Reduction Behaviour of Self-reducing Blends of In-plant Fines in Inert Atmosphere

Hesham Mohamed AHMED,1,2)∗ Amanda PERSSON,3) Lena Sundqvist ÖKVIST3) and Bo BJÖRKMAN1)

1) MiMeR, Luleå University of Technology, 971 87 Luleå, Sweden. 2) Central Metallurgical Research and Development Institute, P.O. Box 87-Helwan, Cairo, Egypt. 3) Swerea MEFOS, 971 87 Luleå, Sweden.

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Large amount of dust and sludge recovered during cleaning of iron and steel making process gases are annually put on landfill or intermediate storage. These by-products have high contents of iron (Fe) and carbon (C) that potentially could be utilized in the steel industry. However, due to the presence of impurity compounds as well as the unsuitable physical properties, these by-products cannot be recycled directly. The main objective of the present study is to investigate the possibilities to recover the valuable components Fe and C in these by-products and thereby decrease the need of landfills at the steel plants as well as reduce the consumption of virgin materials, including fossil coal, and reduce CO2 emissions. A recycling route has been investigated by means of laboratory trials and FactSage thermodynamic modeling. Four different blends of BF and BOF dusts and sludges are prepared in predetermined ratios. Reduction behavior of each blend is studied using TG/DTA/QMS and in-situ high temperature X-ray diffraction. High temperature physical properties like softening, swelling and melting are also investigated by means of heating microscope. The obtained results indicate the feasibility of both minimizing the impurity elements as well as recovering of valuable components.

KEY WORDS: waste materials recycling; self-reducing mixtures; thermodynamics; thermogravimetry; BF dust and sludge; BOF dust and sludge; heating microscope; mass spectroscopy.

1. Introduction

Iron and steel industry consumes large amounts of primary and secondary resources and apart from the main product also large amount of by-products are generated. For instance, 2–4 tons of by-products are produced per ton of produced steel.1) Two important reasons for by-products efficient utilization are;

- Valuable contents of Fe and C can replace virgin materials.
- Available areas for landfilling are decreasing and environmental regulations also become more restricted.

One of the constraints that make recycling of such waste materials difficult is the variation of the chemical composition which depends mainly on variation at its source. The largest volumes of by-products are generated at the blast furnace (BF) and basic oxygen furnace (BOF).2) These by-products are either in the form of dust from dry dust separation in the gas cleaning system or in the form of sludge from wet dust separation.

BF flue dust is a mixture of fines from burden materials expelled from the top of the blast furnace and as the main burden consists of iron ore and coke the dust also contains mainly iron oxide and coke fines. Slag formers or sinter may contribute to compounds found in lesser extent as oxides of silicon and calcium. Elements that originate from the gas phase as e.g. sodium, potassium, zinc and lead can also be found to some extent in the BF dust but the main part in general is recovered in the wet BF sludge. BF sludge is comprised of the fine particles removed by washing of the blast furnace process gas and its main components are Fe and C. In addition it contains oxides of easily volatilized compounds such as zinc and lead.3)

Most zinc and lead are evaporated from the scrap charged to the BOF before start of blowing and are collected separately as dry dust. BOF sludge can be collected in two fractions where the fine fraction contains very fine particles of iron oxide and lime. Other constituents may be e.g. zinc and lead, depending on the type of material charged to the process.4,5) The low zinc and lead content which results from not using e.g. galvanized scrap enables several ways of processing these kinds of by-products.6) Recycling of these materials in existing iron- and steelmaking processes without pre-treatment is difficult due to the adverse impact on the process operation and the product quality which might be caused by the impurities, fine particle size, high moisture content, etc.7)

Attention has been paid by several researchers to investigate different routes of effective utilization of these materials as well as their impact on process performance. Producing agglomerates with self-reducing property which

∗ Corresponding author: E-mail: Hesham.ahmed@ltu.se
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is further processed to produce direct reduced iron (DRI) followed by charging in existing iron and steelmaking processes has been previously suggested as a possible recycling method for dust and sludge that currently are landfilled. This method has the potential to utilize carbon and iron oxides within dust and sludge to produce DRI that can be further used as replacement for scrap. In addition, production of DRI by heat treatment might also contribute to significant reduction of Zn, which enables recycling of by-products with low Zn-contents in the blast furnace.\(^{8-13}\)

In fact, BOF-sludge and BF-sludge in combination with carbon-containing materials such as BF-dust in agglomerates have not been investigated previously. The possibilities to produce agglomerates with chemical- and physical properties suitable for self-reduction need to be studied. Other essential aspects to investigate are the reduction properties and extent of impurity elimination that can be achieved during thermal treatment of these agglomerates.

