

Study of thermal treatment parameters in the obtention of glassceramic materials with the addition of industrial residues

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ABSTRACT

The production of materials from crystallization of glass, called glassceramic, have proved interesting by the possibility of development of different microstructures, with reduced grain size and the presence of residual amorphous phase in different quantities, but with reduced porosity. The method that uses the differential thermal analysis (DTA) provides research on the material properties over a wide temperature range, it's widely applied to crystallization processes of glassceramic materials. Within this context, this paper aims to study the kinetics of nucleation and crystal growth in glassceramic materials in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$, obtained with the addition of mineral coal bottom ash as source of aluminosilicates, through the technique of differential thermal analysis.

1.0. INTRODUCTION

The production of materials from the melting and crystallization of glasses, the so-called glass-ceramic has been shown by the interesting possibility of development of differentiated microstructures with reduced grain size, random orientation, with the presence of residual amorphous phase in different amounts, but with reduced porosity [1]. These features allow to obtain materials with different properties from those obtained in ceramics produced by conventional processes. The glass-ceramic is characterized by a great diversity of behavior and properties technical / technological. Another important feature in the production of glass-ceramic is the possibility of utilization of raw materials that are difficult to be reused in the conventional processes, such as industrial residue, which features: the blast furnace slag, furnace slag, fly and bottom coal ash, among others.

The use of the theories that govern the phenomena of crystallization for the development of glass-ceramic materials from coal bottom ash was an important step for obtaining materials with high technological benefit, generating options that reduce industrial environmental problems enabling reducing costs of raw materials necessary for the proceedings [2].

In terms of participation in the Brazilian energy matrix, According to Electric Power Atlas of ANEEL 2009 [3], the coal is currently responsible for about 11% of the energy matrix and tends to increase its stake to 13% by the year 2030. At the global level, despite the serious impacts on the environment, coal is still an important source of energy. In the case of Brazil, a strong argument for the use of heavy ash is the amount generated by combustion of domestic coals (subbetuminoso), which can reach more than 50% by weight [4].

The crystallization process for the development of a glass ceramic material can be divided into two steps: nucleation or formation of crystalline germs and crystal growth by deposition of material on the nuclei formed. The microstructural control of a glass ceramic material through a controlled crystallization process consists of a great tool for monitoring the properties. For this, it is need to evaluate the behavior of the material in relation to changes in certain parameters such as time of nucleation and crystallization. There are differences between a glass ceramic, obtained by a controlled crystallization of a glass material of origin of a piece of glass that has undergone the process of spontaneous unglassy process, a problem with which the glass industry that has sometimes come across and which consists in the formation of unwanted products that were previously completely glassy.

According to literature [5], differential thermal analysis, DTA, provides simple properties investigations on a wide range of temperatures, being widely applied to studies of crystallization. Other techniques used are the classic method through electronic and optical microscope observations, and the x-ray Diffraction DRX.

The method of differential thermal analysis DTA allows you to evaluate the efficiency of heat treatment nucleation used, through the variation of the peaks of crystallization of temperate sample relative to the specimen previously nucleate. Using this procedure it is possible to estimate the temperature of maximum nucleation rate ($T_{n_{max}}$), and the kinetics of nucleation, i.e. the frequency of nuclei in relation to time (t_n).

The objective of this paper is to study the parameters of heat treatment of nucleation and crystal growth for the development of glass-ceramic system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Li}_2\text{O}$, with the addition of by-product of mineral coal bottom ash, through the technique of differential thermal analysis (DTA).

2.0. MATERIALS AND METHODS

2.1. Obtaining Vitreous Materials

The samples of coal bottom ash where used after drying in an oven at 180°C for 24 hours. The chemical characterization of bottom ash was performed by X-Ray Fluorescence (XRF).

It was used two compositions of glassy materials with the addition of bottom ash from coal for the study of thermal parameters. The glassy materials were named: VT1, material obtained from raw ash and VT2, material obtained from the corrected ash. This correction was made with the removal of magnetic iron oxides present. This process was conducted by submitting the sample to a magnetic field of 1000 Gauss [6]. Were added Al_2O_3 and TiO_2 in the form of commercial rutile, so, the deferrized ashes became the corrected ash. These were obtained by fusing a mixture of composition of 85% ash with the addition of 15% of Li_2CO_3 by weight. The mixtures were calcined in an oven at 800°C for 4 hours. The fusions were performed in alumina-zirconia-silica crucibles.

