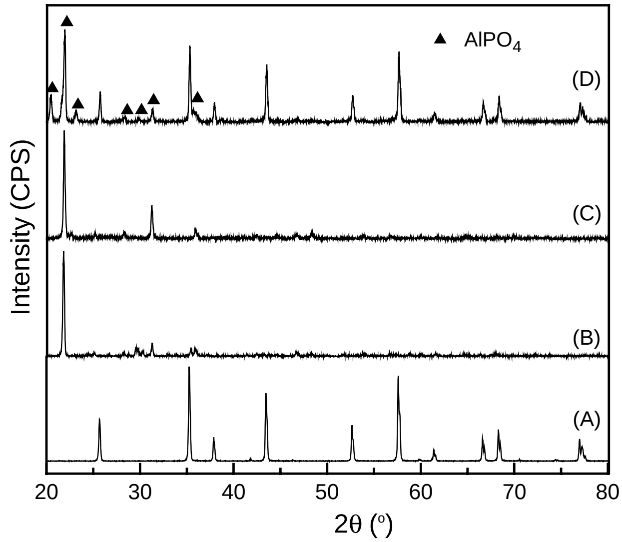

Fig. 1. XRD patterns of glass infiltrated composites. The figure shows (A) the as-sintered alumina perform, (B) composites infiltrated by $60P_2O_5$–15CaO–$10Li_2O$–$10B_2O_3$–$5Al_2O_3$ (mol%) glass at 900 °C for 2 h, (C) composites infiltrated by $57P_2O_5$–26BaO–$10B_2O_3$–$7Al_2O_3$ (mol%) at 1200 °C for 2 h, and (D) composites infiltrated by $LiPO_3$ glass at 1200 °C for 2 h.

Table 1
Properties for various glasses

Composition	Leaching rate (%/min)	Spontaneous infiltration temperature (°C)
$LiPO_3$	$>3.0 \times 10^{-2}$[a]	700
$57P_2O_5$–26BaO–$10B_2O_3$–$7Al_2O_3$ (mol%)	2.1×10^{-5}	1200
$55P_2O_5$–29MgO–$10B_2O_3$–$6Al_2O_3$ (mol%)	6.2×10^{-5}	1200
$60P_2O_5$–15CaO–$10Li_2O$–$10B_2O_3$–$5Al_2O_3$ (mol%)	6.9×10^{-5}	900
$55SiO_2$–$23B_2O_3$–$17Li_2O$–5CaO (wt.%)	6.0×10^{-5}	900
DURAN® glass	1.8×10^{-5}	–

[a] Sample totally dissolved after 63 h.

