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Liquid Phase Sintering of Dense and Porous Glass-Ceramics from Coal Fly-Ash and Waste Glass

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Abstract:

Glass-ceramics were produced utilising fly-ash from coal power stations and waste glass of TV monitors, windows and flask glass. The powder technology route was employed. The mixture of 50% fly ash and 50% waste TV glass increases the bending strength from 12±1 to 56±4 MPa and E-modulus from 6±1 to 26±3 GPa. Using polyurethane foam and C-fibres as pore creators, porosity of 70±4 and 55±5 %, respectively, can be obtained.E-modulus and bending strength of the porous systems obtained by polyurethane foam and C-fibres was 2.7±0.5 GPa and 4.5±1 MPa and 7.1±1 GPa and 9.3±2 MPa, respectively.

***Keywords**: Waste; Fly ash; Glass-ceramic; Sintering; Porosity*

1. Introduction

A great quantity of coal ash (about $15 \cdot 10^6$ tons) is stored in the surroundings of the REK Bitola-thermal power station in the Republic of Macedonia. This waste is a result of burning of lignite in the temperature range of 1100-1450 ^{O}C. Due to the burning procedure fly ash is available in the fine powder form. Waste with a diameter not bigger than 0.1 mm is taken as ash. Other diameters are classed as slag-ashes and slags. A large quantity of waste glass of TV monitors, windows and flasks, can be found at local dumps. This waste can be the basis for obtaining of glass-ceramic materials. A combination of fly ash with waste glasses under a controlled sintering procedure gives bulk or highly porous materials with surface or/and bulk crystallization. The structure of glass ceramics maintains the toxic components in an ecologically harmless matrix phase protected from corrosion [1,2].

The aim of the paper is to make a dense and porous composite between fly ash and glass. Dense materials can be used as a building material, while porous glass- ceramics can be used as filters, thermal insulation, lightweight structural laminates, diffused aeration, dust collectors, acoustic absorbers etc.

The principle of this procedure was presented as a multibarrier–concept by Ondracek [3] and basically investigated for various waste combinations [4,5]. This paper deals not only with the chemical inertisation process and combination of waste materials but also with new application of these waste materials as highly porous glass ceramics.

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2. Experimental procedure

Chemical analysis of the waste materials was carried out using an atomic absorption spectrophotometer (Rank Hilger, Atom Spek H-1580) and wet chemical methods. X-ray diffraction (XRD) studies on the samples were undertaken using a Philips X-ray diffraction unit (Model PV 105-1) operating at CuK_{α}-radiation. Photographs of the samples were made using a stereo microscope (Leica). The materials were ground in a ball mill and screened through a 63μm screen. Glass from TV monitors (only from the screen) was treated with 12%HF and NH_4F to dissolve all non glassy elements [6].

Homogenization of the mineral waste and glass waste was performed in a planetary mill (Fritsch pulverisette). Thermal characteristics were determined by a heating microscope (Leitz) in the temperature interval RT-1400°C with a heating rate of 10°/min. Pressing of the samples was performed by a uniaxial press (Weber Pressen KIP 100). A pressure of 50 MPa was employed to reach green densities of 42% of the theoretical density. Sintering was realized in a chamber furnace in air atmosphere in a temperature region from 800 to 1200°C, using a heating rate of 10°/min and isothermal treatment at the final temperature of 30-120 min. Bulk density of the sintered samples was determined by the water displacement method according to EN-993. The values of theoretical density of the compacts were calculated based on the composition of the initial mixture and known densities of fly ash and glasses. Mechanical properties (E-modulus and bending strength) of the dense and porous specimens (8 pieces, 50x5x5 mm) were investigated at room temperature. The samples were polished with diamond paste of 15 μm and subjected to the 3-point bending tester Netzsch 401/3 with 30 mm span and 0.5 mm/min crosshead speed. Thermal studies of the waste and polyurethane foam were performed by DTA/TG (Netzsch STA 409). Linear thermal expansion of the dense materials was determined by a dilatometer (Netzsch 402E) in air atmosphere and temperature interval RT-650-RT. The measurements were performed with a heating rate of 2°/min. Open celled macrostructures were fabricated by coating the struts of polyurethane foam with a ceramic slurry and then firing the resultant structure to pyrolyse the substrate and sinter the ceramic system [7,8]. Commercial polyurethane foam with a density of 25 kg/m^3 was used as a substrate. The slurry contained 55% solid (fly ash-glass), 27% water glass and 18% Dolapix CE 64 (4% water solution). It coherently coated the polyurethane substrate. The foam was squeezed and dipped into the slurry, looking in that case like a sponge. During expansion to the original shape and size, the mentioned slurry impregnated the foam. After drying, the coated substrates were heated up to 950 °C/1h in a schedule that minimized disruption during pyrolysis and allowed the ceramic to achieve high density. This heating schedule consisted of a heating rate of 0.5°/min up to 500°C and rapid heating of 10°/min from 500 to 950°C, 1h holding at 950°C and then cooling in the furnace. The relative density of the foam material was determined from the ratio of mass and volume.

