Rupture Phenomena of Molten Na$_2$O·2SiO$_2$ Thin Films

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A thin film drawn-out technique was developed to investigate the rupture mechanism of molten sodium silicate thin films. The rupture length of molten sodium silicate films was measured as a function of temperature and the drawn-out rate. It was found that the rupture thickness, $T$, was dependent on the drawn-out rate, $v$, at high drawn out rate, being proportional to the $2/3$rd of $v$, i.e.,

$$T \propto v^{2/3}$$

At low drawn-out rate the rupture thickness was found to be independent from $v$ below a critical value $v_c$.

It was concluded that the rupture at high drawn-out rate was controlled by the external drawn-out rate of the molten slag and the constant rupture thickness at the low drawn-out rate might be determined by the Plateau border suction flow.

KEY WORDS: rupture phenomena; sodium disilicate; molten film; rupture thickness; film thinning.

1. Introduction

Foaming of molten slags has been observed in many steelmaking processes such as the converter process, bath smelting, hot metal treatment and in electric arc furnaces. Because of its importance, many studies on the foaming were carried out over years.$^{1-4}$ Slag foaming has generally been discussed based on the physical properties (viscosity and surface tension) of the slags, and some empirical relations were established to estimate the foam index from the physical properties of the slags.

Despite the efforts in studies of slag foaming, the basic characteristics of the slag foaming are still poorly understood. The process of foaming is a dynamic phenomenon; the deformation of slag films and the film thickness vary with time. Most studies on slag foaming, however, have focused on the foaming column itself. Little attention has been paid to the dynamic behavior of thin slag film. A good understanding of the dynamic behavior of thin slag film is therefore still needed for controlling slag foaming.

It is also very important for an effective application of the lubricant fluxes in the continuous casting process to control the quality of the steel slabs.

Recently, Nexhip et al.$^{5,6}$ have made real time observations and measurements of thickness profiles of films of CaO–SiO$_2$–Al$_2$O$_3$ slag using a laser interferometry technique. It has been shown that non-uniform thinning took place. There is, however, still no clear knowledge of the rupture mechanism of slag films and of the critical film thickness at rupture. In this study, molten sodium silicate thin film was drawn out at varying drawn-out rate and the rupture thickness of slag film was measured to investigate the rupture mechanism of the slag film. The experiments were carried out by varying the drawn-out rate and temperature.

2. Experimental

2.1. Apparatus

The general experimental arrangement is illustrated in Fig. 1. It consisted of a Pt furnace, a molten film drawn-out device, and a stepping motor system. The detail of the film drawn-out arrangement is schematically shown in Fig. 2. A small alumina rod (2.0 mm of diameter and 10 mm height) was inserted between the two wires of a U-shaped thermocouple and maintained contact with the two wires. The diameter of the thermocouple wire is 0.5 mm. The molten slag film was held by the surface tension in the area surrounded by thermocouple wires and the alumina rod as shown in Fig. 2. The film was held horizontally to avoid the effect of gravitational force on drawing the film. The inserted alumina rod was fixed to a supporting alumina tube (7 mm of outside diameter, 150 mm length). This support alumina tube was connected to a slide stage that was driven by a stepping pulse motor controlled by a microcomputer. By this way, the inserted alumina rod could slide, while maintaining the contact with the thermocouple wires, at a constant rate in the rate of 0.01 to 4.0 mm/s to drawn out a molten slag film. Due to geometrical restrictions, the drawn-out length of the molten film was limited to 30 mm.

The thermocouple was connected to a high-speed relay which could switch between a potentiometer and a power supply to function as a so called hot thermocouple, so the heating of the slag and measurement of the slag temperature could be achieved simultaneously, in prac-
tical sense. Details of the hot thermocouple method can be found elsewhere. To keep a uniform temperature within the drawn-out slag film, the whole film drawn-out system was heated by the subsidiary Pt heating furnace. The temperature next to the inserted alumina tube was measured by using another thermocouple placed above the supporting alumina tube. The appropriated temperature of Pt furnace to keep the uniform temperature within the film was determined in preliminary experiments. The Pt furnace had a silica window of 20 mm diameter for observation of the film and the rupture phenomena.

2.2. Procedure

In each experiment, about 20 mg of slag was initially placed at the junction of the thermocouple and melted at the required temperature in air. The alumina tube was then moved in to bring the rod in contact to the molten slag. The initial distance between the alumina rod and the tip of the thermocouple was always fixed to 2 mm. After the establishment of the predetermined temperature of the slag and of the Pt furnace, the stepping motor was activated and a slag film drawn out until the slag film ruptured. The rupture length was calculated from the number of pulses. The experiments were carried out in air by varying the drawn-out rate and temperature.

