The stability of cementite formed from Hematite and Titanomagnetite ore under carburising atmosphere

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Introduction

The decomposition of cememite, formed from iron, was more stable than cememite formed from hematite. From results of experiments, it was found that, in iron containing 0.06% carbon, the decomposition of cememite occurred at 750°C; in iron containing 0.08% carbon, the decomposition began at 670°C; and in iron containing 0.10% carbon, the decomposition began at 650°C. These results suggest that the stability of cememite increases with the addition of carbon to iron. The decomposition of cememite was investigated under various conditions, such as temperature and pressure. It was found that the decomposition of cememite started at a lower temperature in the presence of carbon, while the decomposition was delayed in the absence of carbon.
studied in the temperature range of 500°C to 850°C for the hematite ore, and 450°C to 900°C for the titanomagnetite ore.

2 Experimental

Cementite was formed from hematite iron ore by reaction with a CH₄-H₂-Ar gas mixture in a vertical tube furnace. The experimental set-up was described elsewhere [9]. The gas mixture of given composition was made by mixing ultra-high purity argon, methane and hydrogen whose flow rates were controlled by mass flow controllers. During this study, the gas flow rate was maintained at 1 L-min⁻¹.

The compositions of the two iron ores used are given in Table 1. The hematite ore from Mt. Whaleback was used in the size range of −450 +355 mm. The size fraction used for the New Zealand iron sand was −255 +150 mm. The iron sand was preoxidised by heating it within a muffle furnace in air to 1000°C for 4 days. This changed the ore from the initial titanomagnetite to a more easily reduced titanohematite.

<table>
<thead>
<tr>
<th>Ore</th>
<th>Fe(tot)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>P</th>
<th>CaO</th>
<th>K₂O</th>
<th>S</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt. Whaleback</td>
<td>62.7</td>
<td>5.35</td>
<td>3.61</td>
<td>0.09</td>
<td>0.087</td>
<td>0.016</td>
<td>0.03</td>
<td>0.028</td>
<td>-</td>
</tr>
<tr>
<td>NZ iron sand</td>
<td>57.2</td>
<td>2.17</td>
<td>3.59</td>
<td>7.43</td>
<td>-</td>
<td>0.67</td>
<td>-</td>
<td>-</td>
<td>2.94</td>
</tr>
</tbody>
</table>

Cementite samples were prepared within the lab-scale fixed reactor at 750°C by passing the reducing/carburising gas, with a composition of 35 vol% CH₄, 55% H₂ and 10% Ar, through the sample for 15 minutes for the hematite ore, and 30 minutes for the iron sand. After this, the temperature of the sample was changed to the experimental temperature for cementite decomposition, and the sample held for a prescribed period, after which the sample was quenched under argon.

The phase composition of the samples was determined quantitatively by XRD using a copper Kα source. The scans were done at a rate of 1°/min with a step size of 0.2°-2θ. The morphology of the samples was examined by both optical microscopy and SEM. Etching of the optical microscopy samples in a basic sodium picrate solution allowed differentiation between cementite and metallic iron.

3 Results

The mass fraction of cementite formed from hematite ore during the decomposition of the cementite at different temperatures is shown in Fig. 1(a). This mass fraction only takes into account the iron containing phases, neglecting gangue and free carbon. The cementite is most stable at temperatures around 750-770°C. At temperatures higher than this, the rate of cementite decomposition increased with increasing temperature. At temperatures between 730°C and 600°C, the rate of decomposition of cementite increased with decreasing temperature. Decomposition occurred most quickly at around 600-650°C.
(a) Hematite and pre-oxidized hematite decomposition at different temperatures.

Figure 1: Mass fractions of hematite formed from iron during...

The rate of decomposition never increases to match that seen for hematite. For the hematite, the rate of decomposition is much greater than that seen for the hematite at temperatures between 700°C and 600°C, and indeed the increase in the rate of decomposition is much greater than seen in increase with decreasing temperature from around 700°C to 900°C. However, the increase in the rate of decomposition is much greater than seen in increase with decreasing temperature from around 700°C to 600°C.

The rate of decomposition of hematite formed from iron can be formed from the hematite one.

750°C, and least stable at around 600°C. Hematite is most stable at around 900°C and least stable at around 500°C. The decomposition forms from the hematite forms in hematite. The rate of decomposition increases with temperature. The Figure 1 shows that as the temperature increases in the decomposition forms from hematite. The decomposition rates increase with the decomposition forms from hematite a sharp increase in shown in Figure 2. For example, the decomposition rate and temperature is.

Below 700°C, the rate of decomposition of hematite increased with decreasing temperature.

