

CRYSTALLIZATION KINETICS OF GAHNITE GLASS-CERAMIC FROM COAL GANGUE AND GALVANIZING WASTE

Jaime de Oliveira Filho, Fábio Elyseu, Adriano Michael Bernardin

Ceramic Materials Group, UNESC, Criciúma, Santa Catarina, Brazil

This work aimed at using coal gangue and galvanizing wastes to obtain glass-ceramics. Coal mining, galvanizing and sandstone wastes were used as raw materials for parent glass formulation using mixture design with central points (simplex design). After chemical characterization (XRF), the wastes were dried, milled and blended according to the mixture design. Ten formulations were melted in alumina crucibles at 1600 °C for 3 h and were characterized by differential scanning calorimetry (DSC), dilatometry and X-ray diffraction (XRD). The parent glasses consisted mainly of SiO₂, Al₂O₃, Fe₂O₃ and ZnO. No crystalline phases were observed in the parent glasses, confirming their amorphous nature. For some glasses, the crystallization activation energies and the Avrami coefficients were calculated. As a result, one parent glass could be crystallized into glass-ceramic with gahnite as the only crystalline phase.

1. INTRODUCTION

Glass-ceramics are polycrystalline ceramic materials produced by the controlled devitrification of a parent glass in contrast to an undesirable uncontrolled crystallization. They consist of one or more crystalline phases immersed in an amorphous phase [1,2]. In order to produce glass-ceramics, a conventional glass route is used to form the parent glass that is subsequently crystallized by two-stage heat treatment process: formation of submicroscopic nuclei (nucleation), and their growth into macroscopic crystals (crystal growth). Glass-ceramics are produced from naturally occurring minerals as raw materials. However, they can be prepared from mining and industrial wastes, becoming a suitable way to valorize residues and make them inert [1-3].

Possible residues that can be used as raw material for glass-ceramics manufacturing are coal gangue and hot dip galvanizing waste. Coal gangue is a solid and complex industrial waste that is formed when coal is excavated and washed in its processing. Primarily SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and heavy metals form coal gangue. Quartz, which becomes silica fume when the coal gangue spontaneously decomposes, calcined alumina, after burning, and feldspar are the predominant mineralogical phases, showing the potential use of this waste as a raw material in the production of glass-ceramics. Some studies have been developed about obtaining glass-ceramics from coal mining waste, or coal gangue [1-3].

Therefore, the aim of this study was the use of two common wastes, coal gangue and galvanizing waste containing zinc, as starting materials to obtain a glass matrix that could, by an appropriate heat treatment, be processed as glass-ceramic. DoE was used to design glass compositions that were studied by DSC and dilatometry thermal analyses in order to determine the composition most suitable to be devitrified. Three thermodynamic models were used to determine the activation energies for crystallization.

2. MATERIALS AND METHODS

Three residues were used as raw materials for obtaining the starting glasses in this study: coal gangue, galvanizing waste and sandstone. The residues were characterized by XRF. 10 formulations with three factors and central points were designed in a simplex-lattice mixture design (DoE). The residues were dried, sieved, and mixed according the design. The parent glasses were obtained by melting the raw material mixtures in alumina crucibles at 1600 °C for 180 min in an electric furnace, and subsequently quenching the melts in cold water. The parent glasses were studied by DSC/TG at 10, 20 and 30 °C/min (into synthetic air) and by dilatometry at 5 °C/min. The structure of the glass melts was determined by XRD (Cu K_α ($\lambda=1.5406 \text{ \AA}$), 40 kV and 40 mA, 2θ from 2° up to 72°, 0.05° step for 2 s. Finally, the microstructure of the glass-ceramic was determined by SEM on polished and etched (1 vol% HCl) surfaces.

3. RESULTS AND DISCUSSION

The coal gangue is an aluminosilicate containing sodium and potassium oxides and a high amount of iron oxide. The galvanizing residue consisted mainly of zinc oxide, the waste being refractory. Sandstone was used as a flux, providing a mineralizing effect in the glass compositions. No other component was added to the glass compositions to help melting. Regarding the parent glass compositions the major components are SiO_2 , Al_2O_3 , Fe_2O_3 and ZnO . Regarding the XRD analysis, no peaks related to crystalline phases were observed for all compositions, confirming their amorphous nature.

