Industrial Waste As a Source For Fabrication of Composite Ceramics-Glass With a Controlled Porosity

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Abstract:
Metallurgical slag with granulation (-0.125+0.063mm) and 20 wt% waste TV glass were used for obtaining a glass ceramic composite with a controlled porosity. This material obtained by sintering at 950°C/2h possessed thermal stability, integral porosity of 43.6% and E-modulus and bending strength of 12 GPa and 39 MPa, respectively. The composite was characterized with a permeability of 0.47 Da and generation of air bubbles with size of 1-4 mm in a water medium.

Keywords: Metallurgical slag, Waste glass, Sintering, Porosity, Mechanical properties, Permeability, Diffuser.

1. Introduction

Industrial development over the last decades has generated large amounts of toxic and hazardous inorganic waste like, fly ash, slag, mud etc. which contain appreciable amounts of hazardous elements such as Pb, Cr, Cu, Zn, Cd and Hg. Most of these wastes are buried in landfills, which is costly and environmentally unsatisfactory. Therefore, it is essential to seek new options to recycle or reuse the inorganic residues. The use of waste materials such as metallurgical slag for glass-ceramics is a promising development. A combination of metallurgical slag with waste glass of TV screens under a controlled sintering procedure gives bulk or highly porous materials with surface or/bulk crystallization [1]. Glass-ceramics possess superior mechanical and erosion/wear properties to the parent glass and may also exhibit unique thermal and electrical properties [2]. Considering the experience in the field of the nuclear disposal technique by a multi-barrier-system using glass as a matrix phase, the concept will be transported to the treatment of metallurgical slag and powder technologies basically investigated for various waste combinations [3-5].

The aim of the paper is to make a porous composite between metallurgical slag and glass. This porous composite can be used as a filter, thermal insulation, lightweight structural laminates, diffused aeration, dust collectors, acoustic absorbers etc.
Experimental Procedure

Materials and methods

Metallurgical slag from FENI Kavadarci, R. Macedonia and waste glass of TV screens were used as raw materials. Chemical analysis of the metallurgical slag and TV glass was carried out by using an atomic absorption spectrophotometer (Rank Hilger, Atom Spek H-1580) and wet chemical methods. X-ray diffraction (XRD) investigation on the slag was undertaken using a Philips X-ray diffraction unit (Model PV 10501) operating at CuK$_\alpha$-radiation. Thermal characteristics of the metallurgical slag and TV glass were determined by a heating microscope (Leitz) in the temperature interval RT-1600°C with a heating rate of 10°C/min.

Composites with a controlled porosity were prepared by powder technology. Porous samples were made of slag and TV glass, varying the slag particle size as (-0.500+0.250 mm), (-0.250+0.125 mm), (-0.125+0.063 mm) and (-0.063+0.045 mm); the TV glass particle size was kept constant and lower than 63 μm. The slag and TV glass powders were mechanically mixed in a rotary mixer for 2 hours. The glass content was 10 and 20 wt%. Green bars (60x5x5 mm$^3$) were uniaxially pressed (Weber Pressen KIP 100) using a pressure of 22 MPa, and polyvinyl alcohol as a binder. Greens were sintered in an electrical furnace in air atmosphere with a heating rate of 5°C/min. The sintering temperature was 850, 900, 950 and 1000°C and the soaking time at the final temperature was 2h. Density of the sintered samples was determined by the water displacement method according to EN-993 and from the ratio of mass and volume. The value of the theoretical density of compacts was calculated based on the composition of the initial mixture and known densities of slag and glass. This is not an accurate theoretical density as it does not take into account any change in phases and their proportions that occur during sintering; it is however sufficient for comparison purposes with relatively porous products.

Mechanical properties (E-modulus and bending strength) of porous metallurgical slag-glass composites (8 pieces, 50x5x5 mm$^3$) were investigated at room temperature. 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. Linear thermal expansion was determined by a dilatometer (Netzsch 402E) in air atmosphere and temperature interval RT-600-RT, using a heating/cooling rate of 2°/min. Durability of the composites was tested using standard methods both for glass and ceramics. The durability was determined as a mass lost in 0.1M HCl. After treatment for 24h, 168h and 720h, the leached elements were analyzed by atomic absorption spectroscopy.

Permeability of the porous systems was determined from the gas pressure drop across the porous medium and the resulting gas flow rate. A general view of the equipment used for measurement of permeability of air through the porous glass-ceramic is illustrated in Fig.1.