attributed to the dissolution of alumina into the glass melt. The dissolution of alumina increased the viscosity of the glass melt. As a result, the viscosity of the glass melt at the infiltration front increases with the advancement of the infiltration due to the continuous dissolution of alumina, and the infiltration will stop at certain amount of alumina dissolution where the viscosity in the infiltration front becomes too large. This point was confirmed by two experiments. First, the size of the specimen was found to become smaller after 3 h infiltration at 1200 °C, indicating clearly the dissolution of alumina to the glass melt. Second, alumina was intentionally added to the glass melt to study the effect of the alumina addition on the infiltration behavior. Experiments showed that the glass melt could dissolve at least up to 35 wt.% (concentration in the resultant glass) of alumina at 1100 °C. The viscosity of the glass melt increased with increasing alumina dissolution as confirmed by infiltration tests. For example, 30 wt.% alumina addition ($38.5SiO_2$–$16.1B_2O_3$–$11.9Li_2O$–3.5CaO–$30Al_2O_3$ wt.%) increased the spontaneous infiltration temperature of the glass from 900 to ~1100 °C, and infiltration at 900 °C was thus impossible for the $38.5SiO_2$–$16.1B_2O_3$–$11.9Li_2O$–3.5CaO–$30Al_2O_3$ wt.% glass due to the high viscosity. On the other hand, to prevent the dissolution of alumina into the glass melt, the glass melt should be saturated with alumina at the infiltration temperature, for which a large quantity of alumina addition is required in this particular glass system as indicated by the above-mentioned experiments. If the addition of alumina inevitably increases the viscosity of the glass, low temperature infiltration cannot be achieved in this glass system. Many investigations were, therefore, performed to study the influence of alumina concentration in the glass on the viscosity. It was fortunately found that replacing SiO_2 with Al_2O_3 in the glass could improve the chemical compatibility of the glass with alumina while at the same time keeping low viscosity at 900 °C. For example, for the $(55 - x)SiO_2$–$23B_2O_3$–$17Li_2O$–5CaO–xAl_2O_3 glasses, infiltration tests showed that the chemical compatibility of the glass with alumina increased with increasing alumina concentration (x value) as confirmed by XRD investigations and SEM analyses. The XRD patterns of the glass-infiltrated composites are illustrated in Fig. 2. The composites infiltrated by glasses with 6 wt.% alumina contain reaction-formed Al_5LiO_8 and $AlLiSi_2O_6$ new phases as shown in Fig. 2(B). The intensities of these phases decrease with increasing alumina concentration (Fig. 2(B) and (C)), indicating the improvement in chemical compatibility. For composites infiltrated by glasses with alumina concentrations above 15 wt.%, no new phases were detected by the XRD as demonstrated by Fig. 2(D). SEM analyses confirmed the XRD investigations as shown by the microstructure changes in Fig. 3. The alumina preforms consist of faceted and platelike grains (not shown in Fig. 3) with an equivalent diameter of 3–5 μm. Fig. 3A shows the dramatically changed microstructure of the infiltrated composites, caused by the dissolution of alumina and subsequent precipitation of new phases. For the composites infiltrated from glasses containing 15 wt.% alumina, new phases were indeed not found in the microstructure, but glass strips up to several millimeters width containing some microcracks were observed in the microstructure as illustrated in Fig. 3B. The dissolution of alumina, the precipitation of new phases as well as the formation of the glass strips destroyed the initial faceted and platelike structure of alumina phases and generated microcracks in the composites, which seriously deteriorated the mechanical properties of the composites. The chemical compatibility of the glass with alumina increased with further increasing alumina concentrations in the glass as indicated by the microstructure in Fig. 3C, and it was found that the glass is chemically compatible with alumina when the concentration of alumina reaches ~35 wt.%. The dissolution of alumina and precipitation of new phases were not observed after the infiltration using glasses containing 35 wt.% alumina, so the initial faceted and platelike microstructure of alumina phases was preserved as demonstrated by Fig. 3D. Interestingly, the replacement of SiO_2 with alumina in this glass system has little effect on the viscosity, where spontaneous infiltration was attainable even with the glass containing 35 wt.% alumina (e.g., $21SiO_2$–$24B_2O_3$–$35Al_2O_3$–$15Li_2O$–5CaO wt.%) at 900 °C. Infiltration tests showed that the infiltration speed of the $21SiO_2$–$24B_2O_3$–$35Al_2O_3$–$15Li_2O$–5CaO wt.% glass at 950 °C was comparable with that of Vita In-Ceram glass at 1100 °C,[15] where an infiltration distance of ~4.0 mm was achieved after for 4 h infiltration at 950 °C. Investigations also showed that small variations of the glass composition

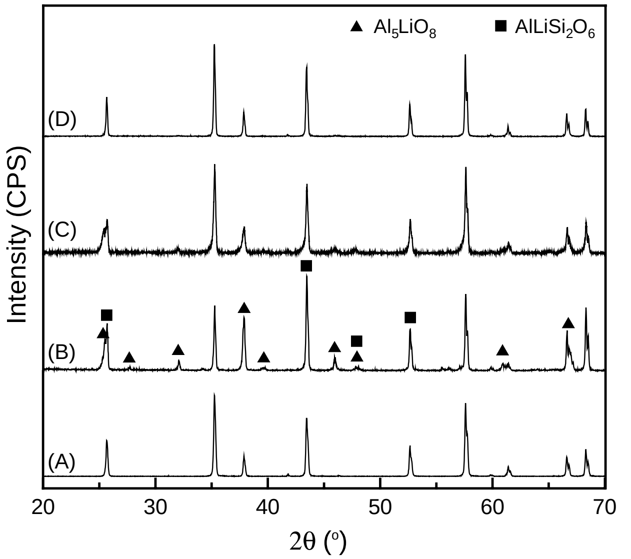

Fig. 2. XRD patterns of alumina performs and glass infiltrated composites. The figure shows (A) the as-sintered alumina perform, (B) composites infiltrated by $49SiO_2$–$23B_2O_3$–$17Li_2O$–5CaO–$6Al_2O_3$ (wt.%) glass at 1200 °C for 2 h, (C) composites infiltrated by $45SiO_2$–$23B_2O_3$–$17Li_2O$–5CaO–$10Al_2O_3$ (wt.%) glass at 950 °C for 4 h, and (D) composites infiltrated by $40SiO_2$–$23B_2O_3$–$17Li_2O$–5CaO–$15Al_2O_3$ (wt.%) glass at 950 °C for 4 h.

