The effect of mica dehydration on the fabrication of cellular glass–mica composite solids

NORMAN M. P. LOW
Centre for Building Studies, Concordia University, Montreal, Canada

Investigations have been conducted to show that hydrated mica flakes are one of the essential starting components for the development of a cellular-structure glass mica composite solid by sintering mixtures of natural mica powders of the phlogopite type and ground glass powders prepared from recycled soda-lime waste glass. Studies show that if the water of crystallization is removed from the mica structure by heating prior to mixing and reaction with the glass grains, the development of the cellular structure in the sintered glass—mica composite solid is partially or totally suppressed depending on the extent of the thermal dehydration of the mica powders.

1. Introduction
Studies of particulate composites based on mica dispersions in a ceramic matrix have attracted some attention in recent years. This arises from the fact that mica—ceramic composites can be used for many engineering applications because of their improved friction and wear behaviour, enhanced fracture toughness, thermal shock resistance and also enhanced machinability. Several investigations dealing with the fabrication of a composite of synthetic fluorine mica (barium mica) and alumina (Al_2O_3) have been reported [1–6]. Although natural mica bonded with glassy material was first produced almost 50 years ago and has since become a widely used ceramic composite for electrical and thermal insulations [7, 8], studies relating to the formation and properties of the glass-bonded mica material have not been well-documented in the literature.

Several previous publications [9–12] have shown that glass—mica composite solids of different physical structures can be fabricated from mixtures of natural mica powders of the phlogopite-type and ground glass powders (prepared from recycled soda-lime waste glasses) by a simple sintering process. It has also been shown that, by means of careful control of the composition of the two starting components, the glass—mica compo-

site solids can be fabricated into a product which exhibits both a cellular structure consisting of closed and open cells and a highly dense structure containing very little porosity. Fig. 1 shows several typical examples of a glass—mica composite solid which combines a layer of the cellular-structure composite material and a layer of the densified composite material in a single unit, made in one sintering operation. These composite materials exhibit great potential as rigid thermal insulators and load-bearing structural elements suitable for building construction applications.

The possibility of transforming the glass—mica mixtures by a solid-state reaction into composite solids with different physical structures has been explained as resulting from thermal dehydration of the mica particles at elevated temperatures during the sintering process. This paper presents further experimental results to support such an hypothesis.

2. Experimental details
The glass powders used for the present study were prepared from recycled amber soda-lime glass cullet. The glass cullet was first pulverized into fine grains (in the range 0.2 to 0.5 mm in diameter) by a mechanical pulverizer. The pulverized glass grains were then ground into fine powders by a ball-mill grinding process lasting about 5 h using corundum
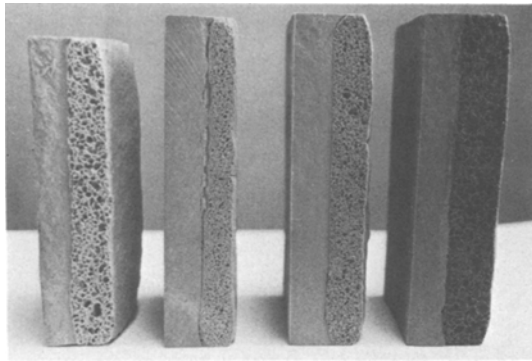
Figure 1 Typical examples of sintered glass—mica composite solid combining a layer of the cellular-structure material and a layer of the densified-structure material in a single unit.

as the grinding medium. The glass powders used for sample preparation had diameters between 150 and 300 μm.

The mica powders used for the investigation were Canadian natural mica of the phlogopite-type and were obtained from the same producer* as used in previous studies. The mica powders used for sample preparation were finer than 300 μm.

Thermal dehydration of the natural mica flakes was first studied. The weight loss of the mica flakes on heating was studied using a batch heating technique instead of a continuous heating thermogravimetric analysis (TGA) technique, as the batch heating process is a more realistic representation of the product fabrication process. The thermal heating of the mica flakes took place in the following steps. A small quantity (exactly 5.0 g) of the as-received mica powders was placed in a flat quartz container. The container and the mica powders were then placed in an electric heating furnace and heated at various temperatures ranging from 500 to 1100° C at 100 degree intervals. The heating time varied from 90 to 240 min. The weight loss was measured to an accuracy of 0.1 mg. All mica powders were heated in the quartz container without cover in air at normal atmospheric pressure.