The dilatometric analysis showed the glass transition temperature (T_g) only for samples A3 (100% sandstone), A5 (50% coal gangue and 50% sandstone), A7 (33% coal gangue, 33% galvanizing residue and 33% sandstone) and A8 (17% sandstone, 66% coal gangue and 17% galvanizing residue), meaning that they formed glass systems. From the DSC studies, only samples A5 and A7 could be crystallized, i.e., devitrified in order to form glass-ceramic systems. Both samples are able to vitrify and both samples show exothermic peaks typical of glass crystallization. It must be noted that, for powdered glasses, sintering starts before crystallization during heat treatment in order to obtain glass-ceramics. Therefore, the sintering and the crystallization processes are competing with each other.

The results from DSC and dilatometry showed that sample A7, containing 33% coal gangue, 33% galvanizing residue and 33% sandstone, undoubtedly forms a glass system and can be devitrified into a glass-ceramic material. Therefore, the activation energy for crystallization and its possible mechanisms were determined for this sample. The DSC analysis provided the data for the determination of the crystallization parameters for sample A7, and the calculation of the activation energy by Kissinger (1014.5 kJ/mol), Ozawa (1034.1 kJ/mol) and Matusita (1014.1 kJ/mol) methods was possible. The activation energy (E_a) is one of the most studied crystallization parameters for glass-ceramic materials. However, its real definition is not entirely clear. In general, E_a is considered a barrier to crystallization, since a minimal amount of energy is required for the crystallization process to begin. Therefore, the activation energy can be defined as the minimum energy required to initiate the crystallization process [5]. The Avrami parameter (n) is related to the nucleation and crystal growth mechanisms. It could be estimated by the Augis-Bennett equation. In this study, the value obtained for the Avrami coefficient was 0.4, which means that the A7 parent glass will undergo surface crystallization [6].

The XRD analysis revealed that the glass-ceramic formed gahnite crystals (ZnAl_2O_4 , JCPDS 005-0669) from the glass matrix, as shown in Figure 1a. All peaks shown in the diffractogram (2θ at 32, 35, 45 49, 55 and 60 degrees) belong only to the gahnite phase. No other phase but gahnite was identified. Gahnite ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$) forms a spinel structure when ZnO is doped with large amounts of Al. Gahnite is a ceramic material with high chemical and thermal stability, also presenting high mechanical strength [7].

Finally, Figure 1b shows the micrograph of the cross-section of sample A7 obtained by SEM. Some crystals protrude from the glass matrix (white coloured particles). The elemental analysis performed by EDS microprobe, not shown, indicates that the main elements are zinc, silicon, aluminium, iron and oxygen.

