GLASS MATRIX COMPOSITES FROM COAL FLYASH AND WASTE GLASS

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ABSTRACT. Glass matrix composites have been fabricated from waste materials by means of powder technology. Flyash from coal power stations and waste glass, residue of float glass production, were used. Commercial alumina platelets were employed as the reinforcing component. For flyash contents up to 20% by weight nearly fully dense compacts could be fabricated by using relatively low sintering temperatures (650°C). For higher flyash contents the densification was hindered due to the presence of crystalline particles in the as-received flyash, which jeopardized the viscous flow densification mechanism. The addition of alumina platelets resulted in better mechanical properties of the composites than those of the unreinforced matrix, despite a residual porosity present. Young's modulus, modulus of rupture, hardness and fracture toughness increase with platelet volume fraction. The low brittleness index of the composites \( B \approx 3 \mu m^{-1/2} \) suggests that the materials have good machinability. A qualitative analysis of the wear behaviour showed that the composite containing 20% by volume platelet addition has a higher wear resistance than the unreinforced matrix. Overall, the results indicate that the materials may compete with conventional glasses and glass-ceramics in technical applications. © 1997 Elsevier Science Ltd

INTRODUCTION

Significant amounts of flyash (for example in the order of 15 million Mg per year in Germany) are produced permanently as a by-product of the coal combustion in power stations. Currently, only a small part of the flyashes is utilized, mainly in the cement industry.1,2 The remaining amounts are used for landfilling, which is an unsatisfactory solution both from an ecological and an economical point of view. In a recently published survey3 the negative environmental impacts of landfilling flyash have been identified, including the leaching of potentially toxic substances into soils and groundwater, the change in the elemental composition of the vegetation growing in the vicinity of the ash, and the accumulation of toxic elements throughout the food chain. Other more efficient uses of flyash have been proposed in the last 40 years, including brick and ceramic tile fabrication, lightweight aggregate, road pavements, filler in plastics and paints, mineral wool and for metal recovery.4 Indeed the attempts to utilize fly ash are not new. As reported by Butterworth5 the addition of coal ashes for brickmaking goes back at least to the eighteenth century in England. The amount of utilized flyash is, however, still very low and consequently new forms for its utilization as a raw material resource are continually sought. Recent papers have reported, for example, on the use of flyash to synthesize mullite ceramics,4 for the fabrication of ceramic tableware and artware,6 for fabricating mineral polymer composites7 and for the production of cordierite8 and other glass-ceramics.9,10 In a previous paper we have reported on an alternative route for the management of coal flyashes by utilizing them in the development of discontinuous reinforced glass matrix composite materials.11 The incorporation of ceramic particles, whiskers or platelets has been shown in the literature12–15 to result in an improvement in the mechanical and fracture behaviour of the glass matrix and to render materials less susceptible to catastrophic fracture and thus with a higher potential for engineering applications. Thus, an
interesting approach would be to develop glass matrix composite materials by using flyash as a component in the matrix and by utilizing a cost-effective fabrication route based on powder technology. This technology comprises the fabrication of dense products from pressed powder compacts by a sintering process at moderate temperatures, i.e. below the melting point of the constituents. In our previous work\textsuperscript{11} a laboratory-synthesized model borosilicate glass, which was available only in small quantity, had to be added to the flyash as a sintering aid. The densities reached, however, were low, with porosities higher than 20\%. In this study we report on the preparation of glass matrix composite materials, where the matrix is composed of flyash and cullet glass residue from the float glass production. Thus, in contrast to the previous study\textsuperscript{11} a different type of glass is added to form the matrix. The chosen reinforcing components were alumina platelets. Similar platelets, which are low-cost and commercially available for use in polishing applications have been shown, in previous studies, to be a useful reinforcing element for glasses and ceramics\textsuperscript{12,16}. The main objective of the present investigation was to optimize a powder technology route in order to maximize the sintered density of the products by keeping a high flyash content and the lowest possible sintering temperature. As the materials produced may have potential for technical applications, for example as floor tiles, machine elements or tool pieces in the chemical industry, their mechanical and tribological behaviour was evaluated.