After the weight loss measurements, the heat-treated mica powders were mixed with the glass powders, which had been prepared from the recycled amber soda-lime waste glass, according to the following specific mixture composition: 90 wt% glass and 10 wt% mica. All specimen pre-

paration procedures were identical to those used in previous investigations [9–12]. These included the addition of 6 wt% of water to facilitate the powder compaction process, compaction of mixed powders at 2 MN m^{-2} and sintering at 850° C for 30 min. Property evaluations of the sintered glass—mica composite solids also followed the same procedures as those used in previous investigations.

3. Results
3.1. Thermal dehydration of phlogopite mica

The rate and extent of thermal dehydration of the hydroxy-micas by heat depends on several factors including: (a) temperature, (b) time or duration of heating at constant temperature, (c) particle size (or exposed surface area), (d) atmosphere, which includes the amount of moisture in the air and whether the crucibles are covered or not, and (e) pressure [13]. In the present study, only the heating temperature and the heating time were varied while the other parameters were maintained constant.

Fig. 2 shows the weight loss of the Canadian natural mica of the phlogopite-type as a function of heating temperature. It is evident that weight loss of the mica flakes began at about 500° C and increased gradually as the heating temperature was increased. At temperatures between 1050 and 1100° C, a significant weight change took place. The weight loss of the Canadian natural mica flakes of the phlogopite-type by heating in air at temperatures up to 1100° C as observed in the present study was found to be in agreement with the results reported in two other studies [13, 14]. The mica producer has reported that a weight loss of about 0.9 wt% mica was observed when the mica flakes were heated by the TGA method up to a temperature of 1050° C, as shown in Fig. 2 [14]. In the present study, the weight loss of phlogopite-type mica flakes at 1100° C after 90 min heating was found to be about 2.44 wt%, which is in good agreement with the result of 2.60 wt% reported by Shell and Ivy based on their study of the Canadian phlogopite mica powders conducted more than 10 years ago [13].

A discoloration of the natural phlogopite mica flakes was observed after heating. The flakes have a light amber colour when unheated or

*The phlogopite-type mica is processed in Boucherville, Quebec (near Montreal), from a high purity ore by Marietta Resources International Ltd in a joint venture with the Société Minéralurgique Laviolette, Inc., Montreal, under the trade name of 'Suzorite' mica.
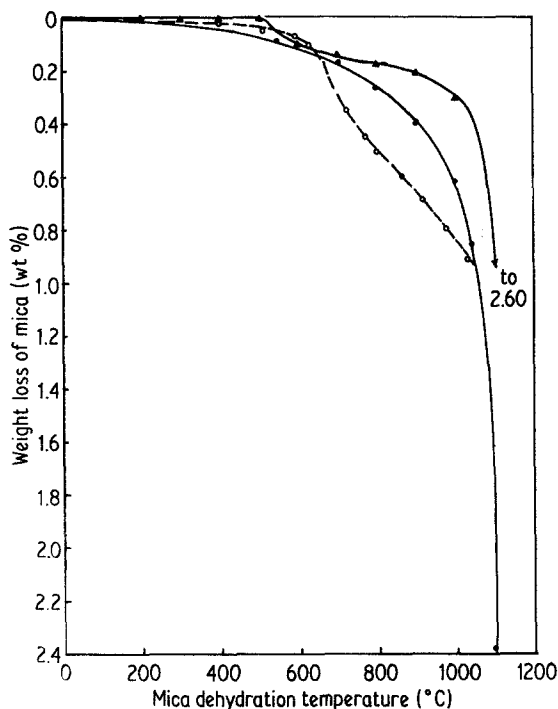
Figure 2 Weight loss of natural phlogopite mica flakes as a function of dehydration temperature. (●) Batch heating method used in present study; (▲) TGA method reported by Shell and Ivy [13]; (○) TGA method reported by mica producer [14].

Figure 3 The dependence of volumetric change (expansion and contraction) of sintered glass—mica composite solids on the weight loss of mica flakes resulting from thermal dehydration.

when heated to temperatures up to 600° C. As the heating temperatures exceeded 600° C and increased to 1100° C, the mica flakes changed to a dark brown colour: the discoloration intensified as the heating increased. However, examination of the dehydrated mica flakes by optical microscopy showed that there was no physical change and the mica flakes retained the foliated structure.

