Crystallization Properties of the Glass Ceramics Prepared from Iron-Rich Nickel Slag

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Abstract For the purpose of broadening the scope of applications of nickel slag, this paper focuses on the crystallization properties of glass ceramics with large amounts of iron-rich nickel slag. In this research, the properties including activation energy of crystallization, crystalline growth pattern, main crystalline phase and micro structure were discussed. It was shown that when KNO_3 was added, the Fe^{2+} oxidized to Fe^{3+} , the activation energy of crystallization increased from 283.70 kJ/mol to 345.45 kJ/mol and the Avrami changed from 2.40 to 2.35. The main crystalline phase for both samples was pyroxene and it grew in one-dimension.

Keywords Crystallization Properties, Glass Ceramics, Iron-Rich Nickel Slag, Pyroxene

be used to prepare the glass ceramics, for example, the system of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-Fe}_2\text{O}_3$, and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O}$ [2-5]. In this research, how to prepare glass ceramics with high content iron-rich nickel slag (more than 90%) was discussed. Considering the chemical composition of iron-rich nickel slag, this study was based on the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$ (FeO) system. The bulk crystallization of the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system was difficult, therefore, TiO_2 , ZrO_2 , Cr_2O_3 or other nucleating agents should be added, which are usually very expensive. Alexander Karamanov found that 0.7wt% Cr_2O_3 could promote the nucleation and crystallization of the iron rich glass [6]. In this experiment, the nickel slag has a certain content of Fe_2O_3 and Cr_2O_3 which could act as nucleating agent. As a result, glass ceramics with iron-rich nickel slag is expected to lower the preparation cost.

1. Introduction

Nickel slag is an industrial waste during the melting of nickel laterite. it occupies large amounts of land and affects our environment due to its lacking of proper application. In view of present studies on nickel slag, the utilization and additional value were very low. The technology with which glass ceramics can be prepared from the industrial wastes is very important not only to solve the environment problems caused by the industrial wastes but also to sustain the development of the related industries. Therefore, it is promising to prepare the glass ceramics from the industrial wastes. The study on preparing the glass ceramics with the industrial wastes has been made since 1960s, and some results were widely reported [1]. And several systems can

2. Experimental

The nickel slag used in this study was an industrial waste obtained during the melting of nickel laterite. The chemical composition of the nickel slag (NS) was given in Tab. 1 and it shows that the iron content was 9.25wt%, while the Cr_2O_3 content was 0.70wt%, both of these were beneficial for the glass crystallization. Sb_2O_3 was used as defoamer and KNO_3 was used for oxidation; both of them were chemical pure. Tab. 2 presents the formulation of each glass ceramic, among them, the parent glass without KNO_3 labeled NK and another with KNO_3 labeled K. All the melting was carried out in an electrical furnace at 1500 °C for 1.5 hours, the molten material was cast into a graphite mold and annealed at 650 °C for 1h, then cooled to room temperature.

Table 1. Chemical composition of nickel slag (wt%)

Composition	SiO_2	Al_2O_3	$\text{Fe}_2\text{O}_3\#$	CaO	Cr_2O_3	MgO	Others	Ignition loss
Content	51.00	5.27	9.25	11.89	0.70	19.95	1.69	0.25

$\text{Fe}_2\text{O}_3\#$ represents the total amount of $\text{FeO} + \text{Fe}_2\text{O}_3$, similarly hereinafter

Table 2. Formulation of the iron-rich glass ceramics(g)

Sample	Nickel Slag	KNO ₃	Sb ₂ O ₃
K	100	2.34	8.44
NK	100	0	8.44

The samples were heated to 700, 750, 800 and 880 °C for 30min respectively. The kinetics of the crystallization of iron-rich nickel slag glass ceramics was determined by DTA which was performed in a Netzsch STA 449 thermoanalyser using 10.5±1mg powder samples with heating rates of 5, 10, 15 and 20 °C/min from ambient temperature to 1200 °C. All the experiments were performed in an air atmosphere with Al₂O₃ powder as reference material. The crystalline phases of these glasses were detected by XRD (D8-Advance, Bruker). The Cu K α radiation ($\lambda=0.15405\mu\text{m}$) was used at 40 kV and 40 mA. X-ray patterns were gathered in the range 10-70° 2 θ with a step size of 0.02° and a step time of 5s. The fractured surface of the glass ceramics was etched in 4% HF solution for 30s at room temperature for FESEM (Ultra plus-43-13, Zeiss) observation.

3. Results and Discussion

3.1. Activation Energy and Growth Pattern

The DTA curves of the glass ceramics are presented in Fig. 1. It shows the glass transition temperature, T_g and crystalline peak temperature, T_p.

