Reduction Behavior of Alumina in Pure Oxygen Blast Furnace for Aluminum Production

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Experimental investigations have been made to clarify the features of the formation of combustion zones as functions of coke size and of oxygen blast rate, because these features should be crucial in forming a hot and reductive zone capable of reducing bauxites outside the combustion zone. Experimental results showed that a hot and reductive zone can be formed at the center of a blast furnace when the combustion zones are formed steadily, without growing up, within a limited space of a furnace. The use of large cokes at a high oxygen blast rate was found to be preferable for this purpose. An investigation has been made to examine an appropriate way of conveying bauxite ores into the hot and reductive region formed. The use of a large amount of calcia as flux for this purpose has been examined experimentally; however, this attempt was failed, since calcia flowed down only in the combustion zone and its vicinity. The observation that calcium oxycarbide melts became fluid in the high temperature combustion zone may imply that increasing the combustion temperature may be effective in improving the mass transfer problem intrisic to an aluminum blast furnace.

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I. Introduction

The production of aluminum alloys in a blast furnace has attracted much attention in recent years. In addition to the high productivity of a blast furnace process, an aluminum blast furnace can, as pointed out by Grjotheim, be categorized as a process that produces aluminum alloys and carbon monoxides. Our investigation on an aluminum blast furnace has been made from the point of view of the energy conservation, from which an aluminum blast furnace can be regarded as a process that produces aluminum alloys using heats generated in coal gasification.

During the course of our experimental investigations on an aluminum blast furnace, the following features have been clarified:

1. When the silica component in ores is relatively large in amount, the severe volatilization can occur because of the evolution of SiO as well as Al₂O; this caused the formation of a heavy bridge in an upper part of a shaft; therefore, the silica component should be lowered in ores.

2. Even when the silica component was lowered and the iron component was added to stabilize aluminum alloys to be produced, the severe volatilization occurred. The extent of the volatilization was found to be severer than those predicted by the chemical thermodynamic considerations. Detailed examinations of the inside of an experimental furnace after operation revealed that no effective reduction zone was formed in the furnace. This suggested us that the severe volatilization may be due to the reaction of produced alloys in an oxidative atmosphere in the vicinity of the combustion zone.

These experiences in operating an experimental blast furnace have led us to the following recognitions:

1. The movement of ores and cokes in a furnace is essentially governed by the feature of the combustion of cokes. In the early stage of our experiments, almost all ores dropped, together with cokes, directly into the combus-
tion zone and reacted with cokes at an oxidative atmosphere resulting in the severe volatilization.

(2) This recognition suggests the necessities of investigating the following aspects:

(i) features of the formation of the combustion zone and their relation with the temperature distribution and the oxygen partial pressure distribution in the vicinity of the combustion zone, and also with the mass transfer of ores toward the combustion zone;

(ii) effects of additives such as calcia on the movement of ores that tend to move toward the combustion zone when no appropriate method is adopted,

In the iron blast furnace, air blast is quite common and the features of the combustion zone have been extensively investigated\(^{(16)}\). However, there has been few work on the behavior of the enriched-air or oxygen blast. Okamoto \textit{et al.}\(^{(17)}\) made an investigation on the effect of use of enriched air in iron blast furnace. They reported that a large amount of white fume was evolved in their operation. This is apparently due to the increase in the combustion temperature which causes the evolution of SiO and Al\(_2\)O gases.

In the present investigation, we have examined the features of the formation of the combustion zone in our experimental blast furnace; experiments was made by changing the particle size of cokes and the oxygen blast rate. An attempt was also made, using calcia, to reduce the volatilization of ash component and also to control the mass transfer.

These experimental results are compared with results of the theoretical investigations on the heat transfer in coke beds and on the combustion behavior for the case of the pure oxygen blast.

\textbf{II. Experimental}

Figure 1 shows the bottom part of an experimental blast furnace; the whole diagram of the furnace is reported elsewhere\(^{(13)}\). Although this furnace has six oxygen lances, three lances were actually used in the present experiments and others were closed. The tuyere diameter was 14 mm except 10 mm for some cases. The oxygen blast speed was changed widely from 7 m/s to 55 m/s; this corresponds to the blast rate of 0.83–8.3 dm\(^3\)/s per lance.

Blast furnace cokes were used of four different particle sizes, that is, 5–10, 10–15, 15–25, and 25–35 mm in diameter. Calcium carbonate lumps were used as slag flux (9–40 mm diameter). The burden was loaded about 1 to 2 m in height.

