Critical Cooling Rates for the Formation of Glass for Silicate Melts

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The critical cooling rate required for the formation of glass is one of the important characteristics for silicate slag. The critical cooling rates have been measured for R_2O ($R=Li, Na$ and K)– SiO_2 and $R'O$ ($R'=Ca, Sr$ and Ba)– SiO_2 systems by the combined use of the hot-thermocouple method and an ordinary melt-quenching method. In all systems, the minima in critical cooling rate corresponded with the composition range of low liquidus temperatures near the eutectics; the critical cooling rates decreased with increasing viscosities at the liquidus temperatures. The measured critical cooling rates were similar to those predicted by the Uhlmann equation and Ota equation. Some factors affecting the critical cooling rate were discussed.

KEY WORDS: silicate; critical cooling rate; glass formation; slag; viscosity.

1. Introduction

The use of metallurgical slag is desirable for some industrial applications. For example, silicate slag is appropriate for concrete aggregates. Excessive expansion of concrete occurs through chemical reactions between cements and certain constituents in the aggregates.¹⁾ The reactivity corresponds mainly to the quantity and quality of aggregates used, *e.g.*, SiO_2 content of residual glass in the silicate slag. Consequently, the critical cooling rate required for the formation of glass is one of the important characteristics for the utilization of silicate slag. However, there are only a few reports on the measured critical cooling rate of silicates. The authors experimentally determined the critical cooling rate for ferro nickel slag.²⁾ Since the composition of practical slag is very complicated, the investigation of the critical cooling rates for simple compositions seems to be desirable. In this study the critical cooling rates have been measured for R_2O ($R=Li, Na$ and K)– SiO_2 and $R'O$ ($R'=Ca, Sr$ and Ba)– SiO_2 systems by the combined use of the hot-thermocouple method and an ordinary melt-quenching method. Also the critical cooling rates determined experimentally were compared with those calculated using the Uhlmann equation³⁾ and the Ota equation,⁴⁾ and factors affecting the critical cooling rate were discussed.

2. Experimental Procedure

Special-grade alkali and alkaline earth carbonates and silicon dioxide were used. Table 1 shows the compositional range for measuring the critical cooling rates required for the formation of glass in R_2O ($R=Li, Na$ and K)– SiO_2 and $R'O$ ($R'=Ca, Sr$ and Ba)– SiO_2 systems. Mixed batches were melted in Pt crucibles at temperatures

100 K above the respective liquidus temperatures for 2 h to remove carbon dioxide. In the hot-thermocouple method,⁵⁾ a several-mg droplet on the Pt and Pt–Rh13% filament was continuously cooled to room temperature in the cooling rate range of 1.0×10^{-2} to $2.0 \times 10^2 \text{ K} \cdot \text{s}^{-1}$. Several ten-mg samples were remelted and cooled at 1.0×10^{-3} , 2.0×10^{-3} and $5.0 \times 10^{-3} \text{ K} \cdot \text{s}^{-1}$ in an electric furnace using a programmed controller.

Crystallization was observed through the microscope. The detectable crystallized volume fraction was about 6×10^{-6} . Since samples with compositions below 31 mol% Li_2O and 28 mol% BaO were phase-separated during cooling,⁶⁾ crystallization was confirmed by the X-ray powder method.

Viscosities of Li_2O – SiO_2 and K_2O – SiO_2 melts were measured with a rotating crucible viscometer. Those of Na_2O – SiO_2 ⁷⁾ and $R'O$ ($R'=Ca, Sr$ and Ba)– SiO_2 ⁸⁾ melts were quoted from previous studies.

3. Results

Figure 1 shows the critical cooling rates required for the formation of glass as a function of composition. The

Table 1. Compositional range for measuring the critical cooling rates to form glasses in R_2O ($R=Li, Na$ and K)– SiO_2 and $R'O$ ($R'=Ca, Sr$ and Ba)– SiO_2 systems.

System	$R_2O, R'O$ (mol%)
Li_2O – SiO_2	20–45
Na_2O – SiO_2	20–60
K_2O – SiO_2	20–50
CaO – SiO_2	40–55
SrO – SiO_2	30–47.5
BaO – SiO_2	20–45

Fig. 1. Measured critical cooling rates for glass formation in (a) $\text{Li}_2\text{O}-\text{SiO}_2$, (b) $\text{Na}_2\text{O}-\text{SiO}_2$, (c) $\text{K}_2\text{O}-\text{SiO}_2$, (d) $\text{CaO}-\text{SiO}_2$, (e) $\text{SrO}-\text{SiO}_2$ and (f) $\text{BaO}-\text{SiO}_2$ systems.

open circles represent noncrystalline samples; the solid circles represent partly crystalline samples. Solid lines represent the critical cooling rates Q^* . Also, the results previously reported by Havermans *et al.*,⁹⁾ Ota *et al.*,¹⁰⁾ and Fang *et al.*,¹¹⁾ are shown for comparison. In all systems, the minima in Q^* correspond with the composition range of low liquidus temperatures near the eutectics seen in the respective phase diagrams. Experimental values for alkali silicates except for the composition below 31 mol% Li_2O closely resemble the results previously reported.

