CHEMICAL DURABILITY OF SINTERED GLASS-COMPOSITE PREPARED FROM GLASS CULLET AND WASTE FOUNDRY SAND

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Abstract

In this study, the glass-composite was prepared using glass cullet and waste foundry sand as raw materials. The powder technology route was employed. The mixtures containing 10-50 wt% of the sand were sintered at $T = 750$ °C for $t = 1$h. XRD and DTA analyses were performed. The chemical durability of the resulting glass-composite was determined by leaching test in HCl, H_2SO_4, NaOH and distilled water at $T = 95$ °C for $t = 1$h. It was shown that the sintering process carried out without the crystallization of the glass matrix. The lowest chemical durability was determined in alkali solution of glass-composite.

Keywords: glass cullet; waste foundry sand; sintering; glass-composite.

Introduction

The adoption of modern recycling technologies is the best way to utilize waste materials. This process reduces the need for natural raw materials, saves energy in production, and reduces environmental pollution. Numerous studies have reported that the waste from different industrial processes can be utilized successfully in the fabrication of new valuable materials [1-7].

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Consequently, the recycling technologies provided the opportunity to prepare a new glass and glass-ceramics materials from waste glasses. Due to a good mechanical, chemical, and thermal properties, a wide application of these waste materials has been made possible, especially in the building industry [8-10].

In addition, toxic and non-toxic wastes can be used in the production of glass and glass-ceramics. One of the most frequently employed technologies for the fabrication of waste glass-ceramics is the sintering of glass powder. The waste glass can be combined with other waste materials to improve some of the properties of sintered materials [11-14].

In the typical foundry processes, sand from collapsed molds or cores can be reclaimed and reused. The used foundry sand consists primarily of silica sand, coated with a thin film of burnt carbon, residual binder (bentonite clay, sea coal, resins) and dust and has been used as a fine aggregate substitute in construction applications and as kiln feed in the manufacture of Portland cement [15].

In the case that this material is not recycled, the waste is discarded at landfills. Landfilling is the most common waste disposal method and is not an appropriate solution for this material because of the negative impact on the environment.

Glass and glass-ceramics production technology is able to absorb complex chemical compounds derived from silicate waste into economically viable and useful materials and that retain hazardous chemical substances inert inside the glass matrix.

In this research, the possibility to obtain a sintered glass-matrix composite using glass cullet and waste foundry sand from collapsed molds for ferrous metal casting is investigated. The powder sintering route was employed for the fabrication of this material. The chemical durability of as-prepared glass-matrix samples containing 10-50 wt % of waste foundry sand was determined.

Materials and methods

Waste bottle glass and waste green foundry sand were used as starting materials for the preparation of the glass-composite body. The glass cullet was washed, dried, crushed in a jaw crusher Retsch 300, and then milled to grain size <100μm by using a laboratory vibrating mill with rings - Humboldt Wedag KHD 953/3. The waste sand, collected in lumps, was previously disintegrated and then used for the preparation of the mixtures. The chemical compositions of starting raw materials were determined using gravimetric and spectroscopic methods (AAS Analyst 300). Quantitative chemical analysis of the samples was determined by the classical silicate method. Content of SiO_2 and l.o.i. (loss on ignition at 900 °C) were determined gravimetrically, while the content of oxides Na_2O, K_2O, Fe_2O_3, MgO, Al_2O_3, CaO, and TiO_2 after the destruction of the sample by melting was determined by analyzing the content of their cations in solution by the method of atomic absorption spectrometry (AAS). The grain size of sand was determined by sieve analysis.

