Sintering and Crystallization Studies of Industrial Waste Glasses

C.H.Oliveira, R.Neumann, & A.Alcover Neto
Centro de Tecnologia Mineral – CETEM/MCT – Rio de Janeiro, Brazil

M.V.A.Fonseca
Instituto de Química – IQ/UFRJ – Rio de Janeiro, Brazil

ABSTRACT: This work evaluated the feasibility of obtaining glass-ceramics (controlledly crystallized glasses) from Brazilian industrial waste glasses. The wastes used were blast-furnace slag, exhaust cracking catalyst and chromite jigging tailings. The glasses were batched only using the wastes, in ratios that generated different contents of iron and chromium (nucleation agents). The careful selection and batching of the wastes allowed not using commercial raw materials, decreasing production costs. The glass crystallization studies (XRD and DTA) showed that higher content of transition metals improved bulk nucleation and lowered crystal growth temperatures. The sintering studies, performed using heating microscopy, showed that the sintering of glasses with lower content of transition metals ranged from 840 to 920°C, while the higher contents one, from 1160 to 1280°C. In the first case, the sintering temperatures were lower because it worked through glassy phase sintering, differently from the other one, where it worked through crystalline particles sintering. The different sintering/crystallization behaviors of the glasses allows glass-ceramic production by bulk crystallization of glass monoliths (higher and intermediate content of iron and chromium) or by simultaneous sintering/crystallization of glass powders (lower and intermediate content). This work shows an alternative usage for industrial wastes, generating a relatively high aggregate value product (glass-ceramics).

1 INTRODUCTION

The huge quantities of solid wastes generated by industries 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. Inorganic solid wastes are already used in glass, ceramic and cement industries.

These wastes can also be used in glass-ceramics (Rabinovich 1982, Pelino et al. 1997), polycrystalline solids prepared by the controlled crystallization of glasses. These materials usually show much better properties than their related glasses or ceramics, but they are 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). So, incorporation of industrial wastes in batch formulations would decrease 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). In a previous work (Oliveira 2000), Brazilian industrial wastes such as blast-furnace slag from iron industry (BFS – rich in CaO, SiO_2, Al_2O_3 and MgO – generated during industrial iron oxide reduction), exhaust cracking catalyst from a refinery (ECC – rich in SiO_2 and Al_2O_3 – cracking catalyst is used for transforming long chain hydrocarbons into smaller ones, but after some time its activity decreases and part of it is removed from the reactor and replaced with fresh catalyst) and chromite jigging tailings from Medrado Mine, Bahia (CJW – rich in SiO_2, MgO, Fe_2O_3, Al_2O_3 and Cr_2O_3 – waste of chromite concentration plant) were used 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).

Glass crystallization comprises nucleation and crystal growth (Navarro 1968). Nucleation provides the sites where the crystals will start to grow (Rincon 1992). When nucleation happens all over the bulk of the glass, fine-grained glass-ceramics can be obtained by heat treatment of a glass monolith (Strnad 1986, Hlavac 1983, McMillan 1979). When nucleation is not effective, the crystal growth starts at the few nuclei formed and external surfaces. An alternative is to ground the glass, cast it just like a ceramic powder, and heat treat it for sintering and crystallization (Strnad 1986, Pannhorst 1997, Rabinovich 1982, Gonzalez-Oliver 1997).

2 EXPERIMENTAL

The maximum nucleation temperature (T_{nuc}) determined with DTA (Buri 1982) demands fast heating the glass until a selected temperature, keeping it stable for two hours, and then heating at a 10°C/min rate. After several analyses with different soaking temperatures, a graph $(1/T_c - 1/T_{c0}) \times T_n$ can be plot (T_n is soaking temperature, T_c is the maximum of the crystallization peak with soaking temperature, and T_{c0} is the maximum of the crystallization peak in a simple DTA – constant heating rate). The maximum of the curve is the maximum nucleation temperature, important issue for heat treatment optimization and for evaluation of the nucleation agents effect.

