Blast-Furnace Slag and Exhaust Cracking Catalyst: Raw Materials for Porcelain Stoneware Tiles of the 21st Century

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Industrial and ore exploration activities, when not aligned to clean technology procedures, use to generate huge quantities of wastes that might be very harmful to the environment. Their disposal is costly and frequently inappropriate, so their usage as raw materials for different applications is an important scientific and technological challenge. Considering the potential value aggregation in processes and products, industrial and mineral wastes recycling can also result in job and profit generation, fundamental aspects nowadays. Glass-ceramics produced from solid inorganic industrial wastes might be alternative products to porcelain stoneware tiles, materials with high aggregate value and increasing application in civil engineering. However, these wastes normally do not present adequate chemical composition for this kind of application, requiring the addition of commercial raw materials, and thus increasing the final product price. The employed technology uses mixtures of different Brazilian inorganic solid wastes, in order to achieve adequate glass batches for glass-ceramics production. Further sintering and crystallization studies of the glasses were performed. The used procedure (glass-ceramic sintering route) allows the generation of materials with low open porosity, the main problem of porcelain stoneware tiles.

Keywords: industrial waste, recycling, porcelain stoneware tile.

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INTRODUCTION

The huge quantities of solid wastes generated by industries and ore exploration might be very harmful to the environment. Their disposal is costly and frequently inappropriate, so their usage as raw materials for different applications is an important scientific and technological challenge. These wastes could be used in glass-ceramics (Rabinovich 1982, Pelino et al. 1997), polycrystalline solids prepared by the controlled crystallization of glasses, usually showing much better properties than their related glasses or ceramics, but more expensive as they demand more energy (Hlavac 1983). Glass-ceramics production can be briefly described as raw materials melting, glass casting and heat treatment (crystallization). Therefore the incorporation of suitable industrial wastes in batch formulations decreases raw materials cost.

Industrial waste glass-ceramics have been produced since the 1970’s in Europe, being used as electric insulators, facing panels, roof coverings, abrading agents, paving tiles and pipes (Rabinovich 1982, Strnad 1986). Oliveira (2000) used Brazilian industrial wastes: blast-furnace slag from iron industry (BFS – rich in CaO, SiO_2, Al_2O_3 and MgO), exhaust cracking catalyst from a refinery (ECC – rich in SiO_2 and Al_2O_3) and chromite jigging tailings from Medrado Mine, Bahia (CJW – rich in SiO_2, MgO, Fe_2O_3, Al_2O_3 and Cr_2O_3), in different proportions for production of glasses with different contents of Fe_2O_3 and Cr_2O_3, possible nucleating agents (Strnad 1986, McMillan 1979).

Porcelain stoneware tiles are ceramic paving tiles with a very compact structure of crystalline phases surrounded by a glassy matrix (similar to glass-ceramic structure), presenting low porosity (< 0,5%) and high technical performance (Menegazzo, 2000). These products are largely used all over the world as a result of their good technical qualities, as well as their beautiful visual aspect (Arantes, 2001). The production of this kind of paving tiles in Brazil is very low when compared to Italy (for example, 3.4 million m^2/year in 1999 in Brazil against 127 million m^2/year in 1997 in Italy) (Menegazzo, 2000). Polished porcelain stoneware tiles present low staining resistance as a drawback. This characteristic is straightly related to the open porosity at the polished surface, where the staining agents penetrate and are hardly removed by domestic cleaning products (Arantes, 2001).

EXPERIMENTAL

The glasses used in this study came from the following batches (Oliveira 2000): glass 1 (70% BFS and 30% ECC) and glass 2 (40% BFS, 30% CJW and 30% ECC). They were ground to 100% below 105 μm in a ceramic ball mill, and characterized by chemical analysis and X-ray diffraction, XRD, (Bruker AXS D5005, Cu $K\alpha$ radiation, 5 to 70º 2θ).

Their crystallization properties were studied with a Perkin Elmer thermodifferential analyzer DTA7 (Pt cups, 20 mg samples and alumina as reference).

Heat treatment of the glasses (according to DTA) was performed in a Thermolyne 46128 furnace, and crystalline phases characterized by XRD.

Shape changes (sintering, softening) of 3 mm side cubic compacts of the glass powders during heating were studied under a Leitz 1A microscope with a heating stage fitted at 10ºC/min rate.