Creation of a porous structure using C-fibres was made by the following procedure: C-fibres as bundles with a diameter of 300/500 μm were embedded in very dense pulp of the mixture of fly ash - 50% TV glass. The number of fibres was cca. 50/cm^2. After drying of the system, it was sintered under the following conditions: in the temperature region from 20-1000°C, the heating rate was 1°C/min, the holding time at 1000°C was 0.5 h.

Durability of the glass-ceramics was tested using standard methods both for glass and ceramics. The durability was determined as a mass lost in 0.1M HCl, 0.1M Na_2CO_3 and distilled water. After treatment of 24 h and 30 days, risky elements like Zn^{2+}, and Pb^{2+} were removed from the tested materials and analyzed by atomic absorbtion spectroscopy.

3. Results and discussion

The chemical composition of the investigated wastes is shown in Table I.

Table I Chemical composition of the Bitola-fly ash and waste glass

Chemical composition	**Fly ash, % wt**	**TV glass, % wt.**	**Window glass, % wt**	**Flask glass, % wt**
ZnO	0.01	0.065	0.09	-
TiO_2	0.09	0.09	0.07	-
SO_3	1.20	0.11	0.37	0.41
K_2O	1.80	6.40	0.19	2.31
Na_2O	0.90	7.10	9.50	8.67
Fe_2O_3	7.31	0.31	0.31	-
CaO	7.42	1.65	8.96	0.21
MgO	2.11	2.42	4.22	7.34
Al_2O_3	22.73	3.75	3.38	4.76
SiO_2	51.36	58.50	71.50	71.62
PbO	0.03	8.18	-	-
CoO	-	0.084	0.12	-
CO_2	1.90	6.30	1.29	-
BaO	-	4.81	-	-
B_2O_3	-	-	-	4.00
Lost of ignition	3.12	-	-	-

The fly ash contained small quantities of harmfull oxides such as PbO.

According to XRD, the as-received fly–ash contained small amounts of crystalline phases such as quartz, mullite, crystoballite, hematite and an amorphous phase. The density of the as-received fly-ash was $\rho_f = 2.58$ g/cm^3. The thermal characteristics of the fly ash and glasses are shown in Table 2

Table II Thermal characteristics of the fly ash and waste glasses (heating microscopy)

Material	significant shrinkage,^oC	softening temperature,^oC	melting temperature,^oC
Fly ash	1050	1280	1303
TV-glass	600	700	800
Window glass	650	850	950
Flask glass	650	850	960

Taking into account the results of DTA and high temperature microscopy, sintering studies of the fly ash were carried out in the temperature range 950-1100^{o}C. Fly ash reached the highest relative density of 70%TD after sintering at 1050^{o}C/2h .One of the reasons for this low relative density is the presence of 3.12 wt% unburned coal in the as-received fly ash. Sintering at a higher temperature of 1050^{0}C exhibits side effects such as bending and degassing.

