Original Paper

Sintered glass-ceramic matrix composites made from Latvian silicate wastes

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Dedicated to Professor Oleg V. Mazurin on the occasion of his 75th birthday

Powder technology and sintering were used to fabricate glass-ceramic matrix composites from Latvian industrial wastes and alumina platelets reinforcement. The optimization of the sintering behaviour of glass-ceramic compositions containing clay and alumina platelets was carried out. Highly crystalline and dense products (> 90 % theoretical density) were fabricated by sintering at temperatures in the range 1040 to 1060 °C, depending on composition. Addition of waste glass to influence the sintering temperature and sintering interval was also investigated. Composites showed higher fracture strength (up to 97 MPa) and hardness than unreinforced glass-ceramics. The "best" composition in terms of density and mechanical properties contained 20 wt% alumina platelets. The matrix exhibited a microstructure composed mainly of elongated crystals of pyroxene type in a residual glassy matrix. These composites are candidates for applications as building materials, such as floor and wall tiles, and for manufacturing machine elements and parts.

1. Introduction

More than 50000 t of industrial waste, e.g. slag and fly-ash, have been accumulated in open storages of the steel plant "Liepajas metalurgs" (Liepaja (Latvia)) during the last 40 years. Environmentally harmful elements have leached out and spread both in the underground water and in the Liepaja lake, which is connected to the Baltic sea, with the related environmental concern [1]. Other forms of inconvenient industrial waste accumulation in Latvia include large amounts of peat and coal ash being stored in the surroundings of the Riga thermal power station and glass cullet from the largest Latvian glass fibre plant (Valmiera).

Although the influence of such industrial wastes to the environment, for example the quantitative effect of harmful elements in the over- and underground water, has been investigated [2], there has been only limited systematic research on the chemical and mineralogical composition of Latvian industrial wastes as well as on the development of alternative technologies for their treatment and recycling.

Taking into account such an unsatisfactory situation, both from economical and ecological viewpoints, research is being carried out focussing on the development of new silicate products from smart combinations of the mentioned residues. In particular, sintered glass-ceramic bodies with high chemical durability for possible applications as building materials have been produced in preliminary research [1, 3 and 4].

The use of powder technology to obtain high-quality products from silicate waste materials is not new. In the past mainly waste glass powders (cullet) or composite mixtures of waste glass and other crystalline ceramic wastes have been used to fabricate building materials such as floor and wall tiles or porous components for thermal insulation or sound absorption [5 to 8]. Also glass matrix composites containing alumina platelet reinforcement have been fabricated using a matrix of recycled glass cullet and fly ash [9]. Further work has been

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published regarding the fabrication of glass-ceramics from powdered waste by sintering, including glass-ceramics from metallurgical slag [10], from coal-fired power station fly ashes combined with waste glass [11], from iron-rich jarosite zinc hydrometallurgical residues [12 and 13] and from municipal incinerator ash [14 and 15]. In recent papers glass composites made from combined waste from municipal waste incinerators and aluminium foundry [16] and magnetic glass-ceramics from sintered coal ash and borosilicate glass combinations [17] have also been reported.

Several advantages appear when using powder technology and sintering to fabricate glass-ceramics. For example, the products can be manufactured using ordinary equipment available in a ceramic plant. Thus, the technology does not require major investment, being particularly suitable for production of articles of complicated shape. Moreover, powder technology and sintering are the technologies of choice when the aim is to fabricate glass-ceramic composite materials reinforced by particles or fibres with enhanced mechanical properties and abrasion resistance [9 and 18]. The relative advantages and limitations of sintering in comparison with traditional melting for the treatment and recycling of silicate wastes have been discussed in a recent paper [19].

In the present study, novel glass-ceramic matrix composite materials have been developed using a combination of Latvian industrial wastes and clay as the matrix. Low-cost commercially available alumina platelets were incorporated as reinforcing component. In order to improve the rheological properties and sintering behaviour of the starting glass-ceramic composition waste glass cullet was investigated as a sintering aid. The sintering heat treatment was optimized in order to obtain high-density glass-ceramic composites with high volume fraction of crystalline phase. Another focus of the work was to maximize the sintering temperature interval by keeping the highest possible content of waste and alumina platelets as well as the highest possible mechanical strength.

2. Experimental methods

Flyash (10 to 30 wt%) from the steel plant "Liepajas metalurgs" and peat ash (90 to 70 wt%) from the Riga thermal power station, combined with a carbon-free clay (20 wt%) were used as the starting materials for production of the glass-ceramic matrix (labelled here 3K0). Clay was added as a binder to improve the plastic behaviour during the pressing step and to increase the bonding strength between particles and particle agglomerates in the pressed green body. Glass-ceramics made from the same waste materials combination and clay additions have been investigated in preliminary studies [1 and 4]. The main chemical constituents of the wastes are compounds of Fe, Si, Ca, Mg, Zn. As reported elsewhere [1], the flyash contains spinel ($ZnAl_2O_4$), sphalerite (ZnS), hematite (Fe_2O_3) and palmerite ($K_2Pb(SO_4)_2$), while the peat ash contains calcite ($CaCO_3$), anhydrite ($CaSO_4$), corundum (Al_2O_3), albite ($(Na,K)AlSi_3O_8$) and quartz (SiO_2). The fly ash contains also trace amounts of hazardous elements (heavy metals), such as Pb, Cd, Sn, Zn and Sr. The nominal chemical composition of the glass-ceramic matrix (3K0) was determined in a previous investigation [4] and is given in table 1. The density of the powdered glass-ceramic matrix was determined by He pycnometry to be 2.923 g/cm^3. The mean particle size of the powdered glass-ceramic was 11 μm with 90 % of the particles having size under 25 μm, as determined by light scattering technique.

