Rupture Phenomena of Molten Alkali Silicate Thin Films

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The rupture length of the iron bearing alkali silicate thin films (the K$_2$O·2SiO$_2$, K$_2$O·2SiO$_2$, and Na$_2$O·
2SiO$_2$–Fe$_2$O$_3$ systems) are measured as a function of the silica content, the Fe$_2$O$_3$ content, temperature, and the drawn out rate. In these melts, it is found that the rupture length, $L$, depends on the drawn-out rate, $v$, at the high drawn-out rate conditions, but is independent from the drawn-out rate at the low drawn-out conditions. For all the systems of K$_2$O–SiO$_2$ and Na$_2$O–SiO$_2$–Fe$_2$O$_3$, the rupture length ($L$) at the high drawn out rate conditions is found to be proportional to the $-2/3$ of the power of the drawn-out rate ($v$),

$$L \propto v^{-2/3}$$

The rupture length at the low drawn-out rate strongly depends on the SiO$_2$ and Fe$_2$O$_3$ contents, but not temperature and drawn-out rate. From these results, it is confirmed that the rupture length at the low drawn-out rate is determined by the Si–O bond strength of the silicate tetrahedral units.

KEY WORDS: rupture phenomena; alkali silicate; thin film; surface tension; bond strength; ferric ion.

1. Introduction

It is very important to understand a rupture phenomenon of molten slag films not only for a theoretical but also a practical viewpoint. Because the break out of the molten slag films routinely takes place in the steelmaking processes such as slag foaming and ruptures of bubbles. Despite the many efforts in studies of these phenomena, the basic characteristics of the rupture mechanism of the slag films still have been poorly understood. In the earlier paper, the authors reported on the measurements of the rupture length of the molten sodium disilicate, Na$_2$O·2SiO$_2$. The rupture length ($L$) was found to be proportional to the $-2/3$rd of the drawn out rate ($v$) at the high drawn out rate conditions,

$$L \propto (v)^{-2/3}$$

but at the low drawn-out rate it was independent from the drawn-out rates. This relation, however, was established only for the sodium disilicate system.

The present work is undertaken to establish if the previously obtained relation (1) can be generally applicable to different slag systems and to obtain more detailed information of the rupture mechanism of a molten slag film, especially at the low drawn-out rate conditions. The drawn-out experiments are carried out on the Na$_2$O–SiO$_2$ and K$_2$O–SiO$_2$ systems with varying the SiO$_2$ content and the Na$_2$O·2SiO$_2$–Fe$_2$O$_3$ system with varying the Fe$_2$O$_3$ content.

2. Experimental Details

The general experimental technique was essentially the same as that described in detail earlier. It consisted of a molten film drawn out system and a hot thermocouple system. A small alumina rod (2.0 mm of outside diameter and 10 mm height) was inserted between two wires of a U shaped thermocouple (I.D. 0.5 mm) and maintained contact with the two wires. The molten slag film was held by the surface tension in the area surrounded by the thermocouple wires and the alumina rod. The film was held horizontally to minimize the effect of gravitational force on the drawn out direction. The inserted alumina rod could slide with keeping slight contact with the thermocouple wires at a constant rate by a stepping pulse motor from the rate of 0.01 to 4.0 mm/s so as to drawn out the molten slag film. To keep the uniform temperature within the drawn-out slag film, the whole drawn-out system was heated by a subsidiary Pt heating furnace. The Pt furnace had a silica window of 20 mm diameter to observe the film drawn-out situation and the rupture phenomena of films.

In each experiment, about 20 mg of the slag was used. After the establishment of the predetermined temperature of slag, the drawn-out of the molten slag was started at the constant rate until the slag was ruptured. The initial distance between the alumina tube and the tip of thermocouple was always fixed to 2.0 mm.