The thermal characteristics of starting samples were determined by the hot stage microscope (HSM) E. Leitz Wetzlar 1750. The samples (<0.50 mm) were pressed into cylinders, then such prepared specimens were placed on a platinum plate, and afterwards on alumina support that is in contact with a thermocouple. The temperature was measured with (Pt/Rh/Pt) thermocouple at a heating rate 10 °C min^{-1}. For the purpose of DSC/TG measurement, the glass cullet powder was prepared by crushing and grinding the bulk

glass in an agate mortar, and then sieving it up to grain size of < 0.50 mm. The experiments under non-isothermal conditions were performed using SDT Q600 v7.0 Build 84TGA/DSC TA Instruments device, and the sample (8.62 mg) was heated in a static air atmosphere in alumina sample pans at $v = 10$ ºC min^{-1} up to $T = 800$ ºC.

The procedure for the synthesis of glass matrix composites samples was as follows. In order to prepare the pellets for sintering experiments (Ø 35 mm, h=10 mm), the glass/sand mixtures containing 0, 10, 20, 30, 40 and 50 wt % of sand were homogenized and then cold pressed at 20 MPa in a laboratory hydraulic press Manfredini C95. These samples were labeled as WGS. The sintering of pellets was performed at $T = 750$ °C for $t =$ 1h in an electric furnace - Carbolite CWF130, and then the pellets were cooled down in the furnace to the room temperature.

The phase composition of sintered glass matrix composite samples was determined by X-ray diffractometry (XRD) and the XRD patterns were collected on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 5 to 70°, counting for 0.50. The surface textures of the resulting glass-ceramics were examined using an optical microscope EU Instruments.

For determining the chemical durability, the sintered samples were crushed and then sieved to a grain size of 0.5-1mm. The leaching procedure was performed in a distilled water (pH = 6.93, conductivity (χ) = 4.91 µS/cm at T=25 °C), HCl, H$_2$SO$_4$ and NaOH solutions (20%) at $T = 95$ °C for $t =$ 1h using 2g of samples [16]. The mass loss of samples (Δm) and ion concentrations released were determined.

Results and discussion

In Table 1, the chemical compositions of waste foundry sand (waste sand) and glass cullet is shown.

Table 1. Chemical compositions of waste glass and waste foundry sand.

Samples	Oxide [wt%]								L.O.I.
	SiO$_2$	Al$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O	Fe$_2$O$_3$	TiO$_2$	
waste sand	92.84	2.55	0.56	0.30	0.17	0.45	0.74	0.20	2.08
glass cullet	70.02	4.28	8.15	2.09	0.81	10.92	3.85	0.17	0.27

In waste foundry sand, a dominant component was silica, with alkali oxides in traces. The chemical composition of glass powder cullet is in accordance with industry technical glass. The results of grain size analysis of waste foundry sand are presented in Table 2.

Table 2. Grain size analysis of waste foundry sand.

(mm)	1+0.5	0.5+0.4	0.4+0.3	0.3+0.2	0.2+0.1	0.1+0.075	0.075+0.063	0.063
wt%	7.86	11.38	60.94	12.52	5.87	0.38	0.70	0.35

In Fig.1, the images of the grains of waste foundry sand obtained by an optical microscope are shown. As seen in Fig.1, the grain size of sand is very uniform, with

contribution > 90 % of the grains with the dimension between 0.5 and 0.1 mm (Table 2). It is obvious that the quartz particles are subangular to round and are partly coated with burnt carbon and a residual bentonite clay binder.
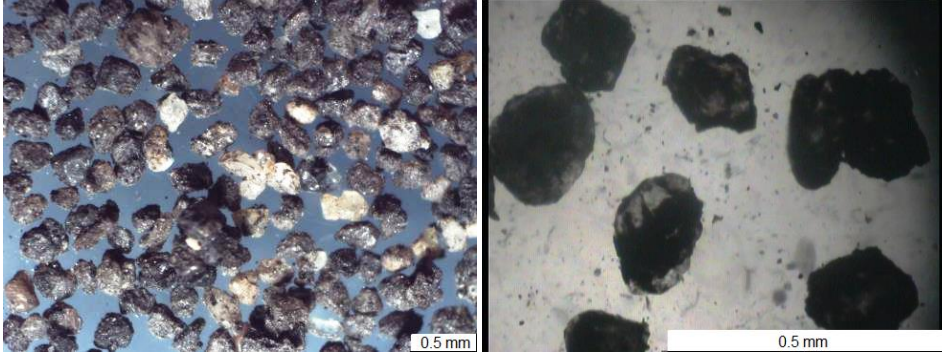

Fig. 1. Optical microscope photographs of waste foundry sand.

