

Crystallization Mechanism of Na₂O-CaO-Al₂O₃-SiO₂-F⁻ Glass Containing Cr₂O₃

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(Received 1998-11-10)

Abstract: The effect of Cr₂O₃ on the nucleation and crystallization of Na₂O-CaO-Al₂O₃-SiO₂-F⁻ glass has been investigated by means of ESR(Electron Spin Resonance), SEM(Scanning Electron Microscope), EDS(Energy Dispersive Spectrometer) and so on. Computer pattern recognition is applied to optimize the heat-treatment schedules. The experimental results show that the base glass containing more than 1.5 % (mass fraction) Cr₂O₃ can be nucleated internally and converted to spheroidal crystal glass materials. The spheroidal crystal consisted of fibrous wollastonite crystals radiating from a center. The residual glass phase filled in the interstices between the fibers and between the spherulites. During heat treatment process, the valence states of chromium changed from Cr⁶⁺ to Cr³⁺, and the Cr-spinel solid solution [CaCr₂O₄] precipitated followed this valence change. At the primary stage of crystallization, the Cr-spinel could act as a nucleating center on which the principal crystalline phase β-CaSiO₃ grew epitaxially.

Key words: crystallized glass; Na₂O-CaO-Al₂O₃-SiO₂; Cr₂O₃; pattern recognition.

Crystallized glass materials are mainly employed in building decorations for their beautiful crystal patterns, good chemical stability and high mechanical strength. The crystals are large enough to be seen by naked eyes, so their microstructures are different from those of glass-ceramics. The preparation of this kind of material is usually based on the surface crystallization mechanism of the CaO-Al₂O₃-SiO₂ system glass [1-3]. This manufacturing process is often complicated, and the sintering pores are difficult to be eliminated from the materials. To simplify the making process and improve the properties of this kind of material, a unique method was used and made the base glass crystallize internally in accordance with large spherulitic crystals. The large spheroidal crystals inlaid the glass matrix and formed beautiful patterns after the sample surface had been polished. From this study, a new kind of building material named crystal pattern glass has been obtained. Nucleating agents play an important role in the crystallization process of this material. The selection of suitable nucleating agents has always been focused on the study of controlled crystallization in glass. A lot of nucleating agents have been studied [4-5]. In this paper, the crystallization mechanism will be dealt with in the Na₂O-CaO-Al₂O₃-SiO₂-F⁻ system glass containing Cr₂O₃.

1 Experimental

The base glass composition was approximately as

follows (mass fraction in %): CaO, 22.0; Al₂O₃, 7.0; SiO₂, 59.0; Na₂O, 6.0; F₂, 2.0. F⁻ ion was used as a catalyst of phase separation in this glass; the sufficient phase separation is an essential condition for the volume crystallization of this glass [4]. Cr₂O₃ was incorporated in the base glass within the range of 1.0%-2.5% (mass fraction, so as the follows). The sample numbers were shown in **table 1**. The glass was melted at 1500 °C

Table 1 The mass fraction of Cr₂O₃ and DTA results in various glasses

Sample No.	C-1	C-2	C-3	C-4
Cr ₂ O ₃ content / %	1.0	1.5	1.75	2.0
Crystallization temperature / °C	892	880	879	878
Activation energy of crystallization / J·mol ⁻¹	341.6	336.2	325.6	322.7

for 2.0 h and annealed at 600 °C for 1.0 h. The peak temperature and activation energy of crystallization were determined by DTA(Differential Thermal Analysis). The valence changes of chromium ions in this glass during heat process have been investigated by ESR (Electron Spin Resonance). The microstructure and phase compositions were studied by SEM (Scanning Electron Microscope) and EDS (Energy Dispersive Spectrometer). The principal crystalline phase was identified by XRD (X-ray Diffraction).

