4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

DEVELOPMENT OF SLAG FOAMING RESTRAINT METHOD BY CARBON ADDITION IN HOT METAL PRETREATMENT PROCESS

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Synopsis: A new slopping restraint method by the injection of fine carbon powder in a foaming slag was developed for the hot metal pretreatment process. Also, a prediction method of slopping by the measurements of the vibration intensity of top blow lance and the sound intensity of operation noise were developed. By the application of these methods, slopping has not taken place under any treatment conditions without having an influence on the reaction efficiency. In a fundamental test, carbon powders existing in the slag film among the bubbles were clearly found and the restraint mechanism was considered.

Key words: hot metal pretreatment, slopping, slag foaming, coke powder, restraint, prediction

1. Introduction

The hot metal pretreatment process of Nippon Steel Corporation was first developed at Kimitsu Works in 1982 and is now in operation also at Yawata, Oita, and Nagoya Works [1]. Although this process has great economic merit, its biggest problem is the temperature drop of hot metal during the treatment. Then, the method of using oxygen gas and the method to shorten the treatment time by the high speed injection of flux were developed to solve this problem [2]. Nevertheless, as the frequency of slopping has abruptly increased with the application of these methods, the amount of oxygen gas consumption and the flux supplying rate are still restricted.

On the other hand, a slopping restraint method by the addition of carbonaceous materials has already been developed in a BOF steel making process [3] and a smelting reduction process [4]. The application of this method for hot metal pretreatment was considered to be difficult, as the addition of carbonaceous materials would cause the reduction of (FeO) and decrease the reaction efficiency.

The authors developed a new slopping restraint method by the use of fine coke powder which was injected in the foaming slag for the hot metal pretreatment process. Also, a prediction method for slopping was developed by the measurements of the vibration intensity of the top blow lance and the sound intensity of operation noise.

2. Industrial tests

2.1 Experimental method

As the hot metal pretreatment process at Yawata Works, desiliconization to adjust [Si] content and dephosphorization are carried out by a torpedo car. In the dephosphorization treatment, lime, fluorspar, and Fe oxide are injected in the hot metal by an immersion lance and oxygen gas is also supplied by a top blow lance. Figure 1 shows the equipment for the restraint and the prediction method of slopping. The foaming restraint materials were injected into the foaming slag with carrier gas (N_2)

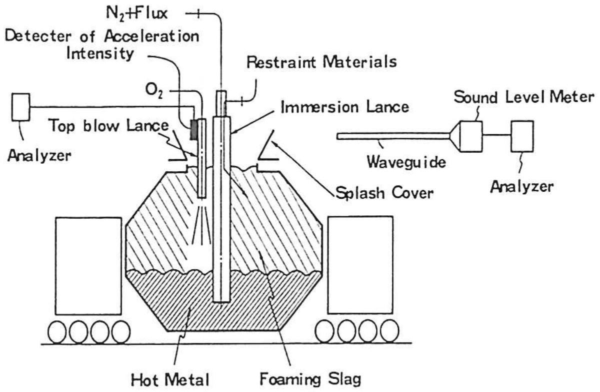


Fig. 1 Experimental setup for restraint and prediction of slopping.

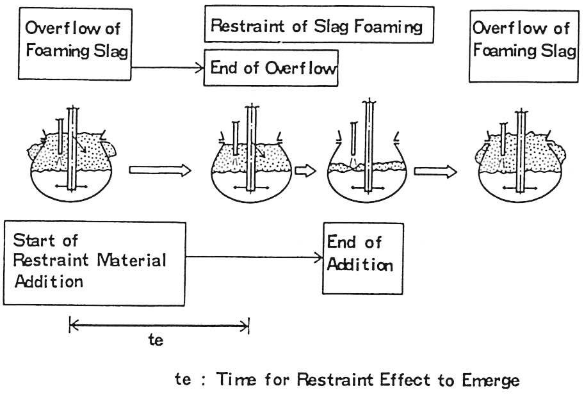


Fig. 2 Definition of time for the restraint effect to emerge ; t_e.

through two holes on the upper side of the immersion lance. As the prediction apparatus, the detector of the acceleration intensity in lance vibration equipped in the top blow lance and its analyzer were set up. Also, the sound level meter to measure the sound intensity during the treatment and its analyzer were installed.