Thermal microscopy revealed that the waste foundry sand sample does not melt below $T = 1630\,°C$ and that the sintering (maximum shrinkage) occurs at $T=1450\,°C$. The glass cullet sample sintering (maximum shrinkage) takes place at around $T=800\,°C$, softening at $T = 900\,°C$ and melting at $T =1030\,°C$.
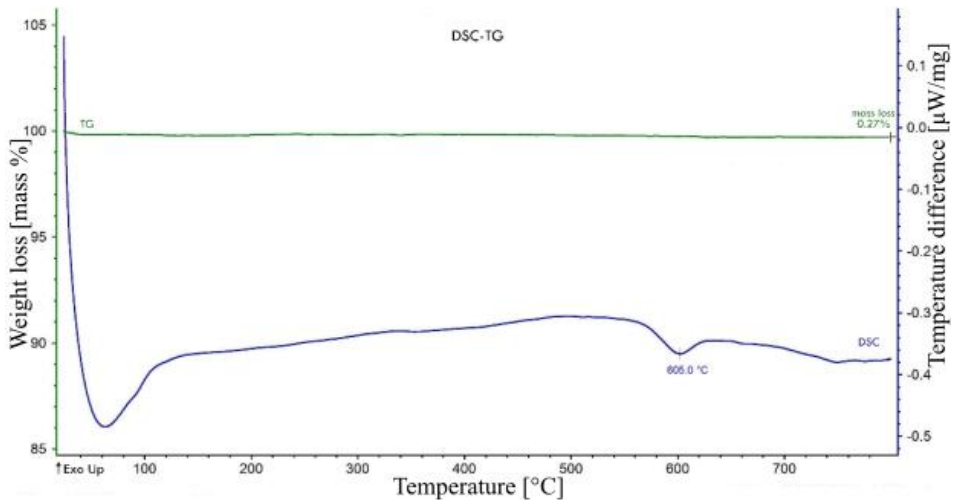

Fig. 2. TG/DSC of powder glass cullet.

From the DSC curve (Fig.2), the glass transformation temperature $T_g = 605\,°C$ was determined for the glass cullet powder. There was no crystallization process observed up to 800 °C.

Glass cullet and waste sand can melt simultaneously and randomly at fused state due to the resemblance of their chemical components. Glass is a noncrystalline solid with no fixed melting point, and while the crystal form of SiO_2 in waste foundry sand subjects

to transformation, the physical state basically stays stable. Thus, the continuum phase of the glass matrix composite is a kind of glass matrix made by sintering.

The HSM analysis showed that during sintering, the shrinkage of pellets decreased with the quantity of the sand added (Figure not shown). This indicates an influence of the rigid sand particles on the viscous behavior of glass matrix composite. Namely, the presence of quartz grains covered with bentonite clay hinders the viscous flow of the glassy phase and that causes poor densification of the samples.
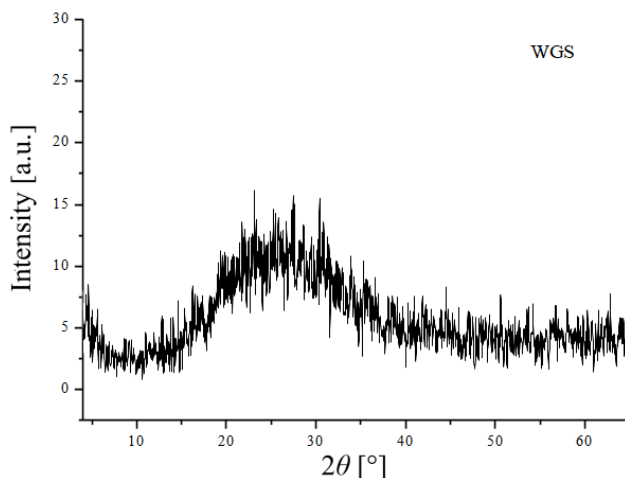

Fig. 3. XRD pattern of WGS sample sintered at   T = 750 °C for t =1h.