The E-modulus, bending strength and technical coefficient of thermal expansion of the fly ash sintered at 1050^{o}C/2h, and glasses are shown in Table 3.

Table III E-modulus, bending strength and thermal coefficient of thermal expansion of the fly ash and glasses

Material	E-modulus,GPa	bending strength, MPa	tech.coeff.therm.expansion .$10^6/^oC$
Fly ash	6± 1	12 ± 1	5.36
TV glass	72±8	136±10	10.61
Window glass	51±7	125±10	10.10
Flask glass	53±7	127±10	10.80

With the purpose of aiding the sintering process and encapsulating the particles of fly ash into a matrix compatible with the environment, waste glasses in the quantity of 10, 20, 30, 40,50 and 60 wt% have been used. The sintering temperature of the compositions was realized at 900, 950, 1000 and 1050°C/1h. The optimal composition of waste composites, sintering temperature, E-modulus, and bending strength are shown in Table 4.

Table IV Optimal composition of the waste composites, sintering temperature, relative density ($\rho_{rel.}$), E-modulus, bending strength (σ)

Composite	Sinter.temp.,°C	$\rho_{rel.}$	E	σ
Fly ash-%glass	°C	%	GPa	MPa
Fly ash-50%TV glass	950	96	26±3	56±4
Fly ash-60% window glass	1050	93	27±3	71±5
Fly ash –50%flask glass	1050	93	23±3	60±4

From Table 4 it is evident that the composition fly ash –50% TV glass sintered at 950°C/1h showed the highest relative density .

Thermal expansion characteristics of these investigated systems in the interval RT-650-RT showed absence of a hysteresis effect, that proves that the systems are in thermal equilibrium. The temperature dependence of the physical coefficient of thermal expansion in the interval RT-650°C can be presented by an II order polynomial form. Table V shows the temperature variation of the physical coefficient of thermal expansion as well as the technical coefficient of thermal expansion.

Table V Temperature variation of the physical coefficient of thermal expansion as well as the technical coefficient of thermal expansion ($\alpha_{tech.}$)

Composite	$\partial(\Delta L/L_o)/\partial T = f(T)$	α_{tech}
Fly ash-50%TV glass	$0.113 - 8.262.10^{-7}T^2$	8.13
Fly ash-60% window glass	$0.477 - 0.004T + 5.220.10^{-6}T^2$	8.23
Fly ash-50% flask glass	$0.422 - 0.002T + 2.450.10^{-8}T^2$	8.19

Durability of the investigated dense materials (mass lost after 30 days) was determined for ceramics containing only fly ash (F) and the composites, fly ash -50% TV glass (TV50), fly ash –60% window glass (W60) and fly ash-50% flask glass(FG50). The composites (TV50) possesses durability of 2.08%, (W60) of 5.18% , (FG50) of 3.65% , whereas (F) possesses durability of 9.43% in 0.1M HCl. The change in mass in 0.1M Na_2CO_3 was –0.47% for (TV50);-0.16% for (W60) ,-0.10% for(FG50) and –0.05 for (F). In all investigated specimens durability in water was 0.001%.

The durability analysis enabled categorization of these materials into definite classes according to DIN EN 122: All investigated composites belong to class B (visible changes of colour). The durabilities show that the ceramics developed meet the requirements of dense unglazed, dust-pressed ceramic tiles according to building ceramic norms DIN EN 106.

Creation of a highly porous macrostructure was realized on the fly ash-50%TV glass system.