In order to calculate the critical cooling rate in the following chapter, the temperature dependence of viscosity for $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$ melts is shown in Fig. 2. It is clear that the isothermal viscosities decrease with increasing content of alkali oxides.

4. Discussion

4.1. Prediction of Critical Cooling Rate

Equations for calculating the critical cooling rates required for the formation of glass have been proposed

by Sarjeant and Roy,¹²⁾ Vreeswijk *et al.*,¹³⁾ Uhlmann and Yinnon,³⁾ and Ota *et al.*,⁴⁾ The predictions of the Uhlmann equation and Ota equation in which homogeneous nucleation and isotropic crystal growth are assumed agreed with previously measured critical cooling rates for alkali silicates to a certain extent.^{11,14)} The data of this study is discussed based on those two equations.

4.1.1. Uhlmann Equation

The volume fraction X crystallized in a time t may, for small X , be expressed as

$$X = \frac{\pi}{3} I_v u^3 t^4, \dots\dots\dots(1)$$

where I_v is the nucleation frequency per unit volume and u is the crystal growth rate.

Taking X as the detectable crystallized volume fraction and calculating the time required at each temperature to develop the indicated degree of crystallinity, one constructs time-temperature-transformation (TTT) curves.¹⁵⁾ The critical cooling rate is the minimum cooling rate for glass formation. Consequently, the critical

Fig. 2. Temperature dependence of viscosity for (a) $\text{Li}_2\text{O-SiO}_2$ and (b) $\text{K}_2\text{O-SiO}_2$ melts.

cooling rate is estimated by the relation

$$Q^* \approx \frac{T_L - T_N}{t_N}, \quad (2)$$

where T_L is the liquidus temperature, T_N is the temperature at the nose of the TTT curve, and t_N is the time at the nose. The temperature of the nose, T_N , can be approximated as the following equation for many materials¹⁶⁾:

$$T_N \approx 0.77 T_L. \quad (3)$$

With the use of Eqs. (1), (2), (3) and the formal theory of transformation kinetics, the critical cooling rate for glass formation, Q^* , can be expressed as³⁾

$$\begin{aligned} \log(Q^*/\text{K} \cdot \text{s}^{-1}) = & -\log(\eta_L/\text{Pa} \cdot \text{s}) + 2 \log(T_L/\text{K}) \\ & - 0.212 B \cdot \log e + \log(A/J \cdot \text{m}^{-3} \cdot \text{K}^{-1}) \\ & + 3/4 \log \left(1 - \exp \left(\frac{0.34 \Delta S_M / J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{R/J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right) \right), \quad (4) \end{aligned}$$

where η_L is the viscosity at $0.77 T_L$, the barrier to crystal $A = 4 \times 10^4 \text{ J} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$ and ΔS_M is the molar entropy of fusion. As can be seen in Eq. (4), the critical cooling rate decreases with decreasing liquidus temperature T_L , increasing viscosity η_L and the molar entropy of fusion, ΔS_M .

4.1.2. Ota Equation

Ota *et al.*⁴⁾ have pointed out that the Uhlmann equation which is based on the TTT curve is not valid in continuous-cooling conditions. When the samples are continuously cooled from T_L to low temperature (*e.g.*, 0 K) at a rate of Q , the crystallized volume fraction X is expressed as

$$X = \frac{4\pi}{3Q^4} \int_0^{T_L} \left\{ \int_0^T u dT \right\}^3 I_v dT. \quad (5)$$

The nucleation frequency per unit volume I_v and the

crystal growth rate u are described with the flow unit v ($\text{m}^3 \cdot \text{mol}^{-1}$), viscosity parameter and thermodynamics parameter. Cooling rate Q can be approximated as⁴⁾

$$\begin{aligned} \log(Q/\text{K} \cdot \text{s}^{-1}) = & -\log(\eta_L/\text{Pa} \cdot \text{s}) - 1.43 \times 10^{-2} E_\eta / T_L (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ & - 3T_0/T_L + 2 \log(T_L/\text{K}) - \log(v/\text{m}^3 \cdot \text{mol}^{-1}) \\ & - 9.08 \alpha^3 \Delta S_M / (J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) - 0.25 \log X - 2, \quad (6) \end{aligned}$$