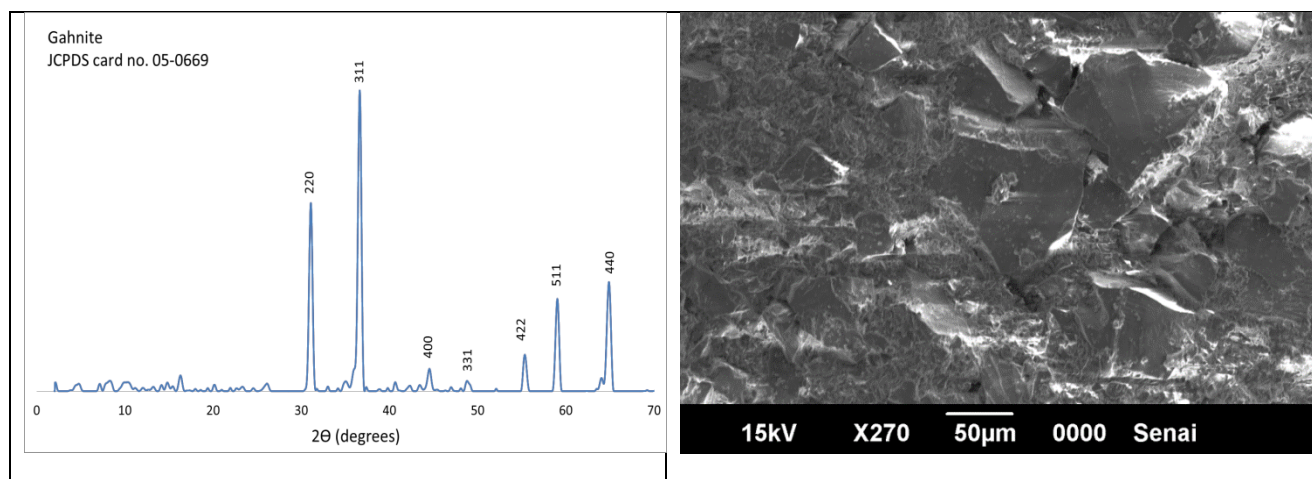


Figure 1. (a) XRD and (b) SEM image of the cross-section of sample A7 after heat treatment

4. CONCLUSIONS

The analysis of the crystallization kinetics for sample A7 (33% coal gangue, 33% galvanizing residue and 33% sandstone) shows that this glass would consume 1034.1 kJ/mol to be devitrified according to the Ozawa method and 1014.5 kJ/mol by the Matusita and Kissinger methods. The Avrami coefficient shows a possible surface crystallization for this glass material.

It is possible to obtain glasses from coal mining waste (gangue) and galvanizing waste containing zinc, using sandstone as flux. The most viable vitreous system able to result in a technological glass-ceramic product would use 2/3 of waste by weight in its composition. The mineral used as a flux, common sandstone, is inexpensive, not impacting the production of glass-ceramic materials.

REFERENCES

- [1] Nicoleau, E., Schuller, S., Angeli, F., Charpentier, T., Jollivet, P., Le Gac, A., Fournier, M., Mesbah, A., Vasconcelos, F. (2015) Phase separation and crystallization effects on the structure and durability of molybdenum borosilicate glass. *Journal of Non-Crystalline Solids*, 427, 17488, pp. 120-133.
- [2] Karamanov, A., Maccarini Schabbach, L., Karamanova, E., Andreola, F., Barbieri, L., Ranguelov, B., Avdeev, G., Lancellotti, I. (2014) Sinter-crystallization in air and inert atmospheres of a glass from pre-treated municipal solid waste bottom ashes. *Journal of Non-Crystalline Solids*, 389, pp. 50-59.
- [3] Vetere, F., Iezzi, G., Behrens, H., Holtz, F., Ventura, G., Misiti, V., Cavallo, A., Mollo, S., Dietrich, M. (2015) Glass forming ability and crystallisation behaviour of sub-alkaline silicate melts. *Earth-Science Reviews*, 150, pp. 25-44.
- [4] Haibin, L., Zhenling, L. (2010) Recycling utilization patterns of coal mining waste in China. *Resour. Conserv. Recycl.*, 54, pp.1331-1340.
- [5] Orava, J., Greer, A.L. (2015) Kissinger method applied to the crystallization of glass-forming liquids: Regimes revealed by ultra-fast-heating calorimetry. *Thermochimica Acta*, 603, pp. 63-68.
- [6] Montedo, O. R. K., Floriano, F. J., Filho, J. O. (2011) Sintering kinetics of a $18.8\text{Li}_2\text{O} \cdot 8.3\text{ZrO}_2 \cdot 64.2\text{SiO}_2 \cdot 8.7\text{Al}_2\text{O}_3$ glass ceramic. *Ceramics International*, 37, pp.1865-1871.
- [7] Battiston, S., Rigo, C., Severo, E Da C., Mazutti, M. A., Kuhn, R. C., Gündel, A., Foletto, E. L. (2014) Synthesis of zinc aluminate (ZnAl_2O_4) spinel and its application as photocatalyst. *Materials Research*. 17 (3), pp.734-738.