For the restraint tests, the injection height of the restraint materials from the surface of the hot metal was determined as a constant value according to the experimental results at Kimitsu works [5] where the optimum values were in the range of 1200mm to 1500mm. As an index to evaluate the efficiency of the restraint, the time for the restraint effect to emerge (t_e) was used. The definition of t_e is shown in Figure 2 schematically. T_e was defined as the interval between the time when the injection of the restraint material started and the time when the overflow of slag stopped. For the restraint materials, coke in various sizes, $CaCO_3$, CaF_2, Al dross, and a mixture of coke and $CaCO_3$ were used. In this report, slopping was defined as the overflow of foaming slag from the torpedo car.

2.2 Results of restraint tests

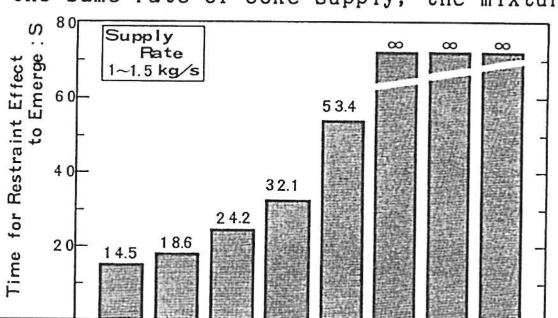
Figure 3 shows the comparision of the restraint efficiency for various materials at a similar rate of supply. From this figure, the following points were clarified.

1) When the coke powder was supplied, only 15s was necessary to restrain the slopping.

2) As the increase in the mixing ratio of $CaCO_3$ to coke, t_e became large and when pure $CaCO_3$ was supplied, about 55s was necessary to restrain.

3) The injection of Al dross and CaF_2 had no restraint effect. The injection of N_2 gas without any restraint materials also did not have any restraint effect.

Figure 4 shows the relation between the rate of coke supply and the time for the restraint effect to emerge. Both the increase in the supply rate and the decrease in coke size shortened t_e. In Figure 5, the effect of $CaCO_3$ mixed with coke is shown. At the same rate of coke supply, the mixture of $CaCO_3$ and coke were slightly efficient



Mixing Ratio of Restraint Materials : %								
Coke	100	75	50	25	0	0	0	0
$CaCO_3$	0	25	50	75	100	0	0	0
Al-dross	0	0	0	0	0	100	0	0
CaF_2	0	0	0	0	0	0	100	0

Fig. 3 Comparision of the restraint effect with various materials.

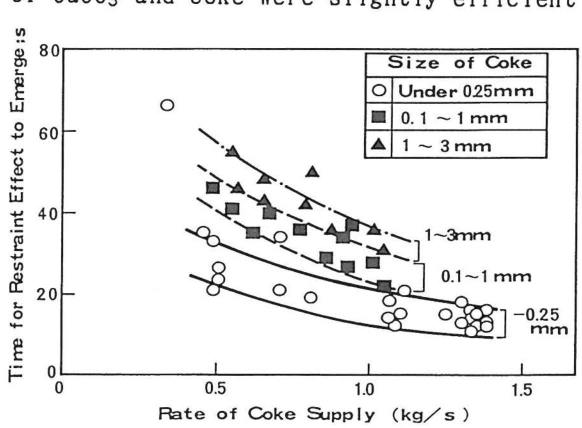


Fig. 4 Influence of coke size on the restraint effect.

than the pure coke.

In Figure 6, the relation between (CaO)/(SiO_2) and (T·Fe) after the dephosphorization treatment is shown. From this result, the influence of the restraint materials on the slag composition was not found. It can be considered that no significant influence was observed in the reaction behavior, because the total amount of restraint materials supplied was less than 1% of slag in weight. No influence of the coke powder addition on oxygen efficiency for dephosphorization was observed either.