The fluid used in the experiments was air at ambient temperature. The air flow rate was measured with rotameters ranging from 20 to 3000 l/h. The pressure drop through a porous sample was measured with U-pipe manometers, one filled with water and the other one with mercury. The pressure drop was plotted as a function of fluid superficial velocity and the results were fitted with the Hazen-Dupuit-Darcy model [6]. A glass vessel (70x50x60 cm$^3$) filled with water was utilized for testing of the diffusers and determining the size of air bubbles produced in a water medium when air flowed through the porous medium.
Fig. 1 Equipment utilized for permeability measurements of porous slag-TV glass composite

The chemical composition of ferronickel slag refers to a multicomponent silicate system, Tab. I. The very high content of iron oxides indicates the potential of this slag to develop magnetic phases upon appropriate processing.

Tab. I Chemical compositions of the Feni metallurgical slag and waste TV glass

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Slag, wt%</th>
<th>Glass, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.80</td>
<td>63.80</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.28</td>
<td>0.09</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.25</td>
<td>4.75</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2.48</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>17.62</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>31.42</td>
<td>0.31</td>
</tr>
<tr>
<td>CaO</td>
<td>4.48</td>
<td>1.85</td>
</tr>
<tr>
<td>MgO</td>
<td>9.66</td>
<td>2.25</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.33</td>
<td>7.30</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.04</td>
<td>6.04</td>
</tr>
<tr>
<td>PbO</td>
<td></td>
<td>8.38</td>
</tr>
<tr>
<td>BaO</td>
<td></td>
<td>4.81</td>
</tr>
<tr>
<td>NiO</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>CoO</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>0.87</td>
<td>0.25</td>
</tr>
<tr>
<td>Σ</td>
<td>99.04</td>
<td>99.80</td>
</tr>
</tbody>
</table>

The XRD pattern of ferronickel slag shows the presence of Forsterite Feroan (Mg·Fe)₂SiO₄, Botriogen (Mg·Fe)(OH)(SiO₄)₂ and a glassy phase, Fig.2.
Fig. 2 XRD pattern of the ferronickel slag

Thermal characteristics of the slag and glass are given in Tab. II.

**Tab. II.** Thermal characteristics of TV glass

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. of significant shrinkage, °C</th>
<th>Softening temperature, °C</th>
<th>Melting temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td>1260</td>
<td>1380</td>
<td>1480</td>
</tr>
<tr>
<td>TV glass</td>
<td>604</td>
<td>711</td>
<td>809</td>
</tr>
</tbody>
</table>

Densities of the slag and glass are shown in Tab. III.

**Tab. II.** Density of slag and glass

<table>
<thead>
<tr>
<th>Material</th>
<th>Density, [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td>3.71</td>
</tr>
<tr>
<td>Glass</td>
<td>2.64</td>
</tr>
</tbody>
</table>

In [3,4] it was shown that the multi-barrier concept for obtaining a glass-ceramics with a controlled interconnected porous structure is dependent on the followed parameters:

- Granulation of the slag in the composite slag-glass;
- Optimal content of the glass phase which will enable a homogenous distribution around the matrix;
- Optimal conditions of sintering: temperature/time.

Regarding the mechanical characteristics of the composite slag-glass, sintered in a temperature interval starting from 850 to 1000°C, the following conclusions have been reached:

Composites (-0.250 +0.125 mm) + 10% TV glass, (-0.125 +0.063 mm) + 10% TV glass and (-0.063+0.045 mm) + 10% TV glass, with a porosity of 41± 0.5% do not change by increasing the sintering temperature. The composite (-0.5+0.25 mm) + 10% TV glass has a porosity in the interval of sintering temperatures of 34.1 ± 1.5%.
Increasing of the sintering temperature, results in values of the E-modulus and the bending strength for the mentioned type of composites in the interval from 6 to 11 GPa, and from 17 to 33 MPa, respectively.

Composites (-0.250+0.125 mm) + 20% TV glass, (0.125+0.063 mm) + 20% TV glass and (-0.063+0.045 mm) +20%TV glass, by all sintering temperatures, have a porosity of 43.3± 1%. For the composite (-0.5+0.25 mm) + 20% TV glass, the porosity has not changed significantly depending on the sintering temperature and it is 39.8±0.5%.

Increase of the sintering temperature results in values of the E-modulus and the bending strength of the mentioned type of composites in the interval from 6-13 GPa, and from 22 to 48 MPa, respectively.

Using the E-modulus, the bending strength and the permeability as a criterion of selection, it has been shown that the composite (-0.125 +0.063 mm) + 20% TV glass, sintered at 950°C/2h possesses optimal properties. This porous composite among the whole spectrum of composites, will be the subject of our consequent investigation. A SEM micrograph of this porous composite is shown in Fig. 3.

