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EFFECT OF Cr_2O_3 ON CRYSTALLIZATION OF CaO-MgO-Al_2O_3-SiO_2(CMAS) SLAG GLASS-CERAMICS

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Using stainless steel slag and iron tailings as main raw materials, the CaO-MgO-Al_2O_3-SiO_2 (CMAS) glass-ceramics with a solid waste utilization rate exceeding 70 % was prepared, and the effects of Cr_2O_3 content on the nucleation and crystallization of glass-ceramics were investigated by X-Ray diffraction (XRD). Research indicates that the main crystalline phases of CMAS are all pyroxene, and the content of Cr_2O_3 increases in a certain range, which promote the crystallization ability of crystals in glass. Besides, the increase of Cr_2O_3 content within a certain rangepromotes the crystal crystallization in glass.

Keywords: stainless steel slag/iron tailings, Cr_2O_3, CMAS, crystallization, glass-ceramics

INTRODUCTION

Due to major crystalline phase is pyroxene, the CaO-MgO-Al_2O_3-SiO_2 (CMAS) glass-ceramics have a wide variety of applications in metallurgy, building materials and chemical industry [1]. CMAS could be produced by solid waste, such as fly ashes [2], red mud [3], waste slag [4] and so on.

Argon oxygen decarburization stainless steel slag (AODS) is refined argon-oxygen decarburizing slag in stainless steel production. The AODS contains a large amount of CaO, SiO_2, Al_2O_3, and MgO, can be used as a CMAS slag glass-ceramics. Iron tailings are another typical waste in the iron and steel industry. For example, Anshan type iron tailings (AIT) have high silica content (SiO_2 > 80 wt.%) [6], which can be used as a raw material for the adjustment of silicon oxide content in CMAS slag glass-ceramics.

For the CMAS, due to the weak self-crystallization ability of the main crystalline phase of pyroxene, it is necessary to add an appropriate nucleating agents to promote the whole crystallizing of the glass-ceramics [1]. The influence of Cr_2O_3 on the crystallization of CMAS investigated by many scholars is mostly concentrated on the amount of crystals, micro-morphology and strength. However, the crystallization mechanism of glass ceramics is rarely studied.

In this paper, CMAS with a solid waste utilization ratio of more than 70 % is prepared from AODS and AIT, and the effect of Cr_2O_3 as nucleating agent on the crystallization of CMAS is also investigated.

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EXPERIMENTAL

The composition of experimental raw materials used in the experiment was shown in Table 1. Other chemicals were all analytically pure and produced by National Pharmaceutical Group.

In the experiment, the raw material ratio /wt.% for preparing the basic glass of CMAS were CaO of 29,15 %, SiO_2 of 42,41 %, Al_2O_3 of 6,04 %, MgO of 5,67 %, CaF_2 of 6,00 % and Fe_2O_3 of 5,15 %. Different amounts of Cr_2O_3 were added to investigate the influence of the content on nucleation and crystallization. With the change of Cr_2O_3 content (0,42, 1,0, 1,5, 2,0, 2,5), the samples are marked as C1, C2, C3, C4 and C5.

The raw materials (300 g) were mixed thoroughly, and then melted at 1 500 °C for 2 h in a high-temperature elevating muffle furnace. The molten glass was cast into a preheated stainless steel mold at 400 °C, while a small amount of glassy water was quenched into glass particles for later characterization. The cast glass samples was placed in a muffle furnace and annealed at 600 °C for 3 h to eliminate the internal stress of the glass. The annealed samples were crystallized and nucleated to prepare glass ceramics.

The thermodynamic properties of the sample were characterized using a integrated thermal analyzer at a heating rate of 10 °C/min (STA 449C, NETZSCH). Phase structure was measured by X-ray diffraction (XRD) (X'Pert PRO MPD, PANalytical). The particle surface of samples were observed by a Scanning electron microscope (SEM) (JSM 6300, JEOL). The bonding mode was analyzed by FTIR (iS50 FTIR, NICOLET)

Table 1 **The main components of the experimental raw materials/ wt/. %**

Raw materials	CaO	SiO_2	CaF_2	MgO	Al_2O_3	Cr_2O_3	TiO_2	Fe_2O_3	Other
AODS	57,90	27,23	4,33	5,51	1,51	0,84	0,78	0,23	1,67
AIT	0,57	82,26	—	—	0,80	—	0,02	14,37	1,65

RESULTS AND DISCUSSION

The nucleation and crystallization temperatures of the samples were determined according to the Differential Scanning Calorimetry (DSC) results. Figure 1 shows the DSC curves of the basic glass with the temperature range of 200 - 1 000 °C). As can be seen from Figure 1, the glass transition temperatures (*T*g) of the sample occur at 699 °C and the crystallization peak temperature (*T*p) is 842 °C. According to the DSC results, the nucleation temperature is 720 °C for 2h and the crystallization temperature is 860 °C for 3h by tow-step heat treatment method.