In the present study, attempts have been made to find out a feasible route to recycle the generated iron and steel industry by-products. The aim is to study the reduction behaviour of BF and BOF dusts and sludges containing self-reducing mixtures. Thermodynamic calculations based on chemical composition are made and proper blending ratios are selected. Reduction mechanism of the produced blends is investigated by means of thermogravimetry and X-ray diffraction (XRD). A detailed study of one selected blend is further conducted to find out the off-gas composition and phases alteration during thermal treatment as well as swelling, softening and melting behaviour.

2. Experimental

2.1. Materials

BF-dust and sludge as well as BOF-dust and sludge have been the main focus in the present study. Samples of freshly produced materials were provided by SSAB MEROX. Table 1 shows average chemical analysis of dry materials using XRF and LECO. The analyses reveal the high iron content of BOF by-products and the high carbonaceous value of BF by-products, especially in dust. BF by-products also contain considerable amount of iron to be recovered.

Average particle size distributions of BF dust and sludge as well as BOF dust and sludge are given in Fig. 1. As can be seen, both BF-sludge and BOF-sludge are fine material compared to dust.

2.2. Blending

In order to obtain agglomerates with self-reducing property, optimal blends have been carefully designed based on chemical analysis given in Table 1. The design of studied blends has mainly been based on the following conditions:

- Fixed relation between BOF-sludge, BOF-dust and BF-sludge
- Content of BF-dust varied to achieve a molar ratio of carbon to reducible oxygen should be larger than 1 (C/O > 1) and Fe(tot) as high as possible
- Simulate available proportions of generated by-products (SSAB EMEA AB steel plants in Luleå and Oxelösund, Sweden, has been taken as a case study)

The proportions of BF and BOF dust and sludge in the designed recipes as well as the corresponding C/O molar ratios and total iron are shown in Table 2.

2.3. Methods

A Netzsch thermal analysis STA 409 instrument with simultaneous thermo-gravimetric measurement with sensitivity ±1 \(\mu\)g (TGA) and differential thermal analysis (DTA) coupled with a quadruple mass spectroscopy (QMS) was used to evaluate and analyze the studied by-products. In addition, it has been applied also to monitor the reduction behavior of different designed blends. A schematic diagram

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**Table 1.** Average chemical analysis of studied by-products.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>BF-sludge</th>
<th>BF-dust</th>
<th>BOF-sludge</th>
<th>BOF-dust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe%</td>
<td>33.3</td>
<td>19.6</td>
<td>49.0</td>
<td>48.7</td>
</tr>
<tr>
<td>CaO%</td>
<td>7.7</td>
<td>8.3</td>
<td>18.7</td>
<td>11.6</td>
</tr>
<tr>
<td>SiO2%</td>
<td>5.3</td>
<td>5.9</td>
<td>1.27</td>
<td>1.5</td>
</tr>
<tr>
<td>MnO%</td>
<td>0.3</td>
<td>0.52</td>
<td>1.07</td>
<td>2.5</td>
</tr>
<tr>
<td>P2O5%</td>
<td>0.13</td>
<td>0.07</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>Al2O3%</td>
<td>2.2</td>
<td>2.3</td>
<td>0.18</td>
<td>0.5</td>
</tr>
<tr>
<td>MgO%</td>
<td>1.7</td>
<td>1.5</td>
<td>3.9</td>
<td>4.31</td>
</tr>
<tr>
<td>Na2O%</td>
<td>0.08</td>
<td>0.05</td>
<td>0.03</td>
<td>3.9</td>
</tr>
<tr>
<td>K2O%</td>
<td>0.12</td>
<td>0.31</td>
<td>0.08</td>
<td>0.40</td>
</tr>
<tr>
<td>V2O5%</td>
<td>0.26</td>
<td>0.33</td>
<td>0.34</td>
<td>0.62</td>
</tr>
<tr>
<td>TiO2%</td>
<td>0.30</td>
<td>0.35</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>Cr2O3%</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td>0.12</td>
</tr>
<tr>
<td>C%</td>
<td>27.2</td>
<td>49.5</td>
<td>2.2</td>
<td>–</td>
</tr>
<tr>
<td>S%</td>
<td>0.4</td>
<td>0.47</td>
<td>0.02</td>
<td>0.74</td>
</tr>
<tr>
<td>Zn%</td>
<td>0.6</td>
<td>0.26</td>
<td>0.10</td>
<td>0.63</td>
</tr>
</tbody>
</table>