Figure 1. DTA curves of K and NK sample

Fig.1 shows that crystalline peak temperatures for the K sample and the NK sample are almost the same, but the exothermic peak of K sample was more pointed, which indicates that the K sample crystallized faster and the degree of crystallization was higher. At the same time, the T_g of the two samples are similar, illustrating their nucleating temperatures would be close. As we all know, the effective nucleating temperature was between T_g and T_g+50 °C, in this study, the K and NK samples were heat treated to 700, 750 and 800 °C for 30min for nucleation [7].

The activation energy of crystal growth, E_c, could be estimated by using the Ozawa equation, shown as equation 1, based on DTA experiments at different heating rates [8, 9]:

$$\ln\beta = -\frac{1.052E_c}{RT_p} + C \quad (1)$$

Where T_p is the crystalline peak temperature of the DTA trace, β is the heating rate, R is the gas constant and C is a constant number. A plot of $\ln\beta$ Vs 1/T_p is a straight line, whose slope corresponds to E_c. The value of n could also be evaluated by a single DTA experiment using the Augis and Bennett equation shown as equation 2 [10].

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E_c} \quad (2)$$

Where n is the Avrami constant, ΔT is the width of the crystallization peak at half height, T_p is the crystallization peak temperature of the DTA trace, R is the gas constant and E_c is the activation energy of crystal growth.

The crystallization peak temperature (T_p) of K sample and NK sample are shown in Tab. 3 and the activation energy of crystal growth (E_c) is shown in Fig. 2.

Table 3. Crystallization peak temperature (T_p) of K sample and NK sample from DTA curves

Sample	Heating rate (K · min ⁻¹)			
	5	10	15	20
K	1199.85	1223.75	1238.45	1246.65
NK	1200.05	1225.75	1246.75	1257.05

Figure 2. Activation energy of crystal growth for K (left) and NK sample (right)

Judging from Fig. 2, activation energy of crystal growth for K sample was 345.45KJ/mol and NK sample was 283.70KJ/mol, so NK sample crystallized easier than K sample. This was owing to the original sample of the nickel slag being formed in a reducing atmosphere, therefore, the iron ions existed as Fe^{2+} ; when enough oxidizing agent KNO_3 was added, they were oxidized to Fe^{3+} . It is known that in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$ (FeO) system, Fe^{2+} destroys the Si-O net structure which leads to a decrease in the viscosity of glass. However, Fe^{3+} could form $[\text{FeO}_4]$ or $[\text{FeO}_6]$, with CaO and MgO forming a net structure and thereby increasing the viscosity [11-15]. Based on this theory, K sample is expected to enhance the control of glass crystallization because the iron exists as Fe^{3+} which tends to increase the viscosity. Fe^{3+} could hinder the Ca^{2+} and Mg^{2+} fusion, go against the adjustment of the net structure, and therefore, increase the activation energy and avoid glass crystallization during cooling.

Different Avrami parameters (n) corresponded to different crystal growth pattern. The higher the value of n , the more crystal dimensions exist, as shown in Tab. 4. Tab. 5 shows the n value of K sample and NK samples at different heating rates calculated by the Augis and Bennett equation.

Table 4. Avrami parameters (n) for different crystallization mechanism [16]

Mechanism-bulk nucleation	Avrami parameters (n)
Surface crystallization	1
One-dimensional crystal growth	2
Two-dimensional crystal growth	3
Three-dimensional crystal growth	4

Table 5. Avrami parameters for K sample and NK sample

Sample	5	10	15	20	Average
K	2.26	2.38	2.45	2.32	2.35
NK	2.35	2.46	2.42	2.38	2.40

It was seen from Tab. 5 that the average Avrami parameters for K sample and NK sample were 2.35 and 2.40, respectively, and the different heating rates had little

influence on the Avrami parameters. From Tab. 5, it can be seen that the crystal grew in a one dimensional chain both for K sample and NK sample, indicating the iron valence state had little effect on the crystal growth pattern, which could be verified by FESEM.

3.2. Crystalline Phase

In order to investigate the different crystallization of nickel slag glass ceramics at different heating temperatures, XRD tests were carried out at 700 °C, 750 °C, 800 °C and 880 °C for 30 min, the results were shown as Fig. 3.