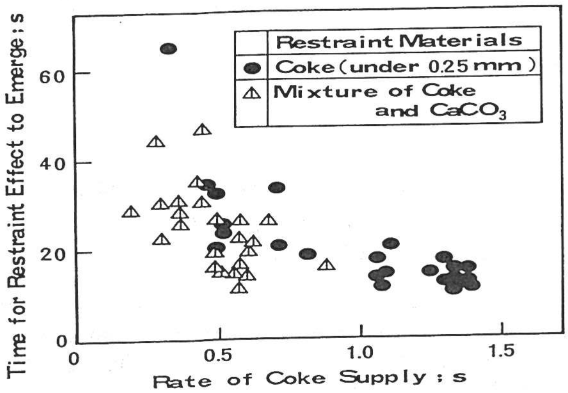


Fig.5 Influence of mixing $CaCO_3$ on the restraint effect.

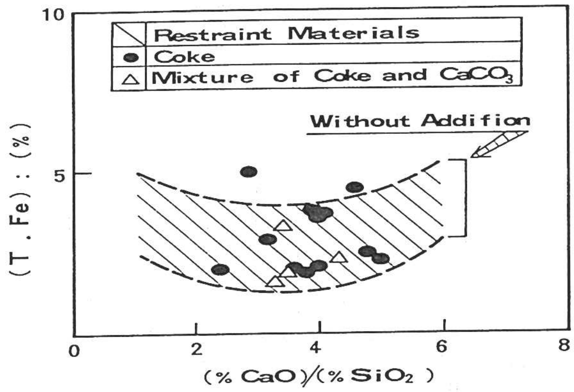


Fig.6 Influence of coke injection on the relation between (CaO)/(SiO_2) and (T·Fe).

2.3 Results for prediction of slopping

Figures 7 and 8 show typical examples of the sound intensity and the acceleration intensity at some typical times in the treatment until the foaming slag overflows from the vessel. In these figures, based on the real intensity change in time, the maximum intensity in an infinitesimal time interval was calculated for each time. The abscissa of these figures shows the time until the overflow of slag was observed. Figures 7 and 8 show the examples for the desiliconization and the dephosphorization treatments respectively.

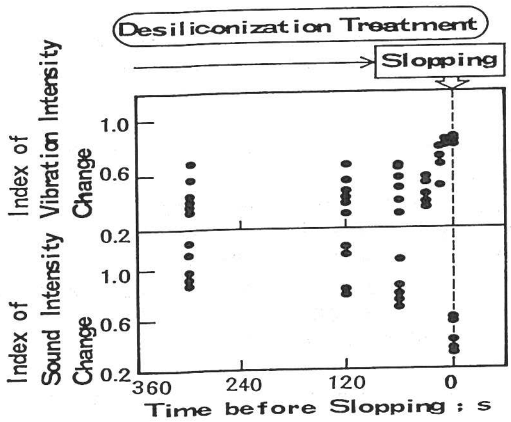


Fig.7 Changes in the sound intensity and the vibration intensity during deslilconization treatment.

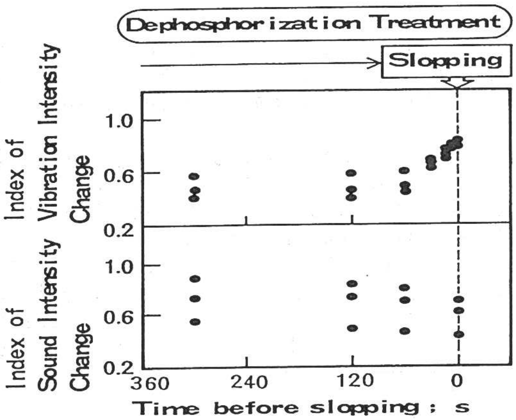


Fig.8 Changes in the sound intensity and the vibration intensity during dephosphorization treatment.

In Figure 7, a noticeable decrease in the sound intensity can be found at about 60s before slopping as well as a noticeable increase in the vibration intensity at about 10s before slopping. On the other hand, for the dephosphorization treatment, a noticeable increase in the vibration intensity can also be found about 20s before slopping but no noticeable decrease can be observed in the sound intensity. The difference of the prediction time would depend on the rising velocity of the slag surface in each treatment condition. When the rising velocity of slag was high, the time interval from the prediction to the overflow was too short by the measurement of the vibration intensity. On the other hand when the rising velocity of slag was slow, the intensity change was too small to predict by a measurement of the sound intensity. Therefore, to predict of slopping accurately, both methods have to be applied simultaneously.