3.2. Mica dehydration and cellular glass—mica formation

As shown in previous studies [9—12], a cellular-structure glass—mica composite solid similar to that shown in Fig. 1 was produced from mixtures consisting of 90 wt% glass and 10 wt% mica when normal hydrated mica flakes were used as a starting component. The reacted composite solid also exhibited a large volumetric expansion in the course of the formation of the cellular structure, thus producing a composite solid with very low bulk density. However, both the formation of the cellular structure and the extent of the volumetric expansion of the composite solid were significantly altered when the starting mica flakes were first
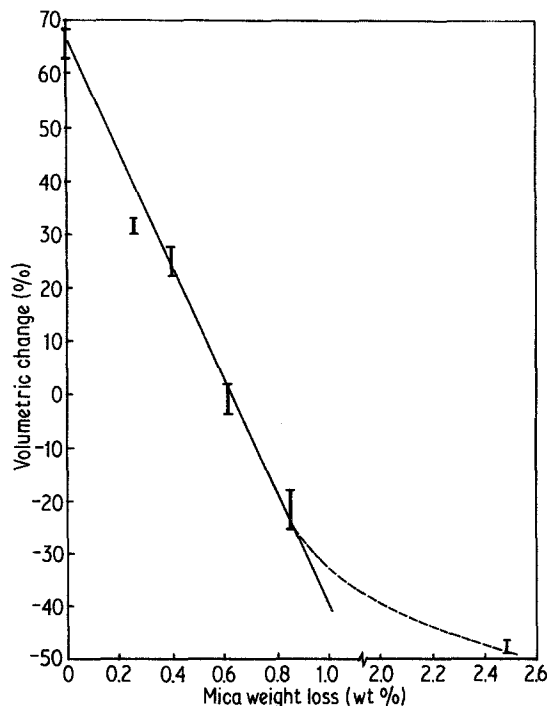
thermally dehydrated and then mixed with the glass grains for subsequent solid-state reaction. These changes varied depending on the extent of the thermal dehydration of the mica flakes. Fig. 3 shows the variation of the volumetric change (positive values are for expansion and negative values are for contraction), expressed as a percentage, as a function of the weight loss of the mica powders. It is evident that the behaviour of the sintered glass—mica mixtures changed from volumetric expansion to contraction as the weight loss of the mica flakes increased. Because of these significant volumetric changes, the bulk density of the sintered glass—mica composite solids formed using the dehydrated mica powders also showed significant changes, as shown in Fig. 4.

Under normal solid-state sintering processes, the physical changes which occur in the bulk of a compacted solid of ceramic material during the firing process are often related to changes in grain size and shape or changes in pore size and shape [15]. The glass—mica mixture is essentially a ceramic system. These parameters are therefore likely to play a role in the physical changes. As
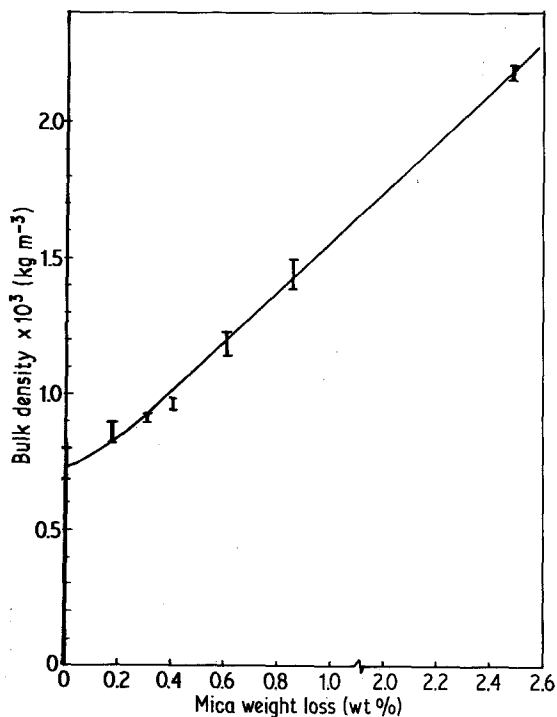
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Figure 4 Variation of bulk density of sintered glass–mica composite solids with weight loss of mica flakes resulting from thermal dehydration.

Figure 5 Variation of open porosity in sintered glass–mica composite solids with weight loss of mica flakes resulting from thermal dehydration.

observed in previous studies [9–12], when 10 wt% of hydrated mica flakes were mixed and reacted with 90 wt% of soda-lime glass powder, the cellular composite solids produced generally contained about 30–40% open porosity. However, when mixtures of similar composition but with dehydrated mica flakes were used, the composite solids produced contained considerably less open porosity. In fact, the open porosity in several samples of the composite solid has been observed to decrease to zero. The decrease of open porosity and the increase of weight loss of the mica flakes resulting from thermal dehydration show a close correlation, as shown in Fig. 5. Thus it is evident that the dehydrated mica flakes and the hydrated mica flakes have different material characteristics when reacted with the soda-lime glass grains.

