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Preparing of glass-ceramics and recovering of iron from copper slag

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Abstract. Copper slag, containing more than 40 wt% iron, is often used for pavement of roads, building bricks and cement etc. The level of this traditional utilization technology is very poor. In this study, a new method of comprehensive utilization of copper slag was investigated. The iron of copper slag was recovered and the residual slag was transformed into glass-ceramics within the same process involving iron reduction, iron-glass separation and glass crystallization. The experimental results indicated that the ratio of iron recovery was more than 99% and the crystalline phase of the obtained glass-ceramics was diopside. With the extension of crystallization time, the content of crystalline phase and the size of crystals of the glass-ceramics increase.

Introduction

The disposal of large quantities of metallurgical slag, which occupies the land resource and causes damage to the ecological environment, is always a big problem to developing countries [1-2]. At present, only part of metallurgical slag is used as the raw material for pavement of roads, building bricks, pigments[3], and starting material for ordinary cement etc [4-6]. Compared with these methodologies of slag treatment, using metallurgical slag for glass-ceramics production is more attractive because glass-ceramics are the advanced materials with outstanding chemical stability, wear resistance, and mechanical properties [7-8].

Though many types of metallurgical slag including slag of ferrous and non-ferrous metallurgy have been considered for glass-ceramics production [9-10], copper slag has not been developed for glass-ceramics production due to its high iron content. The iron mainly exists in form of non-magnetic iron silicate, implying that the iron can not be removed from the waste by using traditional magnetic separation methods [11-12]. Glass-ceramics made from this iron-rich slag are dark in color so that they are not applicable for architectural decoration materials.

In order to prepare glass-ceramics production for architectural decoration materials, this paper investigated the feasibility of recovering the iron and preparing glass-ceramics in the same process by iron-reduction, iron-glass separation and glass-crystallization. The effect of the crystallization time on the crystallization behavior of the obtained glass-ceramics was studied. This work may be valuable in providing the foundation for the application of copper slag in glass-ceramics.

Materials and experimental procedure

The copper slag was provided by HuangShi Dajiang Group Co. Ltd. The composition of the copper slag was identified by X-ray fluorescence analysis and the result was listed in table 1.

Table 1 The composition of the copper slag (wt%)

T Fe	SiO_2	CaO	ZnO	Al_2O_3	MgO	Na_2O	K_2O	SO_3	CuO
41.55	39.41	5.61	3.71	2.84	2.63	1.25	0.88	0.60	0.22

The glass-ceramics and the recovered iron were obtained by first mixing 83.2wt% copper slag, 2.0 wt% alumina, 6.6 wt% limestone, 3.1 wt% sodium carbonate, 5 wt% fluorite and enough coke. Double-crucible method was used of which the mixtures were placed in the inner alumina crucible and the gap between the two crucibles was filled with coke to obtain the reducing atmosphere. Then the melting was carried out at 1450 °Cfor 2 hours. During the melting process, iron ions were reduced by coke and subsequently the melt was divided into two layers with the molten reduced iron at the lower part and the molten slag without iron (melt glass) at the upper part, which lead to liquid-liquid separation. The molten slag without iron was poured into a mould, and then heated at temperature corresponding to the endothermic peaks and exothermic peaks in the DTA curve in the crystal growth stage to obtain the glass-ceramics. The iron at the lower part of the crucible was collected as metallic iron.

The crystallization process of the glass frit was investigated by means of differential thermal analysis (DTA), employing a STA 409 PC apparatus. The heating rate was 10 K/min and the atmosphere was the flowing air. The crystalline phases of the glass-ceramics were determined by XRD technique using a Philips PW-1830 apparatus. After the surface of the glass-ceramics sample was polished and subsequently etched with a 10% HF solution for 30s, the surface microstructure of the sample was observed by a Quanta200 scanning electron microscopy. The iron content of glass frit was measured by titration method.

Results and discussion

Determination of nucleation temperature and Crystallization temperature. Fig.1 shows the typical DTA pattern of the obtained parent glassy slag without iron. As can be seen, a small dip commences at about 698°C and an exothermal peak occurs at 818°C in the curve, which corresponds to the glass transition temperature T_g and the crystallization temperature T_P of the glass, respectively. Nucleation treatment is scheduled at a temperature 50°C above T_g to generate uniform crystal nucleus in parent glass. Therefore, the heat treatment of the obtained glass was scheduled at 748°C in nucleation stage and 818°C in crystal growth stage.

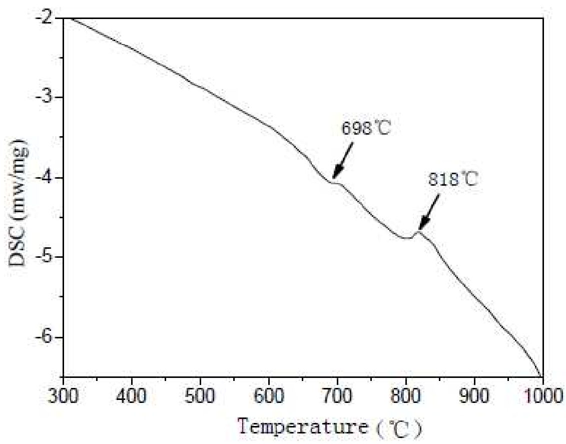


Fig. 1 The DTA pattern of the obtained glass frit without iron

The crystalline phase and microstructure of glass-ceramics. The glass-ceramics samples were prepared by crystallizing the obtained glassy slag without iron. As is well known, the crystallization behavior of the samples was greatly influenced by the crystallization time in crystal growth stage. Therefore, after the nucleation treatment at 748°C for 2h, the samples was subsequently heated at 818°C for 0, 30min, 40min and 60min, respectively. The formation of the crystalline phases in samples was measured by XRD analysis. Fig.2 shows the spectra of the samples after crystallization treatment at 818°C for different times. Diopside ($CaMg(SiO_3)_2$) is identified as the only crystalline phase of these samples.