EXPERIMENTAL

Starting Materials

Flyashes from a Polish coal power station (Lagisza, Katowicie) were used. The chemical composition is shown in Table 1. The relatively high SiO\textsubscript{2} content indicates the feasibility of this flyash to develop glass matrices for the fabrication of composite materials. As reported in the previous study\textsuperscript{11} the as-received flyash contains small amounts of crystalline phases such as quartz and mullite. The density of the as-received flyash was measured by means of an air comparison pycnometer. A value $\rho_f = 2.55 \text{ g cm}^{-3}$ was obtained. Figure 1(a) shows a scanning electron microscopy (SEM) micrograph of the as-received flyash, exhibiting the typical spherical shape of these kind of combustion residues. The mean particle size was 50 $\mu$m with particle diameters varying between 2 and 80 $\mu$m. For the present investigations, the as-received flyash was attrition-milled for 30 s to give a fine powder (mean particle size 10 $\mu$m), as shown in Fig. 1(b). After milling, the particles were irregular in shape with sharp edges. The cullet glass employed was a residue of the float glass production (Vegla, Herzogenrath, Germany). The chemical composition is also shown in Table 1. The density of this glass is $\rho_g = 2.51 \text{ g cm}^{-3}$. The cullet glass, which was received in the form of a frit of 2–5 mm granulate size, was

\begin{table}[h]
\centering
\caption{Chemical Composition of the Investigated Waste Materials}
\begin{tabular}{l c c}
\hline
Oxide & Flyash (wt\%) & Cullet glass (wt\%) \\
\hline
SiO\textsubscript{2} & 61.96 & 71.70 \\
P\textsubscript{2}O\textsubscript{5} & 0.12 & -- \\
Na\textsubscript{2}O & 0.65 & 14.0 \\
CaO & 2.55 & 8.70 \\
MgO & 2.32 & 3.60 \\
Al\textsubscript{2}O\textsubscript{3} & 19.68 & 0.60 \\
TiO\textsubscript{2} & 1.01 & 0.05 \\
K\textsubscript{2}O & 2.72 & 0.20 \\
Fe\textsubscript{2}O\textsubscript{3} & 8.52 & 0.80 \\
SO\textsubscript{3} & 0.08 & 0.25 \\
MnO & 0.27 & -- \\
ZnO & 0.06 & -- \\
PbO & 0.05 & -- \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{image1a}
\caption{(a) SEM micrograph of the as-received flyash showing the typical spherical shape of the particles.}
\end{subfigure}
\hfill
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{image1b}
\caption{(b) SEM micrograph of the flyash after attrition-milling for 30 s.}
\end{subfigure}
\caption{Figures 1 (a) and (b).}
\end{figure}
attrition-milled for 30 s to produce a fine powder having a mean particle size of \( \approx 20 \mu m \). A SEM micrograph of the milled glass powder is shown in Fig. 2. Commercially available alumina platelets (Grade TS100, Lonza-Werke, Waldshut-Tiengen, Germany) were employed as the reinforcing component. The same platelets have been used in previous studies to reinforce borosilicate glass\(^{12}\) and TiO\(_2\)\(^{16}\) matrices. Figure 3 shows a SEM micrograph of the platelets used. They are hexagonal in shape with an average axial ratio of 0.2, while the mean size of the major axis of the platelets is 5 \( \mu m \). The density of the alumina platelets is \( \rho_{al} = 3.99 \text{ g cm}^{-3} \), as determined elsewhere.\(^{12}\)

**Powder Technology**

The main objective of the present study was to develop a cost-effective powder processing route for obtaining composite materials having a matrix made exclusively of residues. This included the determination of an optimum mixture of flyash, glass powder and alumina platelets to obtain a composite material with desired mechanical properties. Thus, different mixtures containing different proportions of flyash and glass powder were prepared, initially, to study their sintering behaviour and to determine the optimal composition of the matrix in terms of the highest flyash content compatible with the lowest possible sintering temperature. The flyash content was varied between 10 and 90\% by weight. The mixtures were attrition-milled for 15 s to improve the mechanical mixing of the powders. Cylindrical samples (60 mm dia., 7 mm h) were pressed uniaxially at room temperature without the addition of any binder. Pressures of 40 MPa were used to reach green densities, i.e. densities before sintering, of \( \approx 55\% \) of the theoretical density. The powder compacts were sintered in air. The heating rate was 10\°C min\(^{-1}\) and the sintering time 120 min for all samples. The sintering temperature was varied between 650 and 800\°C. From the optimized matrix composition, i.e. that with the highest flyash content showing the highest sintered density, three batches of composite mixtures were prepared by adding 10, 20 and 30\% by volume of alumina platelets, respectively. The platelet-containing mixtures were homogenized by dry-mixing in a rotating mixer for 30 min. Attrition milling was not used in this step to avoid breaking and damage of the platelets. Uniaxial cold-pressing, as described above, was used to obtain cylindrical samples with a green density of \( \approx 55\% \) of the theoretical density. The pressed compacts were sintered in air at different temperatures. The heating rate was maintained constant at 10\°C min\(^{-1}\) and the sintering time was 120 min. All samples were cooled down in the furnace.