Table 1. Chemical composition in wt% of the glass-ceramic matrix (3K0) and of the added waste glass

oxide	glass-ceramic (3K0)	waste glass
SiO_2	62.16	72.64
Al_2O_3	12.76	4.44
CaO	5.24	0.91
Na_2O		19.97
MgO		0.34
K_2O	2.54	0.51
TiO_2		0.26
Fe_2O_3	7.94	0.93
ZnO	6.09	
PbO	3.27	

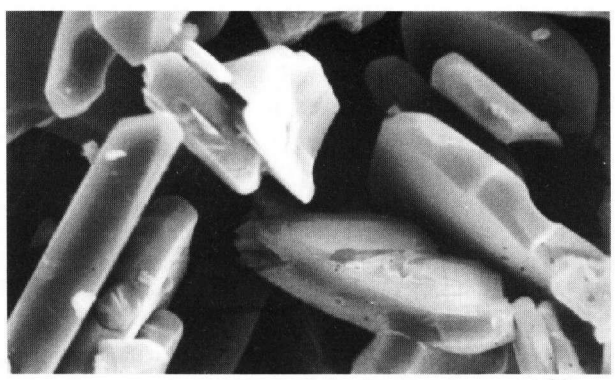


Figure 1. SEM micrograph of the alumina platelets used as reinforcement showing their hexagonal shape.

The alumina platelets used as reinforcement are shown in figure 1 (Lonza Werke, Waldshut-Tiengen (Germany)). They have hexagonal shape with an average axial ratio of 0.2, while the mean size of the platelet major axis is 5 μm. Similar alumina platelets, which are low-cost and commercially available for use in polishing applications, have been shown to be useful reinforcing element for glasses and ceramics [9, 20 and 21]. The density of the alumina platelets is $\varrho_{Al} = 3.99$ g/cm^3 [9]. From the starting glass-ceramic matrix composition three batches of composite mixtures were prepared by adding 10, 20 and 30 wt% of alumina platelets (compositions 3K1, 3K2 and

3K3, respectively). A combined composition with 10 wt% alumina platelets and 10 wt% of waste glass (from Valmiera glass fibre plant) was also investigated (labelled 3KV). A waste glass with relatively low softening temperature (≈850 to 900 °C) was used. The nominal chemical composition of the glass used is given in table 1 and the density of this glass was 2.27 g/cm^3.

The mixtures were milled using dry agate mills for 20 min, in order to homogenize the powders, and subsequently water was added (8 to 12 wt%). The humid powders were sieved (aperture 3 mm) by keeping the moisture content at 12 to 14 %. The sintering behaviour and thermal changes of the mixtures were determined by heating microscopy (Leica, Wetzlar (Germany)) and differential thermal analysis (DTA) (STA 409C) in the temperature range 20 to 1300 °C. Cylindrical samples (diameter = 20 mm; height = 4 mm) were pressed uniaxially at room temperature using pressures of 50 MPa. The green densities achieved were in the range 62 to 67 % of theoretical density. The powder compacts were sintered in air, the heating rate was 8 K/min and sintering time was 60 min. The sintering temperature was varied between 1000 and 1120 °C. The density and water uptake of the sintered samples were determined according to normalized procedures [22]. The values of the theoretical density of the compacts were calculated based on their composition and density of the constituents. X-ray diffraction (XRD) analysis (Siemens, CuK_α radiation) of sintered samples was conducted. The samples for microstructure analysis were polished using SiC abrasive paper and diamond paste. The microstructure of selected sintered samples was studied by scanning electron microscopy (SEM) (LEICA S 440 I). The identification of elements was carried out by EDAX analysis. Four-point bending test on rectangular bars (4 x 3 x 35) mm^3 was used to determine the ultimate fracture strength (modulus of rupture) and Young's modulus. At least five samples of each composition were tested. SEM was used to observe fracture surfaces. Vickers indentation was used to determine the hardness (H_V) of the selected samples using indentation loads of 20 N.

3. Results and discussion

The glass-ceramic used as matrix in the present experiments was developed in a previous study [1]. It has been shown [1 and 4] that the chemical durability of this material, determined by leaching tests, meets the requirements of dense unglazed pressed ceramic tiles according to German standards [23]. These previous results encouraged the use of this glass-ceramic as the matrix for composite materials, as explored in the present study.