The apparent activation energy of crystal growth was determined with the Kissinger (1956) and modified Kissinger (Kemeny & Sestak 1987, Weinberg 1991, 1992) methods. In the Kissinger method, DTAs at different constant heating rates are acquired and plot as $\ln(\beta/T_c^2) \times 1/T_c$ (β is the heating rate and T_c is the maximum of the crystallization peak). The angular coefficient of the obtained straight line is $-E_a/R$ (E_a is apparent activation energy and R is the perfect gas constant). In the modified Kissinger method, the glasses are rapidly heated, soaked at the nucleation temperature and then heated at different constant heating rates. This procedure eliminates the influence of nucleation that may occur during heating. The Avrami parameter (n), present in the kinetic law of most crystallization processes, the KJMA equation (Zanotto 1992)

$$x = 1 - \exp\left(-K \times t^n\right) \quad (1)$$

was determined by means of

$$n = \frac{2.5 \times R \times T_c^2}{\Delta T_{hh} \times \Delta E_a} \quad (2)$$

derived by Augis & Bennett (1978), where ΔT_{hh} is half-height width of the crystallization peak. The Avrami parameter ranges from 1 to 2 for needle-like crystals, from 2 to 3 for lath-like crystals, and from 3 to 4 for three-dimensional ones. The application of a glass-ceramic may depend on crystal dimensionality.

The glasses used in this study came from the following batches (Oliveira 2000): glass 1 (70% BFS and 30% ECC), glass 2 (40% BFS, 30% CJW and 30% ECC), and glass 3 (70% CJW and 30% ECC). They were ground in 100% below 105 μm in a ceramic ball mill, and characterized by chemical analysis and X-ray diffraction, XRD, (Bruker AXS D5005, Cu Kα radiation, 5 to 70° 2θ).

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

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

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

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

3 RESULTS AND DISCUSSION

The chemical composition (acid dissolution, volumetric and gravimetric analyses) of the glasses (Table 1) shows Glass 1 with high CaO, Al_2O_3, SiO_2, and MgO contents while glass 3 contents high MgO, Al_2O_3, SiO_2, Fe_2O_3 and Cr_2O_3. Glass 2 has an intermediate chemical composition.

Glasses 1 and 2 displayed fully amorphous XRD patterns (hump), while glass 3 showed the hump and some small peaks with the diffraction pattern of magnesiochromite, $(Mg,Fe)(Cr,Al)_2O_4$, probably arising from the not fast enough cooling of the melt.

Table 1: Chemical composition of the glasses.

Content (%)	Glass 1	Glass 2	Glass 3
SiO_2	44.1 ± 0.1	50.6 ± 0.1	53.2 ± 0.1
Al_2O_3	22.6 ± 0.1	18.8 ± 0.1	16.3 ± 0.1
CaO	27.5 ± 0.1	15.7 ± 0.1	1.4 ± 0.1
MgO	4.9 ± 0.1	9.8 ± 0.1	18.8 ± 0.1
Na_2O	< 0.1	< 0.1	0.5 ± 0.1
K_2O	< 0.1	0.1 ± 0.1	0.7 ± 0.1
Fe_2O_3*	0.8 ± 0.1	3.2 ± 0.1	4.8 ± 0.1
MnO	< 0.1	0.3 ± 0.1	0.2 ± 0.1
Cr_2O_3	< 0.1	1.4 ± 0.1	4.0 ± 0.1

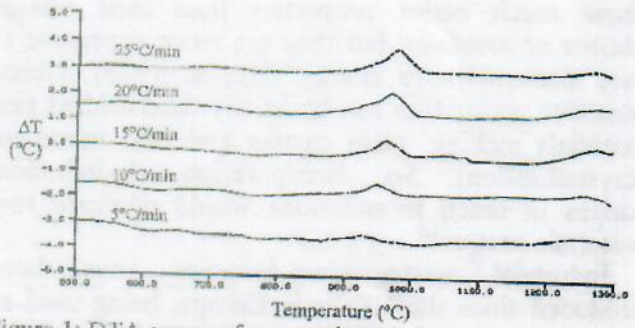

Figure 1: DTA curves of non-nucleated glass 3.