Polyurethane foam was used as the creator of a porous structure, fabricating samples with a porosity of 70±4% (Fig.1). Pores with diameters from 400 to 600 μm are interconnected. The E-modulus of this system was 2.7±0.5 GPa, bending strength was 4.5±1 MPa. Using C-fibres as creators of a porous structure, according to the diameter and number of fibres in the bundle, a correspondent macro porous structure was created. In this case an

integral porosity of 55±5% was achieved. The pores/channels had a cylindrical form with the diameter of 300/400 μm (Fig.2)

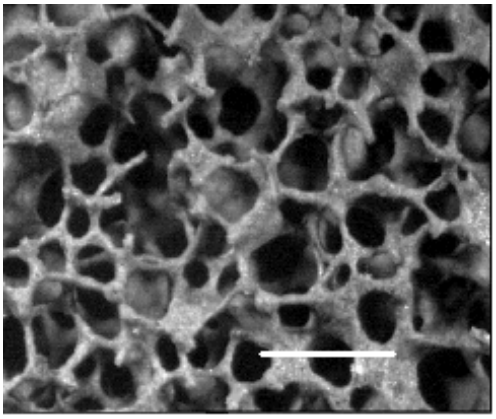

Fig. 1 Macrostructure of cell foam,using polyurethane foam as a pore creator. (bar 1 mm)

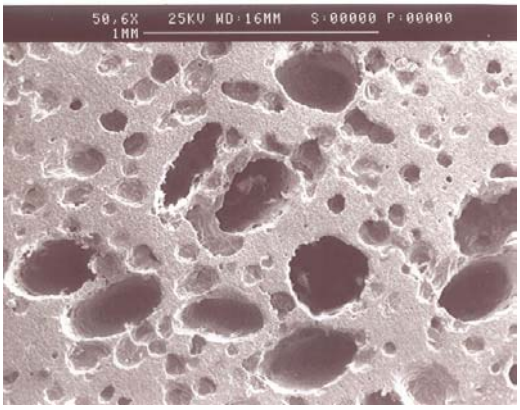

Fig. 2 Macrostructure of cell foam, using C-fibres as a pore creator (bar 1 mm)

Fracture among the pore walls was not evident. This system was characterized with the following mechanical properties: E-modulus of 7.1±1 GPa and bending strength of 9.3±2 MPa.

4. Conclusion

- Ecologically harmless materials (glass ceramics) can be created from fly ash and glass waste.
- The addition of 50% TV glass increases the bending strength from (12.5±1 for fly ash to 56±4 MPa for the fly ash-50%TV glass composite) and E-modulus (6.3±0.5 for fly ash to 25±3 GPa for the fly ash-50% TV glass composite)
- Using polyurethane foam and C-fibres as pore creators, a highly porous system (porosity 70±4 and 55±5%, respectively) can be obtained.
- E-modulus and bending strength of the porous system obtained by polyurethane foam was 4.3±1 GPa and 7.2±2 MPa, respectively.
- The chemical and physical properties of the dense material, makes them suitable for a wide range of applications in the building industry.

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Резюме: *В данной работе исследовано получение стеклокерамики из летучей золы тепловых электростанций стеклянных отходов ТВ мониторов, окон и бутылок.. В данном случае использован способ спорошковой технологии. Смесь 50% золы и 50% отходов ТВ мониторов прочность на изгиб увеличивает от 12±1 до 56±4 МПа и Е-модуль от 6±1 до 26±3 ГПа. При использовании пенополиуретана и С-волокон, в качестве создателей пор, пористость составляет 70±4 и 55±5%; Е-модуль и прочность на изгиб 2,4±0,5 ГПа и 4,5±1 МПа и 7,1±1 ГПа и 9,3±2 МПа, соответственно.*
Ключевые слова*: отходы; зола; стеклокерамика; спекание; пористость.*

Садржај: *Стакло-керамика произведена је коришћењем пепела од угља из термоелектрана и отпадног стакла ТВ монитора, прозора и флаша. Примењен је метод технологије праха. Мешавина 50% пепела и 50% отпадног ТВ стакла увећава крутост од 12±1 до 56±4 MPa и Е-модул од 6±1 до 26±3 GPa. Коришћењем полиуретана и С-влакна као креатора пора добија се порозност од 70±4 и 55±5%. Е-модул и крутост порозних система добијених коришћењем полиуретанске пене и С-влакана била је 2,7±0,5 GPa и 4,5±1 MPa, и 7,1±1GPa и 9,3±2 MPa.*
Кључне речи**:** *отпад; пепео; стакло-керамика; синтеровање; порозност.*