Rupture Phenomena of Alkali Silicate Thin Films

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Abstract

The rupture length of the iron bearing alkali silicate thin films ($K_2O{\cdot}2SiO_2$ and $Na_2O{\cdot}2SiO_2$ systems) are measured as a function of the silica 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_2O-SiO_2 and Na_2O-SiO_2, 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 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.

1.0 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. Slag 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 important to control slag foaming.

Previously the authors reported on the measurements of the rupture length of the molten sodium disilicate thin film by varying the drawn-out rate[1)]. The rupture length (L) was found to be proportional to the -2/3rd of the drawn-out rate (v) at the high drawn out rate conditions,

$$L \propto (v)^{-2/3} \text{ ----- (1)}$$

but at the low drawn-out rate it was independent from the drawn-out rates.

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_2O-SiO_2 and K_2O-SiO_2 systems with varying the SiO_2 content.

2.0 Experimental Details

The general experimental arrangement is illustrated in Fig.1[1)]. It consisted of a molten film drawn out system and a hot thermocouple system[2)]. The detail of the film drawn-out arrangement is schematically shown in Fig.2. 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 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 20mm 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_2CO_3, K_2CO_3, and SiO_2 powder as starting materials. Appropriate dried powders were well mixed and melted in a Pt crucible in a muffle furnace at 1473K 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.

3.0 Results

The measured rupture length of the $K_2O{\cdot}2SiO_2$ slag at 1373K and 1473K as a function of the drawn-out rate from 0.02 to 1.0 mm/min is presented in Fig.3. The rupture length at 1473K 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[1)], 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 $K_2O{\cdot}2SiO_2$ 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 1373K.

From Fig.3, 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.

From the observed relations between the rupture length and the drawn-out rate for the $K_2O{\cdot}2SiO_2$ and the previously measured $Na_2O{\cdot}2SiO_2$ system[1)], 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

To examine the detail of temperature dependence of the L_i, the L_i for the $Na_2O{\cdot}2SiO_2$ and $K_2O{\cdot}2SiO_2$ melts are measured by varying temperature from 1173K to 1473K and is plotted in Fig.4. For the $K_2O{\cdot}2SiO_2$ system, the measurements are carried out from 1373K to 1473K. Because the melting point of the $K_2O{\cdot}2SiO_2$ system is 1318K and to avoid the possible K_2O sublimation at the high temperature. The L_i for the $Na_2O{\cdot}2SiO_2$ system may decrease very slightly with temperature, but almost independent from temperature. The L_i for the $K_2O{\cdot}2SiO_2$ 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 of the silicates on the L_i. The L_i of the Na_2O-SiO_2 and K_2O-SiO_2 systems as a function of the SiO_2 content at 1473K are measured and results are shown in Fig.5. It is clearly shown that the L_i for each Na_2O-SiO_2 and K_2O-SiO_2 melt depends characteristically on the SiO_2 content and increases with the SiO_2 content. The surface tension of the Na_2O-SiO_2 system decreases with the increase of the SiO_2 content, but the K_2O-SiO_2 system has reversed dependency[3,4)]. 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_2O-SiO_2 system is essentially the same as that of the $Na_2O{\cdot}2SiO_2$ system reported in the earlier paper[1)]. Namely, the rupture length (L_d) at the high drawn-out rate is found to be proportional to the -2/3rd 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[1)], -2/3rd dependence of drawn-out rate on the L_d can be well explained from the modified Frankel equation[1,6,7)] and is expressed by,

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

where γ is the surface tension, h is the viscosity of melt, ρ 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 Eq.(2) 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_2O-SiO_2 and Na_2O-SiO_2 systems decreases with temperature[5)]. Based on these results, the dependency of the L_d on temperature shown in Fig.1 and Fig.2 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 ordinary Newtonian fluid.

4.2 The rupture mechanism at the low drawn-out rate condition

The viscosity of silicate melts in this study increases with the SiO_2 content[4)]. 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 related with the macroscopic 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_2O-SiO_2 system decreases with the increase of the SiO_2 content, but the K_2O-SiO_2 system has the reverse dependency[3)]. 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 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[1)], 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 of that 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 anion. 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[8)].

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_2O-SiO_2 glasses[9)]. It has been found that the stretching force constant decreases with increase of the Na_2O 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_2O was also suggested from the X-ray and XPS results on the Na_2O-SiO_2 system[10-12)]. 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[9)]. The relation between the evaluated Si-O stretching force constants[9)] and the rupture length L_i corresponds to the same SiO_2 concentration in the Na_2O-SiO_2 system is shown in Fig.6. There is a good correlation between 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_i 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[8)], 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.

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. 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 that 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 ($K_2O\cdot 2SiO_2$ and $Na_2O\cdot 2SiO_2$) is measured as a function of the SiO_2 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 and increases with temperature.

(2) 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, but increases with SiO_2 content.