During operation, the feature of the combustion zone was inspected visually through the open oxygen lances, through which the temperature of burning cokes was also measured by an optical pyrometer. In order to inspect the inside of the furnace, one of the closed oxygen lances was used; to elongate the path in the lance to the hearth (position “C” in Fig. 1), a graphite pipe was placed on the tip of the lance. A pressure gauze was also equipped to a closed lance to measure the inside pressure directly. A probe lance was furnished at the location of 200 mm
above the tuyere level and between two oxygen lances as shown in Fig. 1. This prove lance was designed as movable horizontally even during operations; since gases inside the furnace can be sampled directly through this lance, the gaseous concentration as well as the inside temperature were observed as a function of the distance from the side wall of the furnace (Line from “A” to “B” in Fig. 1). The wall temperatures were monitored by six sets of W/W-26%Re thermocouples in the furnace wall.

Since effects of heat loss carried away by cooling water seem to be significant in the present small experimental furnace, the heat loss was evaluated from the temperature increment of cooling water between inlet and outlet. The flow rate of cooling waters was fixed at 0.1 m³/s throughout the present experiments.

The furnace was dissected after each operation and the burden bed was dug up in order to inspect the geometrical and other features of the combustion zone.

III. Results

Results are given for the shape of the combustion zone in Fig. 2, the coke combustion temperature in Fig. 3, the temperature of the inside of furnace in Fig. 4, the gaseous concentration in Fig. 5, and the heat loss in Fig. 6.

1. Shape of the combustion zone

Figure 2 shows typical shapes of the combustion zone, which were obtained by digging inspect after several hour operations. After loosely packed cokes were removed, there remained coalesced cokes, which are shown as the shaded area in the Figure.

The depth of combustion zones was about 70 mm below tuyere in all cases. On the other hand, the length and width of the combustion zone depended strongly on the oxygen blast rate. The combustion zone expanded with increasing the blast speed up to 22 m/s; above that blast speed, however, the combustion zone ceased to expand horizontally but in turn grew vertically.

The effect of addition of CaO will be mentioned later.

2. Combustion temperature and temperature distribution

Figure 3 summarizes the coke combustion temperature as a function of oxygen blast speed with a parameter of diameter of coke. These were determined in the visual insight by an optical pyrometer through the open oxygen lances. When small cokes were burnt at a high blast speed, cokes moved around vigorously. Thus, the temperature should be regarded as averaged values. When cokes stayed in front of the tuyere, the surface temperature of cokes elevated very rapidly after cokes started to react with oxygen. It took about 15 to 30 s to attain the maximum surface temperature; this temperature was adopted in Fig. 3, in which the typical temperature drift is indicated by bars. Fig. 3 showed that the combustion temperature increased with coke diameter. There appeared the maximum point for each coke size in the coke combustion temperature versus oxygen blast speed plot. The oxygen blast speed at which the temperature became the maximum increases with the coke size; although no maximum point was observed for
the largest coke, it will be reasonable to assume
the existence of the maximum point beyond
the present region of the blast speed.

The higher combustion temperatures were
observed in the use of 14 mm tuyere than those
observed in the use of 10 mm tuyere.

These characteristic features of the coke
combustion affected the temperature distribu-
tion in the furnace as shown in Fig. 4, in which
the temperature is plotted along the horizontal
line above the tuyere (for geometrical arrange-
ment, see Fig. 1). Note that the temperature
near to the wall well corresponds to the coke
combustion temperature. As mentioned
above, the typical size of the combustion zone
is about 160 mm long; since the hot carbon
monoxide gas tends to go up from the combus-
tion zone, this correspondence seems to be
reasonable. The important observation in Fig.
4 is that although the temperature at the center
of the furnace did not depend strongly on the
size of cokes, there still remained the effects of
the coke size on the temperature at the center.
Note that the temperature difference in the
order of 100 K around 2000 K is quite crucial
in proceeding the reduction of bauxites (the
typical reduction temperature of bauxite is
about 2220 K[14]) and also in promoting the
separation of calcia slags and bauxite ores
from those cokes that tend to drop into the
combustion zone. Figure 4 indicates that the
larger cokes and the higher blast speeds are
effective in obtaining higher temperatures at
the center of the furnace. Note also that the
temperature at the center of the tuyere level, at
the position “C”, depended strongly on the
temperature of the combustion zone.

3. Gaseous concentration

The measured values of the combined con-
centration of oxygen and carbon dioxide along the line of "A" to "B" are plotted in Fig. 5, which shows that the concentration of oxidative gases was quite low at the center of furnace. In the vicinity of the wall, however, the oxidative gaseous concentration was anomalously high especially in the case of fine coke powders (1-4 mm).

The pressure of furnace stayed almost constant (0.101-0.118 MPa) during operations.