Slag samples were prepared by using the reagent grade Na$_2$CO$_3$, K$_2$CO$_3$, SiO$_2$ and Fe$_2$O$_3$ powder as starting materials. Appropriate dried powders were well mixed and melted in a Pt crucible in a muffle furnace at 1473 K in air and the melted mixture was quenched into a water-cooled copper flat mold and then ground to form a powder. These treatments were repeated 2 times to ensure the homogeneity.
3. Results

The measured rupture length of the K$_2$O·2SiO$_2$ slag at 1 373 and 1 473 K as a function of the drawn-out rate from 0.02 to 1.0 mm/min is presented in Fig. 1. The rupture length at 1 473 K below the drawn-out rate of about 0.2 mm/s is almost independent from the drawn-out rate. Above 0.2 mm/s, the rupture length decreases with the drawn-out rate. In the earlier paper, the rupture length was found to be proportional to the −2/3rd of the drawn-out rate at the high drawn-out rate conditions. For the K$_2$O·2SiO$_2$ system, the rupture length also seems to be proportional to −2/3rd of the drawn-out rate, although the results were scattered. The same dependency on the drawn-out rate is observed at 1 373 K.

From Fig. 1, the rupture length at the high drawn-out rate region increases with temperature, but the rupture length at the low drawn-out rate region is almost independent from temperature within experimental scatters.

The rupture length of the Na$_2$O·2SiO$_2$–10mass%Fe$_2$O$_3$ system at 1 373 K and 1 473 K are measured and are shown in Fig. 2. Similar to the result of the K$_2$O·SiO$_2$ system, the rupture length at 1 473 K with the drawn-out rate of less than about 1.0 mm/s is almost independent from the drawn-out rate. Above 1.0 mm/s, the rupture length decreases with the drawn-out rate and is proportional to −2/3rd of the drawn-out rate. The same dependency on the drawn-out rate is also observed at 1 373 K. Similar with the behavior of the system K$_2$O·2SiO$_2$, the rupture length of the Na$_2$O·2SiO$_2$–10mass%Fe$_2$O$_3$ system at the high drawn-out rate region increases with temperature, but the rupture length at the low drawn-out rate region only slightly increases with temperature.

Further experiments were carried out to investigate the effect of the Fe$_2$O$_3$ content of the melts on the rupture length. The rupture length of the Na$_2$O·2SiO$_2$–Fe$_2$O$_3$ system was measured by varying the Fe$_2$O$_3$ concentration from 5 to 10 mass% at 1 473 K. The results are shown in Fig. 3. The rupture length for each system is found to be proportional to −2/3rd of the drawn-out rate. Compared with the rupture length for the Na$_2$O·2SiO$_2$ system without Fe$_2$O$_3$, the rupture length Na$_2$O·2SiO$_2$–Fe$_2$O$_3$ system at the high drawn-out rate region slightly increases with the Fe$_2$O$_3$ content, but the rupture length at the low drawn-out rate region significantly increases with the Fe$_2$O$_3$ content. The rupture length at the low drawn-out rate region at the 1 473 K are plotted as a function of Fe$_2$O$_3$ content in Fig. 4. The rupture length at
the low drawn-out rate region simply increases with Fe$_2$O$_3$ content.

From the observed relations between the rupture length and the drawn-out rate for the K$_2$O·2SiO$_2$, Na$_2$O·2SiO$_2$–Fe$_2$O$_3$ systems, the measured Na$_2$O·2SiO$_2$ system, it is reasonably confirmed that the rupture length of the silicate melt depends on the drawn-out rate at the high drawn-out rate, but does not depend on it at the low drawn-out condition. From these results, we define the rupture length that is independent from the drawn-out rate as $L_i$ and the drawn-out dependent length as $L_d$.

### 3.1. Effect of Temperature on $L_i$

As shown in Fig. 1 and Fig. 2, the rupture lengths, $L_d$, of the K$_2$O·2SiO$_2$ and Na$_2$O·2SiO$_2$–Fe$_2$O$_3$ systems at the high drawn-out rate region increases with temperature, but the rupture length, $L_i$, at the low drawn-out rate region is almost independent from temperature within the experimental errors. In the previous study, the same dependency was also observed for the Na$_2$O·2SiO$_2$ system. To examine the detail of temperature dependence of the $L_i$, the $L_i$ for the Na$_2$O·2SiO$_2$ and K$_2$O·2SiO$_2$ melts are measured by varying temperature from 1 173 to 1 473 K and is plotted in Fig. 5. For the K$_2$O·2SiO$_2$ system, the measurements are carried out from 1 373 to 1 473 K. Because the melting point of the K$_2$O·2SiO$_2$ system is 1 318 K and to avoid the possible K$_2$O sublimation at the high temperature, the $L_i$ for the Na$_2$O·2SiO$_2$ system may decrease very slightly with temperature, but almost independent from temperature. Although the $L_i$ for the K$_2$O·2SiO$_2$ system are relatively scattered, they also seems to be independent from temperature. Based on these results, it can be said that the $L_i$ of the silicate melts will be independent from temperature.

