Study of devitrification in ceramic frit waste to produce glass-ceramic materials

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Abstract: *This work consists of studying the devitrification capacity of ceramic frit waste, using the vitreous powder sintering method. Initially, the frit residue has been characterized by instrumental techniques such as XRF, XRD and DTA. Then, the green glassy tiles obtained using the traditional ceramic method, have been treated at different thermal cycles to cause the crystal growing. The evaluation of the generated crystalline phases has been performed using the XDR and SEM techniques, obtaining that the ceramic frit waste devitrifies in wollastonite crystals as majority phase and without being subjected to the melting step of the glass-ceramic typical method.*

Key words: *Waste, frit, ceramic, devitrification, glass-ceramic.*

INTRODUCTION

The attempt to manage industrial processes with zero residue is an unrealistic issue to what manufacturing processes have to tend, in order to improve the environmental conservation for future generations[1-3]. However, the vitrification process can significantly increase the chemical uniformity of very heterogeneous mixtures even containing hazardous and toxic heavy metals, reaching sufficient compositional stability and modular system to ensure the final properties waste as raw material [4 - 6]. In that sense, the glass-ceramic materials design from industrial waste, particularly, sludge from blast furnaces, started 40 years ago in USSR, thanks to the hard work by Pavlushkin and Kitaigorodski. Some of these glass-ceramic products have become commercial products (Slagsitall, Slagceram, Slagkyston, containing phases of wollastonite and anorthite) or pre-industrial products (Silceram containing pyroxene). Their main applications are focused in the field of abrasion resistive materials (e.g. roofs of industrial buildings, facades) and as high temperature insulating coatings. Thus, the low cost and availability of raw materials make these glass-ceramics materials very attractive from an economical point of view [7 - 13].

The aim of the present research is to study the capability of devitrification of ceramic frit waste in order to produce glass-ceramic materials from industrial waste.

EXPERIMENTAL

Characterization of ceramic frit waste

The ceramic frit waste, from the industrial manufacture of soda-lime type frits, was standardized by mixing to ensure its homogeneity and representability from the total waste. Then, the ceramic frit waste has been wet micronized by means of alumina ball mill with a load of 150 g distilled water, 150 g of sample powder and 250 g of alumina balls as milling agents, enough to obtain a particle size less than 45 microns, proceeding to subsequent drying period.

The instrumental techniques used to characterize the obtained frit material were the elemental analysis (XRF) equipment made by X-ray fluorescence by wavelength dispersion using a Pioneer Bruker model S4; the technique of X-ray diffraction (XRD) through an X-ray diffractometer, model Bruker D4 Endeavor in the range of 10°- 80° (2θ) with a step 0.05°/2s) and thermodifferential analysis (DTA) by an equipment of Bähr model STA 503.

Glassy tiles preparation

The glassy powder after being micronized under 45 micrometres was wetted at 10%wt and afterwards, it was screened again through a 45 micrometres mesh, in order to remove lumps and to prevent cracks in the pressed pieces. Next, the sieved powder was pressed with a uniaxial press Nannetti up to a pressure of 100 kg/cm^2, obtaining rectangular pieces which were then dried to remove residual water from wetting step, before the thermal treatment. The selection of these parameters has been extracted from industrial data.

Thermal treatment of glassy tiles

The glassy tiles were fired in a muffle kiln (Nannetti) at different temperatures such as 800ºC, 825ºC, 850ºC, 875ºC and 900ºC, following the cycle indicated in Table 1.

Table 1 Thermal treatment of glassy tiles in the muffle kiln.

	Initial temperature (ºC)	Final temperature (ºC)	Time (min)	Heating rate (ºC/min)
Step 1	30	T. max	18	48.3
Step 2	T. max	T. max	2	-
Step 3	T. max	30	90	-9.7

The different pieces obtained after the thermal treatment have been characterized by the following techniques. X-ray diffraction were carried out to evaluate the level of crystallisation, using a Bruker-AXS D4 Endeavor, while microstructure of vitrified and crystallized pieces was studied by a Scanning Electron Microscopy (SEM) model JEOL 7001F, supported by an energy dispersive X-ray analyser (EDX).

RESULTS AND DISCUSSION

Ceramic frit waste

The chemical composition of the ceramic frit waste is shown in

Table 2, where it is exhibited the chemical analysis results, acquired for the corresponding oxides in wt%. The frit waste presents as majority elements Si, Ca and Na with a LOI around 3wt%. It means that the potential crystals appeared after the thermal treatment could belong to the Si-Ca-Na system.

Table 2. Chemical analysis (XFR) of ceramic frit waste (wt%).

Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	ZrO_2	BaO	PbO	ZnO	LOI
10,40	0,00	3,96	57,70	1,84	20,30	0,00	0,00	0,10	0,54	0,27	1,09	3,14

The diffractogram corresponding to the frit waste is exhibited in Figure **1**, showing that this waste does not contain any crystalline fractions, so it is completely amorphous material, appropriated for production of glass-ceramics via suitable thermal treatment.