Differential thermal analysis (DTA) results of different compositions investigated are shown in figure 2. The DTA curves for compositions 3K0, 3K1, 3K2 and 3KV

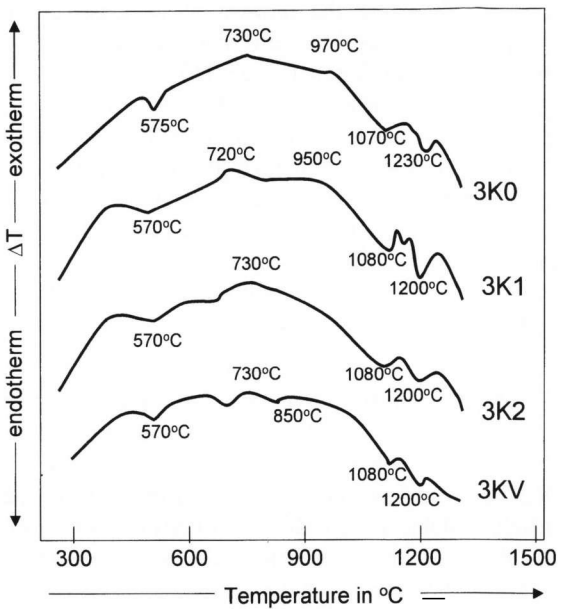


Figure 2. DTA curves of powder samples of different compositions investigated: unreinforced glass-ceramic matrix (3K0), composites with 10 wt% (3K1) and 20 wt% (3K2) alumina platelets, modified matrix with 10 wt% waste glass addition and 10 wt% alumina platelets (3KV).

show shallow exothermal effects at the temperatures in the range 430 to 440 °C, which may be explained due to formation of anhydrite phase ($CaSO_4$). This behaviour has been found in previous DTA studies of the same material (3K0) [1] and it is confirmed by XRD results shown below. These exothermic peaks can be also seen in compositions with alumina platelet addition. In general DTA curves of samples containing alumina platelets are similar to that of the starting composition, indicating no major effect of the presence of alumina platelets on thermal evolution, at least at the temperatures of interest in this study. All DTA curves exhibit endothermic effects at temperatures in the range 570 to 575 °C, which may be connected with transformations of low-temperature quartz (SiO_2) to a high-temperature quartz modification. The next two exothermal effects occur in the ranges 720 to 730 °C and 850 to 970 °C, this last one being more pronounced in the 3K0 and 3K1 samples. The exothermal effect in the 720 to 730 °C range may be connected with oxidation of Fe^{2+} and formation of spinel phases, as also observed by Karamanov et al. [24] in crystallization studies on iron-containing glass-ceramics. Oxidation leads to a decrease of the Fe^{2+}/Fe^{3+} ratio, which increases the viscosity of the materials, making the crystallization process more difficult to achieve. The crystallization of a pyroxene solid solution, as confirmed by XRD analysis shown below and also found in several previous investigations on glass-ceramic production from silicate wastes [14, 25 to 28], should take place at higher temperatures (> 850 °C). This is confirmed in compositions 3K0 and 3K1 by the presence of exothermic effects in the range 850 to 970 °C. This effect seems

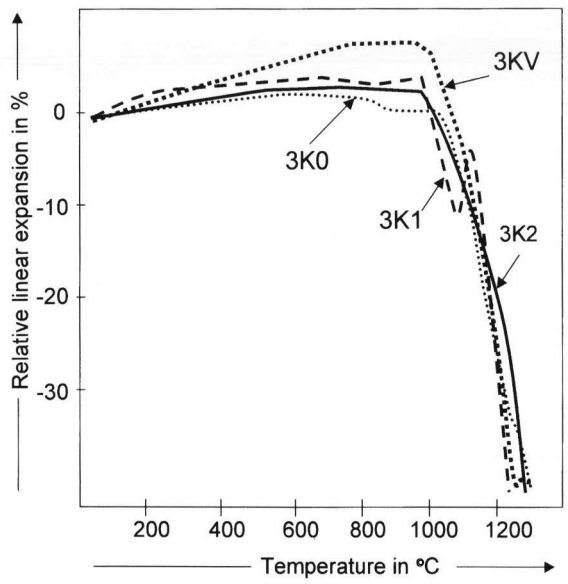


Figure 3. Change of the linear dimension (height) of powder compacts versus sintering temperature for different compositions, as obtained by heating microscopy. Note that the bends in the curves are due to interpolation between discrete experimental points.

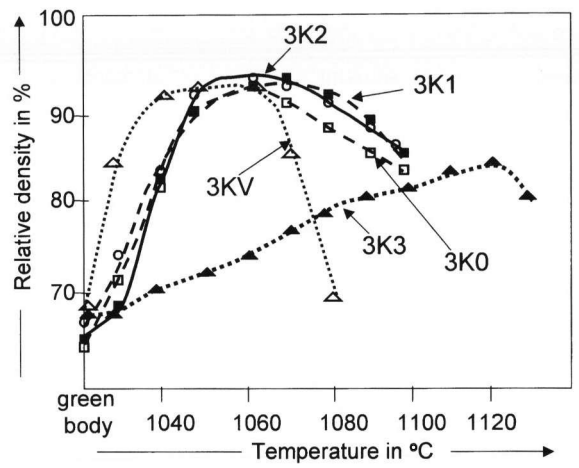


Figure 4. Relative density (as % of theoretical density) of powder compacts of different compositions versus sintering temperature. The heating rate was 8 K/min and the samples were sintered for 60 min at the indicated temperatures.

to be less pronounced in compositions 3K2 and 3KV, according to the results shown in figure 2. At temperatures higher than about 1080 °C partial melting of silicate phases starts to occur, thus explaining the endothermic effects detected by DTA. Endothermic peaks are seen at 1230 °C in the 3K0 composition and at 1200 °C in the other samples, as shown in figure 2. The possibility of crystallization cannot be definitively excluded at > 1080 °C, however the endothermic peaks indicate that the melting of silicates dominates the behaviour of the mixtures at high temperatures. The curve of 3KV composition, which contains waste glass and alumina platelets, shows a small endothermal effect at 850 °C. Melting of the waste glass with a relatively high Na_2O content (19.97 wt%) should start at this temperature.

