Molten Slag Bath Reduction: Carbon-Thermal Reduction of Blast Furnace Dust in Molten Blast Furnace Slag

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Abstract: By adding BF dust into molten BF slag, it was conducted to explore the feasibility of carbon-thermal reduction of BF dust in molten BF slag bath. The experimental results indicate that, BF dust can achieve self-reduction in the bath. It is convenient for the reduction products that are iron-based metal particles separating from slag. Besides, the reduction of BF dust is endothermic. When the mass ratio between BF slag and BF dust is 10:1, the temperature of BF slag after reduction can meet the requirement of dry processing treatment. According to the comparison by X-ray diffraction, the main mineral phases of BF slag are relatively stable before and after reduction. Undoubtedly, it is a novel method to cope with the metallurgical solid waste in molten BF slag bath.

1. Introduction
In China, the disposal of metallurgical solid waste has always been the hot topic in ironmaking and steelmaking industry. With the overproduction of steel in recent years, it is inevitable that the generation of metallurgical solid waste has been growing significantly as well. In ironmaking, the major solid waste are blast furnace (BF) slag and BF dust. For BF slag, it is estimated that the average production of BF slag is up to 346kg per tonne hot metal[1]. Currently, these slags are either water granulated or air cooled. In general, water granulation is the most common treatment used to produce glassy materials that can be widely used in concrete and cement[2-4]. But before water granulation, the high quality sensible heat of molten slag is always wasted in vain without reasonable utilization[5]. It has been estimated that the waste sensible heat of the molten BF slag at 1773K reached 18.5kg CE (kilogram of coal equivalent)[6]. But at present, not only the efficiency of heat recovery is still at a low level, but also the quality of this kind of energy is poor[5]. Therefore, from the view of energy saving, it is important and valuable to use the sensible heat in a high-efficiency way.

In addition to BF slag, BF dust is also a kind of by-product generated in the ironmaking process. It is estimated that the amount of BF dust is 15-50 kg per ton hot metal[7]. Since the various ingredients of BF dust are stemmed from the raw material added in BF, the dust contains high values of carbon and iron accompanied with harmful elements of Zn, K and Na. Based on this, there has been several successful attempts to separate and recycle valuable part of the BF dust, such as carbon and iron as well as zinc[8-10]. But the residual part that is regarded as the so-called useless waste is still a tough problem that has to be faced. Moreover, the disposal of BF dust on the landfill can obviously and inevitably cause environmental pollution as the leaching of some toxic metals (such as Pb and As)[11]. Thus, there needs more appropriate ways to recycle BF dust. Shaheer A. Mikhail et al.[12] reported that carbon-rich BF dust could be regarded as reductant, not only realizing self-reduction, but also...
making the iron oxides in basic oxygen furnace dust reduced at the same time. This research provides an idea that with the help of the high temperature platform, it is feasible to realize the total recycling of BF dust. Therefore, the aim of this paper is to explore the feasibility of both recycling BF dust and the direct use of high-quality sensible heat of molten BF slag. For the sake of achieving the goal, the experiments were carried out with the addition of BF dust into molten BF slag bath. Both the products and mineral phases of slag before and after reduction were studied by several methods, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive spectrometer (EDS). Meanwhile, the heat use of molten BF bath was evaluated as well.

2. Experimental

2.1. Experimental materials

Based on practical composition from AnSteel, BF slag used in the experiment was synthesized by analytical reagents. BF dust was sampled from the spot in AnSteel. The composition of BF slag and BF dust was listed in Table 1. The binary basicity of BF slag and BF dust were 1.11 and 1.04, respectively.

| Sample   | CaO | SiO$_2$ | Al$_2$O$_3$ | MgO | C     | Fe$_2$O$_3$ | Fe$_3$O$_4$ | NiO | CoO |
|----------|-----|---------|--------------|-----|-------|-------------|-------------|-----|-----|
| BF slag  | 40  | 36      | 14           | 10  | --    |             |             | --  | --  |
| BF dust  | 4.93| 8.92    | 3.41         | 1.65| 25.2  | 29.6        | 7.53        | 14.18| 4.58|