2 Results and Discussions

2.1 The crystallization feature

The base glass only crystallized from the surface after being heat-treated. However, when the mass fraction of Cr_2O_3 was more than 1.5%, the glass could crystallize internally. The peak temperature and activation energy of crystallization decreased with the increase of Cr_2O_3 content (table 1). This indicated that Cr_2O_3 could promote volume crystallization in the studied glass. The crystals grew in the form of large spherulites made up of needles radiating from a center. The spherulite diameter ranged from 2.0 to 4.0 mm, depending on the heat treatment schedules. **Figure 1** is the SEM micrograph of a spherulitic crystal near the center area. Phase A are needle-shaped crystals, and phase B are the center area of the spherulitic crystal. The principal crystalline phase of this sample was wollastonite ($\beta\text{-CaSiO}_3$) determined by XRD in **figure 2**.

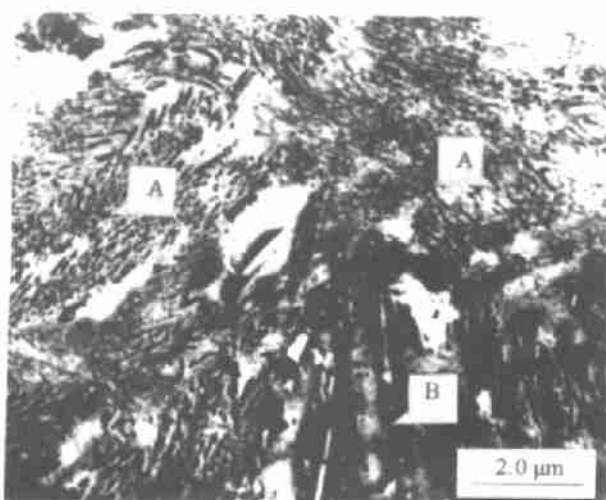


Figure 1 Microstructure of a spherulitic crystal, A- Needle-shaped crystals of CaSiO_3 ; B- Center area of spherulitic crystal.

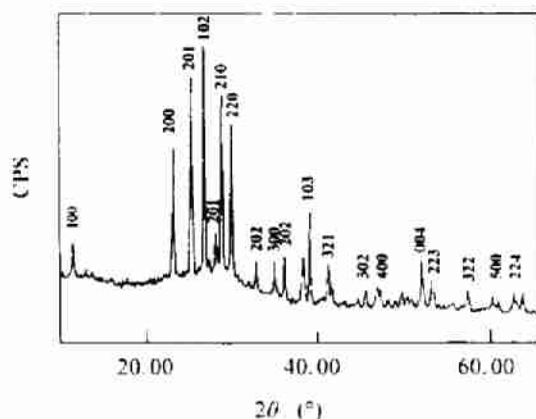


Figure 2 XRD of sample C-3 heat-treated at 940 °C for 2 h

the microstructure and the strength of this material. **Figure 3** shows the relationship between the bending strength and holding time of heat treatment at 980 °C for sample C-4. **Figure 4** shows the microstructure of sample C-4 treated at 980 °C for 3.0 h. When the treatment time was more than 2.5 h, the bending strength would decrease substantially as the time increases. This is due to the formation of coarse crystalline structure. If the crystallization temperature is too high or the holding time is too long, the spherulites would grow large enough and contact each other. The fibrous crystals would convert to clubbed crystals, and this can result in the weakening of binding forces between the crystal and glass phase.

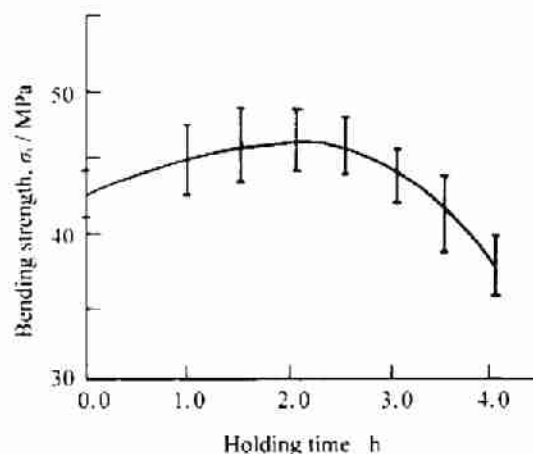


Figure 3 Plots of bending strength against duration time of heat-treatment at 980 °C for sample C-4