Figure 3 shows the results of the sintering experiments obtained by heating microscopy in the form of relative variation of sample height versus temperature. It is seen that the fastest changes of linear dimensions took place at the temperature range 1050 to 1150 °C in composition 3K0 (without platelet additions), while composition 3K2 at temperatures 1000 to 1150 °C shows the slowest decrease of linear dimensions. The increase of the linear dimension for composition 3KV at temperatures between 600 and 1000 °C takes place due to foaming of the waste glass and clay, as reported elsewhere [1], while at temperatures > ≈1000 °C the sample exhibits strong shrinkage. Composition 3K1 showed a different behaviour. Densification of this composition starts at a temperature of 1000 °C, similarly to composition 3K0, while in the temperature range 1100 to 1150 °C an increase of the linear dimension is observed. The next sharp decrease of the linear dimension for composition 3K1 starts at ≈1150 °C. A related thermal effect in the indicated temperature range can be observed in the DTA curve for this composition (figure 2); there are two endothermic effects at 1080 and 1200 °C. The present results do not allow for an explanation of these effects however, which were not observed for the other compositions.

As shown in the literature [29 and 30], the presence of rigid inclusions, such as crystalline inclusions or hard agglomerates, retards the densification of glass matrices because they induce a significant increase of the effective viscosity of the system. Other reason for the detrimental effect of nonsintering inclusions on densification of viscous matrices is the formation of a rigid network of rigid inclusions, which impedes the viscous flow of the silicate phase [31]. This phenomenon has also been found in sintering studies of model alumina-platelet containing aluminosilicate glass powder compacts [30]. For ceramic platelets contents higher than ≈15 vol.%, hot-pressing consolidation techniques must be employed to fabricate highly dense compacts, as most studies in the literature confirm [18, 20, 32 and 33].

The results of the initial studies on densification behaviour of the present materials, in terms of sintering temperature are summarized in figure 4 for mixtures with various volume fractions of alumina platelets and waste glass addition. The samples were sintered for 60 min at the indicated temperatures. The highest sintered density (90 to 93 % of the theoretical density, 3.14 g/cm^3) was obtained in the sample containing 20 wt% of platelets (3K2) at temperatures in the range 1050 to 1070 °C, while for composition 3K1 (with 10 wt% of alumina platelets) the highest densification (up to 91 % of the theoretical density, 3.03 g/cm^3) occurs in the range 1050 to 1080 °C. For higher alumina contents (sample 3K3 with 30 wt% of alumina platelets) densification occurs slowly and samples reached only 80 to 83 % of theoretical density (3.25 g/cm^3) at a maximum

Table 2. Density, water uptake and fracture strength of optimized sintered materials

sample no.	sintering temperature in °C	sintered density in g/cm³	relative sintered density in %[1)]	water uptake in %	flexural strength[2)] in MPa
3K0	1055	2.76	92	0.1	57
3K1	1060	2.76	91	0.1	94
3K2	1065	2.92	93	0.1	97
3K3	1120	2.66	82	5.1−0.1	60
3KV	1040	2.65	91	0.3−0.5	54

[1)] Related to the theoretical density = 3.14 g/cm³.
[2)] The maximum relative error of strength data was 10 %.

sintering temperature in the range 1100 to 1130 °C. This result confirms the negative effect of platelet additions on densification mentioned above, which for the present samples start to be significant for platelet volume fraction > 20 wt%. This result is in agreement with numerous literature data that confirm the existence of a critical concentration of inclusions at which the inclusions form a rigid network opposing further densification [29 to 31]. The critical inclusion concentration depends mainly on the homogeneity of the dispersion and on the shape and orientation of the inclusions. Table 2 shows the final densities achieved in optimized samples at the indicated sintered temperatures. The results of the water uptake measurements, which qualitatively correlate with the density data, are also presented in table 2.

No significant "barrelling" or other shape distortion effects occurred during sintering of samples with the highest concentration of platelet addition (20 and 30 wt%), and the samples retained the cylindrical shape of the "green" bodies after sintering. This indicates that appropriate shape control of the products is possible. This is of practical importance with the aim to fabricate components of complex shapes and high dimensional tolerances for technical applications.

It is interesting to compare also the sintering intervals for the different compositions from the curves in figure 4. A large sintering interval is usually desired in industrial ceramic manufacturing due to possible difficulties in controlling small temperature variations in large furnaces. Defining the sintering interval as the temperature range at which the final relative density varies less than 1 %, Figure 4 shows that for the present samples the largest sintering interval was exhibited by samples 3KV and 3K2, while the starting composition 3K0 has a narrow sintering interval.

