Cold Strength and High Temperature Behaviors of Self-Reducing Briquette Containing Electric Arc Furnace Dust and Anthracite

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Electric arc furnace dust (EAFD) is one of the by-products of steelmaking industry. This research aims at dealing with EAFD by pyrometallurgy through mixing it with anthracite to be used as carbon-containing briquettes in RHF. The effect of the briquetting parameters on the green pellet strength was investigated in this paper. Effects of reduction temperature, reduction time and C/O molar ratio on metallization rate and removal rate of element Zn were also studied respectively. The results showed that: Effect of different factors on the drop number was greater than the compressive strength of briquettes. Green briquette drop number was more sensitive to moisture content and bentonite content. Given 2 wt% content of bentonite, 70 MPa pressure and 1.0 mole ratio of C/O, the drop number of the green pellets increased from 1.4 times to 6.4 times by water content changed from 4 to 10 wt%. Zinc and iron compounds are both easy to be reduced by anthracite. When the reduction temperature is up to 1 200°C, the zinc can be rapidly reduced within 5 min. But if the temperature reduced by 100°C, the total removal time would be prolonged to 20 min. The iron-containing phases were mainly Fe, Ca2Fe2O5 and a small amount of FeO after high temperature reduction. When reduction temperature, reduction time, C/O molar ratio were 1 200°C, 20 min and 1.1 respectively, direct reduction iron was most concentrated.

KEY WORDS: EAFD; briquetting; drop number; direct reduction; dezincification; metallization rate.

1. Introduction

Electric arc furnace dust (EAFD) is generated in considerable amounts by the electric arc steelmaking process. During melting in an electric arc furnace, certain elements volatilize, and form fine dusts after cooling. The EAFD is collected in a baghouse and amounts to approximately 1–2 wt% of the steel produced.1) In China, about 800 million tons of steel was produced in 2015 with more than 9 wt% equipped with electric arc furnaces, generating about a million tons of electric arc furnace dust every year.

On one hand, EAFD has a great amount of iron and it has been widely considered as a kind of secondary resource. On the other hand, EAFD has been designated as a hazardous waste, which means that it cannot be disposed of at landfills without treatment. In order to recover iron element and avoid environmental pollution, most of iron and steel enterprises send EAFD back to sintering machine. However, EAFD has another exceedingly evident characterization that it also has a large amount of zinc. The zinc content varies with the operating conditions such as the characteristics of scraps charged in the furnace, period of operation, specification of the steel produced and so on. Then, the problem is that both the sintering process and the blast furnace ironmaking process could not remove zinc from sintering raw materials. By sintering process, zinc is transferred from EAFD or other metallurgical dust to sintering ore. The zinc compounds embedded in sintering ore or other blast furnace raw materials are reduced to elemental vapor near the bottom of the furnace at high temperature and subsequently condense on the upper walls of the furnace at lower temperature. This process becomes cyclic and leads to an accumulation of Zn compounds in the blast furnace. Since these compounds form solids on the walls, they would eventually cause damage in the blast-furnace operation.

There are currently many different EAFD treatment methods. M. A. T. Alsheyab et al.2–6) aims at solving the problem of this hazardous waste by solidification/stabilization. But it cannot recycle the iron, zinc and other alloying values. R. Sekula et al.7) explored to treat EAFD by mechanical and magnetic separation methods. However, due to the very small particle sizes and formation of mixed phases, a separation of zinc element free form iron compound is not possible. Š. Langová et al.8–16) proposed to extract pure metals Zn, Pb, Cd or Cr from the dust. The final by-product is an iron-rich residue in this kind of process. But a great amount of franklinite embedded in EAFD is considerably refractory against leaching. In addition, hydrometallurgical treatment process would bring in water pollution. F. Santos et al.17) researched the chlorination methods in the field of electric arc furnace dust treatment, but chlorine elements are easy to evolve into hydrogen chloride and it would eventually cause the equipment corrosion. Chloride will also
promote the circulation and accumulation of alkali metal in the blast furnace. S. Itoh et al.) proposed a new EAFD treatment process named as “Lime Addition and Magnetic Separation Process”. But it is lack of kinetic and industrial test verification.