After being mixed with polyvinyl alcohol, the glass powders were uniaxially pressed and heat-treated in the Thermolyne furnace (constrained by the heating microscopy results). Specific weight and porosity were determined by measuring the dry, wet, and immersed weights of the sintered bodies obtained.

RESULTS AND DISCUSSION

The chemical composition of the glasses is in Table 1. Glass 1 has higher CaO and Al_2O_3, and lower SiO_2, MgO, Fe_2O_3 and Cr_2O_3 contents than glass 2. These glasses displayed fully amorphous XRD patterns (Figures 2 and 3).

DTA curves of glass 2 (Figure 1) show three important thermal events: T_g, glassy transition, T_c, crystallization, and T_m, melting. The DTA curves of glass 1 (not shown) show less defined crystallization peaks (wider and less intense) than glass 2. Glass 1 crystallization maximum (T_c), recorded at 10ºC/min heating rate, occurs at 1093 ºC while glass 2 at 1002ºC.

Content (%)	Glass 1	Glass 2
SiO_2	44.1	50.6
Al_2O_3	22.6	18.8
CaO	27.5	15.7
MgO	4.9	9.8
Na_2O	—	—
K_2O	—	0.1
Fe_2O_3*	0.8	3.2
MnO	—	0.3
Cr_2O_3		1.4

Table 1 – Chemical composition of the glasses

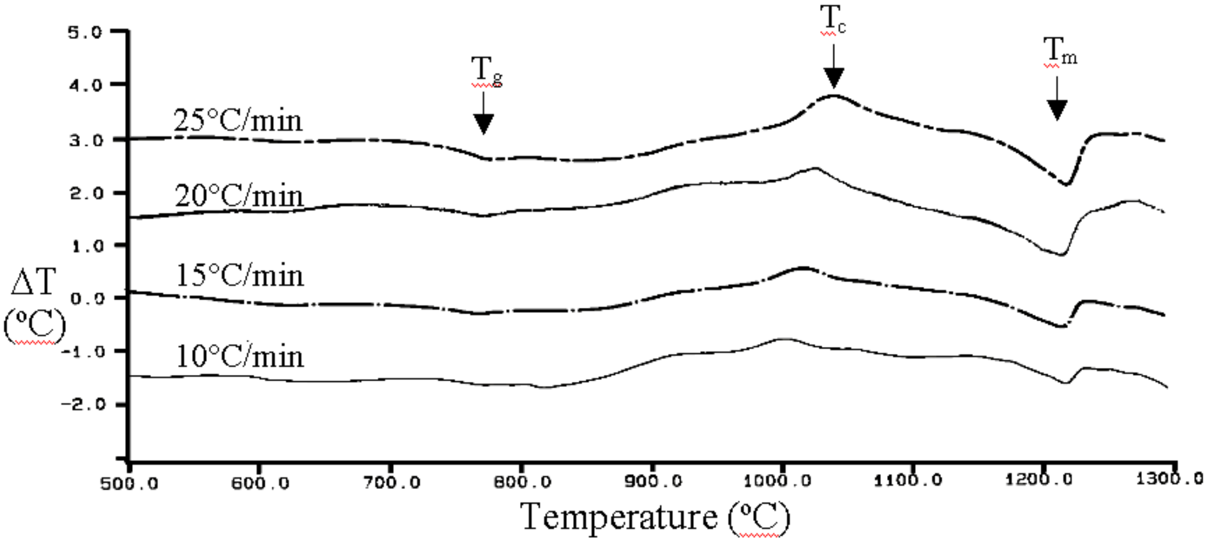

Figure 1 – DTA curves of glass 2

The crystalline phases generated in the heat-treated glasses were identified by XRD (Figures 2 and 3). The chemical formula of these phases agrees with the main components of the glasses. The temperatures where crystalline phases start to appear in XRD agree with the DTA crystallization onset temperatures (not shown).