The XRD patterns of CMAS samples with different content of Cr_2O_3 are shown in Figure 2. As can be seen from Figure 2 (a), the main crystalline phases of samples are all pyroxene phases (JCPDS 41–1483). The secondary phase of calcium silicate phase appears (JCPDS 84-0654) in C1, C2, C3 and C5 but is absent in C4 sample. At the same time, a small amount of spinel phase is formed in C1-C5, and the Cr ions in the glass-ceramics can be fixed inside the crystal lattice by the spinel phase, playing the role of detoxification.

In order to study the effect of Cr_2O_3 addition on the main crystalline phase of glass, the XRD pattern of CMSA slag glass- ceramics is analyzed at diffraction peaks in the range of 28 °- 32 ° shown in Figure 2 (b), the peak position of the main diffraction peak of the pyroxene phase in the glass-ceramics gradually shifts toward a low angle as the content of Cr_2O_3 increases. As Cr_2O_3 addition continues to increase, the diffraction peaks of pyroxene gradually shift toward higher angles. The change of the diffraction peak position of the main crystalline phase of the pyroxene with the addition of Cr_2O_3 indicates that when a small amount of Cr_2O_3 is added, the interplanar spacing of the pyroxene phase increases. It is mainly due to the addition of Cr_2O_3 that partially replaces the smaller radius Al^{3+} ion (radius 0,0535 nm)with Cr^{3+} ion (radius 0,0615 nm). The abnormality of sample C4 is due to the absence of calcium silicate phase in the sample. The content of Ca^{2+} ions (radius 0,1 nm) in the pyroxene phase is relatively high, and the relative replacement of Cr^{3+} ions is relatively small, so the lattice volume increases instead.

Figure 3 (a) shows the infrared absorption spectrum of the basic glass. In the infrared absorption spectrum of the base glass, there are mainly three absorption bands in the wavenumber range of 1 200 to 400 cm^{-1}. The first part appears in the wavenumber range of 1 100 to 900 cm^{-1}. The absorption band is the strongest in this section. This is due to the asymmetric stretching vibration of Si-O-Si in the [SiO_4] tetrahedron. The second part has several weak absorption bands at 800 - 550 cm^{-1}. This is due to the symmetric stretching vibration of T-O-T bridge oxygen of many T ions (T: Tetrahedral coordinated Al^{3+}, Fe^{3+}, Cr^{3+}) and the stretching vibration of Si-O pair due to absorption. The third part has a strong absorption band in the range of 500 - 400 cm^{-1}, which is formed by the bending vibration of the Si-O-Si bond.

Comparing Figure 3 (a) and (b), it can be seen that the infrared spectrum of the basic glass after the crystallization process changes significantly. The wavenumbers of1 100 - 900 cm^{-1} and 500 - 400 cm^{-1} show a tendency to split, and a weak energy shoulder appears at 950 cm^{-1}. Itis related to the vibrational mode of Si-O