2.2. Sample and method

In the present work, analytical reagents were adopted to synthesize BF slag. Firstly, all the ingredients, including SiO$_2$, CaO, MgO and Al$_2$O$_3$, were mixed homogeneously together as the designed mass ratio shown in Table 1. Then the mixture was put into the graphite crucible and heated in a high temperature furnace for 30 mins at 1500°C in pure nitrogen, where the graphite crucible can be protected from oxidation. After synthesis, the BF slag was cooled in the air and crushed for further use. BF dust were made into pellets mixed with 2% bentonite binder and appropriate water by a pelletizer. Then, the pellets were put in a drying oven for 2 hours at 120°C. The diameter of cooled pellets is about 10.6mm shown in Figure 1.

![Figure 1. The scale of BF dust pellets.](image)

Generally, combing with the output ratio between BF slag and BF dust as well as the volume of corundum crucible, the usage of BF slag was confirmed as 80g, while the usage of BF dust was decided to be 8g, 12g and 16g at each experiment respectively.

Figure 2 shows the experimental apparatus used for thermal reduction of BF dust in molten BF slag bath. The experiments were conducted at 1500°C with the temperature duration of 30 mins, so that the solid BF slag could fully melt into liquid. Then, couples of BF dust pellets were added into the molten
slag bath to make carbon-thermal reduction. 30mins later, the corundum crucible was taken out and cooled in the air. The magnet was used to separate the products after reduction. X-ray diffraction (XRD, Cu Kα, λ=1.54178Å, 40kV and 40mA, 2θ=10°-90°, stepsiz=0.013, interval=5s) was used for measuring the mineral phases of slag, and scanning electron microscope (SEM, type: JSM6480LV) coupled with energy dispersive spectrometer (EDS) was employed to make microstructure observation of the product. Actually, though there was obvious reduction weight loss at each experiment, this work is mainly emphasized on the effect of recycling BF dust and the sensible heat use of molten BF slag. The kinetics of reduction of BF dust will be discussed later in another paper specially.

**Figure 2.** Experimental apparatus sketch at high temperature.

### 2.3. Thermodynamics of carbon-thermal reduction in BF slag bath

As shown in table 1, the mole ratio of carbon and oxygen is calculated as 1:0.45, which means that the amount of carbon in BF dust is excess. Figure 3 shows the standard Gibbs free energy changes of different reactions at high temperature[13]. It can be seen that the standard Gibbs free energy changes are all negative under the temperature from 1100°C to 1500°C. And it is obvious that the carbon-thermal reduction reactions of metal oxides, especially NiO, CoO, FeO, Fe₂O₃, Fe₃O₄, are able to happen in molten slag bath.

Figure 3 also shows the diagram of oxygen potential of part of oxides in BF dust[13]. Clearly, carbon is prior to reduce the oxide of Ni and Co instead of Fe. Meanwhile, iron oxides are doomed to be reduced into Fe step by step at 1500°C. Thus, from the view of thermodynamics, molten BF slag bath reduction is able to achieve the recycling of BF dust.

![Graph showing standard Gibbs free energy changes](image-url)
2.4. Mechanism on carbon-thermal reduction of BF dust in slag bath

Since the BF dust pellets were added into the slag bath, solid-solid reactions firstly took place at the reaction point. On account of BF dust containing both carbon and metal oxides, the slag bath reduction of BF dust pellets is similar to the reduction of iron ore-coal composite pellets[14]. The direct reduction reactions can be seen in figure 3. Then, with CO gradually generated, the indirect reduction are simplified as equation (1):

\[ \text{MeO} + \text{CO} = \text{Me} + \text{CO}_2 \]  

Where Me represents metals reduced by CO. In addition to the direct and indirect reduction, the gasification of carbon is supposed to be taken into account for the excess carbon existed in the pellets. Boudouard reaction (gasification of carbon) is expressed as equation (2):

\[ \text{C} + \text{CO}_2 = 2\text{CO} \]  