4. **Heat loss**

Heat loss at the oxygen lance was summarized in Fig. 6. In Fig. 6, (a) open circles indicate the case where the coke of 10-15 mm in diameter was burnt with changing the oxygen blast rate \( F \), and (b) solid circles indicate the case where the oxygen blast rate was fixed at about 3.3-4.2 dm\(^3\)/s per lance with changing the coke particle diameter \( d \). The theoretical heat input was evaluated from the reaction enthalpy for

\[
C + \frac{1}{2}O_2 = CO,
\]

under the assumption that oxygens introduced per unit time of period are reacted completely with cokes; the evaluated values are shown in broken lines in Fig. 4. Heat loss gradually increased with oxygen blast rate when coke diameter was fixed. When the blast rate was small, the observed heat loss became larger.
than the calculated heat input; this is probably due to some bad steadiness in the heat transfer in the present furnace. Heat loss became constant with larger cokes when the oxygen blast rate was fixed. The net heat input, the difference between the calculated heat input and the measured heat loss, increased with oxygen blast rate, whereas it increased with coke size in the small size region and approached a constant value for large cokes.

5. Effect of addition of CaO

When calcia was added with fine cokes, the slags were flooded in front of tuyere; as a result, a large combined zone was formed instead of distinct combustion zones for each lance. Initially, the cokes moved around vigorously; however, the pulverized cokes were combined with calcia to form a kind of slurries, which remained like solidified "lava" after operation.

When large cokes were used with calcia, the cokes did not move so vigorously as the small cokes. In this case, the calcium oxycarbide melts were found in the wall of the combustion zone and also below the combustion zones in a large amount. Three separately formed combustion zones remained after the operation: The center part was about 100-200 mm diameter (see Fig. 2).

IV. Summary of Theoretical Investigations

In order to obtain the complementary information to the present results, some theoretical investigations have been made on the heat transfer in coke beds and on the computer simulation of the combustion zone for the case of pure oxygen blast instead of air blast.

1. Heat transfer in coke beds

The total heat conductance in coke beds were evaluated using the theoretical equation given by Kunui et al.\(^\text{(18)}\) for two cases, that is, small coke particle bed and large coke particle bed.

The major results are as follows: With increasing temperature, the contribution of radiation conduction become significant; this makes the conduction in cokes the rate-limiting step. In view of this, the total heat conductance increases with increasing the particle size of cokes at high temperatures. This is consistent with the observation that the temperature at the hearth (position "C") depended strongly on the coke size. Since the flow rate of the evolved gases was not high at the center of the furnace, the warming of the hearth was achieved through the heat conduction in a coke bed.

2. Computer simulation of oxygen blast

The method adopted is essentially the same as that proposed by Kuwahara et al.\(^\text{(19)}\) Calculational results can be summarized as follows:

(1) Under a condition similar to the present experiments, the partial pressure of oxygen and carbon dioxide are relatively high in the combustion zone. This feature will be discussed later;

(2) On changing blast rate and coke particle size, the length of the combustion zone depends on these conditions, whereas the maximum temperature does not change sensitively (in this analysis, the effect of radiation heat loss is included); this is because when the combustion temperature increases, the radiation heat loss occurs to the corresponding extent. The rough evaluation for the heat loss gave a value of 6 kJ/s, which should be compared with the present observation of 8.8 kJ/s.

V. Discussion

1. Creation of a hot and reductive zone

The present investigation has revealed the following:

(1) To lower the partial pressures of oxygen and carbon dioxide at the center of the furnace, it is necessary to form the separate combustion zones. As confirmed by the calculated results, the concentration of oxygen and carbon dioxide will be still high in the combustion zone. This suggests that when the combined large combustion zone is once formed, the oxygen partial pressure should be high inside the combined combustion zone; this is the case where the calcia was added to the fine
coke particles in the present furnace. On the other hand, in the cases given in Fig. 2, the relatively small combustion zones were formed in the front of each tuyere and provided the reductive zone at the center of the furnace.

(2) The interesting feature has been observed in the effect of the blast rate on the formation of the combustion zone; the combustion zone expanded vertically even when the oxygen blast speed was increased. This phenomena can be regarded as one of the characteristic features of the oxygen blast when compared with the air blast; in the air blast, the momentum of nitrogens is strong enough to extend the combustion zone horizontally.

(3) The effectiveness of large coke can be ascribed to the longer combustion period of an individual coke: Smaller cokes are burnt out before they attain higher temperatures. The high blast speed made more vigorous the movement of cokes in the combustion zones, and gave rise to faster renewal of cold cokes than the low oxygen blast speed. As a result, the effective combustion temperature was lowered.

(4) There was a large temperature gradient in the furnace when the separate combustion zones were formed. Correspondingly, a large concentration gradient was observed along the horizontal line. When fine cokes burnt under the condition of fluidization of cokes in high-speed oxygen blast, oxygen spreaded more widely than in the case of larger cokes.

