Effects of the Content of Blast Slag and Heat-treatment Parameters on the Properties of Slag Glass-ceramics*

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Abstract: A glass-ceramics of $CaO(MgO)$-Al_2O_3-SiO_2 system was prepared by melting with blast slag and other mineral materials as starting materials, and CaF_2, P_2O_5, Fe_2O_3 as multiple nucleation agents. DTA, XRD and SEM were used to ascertain the heat-treatment temperatures and characterize the phase composition and microstructure of the glass-ceramics. The relationship among the content of the blast slag, the heat-treatment parameters and the properties were discussed. Experimental results show that when the content of the slag was 45%, the major crystalline phases are wollastonite ($CaSiO_3$) and diopside ($CaMg(SiO_3)_2$), and the properties of the glass-ceramics are as required. The optimal heat-treatment parameters are: annealed at 670 ℃, nucleated at 850 ℃ for 1 h, then crystallized at 970 ℃ for 1 h. The proper rate for heating is 5 ~ 6 ℃/min before 850 ℃, 1 ~ 2 ℃/min between 850 ℃ and 970 ℃.

Key words: blast slag; glass-ceramics; crystallization; heat-treatment; properties
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1 Introduction

With the booming of industry, the amount of waster is increasing rapidly, which caused a serious imbalance between man and nature. In order to keep the maintainable development of society and economy, scientists in every field are looking for a better way to be in harmony with the environment[1-3]. From the 50s to 60s in the 20th century, a great deal of research had been done in the Soviet Union, Europe, America, Japan and so on to make glass-ceramics using slag and other wastes as starting materials[4]. These works include discussing about the principals and techniques of slag glass-ceramics, design of the chemical compositions, the heat-treatment parameters of slag glass-ceramics and other key factors of this technology. The first industrial line of slag glass-ceramics in the world was put production in 1971 in the Soviet Union, and the products were widely used in construction, metallurgy, chemical industry and so on, which had made a profit of nearly $ 60 000 000[5]. In China, the study and development of slag glass-ceramics are relatively later than abroad. Since 1980s, the research and applications of slag glass-ceramics have been giving more and more attentions. At present, many glass-ceramics plants at home are making products using copper slag, phosphorite residue, fly ash, wolfram waste, blast slag, and other industrial waste[6].

The slag glass-ceramics have many competitive properties such as good wear and corrosion resistance[7], so it is a promising new environmental material. In this paper, the blast slag is used as major material for the preparation of glass-ceramics. The samples were prepared by melting method using fluoride and the phosphate as the complex nucleating agent. Basing on the experimental result, we discussed the effects of the content of blast slag and heat-treatment parameters on the properties of the slag glass-ceramics.

2 Experiments

2.1 Raw materials

The blast slag used in this work was from a steel plant of Hunan province. After removing ferrous impurity by a magnetic filter, the slag was ground to 60 mesh. The compositions of raw materials are listed in Table 1. Some chemicals such as aerolite and calgon are in industrial grade.

2.2 Preparation processing

The basic glass was prepared from blast slag and other minerals by melting in an alumina crucible at 1380 ~ 1420 ℃ for 1 h. The melt was poured onto a preheated (usually up to 500 ℃) ferreous mould to produce a glass plate, then annealed at 670 ℃ for about 30 min and slowly cooled to room temperature. The glass plate crystallized under a certain heat-treatment conditions so as

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to get the glass-ceramics, which were cut into 6 mm × 4 mm × 50 mm pieces for tests.

Tab.1 Compositions of raw materials %

Materials	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	CaF_2
Blast slag	31.71	6.97	36.61	11.84	1.26	-	-	-
Quartz sand	98.5	0.5	-	-	<0.2	-	-	-
Feldspar	67.87	17.32	0.34	0.13	<0.2	8.82	4.56	-
Fluorite	3.5	2.3	2.58	0.8	<0.2	-	-	85
Dolomite	0.57	0.25	31.5	20.5	<0.1	0.04	0.31	-
Calcite	0.5	0.2	54.5	0.5	<0.1	-	-	-

2.3 Testing

DTA was used to determine the optimum nucleation and crystallization temperature, which were heated at 10 K/min in PCR-1 DTA apparatus. XRD analysis (Siemens D5000) was used to confirm the crystal compositions. SEM (JSM-5600LV) was used to show the microstructure of the specimens, which were corroded in 1% HF solution (about 25 ℃) for 1 ~ 5 min and the surface was coated with gold. The bending strength of the specimens were tested with a span of 30mm and a loading rate of 9.8 ± 0.1 $N \cdot S^{-1}$.

