

STUDY ON THE PRODUCTION OF CERAMIC GLASS FROM CALCIUM-SILICA RESIDUE

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Keywords: calcium-silica residue; ceramic glass; comprehensive utilization; melting method

Abstract

Calcium-silica residue is the leaching residue of the lime sinter process which is used to extract alumina from low-grade bauxite or fly ash. The major phases of this residue are dicalcium silicate and calcium carbonate, and the minor phases are aluminates. A large amount of calcium-silica residue is produced because of the high material flow of lime sinter process and most of it is stockpiled. The main contents of the residue, CaO and SiO₂, are the same as the main contents of ceramic glass. Therefore, the production of ceramic glass using calcium-silica residue as the main raw materials, B₂O₃ as fluxing agent and P₂O₅ as nucleation agent is reported on in this paper. XRD and DSC are used to analyze the property of the ceramic glass. The results show that the flexural strength and corrosion resistance of the ceramic glass obtained through a melting method are better.

Introduction

With the development of the alumina industry, the shortage of bauxite is an increasingly serious issue. The A/S (Alumina to Silica mass ratio) of bauxite in the Bayer process in most alumina enterprises is lower than 5, low alumina-leaching ratio and high costs are the associated disadvantages. Dealing with low-grade bauxite and other alumina-containing materials by new technologies has become the research focus, at present. The lime-sintering process has some advantages over other processes [1-2]. Firstly, this process can provide high alumina-leaching ratio of low-grade bauxite and other alumina-containing materials; secondly, the replacement of sodium carbonate with lime made the cost lower than before; finally, this process can cause the self-disintegration of clinker. This method has many advantages in dealing with low-grade bauxite, but its requirement of raw materials and quantity of residue are both huge, and most of the residue is stockpiled.

The comprehensive utilization's study of alumina leaching residue mainly concentrated in the red mud of Bayer process. The calcium-silica residue of lime-sintering process has not been studied. Mishra B. [3] carried out a study on iron making from red mud with coke as the reducing agent. A further study on iron making from red mud with slag-leaching process has been carried out by Mishra [4]. In the former Soviet Union, the red mud of Bayer process has been used in the production of cement [5]. The study of using Bayer process red mud to produce compound barrier, antidrying agent with binder by Kaiser aluminum, the test of using red mud to produce wall tile has been carried out by alumina refinery in Spain [6]. In this study, the red mud was mixed with fly ash before a high pressure shaping, drying and sintering processes. The study of using red mud to produce cement, new-style tile, and filled plastics has been carried out by Japanese workers [7]; the study of using red mud to produce silicon fertilizer, valuable metal, porous ceramic filtration media,

filled plastics, high-classic pavement, glass-ceramic and new sintered cellular brick has been carried out by Chinese workers [8-9].

The study of using red mud, fly ash, and soda residue to reduce eximious glass-ceramic whose main phase is gehlenite has been successfully carried out by Li baoyi et al [10]. The comprehensive utilization of red mud, fly ash, and soda residue was up to 95%. The glass-ceramic which has a high microhardness, high bending strength and high alkali resistance was produced by a melting method, the utilization ratio of red mud was up to 60% [11]. The glass-ceramic which main phase is grossular was produced by a sintering process, the raw material is high CaO and SiO₂ contained red mud, and the the utilization ratio of red mud was up to 65%[12].

Calcium-silica residue and red mud share the same main compositions: SiO₂, CaO, Al₂O₃, but the CaO content of calcium-silica residue is higher than red mud, and the alumina content is lower than red mud. These oxides are the main materials of glass-ceramics. The production of glass-ceramics with cheap calcium-silica residue has both environmental advantages and economic advantages. This paper reports on the study of calcium-silica residue as the raw material for glass-ceramic performance.

1 Experiment

1.1 Materials

Calcium-silica residue is obtained from alumina plant. The other chemicals used: Al₂O₃, SiO₂, B₂O₃, Ca₃(PO₄)₂, are of analytical purity.