**Table 2.** Distribution of by-products in designed recipes B1–B4.

<table>
<thead>
<tr>
<th>Blend</th>
<th>BF-dust (%)</th>
<th>BF-sludge (%)</th>
<th>BOF-sludge (%)</th>
<th>BOF-dust* (%)</th>
<th>C/O molar ratio</th>
<th>Fe(tot) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0</td>
<td>40</td>
<td>58</td>
<td>2</td>
<td>1.1</td>
<td>46</td>
</tr>
<tr>
<td>B2</td>
<td>5</td>
<td>38</td>
<td>55.1</td>
<td>1.9</td>
<td>1.77</td>
<td>45</td>
</tr>
<tr>
<td>B3</td>
<td>10</td>
<td>36</td>
<td>52.2</td>
<td>1.8</td>
<td>1.9</td>
<td>44</td>
</tr>
<tr>
<td>B4</td>
<td>20</td>
<td>32</td>
<td>46.4</td>
<td>1.6</td>
<td>2.04</td>
<td>42</td>
</tr>
</tbody>
</table>

*Mixture of BOF-dust and desulphurisation dust.
of the thermal analysis instrument is given in Fig. 2. Two alumina crucibles, one containing alumina powder as a reference and another one containing sample, were heated 10°C/min from 20 to 1 200°C maintaining argon flow of 100 ml/min during the whole course of reaction.

Further, a PANalytical Empyrean XRD instrument coupled with a heating furnace was used to identify phase development as the reaction proceeds. The obtained X-ray spectra were evaluated using PANalytical software. Furthermore, Leitz Wetzlar Germany heating microscope (Fig. 3) was used to monitor the swelling, softening and flow temperature. Fine ground samples were agglomerated into small briquettes (3 mm height and 2 mm diameter) using specially designed mold provided by the same company. The briquette was then centered on a flat alumina pan and introduced to the hot zone of a horizontal tube furnace. The two endings of the furnace are closed with transparent quartz stoppers to enable atmosphere control and imaging. An argon gas flow was maintained throughout the process. The sample was heated 15°C/min up to 600°C and thereafter 10°C/min up to the sample flow temperature. Imaging was set to carry out automatically according to preset parameters. Size alteration was monitored by analysis of the silhouette of the sample and the change of sample size was calculated accordingly.

3. Results and Discussion

3.1. Thermodynamic Calculations

The thermodynamical calculation database FactSage 5.6 have been used as an auxiliary tool to validate the recyclability of the different designed blends. All calculations have been conducted in the temperature range 25–1 200°C and at atmospheric pressure. Only gas and solid phases have been considered for the calculations.

Based on chemical analysis in Table 1 and preliminary obtained results from XRD and TG, the composition of each by-product and thus, material blends have been adjusted to account for presence of volatile matter and also the iron oxide distribution in the materials. Thermodynamic calculations using FactSage have been conducted for all blends. Figures 4 and 5 show the most significant phases present in the blends.
at temperatures between 25–1200°C for B1 and B4. B1 is corresponding to the blend with no added BF-dust with an expected C/O-molar ratio of 1.10 whereas B4 is containing 20% BF-dust and have an expected C/O molar ratio of 2.04. When comparing the two plots, the major differences found is at temperatures exceeding around 725°C in where all carbon has been transformed to CO/CO2 for B1 but for B4, Fe3C is starting to form. At 1200°C, the major equilibrium phases in the system corresponding to B1 is Fe(s), CO(g), Ca2SiO4(s), CaO(s), CO2(g), MgO(s), Ca3Al2O6 and Ca3MgAl4O10 according to the calculations. While most of the carbon is consumed for B1, a significant part is left in B4 at 1200°C as elementary carbon and Fe3C.

3.2. Starting Materials (by-products)

XRD patterns of received by-products (BF-sludge, BF-dust, BOF-sludge and BOF-dust) are shown in Fig. 6. Hematite (Fe2O3), calcite (CaCO3) and carbon peaks were dominating in BF-dust and sludge whereas no signs of metallic iron (Fe) or magnetite (Fe3O4) could be found. On the other hand, BOF-sludge found to contain portlandite (Ca(OH)2), CaCO3, Fe2O3, Fe3O4, wustite (FeO) and Fe. However, the peak intensity for Fe2O3 and Fe3O4 are small, indicating low concentrations. XRD patterns for BOF-dust does not show any signs of presence of CaCO3, instead it contains calcium oxide (CaO) along with Fe2O3 and traces of Fe3O4.

