

THE USE OF BLAST-FURNACE SLAG AND FLY ASH FOR PRODUCING GLASS-CERAMICS BY SINTERING

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ABSTRACT

The growing interest in developing products and processes for reducing the volume of produced waste, or the use of waste as raw materials, responds to the need to meet environmental protection regulations. These regulations are designed to preserve raw materials sources and suppress waste storage or disposal sites.

In the ceramic tile branch, waste rich in silicates can be reused in body compositions for floor and wall tile production or for obtaining glass-ceramic materials, which are defined as polycrystalline solids, with the presence of an amorphous phase, obtained from glass melting and crystallisation.

The production of glass-ceramic materials from waste has been widely researched over the last three decades. The forerunners in this field developed commercial glass-ceramics from iron and steel industry slag, focussing on the use of blast-furnace slag (slagceram, slagsital and slagkyston). Over the last decade, however, a greater effort has been made to produce glass-ceramics by using fly ash from different industrial processes or from the incineration of urban refuse as a basic raw material. The common characteristic of these two materials, iron and steel industry slag and fly ash, is their high SiO₂ and Al₂O₃ content.

In the case of glass-ceramics from blast-furnace slag, their high CaO and MgO contents give the glass a strong basic character, which causes corrosion in the refractories used. When fly ash is used, the high SiO₂ and Al₂O₃ contents are responsible for melting temperatures exceeding 1500°C. These factors explain the need to adjust the waste composition by adding pure raw materials or a combination of two or more wastes. The current tendency is to research combinations of wastes, and one of these options is the use of mixtures of blast-furnace slag and fly ash. The use of fly ash in these mixtures is designed to facilitate glass production, changing the microstructural characteristics and modifying the type of arising crystalline phase.

Brazil produces 423 Mt.m. of slag yearly, 61% of which is blast-furnace slag. This slag, which can be found raw or granulated, is used almost exclusively in cement compositions. However, fly ash can come from different industrial processes, an important source being thermoelectric power plants. In Brazil, a plant that produces 272000 Mwh/month, consumes on average 172 kt of coal a month, producing 47 kt of fly ash. Only 40% of this is marketed for use in the paving and civil building construction industry. These figures confirm the feasibility of developing processes and products that use these wastes as raw materials.

In the production of glass-ceramics from waste, the crystallisation mechanism as well as the structure and morphology of the arising crystals are greatly affected by factors such as waste composition (with a great influence of the minor components), the presence of nucleating agents, glass thermal history and kiln atmosphere. In general, crystallisation is predominantly by a surface mechanism, which favours use in producing glass-ceramics by sintering, presenting the possibility of making low porosity materials as the main advantage.

In this study, blast-furnace slag and fly ash were combined to produce a glass of the system SiO₂-MgO-CaO-Al₂O₃-R (R=Fe₂O₃, MnO, TiO₂ etc.). The crystallisation mechanism, crystallisation kinetics and crystallised phases were respectively studied by differential thermal analysis, X-ray diffraction, and scanning electron microscopy. The glass-ceramics obtained by sintering were characterised with regard to behaviour during sintering and crystallisation heat treatment, by determining bulk density and arising crystalline phases.

Crystallisation occurred by surface mechanisms, giving rise to the formation of melilite, plagioclase and pyroxene phase groups, the melilite appearing with the greatest volume and the diopside being the most stable phase at high temperatures. Sintering started at about 780°C, attaining maximum densification at 900°C. The maximum density achieved was 2.5g/cm³ and was obtained by sintering at 900°C. Crystallisation initiated at temperatures above 850°C, reducing interaction between the sintering and crystallisation mechanism.

High shrinkage occurs during sintering, which needs to be controlled to ensure appropriate product dimensions. Final density, crystallinity and the type of arising crystalline phase were influenced by heat-treatment temperature, which needs to be defined in terms of desired end product properties.