### 3.2. The Effect of the Silicate Composition on $L_i$

Experiments were carried out to investigate the effect of SiO$_2$ content on the $L_i$. The $L_i$ of the Na$_2$O·SiO$_2$ and K$_2$O·SiO$_2$ systems as a function of the SiO$_2$ content at 1 473 K are measured and results are shown in Fig. 6. It is clearly shown that the $L_i$ for each Na$_2$O·SiO$_2$, and K$_2$O·SiO$_2$ melt depends characteristically on the SiO$_2$ content. The surface tension of the Na$_2$O–SiO$_2$ system decreases with the increase of the SiO$_2$ content, but the K$_2$O–SiO$_2$ system has reversed dependency. Therefore, the tendency that the $L_i$ increases with the SiO$_2$ content for both systems means that the surface tension has a negligible effect on the $L_i$.

### 4. Discussion

#### 4.1. The Rupture Mechanism at the High Drawn-out Rate Condition

The apparent rupture behaviors in the K$_2$O–SiO$_2$ and Na$_2$O·2SiO$_2$–Fe$_2$O$_3$ systems are essentially the same as that of the Na$_2$O·2SiO$_2$ system reported in the earlier paper. Namely, the rupture length ($L_d$) at the high drawn-out rate is found to be proportional to the $-2/3$rd of the drawn out rate ($v$), but at the low drawn-out rate, it is independent from the drawn out rates.

Already discussed in the earlier paper, $-2/3$rd dependence of drawn-out rate on the $L_d$ can be well explained from the modified Frankel equation and is expressed by

$$L_d \propto (\eta v)^{-2/3}(\gamma)^{1/6}(\rho g)^{1/2}$$

where $\gamma$ is the surface tension, $\eta$ is the viscosity of melt, $\rho$ is the density of the molten slag, $g$ is the gravitational constant and $L_d$ is evaluated from the rupture thickness.

From the Eq. (2), the $L_d$ is proportional not only to the drawn-out rate, but also to the liquid viscosity to the $2/3$ power. The $L_d$ shows the very weak dependence of the $L_d$ on the surface tension. Therefore, the $L_d$ can depend on the viscosity but not the surface tension. The viscosity of the K$_2$O–SiO$_2$ and Na$_2$O–SiO$_2$ systems decreases with temperature, and the viscosity of the Na$_2$O·2SiO$_2$–Fe$_2$O$_3$ system in the present experimental region also decreases with increase of the Fe$_2$O$_3$ content. Based on these results, the dependency of the $L_d$ on temperature shown in Fig. 1 and Fig. 2 and that on the Fe$_2$O$_3$ content shown in Fig. 3 can be qualitatively explained from the Eq. (2).

Since the Eq. (2) is derived from a Newtonian fluid dynamical approach, it is reasonably confirmed that the rupture length of the molten alkali silicate film at the high drawn-out rate conditions can be determined by the macroscopic fluid dynamical flow of molten slag. In other words, at the high drawn-out deformation process, the molten alkali silicate film in the present study can be treated as an ordi-
nary Newtonian fluid.

4.2. The Rupture Mechanism at the Low Drawn-out Rate Condition

In the earlier paper, it was suggested that the rupture length at the low drawn-out rate conditions might be determined by the internal suction flow. If the rupture phenomena are related to the fluid flow, regardless whether it is driven by the external drawn-out or the internal suction flow, the rupture length can be decreased with the increase of the viscosity of melts, because the increase of the viscosity decreases the fluidity of melts. The viscosity of silicate melts in this study increases with the SiO$_2$ content. Therefore, the rupture length of the silicates is expected to decrease with the SiO$_2$ content, if the rupture mechanism involves the flow process. As shown in Fig. 5, however, the rupture length, $L_i$, increases with the SiO$_2$ content, or the molten slag film that has a higher resistance to flow is found to be more elongated. It means that the rupture mechanism under the low drawn-out rates cannot be explained from the fluid dynamical viewpoint. Therefore, the rupture mechanism at the low drawn-out rate will not be resulted from the previously suggested internal suction flow.