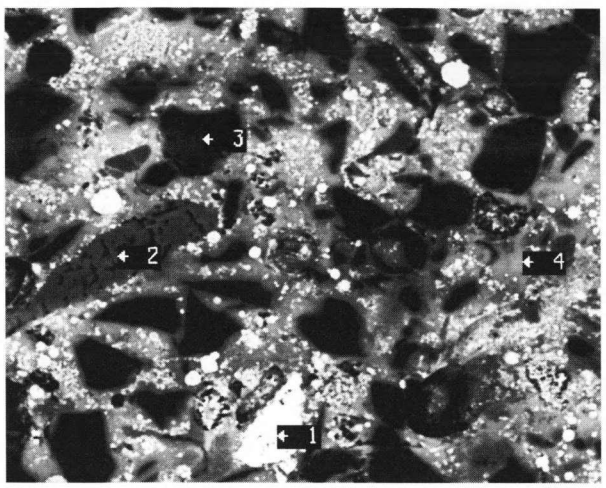
The results of XRD analysis are shown in table 3 for samples 3K0 and 3KV. The results for samples containing alumina platelets did not differ from those for sample 3K0. SEM micrographs showing typical microstructures of sintered samples are shown in figures 5a to c. The different phases observed have been identified by numerical labels. The image of sample 3K0 (figure 5a) shows a complex microstructure comprising a glass matrix (label 4) incorporating different crystalline phases

Table 3. Qualitative data on the mineralogical composition of glass-ceramics 3K0 and 3KV, obtained by XRD analysis of sintered samples

crystalline phases	3K0 (ϑ_{sint}=1055 °C)	3KV (ϑ_{sint}=1050 °C)
$FeFe_2O_4$ (magnetite)	+	
SiO_2 (quartz)	+	+
$CaAl_2Si_2O_8$ (anorthite)	+	+[3)]
$ZnFe_2O_4$ (franklinite)	+	+
$CaSO_4$ (anhydrite)	+	+
$K_2Pb_2O_3$	+	
Fe_2O_3 (maghemite)		
$Al_2(PO_4)(OH)_3$ (augelite)		
$KAlSi_3O_8$ (mycrocline)		
$Ca(Mg,Al)(Si,Al)_2O_6$ (diopside)	+	+
Al_2O_3 (corundum)		+
$CaZnSi_2O_6$ (petedunite)		+
$(Ca,Mg,Fe)_2(Si,Al)_2O_6$ (augite)	+	+

[3)] Sodium-substituted anorthite $(Ca,Na)(Si, Al)_4O_8$

(labels 1, 2 and 3). For example, light-grey inclusions are rich in silicon, as determined by EDAX, and, according to the mineralogical composition shown in table 3, they can be identified as being quartz crystals (label 3 in figure 5a). The other silicate crystalline phases, anorthite ($CaAl_2Si_2O_8$) (label 2) and the spinel phase franklinite ($ZnFe_2O_4$) are distributed in the glass matrix phase as small-size crystalline incorporations. A magnetite phase ($FeFe_2O_4$) was also found, which is labeled 1 in figure 5a. The microstructure in figure 5a, which corresponds to a sample of 92 % relative density, seems to indicate that the viscous flow assisted densification mechanism stops as crystallization and crystal growth proceed and individual crystallized grains start to encounter each other. This negative effect of crystallization during viscous flow densification has been observed in different glass-ceramic systems [14, 34 and 35]. For the present experiments, sintering to achieve high density is further jeopardized by the presence of crystalline phases in the starting material used as matrix (3K0). However, the sintering conditions chosen have led to fairly dense, highly crystalline products as figure 5a shows.



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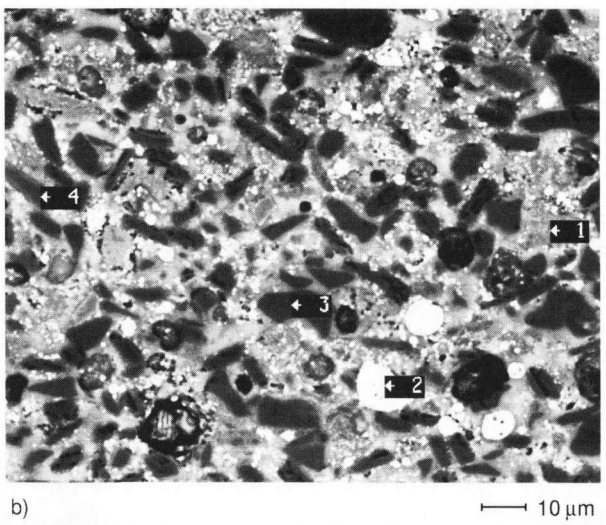

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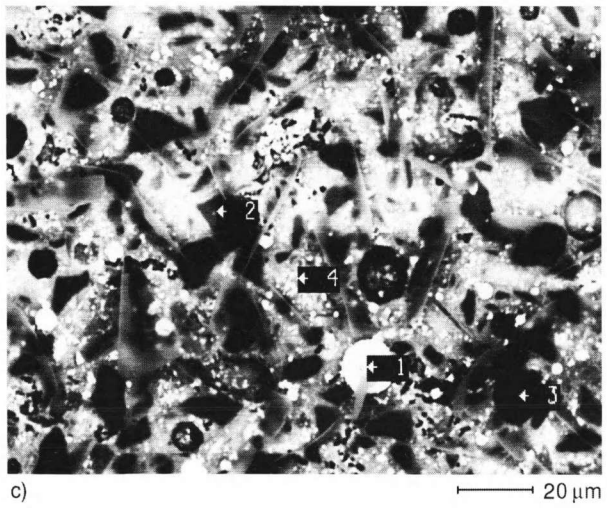


c)