The effect of dehydration time of the mica flakes prior to mixing and reaction with the glass grains on the formation of cellular structure and volumetric changes of the glass–mica composite solid was also clearly observed. When several batches of the mica flakes were thermally dehydrated at 950° C for periods varying from 90 to 240 min and the dehydrated mica flakes then
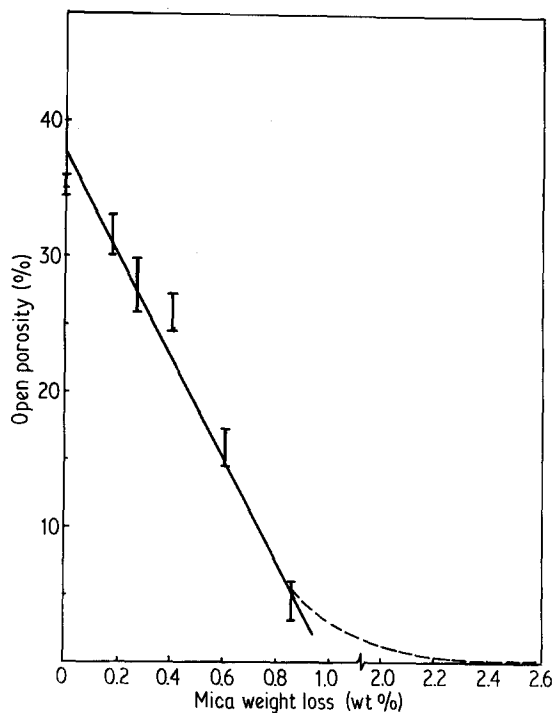
mixed and reacted with glass grains, the reacted composite solids showed a gradual decrease of volumetric change as the dehydration time increasd, as shown in Fig. 6.

Previous studies [9–12] have shown that there is a complex relationship between the volumetric changes of the sintered glass–mica composite solids and the mica content in the composition of the starting mixtures. This complex relationship was further studied by mixing the soda-lime glass powders with various proportions of phlogopite mica powders which had been subjected to thermal dehydration at 1050° C for 2 h prior to use. The mixtures were then sintered at 850° C for 30 min. Results of measurement showed that a similar variation was also observed in the glass–dehydrated mica composite solids. However, the magnitude of the volumetric change for all proportions of the mica content was significantly reduced, as shown in Fig. 7. These results indicate that the removal of the water of crystallization from the mica structure before mixing with the glass grains is an important parameter in controlling the formation of the cellular-structure glass–mica composite solids by the sintering reaction process.
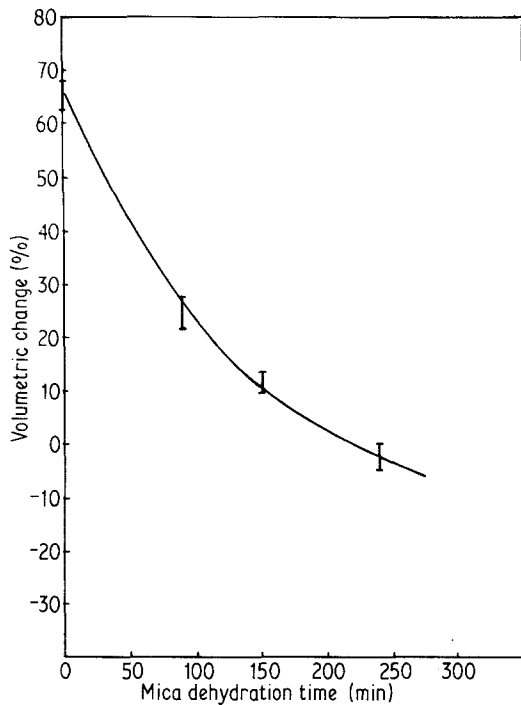
Figure 6 Variation of volumetric change (expansion) of sintered glass–mica composite solids with mica dehydration time.
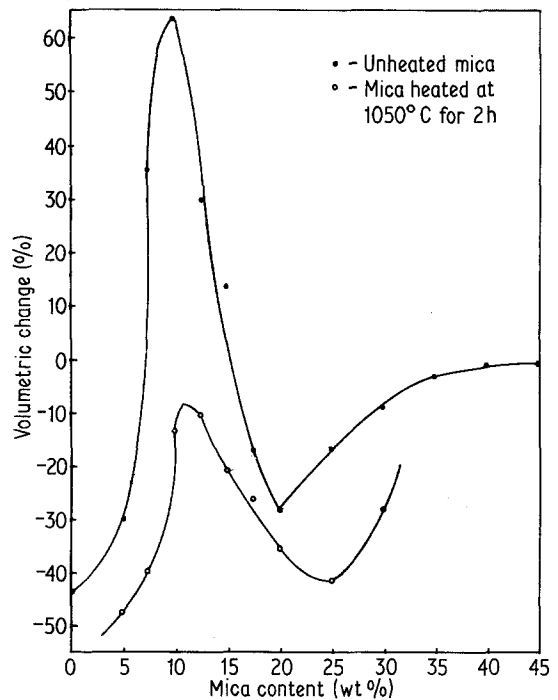