Thermal behavior of each by-product is of quite importance to be understood. TG/DTA curves of thermally treated BOF-sludge, BOF-dust, BOF-sludge and BOF-dust is shown in Fig. 7. Total weight loss of 12.8% was achieved for BOF-sludge, 5.5% for BOF-dust, 33.1% for BF-sludge and 18% for BF-dust. Based on an earlier study of similar materials and from TG curves, it can be concluded that specific reactions occurs at specific temperatures while the sample is being heated. These reactions might occur in a sequence or even simultaneously. Discontinuity of mass loss curve (TG) with accompanied heat release or absorption (DTA) support that theory. Detailed explanation for obtained TG and DTA curves is as follows;

**BOF-dust and sludge:** free moisture as well as chemically bound water are released gradually below 500°C. Chemi-

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**Fig. 6.** XRD patterns of BF-sludge, BF-dust, BOF-sludge and BOF-dust. (Online version in color.)

**Fig. 7.** TG and DTA curves for BOF-sludge, BF-sludge, BOF-dust and BF-dust. (Online version in color.)
cally bound water release is more pronounced for BOF-sludge depicted by the early significant mass loss and the accompanied endothermic feature in DTA curve. This trend is in a good agreement with the chemical analysis. Another series of reactions are occurring in the temperature range 500–800°C coinciding with the presence of an endothermic peak. This can be attributed to the carbon gasification by the released H$_2$O followed by low temperature reduction of higher iron oxides. The mass loss and the accompanied endothermic peak can also be due to the decomposition of carbonates. However, this is unlikely to be the case for BOF-dust as the XRD phase analysis showed insignificant amount of carbonates. Later at higher temperature (above 780°C), the reaction rate seems to be sluggish even with increasing temperature. As the carbon content of BOF by-products is quite low, the available carbon surface area for gasification is heavily decreasing and therefore the produced CO is also decreasing leading to drastic decrease in the reaction rate.

**BF-dust and sludge:** as BF-dust and sludge are known to contain around 50 and 27% carbon and 20 and 33% of iron oxide, respectively (see Table 1) the mass loss is expected to be higher than BOF by-products. The high mass loss values achieved on heating BF by-products is attributed to the presence of carbon and reducible oxygen together. A slight mass loss (5–9%) was observed up to 770°C which is attributed to the release of residual moisture, calcination as well as reduction of higher oxides. At and above 780°C the reaction mechanism is believed to change which is indicated by the sloop discontinuity of TG curves. Based on an earlier investigation by the authors, it is believed that reduction of magnetite and wustite is carried out above 770°C. The change of reaction from reduction of magnetite to wustite reduction is indicated by the sudden increase in the reaction rate which is attributed to the presence of metallic iron. The later is known to have a catalitic effect on gasification reaction. Different temperature intervals have been defined where significant weight losses occurred and reaction mechanism is expected to change, see Table 3.

### 3.3. Blend Mixtures

Thermal behavior of mixed by-products was studied non-isothermally in argon flow with a heating rate 10°C/min up to 1200°C. Weight loss vs temperature curves for B1–B4 are plotted in Fig. 8. Total weight loss of 34.9% for B1, 34.7% for B2, 32.7% for B3 and 31.03% for B4. Thus, highest achieved weight loss was for blends with less BF-dust and more BF-sludge contents. This might be explained by the higher content of reducible iron oxides to be reacted. Irrespective of the blend composition, all TG curves show break points as the reaction proceeds. A step-wise reduction behavior is noticed for all blends which is similar to reduction of simple self-reducing mixtures. The different weight loss intervals have been identified by different temperature intervals, see Table 4.

As the TG curves of the designed blends followed the same trend with a slight difference in the net weight loss, it is decided to differentiate only one of the curves (Blend 1) to keep the diagram clear and easy to read. A slight mass loss was observed early, begins at and above 100°C,
which is due to water release. A sluggish mass loss rate continued till 700°C which is attributed to the chemically bound water release, calcination, carbon loss reaction by the evolved water and reduction of higher iron oxides. At and above 700°C, the reaction rate was improved significantly. Reduction of magnetite is expected to be dominating during this step. The catalytic effect of produced metallic iron on the gasification reaction kinetics can be clearly recognized above 900°C.