![Fig. 3 SEM micrograph of the composite FeNi (-0.125+0.063 mm) + 20% TV glass sintered at 950°C/2h, (bar 100 μm)](image)

The integral porosity of the designated composite was 43.6 % and the E-modulus and bending strength were 12 GPa and 39 MPa, respectively. Pores were interconnected and with a size of 250-400 μm.

The increased temperature of sintering is reflected in the decrease of the viscosity of smelt glass deposited on the surface of the slag particles, forming in this way liquid bridges between particles and favouring liquid-phase sintering, Fig.4.

Durability testing of the ferronickel slag (-0.125+0.063 mm)+20% TV glass composite sintered at 950°C/2h in 0.1 M HCl showed that the weight loss after 24 hours was 0.16 wt%, 0.25 wt% after 168 hours and 0.40 wt% after 720 hours, that indicates that the compacts acted stable in aggressive media.
The thermal expansion characteristics of this composite in the interval RT-600°C-RT, showed absence of a hysteresis effect, which proves the fact that the system was in thermal equilibrium. The temperature dependence of thermal expansion in the interval RT-600°C-RT can be represented by a III order polynomial form:

$$\Delta L / L \cdot 10^{-3} = -0.221 + 0.014T - 1.729 \cdot 10^{-5}T^2 + 1.820 \cdot 10^{-3}T^3$$ (1)

By differentiation of the polynomial (1), the temperature dependence of the physical coefficient of thermal expansion could be derived:

$$\frac{\partial (\Delta L / L)}{\partial T} \cdot 10^{-3} = 0.014 - 3.458 \cdot 10^{-5}T + 5.460 \cdot 10^{-8}T^2$$ (2)

The technical coefficient of thermal expansion in the temperature interval RT-600°C is 11.10·10^{-6}/°C.

The permeability of the porous system, as an intrinsic property of the porous matrix based only on geometrical considerations, is an important characteristic for defining its potential application. Fig. 5 shown the air pressure drop through composite slag (-0.125+0.063 mm) + 20 wt% TV glass versus the volumetric flow rate per unit of cross-sectional area.

The permeability of air through the porous medium and the form coefficient of the porous composite slag (-0.125+0.063 mm) - 20 wt% TV glass were $K_0=0.47$ Da ($Da = 0.987 \cdot 10^{-12}m^3$) and $C_0=6.47 \cdot 10^6m^{-1}$, respectively. The cross-sectional averaged Darcy fluid speed, when the flow is said to have departed from Darcy flow into the quadratic flow regime, was 4.30 m/s.

This porous system was used for construction of a diffuser for water aeration. The diffuser consisted of plastic holders made from aramide and the porous ceramic matrix. The diffusers size was $\phi=30$ cm and $h=6$ cm.

The diffuser was tested in a bottle of water with a volume of 200 dm³. The airflow was varied in the interval $2 \cdot 10^{-3}$ – $7 \cdot 10^{-2} m^3/m^2\cdot s$, but the air pressure varied in the interval 0.1 – 0.6 bars.
Optimal results were obtained for an airflow from $3.83 \times 10^{-2}$ m$^3$/m$^2$/s and the air pressure of 0.15 bars. Air bubbles with sizes from 0.3-0.5 mm were produced. Fig. 6.

From the investigations made so far one can say that, the porous composite (-0.125+0.063 mm)-20% TV glass could potentially be used as a diffuser for water aeration.
Conclusion

- Metallurgical slag with a size of (-0.125+0.063 mm) activated with 20 wt% TV glass can be used for obtaining glass ceramics with controlled porosity.
- Obtained glass ceramics possessed an integral porosity of 43.6% and interconnected pores with a size of 250-400 μm.
- E-modulus and bending strength of this glass-ceramic were 12 GPa and 39 MPa, respectively.
- The obtained glass ceramic composite is in thermal equilibrium.
- The temperature dependence of the physical coefficient of thermal expansion can be expressed as: 
  \[ \frac{\partial (\Delta L/L)}{\partial T} \cdot 10^{-3} = 0.014 - 3.458 \cdot 10^{-5} T + 5.460 \cdot 10^{-8} T^2 \]
- Permeability and form coefficient of this glass-ceramics were \( K_0 = 0.47 \text{ Da} \) (1Da = 0.987·10^{-12} m^2) and \( C_0 = 6.47 \cdot 10^6 \text{ m}^{-1} \).
- Air bubbles from 0.3 to 0.5 mm were produced in a water medium employing a cross sectional air speed of 3.83·10^{-3} m^3/m^2/s, and air pressure of 0.15 bars.
- The obtained slag (-0.125+0.063mm)-20%TV glass could be used for production of diffusers for water aeration.

References