Journal of Cleaner Production xxx (2013) 1–6

Contents lists available at SciVerse ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

# Self glazed glass ceramic foams from metallurgical slag and recycled glass

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A R T I C L E I N F O

*Article history:*
Received 22 February 2013
Received in revised form
14 June 2013
Accepted 16 June 2013
Available online xxx

*Keywords:*
Glass ceramics
X-ray diffraction
Industrial waste
Iron slag
Sintering

A B S T R A C T

Viscous flow sintering of finely powdered glass, at atmospheric pressure, gives the opportunity to prepare new valuable engineering materials, including innovative "glass-based stoneware", as presented in this paper. This new material derives from the substitution of expensive feldspar fluxes with glass, in turn allowing very low processing temperatures (even below 1000 °C) and promoting the incorporation of inorganic waste, such as iron-rich metallurgical slag. In the present case, glass-waste interactions were found to provide a homogeneous foaming, without other additives, and partial crystallization. The specific mechanical properties of the resulting cellular glass-ceramics, being comparable to those of conventional porcelain stoneware, sintered above 1100 °C, suggest an extensive use in the building industry as lightweight panels, considering also the negligible water absorption and the chemical stability.

## 1. Introduction

Traditional ceramics have always been regarded as a reference for the disposal of inorganic waste (Lee, 2006). Since traditional ceramics have a mass market, even a small addition of a given waste to the usual formulations is associated with a remarkable recycling. This concept may be applied even to waste glasses, including glasses from the melting of hazardous waste as well as glasses hardly used in the manufacturing of original articles (Colombo et al., 2003; Kidalova et al., 2012).

Small glass amounts do not determine significant changes in the properties of traditional ceramics, as testified by the experiences with waste glasses introduced in formulations for porcelain stoneware (Brusatin et al., 2005; Karamanova and Karamanov, 2009), but this probably represents an underestimation of the potentialities of glass. A waste glass could be considered, with limited additives, for the preparation of glazes (Schabbach et al., 2012), or as main constituent of ceramic mixtures. In fact, viscous flow sintering may occur at much lower temperatures than those required by conventional feldspar fluxes.

Extensive use of waste glass, either waste-derived or recycled, has been presented in recent papers (Lin, 2007; Bernardo et al., 2008, 2009; Zhao et al., 2013). In particular, glass completely replaced the ordinary feldspar fluxes, allowing the obtainment of dense stoneware tiles ("glass-based stoneware") at temperatures not exceeding 1000 °C (instead of approximately 1200 °C for conventional formulations). The degradation of mechanical properties is prevented by crystallization, caused by interactions between glass and clay components. On the one hand the sintering temperature is not high enough for mullite formation, on the other residues of clay dehydration (i.e. metakaolinite) may react with calcium oxide, provided by the glass (Bernardo et al., 2008) and/or additives (such as $Ca(OH)_2$) (Bernardo et al., 2009), yielding calcium alumino-silicates.

The present paper reports a further extension of the concept of revised formulations for stoneware, with most of the raw materials corresponding to waste; specifically, waste soda-lime glass (SL), i.e. a by-product of municipal glass recycling, was considered combined with a vitreous iron-rich metallurgical slag (MS). This slag, being highly concentrated in $SiO_2$ (see Table 1), cannot be considered for cementer use (Skuza et al., 2009).

The use of metallurgical slag is interesting for the possible interactions between glass and clay components, favouring the crystallization, and for the remarkable content of iron oxide, promoting the development of a highly porous structure by gas release ("bloating" effect, in turn associated to the reduction of $Fe^{3+}$ into $Fe^{2+}$) (Appendino et al., 2004).

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0959-6526/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.jclepro.2013.06.029

Please cite this article in press as: Ponsot, I., Bernardo, E., Self glazed glass ceramic foams from metallurgical slag and recycled glass, Journal of Cleaner Production (2013), http://dx.doi.org/10.1016/j.jclepro.2013.06.029

**Table 1**
Chemical composition of the starting raw materials.

| Component | Soda-lime glass (SL) | Kaolin clay | Metallurgical slag (MS) |
|---|---|---|---|
| Oxides | Contents (wt %) | | |
| $SiO_2$ | 72.3 | 43.5 | 55.3 |
| $Al_2O_3$ | 2.2 | 39.0 | 12.0 |
| $Fe_2O_3$ | 0.3 | Traces | 5.4 |
| $Na_2O$ | 12.0 | | 13.9 |
| $K_2O$ | 0.9 | | 1.0 |
| CaO | 10 | | 12.4 |
| MgO | 2.0 | | Traces |
| $TiO_2$ | 0.1 | | |

Porosity in materials for modern buildings is highly attractive, particularly for lightweight tiles to be placed vertically. Such tiles are interesting, above all, for ventilated façades, i.e. a new generation of coverings applied on the surface of large buildings, aimed at improved thermal insulation (Infield et al., 2004). As recently reported (Bernardo et al., 2010; Garcìa-Ten et al., 2012) a possible solution is represented by foamed porcelain stoneware, produced at high temperatures (those of conventional production), with the help of expensive additives ($CeO_2$ or SiC). Cellular glass-ceramics, owing to their low water absorption, remarkable mechanical properties and good chemical stability, could be a valid alternative, especially when configuring savings in both raw materials and energy (due to the recycling of waste and low firing temperatures), as presented in this paper.