In common, the direct reduction and the gasification of carbon are endothermic process, which means that the enthalpy change of the total reduction reactions is positive (\( \Delta H > 0 \)). So, when the temperature is increasing, it is beneficial for the generation of CO. As the bond of direct reduction and the gasification of carbon, CO plays a key role on the rate of the whole reduction. Due to the limited contact area of solid, the rate of reduction reactions is relatively slow at initial period. However, when the partial pressure of CO rises to some value, the interface of reactions turns from solid-solid area to gas-solid area, causing the reduction rate growing fast. The reduction process of BF dust pellet in slag bath is shown in figure 4. Thus, based on the analysis above, the carbon-thermal reduction of BF dust in slag bath belongs to solid-solid phase reaction and gas-solid phase reaction.

![Figure 4. Reaction periods of BF dust reduction in BF slag bath.](image)

3 Results and discussion

3.1. Metal particles separated from BF slag

When the pellets were added into the molten BF slag, the reduction reactions were violent in the crucible with weight loss significantly, and amounts of smoke generated accompanied with burst-out sound of pellets. Figure 5 shows that the metal particles gather and grow up with different sizes after reduction. And it is clear that most of the particles were attracted by magnet. It indicates that the metal particles are easy to be separated from the slag.
SEM images in figure 6 shows that the main elements of metal particle contains Fe, Ni, Co and Si. It means that most metal oxides in the BF dust are reduced in BF slag bath, and the reduced metals are enriched in the particle where finally iron-based alloy is generated. Moreover, the physical interface of metal particle with the surrounding slag is clear, which indicates that it is easy to separate the metal particles from the slag after cooling. In figure 6(ii), it shows that there are dose of carbon inside the crack. It is probably because during the process of reduction, the metal particles were graphitized by the excess carbon in BF dust. This kind of graphitization is common to be found in the carbon-saturated iron[15].

3.2. Unsinkable behavior of metal particles in slag bath
In this work, it is very interesting to find that most of metal particles are floated on the slag surface after cooling, and it is difficult to find metal particles sinking into the slag or on the bottom of the crucible as shown in figure 5. Though it is seemingly convenient for separating metal products from the surface of slag, still the unsinkable metal particles are disadvantageous for the following treatment.
of BF slag. Because when it is slagging, molten slag and the surface metal products are unavoidable to be mixed together to some extend, which brings unnecessary load to the normal treatment of BF slag. In usual, the density of iron is 7.9 g·cm⁻³, approximately 2.5 times higher than that of BF slag. From this viewpoint, the gathering metal particles are supposed to sink in the slag, even on the bottom of the crucible. But, for one thing, as the stirring capacity of CO is limited in the carbon-thermal reduction, it is hard to make amounts of metal droplets gather and grow up. For another thing, by adding the pellets into the bath, there needs energy supplement for the carbon-thermal reduction of BF dust. As a result, it is inevitable to impact the system temperature that directly affects the viscosity of slag. With the viscosity increasing, it leads to the fluidity of slag turning to bad, which is neither advantageous for the metal particles to sink nor good for the following treatment of BF slag. Therefore, considering the reasons above, it is an alternative way to properly improve the slag bath temperature coupled with the stirring operation, so that not only the metal products are able to sink on the bottom of slag, but also the fluidity of slag can be ensured to meet the requirements of following treatment.

3.3. Heat use of molten BF slag

In China, the slagging temperature of BF slag is usually above 1450 °C, containing heat about 1770 MJ per ton hot metal[16]. Based on this, it can be calculated that 80g BF slag contains heat nearly 146.48kJ at 1500 °C. In order to estimate the heat use of molten BF slag, the enthalpy changes are calculated by the equation of Kirchhoff as follow:

\[
\Delta H^0_m = \Delta H^0_{m,298} + \int_{298}^T \Delta c_p \, dT
\]

(3)