2.4 Operation results

In Figure 9, the frequency of slopping before and after the application of the prediction and the restraint techniques are shown. Before the application, the frequency of slopping also increased with an increase in hot metal temperature. On the contrary, with the application of the techniques, slopping never occurred under any conditions. In addition, an increase in the rate of flux supply and an increase in oxygen gas consumption can be achieved by the use of this method.

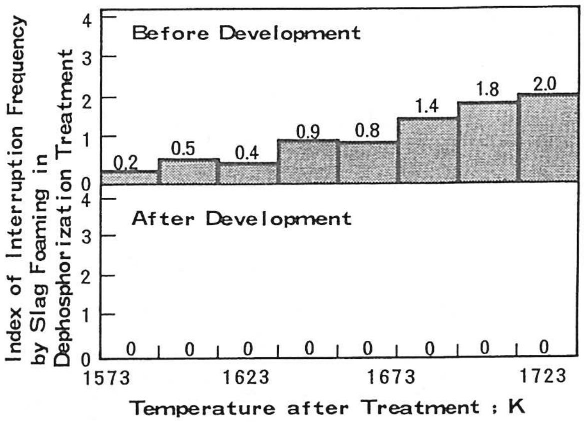


Fig.9 Frequency of slopping.

3. Fundamental tests

3.1 Experimental method

The experiments were carried out in a Tammann furnace. The electrolytic iron (about 400g) and graphite powder (about 40g) were heated to about 1623K in a graphite crucible of 50mm in inner diameter and 180mm in height. A mixture of reagents (about 180 g) without FeO was added and 300s after that, FeO was added three times at 90s intervals. The slag height was measured by the length of the slag adhesion on a steel rod immersed in the crucible. The foaming height was calculated by the subtraction of the slag height before FeO was added to the measured value. The experiments were carried out for an eight component system ($CaO-SiO_2-Al_2O_3-P_2O_5-TiO_2-MnO-MgO-CaF_2$). For the parameter to indicate the slag forming height, the maximum slag height during the experiment was used. To clarify the effect of carbonaceous materials, adequate amounts of coke or graphite powder in various sizes were added before the FeO addition. In some cases, the sample slag was observed by optical microscopy and EPMA to investigate the location of carbon powder in the foaming slag.

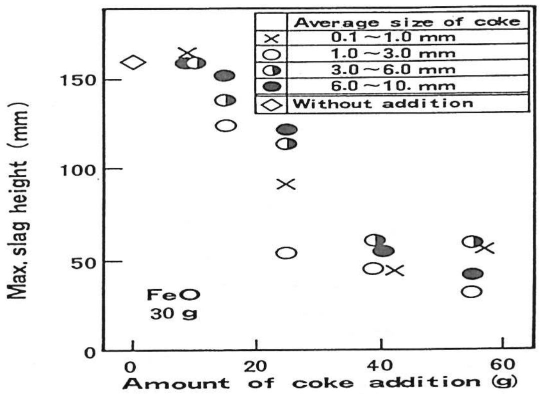


Fig.10 Effect of coke addition in fundamental tests.

3.2 Experimental results

Figure 10 shows the effect of coke addition and the following points were found.

1) As the increase of coke powder, the foaming height decreased. About 40g was necessary to restrain the slag foaming. This value corresponded to about 25% of the coke mixed in the foaming slag.

2) The finer powder was more efficient to restraint.

In addition, no meaningful difference was observed between coke and graphite.