As shown in Fig.3, the glass matrix does not crystallize during sintering. No peaks attributed to any crystallized compound could be identified except a broad diffraction halo (amorphism of between 20° and 30°), which is attributed to the glassy amorphous phase of WGS sample.

Oxides in waste glass samples like Na_2O or CaO used as fluxes could reduce the melting temperature of the glass and accelerate sintering. This may be the explanation for the relatively low sintering temperature of the glass cullet considering the dominant silicon composition.

In Fig.4, the surface textures of sintered samples WGS, WGS 30 and WGS 50 are shown. The sample WGS (without sand addition) revealed numerous cavities on the surface (black spots, Fig.4a) that indicate the formation and separation of gasses during sintering. Such cavities are also visible on the samples containing 10-50 wt% of waste foundry sand in glass matrix composite (Fig.4b)

In Fig.4c, the quartz sand particles are seen to be well-distributed in glass matrix of WGS 50 (50wt % of sand) sample. Macroscopically the configuration of the glass matrix composite is waste foundry sand coated by the waste glass. Glass cullet can be used as a composition corrector for other types of wastes that generally have a lower content of glass-forming oxides and don't always have a composition suitable for direct vitrification.

a)   b)   c)
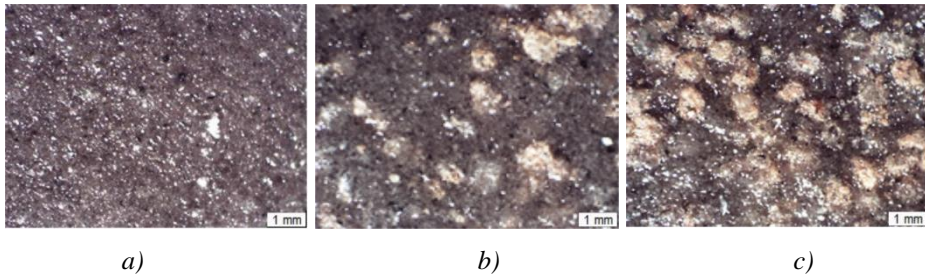
Fig. 4. Surface textures of samples sintered at T = 750 °C for t =1h:
a) WGS; b) WGS 30 c) WGS 50.

The leaching test in different media revealed high durability of the sintered composite in distilled water, Table 3. Mass loss of samples increased with waste foundry sand addition during leaching in acid solutions (0.6-2.5%), as may be seen in Table 3, there is no significant difference between durability in HCl and H_2SO_4. It can be noticed that different type of acid (monoprotic or polyprotic) has no significant effect on the durability of the sintered composite.

The lowest chemical durability of treated samples was determined in 20 % NaOH. In alkali leaching medium, a mass loss increased (1.75-8.11%) with an increase of the content of waste foundry sand in samples.

Table 3. Mass loss of the sintered samples grain size of 0.5-1 mm leached in different
media at T = 95°C for t =1h.

Sample	Distilled H_2O		20 % HCl		20 % NaOH		20 % H_2SO_4	
	Δ m (g)	%	Δ m (g)	%	Δ m (g)	%	Δ m (g)	%
WGS	0.0012	0.060	0.0124	0.62	0.0349	1.75	0.0118	0.59
WGS 10	0.0014	0.070	0.0172	0.86	0.0568	2.84	0.0170	0.85
WGS 20	0.0014	0.070	0.0265	1.33	0.1428	7.14	0.0264	1.32
WGS 30	0.0022	0.110	0.0308	1.54	0.1460	7.30	0.0280	1.40
WGS 40	0.0024	0.120	0.0392	1.96	0.1608	8.04	0.0312	1.56
WGS 50	0.0026	0.130	0.0501	2.50	0.1622	8.11	0.0388	1.94

The dissolution of glass matrix is a complex process that consists of several characteristic steps. Obtained experimental data indicate that there are two possible mechanisms, explaining the release of cations from the glass structure in different aqueous solutions, ion-exchange leaching, and matrix dissolution. [17].