A comparison of achieved weight losses in TG at 1200°C and expected losses according to thermodynamic calculations for blends B1–B4 is given in Table 5. The actual weight losses obtained in TG is decreasing with increasing BF-dust content, implying less reducible oxygen in relation to carbon with increasing BF-dust content. Although the experimental weight loss is close to the calculated one, a clear relation between the calculated weight loss and BF-dust content is difficult to draw. The small difference between the calculated values and the experimental values might arise from the uncertainty in the estimated chemical composition.

After thermal treatment, all blends are found to contain metallic iron, CaO and MgO, see Fig. 9. Since no iron oxides were detected in any of the reduced blends, it can be concluded that the available carbon in each blend was sufficient to achieve complete reduction.

### 3.4. Reaction Mechanism of a Selected Self-reducing Mixture (Blend 1)

As is shown earlier, thermal behavior of the studied blends is similar, therefore it is decided to proceed further with one of these blends for the sake of brevity and to avoid repetition. A deeper look into the thermal behavior of blend 1 (B1) including the accompanied thermal changes as well as the off-gas analysis is depicted in Fig. 10. Mass loss (TG), first derivative of mass loss with respect to time (DTG), differential thermal analysis (DTA) and the off-gas analysis as a function of temperature are given.

It can be seen from Fig. 10 that the sample start to respond to heating at relatively low temperature as it shows sensible mass loss (3%) around 400°C. The mass loss is coinciding with an endothermic peak and appearance of H2O peaks in the mass spectra. This indicates free moisture- and combined water evaporation as well as dehydroxylation. The mass continues to decrease with rising temperature, at 750°C mass loss of more than 7% was detected accompanied with an endothermic peak and appearance of CO2 and CO in the off-gases stream. This behavior can be attributed to the dissociation of some residual carbonates or the reduction of higher iron oxides. As the temperature approaches 1000°C, reduction of wustite and gasification reaction reach its maximum rate indicated by the DTG curve and detected maximum concentration of CO as well as the heat absorbed

![XRD patterns of reduced blends B1–B4. (Online version in color.)](image1)

### Table 5. Weight losses achieved in TG at 1200°C compared to calculated losses by FactSage for B1–B4.

<table>
<thead>
<tr>
<th>Wt-loss at 1200°C</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>33.1%</td>
<td>34.5%</td>
<td>33.9%</td>
<td>31.7%</td>
</tr>
<tr>
<td>In TG</td>
<td>34.9</td>
<td>34.68</td>
<td>32.67</td>
<td>31.03</td>
</tr>
</tbody>
</table>

![Thermal analysis curves of B1 as a function of Temperature. (Online version in color.)](image2)

![XRD patterns of reduced blends B1–B4. (Online version in color.)](image3)
by the gasification reaction. Total weight loss achieved at 1200°C is around 35%. TG curve manifest discontinuity during the course of the reaction confirming the step wise process as the temperature goes up. DTG curves trend clarify the changeover of process mechanism as the temperature rises.

In-situ High temperature XRD was performed for the same blend (B1) to figure out the reaction mechanism and phase development as the reaction proceeds. The samples were introduced into the even temperature zone of a small furnace. The furnace is assembled in such a way to enable in-situ X-ray scanning and enables continuous inert gas flow. The samples were subjected to the first scan at ambient temperature. The second scan was carried out at 300°C while the third was at 600°C with 10°C/min fixed heating rate. The sample was then scanned every 75°C until the temperature reached 1100°C. Figure 11 shows the XRD patterns and the corresponding detected phases of the processed samples.

It can be observed from the above XRD patterns that the dominating phases of the green samples are Ca(OH)2, CaCO3, Fe2O3, Fe3O4, FeO and Fe. On heating, the existing wustite and metallic iron get oxidized by either the trapped oxygen or residual water in the sample or even by oxygen transfer (solid diffusion) from higher oxides to lower ones. In addition, the hydroxide phase disappears as a result of dehydroxylation. Later at 750°C as a result of carbonate decomposition and primary slag formation, new phases appear like CaO, Ca2Fe2O5 and Ca2Al2SiO7. Reduction of hematite into magnetite was almost completed at 850°C and wustite phase start to be dominating. Moreover, the step wise-reduction of waste material containing mixtures could be proved also by XRD patterns.

Further, the powder mixture was pressed into small compact briquettes and then heated in inert atmosphere with continues imaging to capture swelling, deformation and melting phenomena. Figure 12 shows the silhouette sample area change as a function of temperature. On the right hand side of Fig. 12, three images show the sample shape alteration as the temperature increases, the first one (a) at ambient temperature, the second one (b) at 1200°C and the third one (c) at 1270°C.