Carbothermic reduction is an effective way to treat zinc-bearing dust, and the waalz process (Rotary kiln) and RHF (Rotary hearth furnace) process have been applied into production. H. N. Zhang et al. have studied abnormal swelling behavior and the zinc and iron reduction temperature condition of self-reducing pellets containing EAFD. But they did not clarify clearly how different parameters affect the drop number and the compressive strength of the green briquettes containing EAFD and anthracite. They also did not explain clearly the microstructure evolved process of the EAFD briquettes. In this paper, the mineral characterization of the EAFD was studied firstly. Then the green briquetting strength under different water content, bentonite content, pressure and C/O molar ratio were investigated. Effects of temperature and C/O molar ratio on metallization rate and removal rate of Zn were also investigated. The mineral composition and microstructure of reduced briquette were also studied.

2. Experiment

Firstly, the mineral elements of raw EAFD were detected using an X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan) and total C was determined by the Carbon and sulfur analyzer (EMIA-820 V, Horiba, Japan).

Then, the dust granulometric distribution and the mean size of its particles were evaluated. A laser granulometer model SEISHIN LMS-30 from Japan was used, with anhydrous ethanol as dispersing medium. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Five points were used representing equilibrium condition of self-reducing pellets containing EAFD particles. Effects of temperature and C/O molar ratio on metallization rate and removal rate of Zn were also investigated. The mineral composition and microstructure of reduced briquette were also studied.

The main mineral composition of the EAFD briquettes was evaluated by X-ray diffraction analysis (Dmax-RB 12 kW, Rigaku, Japan). Scanning electron microscopy (SEM) was conducted to gain further knowledge of the EAFD particles structure and morphology. In addition, SEM was used to observe the size distribution of zinc-bearing particle. Fourier transform infrared spectroscopy (FTIR) spectra were collected on an Infrared spectrometer (NEXUS 670-FTIR, Nicolet, America), on KBr pellets, between 4000 and 400 cm⁻¹ with a 4 cm⁻¹ resolution and 32 scans.

TG/DSC analysis was made using integrated thermal analyzer (STA409C, Netzsch, Germany). The samples were 20~30 mg in weight. Two alumina crucibles, one containing alumina powder as a reference and the other a dust sample, were heated from 20 to 1000°C at a heating rate of 10°C/min in argon with a constant flow rate of 30 ml/min. The derivative thermogravimetry curves were also provided to get a better understanding of weightlessness course.

Magnetization measurements were carried out by using an integrated physical property measurement system (PPMS-9, Quantum, America). The sensitivity of vibrating sample magnetometer was over the range from 2×10⁻⁷ emu to 3 emu. The saturation magnetizations of the samples were measured at the external magnetized field of 10 000 Oe.

Secondly, the procedure of making pellet was as follows for fundamental investigation:

(a) Raw materials and binders were weighed and dry mixed and then were mixed with some water.
(b) Cylindrical pellets were made using steel die and punch with a constant impact.
(c) The drop number and the compressive strength of briquettes were evaluated one by one.

The briquettes have a diameter of 20 mm and a height about 14 mm.

At last, the briquettes, which were put in a graphite boat, were sent to the high temperature zone of a muffle furnace after being preheated at 400°C for about 300 s. Chemical analysis, X-ray diffraction analysis and SEM analysis were performed on the reduction product. The metallization rate of iron components, η, is defined as follows:

$$\eta = \frac{M_{\text{Fe}}}{T_{\text{Fe}}} \cdot 100\% \quad (1)$$

Where, $M_{\text{Fe}}$ and $T_{\text{Fe}}$ represent metallic iron content and total iron content, respectively, in the reduced briquettes. Removal percentage of Zn from the briquettes, $R_{\text{Zn}}$, can be described as:

$$R_{\text{Zn}} = \frac{(m_{\text{Zn}} - m_{\text{iZn}})}{m_{\text{Zn}}} \cdot 100\% \quad (2)$$

Where, $m_{\text{Zn}}$ and $m_{\text{iZn}}$ refer to total mass of zinc element in the initial briquettes and that in the briquettes after being reduced, respectively.

