Slag-foaming Phenomenon in Pyrometallurgical Processes

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The slag-foaming phenomenon is observed in many pyrometallurgical processes such as basic oxygen steelmaking, pretreatment of molten pig iron and bath smelting of iron or chrome ore. The current state of understanding of this phenomenon is reviewed and particular attention is paid to its surface chemical view.

KEY WORDS: review; slag foaming; pyrometallurgy; iron and steel; bubble creation; foam stability; suppression of foam; Marangoni effect.

1. Introduction

The slag-foaming phenomenon related to slopping is a problem in the basic oxygen steelmaking process. In some cases, the slag froth overflows from the lip of the furnace, causing metal loss and interruption of the furnace operation. The foaming phenomenon is also observed in newly developed pretreatment of hot metal, such as desiliconization, dephosphorization, desulfurization of pig iron and bath smelting of iron or chrome ore. Its suppression is an important target to be resolved. The Committee on Interfacial Transport Phenomena was organized in 1986 as the Joint Society on Iron and Steel Basic Research, ISIJ, and its activities were completed successfully in April of 1991. One of the aims of the committee was to identify the mechanism of the slag-foaming phenomenon and the methods of suppressing it. The committee's final report¹⁾ was published in June of 1991 by the Iron and Steel Institute of Japan. We review here the current progress of understanding of the phenomenon which considerably owes to discussion in the committee.

2. Basic Research on Slag-foaming Phenomenon

2.1. Creation of Slag-foam

In practical processes, the slag foaming phenomenon originates from the expansion of molten slag by gas bubbles evolving from chemical reactions at the slag-metal interface; hence the phenomenon is caused by two principal factors; (1) the rate of gas evolution by the reactions and (2) the stability of the foam in the melt. The second factor is dependent on the foam structure. When air is blown into a foamable oil, the upper foam layer and the lower gas-dispersed liquid layer can be clearly distinguished from each other as shown in Fig. 1. To understand the slag-foaming phenomenon, it is important to know which layer plays the predominant role in the foaming because the two layers have a dif-

ference in nature as well as in appearance. The stability of the foam layer depends on the stability of the bubble lamella, so that breakdown of the lamella results in the disappearance of the foam. On the other hand, the stability of the gas-dispersed liquid layer is controlled by the viscosity and the movement of bubbles in the liquid, and breakdown of the bubbles promotes the stability of the layer because it increases dispersion of the bubbles in the liquid. It is essential to determine which structures predominate in the slag-foaming phenomenon in a pyrometallurgical system. The answer can be found by direct observations at the slag-metal interface where gas (mainly CO gas) evolves by chemical reactions such as the reduction of iron oxide. Direct observation of the slag-foaming phenomenon by X-ray fluoroscopy technique revealed the structure. According to Amatatsu,²⁾ fine bubbles are produced at the slag-metal interface during the reduction of iron ore by carbon dissolved in the molten iron or solid carbon; the bubbles accumulate at the top of the slag layer, because it is difficult for them

Fig. 1. Foam layer and dispersed gas layer.

Fig. 2. Effect of iron oxide content in slag on bubble diameter.⁴⁾

Fig. 3. Changes of foam height and bubble diameter during the reaction.⁴⁾

to pass through the slag layer. These results in a foam layer composed of fine spherical bubbles ("Kugelschaum") to be developed on the top of the slag layer. Thickness of the bubble lamella is greater than that observed for typical soap bubbles, but not as thick as that for a typical gas-in-liquid dispersion system. Polyhedral foam, in contrast, which was observed by Hara *et al.*,³⁾ is the result of Ar gas injection into molten slag. The foams created by the two methods differ in appearance, but acceleration of drainage of the liquid in the lamella decreases the stability of the foam layer. Ogawa and Tokumitsu⁴⁾ also observed the foaming phenomenon by the X-ray fluoroscopy during the bath smelting process. According to their results, size of the CO gas bubbles created at the slag-metal interface is governed by the rate of the reaction (Fig. 2). As shown in Fig. 3, the foam is remarkably stabilized when the bubble diameter is less than 2 mm. These observations suggest that the slag foaming is caused by retardation of drainage of the liquid in the lamella, although it is not a typical stable foam. Two questions then arise; (1) why are fine bubbles produced by the rapid chemical reaction, and (2) what factors affect the drainage of the liquid in the bubble lamella. Several models have been proposed to answer the first question. Terashima *et al.*,⁵⁾ Ogibayashi,⁶⁾ and Ogawa and Tokumitsu⁷⁾ calculate the bubble size created at the slag-metal interface on the basis of the force balance among buoyancy of a bubble