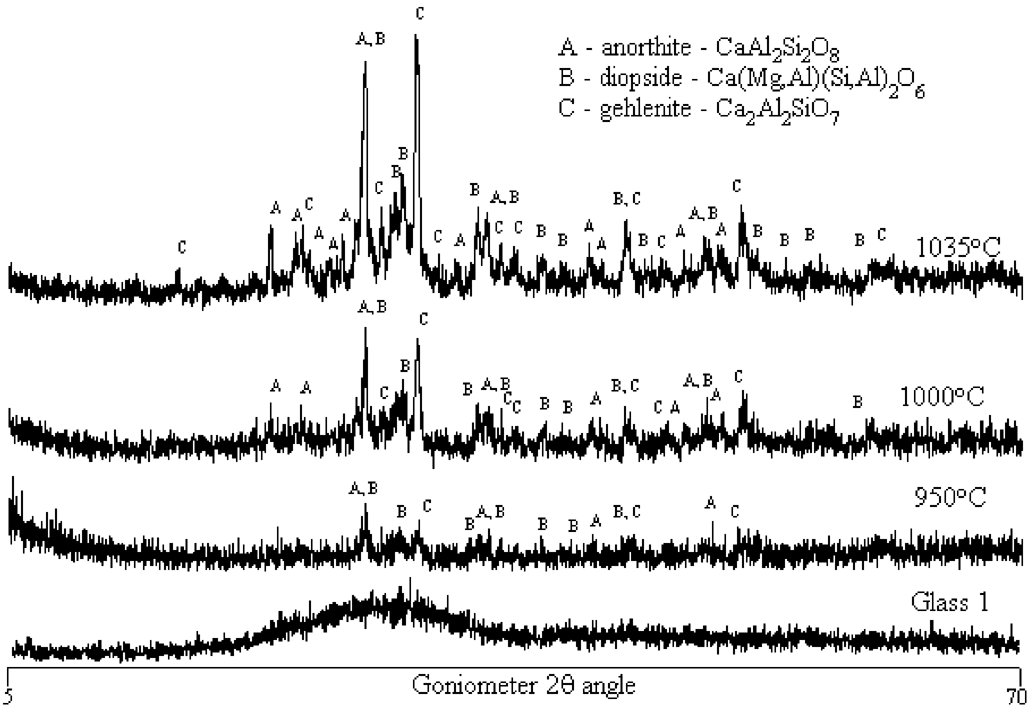

Figure 2 – XRD of glass 1, before and after heat treatments.