where η_L is the viscosity at the liquidus temperature, E_η is the activation energy for viscous flow, T_0 is a constant in the Fulcher equation¹⁷⁾ and α is a molar surface energy/molar heat of fusion ratio.¹⁸⁾ The viscosity at the liquidus temperature is hereinafter referred to as the liquidus viscosity. For a minimal constant value of the detectable degree of crystallinity, X , one can estimate the critical cooling rate for glass formation, Q^* . From Eq. (6), the favorable conditions for glass formation, Q^* . From Eq. (6), the favorable conditions for glass formation are that the liquidus viscosity η_L is high; the activation energy for viscous flow, E_η , is high; the liquidus temperature T_L is low; a constant in the Fulcher equation, T_0 , is high; the flow unit v is high; and the molar entropy of fusion, ΔS_M , is high.

4.1.3. Comparison of Theory with Experimental Data

Table 2 shows the values for calculating the critical cooling rate: the liquidus temperature T_L , liquidus viscosity η_L , activation energy for viscous flow, E_η , a constant in the Fulcher equation, T_0 , and viscosity at the nose ($0.77 T_L$), η_N . Liquidus viscosities and the activation energies were determined from the temperature dependence of viscosity for silicate melts shown in Fig. 2 and those in the previous studies.^{7,8)} To estimate the viscosity at the nose ($0.77 T_L$), the previously reported glass transition temperature T_g ¹⁹⁾ was used as a corresponding state parameter ($\eta = 10^{12} \text{ Pa} \cdot \text{s}$), and a least squares fit of the appropriate Fulcher equation was employed for the flow data of melts. A flow unit v of

$30 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$,⁴⁾ a detectable crystallized volume fraction X of 10^{-6} ³⁾ and a molar surface energy/molar heat of fusion ratio α of 0.25¹⁷⁾ were used. The values of nucleation barrier B are taken as 60¹¹⁾ for alkali silicates and 80 for alkaline earth silicates, the latter being the value for anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$).²⁰⁾ Because the relation of the nucleation barrier B with the molar entropy of fusion, ΔS_M , is expressed as $B = 12.6 (\Delta S_M/R)^3$, ΔS_M for alkali silicates is $39.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and that for alkaline earth silicates is $52.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

Table 2. The values for calculating the critical cooling rates: liquidus temperature T_L , liquidus viscosity η_L , activation energy for viscous flow, E_η , a constant in Fulcher equation, T_0 , and viscosity at the nose, η_N for $\text{R}_2\text{O}(\text{R}=\text{Li, Na and K})\text{-SiO}_2$ and $\text{R}'\text{O}(\text{R}'=\text{Ca, Sr and Ba})\text{-SiO}_2$ systems.

Composition (mol%)	T_L (K)	η_L (Pa·s)	E_η (kJ·mol ⁻¹)	T_0 (K)	η_N (Pa·s)
Li₂O-SiO₂					
25.0 75.0	1 536	16.6	154	449	1.13×10^3
30.0 70.0	1 323	38.1	140	537	5.75×10^3
35.0 65.0	1 326	15.1	137	551	2.18×10^3
40.0 60.0	1 392	37.8	156	487	5.28×10^2
Na₂O-SiO₂					
20.0 80.0	1 400	170	174	423	3.29×10^4
30.0 70.0	1 136	831	152	535	1.12×10^6
40.0 60.0	1 216	75.9	153	494	2.94×10^4
50.0 50.0	1 357	1.07	129	518	80.7
60.0 40.0	1 466	0.04	29.7	658	0.11
K₂O-SiO₂					
30.0 70.0	1 284	3.58	178	513	2.43×10^5
35.0 65.0	1 309	116	169	534	5.37×10^4
40.0 60.0	1 197	192	174	577	4.59×10^5
45.0 55.0	1 117	90.0	174	627	2.00×10^6
50.0 50.0	1 252	1.15	257	484	1.57×10^4
CaO-SiO₂					
35.0 65.0	1 837	2.69	154	846	1.83×10^2
38.8 61.2	1 720	2.08	186	838	6.21×10^2
41.6 58.4	1 756	0.98	167	856	1.48×10^2
43.6 56.4	1 787	0.68	164	854	79.6
48.7 51.3	1 809	0.35	149	883	26.7
49.7 50.3	1 817	0.29	148	889	21.4
50.7 49.3	1 804	0.29	151	891	25.4
51.7 48.3	1 800	0.27	146	907	22.1
52.7 47.3	1 790	0.26	147	921	25.1
53.7 46.3	1 780	0.27	149	927	30.0
SrO-SiO₂					
40.5 59.5	1 768	1.57	166	822	1.89×10^2
44.4 55.6	1 816	0.65	159	836	52.8
50.3 49.7	1 851	0.35	143	884	19.1
BaO-SiO₂					
30.7 69.3	1 682	6.21	184	760	1.43×10^3
33.5 66.5	1 693	4.48	178	768	843
40.2 59.8	1 726	2.04	147	807	158
42.0 58.0	1 709	1.55	162	795	177
49.8 50.2	1 873	0.27	99.5	882	4.03