1.2 Equipments

Electronic balance, SFM-II planetary four head mixer, crusher, SFM-I planetary ball mill, KSL-1700X box-type high temperature sintering furnace, blower type constant temperature drying box, FY-24-A type powder tablet press machine, circular saw, ZBC1151 impact testing machine, D/MAX-2500 X-ray diffractometer (Rigaku Japanese company), S-4800-I SEM and EDX (Hitachi), STD-2960 DSC-TGA (TA).

1.3 Synthesis and analysis

Calcium-silica residue and pure reagents were weighed at a certain proportion using the electronic balance. And then they were mixed by SFM-II planetary four head mixer for 2h. The mixture was put into box-type high temperature sintering furnace and sintered for 2h at 350°C, and then sintered for 2h at 1500°C. and then was taken out at 1500°C and casted. After cooling, the mixture was put into high temperature sintering furnace and

annealed at 600 °C for 3h, and then, the preparation of the basic glasses was done.

Parts of the basic glasses were crushed and ground at the speed of 250r/min for 1h. Then they were identified by X-ray diffraction and DSC. Nucleation temperature and crystallization temperature can be obtained from the DSC results. After that, the glass-ceramic is heated under the two temperatures.

The glass-ceramic was incised into samples of 4×4×40mm for flexural strength analysis. The rest of glass-ceramic was crushed for XRD analysis. And the conditions were: 40 kv pressure pipe, 150 mA pipe flow, Cu Kα1 (λ=0.154056nm), 10 to 90° scanning range and 2 °/min scanning speed.

2 Results and discussions

2.1 Characterization of calcium-silica residue

XRD, SEM and XRF results of calcium-silica residue are shown in Fig. 1 and Fig. 2

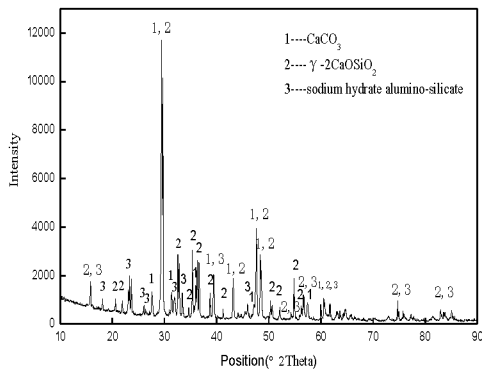


Figure 1. X-ray diffraction spectrum of calcium-silica residue

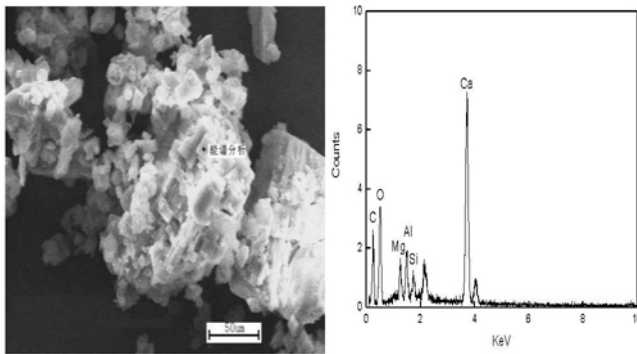


Figure 2. Apparent morphology of residue and EDS analysis results

Fig. 1 shows that CaCO_3 and $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ are two main phases of calcium-silica residue, there exists sodium hydrate alumino-silicate as well. The SEM results show that the microstructure of the leaching residue is agglomerated and irregular. The EDS result shows that the composition of the agglomerates is complex. According to the alumina leaching process and the XRD result, CaCO_3 , $2\text{CaO}\cdot\text{SiO}_2$, $\text{Mg}(\text{OH})_2$ and a small quantity of sodium

hydrate alumina-silicate are the main phases of the leaching residue.

In order to determine amount of the oxides, XRF analysis was carried out, and the result are listed in Table 1.

