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The influence of various additions on a glass-ceramic matrix composition based on industrial waste

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Abstract

The influence of chamotte additions on the microstructure and mechanical properties of glass-ceramics made from a combination of silicate wastes is investigated, in order to obtain reinforced glass-ceramic composites by powder technology and viscous flow sintering. The base glass-ceramic matrix was formulated from fly ash, peat ash and clay from Latvian origin and, in once case, addition of waste glass. Chamotte particles obtained from clay in concentrations of 10, 20 and 30 wt.% were added to the starting silicate composition. The optimal concentration of chamotte additive was found to be 20 wt.%, which resulted in a material with high relative density (96% theoretical density), relatively high ultimate bending strength (72 MPa) and large sintering interval ($\Delta T > 50$ °C). The results confirmed that chamotte particles are useful and cost-effective additions as reinforcing phase to produce improved silicate glass-ceramics from wastes.

Keywords: A. Sintering; B. Porosity; D. Glass-ceramics; Chamotte; Silicate waste

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1. Introduction

Previous studies of sintered glass and glass-ceramic matrix composites from silicate wastes have concentrated on the use of commercially available and relatively costly reinforcements, such as Al_2O_3 platelets [1,2], and SiC, TiC [3,4] or metallic particles [5]. The influence of the reinforcement addition on the microstructure and mechanical properties of waste derived glass-ceramics has been investigated and usually a better mechanical behaviour with increasing volume fraction of reinforcement addition has been achieved [1–5]. It is interesting therefore to investigate other kinds of reinforcing components, coming from less expensive sources, for production of waste derived glass-ceramic matrix composites. There are a few previous investigations where this approach has been explored, but mainly composites with glass matrices rather than with glass-ceramic matrices have been developed. These include an early experiment using coal fly ash from Polish power stations combined with a borosilicate glass to produce a glass matrix composite [6] and, more recently, the development of glass matrix composites from a combination of municipal solid waste incinerator fly ash and solid wastes from aluminium alloy production by an Italian group [7].

The preparation of glass matrix composite materials, where the matrix is composed of fly ash, peat ash and clay of Latvian origin, has been carried out in the past and commercially available Al_2O_3 platelets were used as reinforcement [1]. In contrast to the previous investigation, in the present study, chamotte was added to the silicate matrix as a reinforcing component. Chamotte made from the same clays has been described in the literature originated in Latvia [8] and Russia [9] as suitable reinforcing addition for producing stoneware materials and fine ceramics articles. The main objective of the present investigation was thus to

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optimise a powder technology route for production of improved glass-ceramics from silicate wastes of Latvian origin and chamotte as reinforcement. Process parameters were chosen in order to maximize the sintering temperature interval by keeping as high as possible the silicate waste content, highest sintered density as well as the highest possible mechanical strength of the materials obtained.

2. Experimental

The starting materials for the glass-ceramic matrix (labelled 3S0) are fly ash from the steel plant ‘‘Liepajas metalurgs’’ (Latvia) and peat ash from the Riga coal power station, as well as limeless clay, as reported elsewhere [1,10]. Clay was added as a binder to improve the bonding properties between particles during the pressing process. The waste materials contain as main chemical elements: Si, Ca, Al, Fe, Zn, Mg, Pb as well as trace amounts of Sr, Mn, Ni, Cu, Cd and Sn [11]. As reported in previous studies [11,12], the fly ash contains spinel ($ZnAl_2O_4$), sphalerite (ZnS), hematite (Fe_2O_3) and palmerite ($K_2Pb(SO_4)_2$), while peat ash contains calcite ($CaCO_3$), anhydrite ($CaSO_4$), corundum (Al_2O_3), albite ($(Na,K)AlSi_3O_8$) and quartz (SiO_2). The ecologically incompatible element lead, which is contained in the fly ash, has been found included in the palmerite phase. The relatively high SiO_2 content in the peat ash indicates the feasibility to use this waste composition to develop glass matrices for composite materials, and the nominal chemical composition of the optimal glass-ceramic matrix has been determined in previous studies [1,10,11]. As reinforcing addition, chamotte made from the mentioned clay was used. Limeless clay from deposit Liepa (Latvia) was thermally treated at 900 °C for 1 h and milled using a ball mill for 24 h up to an average particle size of 10 μm. The density of the powdered glass-ceramic matrix and the chamotte, determined by He pycnometry, are 2.923 g/cm^3 and 2.715 g/cm^3, respectively. From the starting glass-ceramic composition (labelled 3S0) two batches of composite mixtures were prepared by adding 20 and 30 wt.% of chamotte, these were labelled compositions 3S2 and 3S3, respectively. Combined compositions with 10 and 20 wt.% of chamotte and the addition of 10 wt.% of waste glass (from Valmiera Glass Fibre Plant, Latvia) were also investigated, these samples are labelled 3SV and 3SV2, respectively. The density of the waste glass was determined to be 2.267 g/cm^3. Mixtures in dry state were milled using agate mills for 20 min and subsequently water was added (8–12 wt.%). The humid powders were screened (screen aperture: 3 mm) by keeping the moisture content at a level of 12–14%. The sintering behaviour and thermal changes of the mixtures were determined by heating microscopy (Leica Wetzlar 38818) and differential thermal analysis (DTA) (STA 409C) in the temperature range 20–1300 °C. Cylindrical samples (diameter = 20 mm; height = 4 mm) were uniaxially pressed at room temperature using pressures of 50 MPa. The powder compacts were sintered in air, the heating rate was 8 °C/min and sintering time was 60 min. The sintering temperature was varied between 1000 and 1120 °C. Rectangular test bars (25 mm × 5 mm × 5 mm) were also fabricated by sintering at the optimum temperature for each composition. The sintered bars were used for bending strength tests, as described below.