3. Results and Discussion

3.1. Characterization of the EAFD

The main chemical composition of EAFD is shown in Table 1. The main components of the EAFD in the present study are 43.17% T. Fe, 8.25% zinc oxide and 8.77% calcium oxide.

Figure 1 shows the particle size distribution of EAFD. EAFD has a relatively heterogeneous distribution of particle size, where 100% has size between 0.33 and 4.24 micron, having a large number of fine particles. Total pore volume was calculated at the relative pressure close to saturation in the adsorption branch. The average pore size of its particles were evaluated. A laser granulometer model SEISHIN LMS-30 from Japan was used, with anhydrous ethanol as dispersing medium. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Five points were used representing equilibrium condition of self-reducing pellets containing EAFD particles. Effects of temperature and C/O molar ratio on metallization rate and removal rate of Zn were also investigated. The mineral composition and microstructure of reduced briquette were also studied.

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Figure 1 shows the particle size distribution of EAFD. EAFD has a relatively heterogeneous distribution of particle size, where 100% has size between 0.33 and 4.24 micron, with granularity specific surface area up to 6.141 m²/cm³.

The nitrogen adsorption and desorption isotherms of EAFD is shown in Fig. 2. The surface area and porosity are analyzed. In spite of the small particle size, the specific surface area of EAFD is limited to 4.780 m²/g, mainly because of the dense spherical morphology of the particles. Total pore volume was calculated at the relative pressure close to saturation in the adsorption branch. The average pore

<table>
<thead>
<tr>
<th>Component</th>
<th>MFe</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>MnO</th>
<th>C</th>
<th>S</th>
<th>ZnO</th>
<th>PbO</th>
<th>K₂O</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>0.62</td>
<td>3.53</td>
<td>56.91</td>
<td>8.77</td>
<td>3.40</td>
<td>0.59</td>
<td>3.25</td>
<td>3.77</td>
<td>1.39</td>
<td>0.56</td>
<td>8.25</td>
<td>0.34</td>
<td>1.49</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Table 1. The main chemical composition of EAFD.
diameter, $D_p$, can be calculated based on the assumption that no surface other than the inner walls of the pores exits and that pores are of cylindrical geometry using Eq. (3):20–22)

$$\frac{V_p}{S_{BET}} = \frac{D_p}{4} \quad \text{................................. (3)}$$

This equation yields $D_p$ value 39.82 nm for the dusts which may be accordingly considered meso-porous materials. Pore size distribution of dust analyzed by adsorption branch of the isotherm under BJH theory is shown in Fig. 3. The most fraction of pore size is between 1 and 4 nm.

Figure 4 shows the XRD pattern of EAFD. In this work, as can be seen in Fig. 4, iron was identified as franklinite ($\text{ZnFe}_2\text{O}_4$), magnetite ($\text{Fe}_3\text{O}_4$), manganese iron oxide ($\text{Mn}_{0.15}\text{Fe}_{2.5}\text{O}_4$), magnesiomafite ($\text{MgFe}_2\text{O}_4$) and calcium iron oxide ($\text{Ca}_{0.15}\text{Fe}_{2.5}\text{O}_4$). These mineral phases that belong to the spinel group phases come with overlaid peaks and they are the minerals in a larger abundance in the EAFD. In addition, zinc was identified as franklinite and zincite($\text{ZnO}$).