From these observations and the calculated results, the following important features can be derived under the present experimental conditions:

(1) Hot but quite oxidative gases tend to ascend immediately after their evolution in the reaction between cokes and oxygen;

(2) In the ascending stream, the further reaction of the gases with cokes does not proceed significantly;

(3) On contrary, the reaction of gases with cokes proceeds completely in the center of furnace.

The dissection of the furnace suggests that cokes to be burnt also descend through the same path as that of the hot and oxidative gases, and finally drop directly into the combustion zone. When bauxites are loaded under these experimental conditions, it is expected that the bauxites drop, together with cokes, into the combustion zone; this was the case in our previous experiments.

In order to avoid the direct drop of bauxites into the combustion zone, a hot and reductive zone must be formed outside the combustion zone as well as outside the hot and oxidative gaseous stream; in addition, bauxites to be reduced must be conveyed to this zone in an appropriate way.

The present results shown in Figs. 4 and 5 indicated that a hot and reductive zone can actually be formed at the center of furnace for the case where the combustion zones were formed within a limited space in a steady state.

2. Behavior of slag and control of solid briquettes transfer

Finding an appropriate way of conveying bauxite into a hot and reductive zone is one of the most important key points in establishing an aluminum blast furnace. This will be clearer when an aluminum blast furnace is compared with the iron blast furnace. The essential difference between the iron and the aluminum blast furnaces comes from the nature of solid mass transfer in furnaces. In iron blast furnace, ascending hot CO gases reduces descending iron ores in the furnace shaft and the ferrous oxide/pig iron mixture can flow down as the liquid state. In an aluminum blast furnace, however, bauxites stay in the solid state until they are heated to a temperature (2200 K) hot enough to proceed the reaction with cokes\(^{(14)}\). Bauxites will thus descend, together with solid cokes, into the combustion zone where the oxygen exists abundantly.

We have investigated the effect of addition of CaO in experimental operations with an aim that CaO may work in controlling the mass transfer associated with bauxites. The reasons of using CaO can be summarized as follows:

(1) CaO reacts with Al\(_2\)O\(_3\) to form the double oxide melt at a relatively low temperature;

(2) CaO reacts with carbon to form the calcium oxy carbide melts; the stability region of this melt is wider that of the aluminum oxy carbide melt.
There is no calcium oxide gaseous species. Therefore, the calcium component exists in the form of CaC$_2$ or Ca vapor in the reductive atmosphere and in the oxydative atmosphere in the form of CaO. This should be compared with the features in the Al–O–C system in which the aluminum oxide vapors evolve in both reductive and oxydative atmospheres.

The present results are not confirmative about the effects of addition of calcia: The calcium component was found in the wall and bottom of the combustion zone, and there was little evidence for the flowing of calcia to the hot and reductive zone formed at the center. To improve this situation, the temperatures should be elevated further at the center of furnace.

The present results revealed other effects of the addition of CaO. As shown in Fig. 2, the combustion zone formed in the presence of CaO exhibited a slightly different feature; that is, the width of the zone was widened. This implies that the presence of CaO may affect the heat and mass transfer in the combustion zone, although a possible mechanism remains unknown. The present results indicated that when CaO is added, the larger cokes should be used; this is because the pulverized cokes combined with CaO prevent the continuous and smoothed flowing away of the melts out of the combustion zone. This is one of the key points of keeping the combustion zones in a steady state, which is required to form a hot and reductive zone as mentioned above. To promote the smoothed flowing away of the calcium component, the higher combustion temperature will be appropriate, since the viscosity can be lowered at higher temperatures. In view of these features, the increase of the combustion temperature and use of large cokes may improve the situation.

When the combustion temperature increases, the heat loss may increase correspondingly. In the present experimental furnace, the cooling water at the tuyere carried away a large portion of heat input as shown in Fig. 4. The increase of heat loss with coke diameter and blast rate seems to be reasonable because at such a high temperature, heat is transferred mainly by radiation; note also the increasing heat conductance in a large coke bed. Nevertheless, the heat loss can be reduced in larger furnaces.

V. Conclusion

(1) A hot and reductive zone was created at the center of furnace when large cokes were burnt with oxygen in a high blast rate. This makes it possible to prevent the severe volatilization of the aluminum component in bauxite due to its reaction with the oxidative atmosphere.

(2) In the present experimental small furnace, heat loss, carried away by cooling waters at oxygen lances, was extraordinary significant. This heat loss can be reduced in larger furnaces in an appropriate way, for example, by improving the structure of oxygen lance.

(3) Liquefaction of briquettes in the presence of calcia was not successful enough. Further warming up of furnace will be required especially at the shaft part to surmount the mass transfer associated with an aluminum blast furnace.

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