At higher temperatures, the decomposition occurred slightly faster. However, the decomposition was found to have little impact on the rate of decomposition. The temperature range between the temperatures from 700-850°C. In this range, the hematite formed from the hematite. The hematite was found to most

The mass fraction of hematite formed from iron factors of (hematite)
Fig. 2: The rate of decomposition of cementite as a function of temperature.

4 Discussion

The following mechanism for the decomposition of the cementite formed from iron ore under carburising atmosphere is proposed. After conversion of iron to cementite, solid carbon is deposited onto the surface of cementite. This decreases the carbon activity at the cementite/carbon interface to unity, making cementite thermodynamically unstable. Because of this, cementite is transformed to super-saturated carbon solution in metallic iron. This stage includes the nucleation and growth of the new super-saturated iron phase within the cementite. The final stage is carbon precipitation from the super-saturated solution by diffusion under gradient of carbon chemical potential. The location of the carbon could not be determined from either optical or electron microscopy. However, it is speculated that the carbon would be deposited onto the surface of the metallic iron (or existing iron-carbon interfaces), either at the outside of the particle, or inside of the pores within the particle.

The TTT curves of cementite decomposition are typical C-curves, which are explained by different rates of nucleation and growth of phases at different temperatures: slow nucleation rate at high temperatures, and slow mass transfer at low temperatures. Nucleation rate in the process of cementite decomposition is low at high temperatures because of a weak thermodynamic driving force. This driving force increases with decreasing temperature, causing the cementite decomposition rate to increase with decreasing temperature from 730°C to 550°C for hematite ore and from 700°C to 400°C for the titania-ferrous ore.

For cementite formed from both ores, the mechanism of cementite decomposition is the same, but the rate of nucleation of iron phase is different. For cementite formed from iron sand, nucleation is the rate controlling stage between 400°C and 700°C, while for cementite produced by reduction of hematite it is controlling between 550°C and 730°C.
The amount of lanthanum in the cementite is higher than expected. The amount of lanthanum in the carbide significantly affects the thermodynamic properties. This phase, which is carbide, takes up more lanthanum. Roughly the same concentration is found in other phases, whether or not the cementite has decomposed. This phase, which is either carbide or metallic iron, depending on the decomposition process, is either carbide or high temperature cementite in composition to lanthanum in the form of oxide. Lanthanum and other elements are well as iron. If containing relatively little calcium and other elements, as well as iron, the cementite formed has decomposition products consist of lanthanum carbide and lanthanum oxide. The denser phase with the least amount of lanthanum concentration and the amount of basic decomposition is relatively less stable than the other phase. The amount of lanthanum is below the level needed for the cementite to form. In this case, carbon activity is below the level needed for the cementite to form. At low temperatures, iron precipitates in the particles into iron carbide. The decomposition process progresses slowly toward the carbide phase (3). The decomposition process progresses slowly toward the carbide phase (3).
from the literature, where it was generally reported that titanium forms TiC preferentially to cementite [15,16]. Under the experimental conditions in this work, titanium carbide was not formed, due to the low temperatures used.

Fig. 4: SEM images of cementite formed from ironsand, decomposed at 500°C for 60 minutes, indicating the three titanium containing phases. (a) gangue material at the particle edge; (b) oxide phase (grey) and metallic phase (bright) inside the particle.

Cementite formed from the ironsand at 750°C contains a high amount of titanium, which stabilises cementite. Titanium is known to have a strong affinity for carbon, reducing the activity of carbon within the cementite and the driving force for nucleation. Because of this, the decomposition occurs more slowly.

5 Conclusions

The decomposition of cementite formed from hematite was investigated in the temperature range from 500°C to 925°C under a carburising atmosphere. Cementite was most stable at temperatures around 750-770°C. Between 730°C and 550°C, the rate of decomposition of cementite increased with decreasing temperature, with the highest rate at around 600°C to 650°C. At temperatures both higher and lower than this interval, the rate of cementite decomposition increased.

Cementite formed from ironsand, was stable in the range of 700°C to 900°C, with no significant effect of temperature on the decomposition rate. At lower temperatures, between 700°C and 400°C, the rate of decomposition of cementite increased with decreasing temperature. At higher temperatures, the decomposition became faster, especially at temperatures above 1000°C. Cementite formed from ironsand decomposed much more slowly than that formed from hematite, especially at temperatures below 700°C.

The mechanism of decomposition of cementite was proposed. Firstly, carbon is deposited onto the surface of the cementite, decreasing the carbon activity in the system to unity, making cementite thermodynamically unstable. Cementite decomposition follows, including stages of nucleation and growth of a metallic iron phase and carbon diffusion to form graphite on a free surface.