Preparation of Mono-, Di- and Hemicalcium Ferrite Phases via Melt for Reduction Kinetics Investigations

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Iron ore concentrates that are used in the iron production are usually agglomerated into sinter or pellets in order to improve their properties in the blast furnace. The main minerals in the magnetite base sinters are hematite, magnetite and Si and Al containing calcium ferrites of which the latter can exist as either monocalcium ferrite, dicalcium ferrite or hemicalcium ferrite depending on the conditions and on the material’s iron/calcium-ratio. In order to study the reduction behaviour of the sinter in the iron production, samples of monocalcium ferrite, dicalcium ferrite and hemicalcium ferrite were prepared by melting different proportions of pure calcium and iron oxides. After melting the samples were cast and cooled. Samples of hemicalcium ferrite were also heated at a certain temperature before the actual reduction experiments in order to ensure the wanted phase composition of the samples. The mineral compositions of the samples were verified using scanning electron microscopy (SEM-EDS) as well as X-ray diffraction (XRD). The verification showed that it was possible to produce the samples of calcium ferrites via melting. The conditions needed to reduce the calcium ferrites were estimated with thermodynamic calculations.

Keywords: calcium ferrites, sample preparation, reduction, SFCA, hemi-calcium ferrite, monocalcium ferrite, dicalcium ferrite

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Introduction

In order to improve the properties of blast furnace burden materials, iron ore concentrates are usually agglomerated into sinter or pellets. The mineralogical as well as the macroscopic structure of the material is changed due to melting and crystallization phenomena that take place in the sintering due to high temperatures (close to 1400°C). The main minerals in the magnetite based sinters are hematite, magnetite and Si and Al containing calcium ferrites (SFCA; Silico Ferrite of Calcium and Alumina). Although the content of calcium ferrites is low compared with the amount of hematite and magnetite, it is a determining factor in melt formation and crystallization of high basicity, magnetite based sinters (CaO/SiO₂ > 2).

Calcium ferrites have a significant effect on the cold strength and reduction strength of the sintered material since it causes particles to stick to each other. In oxidizing conditions the calcium ferrites can exist as either monocalcium ferrite (CaFe₂O₄), dicalcium ferrite (Ca₂Fe₂O₅) or hemicalcium ferrite (CaFe₂O₅) depending on the conditions and on the material’s and especially melt’s iron/calcium ratio. It should be noted that in real processes the sinters - as well as the iron concentrates they are made from - always include some impurities (e.g. aluminium and silicon) and therefore it is very unusual for calcium ferrites to exist as pure phases.

A lot of examinations concerning the preparation of synthetic calcium ferrite and SFCA samples for the reduction tests have been published. The methods presented in the literature can be divided in three categories (i.e. solid state sintering, sintering in a partly molten state and via melt) of which the first two were reported to be functional in practice. In most cases the calcium ferrites were prepared using a solid state sintering method [1,2], in which the formation of calcium ferrites takes place in solid state via diffusion between CaO and Fe₂O₃ at low temperatures (below 1200°C). In another method (sintering in a partly molten state) the temperature is slightly higher (approximately 1300 - 1400°C) than in the solid state sintering method, which causes calcium ferrite formation to take place via solid-melt reaction [3-6]. In order to achieve crystallisation from completely molten material, the temperature has to be even higher depending on the ratio of CaO and Fe₂O₃. However, there are problems such as high reactivity of calcium ferrite melt that has been reported in the literature concerning the preparation of calcium ferrites via melt [7,8]. In this study the purpose was to prepare all main calcium ferrite types (hemi-, mono- and di-) via melt.

This study consists of two main topics. In the first part thermodynamic calculations were used to estimate the equilibrium conditions to be used in the preparation of calcium ferrite samples as well as in the reduction tests of these materials in which the reaction kinetics and mechanisms of the calcium ferrites were defined. The second part of this study consists of actual preparation of the calcium ferrite samples via melt. The purpose of the study was to investigate the stability of calcium ferrites in various gas atmospheres and temperatures. Thermodynamic calculations were used to estimate the partial pressures of oxygen in equilibrium with different oxide phases with various iron/calcium ratios.

Methods

Thermodynamic calculations. In order to estimate the partial pressures of oxygen (p(CO)/p(CO₂) ratio to be
In equilibrium with different oxide phases with various iron/calcium ratios, equilibrium compositions of the Ca-Fe-O-C-systems were determined computationally using a FactSage software and its databases [9]. The software, its database and its possibilities and restrictions have been presented thoroughly elsewhere by the authors of the software [10], thus making it unnecessary to present the software here.