**Characterization of Sintered Materials**

The characterization of the samples was conducted using standard methods of current use for the testing of ceramic materials.\(^{17}\) The density of the sintered samples was determined by the well-known Archimedes' technique. The values of the theoretical density of the compacts were calculated based on their composition and on the density of the constituents. The microstructure was studied by optical microscopy and SEM of polished surfaces of selected samples. The same polished surfaces were employed for Vickers indentation tests, which were conducted to determine the hardness (\( H_v \)) and the indentation fracture toughness (\( K_{ic} \)) of the materials. A load of 500 g was used. The fracture toughness was estimated from the length of the cracks arising at the corners of the Vickers pattern and the \( K_{ic} \) values were obtained by using the equation of Antis \textit{et al.}\(^{18}\) From the values of hardness (\( H_v \)) and indentation fracture toughness (\( K_{ic} \)) the brittleness index (\( B \)) was calculated by means of the equation:\(^{19}\)
RESULTS AND DISCUSSION

The results of the initial studies concerning the optimization of the matrix material in terms of flyash content, sintering temperature and sintered density are summarized in Fig. 4. From these results, a composition containing 20% by weight of flyash was chosen as the matrix for the fabrication of composite materials. Higher flyash contents result in a drop of the final density of the material, even by using higher sintering temperatures. It is suggested that the presence of crystalline particles (such as quartz and mullite) in the as-received flyash, as determined elsewhere, can negatively influence the densification by hindering the viscous flow of the amorphous glass. It is well-known that the presence of rigid inclusions, such as crystalline inclusions or hard agglomerates, retards the densification of glass matrices, especially at volume fractions higher than \( \approx 15\% \), because they induce a significant increase of the effective viscosity of the system. In the present mixtures, for flyash contents lower than 20% by weight, the presence of crystalline phases does not have a major effect on the viscous flow densification and sintered densities higher than 96% of the theoretical density could be obtained. Higher flyash contents and consequently higher concentrations of crystalline particles result in poor densification of the compacts. Figure 5 shows a SEM micrograph of a sample containing 20% by weight of flyash sintered at 650°C. Residual spherical porosity as well as the crystalline inclusions in the glass matrix can be observed. The light grey inclusions are rich in Si (presumably quartz inclusions) while the darker inclusions have mullite composition, as determined by EDX spot analyses. A complete analysis of the mineralogical composition of these mixtures has been presented elsewhere.

![Figure 4](image-url)  
**FIGURE 4.** Relative sintered density, i.e. the measured density divided by the theoretical density, for different flyash/waste glass mixtures as a function of the flyash content for different sintering temperatures: (■) 630°C, (●) 650°C, (○) 690°C, (□) 710°C. The lines serve as a guide for the eye.

![Figure 5](image-url)  
**FIGURE 5.** SEM micrograph of a sample containing 20% by weight of flyash sintered for 2h at 650°C showing the presence of residual (mainly isolated, spherical) porosity. The light grey inclusions are rich in Si, while the darker inclusions have mullite composition.
Figure 6 shows the variation of the sintered density of the platelet-containing composite materials as a function of the sintering temperature. It is seen that the alumina platelets have a strong effect on the densification behaviour. For low platelet concentration (10% by volume) an increase in the sintering temperature promotes densification. This can be correlated with a decrease in the viscosity of the glass matrix allowing for counteracting the constraining effect of the rigid platelets. For higher platelets contents, however, an increase in the sintering temperature does not bring any significant improvement in densification. It is seen that densification essentially stops for platelet contents greater than 20% by volume as a consequence of the rigid network formed by the platelets. This phenomenon has also been found in pressureless sintering studies of model platelet containing borosilicate glass. In that work, a platelet volume fraction of 15% was found to be the upper concentration limit for achieving fully dense composites. For higher volume fractions of rigid inclusions in glass or glass-ceramic matrices, hot-pressing consolidation techniques must be employed to fabricate highly dense compacts, as most studies in the literature confirm. Achievement of high densities is important because the final properties of the products, especially the mechanical properties, increase with increasing density. Figure 7 shows an optical micrograph of a polished section of a sample containing 20% by volume of platelets and sintered at 700°C. The platelets are seen to be well-distributed in the glassy matrix and the residual porosity is closed and spheroidal in shape. It is assumed that a strong bond at the platelet/matrix interface exists, since no platelets removal (debonding) during the polishing procedure was observed. The mechanical properties and tribological behaviour of the composites are expected to be related to this strong interfacial bond.