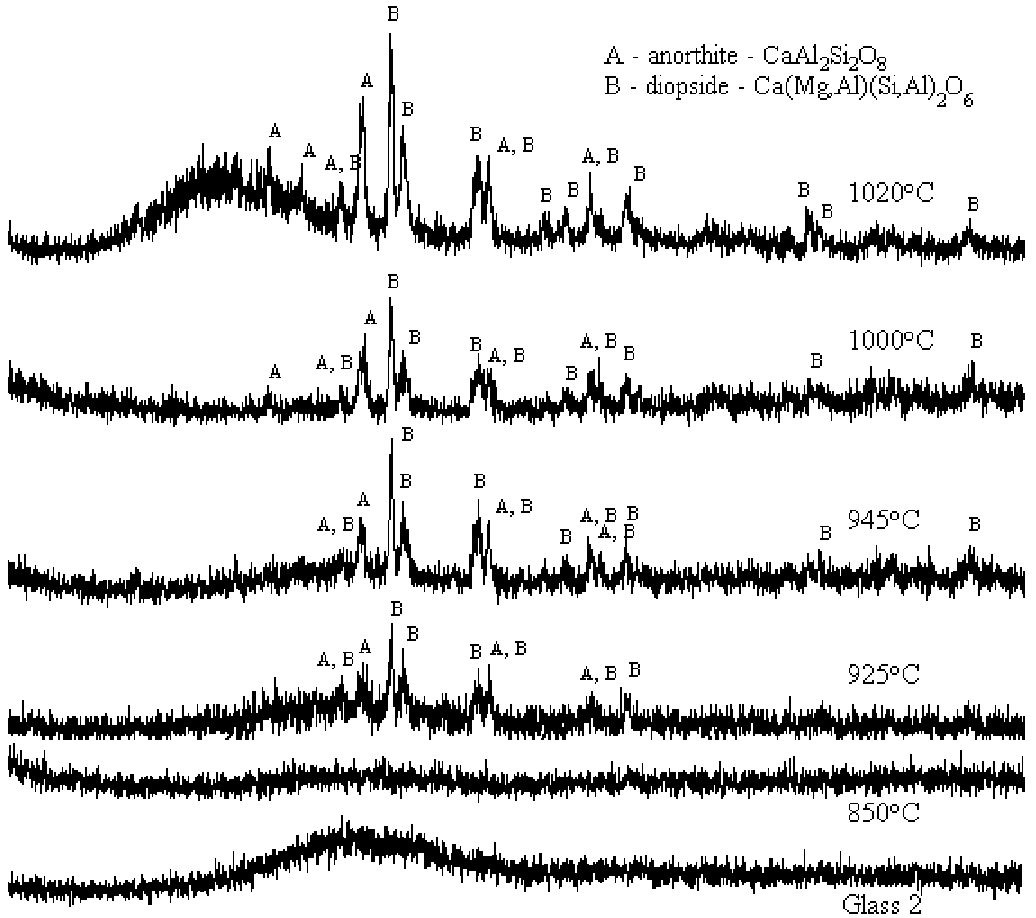

Figure 3 –XRD of glass 2, before and after heat treatments.

Heating microscopy (Figure 4 and Table 2) indicated similar sintering and softening behavior for both glasses. Their sintering temperature range ends before the beginning of crystallization (XRD and DTA) indicating that they sinter while still glassy.