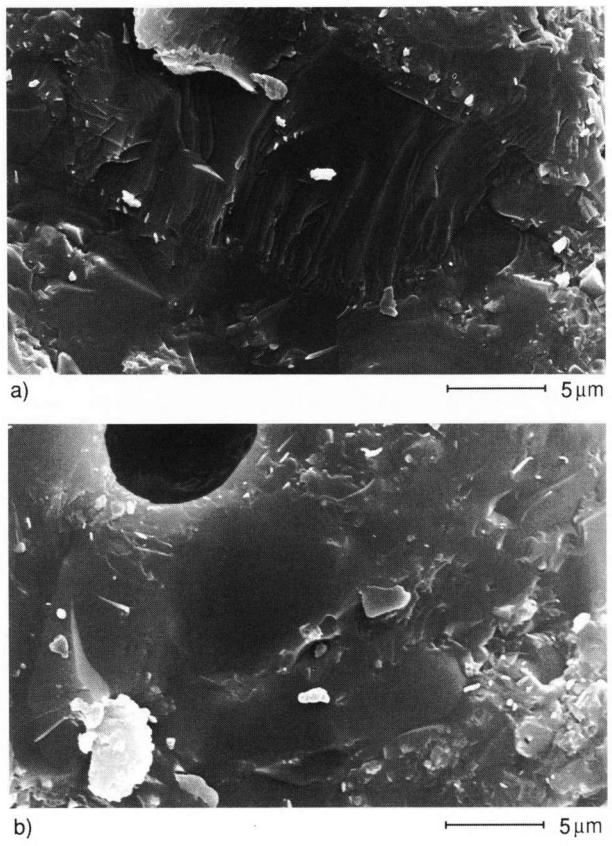
Figures 5a to c. SEM micrographs showing the microstructures of sintered samples; a) 3K0, b) 3K2 and c) 3KV. Sintering temperatures are given in table 2. Phases identified are: in a): glassy matrix (4), quartz (3), anorthite (2) and magnetite (1), in b): glass matrix (1), alumina platelets (3 and 4) and franklinite (2), in c): franklinite (1), quartz (2), porosity (3) and sodium-substituted anorthite (4).

The microstructure of the sample with 20 wt% reinforcing alumina platelets (figure 5b) reveals a regular distribution of small-size crystalline incorporations in a glassy matrix (label 1), which according to EDAX and XRD analysis can be ascribed to quartz (SiO_2), diopside ($Ca(Mg,Al)(Si,Al)_2O_6$) and augite ($Ca(Mg,Fe)Si_2O_8$). The bright phase (label 2) is an iron-containing phase, most probably franklinite ($ZnFe_2O_4$). In figure 5b the alumina platelets are labelled 3 and 4. The appearance of pyroxene phases (diopside, augite), similar to those formed in crystallized basalt glasses [36], which possess high chemical and thermal stability, is significant when considering possible industrial applications of these materials. Indeed diopside and other pyroxene phases frequently develop in glass-ceramics prepared from silicate waste materials. For example, the formation of augite has been reported during crystallization of a waste material obtained by vitrification of electric arc furnace dust [25]. Moreover, pyroxene crystals have also been observed in crystallized glasses obtained from other industrial waste rich in iron, such as flyash from thermal power stations [26], goethite industrial waste [27] and flyash from municipal waste incinerators [14 and 28].

The fine-grained interlocking texture of crystals in the range of 1 to 5 µm in the matrix (figure 5b) contributes to the high mechanical strength and elastic modulus of these composite samples, as reported below. The presence of anisotropic rod-shaped crystals that can act as reinforcing whiskers may further increase strength (and toughness). The added alumina platelets, seen as large grey inclusions in figure 5b (labelled 3 and 4), are homogeneously distributed in the glass matrix. Moreover, the material is seen to be fairly dense with only small, dispersed pores, mostly located around the alumina inclusions.

Figure 5c shows the microstructure of the 3KV sample, confirming the relative high densification achieved in this material after sintering at 1040 °C. The microstructure of this sample however is rather inhomogeneous with the presence of large quartz crystals (label 2), large glassy regions and isolated pores (label 3). Due to the large amount of sodium in this sample from the waste glass added (see table 1), sodium-substituted anorthite ($(Ca,Na)(Si, Al)_4O_8$) is found as reported in table 3, which is identified as small white particles in figure 5c (label 4). The bright phase (label 1) is an iron-containing phase, most probably franklinite ($ZnFe_2O_4$), as found in the previous samples.

The fracture strengths of optimized samples, as determined in 4-point flexural strength tests, are shown in table 2. The Young's modulus of the platelet-containing samples was in the range 116 to 120 GPa. The highest fracture strengths reached are 94 and 97 MPa for compositions 3K1 and 3K2, respectively. This represents a notable improvement over the strength of the starting "unreinforced" glass-ceramic composition 3K0 (57 MPa). For glass-ceramics containing 10 wt% waste glass and 10 wt% alumina platelets (3KV) the fracture strength at the optimal sintering temperature was only 54 MPa. This relatively low mechanical strength may be



Figures 6a to b. SEM images of the fracture surfaces of sintered samples; a) composite sample 3K2, b) glass-ceramic sample 3K0, showing different surface roughness due to the presence of alumina platelets in sample 3K2.

the consequence of the larger glass and lower alumina platelet contents of this sample as well as its rather inhomogeneous microstructure, as shown in figure 5c. Thus this material is, in terms of mechanical properties, comparable to the starting glass-ceramic (3K0). It has however the benefit of reaching high density (> 90 % of theoretical density, 2.96 g/cm^3) at a lower temperature than the starting composition (1040 versus 1060 °C). Moreover, it has a larger sintering temperature interval, as defined above (> 30 K compared to only ≈10 K of the 3K0 composition, see figure 4). This is of practical interest for fabrication of waste-containing building materials using standard ceramic equipment, as mentioned above.