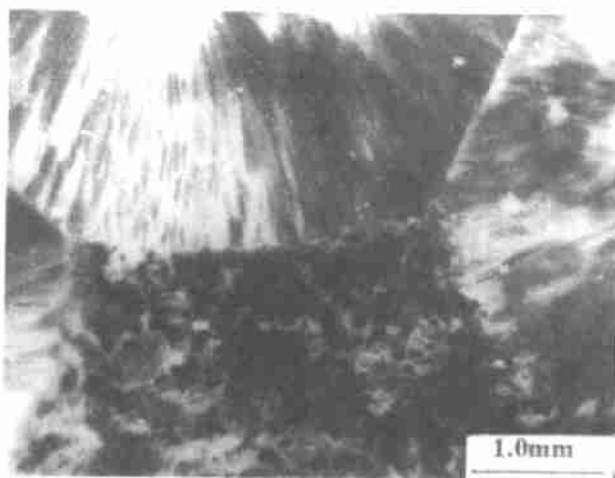


Figure 4 Optical microstructure of sample C-4 heat-treated at 980 °C for 3.0 h

Therefore, it is very important to select a suitable heat treatment process for making high strength materials. Of course, the bending strength of this material is affected by many factors, among which four main factors are as follows: base glass composition, especially

The heat treatment schedules have great effects on

the mole ratio of CaO to SiO₂ (R); nucleating agent content of Cr₂O₃ (C); heat-treatment temperature (t) and holding time (τ). To optimize the heat-treatment schedules, computer pattern recognition is applied to determine the target parameter region with good mechanical properties. The four main factors mentioned

above were chosen as classifying characteristics, and the bending strength at room temperature is selected as criterion. The samples with the values of bending strength σ_f more than 44 MPa were regarded as good points; the others were bad ones. The experimental results consisting of 18 samples are shown in table 2. A

Table 2 The experiment data groups consisted of 18 samples

No.	R	C (mass fraction) %	t / °C	τ / h	σ_f / MPa	X	Y
1	0.4	2.0	900	1.75	46.99	1.4941	-0.1414
2	0.4	2.0	940	2.00	44.67	1.5220	-0.1246
3	0.4	2.0	980	0.00	42.50	1.5287	0.0128
4	0.4	2.0	980	1.00	45.05	1.5382	-0.0408
5	0.4	2.0	980	1.50	46.88	1.5429	-0.0676
6	0.4	2.0	980	2.00	47.50	1.5476	-0.0944
7	0.4	2.0	980	3.00	44.30	1.5571	-0.1480
8	0.4	2.0	980	4.00	38.13	1.5665	-0.2016
9	0.4	2.0	1000	1.50	45.82	1.5557	-0.0525
10	0.4	2.0	1000	2.50	43.65	1.5651	-0.1061
11	0.4	1.0	900	1.75	39.46	1.3103	0.0059
12	0.4	1.0	940	2.00	40.83	1.3382	0.0228
13	0.4	1.0	980	2.00	41.02	1.3639	0.0530
14	0.4	1.5	900	1.75	40.90	1.4022	-0.0678
15	0.4	1.5	940	2.00	42.78	1.4302	-0.0509
16	0.4	1.5	980	2.00	44.98	1.5257	-0.0837
17	0.3	2.0	940	2.00	39.12	1.3884	-0.0164
18	0.3	3.0	940	2.00	40.23	1.5722	-0.1637

target optimum region with better differentiation ability is obtained by principal analysis method [6], and the project diagram of samples on classifying plane is shown in figure 5. It exhibits that the good point was dif-

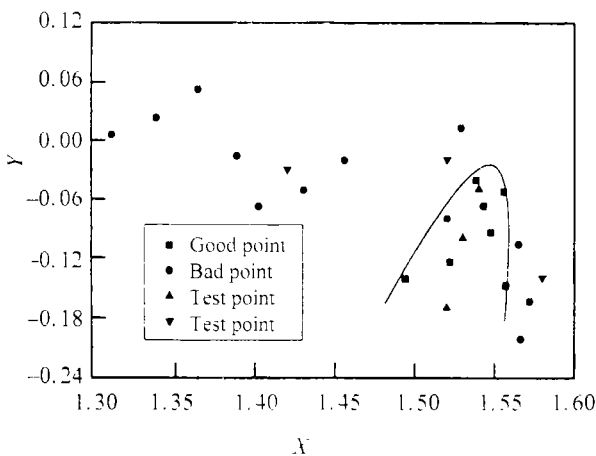


Figure 5 The project diagram of samples on classifying plane

Method: 1; matrix: 1; $i=1, j=2$;

$$X = 1.3362R + 0.1838C + 0.0006t + 0.0095\tau,$$

$$Y = -1.0826R - 0.1474C + 0.0008t - 0.0536\tau;$$

Recognition rate is 100%.