Table 2 shows the results of the mechanical properties determination for the unreinforced glass matrix and for the composites containing 10 and 20% by volume of platelets. Due to the poor densification achieved (less than 70% of theoretical density) the mechanical properties of the composite containing 30% by volume of platelets were not determined. It is seen that despite the residual porosity present, all properties increase with increasing platelet content. The Young's modulus and the fracture strength

<table>
<thead>
<tr>
<th>Vol% alumina platelets</th>
<th>Young's modulus (GPa)</th>
<th>Bending strength (MPa)</th>
<th>Hardness (GPa)</th>
<th>Indentation toughness (MPa√m)</th>
<th>Britteness index (μm⁻¹/₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61</td>
<td>59 ± 6</td>
<td>3.2</td>
<td>0.7</td>
<td>4.6</td>
</tr>
<tr>
<td>10</td>
<td>78</td>
<td>71 ± 7</td>
<td>3.4</td>
<td>1.1</td>
<td>3.1</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>90 ± 8</td>
<td>4.0</td>
<td>1.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>
The increase of the hardness is, on the other hand, negligible, due to the porosity present. Several mechanisms have been proposed in the literature to explain the increase of toughness in platelet-containing materials. It was not the objective of this work to further investigate which are the active toughening mechanisms in the materials developed. However, since a strong interfacial bond exists at the interface, it is suggested that the system behaves similarly to a model borosilicate glass/alumina-platelet system previously investigated. Crack deflection due to elastic and thermal residual stresses should contribute to the toughness increment, while platelet debonding and pull-out should play a minor role. The mechanical properties are similar to those of glass-ceramic materials made from a controlled devitrification heat-treatment of melted flyashes and also comparable to those of in situ reinforced lithia-alumina-silica glass-ceramics. The calculation of the brittleness index [equation (1)] is important because it gives an assessment of the simultaneous response to both deformation and fracture, as it represents the ratio of hardness to fracture toughness. The values calculated for the present materials are extremely low, (typical values for glasses and glass-ceramics are in the range 4-7 \( \mu \text{m}^{-1/2} \), as shown in the literature. Both the presence of porosity and the platelet reinforcement contribute positively to yield “less brittle” materials, however with limited hardness \( (H_v < 4 \text{ GPa}) \). The low value of the brittleness index of these materials should result in a good machinability of the compacts. It has been shown that machinable brittle materials (glass-ceramics) have brittleness index values \( B < 4 \mu \text{m}^{-1/2} \).

A comparison of the wear behaviour of the unreinforced sample and a composite sample containing 20% by volume of platelets is shown in Fig. 8. The plot serves as a qualitative assessment of the variation of the wear behaviour with the testing time during sliding against a hard steel pin. The composite sample is shown to have a higher wear resistance since its friction parameter, which is proportional to the friction coefficient, remains lower than that of the unreinforced sample for the whole experiment. The better wear behaviour of the composite can be related directly to the presence of the hard, well-bonded alumina platelets. The positive influence of a hard second phase on the wear behaviour of brittle materials is well-known in the literature. A quantitative assessment of the wear behaviour, also under different environments, and the comparison with other glasses and glass-ceramics, is still to be done, however. This will be necessary in order to realistically assess the potential of the present materials for applications where a good wear resistance is required.

Moreover, in the exploration of potential applications for the materials developed here, the knowledge of their thermomechanical properties, such as the coefficient of thermal expansion and the thermal shock resistance, and the assessment of their chemical durability and leaching behaviour will be essential, this being the focus of current studies.

**CONCLUSIONS**

The present study was conducted to develop glass matrix composites from waste materials. Flyash from a coal power station and cullet glass residue from the float glass production were used. Low-cost, commercially available alumina platelets were used as reinforcing component. Using a simple, cost-effective powder technology method and relatively low sintering temperatures sufficiently dense flyash containing materials were produced. The addition of alumina platelets resulted in better mechanical properties of the composites than those of the unreinforced matrix, despite a residual porosity. The low brittle index suggests that the materials have good machinability. This, together with the qualitatively better wear behaviour of the composites, indicates an interesting potential of these materials for technical applications, for example as floor tiles, machine components or in the chemical and food industry. The full potential of the materials will only be realistically estimated, however, when more information concerning the thermomechanical behaviour and the chemical durability of the products becomes available, this being the focus of on-going research.
REFERENCES