It is assumed that the effect of the type of cation on the molar entropy is negligible.¹⁴⁾

The measured and calculated critical cooling rates for glass formation are shown in Fig. 3. In all systems, the experimentally determined values agree approximately with calculated values. Since the measured values are slightly smaller than predicted values, which consider only homogeneous nucleation, heterogeneous nucleation may not have occurred in this experiment. The differences between the measured and calculated values are derived from quoted values for the molar surface energy/molar heat of fusion ratio α , the nucleation barrier B and the molar entropy of fusion, ΔS_M . The critical cooling rates predicted from the Uhlmann equation are one order larger than those predicted from the Ota equation. The difference between those results is that the use of TTT curves results in overestimation of the critical cooling rates required for the formation of glass.

4.2. Factors Affecting Critical Cooling Rate for Glass Formation in Silicates

It is experimentally known that a melt with a large viscosity at a liquidus temperature forms glass easily during cooling. The Uhlmann equation and Ota equation also indicate that the critical cooling rate ($\log Q^*$) decreases with increasing liquidus viscosity ($\log \eta_L$). If each term on the right-hand side of Eqs. (4) and (6), except for $\log \eta_L$, is constant, in other words, the critical cooling rate depends only upon the liquidus viscosity, a slope of -1 in the $\log Q^* - \log \eta_L$ relation should be obtained.

Figure 4 shows the relationship between $\log Q^*$ and $\log \eta_L$. In all systems, $\log Q^*$ decreases with increasing $\log \eta_L$. The slopes for alkali silicates are -0.98 , -0.87 and -0.58 ; those for alkaline earth silicates are -7.90 , -2.98 and -2.02 . The results show that the critical cooling rates for alkali silicates depend only upon the liquidus viscosity; another factor contributes to those for alkaline earth silicates. The factors determining the critical cooling rate for alkaline earth silicates are discussed below using the Ota equation.

Table 3 shows the measured critical cooling rates and the experimentally determined parameters of the Ota equation of Eq. (6) for some compositions of alkaline earth silicates. Liquidus viscosities for these compositions are almost equal. It is difficult to measure the molar entropy of fusion, which is one of the parameters.³⁾ It can be seen in this table that $\log Q^*$ is not correlated with these parameters. The results suggest that the molar entropy of fusion, the only residual parameter in the Ota equation, is important in determining the critical cooling rate for alkaline earth silicates.

Table 3. Critical cooling rates and parameters in the Ota equation for alkaline earth silicate.

Composition (mol%)	$\log(Q^*/\text{K} \cdot \text{s}^{-1})$	$-\log(\eta_L/\text{Pa} \cdot \text{s})$	Parameters in Ota equation		
			$-1.43 \times 10^{-2} E_\eta/T_L$ ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$-3T_0/T_L$	$2\log(T_L/\text{K})$
49.8BaO-50.2SiO ₂	3.13	0.575	-0.76	-1.41	6.55
50.3SrO-49.7SiO ₂	2.62	0.453	-1.11	-1.43	6.54
53.7CaO-46.3SiO ₂	-0.395	0.573	-1.20	-1.56	6.50
48.7CaO-51.3SiO ₂	-0.803	0.458	-1.18	-1.46	6.51

Fig. 3. Comparison of experimental and calculated critical cooling rates in (a) Li₂O-SiO₂, (b) Na₂O-SiO₂, (c) K₂O-SiO₂, (d) CaO-SiO₂, (e) SrO-SiO₂ and (f) BaO-SiO₂ systems.

Fig. 4. Relationship between $\log Q^*$ and $\log \eta_L$.

5. Conclusions

The critical cooling rate required for the formation of glass is one of the important characteristics of silicate slag. For fundamental study, the critical cooling rates in $R_2O(R=Li, Na \text{ and } K)\text{-SiO}_2$ and $R'O(R'=Ca, Sr \text{ and } Ba)\text{-SiO}_2$ systems have been measured by the combined use of the hot thermocouple method and an ordinary melt-quenching method.

In all systems, the minima in critical cooling rate corresponded with the composition range of low liquidus temperatures near the eutectics; the critical cooling rates decreased with increasing liquidus viscosities. The measured critical cooling rates were similar to those predicted by the Uhlmann equation and Ota equation. The results suggested that the molar entropy of fusion was one of the important parameters for determining the critical cooling rate for alkaline earth silicates.

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