The purpose of the computations was to determine predominance area diagrams describing the stability regions of different phases as a function of partial pressures of CO and CO₂ at different temperatures. The stabilities of different calcium ferrites and iron compounds (oxides, carbide and metallic iron) were considered using three different Ca/Fe ratios. The systems that were considered computationally are presented in Table 1. In all the calculations, all the solid compounds were assumed to be pure phases with a single composition.

Table 1. Descriptions of the systems considered for thermodynamical calculations.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Variables</th>
<th>Temp. [°C]</th>
<th>Fe/(Ca+Fe) -ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-Fe-O-C</td>
<td>950</td>
<td>0.50...0.67</td>
<td>0.67...0.80</td>
</tr>
<tr>
<td>Ca-Fe-O-C</td>
<td>1000</td>
<td>0.50...0.67</td>
<td>0.67...0.80</td>
</tr>
<tr>
<td>Ca-Fe-O-C</td>
<td>1050</td>
<td>0.50...0.67</td>
<td>0.67...0.80</td>
</tr>
<tr>
<td>Ca-Fe-O-C</td>
<td>1100</td>
<td>0.50...0.67</td>
<td>0.67...0.80</td>
</tr>
<tr>
<td>Ca-Fe-O-C</td>
<td>1150</td>
<td>0.50...0.67</td>
<td>0.67...0.80</td>
</tr>
<tr>
<td>Ca-Fe-O-C</td>
<td>1200</td>
<td>0.50...0.67</td>
<td>0.67...0.80</td>
</tr>
</tbody>
</table>

Table 2. CaO/Fe₂O₃ ratios and chemical compositions of calcium ferrites.

<table>
<thead>
<tr>
<th>Fe₂O₃ (wt.%)</th>
<th>CaO (wt.%)</th>
<th>Fe₂O₃ (wt.%)</th>
<th>Ca (wt.%)</th>
<th>Fe (wt.%)</th>
<th>O (wt.%)</th>
<th>Fe/(Ca+Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.3</td>
<td>58.7</td>
<td>29.5</td>
<td>41.1</td>
<td>29.4</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>2CaO·Fe₂O₃</td>
<td>26.0</td>
<td>74.0</td>
<td>18.6</td>
<td>51.8</td>
<td>29.7</td>
<td>0.74</td>
</tr>
<tr>
<td>Ca₂Fe₂O₅</td>
<td>14.9</td>
<td>85.1</td>
<td>10.7</td>
<td>59.2</td>
<td>29.8</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Preparation of calcium ferrites. Calcium ferrites were prepared from synthetic CaO and Fe₂O₃ powders with the purities of 99.95 wt.% and 99.998 wt.%, respectively. In order to ensure that the CaO powder is free of hydroxides, it was calcinated before the powder mixtures with different CaO/Fe₂O₃ ratios were prepared. CaO/Fe₂O₃ ratios and chemical compositions of calcium ferrites are described in Table 2.

The powder mixes with certain CaO/Fe₂O₃ ratios were set in a platinum crucible placed in a spinel (MgO-Al₂O₃) crucible and melted in a chamber furnace in air. The Temperature was increased slowly to 1500 or 1600°C depending on the type of calcium ferrite (cf. Figure 1 in which the numbers 1-3 describe conditions and compositions of the initial melts). Calcium ferrite melt was quickly cast into a mould and cooled down as described in Figure 2.

Metastable hemicalcium ferrite samples were annealed at 1170°C which is located in the stability area of hemicalcium ferrite in air (cf. number 4 in Figure 1).

Polished sections were prepared from the calcium ferrite samples for optical and scanning electron microscopy and analyses.

Figure 1. Binary phase diagram of system CaO-Fe₂O₃ [11].

Figure 2. Casting of calcium ferrite melt into a copper mould placed on a water cooled copper plate.

Results and Discussion

Predominance area diagrams describing the phase stabilities of the Ca-Fe-O-C system at 950°C (with two different Fe/Ca-ratios) and 1200°C (with one Fe/Ca-ratio) are presented in Figures 3 to 5 as examples of the results from the thermodynamics computations.