In Photo.1, the result of the optical microscopy observation of slag is shown. This photograph shows the cross sectional area of the solidified slag which was fixed with resin to preserve its shape during polishing. The characteristic X-ray images at the interface of the slag

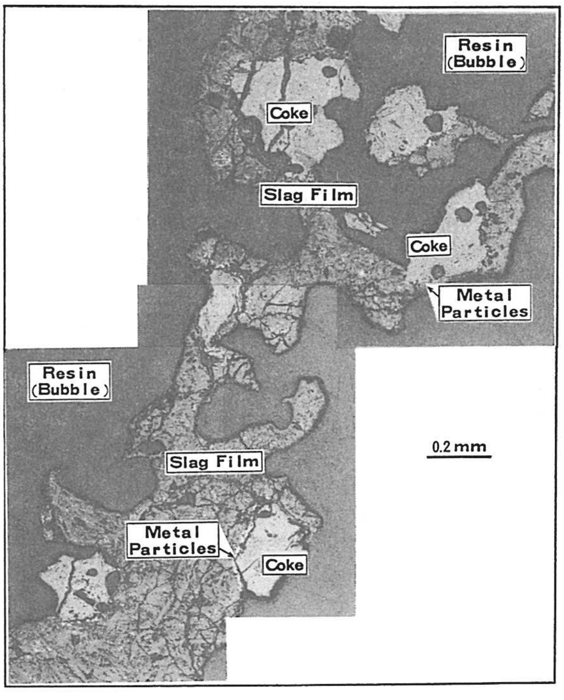


Photo.1 Coke powders in the slag film among the bubbles.

and coke powder are shown in Photo.2. According to these pictures, the following points were found.

1) Coke powders located at the slag film surface and partially intrude into the film.
2) Fine metal particles were found at the slag and coke interface.

From the results of EPMA analysis, the composition of slag near the interface was not different from that of slag bulk.

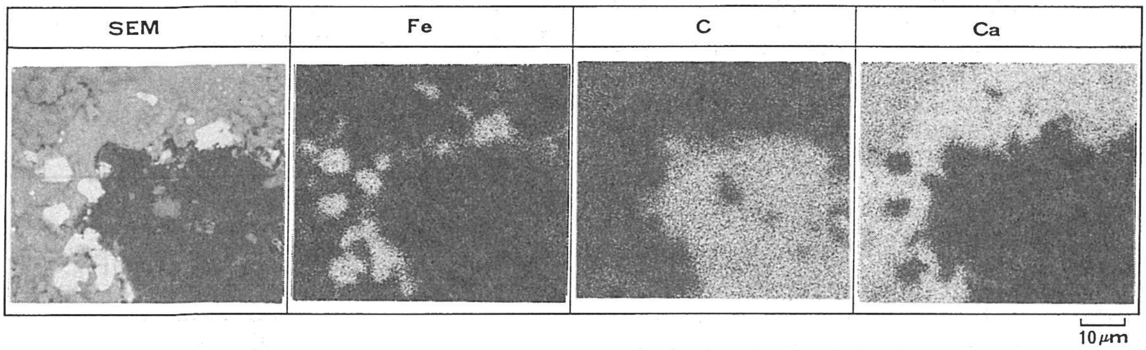


Photo.2 Characteristic X-ray images at the slag and coke interface.

4. Discussion

In this experiment, no macroscopic change in slag composition was observed. Therefore, the restraint mechanism of the fine coke powder should be discussed as an interfacial phenomena at the slag and the coke interface. From the results shown in Photos.1 and 2, the following restraint mechanism can be considered. In these photographs, metal particles which partially adhered on the coke surface were found. The wetness between slag and liquid metal can be considered as much better than that between coke and slag. Therefore, the coke powder on which the metal particles partially adhered would easily intrude into the slag films. After the intrusion, the neighboring two bubbles would be combined because the gas in the two bubbles was able to move through the coke surface where the metal particles did not adhere.

In addition to this, when the fine coke powder comes in contact with the slag liquid film, the following mechanisms have been proposed :

(A) If the coke powder had movement, relative to the foaming slag, the powder would intrude into the slag film by kinetic energy [4].

(B) The CO gas, which was formed by the reaction between the coke powder and (FeO) in the slag film, increased the bubble size and decreased the thickness of the slag film.

(C) The change in (FeO) concentration in the slag film, which was also formed by the reaction between the coke powder and (FeO) in the slag film, caused the Marangoni flow and decreased the thickness of the slag film [6].