ferentiated from the bad one in different area, projecting points surrounded by parabola present the samples whose bending strength exceeds 44 MPa, and absolutely all the good points located in target parameter optimum region. The projection coordinate (X, Y) corresponding to each sample point is also shown in table 2. In order to verify the pattern recognition program, 2 points in good area and 2 points in bad area are chosen, respectively, and its corresponding technological parameters are calculated with inverse mapping program. The experimental results based on these technological parameters show that this pattern recognition program is reliable. The corresponding technological parameters and experiment results are shown in table 3. The optimized heat-treatment schedules have been obtained from the target parameter region with good mechanical properties.

2.2 Nucleation mechanism

In order to study the catalytic effect of Cr₂O₃ on the nucleating process, the composition of a spherulite center was determined by EDS. The results showed that the center phase was rich in Cr³⁺ and Ca²⁺ ions (figure

Table 3 The optimum parameters gained with reverse project program

Sample No.	Coordinate		Assumed factors		Recognition factors		Property σ MPa
	X	Y	R	C (mass fraction) %	t °C	τ h	
1	1.54	-0.05	0.4	1.75	1037.5	2.670	46.04
2	1.53	-0.10	0.4	2.00	962.1	1.850	46.49
3	1.52	-0.02	0.4	2.00	957.7	0.300	42.75
4	1.58	-0.14	0.3	3.00	955.5	1.776	39.89

6 (b)). The needle-shaped phase was rich in Si^{4+} and Ca^{2+} ions (figure 6 (a)). This result is consistent with the XRD spectra in figure 2. The needle-shaped phase was wollastonite ($\beta\text{-CaSiO}_3$). Wollastonite crystals grew on

the surface of the center crystals. This implies that it is the center phase containing more Cr^{3+} and Ca^{2+} ions that contributes to the forming of spherulitic wollastonite crystals.

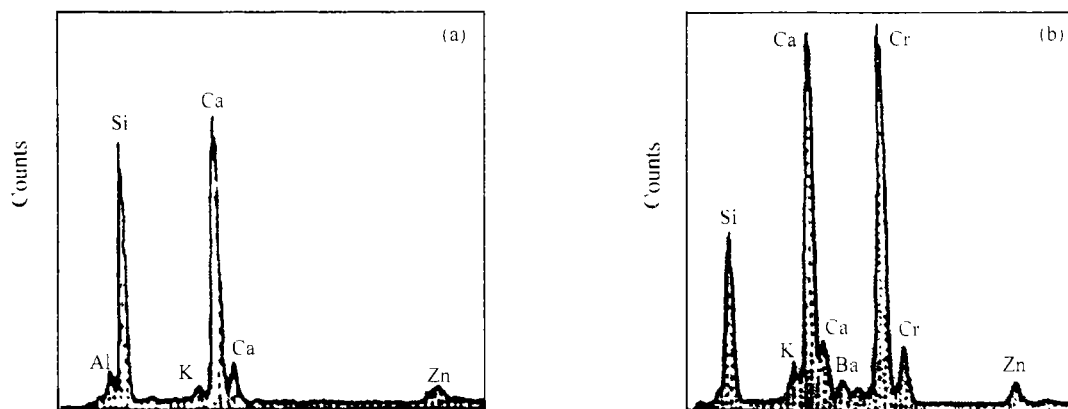


Figure 6 EDS spectra of the phase A and B of spherulitic crystal in figure 1, (a) Needle-shaped crystals; (b) Center phase of spherulitic crystal

To investigate the effect of Cr_2O_3 on the nucleation of this designed glass, the valence change of chromium during heat treatment process has been studied by ESR. ESR spectra at room temperature of the original glass

and heat-treated samples were shown in figure 7. The original glass appears two ESR absorption signals (figure 7(a)). The resonance absorption at $g = 1.96$ results from the contributions of both Cr^{3+} and Cr^{2+} ions [7].