Table 1 Oxides content of calcium-silica residue by XRF (%)

CaO	Al_2O_3	SiO_2	TiO_2	Fe_2O_3
53.47	4.74	12.03	1.15	5.15

2.2 Determination of sintering process parameters

At present, there are two main methods for glass-ceramic production: a sintering process and a melting process. There are both advantages and disadvantages with both of these two methods. The melting process can use any kind of glass forming material, can produce complex-shape products, and there are less restrictions for the final glass composition than with the sintering process. Furthermore, there are no bubbles in the products from the Melting process (bubbles exist in the products from the sintering process), and the density of the Melting process products is higher than the density of the products using the sintering process. In this study the Melting process was used to deal with calcium-silica residue in order to produce glass-ceramics. The main crystal phases of the glass-ceramic are wollastonite, diopside and forsterite/gehlenite.

Because the content of CaO of calcium-silica residue is high, the main phase of ceramic glass was chose as gehlenite in this paper. B_2O_3 was used as flux and P_2O_5 was used as nucleating agent. The target composition of the ceramic glass was as follows: SiO_2 22~32%, CaO 41%, Al_2O_3 10~17%, MgO 7%, P_2O_5 4% and B_2O_3 2%. Calcium-silica residue was the raw material and purified reagents were added as auxiliary materials in the preparation of the glass-ceramic.

2.3 Characterization of ceramic glass

Basic glass was produced under the conditions in section1.3. a part of the glass-ceramic was crushed and grinded to below 75 micron, and then analyzed by DSC under atmosphere condition, the result are shown in Figure 3.

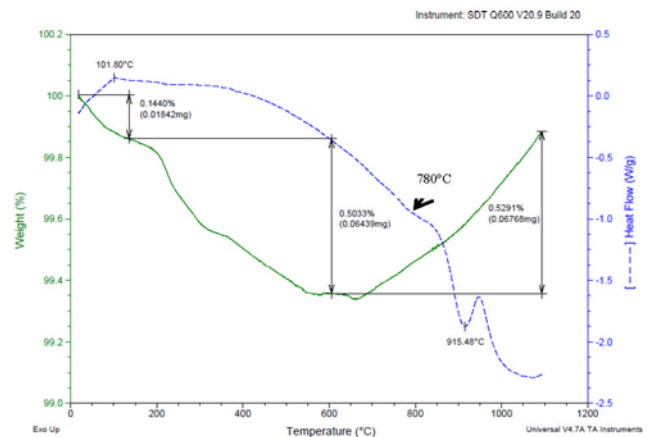


Figure 3. DSC results of basic glass

The DSC result showed that the nucleation temperature was 780 °C (starting point of easy curve), the maximum crystallization

temperature was 916°C (the peak value). The heat treatment of glass-ceramic is as followed:

- 1.heating rate: 8°C/min, (to 780°C);
- 2.holding time: 2h;
- 3.heating rate: 2°C/min, (to 916°C); in case of the deformation of glass-ceramic, the temperature should be rose slowly to form the crystal ;
- 4.holding time: 2h(916°C);
- 5.natural cooling.

After crystallization, the surface topography of the glass-ceramic was examined, as shown in Figure 4.



Figure 4. Surface topography of glass-ceramic

Figure 4 shows that the glass-ceramic of silicium-calcium slag is milk white without discolorations. The section of transversal truncation is clean, and there are hardly any bubbles visble.

The glass-ceramic was incised into samples of 4×4×40mm for flexural strength analysis. The results show that the flexural strength is up to 75Mpa. The water absorption of the sample was 0.22%, the bulk density was 2.78 g/cm³.

3 Conclusions

Because of the high CaO content of calcium-silica residue, gehlenite is the main crystal phase of the glass-ceramic after smelting and heating treatment. In this study, the obtained glass-ceramic has a uniform color, nearly no bubbles, and a bending strength of up to 75Mpa. This process can be used for the comprehensive utilization of silicon-calcium containing slags. If the pure reagents are replaced with fly ash, the comprehensive utilization will be even better.

Acknowledgements

The authors greatly acknowledge the financial support of the National Nature Science Foundation of China (No: 51104053), and the National Nature Science Foundation of Hebei Province (No: E2012208047).

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