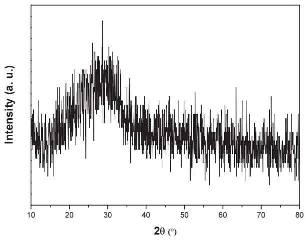


Figure 1. XR diffractogram of ceramic frit waste

The DTA result represented in Figure 2 indicates that the ceramic frit waste has the maximum crystallizing rate at 848 ºC. Hence, the range of temperatures tested in the thermal treatment must be between 800 ºC and 900 ºC, in order to study the crystal growing rate.

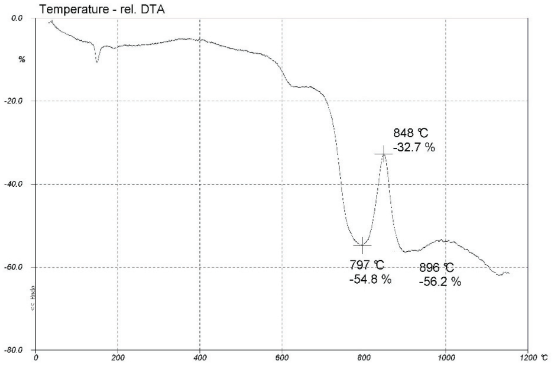


Figure 2. DTA of the ceramic frit waste

Thermal treatment

The XRD results, acquired for the treated glassy tiles obtained from the ceramic frit waste are plotted in Figure 3, where the diffractograms corresponding to different temperatures are compared. No crystals appear until 850 ºC. The thermal treatment at 850 °C has caused appearance of wollastonite as predominant crystalline phase with calcium sodium silicate as residual phase, when glassy tiles have been heated. Furthermore, intensification of these peaks was observed with increase of the treatment temperature. Their intensification coincides with the maximum crystallization peak increment registered by DTA analysis (Figure 2).

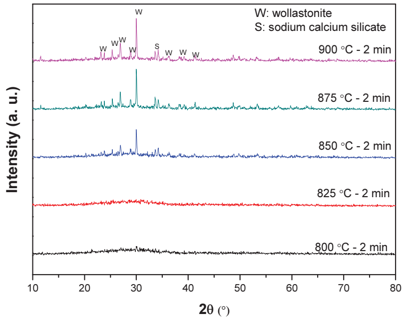
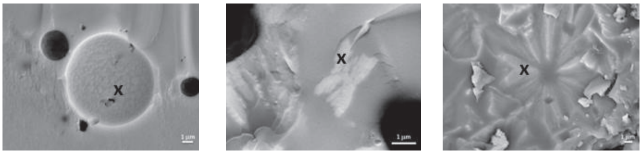


Figure 3. XR diffractograms of ceramic frit waste treated at different temperatures

Figure 4 shows the progression in the formation of crystals from a range between 800ºC and 900°C, which includes the maximum sintering temperature within a residence time only for 2 minutes, in order to avoid an excessive growth of crystalline phases formed with increasing temperature. The sizes of the crystals obtained are shown in the micrographs made with a scanning electron microscope (SEM). The chemical analysis by EDX, makes a rise in the percentage of CaO as the temperature rises, tending to approach the theoretical formula of wollastonite (48.3% CaO and 51.7% SiO_2), although the fact that the microanalysis has shown a mixture of the two distinguishable crystalline phases detected by XRD.

a) **b)** **c)**



800ºC		850ºC		900ºC	
Na_2O	11.72	Na_2O	5.9	Na_2O	4.39
Al_2O_3	2.68	Al_2O_3	2.62	Al_2O_3	1.61
SiO_2	63.06	SiO_2	60.26	SiO_2	60.99
K_2O	1.46	K_2O	1.13	K_2O	0.74
CaO	20.40	CaO	30.09	CaO	32.27

Figure 4. SEM micrographies and microanalysis (%wt) of glassy tiles sintered at different temperatures: a) 800ºC, b) 850ºC and c) 900ºC.

CONCLUSIONS

The thermal treatment of the glassy tiles of ceramic frit waste at temperatures above 850°C, has facilitated the crystallization of wollastonite as predominant phase and also sodium-calcium silicate as residual phase, embedded in a sodium enriched vitreous matrix. Hence, the ceramic frit waste material, studied can be successfully used as a precursor of glass-ceramic material, because it can easily devitrify. Moreover, it is not necessary to subject it to a conventional melt processing, since it already has a completely amorphous nature of departure, as its diffractogram indicates. Thus, significant energy savings produced by melting excluding the melting stage as an intermediate technological operation, which usually demands at least 1400 ºC, placing it in a traditional way ready to process ceramic waste. Also noteworthy is that crystals have formed in unfavorable conditions, only 2 minutes hold at maximum temperature without the addition of nucleating agents that promote devitrification. Thus, it appears that the ceramic frit waste has a great potential to become a glass-ceramic material, by the thermal procedure proposed in the present study. The present research provides a suitable heat treatment, designed by modifying the crystallization temperatures and residence times at such temperatures. Finally, this glass-ceramic material is applicable for the high performance construction industry, due to its remarkable mechanical performance [14 - 15].

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