## 2. Material and methods

The chemical composition of the employed starting materials is reported in Table 1. Pure kaolin clay (Carlo Erba Reagenti SpA, Milan, Italy) was mixed with soda-lime glass (SL), recovered from municipal recycling, and a metallurgical slag (MS), both kindly provided by SASIL SpA (Biella, Italy), in shape of fine powders (<100 μm). SL does not refer to the fraction of recycled materials, after sorting, which consists of almost pure glass, ready for the industry, but to the fraction enriched in contaminants, which remains practically unemployed and mostly landfilled, in huge quantities (SASIL treats this waste in a quantity of about 180,000 t/y). MS corresponds to slag from recovery and refining processes of precious metals.

Kaolin clay, SL and MS were considered in three proportions, according to Table 2, showing also the overall oxide contents. Mixture A (SL and MS in equal amounts) can be seen as the reference composition; it was conceived according to previous experiments with sintered glass-ceramics (Bernardo et al., 2012), in which pure kaolin clay, in an amount of 10wt%, was successfully employed as binder for fine glass powders. Mixture B and C were conceived to evaluate the impact of an increased glass content, which was thought to enhance viscous flow (mixture B), and of an increased slag content, thought to favour crystallization and gas release, by reduction of $Fe_2O_3$.

**Table 2**
Formulation of the investigated mixtures.

| Mix | A (reference) | B (glass rich) | C (slag rich) |
|---|---|---|---|
| Formulation | Contents (wt %) | | |
| SL | 45 | 54 | 36 |
| MS | 45 | 36 | 54 |
| Kaolin clay | 10 | 10 | 10 |
| Oxides | Contents (wt %) | | |
| $SiO_2$ | 61.8 | 63.3 | 60.2 |
| $Al_2O_3$ | 10.3 | 9.4 | 11.2 |
| $Na_2O$ | 13.0 | 12.8 | 13.1 |
| CaO | 11.2 | 11 | 11.4 |
| $Fe_2O_3$ | 2.6 | 2.1 | 3.0 |

The components were mixed together and added with water (35%–40% of the total solid), in order to obtain aqueous slips, homogenised by mechanical stirring. The slips were cast in wide glass containers and left at 110 °C overnight. Fine granules of about 200 μm were obtained by manual grinding of the dried slips and pressed at 40 MPa in rectangular steel dies, to obtain tiles of dimensions 50 mm × 35 mm × 6 mm. Sintering experiments were performed in an electric muffle furnace, by direct introduction of samples, i.e. without heating stage, at various temperatures (from 900 °C to 1050 °C), for 30 min. Sample were naturally cooled down.

Immersion in boiling water was used for the evaluation of the water absorption, according to the current norm (ISO 10545-3). The apparent density of the sintered materials was estimated by means of the Archimedes' principle. Mineralogical analysis was conducted by X-Ray Diffraction analysis (XRD) on powdered samples (Bruker D8 Advance, Karlsruhe, Germany – CuKα radiation, 0.15418 nm, $2\theta = 10–60°$). Phase identification was achieved by means of the Match!® program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA). Scanning Electron Microscopy (ESEM Quanta 200, FEI Company, Eindhoven, The Netherlands) was used for microstructural characterization.

For the evaluation of mechanical properties, small beams of 45 mm × 3 mm × 4 mm were cut from bigger tiles and carefully polished up to a 5 μm finish and chamfered at the edges, by using diamond tools. One set of beams was left unpolished. The elastic modulus was measured by non-destructive resonance frequency testing (GrindoSonic Mk5, Leuven, Belgium). Three-point flexural tests (span of 28 mm) were carried out by using an Instron 1121 UTS (Instron, Danvers, MA), at a cross-head speed of 1 mm/min; each data point represents the average of ten individual tests.

The release of heavy metals was evaluated by application of Toxicity Control Leaching Procedure or TCLP: 4 mm diameter fragments from bending strength determinations were placed in an extraction solution consisting of distilled water, with a pH value of about 7, prepared according to European Standard for waste toxicity evaluation (EN 12457-2) for a liquid to solid ratio of 20, and softly stirred at 25 °C for 24 h. The resulting solutions were filtered through a 0.6 μm filter and analysed by using inductively coupled plasma (ICP, SPECTRO analytical Instruments GmbH, Kleve, Germany).

## 3. Results and discussion

The amorphous character of MS is confirmed by the preliminary diffraction analysis shown in Fig. 1. The same figure testifies the remarkable crystallization tendency of MS powders, fired at 1000 °C without additives. The developed crystal phases consist of calcium-sodium alumino-silicate ($2CaO\cdot Na_2O\cdot Al_2O_3\cdot 4SiO_2$, PDF#76-0479), nepheline ($Na_2O\cdot Al_2O_3\cdot 2SiO_2$, PDF#79-0993) and hematite ($Fe_2O_3$, PDF#87-1166). The separation of an iron oxide is interesting, since it reasonably acted as a nucleating agent, thus justifying the extensive crystallization (in Fig. 1, the amorphous halo is practically absent for fired MS). This situation is rather similar to that of glass-ceramics from melted basalts, for which the separation of iron oxides is even promoted by adding oxidising agents in the melt (Höland and Beall, 2002). In the present case, the oxidation (with the formation of ferric oxide, $Fe_2O_3$, i.e. the oxide associated to the higher valence state of iron ions) was favoured by the high specific surface of glass powders (Chinnam et al., 2013).

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