The compositions studied were melted under thermal cycles that sowed, for glass VT1, a dwell at 1310°C for 30 minutes, which occurs the decomposition of lithium carbonate and a dwell at 1400°C, aiming at the homogenization of the glassy mass. For glass VT2, the temperature

programming differs from the glass used in VT1, since iron oxide is present in smaller quantities, which strongly influences the viscosity of the glassy mass. For VT2, the steps includes a dwell for the fusion at 1310°C for 30 minutes, which is the decomposition of lithium carbonate and a dwell at 1550°C.

2.2. Determination of the Maximum Rate of Nucleation

The equipment used for the study of thermal behavior of the glass by DTA analysis was an STA Netzsc, model 409 C. Both crucibles used, the port and the reference sample, were alumina. The studies was performed under air atmosphere at a heating rate of 20°C/min. The material was embedded in beeswax and cut into diamond disc-shape in a "cut off" of brand Isomet. The specimens relating to the tests of DTA were cut in size of 3mm³.

According to the literature [7], the difference between the peak crystallization temperature of the sample tempered (T_p') and the value of T_p , for the samples previously nucleated versus the annealing temperature, nucleation, can express the curve of maximum nucleation rate.

The nucleation temperatures were set from the prior determination of the glass transition temperature by differential thermal analysis at a heating rate of 20°C/min. The temperate and previously nucleated samples for 15 minutes in different temperatures from T_g , were tested at a heating rate of 20°C/min. The value of 15 minutes has been optimized through several preliminary analysis, along with information drawn from the literature [8].

2.3. Kinetics of Nucleation

Threatening previously the samples at different times in maximum temperature nucleation rate ($T_{n_{max}}$), i.e. $T_p' - T_p$ versus thermal treatment times, it is obtained a curve of isothermal nucleation, whose behavior that allows to evaluate a number of cores, that increases with the duration of treatment crystalline.

In the nucleation kinetics curve, the optimum time (t_0) is determined as being the time of heat treatment maximum in T_n , that does not cause comparatively modifications of XRD glass precursor.

2.4 Obtaining the glass-ceramic materials

The heat treatment of nucleation and crystallization were performed in oven model Lab 0.36/TB - 1300°C, brand Schaly. The maximum values of nucleation rate and kinetic studies were used as a criterion for the choice of heat treatment temperatures.

To obtain the VCR1 material, vitro-ceramic derived from raw ash was applied to a thermal cycle of 15 minutes at a temperature of maximum nucleation rate determined (720.0°C), followed by 20 minutes in the crystallization temperature (830.0°C) in the origin glass VT1. To VCR2, the permanence of glass VT2 in temperature of maximum nucleation rate was 730.0°C for 15 minutes, followed by 30 minutes at 870.0°C.

3.0 RESULTS AND DISCUSSION

3.1. Characterization of Residue

The chemical analysis of raw bottom ash, collected at Jorge Lacerda/SC thermoelectric plant, after the process of iron removal are presented in Table 1.

Table 1. Chemical analysis of bottom ash collected and bottom ash deferrized in oxides (wt%).

Oxide	bottom ash	deferrized bottom ash
SiO ₂	54,34	55,48
Al ₂ O ₃	22,82	23,21
Fe ₂ O ₃	9,96	5,36
Cão	1,55	1,36
Na ₂ O	0,17	0,16
K ₂ O	2,40	2,39
MgO	0,03	0,51
TiO ₂	1,07	1,05
MnO	0,52	0,03
P ₂ O ₅	0,06	0,06
LOI	7,07	9,41

Table 1, shows that, of the total of 9.96% of iron oxides present in the raw bottom ash, it was retired about 54%. The TiO₂ content present in about 1% acts as a intrinsic nucleating agent of the system, favoring the appearance of crystalline germs during the heat treatment process of crystallization.

The mineralogical analysis shows that the crude bottom ash (CPB) is composed of two majority crystalline phases: quartz (SiO₂ - JCPDS 5-490) [9] and mullite (3Al₂O₃.2SiO₂ - JCPDS 15-776) [9], and two minority phases of magnetite (Fe₃O₄ - JCPDS 19-629) [9] and hematite (Fe₂O₃ - JCPDS 13-534) [9], associated with high content of iron oxide present in its composition.