Examples of DTA and nucleation curves are in Figures 1 and 2, respectively. The exothermal peaks due to crystallization show up on the DTA at Figure

1, and the maximum nucleation temperature might be derived from Figure 2.

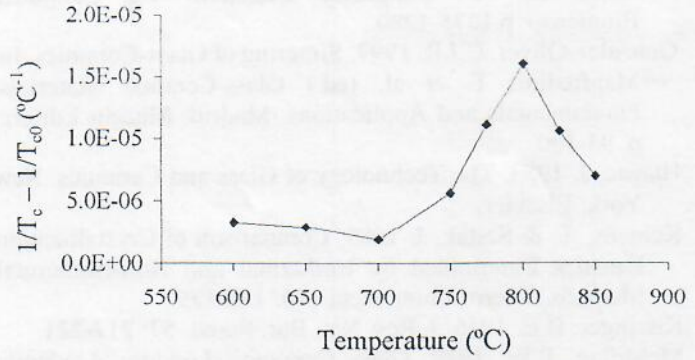

Figure 2: Nucleation curve of non-nucleated glass 2.

Table 2 summarizes the results obtained with DTA for the performed crystallization studies.

Table 2: Crystallization Properties.

Glass	E_a (kJ/mole)	n	T_c (°C)	T_{nuc} (°C)	E_a* (kJ/mole)	n*
Glass 1	396	1.3	1093	925	-	-
Glass 2	338	2.8	1002	800	489	1.9
Glass 3	369	2.2	948	800	418	1.7

* Glasses nucleated before the crystal growth exotherm.

The DTAs of glass 1 showed wide and not intense crystallization peaks, that disappeared after nucleation. The higher T_{nuc} (error ± 5 °C) of this glass, occurring very close to the crystallization peak onset (not shown), could indicate simultaneous crystal growth and nucleation. The Avrami parameter (error ± 0.2) of this glass near 1 and the wide exotherms are indicative of surface crystallization mechanism (Fonseca et al. 1993, 1994, Oliveira et al. 1995, 1997).

Glasses 2 and 3 show the same T_{nuc}, and when pre-nucleated E_a (error ± 20 kJ/mole) increases n decreases. Differently from glass 1, their T_{nuc} values are just a little higher than glassy transition, T_g, (≈ 770°C for glass 2 and ≈ 750°C for glass 3). Glasses 2 and 3 Avrami parameters indicate bulk nucleation and lath-like crystals (for just one crystalline phase).

The crystalline phases generated in the heat-treated glasses were identified by XRD (Table 3). The chemical formulas of these phases are in agreement with the main components of the glasses. The crystalline phases start to appear in XRD at the temperatures assigned in Table 4, agreeing with the DTA crystallization onset temperatures (not shown). Glasses 2 and 3 when heat-treated generate two crystalline phases, one of them presenting uni-dimensional growth (the pyroxenes diopside and enstatite) and the other one, three-dimensional structure (the feldspar anorthite and the spinel magnesiochromite). Therefore the Avrami parameter values for these glasses near 2 reflect the effect of both phases in the crystallization kinetics.

Table 3: Crystalline phases generated in the glasses.

Crystalline Phases	1	2	3
$T_{cryst,XRD}$ (°C)	950	925	925
Anorthite $CaAl_2Si_2O_8$	•	•	
Gehlenite $Ca_2Al_2SiO_7$	•		
Diopside $Ca(Mg,Al)(Si,Al)_2O_6$	•	•	
Enstatite $MgSiO_3$			•
Magnesiochromite $(Mg,Fe)(Cr,Al)_2O_4$			•

Heating microscopy (Table 4, Figures 3, 4) indicated higher characteristic temperatures (error ± 5 °C) for glass 3, also showing sintering temperature range very close to softening temperature, indicating that crystallization precedes sintering.