The predominance area diagrams were used to define the partial pressures of oxygen (p(CO)/p(CO₂) ratio to be exact) in equilibrium with different phases. As an example a phase boundary between the stability areas of CaFe₂O₄ + Fe₃O₄ and Ca₂Fe₂O₅ + Fe₃O₄ (i.e. the phase boundary between mono- and dicalcium ferrites in contact with magnetite) in Figure 3 can be examined. It is seen that the ratio between the partial pressures of CO and CO₂ has a constant value of approximately 0.24·10⁻³, which corresponds to a partial pressure of oxygen of approximately 1.6·10⁻⁸ atm. At higher values of pO₂ monocalcium ferrite is thermodynamically more stable than dicalcium ferrite and at lower values the situation is opposite. A similar approach can be used to define the equilibrium values of pO₂ (or pCO/pCO₂) for other phase boundaries in the system. The plus symbols (+) in Figures 3 to 5 signify the area in which the sum of partial pressures of CO and CO₂ equals 1 atm (i.e. the atmospheric pressure with only these two components in the gas phase).
According to the calculations the CO/CO₂ ratio in the gas is approximately 22/78 at the phase boundary between magnetite and wüstite in equilibrium with dicalcium ferrite. This differs from the value of pure magnetite reduction, where the CO/CO₂ ratio is 10/90 [12].

Thermodynamic computations were used to estimate the stability regions of pure calcium ferrites in order to define the conditions in which different phases were prepared experimentally and especially to define the conditions for reduction experiments. However, due to limitations of available databases, it was not possible to computationally estimate the distribution of trace elements (e.g. silicon) in different solid solutions.

Dicalcium ferrite was crystallized straight from the melt, and it formed a homogeneous matrix in which distinct dicalcium ferrite crystals could be observed as is seen in Figure 6. The stoichiometric composition of the calcium ferrites (C₂F, CF and 2CF) are presented in the same diagram as a bar chart together with the compositions from the sample. This bar chart shows that the composition of the crystals in the sample is close to the stoichiometric composition of the dicalcium ferrite.

In the casting of the melt, corresponding to the composition of monocalcium ferrite, the formation of columnar dicalcium ferrite crystals was observed to take place from the surface to the core of the samples (Figure 2). Between the dicalcium ferrite crystals there was a streaky area where the chemical composition varied between hemicalcium ferrite and monocalcium ferrite as can be seen in Figure 7.

It is proposed that both phases co-exist due to quick cooling. Quenching caused a situation in which the samples did not have enough time to form the thermodynamically most stable phases. Thus both calcium ferrites are proposed to occur in the area.

Homogenous hemicalcium ferrite was not achieved by only casting the melt to the mould. The sample had to be annealed after the casting in order to achieve the wanted structure. The crystallised sample before annealing was full of CaO-bearing iron oxide and one or two calcium ferrites as seen in Figure 8.

The chemical analyses of the present phases did not correspond accurately to the stoichiometric phases. This implies that two separate phases exist that cannot be detected separately by electron microscopy due to the tiny crystal size in proportion to the analysis spot of the electron microscope. Therefore, they did not match the composition of either hemi- or monocalcium ferrite as described in Figure 9.

After heating at 1170°C, the sample consisted mainly of hemicalcium ferrite, although a few hematite crystals could also be observed in the sample (cf. Figure 10). The chemical composition was close to the composition of stoichiometric hemicalcium ferrite as can be seen in Figure 11.
Figure 6. Optical microscope images from a polished section made from the cast sample with the total composition corresponding to dicalcium ferrite.

Figure 7. SEM-image and analysis from a polished section made from the cast sample with the total composition corresponding to monocalcium ferrite.

Figure 8. Microscope images from polished sections made from the cast sample with the total composition corresponding to hemicalcium ferrite.

Figure 9. Results of analysis from cast melt corresponding to the composition of hemicalcium ferrite. The last five patterns on the right show chemical compositions of calcium ferrites, hematite and magnetite.
Small areas of monocalcium ferrites could also be observed in the core of the sample as seen in Figure 12. This means that the annealing time should have been longer in order to have enough time for the formation of hemicalcium ferrite from the CaO-rich monocalcium ferrite and CaO-pore hematite.

In addition to the predominance area diagrams presented in Figures 3 to 5 computational thermodynamics were used to define the reduction route for the calcium ferrites as well as the p(CO)/p(CO₂) ratios at which the different phases are in equilibrium with each other. The results of these computations are presented in Figure 13.

Conclusions

Thermodynamic computations were used to support the experimental procedures for the reduction of hemi-, mono- and dicalcium ferrites, and the main results are described in Figure 13. However, due to the limited resources of available databases, it was not possible to computationally estimate the behaviour of trace elements in solid solutions.

Preparations of hemi-, mono- and dicalcium ferrites were executed and confirmed. Dicalcium ferrite demanded the highest casting temperature but was the easiest to prepare as nearly homogeneous phase. The other calcium
ferrites demanded either very slow cooling (for the preparation of the monocalcium ferrite samples) or heating after casting (for the preparation of the hemicalcium ferrite samples).

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References

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