3 Results

3.1 Design of compositions

The characteristics of glass-ceramics mainly depend on the types of crystal - phases, the ratio between the crystal and the vitreous phase, and the size and distribution of crystals. Therefore, when designing the compositions of basic glass, we must take two factors into consideration, the stability of basic glass and the phase compositions of the final material[8]. According to the crystal chemistry, different ratio of Si/O results in different phase compositions[9]. If the content of SiO_2, Al_2O_3 is relatively low, a silicate of lower Si/O ratio (e.g. wollastonite) will be formed. On the contrast, the silicate with frame construction, such as feldspar, will be formed. If the ratio is big enough, the melting point of glass will be improved. The blast slag provides a good deal of CaO. The Ca^{2+} and Mg^{2+} are ions with small ionic radius and strong field intensity, which can make phase separation more easily. Moreover, this will indirectly accelerate the nucleating and crystalline of the basic glass[10]. F and P were added as nucleating agent together with Fe in the slag. Some fusing agents such as borax and feldspar were added to decrease the melting point. Too much borax tends to the distortion of the products and corrodes the crucible. Aerolite was added as fining agent. Considering that the products are expected to gain good mechanical property and chemical stability, and according to the compositions of the blast slag, we chose the CaO (MgO)-Al_2O_3-SiO_2 system as the basic glass system, and the pyroxene (mostly including the augite and the diopside) as the major crystalline phase. Furthermore, the utilization ratio of the blast slag should be as much as possible to decrease the cost and improve the environmental benefit. Consulting the phase diagram of CaO-Al_2O_3-SiO_2 ternary system with 10% MgO, the reasonable compositions of the basic glass are as follows. $w/\%$: SiO_2, 35 ~ 55; Al_2O_3, 3 ~ 6; CaO, 14 ~ 24; MgO, 4 ~ 8; B_2O_3, 1 ~ 5; KNaO, 2 ~ 4; CaF_2, 5 ~ 7; P_2O_5, 3 ~ 6; Fe_2O_3, 0 ~ 3.

3.2 Effects of the content of blast slag on phase composition and mechanical properties

We adopted the method of gradually substituting the blast slag for the other minerals such as dolomite, calcite and feldspar. The content of the blast slag was 20% ~ 50%. Observing the annealed glass, we found that while the content of the blast slag increasing, the opaque degree of the glass deceased. When the content of the slag was 20%, the annealed glass was ivory-white, which suppose a serious phase separation in the glass. If once the content was higher than 50%, the annealed glass was transparent. This is possibly caused by the increase of the stability of the glass network, which decreases the tendency of phase separation[11].

The curves of differential thermal analysis (DTA) of the glass with different blast slag are showed in Fig. 1. The fovea on the graph represents a light endotherm, corresponding the softening temperature of the glass. With the increase of the temperature, the exothermic peak occurs, which represents the emergence of the crystallization. The sharper the peak is, the higher the crystallization rate will be. The area of the peak reveals the degree of crystallization. With the increase of the slag content, the softening, nucleating and crystallizing temperature of the basic glass were increased, and the area of the exothermic peak were lessened, which showed that the stability of the glass improved. The blast slag is not good for the crystallization of the basic glass. The bending strength of the specimens nucleated at 800 ℃ for

1 h and crystallized at 950 ℃ for 1.5 h was listed in Tab. 2. It is evident that the strength of the glass-ceramics also decreased with the increase of the slag content.

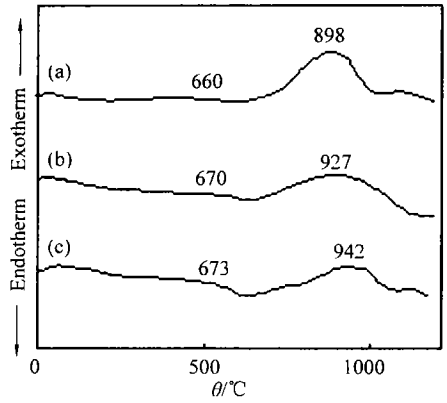

Fig.1 DTA curves of glasses with slag content of *w*/%: (a) 20, (b) 30, (c)45

Tab.2 Effects of the contents of slag on the strength of glass-ceramics

	(a)	(b)	(c)
Content of slag/%	20	30	45
Bending strength/MPa	91	86	54

Fig.2 shows the XRD patterns of glass-ceramics with different contents of blast slag. The major crystalline phases of these specimens are wollastonite and diopside. With the increase of slag content, the diffraction peak of crystals decreases. The result shows that the addition of blast slag decreases the amount of the crystalline phase. Fig.3 shows the SEM photographs of the fracture section of glass-ceramics specimens, which were nucleated at 800 ℃ for 1h and crystallized at 930 ℃ for 1 h. The microstructure of Fig. 3 (a) shows that the material has well crystallized, and the branched crystallites interweave each other to form a network structure. The particle size is about 0.5 μm and with narrow size distribution. It is reasonable that the specimen has a higher bending strength. Fig. 3 (b) shows the microstructure of the specimen with 45% slag. The material is just nucleated with fine spheric nuclei located homogeneously in the glass. The strength of the specimen is not good as the glass phase is high. It is necessary to increase the crystallizing temperature to obtain better microstructure and strength.