The other phases found in EAFD were calcium hydroxide ($\text{Ca(OH)}_2$), lime($\text{CaO}$), calcium silicate ($\text{Ca}_2\text{SiO}_4$), sylvine sodian ($\text{Na}_0.49\text{K}_0.5\text{Cl}$), sodium silicate ($\text{Na}_6\text{Si}_8\text{O}_{19}$) and Magnesia($\text{MgO}$).

As Fig. 5 shows, most particles in EAFD are spherical. It is in agreement with the main generation mechanism, i.e., ejection of the slag and metal particles by bubble-burst. Based on this microphotograph and the results of X-ray energy dispersive spectrometry (EDS), it can be seen that the samples were not completely homogeneous.

![Figure 1. Particle size distribution of EAFD.](image)

![Figure 2. Nitrogen adsorption and desorption isotherms of EAFD at 77 K.](image)

![Figure 3. Pore size distribution of EAFD.](image)

![Figure 4. X-ray diffraction (XRD) pattern of EAFD.](image)
content in white powders is evidently higher than the dark smooth spherical particle. By magnifying the zone of white powders step by step, the dissemination size of zinc-bearing particles in electric arc furnace dust was measured by SEM under 20 000 times magnification. The results show all zinc-bearing spherical particles stick together. Almost all zinc-bearing particles have a major size distribution lower than 1.45 μm. For the chemical compositions of the single particle, Li et al.23 declared that a series of oxide layers form on the molten steel. From the surface to interior of the liquid, these are: (Mn, Zn) Fe₂O₄, (Mn, Zn) Fe₂O₄–Fe₃O₄, Fe₃O₄–(Mn, Fe) O and (Mn, Fe) O.

The infrared spectra of EAFD can be seen in Fig. 6. The spectra present a broad band, around 3 425 cm⁻¹ due to the O–H stretch of hydrogen bonded water. O–H bend of hydrogen bonded water is also found near 1 639 cm⁻¹. These are the typical absorption peaks of calcium hydroxide, which confirms the XRD result. Asymmetric stretching vibration and out of plane bending vibration feature reveal that carbonate presences in EAFD. It makes the mineral composition testing results from XRD more accurate and complete. The band around 1 107 cm⁻¹ is assigned to Si–O stretch vibrations and implied that quartz or silicate exists in EAFD. The bands located at 571, 440 cm⁻¹ in EAFD are arranged to vibrations of spinels (AB₂O₄), such as franklinite, magnetite and so on.

Figure 7 shows the TG, DTG and DSC curves of EAFD. For electric arc furnace dust, except free water molecules, the TG curve shows three distinct stages of weight loss at 330–500, 550–730 and 900–1 000°C, accompanied by variable-intensity endothermic peaks on the DSC curve. The first two activities are typical of the dehydroxilation of calcium hydroxide and the decomposition of calcium carbonate, respectively, according to the following reactions

\[
\text{Ca(OH)}_2 = \text{CaO} + \text{H}_2\text{O} \quad (4)
\]
\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2 \quad (5)
\]
The first weight loss is 3.09 wt%, indicating the presence...
of maximum 12.7 wt% Ca(OH)₂ and the second is 1.83 wt% indicating the presence of maximum 4.16 wt% CaCO₃. Such differential thermal analysis results further verified the results of XRD and FTIR. The third weight loss may take place at 900–1000°C or even high temperature by reduction reaction between small amounts of carbon and spinel minerals, and disappearance of volatile substances, such as, zinc and halides.

The result of magnetic analysis of EAFD is shown in Fig. 8. Specific magnetic susceptibility plot are derived by differential of M-H curves. By analyzing the result, EAFD belongs to strong magnetic minerals. The specific magnetic susceptibility of EAFD is up to 4.20×10⁻⁴ m³/kg when the magnetic field strength is 23 500 A/m. In fact, different size particles have different chemical composition and magnetic. We have obtained that zinc-bearing particles mostly exists in particles less than 2 μm by the SEM. But in the surface layer of the slightly larger smooth spherical particle, zinc also exist in the form of spinel mineral ZnFe₂O₄. And it is these spinel group phases that lead to EAFD own strong magnetism. In consequence, as the experiment result of R. Sekula et al., mechanical separation methods can be used to separate or concentrate zinc and iron between high zinc content of fine particles and low zinc content of coarse particles. But the efficiency is very limited. In summary, magnetism separation can only be used as a simple pretreatment process for recycling and usage of the dusts like mechanical separation.