Figure 7 Variation of volumetric change (expansion and contraction) of sintered glass–mica composite solids with mica content between hydrated and dehydrated mica flakes.

4. Discussion

The display of the formation of the cellular structure and the development of volumetric expansion in the sintered glass–mica composite solids when hydrated mica powders were used, as observed in previous studies, and the display of the gradual suppression of the formation of the cellular–structure and the reversal to volumetric contraction when dehydrated mica powders were used, as observed in the present study, clearly indicate that the water molecules released from the mica structure by the thermal dehydration process are the primary driving force in inducing a dynamic reaction between the mica flakes and the glass grains. Results of the present study show clearly that when the water of crystallization is removed from the mica structure prior to mixing and reaction with the glass grains, it is no longer possible to develop a cellular structure in the sintered glass–mica composite solid, as this driving force is absent in the system. Hence, control of the removal of the water of crystallization from the mica powders before or during the sintering of the glass–mica mixtures becomes

a very important processing parameter in modifying the formation of the cellular structure of the glass–mica composite solids.

The overall experimental results observed in the various studies justifiably support the following proposed hypothesis for the development of the cellular structure in the glass–mica composite solids. As the sintering temperature is raised gradually and continuously to a level such as 850° C, most of the glass grains near the surface of the powder compact melt and the melting process then gradually propagates to the interior of the compact. Meanwhile, the mica particles undergo a dehydration process, thereby releasing both their free water and combined water. As the water is released from the mica particles in the matrix, a small portion of the water will be dissolved in the liquid-phase glass. The dissolution of water in the liquid-phase glass will consequently cause a lowering of the viscosity of the glass–mica system, as has been observed in the reaction of water with glass by other workers [16, 17]. The dissolution of the water molecules in the liquid glass phase probably takes place in the form of

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hydroxyl (OH) groups according to the following chemical reactions:

$$(=Si-O-Si=) + H_2O \rightarrow 2(=Si-OH).$$
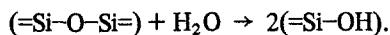
The undissolved portion of the water, on the other hand, will be trapped in the interior of the sintered bulk because of the presence of the viscous liquid-glass envelope. As a result, the entrapped water vapour develops a strong internal vapour pressure which forces the molten glass mass apart, and causes the glass matrix to expand. As the liquid glass—mica is cooled suddenly, solidification of the composite matrix takes place with the formation of a cellular structure.

The amount of water vapour released from the mica flakes by the thermal dehydration process is fundamentally important as it affects both the solubility of water and the development of internal vapour pressure in the glass melt. Information from the literature indicates that the solubility of water vapour in glass melts is proportional to the square root of the partial pressure of the water vapour [14]. The volumetric contraction observed in the glass—mica composite solid when overheated mica flakes were used was very similar to that observed in the pure soda-lime glass alone. This is a clear indication that no water molecules were released from the mica flakes to modify the viscosity of the glass phase or to generate vapour pressure to cause expansion of glass—mica mass. However, this extensive contraction of the glass—mica composite solid could also have been caused by structural modification of the mica flakes resulting from excessive thermal heating. It has been reported that phlogopite tends to lose its micaceous structure at about 1000° C and the material transforms to a spinel crystalline phase [18].

5. Conclusion

The substantiation of the theoretical consideration that the water of crystallization released from the mica structure by thermal dehydration is the driving force for the formation of the cellular structure and for the associated volumetric changes during the fabrication of the glass—mica composite solids from mixtures of natural mica powder of the phlogopite-type and ground glass powder prepared from recycled soda-lime waste glass establishes a scientific basis to account for the phenomenon. It also provides an alternative approach, apart from the composition control as suggested in previous studies, to develop further the glass—mica composite solids into rigid thermal insulators with optimum properties for practical engineering applications.

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