The density and water uptake of the sintered samples were determined according to DIN EN 993-1, while the values of the theoretical density of the compacts were calculated based on their composition and density of constituents. The microstructure of sintered materials was studied by scanning electron microscopy (SEM) (LEICA S 440 I). The chemical identification of elements was carried out by EDX spot analysis (OXFORD 5431). Four-point bending test on rectangular bars (25 mm × 5 mm × 5 mm) was used to determine the ultimate fracture strength (INSTRON 430) according to DIN EN 100. At least five test bars were tested for each composition and the results were averaged.

3. Results and discussion

Differential thermal analysis (DTA) results of various compositions investigated are shown in Fig. 1. All DTA curves exhibit shallow endothermic effects in the temperatures range 570–575 °C, which indicates transformations of low-temperature quartz (SiO_2) to a high-temperature quartz modification (α-quartz to β-quartz), in agreement with the literature [13]. The next two exothermal effects occurred in the temperature ranges 720–730 °C and 930–970 °C. The first of them (720–730 °C) may be related to oxidation of Fe^{2+} and formation of spinel phase at the same time. The crystallization of a pyroxene solid solution takes place in the temperature range 920–970 °C, as observed on crystallization studies of iron-containing glass-ceramic [14,15]. In our case, a second exothermic effect in the range 930–

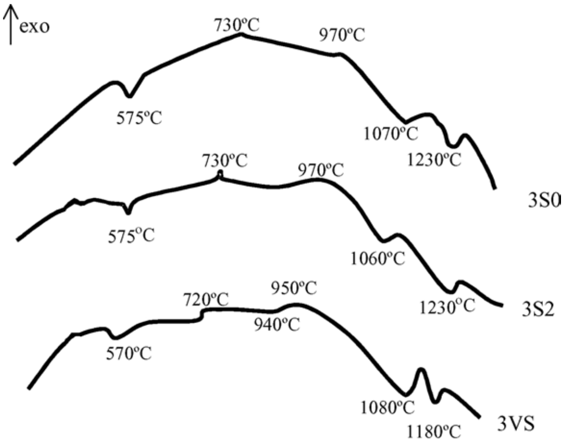

Fig. 1. DTA curves of powder samples of the different compositions investigated: unreinforced glass-ceramic matrix (3S0), composites with 20 wt.% of chamotte (3S2) and combined matrix with 10 wt.% waste glass and 10 wt.% chamotte (3VS).

970 °C in all DTA curves is observed, which can be connected with this process and it is confirmed by the XRD results shown below. The partial melting of silicate phases for composition 3S2 and 3S0 at temperatures 1060 °C and 1070 °C, respectively, can explain the appearance of the endothermic peak. The exothermal peaks of all compositions in the temperature range 1090–1150 °C can be explained by formation of crystalline phases while the last endothermic peaks (in the range 1180–1230 °C) characterize the melting of the parent glass composition.