3.2. Cold Strength of Self-Reducing Briquette Containing EAFD and Anthracite

The preparation of metallurgical dust and sludge pellets has two types, disc balling and briquetting. Differently from blast furnace dust or basic oxygen furnace dust, the practice shows the disk pelletizer is not suitable for EAFD. It is mainly because EAF has extremely fine particle size distribution and smooth spherical particle. The experiment was conducted in a simple manual briquetting apparatus. The variation trend of green briquette strength affected by water dosage, bentonite dosage, operating pressure and the content of anthracite was investigated. The main chemical composition of bentonite and anthracite are shown in Tables 2 and 3. Table 4 gives the chemical composition of the ash in anthracite. The mean size of anthracite particle was crushed to about 200 meshes. Figure 9 shows the green strength of self-reducing briquette containing EAFD and anthracite under different content of water and Bentonite, operating pressure, mole ratio of C/O.

The effect of water dosage on the green pellet strength is illustrated in Fig. 9(a). The drop number of the green pellets increases with an increase in water dosage, and it basically keeps unchanged when the water surpasses 10 wt%. The compressive strength increases when water dosage increases from 4 wt% to 10 wt%, while it goes down when more water was applied. Under the conditions of 70 MPa pressure, and with 2 wt% bentonite and 1.0 mole ratio of C/O for balling, the highest strength of green pellets reaches at 10 wt% moisture and the drop number and compressive strength reach 6.4 times and 70.2 Newton per pellet (N/pellet), respectively, in the tested moisture range.

Figure 9(b) shows the effect of the bentonite dosage on green pellet strength under 70 MPa pressure, with 1.0 mole ratio of C/O and 10 wt% moisture for balling. It was found that the drop number of green pellet increased from 3.0 to 8.2 times as the bentonite dosage increases from 0 to 3 wt%, whereas it decreased when more bentonite was added. Similarly, the compressive strength increases from 67.5 to 78.1 Newton per pellet (N/pellet) with increasing the bentonite from 0 to 1 wt%, while it decreased a little with increasing the bentonite from 1 to 4 wt%. In fact, the addition of bentonite could really improve the green pellet strength of briquette containing EAFD and anthracite. However, it will also bring in the mass content increase in such briquette. Therefore, considering the requirement of rotary hearth furnace on the green pellet strength, 1 wt% content of bentonite is enough in EAFD briquette.

The drop number and cold compressive strength of the produced briquettes with respect to different pressing load at constant amount of water and bentonite are shown in Fig. 9(c). As it can be seen, the drop number and cold compressive strength have a similar trend. The strength of the green pellets gradually increases with an increase in pressing load.

| Table 2. Chemical composition of bentonite (wt%). |
|-------------------------|--------|--------|------|-------|-------|-------|-------|-------|
| SiO₂                  | Al₂O₃  | CaO    | Fe₂O₃ | MgO   | Na₂O  | K₂O   | TiO₂  | MnO   |
| SiO₂                  | 63.21  | 19.48  | 4.34  | 4.16  | 3.40  | 3.22  | 1.54  | 0.26  |
| Al₂O₃                 | 4.34   | 4.16   | 3.40  | 3.22  | 1.54  | 0.26  | 0.09  | 0.04  |

| Table 3. Chemical composition of anthracite (wt%). |
|-----------------|--------|--------|-------|
| Moisture        | Ash    | Volatile matter | Fixed Carbon |
| 1.85            | 11.41  | 6.34   | 82.25   |