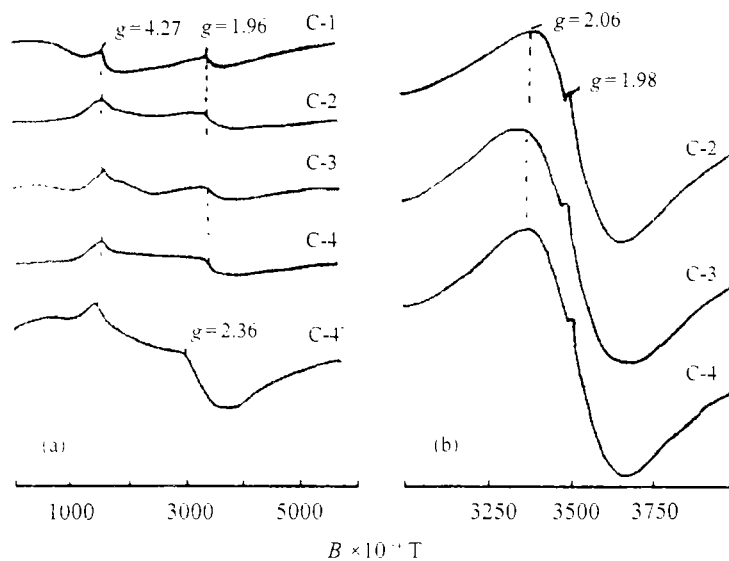


Figure 7 ESR spectra of the original glasses and heat treated samples at room temperature, (a) The original glasses before heat-treatment, C-4' is C-4 after heat-treated at 860 °C for 2.0 h; (b) The samples after heat-treated at 960 °C for 2.0 h.

The intensities for signals at $g=1.96$ increases as the Cr_2O_3 content increases. For samples after being heat-treated, the ESR spectra are characterized by the appearance of resonance absorption at $g=2.06$ and $g=1.98$. The narrow and weak resonance with $g=1.98$ is due to Cr^{5+} ions. The broad and symmetric resonance absorption with $g=2.06$ is due to exchange-coupled Cr^{3+} pairs [8], its intensity is about seven times more than that of corresponding original glass. In original glass the chromium is mainly in the form of Cr^{6+} , while the concentration of Cr^{3+} is comparatively smaller. In the heat-treated samples the chromium predominantly existed as Cr^{3+} ions. This indicated that the valence states of chromium changed from Cr^{6+} to Cr^{3+} ions during heat-treatment process. This valence change would contribute to the precipitation of Cr-spinel solid solution in glass [9]. Combining the EDS result in figure 6 and the ESR spectra, it can be inferred that this Cr-spinel precipitated in the form of CaCr_2O_4 . CaCr_2O_4 has a cubic close-packed structure, its lattice parameter is $a_0=0.83$ nm, $\beta\text{-CaSiO}_3$ is triclinic crystal, and its lattice parameters are $a_0=0.794$ nm, $b_0=0.73$ nm, $c_0=0.71$ nm. The mismatch of the parameters between them is less than 15%. The close similarity of lattice parameters in some direction makes wollastonite nucleate heterogeneously on the surface of CaCr_2O_4 crystals.

4 Conclusions

(1) The structure of macrocrystal glass material is that a number of large spheroidal crystals in the matrix glass phase. This material has beautiful crystal patterns after the surface is polished.

(2) Cr_2O_3 could effectively catalyze the volume cry-

stallization of the $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-F}^-$ system glass. During heat-treatment process, the valence states of chromium changed from Cr^{6+} to Cr^{3+} , and the Cr-spinel (CaCr_2O_4) precipitated followed this valence change. The CaCr_2O_4 crystal could act as a nucleating center on which the principal crystalline phase $\beta\text{-CaSiO}_3$ grew epitaxially.

(3) The computer pattern recognition is very useful to optimize the heat-treatment schedules by determining the target parameter region with good mechanical properties.

Acknowledgment

This project was supported by the Natural Science Foundation of Shandong Province.

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