Table 4: Characteristic Temperatures (DIN 51730).

	Sintering (°C)	Softening (°C)	Melting (°C)
Glass 1	840-920	1230	1260
Glass 2	840-920	1222	1237
Glass 3	1180-1270	1298	1350

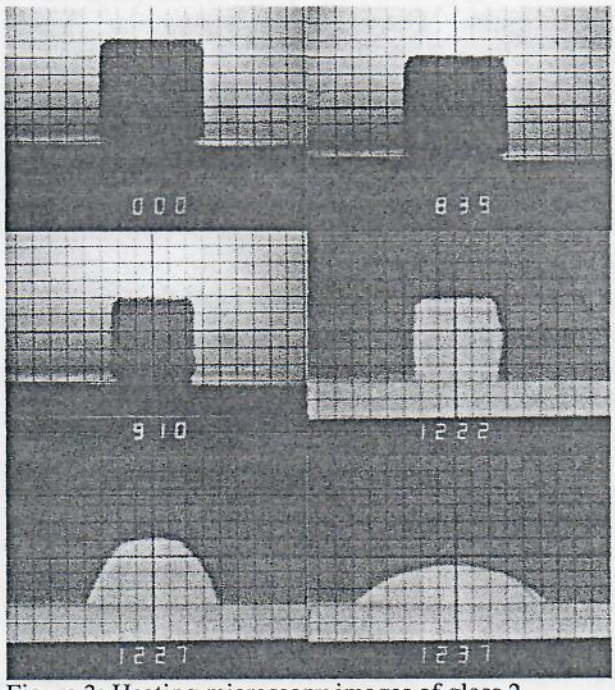

Figure 3: Heating microscopy images of glass 2.

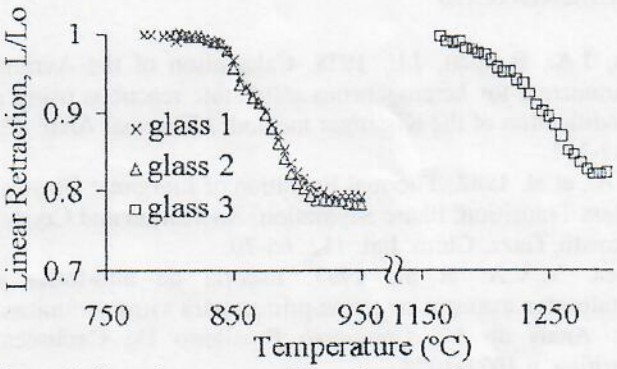

Figure 4: Sintering curves of the glass powders.

Glasses 1 and 2 sinter while still glassy, and their sintering curves end before the beginning of crystallization (XRD and DTA).

Table 5 shows the sintering temperatures applied to the glass compacts (determined by sintering curves in Figure 4) and some properties of the solid bodies obtained. The high specific weight (closed pores + solid) and low open porosity values indicate effective sintering and possibility of obtaining good quality glass-ceramics.

Table 5: Properties after heating the compacts.

Glass	Sintering Temperature (°C)	Specific Weight (g/cm^3)	Open Porosity (%)
1	900	2.80 ± 0.02	1.2 ± 0.1
2	900	2.84 ± 0.02	0.8 ± 0.1
3	1200	2.83 ± 0.02	0.5 ± 0.1

4 CONCLUSIONS

The sintering and crystallization studies indicated the best suited glass-ceramic production procedures for each glass. Glass 1 (sintering at lower temperatures than surface crystallization) is adequate for glass-ceramic sintering route. Glass 3 (sintering at temperatures much higher than bulk crystallization and near melting point) is adequate for glass-ceramic production by heat treating glass monoliths. Glass 2 (sintering at lower temperatures than bulk crystallization) is adequate for both routes.

Iron and chromium oxides confirmed their nucleating properties in the glasses studied.

Glass-ceramic production from only industrial wastes as raw materials is technically feasible.

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