The newly proposed mechanism and the mechanism (A) are based on the wetness and the mechanism (C) is based on the reaction between slag and coke. For these mechanisms, the interfacial area of slag and coke will be a predominant factor in the restraint.

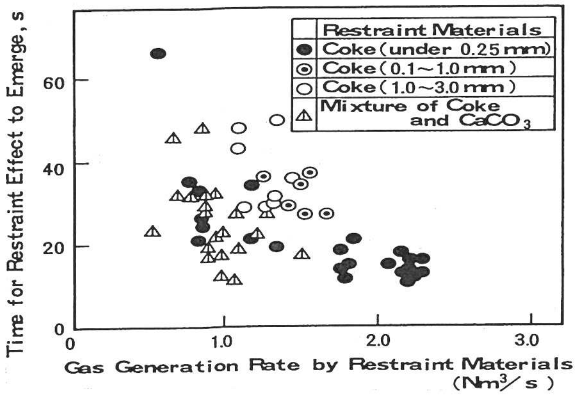


Fig.11 Relation between the restraint effect and the gas formation rate.

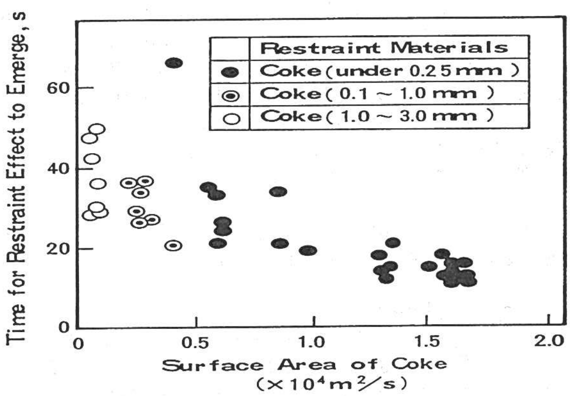


Fig.12 Relation between the restraint effect and the surface area of coke.

On the contrary, the mechanism (B) is based on gas formation. Therefore, the gas formation rate will be a predominant factor.

Figure 11 shows the relation between the time for the restraint effect to emerge and the gas formation rate by the addition of the restraint materials. The gas formation rate was calculated by the following assumptions.

1) The added coke was oxidized by the FeO in slag or oxygen gas and formed CO gas instantaneously.

2) The added $CaCO_3$ decomposed and formed CO_2 gas instantaneously.

From this figure, the influence of the supply rate, $CaCO_3$ mixing, and the difference between coke and $CaCO_3$ can be explained by the difference in the gas formation rate. The effect of coke size could be explained if the CO gas formation rate increased with the decrease in size.

On the other hand, Figure 12 shows the relation between t_e and the surface area of the coke supplyed in an unit time. The surface area was calculated under the assumption that the coke was a sphere with an average diameter. From this figure, the influence of the rate of supply and the effect of coke size can be explained. However, the difference between coke and $CaCO_3$ and the effect of $CaCO_3$ mixing could not be explained.

In this discussion, the effectiveness of the four mechanisms could not be evaluated quantitatively. Investigation should be continued to understand the restraint mechanism of slag foaming by coke powder.

5. Conclusions

A new slopping restraint method by the use of fine coke powder which was injected in the foaming slag was developed for the hot metal pretreatment process. Also, a prediction method for slopping was developed by a measurement of the vibration intensity of the top blow lance and a measurement of the sound intensity. This investigation, clarified the following points :

1) When the coke powder was supplied, only 15s was necessary to restrain the slopping. As an increase in the rate of coke supply and a decrease in the coke size, the restraint effect became more significant.

2) Although the injection of $CaCO_3$ had a restraint effect, the injection of Al dross and CaF_2 had no effect.

3) The injection of coke powder had no influence on the reaction behavior.

4) For the accurate prediction in any case with a the rising velocity of foaming slag, the measurement of the vibration intensity and the sound intensity has to be performed simultaneously.

5) The coke powders in the slag film between the bubbles were clearly found in the observation by optical microscopy.

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