The positive effect of platelet addition on enhancing mechanical properties is evident for samples containing 20 wt% platelets. The flexural strength and Young's modulus of these composites are very similar to data reported in the literature for glass-ceramics and particle-reinforced glass and glass-ceramic matrix composites [9, 18, 20 and 33]. For higher platelet content (30 wt%), due to the insufficient densification, the mechanical properties were poor, the reinforcing effect of the platelets being offset by the residual porosity. A typical fracture surface of the 3K2 material is seen in figure 6a. The equivalent fracture surface of the unreinforced matrix (3K0) is shown in figure 6b for comparison. The micrographs demonstrate the different degree of roughness of the fracture surfaces. As recently found [37], the level of toughening effect of alumina platelets in glass matrices, due to crack deflection process at platelet/matrix interfaces, may be related to fracture surface roughness. Thus, it can be stated in qualitative terms that the fracture toughness of the platelet-containing samples should be higher than that of the unreinforced matrix, as a propagating crack will encounter more obstacles and interfaces during failure, and so a higher fracture energy will be required. A more detailed analysis of the fracture process and the measurement of the fracture toughness were however not attempted here.

The Vickers hardness of the optimized sample with 20 wt% platelet addition was 4.7 GPa, which is higher than values obtained in other alumina platelet reinforced glass-ceramics [9]. Combination of high hardness and high fracture toughness should result in the present material having high wear and erosion resistance, which is relevant for its possible applications as high-performance tiles and for construction of machine elements and tools.

4. Conclusions

The present study was conducted to develop glass-ceramic matrix composites using industrial wastes of Latvia. Low-cost, commercially available alumina platelets were used as reinforcing components. In order to decrease the sintering temperature of compositions, addition of a waste glass with relatively low softening temperature was also investigated. Using a simple powder technology route; uniaxial dry pressing and pressureless sintering, fairly dense glass-ceramic composites were produced. The addition of 20 wt% alumina platelets resulted in a material with high fracture strength (97 MPa) and hardness (4.7 GPa). The products have a large application potential. They could be, for example, candidate materials for applications in floors of industrial buildings and constructions, and for outside and inside facings of walls as tiles and pavements. Moreover, fracture toughness imparted by the platelet addition coupled with relatively high hardness should lead to a material with high wear and erosion resistance enabling applications also in specialty areas, for example for constructing diverse equipment and tool pieces, such as threads guides for textile machines.

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5. References

[1] Rozenstrauha, I.: Glass-ceramics materials with multibarrier structure from industrial waste. Riga Technical University, Ph.D. thesis 1999. (English short version.)