Fig. 4. A bubble at the slag-metal interface.⁷⁾

Fig. 5. Formation of a CO bubble at the slag-metal interface under the generation of small roll cell.⁸⁾

Fig. 6. A model of generation of small bubbles by surface tension driven flow.

and interfacial tensions worked at the slag-gas-metal three phase boundary (Fig. 4). The calculated values are in fairly good agreement with those observed by X-ray technique when the rate of the chemical reaction is relatively slow, but the model may not always be the case, if the rate of gas evolution is very high.

Another model was proposed by Mukai,⁸⁾ and Hara and Ogino,⁹⁾ who focus on the Marangoni effect at the interface. Mukai considers that a transfer of surface active FeO from slag to metal causes an interfacial turbulence of the roll cell type at the slag-metal interface (Fig. 5), and that the gas bubbles on the metal are released from the metal, before the force balance is achieved at the boundary. Hara and Ogino found that bubbles created by Ar + 3% H₂ gas injection into iron oxide-based slags were smaller in size than those by Ar gas.³⁾ This can be explained as follows; the reaction rate at a moving boundary being higher than that at a stationary one, so that the concentration of iron oxide at the growing gas-slag interface becomes lower than that near the blowing tube (Fig. 6(a)), and this creates a local difference in the concentration of iron oxide, which, in turn, causes a surface tension driven flow (the Marangoni effect), because the less iron oxide is in the slag, the lower is the surface tension. The result may be that a small part of the bubble is torn off by the flow. The same mechanism may work at the gas-metal-slag interface to create small bubbles as shown in Fig. 6(b).

Another question is why small bubbles produce a relatively stable foam. Ogawa and Tokumitsu,⁷⁾ who theoretically treated the effect of bubble size on the rate of bubble rupture, pointed out that life time of the bubbles increases remarkably with decreasing bubble diameter and become minimal at some critical diameter. They also considered that increase of the melt viscosity decrease the rupture rate, although the effect of surface tension is not high. Current work on the stability of a single bubble by the authors,⁹⁾ however, shows that a small addition of surface active component to slag melts is effective in stabilizing the bubble lamella; it is also observed in practical processes that the existence of surface active components in the slag stimulates foaminess. Accordingly, it should be noted that physicochemical properties of the foam lamella relate to stability of the foam.

2.2. Stabilization of the Bubble Lamella

According to Tachikawa *et al.*¹⁰⁾ for the foaming in a 2.5 T LD converter, the variation of slag height with time is approximately given by the Eq. (1).

$$dH_s/dt = Q - (H_s - H_0)/\tau \quad \dots\dots\dots(1)$$

in which H_s and H_0 are the slag heights at the time t and at the datum level, and Q and τ are rate of bubble generation and time constant for decay of bubbles (namely, foam life), respectively. A similar relation (Fig. 7) was also observed, when an Ar gas was injected into molten slags at the flow rate of 30 cc/min through a platinum nozzle.³⁾ This suggests that the slag-foaming is controlled by two factors; bubble creation (the rate and size) and stabilization of the bubble lamella. Foam life is used as a measure to determine what factor controls the stability of the foam. The time required for the surface of the foam to fall down between two marked points after the gas injection has ceased is usually defined as the foam life. This kind of measurement was first carried out by Cooper and Kitchner for CaO-SiO₂ melts.¹¹⁾ According to their results, CaO-SiO₂ melts are non-foaming, but stable foam is observed when a small amount of surface active P₂O₅ is added in silica-rich CaO-SiO₂ melts. An increase of SiO₂ content and a small addition of P₂O₅ may increase the viscosity of the melt on the surface as well as in the bulk. Although the stability decreases with increasing temperature, the temperature dependency of foam life is greater than that of the bulk viscosity. Accordingly, they concluded that a higher

