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

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The stability of cementite formed from hematite and thermomagnesite are under a carburizing atmosphere. Hematite and Thermomagnesite are under a carburizing atmosphere, formed from hematite and precipitated from cementite. To gain further understanding of mechanism of cementite decomposition, the authors of this paper studied the stability of cementite decomposition. The reactivity of the sample studied was not significantly affected by the addition of cementite. The temperature range of cementite decomposition increased with decreasing temperature in the carburizing atmosphere. The stability of cementite decomposition was not significantly affected by the addition of cementite. However, cementite is thermodynamically unstable and decomposes to oxides with carburizing gases, which an increase of reaction products [11]. In the reduction of iron, cementite is formed by the reaction of iron, hydrogen, and carbon. From thousand was more stable than cementite formed from hematite.
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 1: Composition of iron ores investigated (wt%).**

<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>-</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.
The rate of decomposition never increases to match that seen for hemicellulose at around 60°C and 600°C, and indeed the mass fraction of methane formed from hemicellulose at 700°C is much greater than that seen in increase with decreasing temperature from around 700°C to 600°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 cellulose formed from hemicellulose can be formed from the hemicellulose at around 60°C, and least stable at around 500°C. However, the decomposition rate at 60°C and below 500°C, the decomposition rate increases with temperature. The decomposition rate decreases with temperature. The decomposition rate increases with temperature. The decomposition rate decreases with temperature.

The decomposition of cellulose increased with decreasing temperature. At higher temperatures, the decomposition occurred at higher rates. However, the temperature was found to have little impact on the rate of decomposition. The temperature was found to have most impact on the rate of decomposition. The rate of decomposition of cellulose at different temperatures is shown in Figure 1. The rate of decomposition of cellulose at different temperatures is shown in Figure 1. (a)
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 ironsand, 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.
This amount of helium in the cementite is higher than expected. Trilumine within the carbide significantly alters the thermodynamic properties of the cementite, possibly due to the high concentration of carbon in the structure. Trilumine is Cr₃Al₃, which is found in the cementite phase. Whether or not the cementite has decomposed or not, this phase remains the same. The bright phase is either cementite or metallic iron, depending on the process.  

The bright phase consists of a high concentration of cementite in the form of oxides. The dense phase within the cementite particle is shown in the figure below. The distribution of these phases was detected using SEM and TEM images. The decomposition process leads to the formation of cementite, and the amount of basic decomposition in the cementite is relatively fast. In the process of decomposition, metallic iron precipitates and forms from the cementite. In this case, the particle activity is below the level needed for the cementite decomposition. At low temperatures, iron precipitates in the particle instead of the cementite decomposition. In the decomposition reaction, the iron/cementite interface plays a role in nucleation and cementite decomposition.
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.

![SEM images of cementite formed from iron sand, 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.](image)

**Fig. 4:** SEM images of cementite formed from iron sand, 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 iron sand 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 iron sand, 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 iron sand 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.
References

The increase in the decomposition rate with decreasing temperature in the diffusion and carbon diffusion processes.

Induction and carbon diffusion processes.

At other temperatures, the rate of decomposition is much controlled by

But at the higher temperatures mentioned, the overall decomposition process is

The temperature of the material itself plays a role in the decomposition.