The curve of sample 3VS containing waste glass shows a small endothermic peak at 940 °C. The melting of waste glass with relatively high Na_2O content (19.97 mass%) should start at this temperature.

Fig. 2 shows the relative linear thermal expansion versus temperature for samples 3S0 and 3VS, obtained by heating microscopy. Linear dimensions change most rapidly for the composition 3S0 (without additions) in the temperature range 1050–1150 °C. Composition 3SV shows a different behaviour. The increase of the linear dimensions for this composition (3SV) at temperatures between 400 and 900 °C takes place due to foaming of the waste glass and clay, as reported elsewhere [1,11]. In the temperature interval 950–1050 °C, a rapid decrease of the linear dimensions of the sample can be observed, indicating the occurrence of sintering. The next fast decrease of linear dimensions for composition 3VS starts at a temperature of 1120 °C. In the temperature range 1050–1120 °C a shoulder was observed, perhaps due to the formation of a crystalline phase, which in part hinders the melting of the parent composition. A related thermal effect in the same temperature range can be detected in the DTA curve for composition 3VS, as seen in Fig. 1, which shows two endothermal effects at 1080 and 1180 °C. The endothermal effect at 1080 °C can be explained by the considerable changes in the crystalline structure of the materials.

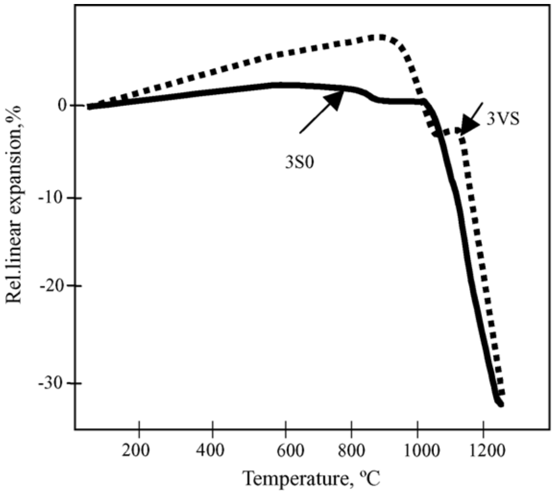

Fig. 2. Change of the linear dimension (height) of powder compacts vs. sintering temperature for unreinforced matrix (3S0) and modified matrix with 10 wt.% waste glass and 10 wt.% chamotte (3VS).

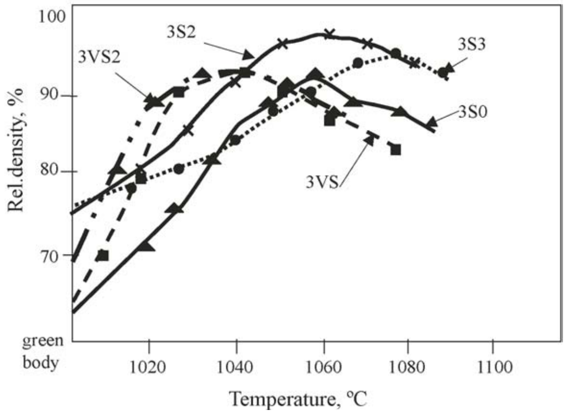

Fig. 3. Relative density (% of theoretical density) of powder samples sintered at different temperatures.

The results of the measurements on the different materials in terms of sintered density as well as water uptake and flexural strength are summarised in Fig. 3 and Table 1. The sintering process occurs by solid phase reactions between the crystalline particles and by viscous flow of soften glass particles. At the same time, crystallization process in the silicate matrix is progressing by a combination of bulk and surface crystallization processes, typical mechanisms in glass-ceramics made of wastes [16,17].

