Characterization of glass and glass-ceramics obtained from industrial by-products

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Abstract

In the current study the utilization of industrial by-products for the production of glass and glass-ceramics was examined. Three industrial wastes were selected due to their mass production: fly ash derived from the combustion of lignite, blast furnace slag from the production of Fe-Ni and blast furnace slag from the production of steel. The capability of the above materials to be vitrified and subsequently devitrified was investigated. Mixtures were obtained using the fly ash, slag, glass cullet, quartz and melting agents at the appropriate proportions and the vitrification process, which took place at 1350-1450°C, was followed. Crystallization was achieved by heat treatment at 900, 950 and 1000°C. The chemical durability and the stability of the raw materials as well as of the final products were determined using standard procedures. X-ray and Scanning Electron Microscopy techniques were employed to identify the microstructure of the stabilized products before and after the heat treatment. The glasses obtained displayed good durability and negligible leachability. Furthermore, the results showed that the crystalline phase is greatly dependent on the structure of the by-product and the heat treatment.

Keywords: industrial waste, vitrification, de-vitrification, glass, glass-ceramics, fly ash, blast furnace slag.

1 Introduction

The use of waste materials as a partial or total replacement of virgin raw materials for the production of construction or other purposes has become a vital part of the waste management in developed countries. Great amounts of solid
waste are derived from the industrial and domestic activity which needs to be disposed of in a safe and economical way.

For that reason there is an effort in extending the application of waste mainly by innovative technologies for the production of new products. The construction materials area seems to be the most attractive one because of the volume of materials involved and the capacity for use of the material in bulk. Many attempts have been made to incorporate fly ashes, slags or domestic waste into cementitious materials [1-4].

The most promising applications are based on the total use of waste for the production of new materials. In the last few years waste vitrification has been considered an attractive procedure for the treatment of different type of waste and mixtures of waste. Vitrification is a known technology for the inertization of various industrial residues [5-7]. The main advantage of vitrification is the high chemical stability, the immobilization of heavy metals and radioactive elements, the destruction of organic components and also the vitrification process usually affords a great reduction of the volume of waste [8]. Moreover by the proper selection of glass compositions and the efficient thermal treatment the production of glass and glass-ceramics with better mechanical and chemical properties could be achieved.

The present study is a first approach of investigating the capability of the common industrial waste to be utilized as a raw material in glass and glass ceramics. Three industrial/metallurgical waste rich in SiO$_2$ content that are produced in large quantities as by products were selected. In a first series of experiments the potentiality of waste vitrification without any other additives was examined. Moreover, further specimens were made so as to evaluate the influence of SiO$_2$ addition in the mixtures. The source of SiO$_2$ was either Egyptian sand, or Fly ash or Glass Cullet. The presence of cullet in the batch could lower the glass melting temperature due to the increase of Na$_2$O.

In order to obtain the production of glass-ceramics the vitrified materials were subject to a devitrification process. The mineralogical structure and the physical and chemical properties of the material before and after the devitrification process were examined.

2 Experimental part

2.1 Materials

Three industrial waste were selected using as criterion their mass production: fly ash which is produced in a large amount as a by – product of combustion (at 1000-1050°C) of lignite in Greek electro-power stations, blast furnace slag from the pyrometallurgical treatment of iron nickel ore for the production of Ferro-nickel and blast furnace slag from the production of steel.

Chemical analysis of the above materials was determined using XRF analysis (PHILIPS 1606) and it represents average values. The chemical compositions are shown in Table 1 as well as the average chemical analysis of amber coloured
glasses which was used in some specimens as a melting agent. The cullet is collected from glass recycling units.

Table 1: Average chemical composition of the raw materials used.

<table>
<thead>
<tr>
<th></th>
<th>Blast Furnace Fe-Ni Slag</th>
<th>Blast Furnace Steel Slag</th>
<th>Lignite Fly Ash</th>
<th>Amber glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>41.10</td>
<td>17.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.60</td>
<td>-</td>
<td>8.44</td>
<td>0.35</td>
</tr>
<tr>
<td>MnO</td>
<td>-</td>
<td>7.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni-Co</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
<td>33.70</td>
<td>16.00</td>
<td>51.26</td>
<td>71.20</td>
</tr>
<tr>
<td>CaO</td>
<td>3.30</td>
<td>41.00</td>
<td>11.82</td>
<td>10.35</td>
</tr>
<tr>
<td>MgO</td>
<td>3.40</td>
<td>4.50</td>
<td>2.27</td>
<td>2.60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.30</td>
<td>7.00</td>
<td>19.39</td>
<td>1.90</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>-</td>
<td>0.53</td>
<td>13.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>-</td>
<td>1.81</td>
<td>0.60</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>4.30</td>
<td>0.56</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.85</td>
<td>6.63</td>
<td>2.91</td>
<td>0.30</td>
</tr>
</tbody>
</table>


All the materials were ground in ball mills under 90µm (DIN 4188), except from fly ash. The fineness of fly ash is measured using Laser Granulometre
(CIALAS GRANULOMETRE 715 D314) and it was found that fly ash samples have a retained amount fluctuate at 60% on 48µm.

Moreover, x-ray analysis XRD (Siemens D5000 diffractometer, Cu Ka radiation, Ni Filter) was used for the examination of crystallinity of each waste. Glass cullet and Blast Furnace Fe-Ni Slag spectrums revealed amorphous materials, while the spectrums of fly ash and Blast Furnace Steel Slag present except from the crystalline formation and amorphous phase.

2.2 Experimental procedure

Glasses were prepared from the industrial waste by melting in a preheated electric furnace at 1450°C for 2 hours. Fire resistant ceramic crucibles were used for the vitrification process. After fusion the glass was cast in a metallic mould in air and the material was solidified. The annealing of the glasses took place at 550°C for 2h.