[2] Vircavs, M.; Taure, I.; Njastad, O. et al.: An evaluation of the environmental state of lake Liepaja (Latvia) using elemental distributions in sediments. Chem.-Geol. (1995) p. 135–141.
[3] Berzina, L.; Cimdins, R.; Rozenstrauha, I. et al.: Glass-ceramics with multibarrier structure obtained from industrial waste. *Key Eng. Mat.* **132–136** (1997) p. 2228–2231.
[4] Cimdins, R.; Rozenstrauha, I.; Berzina, L. et al.: Glass-ceramics obtained from industrial waste. Resour. Conserv. Recycl. **29** (2000) p. 285–290.
[5] Shutt, T. C.; Campbell, H.; Abrahams, J. H.: New building materials containing waste glass. Ceram. Bull. **51** (1972) p. 670–671.
[6] Brown, I. W. M.; Mackenzie, K. J. D.: Process design for the production of a ceramic like body from recycled waste glass. J. Mat. Sci. **17** (1982) p. 2164–2170.
[7] Liu, W.; Li, S.; Zhang, Z.; Sintered mosaic glass from ground waste glass. Glass Technol. **32** (1991) p. 24–27.
[8] Boccaccini, A. R.; Bücker, M.; Trusty, P. A. et al.: Sintering behaviour of compacts made from television tube glasses. Glass Technol. **38** (1997) p. 128–133.
[9] Boccaccini, A. R.; Bücker, M.; Bossert, J. et al.: Glass matrix composites from coal flyash and waste glass. Waste Manage. **17** (1997) p. 39–45.
[10] Kim, H. S.; Rawlings, R. D.; Rogers, P. S.: Sintering and crystallization phenomena in silceram glass. J. Mat. Sci. **24** (1989) p. 1025–1037.
[11] Boccaccini, A. R.; Bücker, M.; Bossert, J.: Glass and glass-ceramics from coal flyash and waste glass. Tile Brick Int. **12** (1996) p. 515–518.
[12] Rincon, J. M.; Pelino, M.; Romero, M.: Glass-ceramics obtained from axial pressing and sintering of vitrified high iron content red muds. In: Pelino, M.; Pellacani, G. C. (eds.): Proc. 1st Nat. Congress Valorisation and Recycling of Industrial Wastes, Tenerife 1992. Modena: Mucchi Editore, (1997) p. 169–182.
[13] Kamaranov, A.; Pelino, M.; Taglieri, G. et al.: Sintered building glass-ceramics based on jarosite. In: Choudhary, M. K.; Huff, N. T.; Drummond III, C. H. (eds.): Proc. XVIII International Congress on Glass, San Francisco, CA, 1998. Westerville, OH: Am. Ceram. Soc., 1998. Available only on CD-ROM.
[14] Boccaccini, A. R.; Schawohl, G.; Kern, H. et al.: Sintered glass-ceramics from municipal incinerator fly ash. Glass Technol. **41** (2000) p. 99–105.
[15] Barbieri, L.; Corradi, A.; Lancellotti, I.: Bulk and sintered glass-ceramics by recycling municipal incinerator bottom ash. J. Europ. Ceram. Soc. **20** (2000) p. 1637–1643.
[16] Ferraris, M.; Salvo, M.; Smeacetto, F. et al.: Glass matrix composites from solid waste materials. J. Europ. Ceram. Soc. **21** (2001) p. 453–460.
[17] Francis, A. A.; Rawlings, R. D.; Boccaccini, A. R.: Processing of coal ash into glass-ceramic products by powder technology and sintering. Glass Technol. (2002). In press.
[18] Rawlings, R. D.: Glass-ceramic matrix composites. Compos. 25 (1994) p. 372–379.
[19] Boccaccini, A. R.; Lancellotti, I.; Barbieri, L.; Sintering: an alternative to fusion for the recycling of silicate wastes? Glastech. Ber. Glass Sci. Technol. **73 C2** (2000) p. 85–94.
[20] Boccaccini, A. R.: Trusty, P. A.: Toughening and strengthening of glass by Al_2O_3 platelets. J. Mat. Sci. Lett. **16** (1996) p. 60–63.
[21] Boccaccini, A. R.; Fredel, M. C.; Processing and mechanical properties of biocompatible of Al_2O_3-platelet reinforced TiO_2. J. Mat. Sci. **31** (1996) p. 4375–4380.
[22] German standard DIN EN 993-1 (April 1995): Prüfverfahren für dichte geformte feuerfeste Erzeugnisse. T. 1. Bestimmung der Rohdichte, offenen Porosität und Gesamtporosität. Berlin: DIN, 1995.
[23] German standard DIN EN 106 (Sept. 1980): Kalksandsteine, Vollsteine, Lochsteine, Blocksteine, Hohlblocksteine. Berlin, DIN, 1980.
[24] Karamanov, A.; Taglieri, G.; Pelino, M.: Iron-rich sintered glass-ceramics from industrial wastes. J. Am. Ceram. Soc. **82**(1999) p. 3012–3016.
[25] Gao, Z.; Drummond III, C. H.: Thermal analysis of nucleation and growth of crystalline phases in vitrified industrial wastes. J. Am. Ceram. Soc. **82** (1999) p. 561–565.
[26] Barbieri, L.; Manfredini, T.; Queralt, I. et al.: Vitrification of fly ash from thermal power stations. Glass Technol. **38** (1997) p. 165–170.
[27] Romero, M.; Rincon, J. M.: Preparation and properties characterisation of high iron content glasses obtained from FeOOH industrial wastes. J. Europ. Ceram. Soc. **18** (1998) p. 153–160.
[28] Boccaccini, A. R.; Kopf, M.; Stumpfe, W.; Glass-ceramics from filter dusts from waste incinerators. Ceram. Int. **21** (1995) p. 231–235.
[29] Rahaman, M. N.; De Jonghe, L. C.: Effect of rigid inclusions on the sintering of glass powder compacts. J. Am. Ceram. Soc. **70** (1987) p. C348–C351.
[30] Boccaccini, A. R.: Sintering of glass matrix composites containing Al_2O_3 platelet inclusions. Mat. Sci. **29** (1994) p. 4273–4278.
[31] Boccaccini, A. R.; Olevsky, E. A.: Effect of rigid inclusions on sintering anisotropy of composite glass powder compacts. J. Mat. Proc. Technol. **96** (1999) p. 92–101.
[32] Kageyama, K.; Enoki, M.; Kishi, T.: Mechanical properties of alumina particulate and platelet-reinforced glass composites with a crystalline phase at the interface. J. Ceram. Soc. Japan **103** (1995) p. 205–210.
[33] Wadsworth, I.; Stevens, R.; Strengthening and toughening of cordierite by the addition of silicon carbide whiskers, platelets and particles. J. Mat. Sci. **26** (1991) p. 6800–6808.
[34] Clark, T. J.; Reed, J. S.: Kinetic processes involved in the sintering and crystallisation of glass powders. J. Am. Ceram. Soc. **69** (1986) p. 837–846.
[35] Zimmer, J.; Raether, F.; Müller, G.: In-situ investigations of sintering and crystallisation on lithium aluminosilicate glass-ceramics. Glastech. Ber. Glass Sci. Technol. **70** (1997) p. 186–188.
[36] Chick, L. A.; Lokken, R. Q.; Thomas, L. E.: Basalt glass-ceramics for the immobilization of transuranic nuclear waste. Ceram. Bull. **62** (1983) p. 505–516.
[37] Boccaccini, A. R.; Winkler, V.: Fracture surface roughness and toughness of Al_2O_3-platelet reinforced glass matrix composites. Compos. **A 33** (2002) p. 125–131.

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