2.3. Materials

Slag samples were prepared by using reagent grade Na$_2$CO$_3$ and SiO$_2$ dried powders as starting materials. Dried powders were well mixed and melted in the Pt crucible in a muffle furnace at 1473 K in air and quenched on a water-cooled copper plate. Pieces of crushed slags were stored in a dessicator for later use.

3. Results

3.1. Distribution of Film Thickness

Molten films were quenched at various drawn-out lengths and their thickness along the length was measured by using a digital micro thickness meter. Typical results of the thickness of Na$_2$O-2SiO$_2$ films (of 11-mm length) at 1173 and 1473 K along the drawn out direction after drawn out about 11 mm were shown in Fig. 3. The thickness of film gradually became thinner from the tip of the thermocouple and became almost constant for major part of the film and then quickly increased near the alumina rod at both temperatures. For another sodium silicate systems, the same tendency of distribution was also observed. As a first approximation, it can be said that the drawn-out film had nearly constant film thickness except at both ends and this constant thickness was defined as the horizontal thickness, $T_h$. The results of thickness measurement at different drawn-out length are shown in Fig. 4. The values of $T_h$ were scattered, but it was almost reciprocally proportional to the drawn-out length. Therefore, the rupture thickness can be estimated from the rupture length based on this relation.
3.2. Effect of Alumina Dissolution

In the present experiment, the alumina tube was always in contact with the molten silicate slags. To examine the effect of the dissolution of alumina from the alumina rod into the molten silicate slags on the rupture length, slag films just before rupture was quenched and the slag composition was analyzed by using the EPMA technique. Typical results of the distribution of Na₂O, SiO₂ and Al₂O₃ in Na₂O·2SiO₂ slag along the drawn-out direction at 1473 K were shown in Fig. 5. The content of Na₂O and SiO₂ were almost constant over whole film length. The dissolution of alumina was almost negligible except near the alumina tube. The alumina enriched area was restricted within about 0.5 mm from the alumina surface and this area formed a thick meniscus as already shown in Fig. 4. It was observed that the film rupture always took place far from the alumina rod. It can be said that the dissolved alumina had little effect on the rupture of the slag films.

3.3. Effect of Drawn Out Rate

The rupture length of Na₂O·2SiO₂ slag at 1173 and 1323 K as a function of drawn-out rate from 0.01 to 2.0 mm/min was presented in Fig. 6 and the result at 1473 K in Fig. 7. The rupture length at 1173 K below a drawn-out rate of about 0.2 mm/s was almost independent from the drawn-out rate. At drawn-out rate above this value of 0.2 mm/s, the rupture length decreased with the drawn-out rate. The same tendency was also observed at 1323 and 1473 K, but the rupture length at 1473 K decreased again with the drawn-out rate decreasing below about 0.05 mm/min. In experiments with the drawn-out rate of less than 0.05 mm/min at 1473 K, the small bubbles around Pt wire was observed. The presence of these bubbles might be the reason for the rupture length decrease at drawn-out rate lower than 0.05 mm/min. Details of the bubble formation mechanism, however, were not yet established. Of all these results, the most intriguing was that the molten slag film was always ruptured once it reached some critical thickness, no matter how slow the external drawn rate was.

We may define the rupture length that was independent from the drawn-out rate as L₁ and the dependent length as L₄. The rupture length (L₄) was found to be apparently proportional to (2/3)⁻¹ of the drawn-out rate within experimental scatters for all measurements. The drawn-out rate where the dependency of stretching rate changed from independent to dependent was defined as vₑ.

The two observed drawn-out rate dependencies of the rupture length strongly suggested two rupture mechanisms, as will be discussed later in this paper.

3.4. Effect of Temperature

A series of experiment was carried out with Na₂O·2SiO₂ slag at temperatures from 1173 to 1473 K. The measured drawn-out rate independent rupture length (L₁) for Na₂O·2SiO₂ slags was plotted as a function of temperature in Fig. 8. It was found that the L₁ had only a very slight decease with temperature except at 1173 K. From the phase diagram of Na₂O·2SiO₂ system, the melting point of Na₂O·2SiO₂ was 1410 K. Since the experimental temperature of 1173 K was relatively close
to the melting point, slight fluctuations of temperature could easily introduce the solid precipitation. Solid precipitation or near melting point clustering in the melt could have something to do with the sharper temperature dependence near 173 K.

As can be seen from Figs. 6 and 7, the drawn-out rate dependent thickness, \( L_d \), at a given drawn-out rate would increase with temperature.