Fig. 7. Foam height as a function of the foam life.³⁾

viscosity of melt is not enough to stabilize the foam by itself, and that the existence of P₂O₅ as a surface active component may relate to an increase in the surface elasticity. Swisher and McCabe¹²⁾ found that a small addition of surface active Cr₂O₃ to the melts also stabilized the foam, but after the melts arrived in the liquid immiscibility region by further Cr₂O₃ addition, the stability suddenly decreased (Fig. 8). However, the calculated surface excess quantity for slag melt by the Gibbs adsorption isotherm is smaller than that on an aqueous system. This means that the Gibbs elasticity mechanism does not work to stabilize the slag foam. Swisher and McCabe thus presumed that the Marangoni effect is an important factor in foam stability. The stability mechanism by Fe₂O₃ and V₂O₅ additions is thought to be similar.¹³⁾ Hara *et al.*³⁾ found that the foam is stabilized by the additions of CaF₂, Na₂O and P₂O₅ into iron oxide-based slags, which decrease the surface tension of the melts, namely surface active components.

To know the role of surface active components, the surface viscosity was measured for some phosphate, borate and silicate melts.¹⁴⁾ The results are shown in Fig. 9, in which numerals show the foam height (cm) when

Fig. 8. Effect of Cr₂O₃ content in CaO-SiO₂ melt on the foam life.¹¹⁾

Fig. 9. Effects of surface tension, η_s and surface tension depression by unit concentration change of melt, $\Delta\gamma$ on foaminess (numerical value: foam height (cm) at Ar gas flow rate of 5 cm³/min).¹⁴⁾

 Fig. 10. Effect of slag composition on foaminess.¹⁵⁾

an Ar gas is injected at a constant flow rate (5 cc/min). From the measurements, it is concluded that higher surface viscosity of a melt does not work to stabilize the foam by itself and the stable foam appears, when surface viscosity of the melt is relatively high and the surface tension of the melt depends remarkably by the composition. The highest foaminess was observed for BaO–82.2mol%B₂O₃ uniform melt near the liquid immiscible region, however, no foaming was detected within the region where the surface tension depression by the composition is negligible. A similar phenomenon was reported by Kitamura *et al.*¹⁵⁾ who injected an Ar gas into Fe₂O₃–MnO–CaO–SiO₂ melts to measure the foaminess. As shown in Fig. 10, the highest foaminess was observed near the silica saturation, but in the silica saturated region, the foaminess decreased. These facts suggest that surface tension driven flow caused by local difference in concentration of surface active component, namely Marangoni effect relates to the foam stability.

3. Slag-foaming in Practical Processes

The slag-foaming phenomenon in the steelmaking processes has already reviewed by Kozakevitch¹⁶⁾ and Yaboiskii,¹⁷⁾ and is therefore explained only briefly here. Generally, it was found that foamy slags were highly viscous and that the foaminess of acid slags was high, but this is not always the case. According to Kozakevich, who analyzed the data by Fellcht¹⁸⁾ and Lundemann,¹⁹⁾ slag foaminess seemed to be increased with the increase of silica content beyond the composition of 2CaO·SiO₂. Although Davis²⁰⁾ found that partial precipitation of 2CaO·SiO₂ crystal stimulates the foam, the highest foaminess was observed at CaO/SiO₂=1.6 by Nechkin *et al.*,²¹⁾ while Tachikawa *et al.*¹⁰⁾ found that the stability of the foam remarkably increases, when the CaO/SiO₂ ratio is below 1.2. These differences suggest that slag foaming is affected not only by the foam stability but also by the rate of bubble generation (rate of decarburization).

Slag foaming is also observed in widely practiced desilicization of pig iron. In this process, it is accepted that decrease of the CaO/SiO₂ ratio in the molten slags stabilized the foaming.^{15,22)} However, another report shows that foaming level passes a minimum point with increase in CaO/SiO₂ ratio as shown in Fig. 11.²³⁾ Ito *et*

 Fig. 11. Slag foaming in a 400 T torpedo car during desilicization of hot metal.²³⁾

 Fig. 12. Effect of surface tension of slag melts on foaminess in the bath smelting of iron ore.²⁶⁾

 Fig. 13. Effect of P₂O₅ in slag melts on the foaminess in the bath smelting of iron ore.²⁶⁾

*al.*²⁴⁾ investigated the slag-foaming phenomenon during the desilicization in a 300 T torpedo car and discussed the method of suppression. They found that the foaming slag level during the process strongly depends on slag volume and surface tension, but that the effect of viscosity is minimal. Okuda *et al.*²⁵⁾ found that the surface active component P₂O₅ in the slag promotes the slag foaming.