In neutral and acid media, the initial dissolution is characterized by ion exchange processes between protons in solution and glass network modifier cations, resulting in the formation of a hydrated layer, through which the aqueous species diffuse. Therefore, in neutral and acid media, the initial stage of the reactions is the diffusion of alkali ions through the glass network and across the leached layer into the solution [18].

At the same time, the glass network composed of network forming tetrahedrons hydrolyzes, causing the release of cations into solution. As a consequence, the complete destruction of the polyanionic glass network occurs.

In alkaline media, the dissolution of the Si-glass network by which the glass dissolves directly into the solution takes place. This type of chemical reaction leads to a

higher weight loss as a function of time as determined for the leached ions in NaOH solution.

In Fig.5, the concentration of ions released during leaching in different media as a function of waste sand content present in the samples is shown.
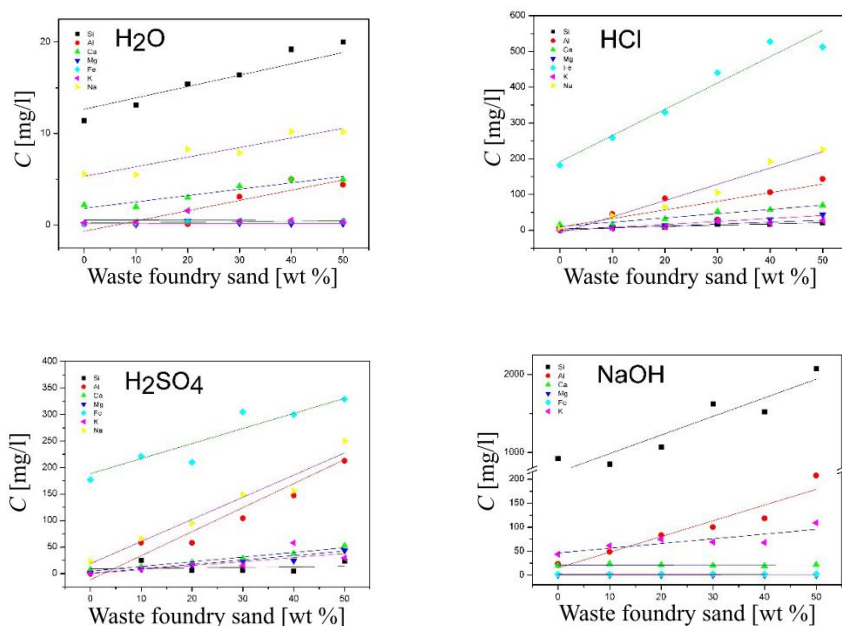

Fig. 5. Concentration of ions released during leaching in different media as a function of waste sand content present in the samples sintered at T = 750 °C for t =1h.

As seen in Fig.5, a high concentration of Si-ions in NaOH solution was determined, which indicates the intensive destruction of Si-glass network. Bunker explained that the tetrahedral SiO_4 sites common to all silicate glasses were susceptible to nucleophilic attack primarily by OH^- anions to form a reactive five-coordinated intermediate, which can be decomposed to rupture the Si–O–Si bond [19]. Therefore, a significant quantity of OH^- anions could improve the formation of a five-coordinated intermediate, which could lead to the great destruction of the glass network.

Otherwise, in the case of distilled water, HCl and H_2SO_4, the diffusion of alkali ions through the glass network into the solution took place as the first step of dissolution. The concentration of all ions released during leaching in different media increased by increasing the quantity of waste foundry sand in the samples.