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

(4) 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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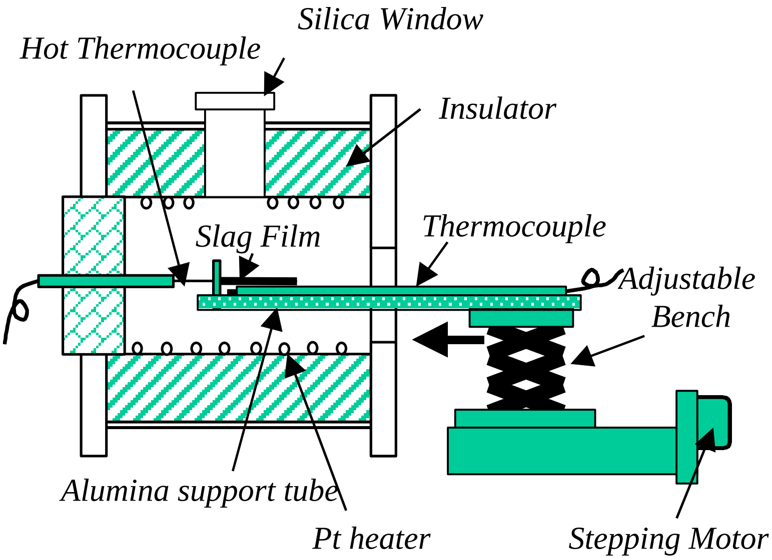

Fig.1 Experimental apparatus

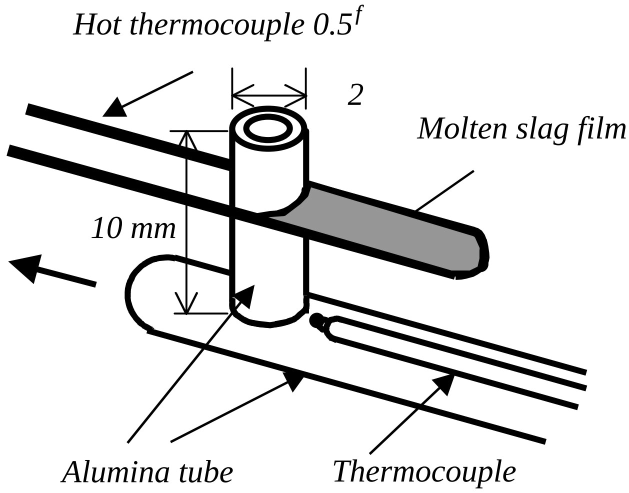

Fig.2 Schematic of film drawn-out system.

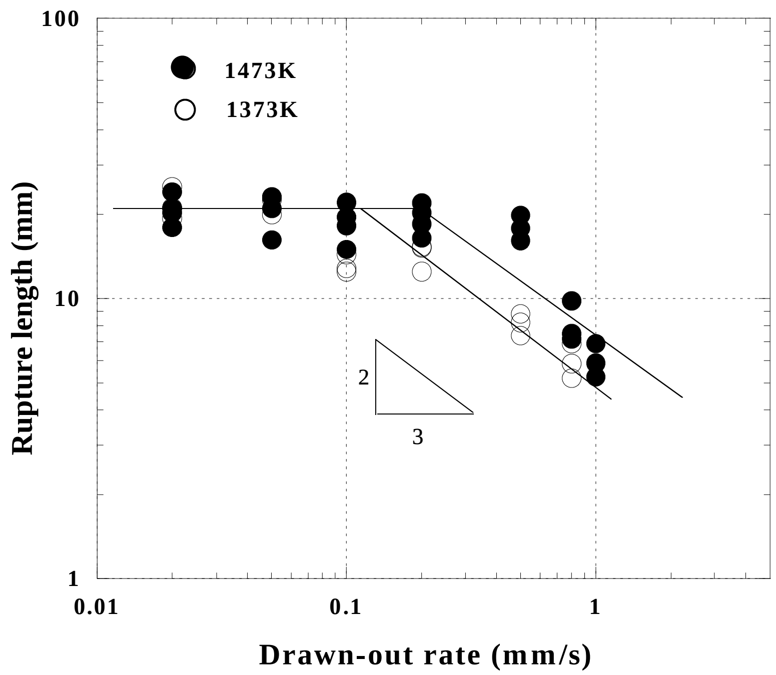

Fig.3 The rupture length of $K_2O \cdot 2SiO_2$ slag at 1173K and 1323K as a function of drawn out rate.