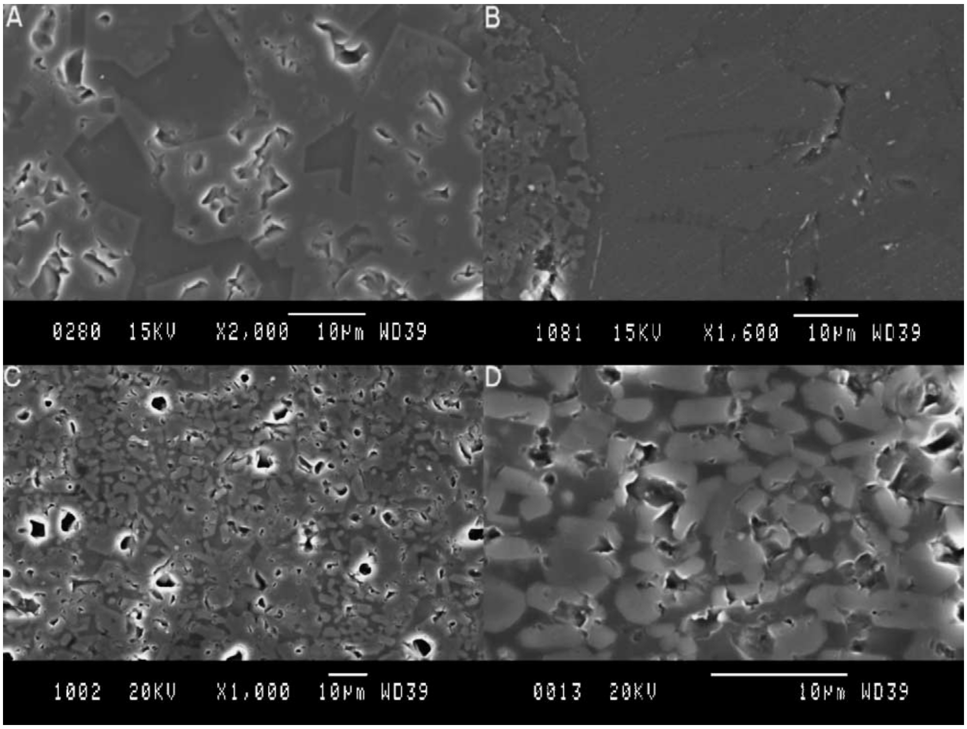

Fig. 3. Microstructure of the glass infiltrated composites. The figure shows composites infiltrated by (A) $49SiO_2–23B_2O_3–17Li_2O–5CaO–6Al_2O_3$ (wt.%) glass at 1200 °C for 2 h, (B) $40SiO_2–23B_2O_3–17Li_2O–5CaO–15Al_2O_3$ (wt.%) glass at 950 °C for 4 h, (C) $25SiO_2–23B_2O_3–17Li_2O–5CaO–30Al_2O_3$ (wt.%) glass at 950 °C for 4 h, and (D) $21SiO_2–24B_2O_3–15Li_2O–5CaO–35Al_2O_3$ (wt.%) glass at 950 °C for 4 h.

do not significantly change the glass properties (viscosity, chemical compatibility with alumina, leaching resistance, etc.). Based on the above investigations, the glass of $21SiO_2–24B_2O_3–35Al_2O_3–15Li_2O–5CaO$ (wt.%) was successfully developed for the infiltration of alumina. The glass meets the development criteria as: (1) it is chemical compatible with alumina at elevate temperatures, (2) the glass has a relatively good leaching resistance, where the leaching rate was determined to be 4.4×10^{-5}%/min, (3) the viscosity of the glass is low enough for spontaneous infiltration at 900 °C. Dense alumina glass composites can be fabricated through infiltrating the glass into presintered porous alumina performs at 900–950 °C, which is ∼150 °C lower than the current-state-of-art. The relative density of the infiltrated composites was estimated to be ∼95% of the theoretical density. Uninfiltrated pores up to 40 µm were observed in the microstructure. These pores are mainly attributed to presintering-induced closed pores in the preform that cannot be reached by the molten glass during the infiltration process. Further increase in composite density might be possible through optimizing the presintering and the infiltration process.

