Synthesis and Characterization of Glass-ceramics From Magnetic Separation Tailings of Ferrochromium Slag

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1. Introduction

High-carbon ferrochromium slag (HCFS), a kind of by-product from the production of ferrochrome, is a heavy hazardous waste and a promising secondary resource. Producing one ton of high-carbon ferrochromium (HCFC) will generate 1.3 tons of HCFS. Considering the shortage of chromium resources in China, the comprehensive use of chromium slag becomes meaningful.[1] The treatment is usually stockpiling or using chromium slag as landfill. At present, chromium slag brick, calcium magnesium phosphate, glass colourant, colour cement made of reduced chromium slag and mineral wool products of chromium slag have been experimentally studied. However, such processes do not achieve total recycling of the chromium slag.[1]

In this work, after the magnetic separation of high-carbon ferrochromium slag, the obtained concentrate can be used as raw materials returning back to the electric furnace for high-carbon ferrochromium production, but the tailing(HCFT) is remained in large quantities, which should be treated in low cost, clean use and large quantities ways. Glass-ceramics are is polycrystalline materials which are not fully crystalline, that is, they are approximately 50-95 vol% crystalline phase with residual glass. Glass-ceramics have finer mechanical properties compared to the parent glass. Glass-ceramic materials have been successfully prepared from the solid waste, such as blast furnace slag.[2,3] So that the use of HCFT is reasonably suggested for the synthesis of glass-ceramics. Thus, this study is motivated to comprehensively use the tailing of HCFS obtained after magnetic separation. The characterizations of tailing are investigated, and a tailing-based glass-ceramic is synthesized.

2. Material and methods

The high-carbon ferrochromium slag (HCFS) used in this study was received from a ferrochromium plant, after the magnetic separation, the phases of the tailing were obtained using an X-ray diffraction analysis. In order to decrease the synthesis temperature, waste glass (WG) was selected for the composition adjustment, limestone and soda (≤ 75μm) were used as the fining agent, and fluorite (≤ 75μm) was added as the flux. All of the chemical compositions are shown in Table 1. Five samples with different mass ratios of tailing to WG (R(T/W)) were investigated, and their compositions are shown in Table 2.

Table 1 Chemical characterization of raw materials (wt %).

Raw Materials	SiO_2	MgO	Al_2O_3	CaO	Na_2O	Cr_2O_3	Fe_2O_3	K_2O	CaF_2
Tailing	31.89	33.61	24.5	1.99		5.15		0.11	
WG	75.68	3.40	0.94	8.95	9.73	0.024	0.27	0.68	

Table 2 Compositions of the samples (mass/g).

Sample NO.	Tailing	Waste glass (WG)	$CaCO_3$	Na_2CO_3	CaF_2(extra addition)	Mass ratio of tailing and WG, R(T/W)
1#	30.0	50.0	15.0	5.0	5.26	0.60
2#	35.0	45.0	15.0	5.0	5.26	0.78
3#	40.0	40.0	15.0	5.0	5.26	1.00
4#	45.0	35.0	15.0	5.0	5.26	1.29
5#	50.0	30.0	15.0	5.0	5.26	1.67

Appropriate amounts of tailing and WG were first ground to 75 μm and subsequently evenly mixed with the other materials. The mixture was put into a crucible, melted at 1550 °C in a muffle furnace for 2h. Subsequently, the melting samples were poured into a mould that was pre-heated to 500 °C, and annealed at 500 °C for 1h, thus the parent glass was obtained. The parent glass was followed investigated by TG-DSC to determine the

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nucleation and crystallization temperatures. Finally, a two-stage heat treatment was used to prepare the glass-ceramics, which included the nucleation and crystallization processes.

3. Results and discussions

The nucleation temperatures (T_n) and crystallization temperatures (T_g) were detected using Differential Scanning Calorimetry (DSC, NETZSCH-STA409) and the results are shown in Table 3.

Table 3 Nucleation and crystallization temperature of the samples.

R(T/W)	0.60	0.78	1.00	1.29	1.67
Nucleation temperature/℃	640	648	652	656	663
Crystallization temperature/℃	865	868	873	878	882

The five parent-glass samples were separately heat-treated considering their respective nucleation and crystallization temperatures, and the glass-ceramics were finally prepared. The main phases of the tailing-based glass-ceramic samples were diopside ($CaMg(SiO_3)_2$), nepheline ($(Na,K)AlSiO_4$), pyroxene ($Ca(Mg,Fe)Si_2O_6$, and $Ca(Mg,Al,Fe)(Al,Si)_2O_6$), respectively.

The mechanical properties of the tailing-based glass-ceramics were determined using the microhardness and 3-point bending tests. The hardness values firstly increase with the increase with R(T/W), then decrease. When the value of R(T/W) increases to 1.00, it reaches a maximum of 9188 MPa, which is higher than that of other glass-ceramics made from metallurgical slags with a maximum value of 7000 MPa. With the increase in R(T/W), the bending strength of the samples firstly increases to the top and then slightly decreases. When the value of R(T/W) reaches 1.29, the microhardness of glass-ceramic sample reaches the maximum of 112 MPa.[3-5]

The leaching performance of each sample was tested by the toxicity characteristic leaching procedure (TCLP) developed by the U.S. Environmental Protection Agency (EPA).[6] It indicates when the R(H/W) reaches 1.67, the leaching concentration of total chromium ions achieves its maximum of 0.257 mg/L, which is far lower than the international standard of toxic emission of chromium (5.0mg/L).

4. Conclusions

In this paper, tailing-based glass-ceramics are prepared from the magnetic separation tailings of high-carbon ferrochromium slag and waste glass using the two-stage heat treatment, and the microstructural characterization and mechanical properties of the glass-ceramics are investigated. With the increase in R(T/W), the nucleation and crystallization temperature increases. The microhardness and bending strength increase with the increase in R(T/W), whereas when the value of R(T/W) beyond 1.29, the bending strength begins to decrease. The optimal bending strength and microhardness of HCFT-based glass-ceramics are 112 MPa and 9188 MPa, respectively. Besides, the maximum leaching concentration of total chromium ions is 0.257 mg/L, which is far lower than the international standard of toxic emission of chromium.

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