| Table 4. Chemical composition of the ash in anthracite (wt%). |
|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| T. Fe         | CaO    | SiO₂   | Al₂O₃  | MgO    | TiO₂   | P₂O₅   | MnO    | S      | Na₂O   |
| 0.85          | 1.38   | 10.89  | 5.70   | 0.12   | 0.19   | 0.065  | 0.02   | 0.194  | 0.162  |
| K₂O           | Zn     | Pb     |
| 1.62          | 0.406  | 0.001  | 0.018  |
But it changes little when the pressure exceeds 90 MPa. Under the conditions of 1.0 mole ratio of C/O, and with 2 wt% bentonite and 10 wt% moisture for balling, the highest strength of green pellets occurs at 90 MPa pressure and the drop number and compressive strength reach 6.6 times and 75.4 Newton per pellet (N/pellet), respectively, in the tested pressure range. It is worth noting that, although the increase of pressure has a positive influence on the green pellet strength of briquette containing EAFD and anthracite, it will also lead to the decrease of its porosity. It is harmful to the gas emission during the high temperature direct reduction and will aggravate the occurrence possibility of abnormal swelling of such pellets. Therefore, the pressure is suggested between 70 MPa and 90 MPa.

The effect of C/O molar ratio on drop number and cold compressive strength of the produced briquettes at constant pressure is shown in Fig. 9(d). It was clear that as the C/O molar ratio increased the drop number of produced briquettes gradually increased while the compressive strength decreased. In general, the green briquettes of EAFD with 10 wt% water and 1 wt% bentonite pressured at 70 MPa had a good performance in strength, even with excess content of anthracite.

In summary, considering both the green pellet strength and the direct reduction of briquette containing EAFD and anthracite, the suitable briquetting parameters are: 10 wt% content of water, 1 wt% content of bentonite, pressure between 70 MPa and 90 MPa, C/O molar ratio between 1.0–1.1.

3.3. High Temperature Properties of Self-Reducing Pellets Containing EAFD

As the chemical composition shows, EAFD has 6.62 wt% zinc. Mainly due to the existence of zinc, EAFD cannot directly be used in sintering, blast furnace, or steelmaking process. Therefore, zinc must be removed first. Although EAFD belongs to strong magnetic minerals, the magnetic separation method is not suitable for recovering EAFD. In addition, the efficiency of hydrometallurgical extraction of zinc from EAFD is also limited. Pyrometallurgical removal or recovery of zinc in EAFD is the most effective way. According to the thermodynamic analysis, zinc compounds can be easily reduced by carbon at 906°C, which is zinc boiling temperature. In order to clarify removal regularity of elements Zn from the prepared briquettes, effects of reduction temperature, reduction time and mole ratio of C/O on its removal rate were investigated. Table 5 shows the reduction conditions for tests, and the result is shown in Fig. 10.

Table 5. Reduction conditions for tests on the removal of zinc.

<table>
<thead>
<tr>
<th>Case</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>mole ratio of C/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 000</td>
<td>5</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>1 050</td>
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<td>3</td>
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<td>11</td>
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</tr>
<tr>
<td>12</td>
<td>1 150</td>
<td>5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Fig. 9. The green briquette strength vs. content of water and Bentonite, operating pressure, mole ratio of C/O.
and C/O molar ratio on metallization rate of the briquettes are shown in Fig. 11. As illustrated in Fig. 11, the metallization rate increases with the increasing of the reduction temperature. It increases from 73.8% to 91.3% when the temperature increases from 1000°C to 1200°C. Under the conditions of 1200°C and 1.1 mole ratio of C/O, the metallization rate increases with the increasing of the reduction time. A little oxidation of Fe may occur when the reduction time exceeds 20 min. Besides, C/O molar ratio also has a positive effect on the metallization rate of the EAFD briquettes. Under the conditions of 1200°C and 20 min reduction time, the metallization rate increases from 87.7% to 92.1% with C/O mole ratio increasing from 0.9 to 1.2.