The production process of glass matrix composite is simple, the chemical durability in neutral, alkali and acid media (WGS, WGS 10) is very good, and there is a possibility for application of this material in the building industry. The composite samples with the addition of more than 20% sand (WGS 20, 30, 40 and 50) have good acid but poor alkali durability. The chemical durability decreased with the increased content of sand in glass composite.

The advantages of the production process include the bypassing of the waste material vitrification, sintering temperatures below 900 °C and the ability to strengthen the glass matrix by introducing other solid components with good mechanical and thermal properties.

Conclusions

The glass-matrix composites were prepared using the powdered glass cullet and waste foundry sand as raw materials. It was determined that the increase of sand quantity in the composites causes poor densification of sintered samples. As confirmed by XRD analysis, the sintering process at $T = 750$ °C for $t = 1$h was carried out without crystallization. The results of the leaching test revealed high durability in distilled water of the sintered samples. Durability in acidic medium is low, however no significant difference of leaching in HCl and H_2SO_4 was noted. Weight loss determined after leaching in NaOH solution confirmed poor alkali durability of the samples. For all leaching media, the durability decreased with the increase of the quantity of waste sand in the glass matrix composite. It has been shown that industrial waste materials that have a negative impact on the environment ought to be converted into environmentally friendly new materials with wide applications.

Acknowledgment

References

[1]   L. Maccarini Schabbac, F. Andreola, E. Karamanova, I. Lancellotti, A. Karamanov, L. Barbieri: J Non-Cryst Solids, 357(1) (2011) 10–17.
[2]   M. Rafieizonooz, J. Mirza, M. Salim, M. Hussin, E. Khankhaje: Constr Build Mater, 116 (2016) 15–24.
[3]   I. Ponsot, E. Bernardo, E. Bontempi, L. Depero, R. Detsch, R. Chinnam, A. Boccaccini: J Clean Prod, 89 (2015) 224-230.
[4]   L. Aranda, T. Schweitzer, P. Berthod, C. Rapin, D. Souchon, F. Maad, J. Brossard: J. Mater Sci Technol Res, 5 (2018) 6-10.
[5]   G. Qian, Y. Song, Y. Zhang, Y. Xia, H. Zhang, P. Chui: Waste Manage, 26 (2006) 1462.
[6]   P. Trifunović, S. Marinković, R. Tokalić, S. Matijašević: Thermochim Acta, 498 (1-2) (2010) 1-6.
[7]   Ž. Kamberović, Z. Anđić, M. Korać, N. Gajić, B. Tomović: Metall Mater Eng, 23(2) (2017) 167-181.
[8]   R. Cimdins, I. Rozenstrauha, L. Berzina, J. Bossert, M. Bucker: Resour Conserv Recycl, 29 (2000) 285-290.
[9]   V. Gomes, C. De Borba, J. Riella: J Mat Sci, 37 (12) (2002) 2581-2585.
[10]   K. Dana, S. Das: J Mater Sci Lett, 22 (2003) 387-389.
[11]   A. Francis: J Eur Ceram Soc, 24 (2004) 2819-2824.
[12]   A. Boccaccini, M. Bucker, J. Bossert, K. Marszalek: Waste Manage, 17 (1997) 39-45
[13]   R. Rawlings: Composites, 25 (1994) 372.
[14]   R. Rawlings, J. Wu, A. Boccaccini: J Mater Sci, 41 (2006) 733–761.

[15]   A. Torres, L. Bartlett, C. Pilgrim: Constr Build Mater, 135 (2017) 674-681.
[16]   A. Karamanov, M. Pelino, M. Salvo, I. Metekovits: J Eur Ceram Soc, 23 (2003) 1609-1615.
[17]   W. B. White, Corrosion of glass, ceramics and ceramic superconductors, Noyes Publications, New Jersey, 1992, 2-28.
[18]   S. Gin, C. Jégou, P. Frugier, Y. Minet: Chem Geol, 255 (2008) 14-24.
[19]   B. Bunker, D. Tallant, T. Headley, G. Turner, R. Kirkpatrick: Phys Chem Glasses, 29 (1988) 106-120.