From Fig. 3 (left) showed that there was little difference between K sample and NK sample during nucleation process and an obvious broad amorphous peak between 20 ° and 40 ° at all the nucleating temperatures at 700, 750 and 800 °C for both K and NK sample, indicating few crystals were formed in nickel slag glass ceramics. As for Fig. 3 (right), when the heating temperature was at 880 °C, an obvious crystal peak could be observed, suggesting a crystal precipitation of nickel slag with main crystalline phase being pyroxene, known as $\text{Ca}(\text{Mg}, \text{Fe})(\text{Si}, \text{Al})_2\text{O}_6$ both for K and NK samples. Because the composition of the original glass was complicated, the crystalline structure formed was a solid solution-pyroxene. A small but broad amorphous peak existed, showing a perfect crystallization precipitation and indicating different valence state of Fe had little influence on the main crystalline phase [17]. Though the peak positions were almost the same between K and NK sample, the peak intensity of K sample was much higher than NK sample, and compared with Fig. 1, the peak of K sample in DTA curve was also more pointed than for NK sample, both of these could illustrate that Fe^{3+} could promote crystalline growth, although the iron ion valence state did nothing to the main crystalline phase. Because the activation energy of NK sample was lower than K sample, the phase separation was more obvious and nucleation positions were huge; all of these would lead to easier crystallization. However, with the crystalline structure growing, the glass phase decreased, the crystalline structure competed with each other, excess crystal

nuclei hindered the growth of crystalline structures and the crystallization was worse than that for K sample [18]. All of these results confirmed that the KNO_3 could improve the glass ceramics properties.

3.3. Micro Structure

For the purpose of clearly observing K and NK samples' growth, K and NK samples were kept at 700, 750 and 800 °C for 30 min and then immersed in 4% HF for 30s. After that, the samples were tested by FESEM for morphology structure. The results were shown at Fig. 4.

From Fig. 4, at the same heating temperature, NK sample phase separation was more obvious than K sample, confirming the lower activation energy once again and coinciding with the previous result calculated by equation 2. At the same time, for K sample, obvious phase separation existed for all the heating temperature. However, based on the XRD results, there was no crystalline structure, so all the precipitation in K sample was liquid droplets. For NK

sample, when heated to 700 °C, a lot of spherical liquid existed with diameter about 20nm, amongst which, a certain quantity of droplets began vertical growth and formed needle like structures. When heated to 750 °C, the needles disappeared and the droplets' diameter increased to 40nm; when the temperature increased to 800 °C, the droplets' sizes changed little, but were connected with each other even in aggregation. Based on the previous study, the spherical droplets perhaps were an iron-rich phase while the other was a silicate-rich phase; at the interface, it was much easier to undergo heterogeneous nucleation, provided numerous nucleation positions existed which made it much easier for crystallization to occur [19, 20]. The higher the nucleating temperature gets, the more obvious the difference of phase separation for K and NK samples is. When heated to 800 °C, NK sample droplets began to aggregate, while K sample did nothing, indicating Fe^{2+} could promote to phase separation, made crystallization easier, and thus affect the original glass in cooling process.

Figure 3. Heat treated at 700,750,800°C (left) and 880°C (right) for 30 min

Figure 4. FESEM of different sample: a) K sample at 700°C for 30 min; b) K sample 750°C for 30 min; c) K sample 800°C for 30 min; d) NK sample at 700°C for 30 min; e) NK sample at 750°C for 30 min; f) NK sample at 800°C for 30 min

Figure 5. FESEM of the glass ceramics: a) K sample at 880°C for 30 min; b) NK sample at 880°C for 30min

In order to confirm the crystalline growth in crystallization, K and NK samples were heated to 880 °C for 30 min, then observed the FESEM, shown as Fig. 5.

It could be seen from Fig. 5 that K and NK samples grew in one dimensional chain. From the result of XRD in section 3.1, the main crystalline phase was pyroxene growing in a chain, which corresponded with the FESEM result. What's more, taking the Avrami constant discussed in section 3.1 into consideration, which was calculated to be 2.40 and 2.35 respectively, a one-dimensional growth style is confirmed, corresponding with the FESEM result. That is, all the tests showed the same result: that the crystalline main phase was pyroxene and confirmed it to be a reliable result. Besides, the crystals' horizontal size for NK sample was about 100nm while being 120nm for K sample, so there were more crystals in NK sample. However, numerous crystals led to more interaction with each other and worsened the mechanical properties because of competing growth. Both the samples grew in the c axis and were arranged densely in a horizontal direction, so there were good mechanical properties in nickel slag glass ceramics [21].

4. Conclusions

It was feasible to prepare glass ceramics with a high content of iron-rich nickel slag without any crystallization agent, the main crystalline phase being pyroxene. When KNO_3 was added, the activation energy increased from 283.70kJ/mol to 345.45kJ/mol, the Avrami constant changed from 2.40 to 2.35, while still growing in a one dimensional chain pattern; Fe^{2+} was oxidized to Fe^{3+} in KNO_3 ambient, increasing the activation energy of crystallization, avoiding to rapid crystallization, enhancing the control of crystallization, thus benefiting crystalline growth, and increasing the crystalline phase content.

Abbreviations

XRD X-ray diffraction
DTA differential thermal analysis

FESEM field emission scanning electron microscope

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