Since the elongation rate of the thin film at the low drawn-out rate condition is very small, it is reasonable to assume that the molten thin film is essentially in mechanical equilibrium condition. Under the mechanical equilibrium condition, the surface shape or the distribution of the film thickness can be determined by the surface tension. Therefore, if the $L_i$ is determined by the break out of the mechanical balance, the $L_i$ will be related to the surface tension of melts. But already remarked, the surface tension of the Na$_2$O–SiO$_2$ system decreases with the increase of the SiO$_2$ content, but the K$_2$O–SiO$_2$ system has the reverse dependency. Despite of this different dependency of the surface tension, the $L_i$ of the both systems decrease with the SiO$_2$ content. It means that the surface tension has a negligible effect on $L_i$. Namely the rupture of the slag film at the low drawn-out rate condition is not determined by the break out of the mechanical balance. It is very intriguing that the $L_i$ has no relations to the surface tension, the viscosity, temperature and the drawn-out rate and only depend on the compositions, although the surface tension and the viscosity is a function of compositions.

The molten silicate film simply ruptures once the length of the molten film reaches to the certain length even if the film is under a fluid dynamically or a mechanically stable condition. In the earlier paper, the film thickness is found to be reciprocally proportional to the length of elongated slag film within experimental errors. So it can be said that the molten slag film at the low drawn-out condition is ruptured once it reaches to the certain thickness, $t_c$. Already mentioned, the molten alkali silicate behaves as an ordinary Newtonian fluid until it reaches to the $t_c$. In other words, the molten film, which thickness is less than $t_c$, cannot be regarded as the Newtonian fluid.

It is well known that molten silicates are consisted of many bent and tangled silicate chain and sheet polymers of different molecular weights. Until the film reaches to $t_c$, there is enough room for the silicate polymers to move and rotate in the melt volume, and they can move freely or rotate easily and the strain in the melt due to the elongation driven by the external force can dissipate quickly and cannot be accumulated. However, once the film thickness of the silicate melt becomes less than the $t_c$, the consisted silicate polymers cannot move or rotate freely in the melts due to the restriction of the volume space. At this condition, the elongation process will be mainly maintained by the stretching or straightening of bent and/or tangled silicate polymers, but not by the macroscopic transfer of silicate polymers. It is known that the molten slag is a viscoelastic body. Namely the slag has not only the viscosity but also the elastic property. The origin of elasticity can be resulted from the stretching or straightening of bent and/or tangled silicate polymers. The similar elongation mechanism takes place in the behavior of rubber or organic polymer elongation.

Due to this elongation mechanism, the strain due to the stretching of silicate chains gradually accumulates in the molten film with proceeding the elongation, and finally the film cannot sustains this strain and breaks out. Namely, the elongation of the molten thin slag at the low drawn-out rate condition is proceeded by the stretching or straightening of the silicate anion, and the rupture is caused by the break out of the Si–O bond caused by the accumulated strain. H. Toyuki evaluated the Si–O bond stretching force constant applying the normal coordinate treatment on the infrared spectra of the Na$_2$O–SiO$_2$ glasses. The details of force constant are presented in the Appendix. It has been found that the stretching force constant decreases with increase of the Na$_2$O concentration in glasses and, as the results, the Si–O bonds are weakened. This weakening is due to the decrease of the double bond character of Si–O bond and the increase of the Si–O bond length. The Si–O bond weakening due to the increase of the Si–O bond length with the addition of the Na$_2$O was also suggested from the X-ray and XPS results on the Na$_2$O–SiO$_2$ system. The attention must be given to the fact that this weakening is the weakening of Si–O bond itself and is totally different from that being due to the breakage of the silica network by a cation modifier. The relation between the evaluated Si–O stretching force constants and the rupture length $L_i$ corresponds to the same SiO$_2$ concentration in the Na$_2$O–SiO$_2$ system is shown in Fig. 7. There is a good correlation be-
tween them. This result supports the proposed rupture mechanism that the rupture length at the low drawn-out condition is determined by the Si–O strength.