3.2 Determination of Maximum temperature nucleation rate for Vitreous Materials

The glass transition and crystallization for the tempered sample glass VT1 were determined as 639.0°C and 832.36°C respectively. Table 2 shows a summary of the results obtained through the thermal analysis performed on the sample VT1 nucleated at different temperatures.

Table 2. Summary of results obtained by differential thermal analysis to VT1.

Nucleation Temperature (°C)	Crystallization Temperature (°C)	Tp' - Tp (°C)
640	822,48	9,88
660	826,06	6,30
680	829,50	2,86
700	818,10	14,26
710	817,50	14,86
720	808,59	23,77
730	820,20	12,16
740	823,88	8,48

The differences Tp'-Tp versus the temperatures of previous treatment nucleation resulted in the curve of maximum nucleation rate. The temperature of maximum nucleation rate was determined was approximately 720.0°C. In this temperature occurs the largest formation of nuclei, the temperature at which nucleation is favored.

Compared to glass VT2, the glass transition temperature and crystallization for the tempered sample where obtained as 642.0°C and 866.0°C respectively. According to Varshenya [10], the redox reactions involved in nucleante agent used, as well as some constituents of heavy gray, such as

iron oxide, are related to the most critical part of the melting of the glass, the refinement operation and, also, with the nucleation process. According to Magella [11], the dislocation of the crystallization temperature, noted by the crystallization temperature reduction with increasing temperature treatment, represents the largest formation of nuclei.

Table 3 presents a summary of the results obtained through the thermal analysis performed on the sample VT2 nucleated at different temperatures. Analyzing the obtained diagrams, there is also a difference in intensity between the exothermic peaks, which relates the energy of crystallization released.

Table 3 - Summary of results obtained by differential thermal analysis for VT2.

Nucleation Temperature (°C)	Crystallization Temperature (°C)	Tp' - Tp (°C)
680	830,16	35,84
700	827,66	38,34
710	826,28	39,72
720	825,17	40,83
730	814,08	51,92
740	839,43	26,57

The maximum rate nucleation temperature was determined as being approximately 730°C. From this temperature, the values of Tp'-Tp start decreasing as a result of increased formation of nuclei, which is a consequence of the tendency to stabilization of the system. It is possible say that from the maximum temperature nucleation rate begins to process the crystallization.

3.3. Determination of Nucleation Kinetics

The samples previously nucleated in $T_{n_{\max}}$ in increasing time from 5 minutes, were tested in the DTA, the heating rate of 20°C/min. Through of the Tp'-Tp values versus the time of previous thermal treatment of nucleation, we obtained the curve of kinetic nucleation to VT2, i.e. the qualitative frequency of nuclei in relation of time (Fig. 1).

The tendency of the obtained curve is related to the results described in the literature [9]. The optimal time for nucleation for $T_{n_{\max}}$ was determined to be 15 minutes. This result means that this maximum time of heat treatment on $T_{n_{\max}}$ were not observed in comparison with tempered glass, changes in diffractometry of the sample neither crystalline phase formation.

The importance of determination of kinetic parameter is in function of a controlled heat treatment process for glass-ceramic materials with specific characteristics, i.e. a proper monitoring of the nucleation phase.

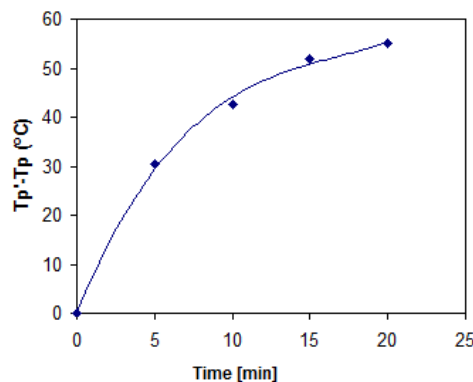


Fig. 1 - Tp'-Tp values versus the time of previous thermal treatment of nucleation.

4.0 CONCLUSION

The study of heat treatment parameters, involving nucleation and crystal growth, for the development of glass-ceramic materials by a controlled crystallization process consists of a great tool for monitoring the properties. The method used, using DTA, allows to determinate these parameters. This approach has, as main advantages, compared with other techniques, speed and ease of measurements, small sample size (for glassy material) are needed and the fact that heat treatments can be performed in the equipment's oven.

5.0 REFERENCES

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