XRD analyses of the reduced briquette under different reduction temperatures and reduction times are shown in Fig. 12. As seen in Fig. 12(a), the main phases contain: Fe, FeO and Ca2Fe2O5. With the increasing of reduction temperature, the peak intensity of Ca2Fe2O5 gradually decreases, while the peak intensity of Fe gradually increases. The FeO disappears when the temperature is up to 1050°C, while it presents again under 1150°C because of secondary oxidation. At the temperature of 1200°C, none of Ca2Fe2O5 peak is found, indicating that Ca2Fe2O5 can be totally reduced at this temperature. Similarly, as shown in Fig. 12(b), with the increasing of reduction time, the peak intensity of Ca2Fe2O5 gradually decreases, while the peak intensity of Fe gradually increases. Besides, the variation trend of X-ray diffraction peaks is consistent with the results shown in Fig. 12(a).
tion peak of FeO suggests that secondary oxidation occurs seriously after reduction of 25 min. Therefore, 20 min of reduction time is more suitable. It is widely considered that basicity is an important factor on the reduction process. For example, CaO·Al₂O₃ and Ca₂SiO₄ was found in self-reducing briquettes composed of flue dust and mill scale. These are mainly influenced by its own initial binary basicity of the dust. This is another typical characteristic of EAFD that is different from other metallurgical dust, such as sintering dust and blast furnace dust.

XRD analysis of the reduced briquette with different C/O mole ratio after reduced 20 min at 1 200°C is shown in Fig. 13. With the increasing of C/O mole ratio, the peak intensity of Ca₂Fe₂O₅ gradually decreases, while the peak intensity of Fe gradually increases. Moreover, the variation trend of X-ray diffraction peak of FeO here illustrated that excessive carbon in the EAFD pellet cannot prevent it from secondary oxidation. These results emphasize the importance of protection by inert or reductive atmosphere in the late period of direct reduction in such carbon-containing briquettes.

Samples from the muffle furnace reduction experiments were cast in epoxy resin and polished before observation with SEM-EDS. Figure 14 shows the microstructure of a self-reducing EAFD briquettes with 1.1 mole ratio of C/O after heating 20 min between 1 000°C and 1 200°C. It is evident that the particles of EAFD maintain the original spherical morphology at 1 000°C. The images show that significant change has occurred in the sample between 1 050°C and 1 150°C. It presents a relatively uniform distribution of fine metallic iron. Only when the temperature increased to 1 200°C, the Fe phase evidently gathered together. Concerning the chemical composition, particles rich in zinc, calcium, and iron were identified in the spherical particle (phase A, 8.1 wt% Zn, 14.0 wt% Ca and 25.0 wt% Fe). It implied that part ZnFe₂O₄ was transferring to CaFe₂O₅ directly and this process didn’t complete at this temperature. This phenomenon indicated that ZnFe₂O₄ mainly experienced the following two reactions in the former period:

\[
\text{ZnFe}_2\text{O}_4(s) + 2\text{CaO}(s) = \text{ZnO}(s) + \text{Ca}_2\text{Fe}_2\text{O}_5(s) \quad (6)
\]

\[
\Delta G^\circ = -32 114 + 11.329T + 4.201 \times 10^{-3}T^2 - 5.46 \times 10^3/T - 3.373 T \ln T \quad \text{J/mol} \quad (7)
\]

\[
\text{ZnFe}_2\text{O}_4(s) + 2\text{C}(s) = \text{Zn}(g) + 2\text{FeO}(s) + 2\text{CO}(g) \quad (8)
\]

\[
\Delta G^\circ = 603 178 - 943.185T - 6.715 \times 10^{-3}T^2 - 50.21 \times 10^3/T + 58.316 T \ln T \quad \text{J/mol (906°C < T < 1 377°C)}
\]

Free magnesia (phase B) surrounded by a phase contains Mg > Fe > Mn > Ca > Si (phase C). The Metallic iron contains a little manganese (phase D, 96.9 wt% Fe and 2.3 wt% Mn), while joined crystal interface of Metallic iron grain have a relatively high content of manganese (phase E, 93.2 wt% Fe and 5.0 wt% Mn). This phenomenon verified that spinel group phases have some content of manganese iron oxide, especially in the surface layer. The slag phase mainly contains calcium, silicon, manganese, aluminum (phase F, 41.3 wt% Ca, 34.0 wt% Si, 9.3 wt% Mg, 9.2 wt% Al).