4. Discussions

4.1. High Drawn-out Rates

When a molten film is drawn from the border at a finite rate, the pressure and the surface curvature change continuously in the transition region. A quantitative theory of thin films relating the velocities and forces involved has been developed under simplifying assumptions that only hydrodynamic forces are involved and the surface of the film is in inextensible in the region considered.\(^7,8)\)

Two quantities are involved here; the velocity \( v \) with which the film is drawn out of the border, its limiting thickness \( T \). In the case of the horizontal bulk liquid surface, these are related by

\[
T = 2x_0(\kappa_0)^{-1}(v/v_0)^{2/3} \quad \ldots \ldots \quad (1)
\]

\[
= 0.93(\eta v)^{2/3}(\gamma)^{1/6}(\rho g)^{1/2} \quad \ldots \ldots \quad (1')
\]

where \( x_0 \) is a constant and numerically computed to 0.64.\(^7\) \( \kappa_0 \) is the curvature of the so called Plateau border. \( v_0 = \gamma/3\eta \), is a velocity related to the speed of retraction of a thin broken film, where \( \gamma \) is the surface tension, \( \eta \) is the viscosity of melt, \( \rho \) is the density of the molten slag and \( g \) is the gravitational constant. Eq. (1') showed that the limiting thickness of the drawn-out film was proportional to the drawn-out rate and to the viscosity to the 2/3 power. The limiting thickness was but a very weak function of the surface tension. At the early stage of film drawing, the film thickness was thicker than the limiting thickness, it could thin while being drawn. Once it reached the limiting thickness, the film could not become thinner and further drawing would then rupture the film.

The curvature of the Plateau border, \( \kappa_0 \), might change while the film was drawn out. As shown in Fig. 3, however, after some drawn-out length, almost parallel plane was established. Therefore, the \( \kappa_0 \) may not change so much once the parallel plane formed. Then, the rupture thickness is proportional to the 2/3 power of the drawn-out rate from Eq. (1)

\[
T \propto (v)^{2/3} \quad \ldots \ldots \quad (2)
\]

As shown in Fig. 4, the measured rupture thickness \( T \) was reciprocally proportional to the rupture length \( L_d \).

\[
T \propto 1/L_d \quad \ldots \ldots \quad (3)
\]

Combination of the Eqs. (2) and (3) gives

\[
L_d \propto (v)^{-2/3} \quad \ldots \ldots \quad (4)
\]

The relation Eq. (4) means that the rupture length can be proportional to the \((2/3)^{-1}\) of the drawn-out rate. This dependency was apparent in Fig. 3 with the drawn-out rate above \( v_c \). In other words, the rupture length \( L_d \) dependency of \((2/3)^{-1}\) on the drawn-out rate above \( v_c \) was in good accord with the fluid dynamical consideration.

4.2. Low Drawn-out Rates

As shown in Figs. 6 and 7, at drawn-out rate less than \( v_c \), the rupture length or the rupture thickness was almost independent from the drawn-out rate. Similar phenomena were also reported for very thin soap film system.\(^2\)

In the soap film system, the surfaces were covered with carbonic acid and the two surfaces were negatively charged. The independent thickness of soap film from the drawn-out rate was explained by the repulsion of these negative charges (double layers). It is estimated that the double layers repulsion force can reach about 10–100 nm. In the present system, the rupture thickness was in all cases no less than several micrometers. This double layers repulsion mechanism was therefore not expected to operate in the molten slag system under conditions in this study.

In the present work, the film was drawn out by an external force. There is, however, always a suction flow in a thin film towards the border even without the external forces. This suction flow is due to the pressure difference between the almost horizontal region of the film and the curved Plateau border region around Pt wire. Since the suction flow rate was probably independent from the drawn-out rate, at sufficiently high drawn-out rate, film thinning due to the suction flow would fall below that due to the external drawing, and therefore the film thinning would be under the control of the latter.

With the decrease of the drawn-out rate, however, the rate of suction flow could eventually overtake the external drawn-out rate. Once the suction flow became dominant, the suction flow rate rather than the external drawn-out rate would determine the rupture and the rupture thickness. The rupture thickness, therefore, became independent from the external drawn-out rate. To establish the detailed rupture mechanism at low drawn-out rate, however, further quantitative work is necessary.

5. Summary and Conclusions

A thin film drawn-out technique was developed to investigate the rupture of molten soda silicate thin film. The rupture length was measured as a function of drawn-
out rate from 0.01 to 2.0 mm/min at temperatures from 173 to 1473 K. Under the present experimental conditions, the rupture thickness was found to be proportional to the 2/3rd of the drawn-out rate at high drawn-out rate, but became almost independent from the drawn-out rate in the low ranges. It was concluded that the rupture thickness at the high drawn-out rate was controlled by the external drawn-out rate of the molten slag. At low drawn-out rate, however, it might be determined by the internal suction flow rate from the horizontal region of thin film to the Plateau border.

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