No crystalline phases form in the sample without crystallization treatment because the sample shows an amorphous spectrum. After 30min of crystallization time, the trace of crystalline phase formation is very weak, indicating that few diopside phases form in the sample because crystal nucleus hardly grows fully. With the extension of crystallization time from 30min to 60min, the peaks of the spectra increase in number and become sharper, implying that the content of crystalline phase significantly increases and the crystal nucleus grow more fully. Hence, the crystallization time influences not the type of crystalline but the content of crystalline in the glass-ceramics.

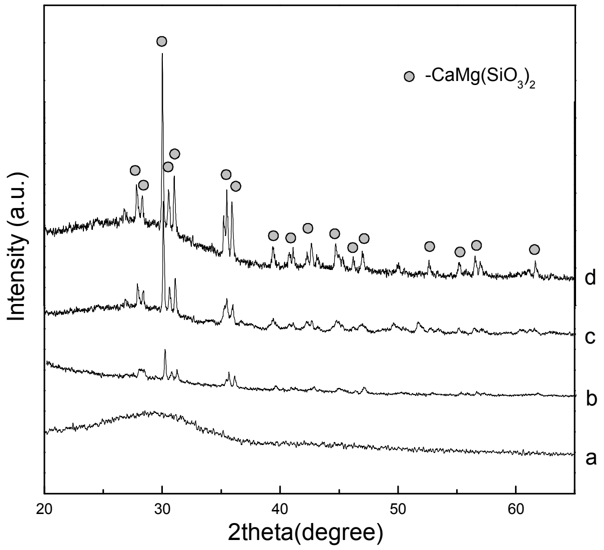
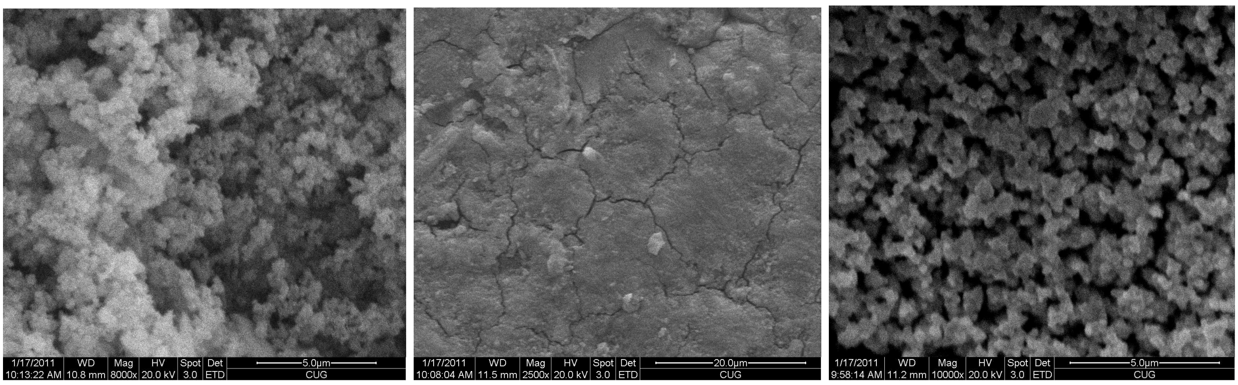


Fig.2 XRD spectra of the glass-ceramics samples with different crystallization time at 818°C. (a) without crystallization treatment; (b) 30min;(c) 40min;(d) 60min.

Microstructure of glass-ceramics samples. Fig.3 shows the surface micrographs of the obtained glass-ceramics samples after corrosion in HF solution. Being consistent with the result of XRD, no crystals were observed on the surface of the samples heated for 30 min, implying that crystal nucleus grow slowly during this process. After another increase of 10min, the growth of the crystals becomes obvious because a great number of fine crystals present in the form of granular. Extending to 60min, much bigger crystals of average size of about 500nm are detected, uniformly dispersing in glass matrix. It can be easily deduced that the size of granular crystals will continue to increase if crystallization time further increases. Therefore, the crystallization treatment time determines the content of crystalline phase and the size of crystals, which affect chemical stability, wear resistance, and mechanical properties of the glass-ceramics.



(a) (b) (c)

Fig. 3. SEM image of the surface of the glass-ceramics samples with different crystallization time at 818°C. (a) 30min;(b) 40min;(c) 60min.

Conclusions

Though many kinds of metallurgical slag were well developed for glass-ceramics production, copper slag has not been considered for application in this area because of its high iron content. In this study, the glass-ceramics were prepared and more than 99% of iron was successfully recovered from the copper slag within the same process. The crystal phase of the glass-ceramics was diopside. The extension of crystallization time enhanced not only the content of crystalline phase but also the size of crystals. Glass-ceramics samples with crystallization time of 60min showed that the average size of diopside crystals was about 500nm and the crystals uniformly dispersed in glass matrix. The crystallization behavior may be affected by nucleation treatment like nucleation time and nucleation temperature, which will be investigated later. Results obtained from this study suggest that it is feasible to prepare the glass-ceramics and recover the iron from copper slag, which can greatly improve the comprehensive utilization of copper slag.

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