Figure 15 shows the microstructure of a self-reducing EAFD briquettes with 1.1 mole ratio of C/O after heating 5 to 25 min at 1 200°C. It presented totally different distribution of metallic iron phase and other phases. From the previous results, we know that the reduction of iron oxide and zinc oxide by anthracite promptly conducted. After 5 min
of reduction, the dendritic structure of spinel-ferrite crystal still exists in the initial spherical particle. With the heating time prolonged, the dendritic structure of spinel-ferrite crystal gradually disappeared and the metal phase gradually gathered together, which further benefit to the recovery of iron. After crushing and magnetic separation, magnetic part could return to electric arc furnace.

Figure 16 shows the microstructure of a self-reducing EAFD briquette with different mole ratio of C/O after reducibility for 20 min at 1200°C. Provided that mole ratio of C/O is only 0.9, the fine metallic iron presents uniformly dispersive distribution. Provided that mole ratio of C/O is up to 1.2, excess anthracite particles brought abundant of ash, which also hindered the cluster of metallic iron. Therefore, the suitable mole ratio should be controlled between 1.0 and 1.1.

To sum up, heating the self-reducing briquette with 1.1 mole ratio of C/O at 1200°C for 20 min, zinc and iron could be promptly reduced by carbon within 5 and 15 min, separately. Given that EAFD has lot of calcium-based compound, some ZnFe₂O₄ converted to Ca₂Fe₂O₅ directly, and then Ca₂Fe₂O₅ was gradually reduced. It was the form of Ca₂Fe₂O₅ that decreased the reduction rate of EAFD.

4. Conclusion
In order to make full use of EAFD by virtue of Rotary hearth furnace process, mineralogical characterization tests
of EAFD were detected first. Then, effects of different briquetting parameters on the green pellet cold strength were studied. Besides, the high temperature behaviors, such as metallization rate, removal rate of Zn, the mineral composition and microstructure of reduced briquette, were all analyzed. The conclusions can be drawn as follows.

1. The mass fractions of Fe, Zn and Ca are 43.17 wt%, 6.62 wt% and 6.26 wt% in EAFD, respectively. Apart from the common spinel minerals and ZnO, other mineral composition, such as Ca(OH)\(_2\), CaCO\(_3\), Ca\(_2\)SiO\(_4\), Na\(_{0.4999}\)K\(_{0.5001}\)Cl are also found in EAFD. In addition, almost all zinc-bearing particles have a major size distribution lower than 1.45 micron. The most fraction of pore size distribution is between 1 and 4 nm.

2. Effect of different factors on the drop number is greater than the compressive strength of briquettes. Green pellet drop number is more sensitive to moisture content and bentonite content. Under the test conditions, the drop number of the green pellets increases from 1.4 times to 6.4 times by water changed from 4 to 10 wt%, and it increases from 3.0 times to 8.2 times when bentonite mass content increased from 0 to 3 wt%. The parameters of briquetting for pretreating the EAFD are optimized as follows: 10 wt% content of water, 1 wt% content of bentonite, 70–90 MPa pressure, and C/O molar ratio 1.0–1.1.

3. Generally, with the reduction temperature or reduction time increasing, the Zn removal and metallization rate gradually increased. Heating the self-reducing briquette with 1.1 mole ratio of C/O at 1 200 °C, 20 min and 1.1 respectively, direct reduction iron was most concentrated.

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