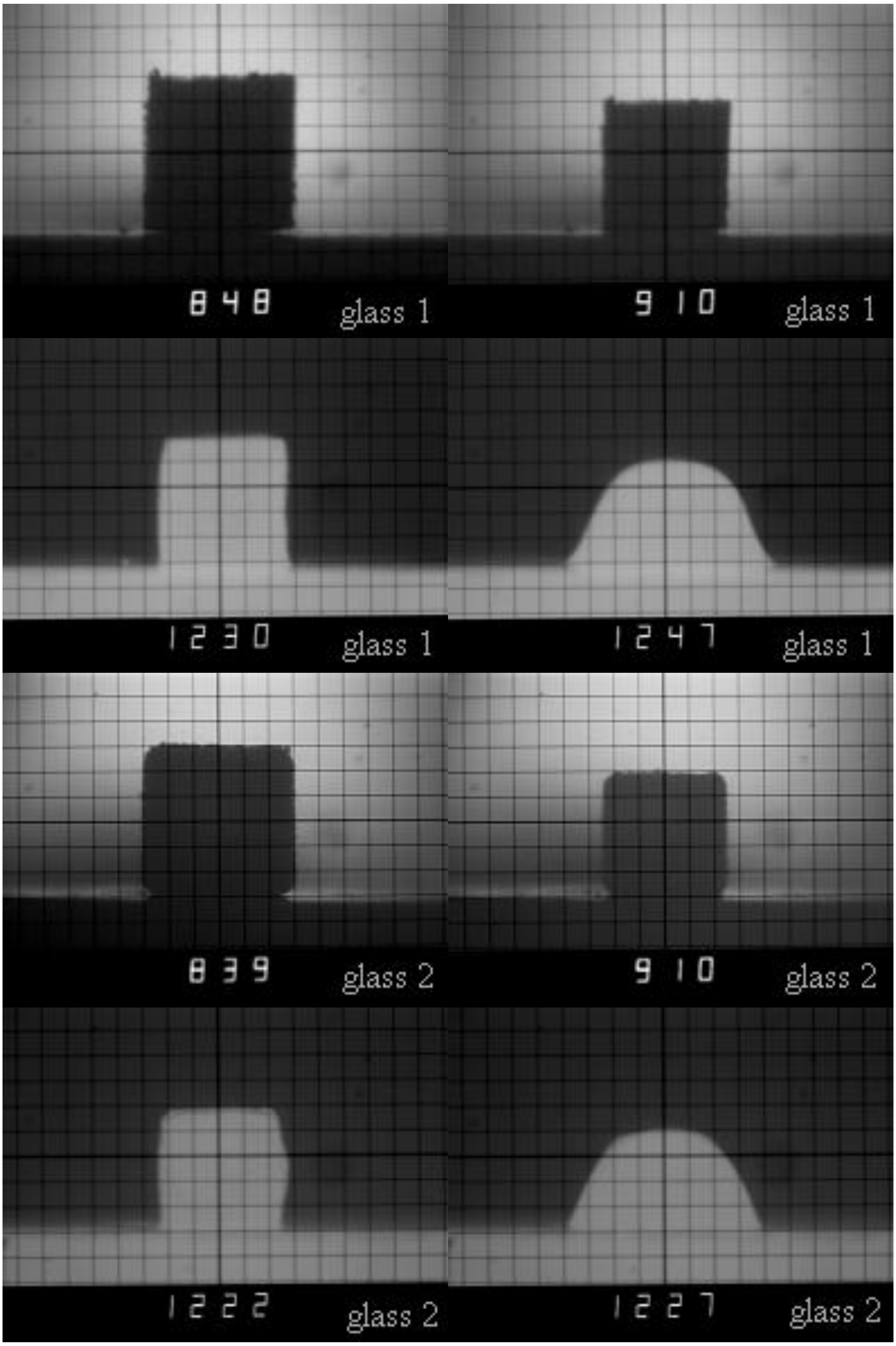

Figure 4 – Heating microscopy images of powder compacts of glasses 1 and 2.

	Sintering (ºC)	Softening (°C)
Glass 1	840-920	1230
Glass 2	840-920	1222

Table 2 – Temperatures of Dimensional Changes

Figure 5 shows the similarity of the sintering curves of both glasses. As they show different colors after crystallization, a mixture of them could be sintered together and generate a texture similar to the obtained in porcelain stoneware tiles.

Table 3 shows the sintering temperatures applied to the glass compacts (determined by sintering curves in Figure 7) and some properties of the obtained solid bodies. The high specific weight (closed pores + solid) and low open porosity values indicate effective sintering, and the possibility of obtaining good quality glass-ceramics, that might be used as porcelain stoneware tiles. As sintering occurs with the particles still glassy, porosity values might be even lower, reaching the porcelain stoneware tiles range.

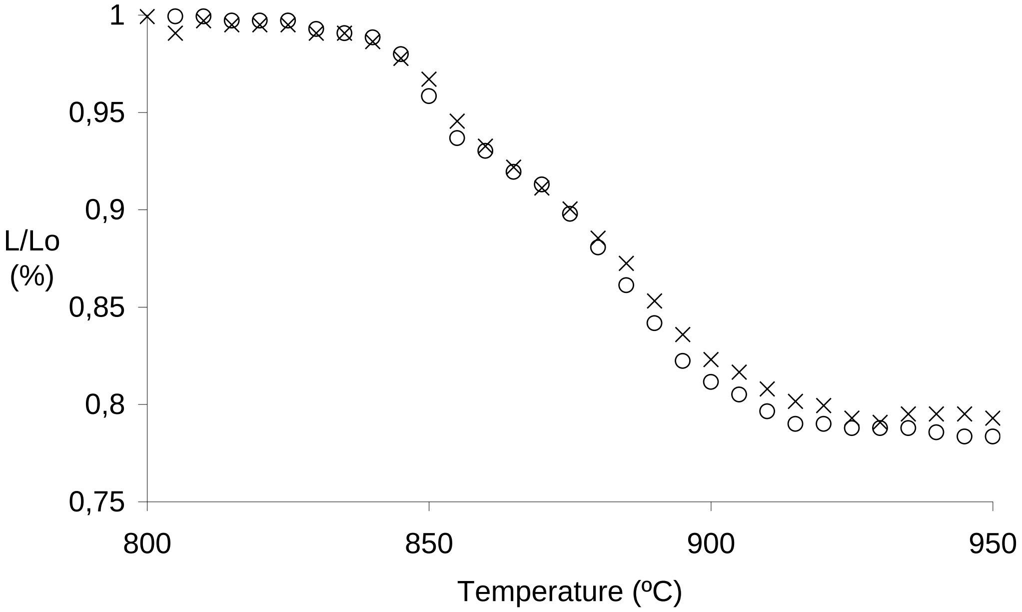

Figure 5 – Sintering curves: X – glass 1, O – glass 2.

Glass	Sintering Temperature (ºC)	Specific Weight (g/cm^3)	Open Porosity (%)
1	900	2.80	1.2
2	900	2.84	0.8

Table 3 – Properties after heating the compacts.

CONCLUSIONS

This work indicated industrial wastes glass-ceramics obtained by sintering route as good candidates for usage as porcelain stoneware tiles, as they showed low open porosity that might be reduced even more by optimization of the sintering/crystallization heat treatment.

Iron and chromium oxides changed the color of the glass and the resulting glass-ceramics.

The different color and the chemical and sintering similarities of the glasses indicate the possibility of obtaining color texture similar to porcelain stoneware tiles, when a coarse mixture of glass powder agglomerates is cast and heat-treated.

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