Using chamotte as reinforcing addition, the highest relative density (up to 96% of theoretical density) was obtained for the compositions 3S2 and 3S3, containing 20 wt.% and 30 wt.% of chamotte addition, respectively, at temperatures in the range 1070–1090 °C (for composition 3S3) and 1050–1080 °C (for composition 3S2). In contrast to this, for compositions 3VS (with 10 wt.% of chamotte and 10 wt.% of waste glass) the relative density reached only 87% of the theoretical density (2.94 g/cm^3) and densification occurs in the temperature range (1030–1070 °C), which is notable lower than the sintering temperature for composition 3S0 without additions. For the second modified composition 3VS2, with 10 wt.% of waste glass and 20 wt.% of chamotte, the relative density of the glass-ceramic was 92% of theoretical density (2.82 g/cm^3), while the sintering temperature was relatively low too (1020–1060 °C). For higher concentrations of chamotte, the densification of the silicate mass during sintering takes place at higher temperatures; e.g. for composition 3S3 containing 30 wt.% chamotte, sintering occurs at temperatures of 1070–1100 °C. These results show that densification is limited by chamotte contents greater than 20 wt.% as consequence of the rigid network formed by the chamotte particles. The studies of sintering behaviour of the modified compositions indicated a larger temperature interval for sintering ($\Delta T > 40$ °C), in which the relative density varies less than 1% in comparison with the starting (unreinforced) composition 3S0 ($\Delta T < 20$ °C). The large sintering interval is of practical relevance, if these materials are to be fired in conventional industrial kilns for production

Table 1
Density, water uptake and fracture strength of raw materials and optimised sintered materials

Sample no.	Sintering temperature (°C)	Sintered density (g/cm^3)	Relative sintered density (%)	Water uptake (%)	Flexural strength (MPa)
3S0	1055	2.76	92	0.1	57
3S2	1070	2.62	96	0.5	72
3S3	1080	2.64	96	0.1	66
3VS	1040	2.56	87	0.1	63
3VS2	1040	2.59	92	0.4	67

of building materials such as tiles. Moreover, the low water uptake measured on all materials (Table 1) is evidence that these glass-ceramic composites can be used as frost-resistant building plates or road stones.

Typical microstructures of sintered glass-ceramics (matrix only) and glass-ceramic matrix composites with chamotte additions are shown in Fig. 4a and b, respectively. The images show the regular crystalline structure, where well-shaped crystals are incorporated in a glassy phase, also few remaining pores can be seen. The ratio between the amount of crystalline phase and glassy phase is approximately 1.

According to the results of XRD analysis (summarised in Table 2), for both discussed materials similar crystalline phases, i.e. quartz (SiO_2), anortite ($CaAlSi_2O_8$) as well as franklinite ($ZnFe_2O_4$) have been detected. Quartz crystals (label 3 in Fig. 4a) are well distributed in the glassy matrix (label 2 in Fig. 4b). The addition of chamotte changes the microstructure of the glass-ceramic matrix by inducing the crystallization of the following phases: maghemite (Fe_2O_3), augelite ($Al_2(PO_4)(OH)_3$) and the silicate phases mycrocline ($KAlSi_3O_8$) and diopside ($Ca(Mg,Al)(Si,Al)_2O_6$), which can be created during the thermal treatment of clay minerals (labels 3 and 4 in Fig. 4b). Diopside ($Ca(Mg,Al)(Si,Al)_2O_6$) is a desired crystalline phase, which can develop a rigid network in glass-ceramic materials during sintering, impacting to the final products good shape tolerance and chemical durability [13,17]. The spinel crystalline phase franklinite ($ZnFe_2O_4$) as well as iron-containing maghemite (Fe_2O_3) (for composition 3S2, label 1 in Fig. 4b) and magnetite ($FeFe_2O_4$) (for composition 3S0, label 1 in Fig. 4a) are seen as small incorporations in the microstructure of the materials made from this type of waste, which according to results of EDAX spot analysis contains notable amounts of iron.

Table 2
Mineralogical composition of glass-ceramics 3S0 and 3S2

Crystalline phases	3S0 (t_{sint} = 1055 °C)	3S2 (t_{sint} = 1070 °C)
$FeFe_2O_4$ (magnetite)	+	
SiO_2 (quartz)	+	+
$CaAlSi_2O_8$ (anorthite)	+	+
$ZnFe_2O_4$ (franklinite)	+	+
$CaSO_4$ (anhidrite)	+	
$K_2Pb_2O_3$	+	
Fe_2O_3 (maghemite)		+
$Al_2(PO_4)(OH)_3$ (augelite)		+
$KAlSi_3O_8$ (mycrocline)		+
$Ca(Mg,Al)(Si,Al)_2O_6$ (diopside)		+

Due to the suitable reinforcing additions, the developed materials exhibit significant improvement of mechanical properties as the results of fracture strength tests show. The highest ultimate strength of glass-ceramics, measured by 4-point bending tests, reaches 72 MPa for composition 3S2 and 66 MPa for composition 3VS2. This represents a notable improvement over the strength of the starting composition (unreinforced glass-ceramic matrix 3S0) which is 57 MPa. For the combined glass-ceramic composition containing 10 wt.% waste glass and 10 wt.% chamotte additives (3VS)