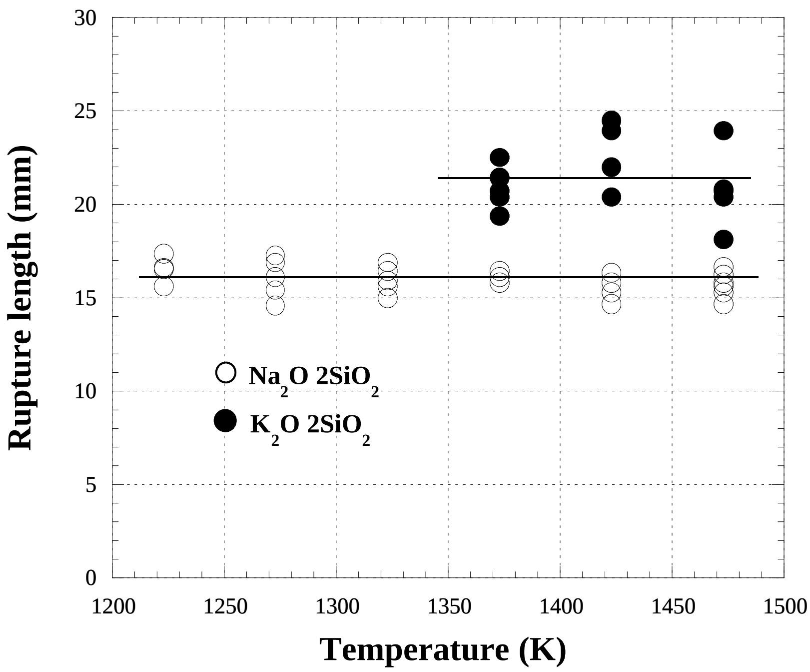

Fig.4 The measured L_i for $Na_2O \cdot 2SiO_2$ and $K_2O \cdot 2SiO_2$ melt as a function of temperature from 1173 to 1473K.

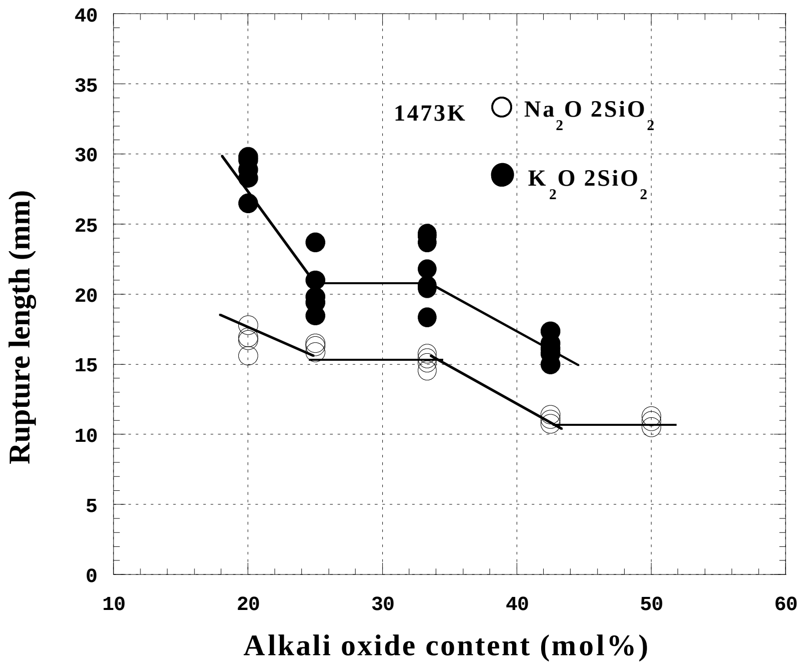

Fig.5 The measured L_i for $Na_2O{\cdot}2SiO_2$ and $K_2O{\cdot}2SiO_2$ melt as a function of SiO_2 content.

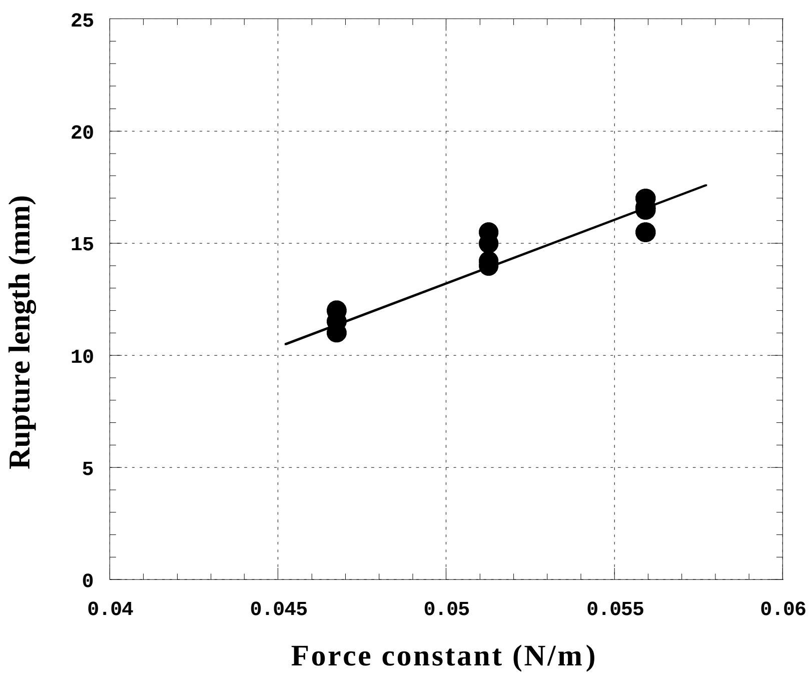

Fig.6 The relation between the rupture length and the Si-O stretching force constant.