In the bath smelting process of iron ore, where slag foaming is also observed, it is required to suppress the height of the foaming slag suitably, because post-combustion process of CO-rich exhaust gas expected to

be carried out in the slag bath. Hirata *et al.*²⁶⁾ found in a laboratory test (100 kg of hot metal) that the foaming level increases with decreasing surface tension (Fig. 12) and that existence of surface active component P_2O_5 in the slag promotes the foaminess (Fig. 13), while the viscosity of slag has no clear effect on it.

There is no doubt that vast amounts of fine gas bubbles created by the reaction at the slag-metal interface cause the slag-foaming in many pyrometallurgical processes. However, it is difficult to reveal the phenomenon without considering the stability of the bubble lamella, because the foamy slags observed in these processes seem to have common characteristics, that is to say, the foaminess strongly depends on slag composition, especially existence of surface active components in the slag melts.

4. Suppression of the Slag-foaming

It had been widely recognized even before the committee was formed that the addition of a carbonaceous material like coke in slag suppresses the slag foaming.¹⁰⁾ However, the reason for this was not clear. Figure 14 for the bath smelting process of iron ore is a typical example, where excess coke in the slag melt is very effective to suppress the foaming.²⁶⁾ Direct observation by X-ray fluoroscopy revealed that the carbonaceous material promotes the coalescence of fine bubbles by destroying the bubble lamella, so that larger bubbles are formed which can more easily escape from the slag phase.^{4,26,27)} It is considered that the movement of carbonaceous materials being non-wet to liquid slags destroys the lamella (Fig. 15).²⁶⁾ Recent study on the stability of a single oxide bubble by the authors,⁹⁾ however, found that the Marangoni effect also works on the rupture mechanism of the bubble lamella. After a single gas bubble made of $BaO-B_2O_3$ melt forms under air and then a part of bubble film touches solid iron ore (in Fig. 16(a)), the concentration of iron oxide in portion 1 is increased due to the dissolution of the iron ore. The concentration difference in iron oxide between portions 1 and 2 causes a surface tension-driven flow from 1 to 2, because surface tension of iron oxide is higher than that of bulk melt. The flow promotes the thinning of the bubble lamella, so that it accelerates the rupture. While a bubble is easily ruptured, if a graphite plate is moved near a single bubble of a $BaO-B_2O_3-Fe_2O_3$ melt (Fig. 16(b)). This occurs without contact with the graphite. In that case, a flow from portions 2 to 1 can be observed. This can also be explained by the surface tension driven flow, because the concentration of iron oxide in portion 1 is reduced by the reaction with CO gas, generated by combustion of the graphite under air.

It is thus concluded that the Marangoni effect works to stabilize the foam, while in some cases the effect also causes rupture of the bubble lamella. Accordingly, it is expected that sprinkling of surface active reagents on the foaming slag may be effective to suppress the foaming, but that such suppression may be transient, because these reagents also act to promote the foaming after it dissolves in the slag melt. By contrast, carbonaceous material such as coke works only to destroy the bubble lamella.

Fig. 14. Suppression of slag-foaming by excess coke in the bath smelting of iron ore.²⁶⁾

Fig. 15. Role of carbonaceous materials in suppression of the slag-foaming.²⁶⁾

Fig. 16. Effect of surface tension driven flow on stability of a single bubble.

5. Summary

The slag foaming phenomenon is caused by a vast quantity of fine CO gas bubbles generated at the slag-metal interface, although the slag foam is unstable. Vigorous foaming appears when the slag contains components which stabilize the bubble lamella, especially surface active components such as SiO_2 , P_2O_5 , and CaF_2 . The mechanism of the stabilization of the foam is now considered to be a surface tension driven flow, namely the Marangoni effect. This effect also has an important part in suppression of the foaming by coke addition.

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