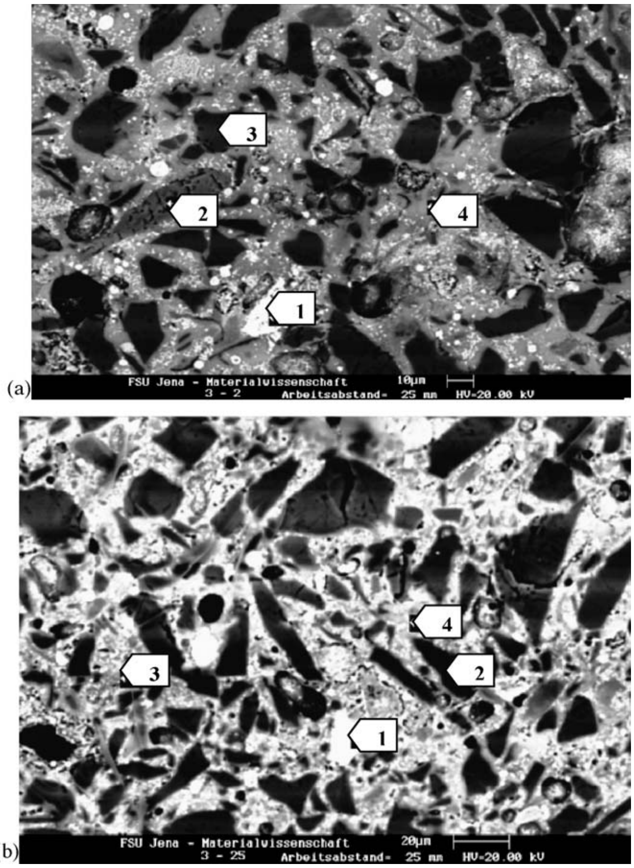

Fig. 4. Microstructure of samples: (a) 3S0 (glass-ceramic matrix) and (b) 3S2 (composite with 20 wt.% of chamotte additions). Phases are identified by numbers. In (a): magnetite (1), anorthite (2), quartz (3) and glassy matrix (4); in (b): iron-containing franklinite and maghemite (1), quartz (2), augelite or mycrocline (3) and anorthite or diopside (4).

the ultimate strength at the optimal sintering temperature was 63 MPa. It is interesting to note that the value of ultimate strength for all compositions made with chamotte addition was higher than those of composition 3 KV (with 10 wt.% alumina platelets and 10 wt.% waste glass addition) developed in the previous work [1], where the ultimate strengths reached only 54 MPa. However the highest ultimate strengths value of samples sintered with chamotte incorporation (72 MPa in composition 3S2 with 20 wt.% chamotte) is approximately 20% lower than the most successful composition produced using the same wt.% of commercial Al_2O_3 platelets described in the previous paper [1]. This indicates the need to rely on commercial reinforcing elements (alumina platelets, SiC particles) if the mechanical strength of glass-ceramic matrices must be optimised to a very high value a (~100 MPa). Nevertheless, the composite materials produced in the present study, which are totally made of residues, exhibit in all cases comparable mechanical strength values, to those of the equivalent waste-only glass composites produced by Ferraris et al. [7].

4. Conclusions

The present study was conducted to develop high-strength glass-ceramic matrix composites totally made from industrial wastes of Latvia. The additions of chamotte particles (10, 20 and 30 wt.%) to the starting composition (formulated from fly ash, peat ash and clay) resulted in a material with relatively high ultimate strength, 72 MPa for composition 3S2 and 66 MPa for composition 3VS2. The chamotte additives have increased the sintering interval from ~ 20 °C for the starting composition (3S0) to ~40 °C for composition with 20 wt.% of chamotte addition. The optimal concentration of chamotte additive was found to be 20 wt.%. The results confirmed that using chamotte from thermal treated clay as reinforcing addition can essentially reduce the real fabrication costs of glass-ceramic matrix composites from waste materials, as no expensive commercial reinforcements are required. However it is apparent that if high fracture strengths are required, of the order of 100 MPa, then the use of commercial reinforcements might be unavoidable.

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