Moreover, specimens made from mixtures of lignite fly ash and Blast Furnace Steel Slag and Blast Furnace Steel Slag and quartz or amber glass cullet were prepared in order to estimate the influence of SiO₂ enrichment which either derive from a waste material or a primary raw material.

Every specimen was subjected to devitrification thermal treatment at 900, 950, 1000°C for 2 hours.

Furthermore, leaching tests were performed on both glass and glass – ceramics according to DIN 38414 S4. It is important to pinpoint that although the above test is not applied to extra fine particles, the used glass and glass – ceramic powders were less than 45µm in size, so as to assess the worst case.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Sample name</th>
<th>G-S1</th>
<th>G-S2</th>
<th>G-S3</th>
<th>G-S4</th>
<th>G-S5</th>
<th>G-S6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite Fly Ash</td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Blast Furnace Fe-Ni Slag</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blast Furnace Steel Slag</td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>60</td>
<td>40</td>
<td>77</td>
</tr>
<tr>
<td>Amber glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Egyptian Sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23</td>
</tr>
</tbody>
</table>

The color evaluation of the glass samples was performed according to the C.I.E. system. Dominant wavelength L (mm), purity (%) and brightness (%) were carried out with a UV/Vis spectrometer Perkin Elmer model L-20,
equipped with an integrated sphere. In particular, the samples presented in table 2 shown an olive-green to dark amber color.

In order to characterize the produced glass and glass ceramics based on its physicochemical characteristics, samples density and hardness were measured.

The microhardness has been tested by the Vickers indentation method for glasses stable atmosphere conditions were kept during the measurements (RH = 45%). The calculated results were mean values for at least five measurements.

The density was measured according to ASTM C729-75.

The crystalline phase composition of the produced glasses and glass ceramics was investigated using X-ray powder diffraction.

In order to estimate the resistance of the produced glass and glass-ceramics to chemical attack the standard test method for the resistance of glass containers to chemical attack (ASTM C 225-85) was employed.

3 Results and discussion

In figures 2, 3 the XRD spectrums of the produced glasses and glass-ceramics are illustrated. As XRD analysis verified all the vitrified specimens were amorphous materials except from Blast Furnace Fe-Ni Slag.

![Figure 2: XRD spectrums of the produced glasses.](image_url)

At vitrify Blast Furnace Fe-Ni Slag spectrum crystalline phases of Augite aluminian (Ca(Mg, Al,Fe)Si₂O₆), Diopside aluminian (Ca(Mg, Fe, Al) (Si, Al)₂O₆), anorthite (CaAl₂Si₂O₈), Chromite (FeCr₂O₄), Iron Nickel (Fe-Ni), Leucite KAlSi₂O₆), Magnetite (FeFe₂O₄) are presented.
Figure 3: XRD spectrums of the produced glass-ceramics (devitrification 1000°C).

Figure 4: XRD spectrums of the produced glass-ceramics from blast furnace steel slag.

In figure 3 one can see the different products from the devitrification of various glasses produced by waste materials. Regarding Blast Furnace Fe-Ni Slag the derived product from the vitrification process is a crystalline material
and there are not distinct changes due to devitrification process. Vitrified lignite fly ash could provide glass-ceramics. The main crystalline phases that could be recognized from the XRD spectrums are anorthite and quartz. All the vitrified mixtures with Blast Furnace Steel Slag have shown analogous crystalline formation. The main crystalline phases were diopside, anorthite, albite calcian. The resulted glass-ceramic from Lignite Fly Ash and Blast Furnace Steel Slag was similar to that made from Blast Furnace Steel Slag. On the other hand the presence of Egyptian sand favours the production of anorthite and the presence of glass cullet promote the production of albite calcian.

Thermal treatment of the produced amorphous materials at different temperatures has shown that glass from Lignite Fly Ash and Blast Furnace Steel Slag could not be de-vitrified at 900°C and gradually is crystallized at higher temperatures. There is not significant heat effect from 900-1000°C for Blast Furnace Steel Slag glass-ceramics.

The results from XRD are reinforced by the Scanning Electron Microscopy observations. In figure 6a an amorphous vitrified material is illustrated. At SEM photo 6b the formation of crystalline phase could be observed. Regarding the density values the produced glass and glass ceramics had shown higher values than the common glass, which fluctuated from 2.5626 to 2.5712 g/cm³.

The hardness measurements varied from 525-595 Hardness (kgf/mm²). At this point, it should be mentioned that the results from Vickers indentation method should be reconsidered owing to the fact that the specimens fractured and not just marked during the measurement.
Each sample which analyzed according to DIN 38414 S4 has insignificant leachability characteristics for Cr, Mn, Ni, Cd, Cu. It is obvious that the vitrification and devitrification technique immobilize the above heavy metals. Still, the leaching of Fe and Zn ions was not negligible, possible due to the extra fine granulometry of the testing material.

The results of the resistance of glass to chemical attack were similar to soda lime flint glass, which shows an average value 7.67 ml acid per 10g glass.

![SEM observations of the produced glass and glass - ceramics from lignite fly ash.](image)

4 Conclusions

Glass and glass-ceramics were prepared from industrial waste. The formation of amorphous materials from Lignite Fly Ash and Blast Furnace Steel Slag was accomplished at 1450°C without using any fluxing additive. Blast Furnace Fe-Ni Slag has not been vitrified at the same temperature. Adequate heat treatment of the amorphous materials showed that it was possible to crystallize them into glass-ceramics. Samples have shown good durability and negligible leachability. However, further investigation is needed in order to estimate the optimum ratios of raw materials in relation to the products properties.

References