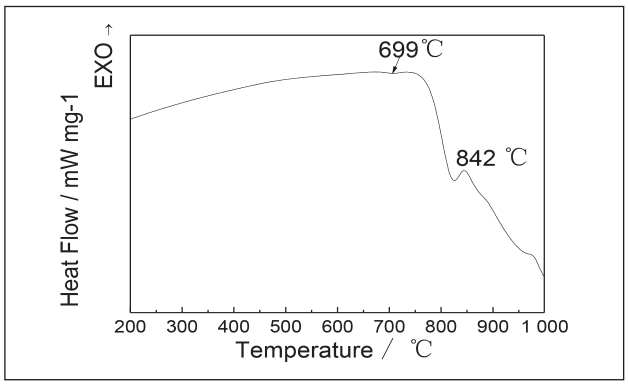

Figure 1 The DSC curves of basic glass

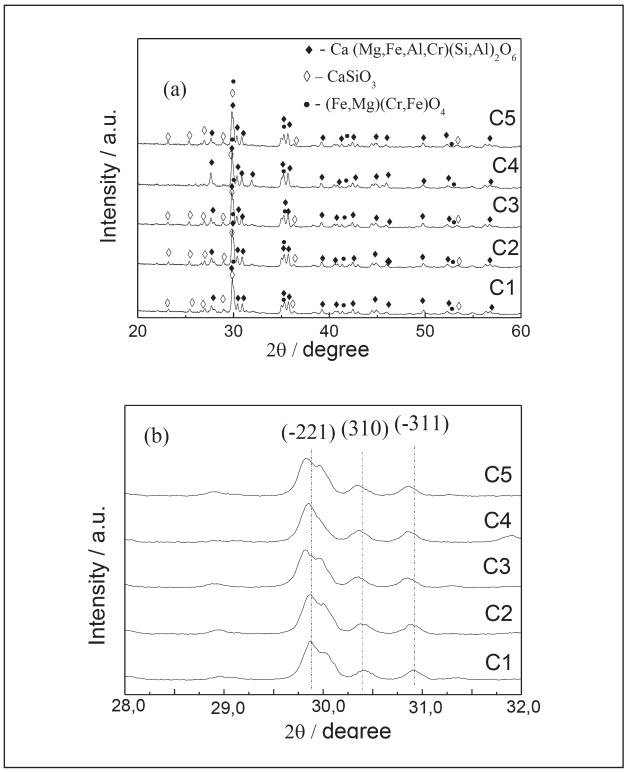

Figure 2 XRD patterns of CMAS
(a) The 2θ angle is between 20 and 60 °
(b) The 2θ angle is between 28 and 32 °

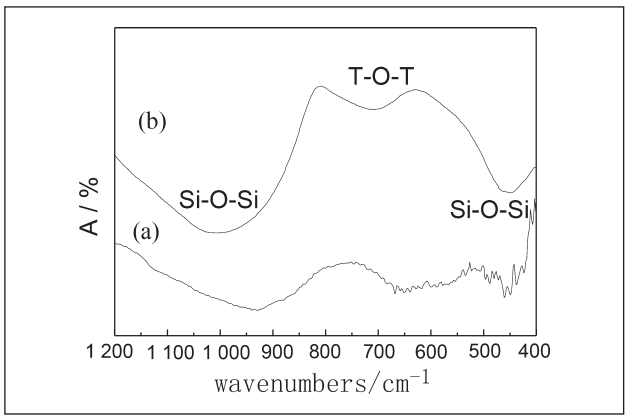

Figure 3 Infrared absorption spectrum of the sample
(a) basic glass
(b) crystallized glass

bonds, indicating that more non-bridge oxygen appeared in the glass. When the X ion has two coordination states of [XO_4] and [XO_6], the coordination number increases and the absorption band moves toward the long wave direction. At the same time, the band is significantly broadened, indicating that the T-O-T bridge oxygen structure is adjusted, and the non-uniformity of the glass structure is increased, which is also conducive to the crystallization of the glass.

Figure 4 is SEM images of the CMSA sample. As can be seen from Figure 4, due to the small content of Cr_2O_3 in the sample, the spinel phase formed in the glass sample. The spinel in CMAS slag glass-ceramics can become a heterogeneous nucleation "crystal nucleus", and the pyroxene phase grows into a granular shape with a spinel phase as "crystal nucleus". Due to the large amount of spinel phases generated, the mutual spacing decreases, resulting in mutual interference of the main crystalline pyroxene phase and the gradually decrease of grain size.

CONCLUSIONS

AODS and AIT were used as the main raw material, and the crystallization process was used to prepare the CMAS based on the pyroxene phase. XRD analysis shows that the main crystalline phases of CMAS are all pyroxene, and the content of Cr_2O_3 increases in a certain range, which promote the crystallization ability of crystals in glass. Infrared analysis shows that the conversion from low coordination to high coordination plays a role of disconnection and promotes the crystallization of the glass. The band is obviously broadened, indicatingthat the non-uniformity of the glass structure is increased, which is beneficial to the crystallization of the glass.

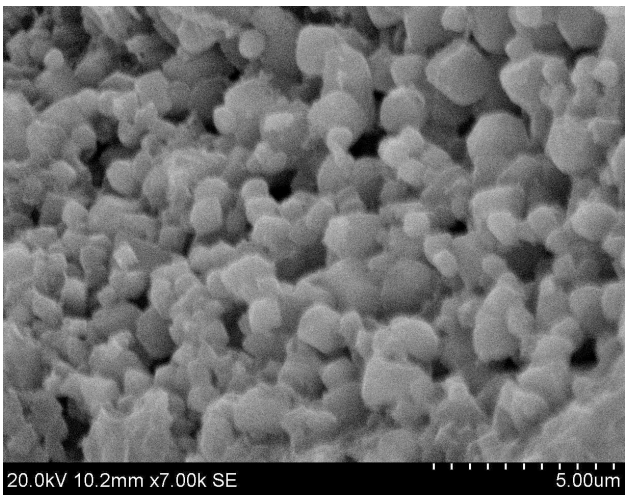

Figure 4 SEM pictures of CMAS

Acknowledgements

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Note: The responsible translator for English language is K. Bei, Hangzhou Qihang translation Co.LTD, China