Where, \(\Delta c_p\): heat capacity from 298K to the certain temperature, kJ·mol⁻¹·K⁻¹; \(\Delta H^0_{m,298}\): standard enthalpy change of reactions at 298K, kJ·mol⁻¹; \(\Delta H^0_m\): standard enthalpy change of reactions from 298K to the certain temperature, kJ·mol⁻¹. Here, it is assumed that ferrous oxides are reduced to Fe by one step. According to the chemical composition of BF dust in Table 1, the calculated results of \(\Delta H^0_m\) for each reaction are shown in table 2.

| No. | Reactions                       | \(\Delta H^0_m / (kJ \cdot mol^{-1})\) |
|-----|--------------------------------|---------------------------------|
| 1   | Fe₂O₃+3C=2Fe+3CO                | 494.00                          |
| 2   | Fe₃O₄+4C=3Fe+4CO                | 676.38                          |
| 3   | NiO+C=Ni+CO                     | 138.08                          |
| 4   | CoO+C=Co+CO                     | 128.41                          |

Clearly, the results of \(\Delta H^0_m\) are all positive in table 2, it means that the absorption of heat is apparent. Besides, due to not participating in the reduction, these ingredients such as SiO₂, CaO, MgO and Al₂O₃ in BF dust are heated in the slag bath, so the physical absorption of heat is taken into account as well. Therefore, the total heat consumption of pellets is calculated by the income and outcome of heat caused by physical absorption and chemical reactions. The calculated results are that when the reactions were complete, the system temperature was predicted to be 1358.3 °C, 1288.1 °C and 1217.8 °C with the added pellets of 8g, 12g and 16g, respectively. The temperatures above were almost in accord with the results showing in the experimental controlling system. Particularly, when the amount of BF dust pellets is 8g, namely the mass ratio between BF slag and BF dust is 10:1, the temperature after carbon-thermal reduction is just fit for the dry processing at 1348 °C to 1361 °C for BF slag[17]. Hence, in order to meet relevant requirement of various slag treatment, the amounts ratio between BF dust and BF slag should correspondingly make some adjustment.

3.4. Mineral phases of BF slag

The mineral phases of BF slag before and after slag bath measured by XRD is shown in figure 7. It
can be found that, there are no Fe diffraction peaks in the BF slag after slag bath. Based on this, it is in accordance with the mentioned results of few metal particles sinking in the BF slag. Moreover, compared with the original BF slag, the main mineral phases of BF slag after slag bath are basically the same. Besides, the mineral phase gehlenite (Ca$_2$Al(AlSiO$_7$)) disappeared in the BF slag, while grossularite (Ca$_3$Al$_2$Si$_3$O$_{12}$) appeared. This transformation is probably caused by the added ingredients of CaO and SiO$_2$ in BF dust as shown in equation 4.

$$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{CaO} + 2\text{SiO}_2 = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$$

(4)

Generally speaking, it is still common to find grossularite in CaO-SiO$_2$-Al$_2$O$_3$ system. The XRD results show that the main mineral phases of BF slag is not changed violently by the addition of BF dust. Also, it means that BF slag successfully contains the residual part of BF dust that can not be reduced during the slag bath. Undoubtedly, the method of BF slag bath is an alternative choice to be taken seriously in the field of energy saving and solid waste recycling in the future.

![XRD images of BF slag before and after slag bath.](image)

**Figure 7.** XRD images of BF slag before and after slag bath.

### 4. Conclusions

(1) With the sensible heat of slag bath at high temperature, self-reduction of BF dust is able to be realized. The reduction products are iron-based alloy particles, which remain on the surface of slag and are easy to be separated and recycled by magnet.

(2) The process of BF dust reduction in molten slag bath is endothermic. In this work, when the mass ratio between BF slag and BF dust is 10:1, the temperature of BF slag after reduction is able to meet the requirement of dry processing treatment.

(3) The residual part of BF dust after reduction is fully dissolved in the BF slag, and the main mineral phases of BF slag are relatively stable before and after reduction. Meanwhile, XRD results show that there are not metal particles in the BF slag after reduction.

### 5. References

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