Previously mentioned, \( L \), depends on the composition of silicates, but independent from the surface tension and the viscosity, although the surface tension and the viscosity varied with compositions. This intriguing result can be explained by that the microscopic Si–O bond strength vary with composition as already mentioned, but the viscosity and the surface tension of molten silicate is related to the interactions between the consisted complex silicate anions, but not silicate anion’s Si–O bond strength.

As shown in Fig. 5, the rupture length at the low drawn-out rate region is independent from temperature. This independence is also simply explained if \( L \) is determined by the Si–O bond strength. Because the Si–O bond in the silicate tetrahedral units is highly covalent and its bond strength can be independent from temperature.

Generally speaking, the amount of the long length polymers in the molten silicate increases with the silica content. Since the long polymer has many bending points, the longer silicate polymer can be elongated much more than that of shorter one. It was reported that Fe\(^{3+}\) ion in alkali silicate works as a network former and promotes the silicate polymerization. Therefore, with increase of Fe\(^{3+}\) in the silicate melt, the number of bending points of the silicate polymer in the melt also increases. Then, the iron bearing molten silicate can be elongated with increase of Fe\(^{3+}\) content just as shown in Fig. 4.

Thus, all elongation behaviors of molten thin film in the present study at the low drawn-out rate condition are reasonably well explained based on the stretching or straightening of bent silicate polymers. Further work, possibly by studying the stress-strain relation as a function of drawn-out rate, is needed to provide quantitative information which is required to examine the proposed rupture mechanism at the low drawn-out rate condition.

5. Conclusions

The rupture length of iron bearing molten alkali silicate, \((\text{K}_2\text{O} \cdot 2\text{SiO}_2, \text{Na}_2\text{O} \cdot 2\text{SiO}_2 \text{ and Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot \text{Fe}_2\text{O}_3)\), is measured as a function of the \(\text{SiO}_2\) content, the \(\text{Fe}_2\text{O}_3\) content, temperature, and the drawn-out rate. The following results were obtained.

(1) The rupture length of the measured silicate films at the high drawn-out rate condition is found to be proportional to the \(-2/3rd\) of the power of the drawn-out rate.

(2) The rupture length of the measured silicate films at the high drawn-out rate condition increases with temperature.

(3) The rupture length of the measured silicate films at the low drawn-out rate condition is almost independent from the drawn-out rate and temperature.

(4) The rupture length of the measured silicate films at the low drawn-out rate condition increases with \(\text{SiO}_2\) and \(\text{Fe}_2\text{O}_3\) content.

(5) The rupture length of the measured silicate films at the high drawn-out rate is determined by the macroscopic fluid dynamical flow of molten silicate.

(6) The rupture length of the measured silicate films at the low drawn-out rate is determined by the Si–O bond strength of the silicate.

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Appendix

Force Constant

Through quantum mechanical considerations, the vibration of two nuclei in a diatomic molecule can be reduced to a simple harmonic oscillation that the restoring force on a body is proportional to its displacement from equilibrium. The restoring force can be expressed by

\[
\text{force} = -kx
\]

where \( k \) is force constant of the proportionality between the restoring force and the displacement \( x \) from equilibrium point. As the unit of force constant, \( \text{mdyn/Å} (=100 \text{N/m}) \) is often used. The importance of the force constant in quantum theory is that it is a measure of the stiffness of bonds between atoms, and therefore governs (together with the atomic mass) the vibrational frequencies of molecules. Reversibly the force constant can be evaluated from the vibrational frequency.

Generally the vibration of polyatomic molecules is quite complex. When there is more than one vibrational displacement, a displacement of one atom may influence the restoring force experienced by other. However, under the harmonic normal mode approximation, vibrations of any polyatomic molecules can be expressed by the superposition of so-called normal vibration. In normal vibration, all atoms move with the same frequencies and in phase. In the normal vibration treatment in the polyatomic molecules, normal vibrations corresponds to the stretching, bending and rotation movement, the force constant is consisted of stretching and bending force constants, as well as the interaction force constants between them.