The alumina powder used in the present investigation has the mean particle size of 3–5 µm. The pore structure (pore size and distribution) and the green density of preforms were characterized using a mercury porosimeter. Fig. 4 shows a typical result obtained by the mercury porosimeter, which indicates that the average pore diameter for preforms pre-sintered at 1100 °C for 3 h is 0.58 µm, distributed from 0.3 to 1.0 µm. The relative density is 0.40 for preforms sintered 950 °C for 3 h and 0.44 for preforms sintered 1100 °C for 3 h. The dimensional changes during the sintering and the infiltration process at 950 °C were characterized and compared with those at 1100 °C. Within the measurement resolution of 10 µm, the physical dimensions of samples ($\Phi 12 \times 5\,mm^3$) are identical before and after the sintering at 950 °C. So, the shrinkage during the sintering process is less than 10 µm, indicating that the linear shrinkage is less than 0.08%. While at the same conditions, samples sintered at 1100 °C caused linear shrinkage of 0.4% (50 µm). Investigations showed that infiltration at 1100 °C by In-Ceram

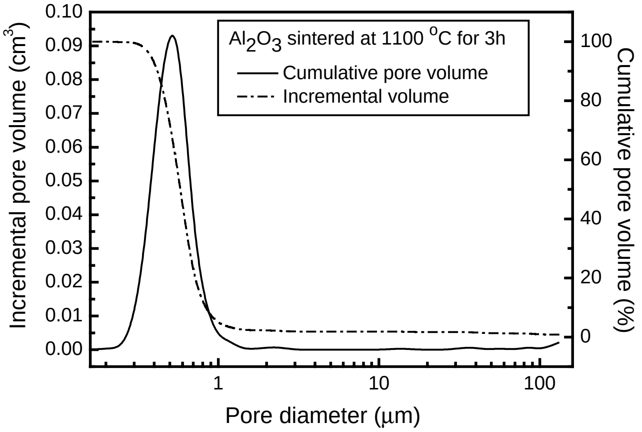

Fig. 4. Pore distribution of alumina preforms sintering at 1100 °C for 3 h.

Table 2
Properties of alumina glass composites

Composite	Infiltration temperature (°C)	Shrinkage (%)	Fracture strength (MPa)	Fracture toughness (MPa $m^{1/2}$)
Newly developed	950	<0.1	303 ± 25	3.4 ± 0.2
In-Ceram	1100	0.5	321 ± 31	3.6 ± 0.2

glass induced linear shrinkage of 0.1%, whereas the shrinkage caused by the infiltration at 950 °C with the newly developed glass was undetectable on the micrometer level. These investigations demonstrated that the shrinkage for the newly developed alumina–glass composites could be kept below 0.1% as required by a number of applications[5] due to the low presintering as well as infiltration temperature. The lower processing temperature together with excellent net-shape capability should be helpful in reducing production cost and achieving accurate dimensional control as well.

Preliminary tests were performed to determine mechanical properties of the infiltrated alumina glass composites. The fracture strength and toughness of the composite are listed in Table 2. The composite has a strength value of 303 MPa and a toughness value of 3.4 MPa $m^{1/2}$. In comparison, the strength and toughness of the In-Ceram alumina glass composites were determined to be 321 MPa and 3.6 MPa $m^{1/2}$. Therefore, it can be concluded that the fracture strength and toughness of the newly developed alumina glass composite are comparable with those of In-Ceram alumina glass composite.

4. Conclusions

To reduce the infiltration temperature for melt-infiltrated alumina glass composites, new infiltration glasses aiming at achieving good chemical compatibility with alumina and low viscosity at 900–1000 °C were explored. It was found that phosphate glasses are very reactive to alumina and it is difficult to find suitable phosphate glasses for the infiltration of alumina. After extensive investigations in the borosilicate glass system, glasses of $21SiO_2$–$24B_2O_3$–$35Al_2O_3$–$15Li_2O$–5CaO wt.% were successfully developed. The glass has good leaching resistance, is chemical compatible with alumina at elevated temperatures and has low viscosity at 900 °C and above. Dense alumina glass composites can be fabricated by the melt infiltration process at 950 °C, which is 150 °C lower than the current state-of-art. The total shrinkage for the presintering and infiltration process at 950 °C is less than 0.1%. In comparison, the shrinkage is ∼0.5% when the presintering and the infiltration are performed at 1100 °C. Mechanical tests showed that the fracture strength and toughness of the composites are 303 MPa and 3.4 MPa $m^{1/2}$, respectively. The lower processing temperature and better dimensional control are the major advantages for the newly developed alumina glass composites.

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