Figure 11. XRD patterns of in situ heated sample of B1. (Online version in color.)

Figure 12. Selected images show the sample deformation and swelling as the temperature increases (on the right hand side) and the change of sample silhouette area as a function of temperature (On the left hand side).
but small difference in the net mass loss. XRD patterns approved the high degree of metallization even for the sample with lowest C/O molar ratio. The heating process of different blends was found to proceed through simultaneous and consecutive steps as follows;

- Water release and dehydroxylation below 450°C
- Reduction of higher oxides along with calcination and primary slag formation below 870°C followed by magnetcite reduction.
- Wustite reduction and gasification reactions then dominate the process at temperatures higher than 850°C accompanied with significant swelling.
- Deformation and then melting above 1 200°C

Further, predictions based on thermodynamic calculations using FactSage were in reasonable agreement with the experiment results. It showed that complete reduction is still yet to be reached.

Generally, effective utilization of BF and BOF by-products dusts and sludges could be realized by thermal pretreatment. It results in high metallized product with low zinc and lead content which likely can be charged into existing iron and steel industry processes without negative impact on operation or final product.

Acknowledgement

The financial support from the energy agency of Sweden, Jernkontoret and CAMM center is greatly acknowledged. The authors express their deep thanking to the project committee members “JK21068 Energy efficient recycling of in-plant fines in rotary hearth furnace (RHF)”, for their instructive feedback and fruitful discussions especially Anita Wedholm, SSAB MEROX and Jenny Wikstrom, LKAB.

REFERENCES


Table 6. Summary of steps occurring during heating of iron-making waste materials containing blends in an inert atmosphere.

<table>
<thead>
<tr>
<th>Nr</th>
<th>On going process</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water evaporation</td>
<td>0–400</td>
</tr>
<tr>
<td>2</td>
<td>Dehydroxylation, Ca(OH)₂ = CaO + H₂O</td>
<td>400–425</td>
</tr>
<tr>
<td>3</td>
<td>Oxidation of iron to higher oxides</td>
<td>Below 600</td>
</tr>
<tr>
<td>4</td>
<td>Calcination and primary slag formation; CaCO₃ = CaO + CO₂, 2CaO + Fe₂O₃ = Ca₂Fe₂O₅</td>
<td>650–825</td>
</tr>
<tr>
<td>5</td>
<td>Hematite reduction; 3Fe₂O₃ + CO = 2Fe₂O₄ + CO₂</td>
<td>570–675</td>
</tr>
<tr>
<td>6</td>
<td>Magnetite reduction; Fe₃O₄ + CO = 3FeO + CO₂</td>
<td>750–870</td>
</tr>
<tr>
<td>7</td>
<td>Wustite reduction; FeO + CO = Fe + CO₂</td>
<td>900–1 000</td>
</tr>
<tr>
<td>8</td>
<td>Gasification reaction; CO₂ + C = 2CO</td>
<td>850–1 000</td>
</tr>
<tr>
<td></td>
<td>Swelling</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Deformation temperature</td>
<td>1 201</td>
</tr>
<tr>
<td></td>
<td>Hemisphäre temperature</td>
<td>1 233</td>
</tr>
<tr>
<td></td>
<td>Flow temperature</td>
<td>1 270</td>
</tr>
</tbody>
</table>

condition, the second (b) is for deformed briquette and the third (c) is for completely melted sample. On the left hand side, sample swelling as a function of temperature is being captured and presented by the change of silhouette sample area vs temperature. No swelling is detected before 650°C. As the temperature rises, the sample manifests gradual swelling up to 5% followed by melting above 1 200°C.

The studied blend shows a narrow range of melting temperature which has a good impact on the cohesive zone thickness in blast furnace. Based on the above mentioned results, reduction behavior of iron-making waste materials containing mixtures can be considered to go through simultaneous and consecutive steps which are summarized in Table 6.

4. Conclusion

In the present study, effective utilization of iron and steel industry by-products in producing direct reduced iron was investigated. Dusts and sludges generated from both blast furnaces and basic oxygen furnaces at SSAB were mixed in different ratios based on the chemical composition keeping the C/O molar ratio higher than unity. Thermal behavior of produced mixtures was studied non-isothermally under inert atmosphere by means of thermogravimetry and X-ray diffraction.

Irrespective of the chemical composition of the designed mixtures, TG tests showed similar trend for all mixtures...