3.3 Effects of the heat-treatment on mechanical properties

Nucleation is a key factor to develop a great deal of fine nucleus effectively; and crystallization is important for the growth of crystallite. In order to prevent the

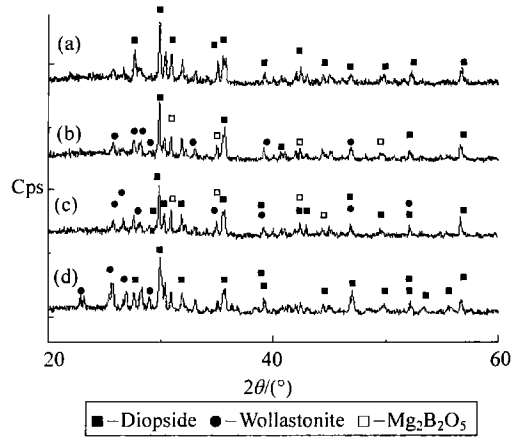

Fig.2 XRD patterns of glass-ceramics with slag content of *w*/%: (a) 45, (b) 40, (c)30, (d) 20

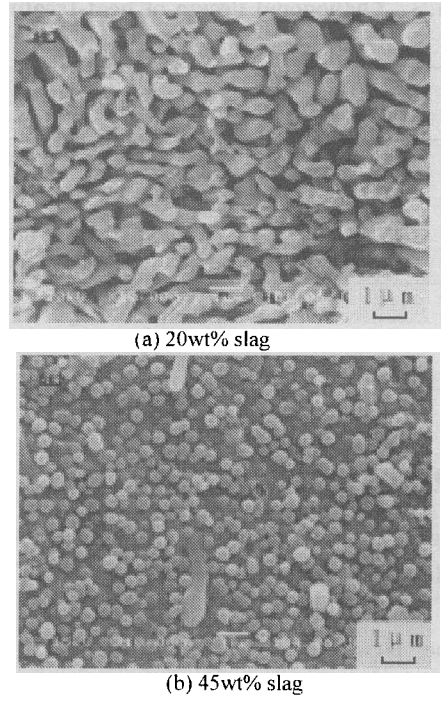

Fig.3 SEM photographs of the fracture section of glass-ceramics with differnt contents of slag

distortion of the sample[4], the heating rate is also important. If the temperature rises too fast, the glass will soften before the crystal growth enough to form a strong "framework". From the results of our experiments, the heating rate is optimized as follows: from room temperature to nucleating temperature at 5 ~ 6 ℃/min, and from nucleating temperature to crystallization temperature at 1 ~ 2 ℃/min. The time for crystallization should not be too long to avoid the abnormal growth of crystals which will decrease the strength of the material[12].

With the heating rate mentioned above, an orthogonal design was used for Fig.2(a) specimen. Based on $L_4 2^3$ orthogonal table, heat-treatment parameters are

listed in Tab.3. The bending strengths of each specimen prepared under different parameters are also listed in Tab. 3. It can be concluded that nucleating temperature (factor 1) affected the bending strength more dramatically (R = 58) than other factors, while the time for crystallization (factor 3) affected the least (R = 10). In a word, when ignoring the effect of the holding time for nucleating, the effect of nucleating temperature on the bending strength is the maximum and the holding time for crystallization is the minimum. Based on the maximum sum of each level, the optimal heat-treatment parameters for 4 # specimen are: nucleated at 850 ℃ for 1h, and crystallized at 970 ℃ for 1h, that is the 4 – 4 # in Tab.3, whose bending strength is 99 MPa.

Tab.3 Orthogonal design of heat-treatment parameters and results analysis

	T_n/℃	t_n/h	T_c/℃	t_c/h	Bending resistance/MPa
4 – 1 #	800	1	950	1	54
4 – 2 #	800	1	970	1.5	65
4 – 3 #	850	1	950	1.5	78
4 – 4 #	850	1	970	1	99
Level 1	119	–	132	153	–
Level 2	177	–	164	143	–
R	58	–	32	10	–

4 Conclusions

A glass-ceramics with homogeneous microstructure and good properties was prepared by melting the blast slag (45%) and other mineral materials. The major crystalline phases were wollastonite ($CaSiO_3$) and diopside ($CaMg(SiO_3)_2$). With the increase of blast slag content, the stability of the basic glass will improve, and the temperature for nucleation and crystallization will increase. Under optimized heat-treatment conditions, the glass-ceramics has homogeneous and dense microstructure and preferable bending strength. Heat-treatment parameters affected dramatically the strength of the material. The bending strength of the blast glass-ceramics can be greatly improved by optimizing the heat-treatment parameters.

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高炉渣含量与热处理制度对矿渣微晶玻璃性能的影响

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摘 要:运用 DTA、XRD 和 SEM 等现代分析技术对 CaO(MgO)-Al_2O_3-SiO_2 系矿渣微晶玻璃的核化晶化温度、物相组成和显微结构进行了分析,探讨了高炉渣引入量和热处理制度的影响。试验结果表明,当高炉渣引入量为 45%时,主晶相为硅灰石($CaSiO_3$)和透辉石($CaMg(SiO_3)_2$),材料结构均匀致密,性能良好。本文适宜的热处理工艺参数为:退火温度 670 ℃;核化温度 850 ℃,晶化温度 970 ℃,各保温 1 h。

关键词:高炉渣;微晶玻璃;晶化;热处理;性能

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