Effect of Sulphur on Iron Carbide Formation and Stability

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Effect of sulphur on iron carbide process was investigated by examining iron ore reduction, iron cementation and cementite decomposition under gas atmosphere with and without sulphur. Sulphur added to H$_2$–Ar gas in the form of H$_2$S slightly decreased the rate of iron ore reduction at 750°C, but had a negligible effect at 850°C. Sulphur strongly retarded iron cementation. At 850°C, cementite was formed in 10 min by sulphur-free gas, 100 min when gas contained 50 ppm H$_2$S, and 180 min when H$_2$S was in the amount of 100 ppm. The rate of cementite formation increased with increasing temperature from 750°C to 925°C. Sulphur also strongly retarded free carbon deposition and stabilised cementite. However sulphur had no significant effect on the rate of cementite decomposition when it was introduced to the gas atmosphere after the completion of the cementation process.

KEY WORDS: sulphur; iron ore; reduction; iron carbide; cementite formation; cementite stability; methane cracking.

3. Results and Discussion

3.1. Effect of Sulphur on Iron Ore Reduction

Effect of sulphur on iron ore reduction was investigated by adding H$_2$S to H$_2$–Ar gas. The reducing gas contained 25 vol% H$_2$, 0–600 ppm H$_2$S and Ar the rest. Sulphur activity, $a_s$, defined as $(P_{H_2S}/P_{H_2})/(P_{H_2S}/P_{H_2})^{eq}$, where $(P_{H_2S}/P_{H_2})^{eq}$ is $P_{H_2S}$ to $P_{H_2}$ ratio in the gas phase in equilibrium with metallic iron and FeS, was in the range of 0–1. In some experiments, H$_2$S was introduced into the reactor during sample heating, prior to the reduction. Sulphur effect on iron ore reduction at 750°C and 850°C is shown in Figs. 1(a) and 1(b). At 750°C, increasing H$_2$S from 50 ppm ($a_s=0.16$) to 210 ppm ($a_s=0.66$) decreased the rate of iron oxide reduction. Sulphur being introduced into reactor before reduction (heating of a sample in Ar–H$_2$S atmosphere) had a stronger

Table 1. Chemical composition of iron ore, wt%.

| Element | Fe | FeO | SiO$_2$ | Al$_2$O$_3$ | TiO$_2$ | P | Mn | S |
|---------|----|-----|---------|------------|---------|---|----|---|
| Fe      | 62.7 | 89.56 | 4.81 | 2.81 | 0.08 | 0.087 | 0.04 | 0.026 |
retarding effect on the reduction than sulphur introduced with reducing gases. The effect of sulphur on iron ore reduction at 850°C was rather slight (Fig. 1(b)).

Hayashi and Iguchi reported that the introduction of a small amount of sulphur to gas with activity $a_s/H_{11005}$ 0.01, retarded wustite reduction due to formation of dense iron. While increase in sulphur activity to 0.1, accelerated the reduction because of formation of porous iron. This effect was not observed in our experiments. In contrast to Hayashi and Iguchi experiments with wustite, in these experiments hematite was reduced. A porous structure was formed, which insured a quick reduction. Sulphur, being added to the reducing gas, tended to adsorb on impurities and surface defects to lower surface and interfacial energies. As a result, the rate of iron oxide reduction decreased because metallic iron nucleated namely on these active sites in the iron ore. At high temperature of 850°C, reduction of iron ore was very fast, and this effect was of less significance than that at lower temperatures.

3.2. Effect of Sulphur on Cementite Formation

Effect of sulphur on cementite formation was studied at 750°C, 850°C and 925°C. The reacting gas contained 35 vol% CH₄, 55 vol% H₂, 0–1 360 ppm H₂S (sulphur activity 0–0.7), and Ar the rest. Effect of sulphur on cementite fraction in samples of iron ore reduced/carburised at 750, 850 and 925°C is illustrated in Figs. 2(a)–2(c). Total carbon contents in samples reduced at 850°C (reaction time: 30, 60 and 120 min) using gas with different sulphur contents are shown in Fig. 3.

Sulphur had a very strong retarding effect on cementite formation. At 750°C, iron oxide reacting with sulphur-free gas was converted to cementite in about 15 min. However, the conversion time increased to about 30 min when reaction gas contained 3 ppm H₂S ($a_s/H_{11005}$ 0.004). When reaction time increased further to 60 min, cementite fraction in the sample exposed to gas with 3 ppm H₂S decreased to 0.94 as a result of cementite decomposition. When gas contained more than 11 ppm H₂S ($a_s/H_{11005}$ 0.015) the conversion of iron oxides to cementite was not completed. The maximum attainable cementite fraction was 0.93 for gas containing 11 ppm H₂S ($a_s/H_{11005}$ 0.015) and 0.76 for gas with 16 ppm H₂S ($a_s/H_{11005}$ 0.023). Further increase in reaction time caused cementite decomposition. It indicates that at this temperature the retarding effect of sulphur on cementite formation was much stronger than that on cementite stability. It was found that when 16 ppm H₂S was introduced into the reactor in the process of a sample heating (about 60 min before reaction) it was not possible to produce cementite at all. In this case, as soon as metallic iron was formed, sulphur covered
the surface of iron and prevented cementite formation. However, when H2S was introduced with reaction gases, adsorption and cracking of methane and adsorption of sulphur occurred simultaneously, which retarded the iron cementation, but did not stop it.

At 850°C, cementite was formed in about 10 min when reducing/carburising gas was sulphur-free. This process took about 100 min when the gas contained 50 ppm H2S (αs = 0.04), and 180 min when H2S was added in the amount of 100 ppm (αs = 0.08).

At 925°C, conversion of iron oxides to cementite was completed in about 30 min when the gas contained 160 ppm H2S (αs = 0.08) and 40 min using the gas with 270 ppm H2S (αs = 0.14). However, in the reduction/cementation process using sulphur-free gas, maximum cementite fraction at this temperature was below 75%, because of very rapid cementite decomposition.

Increasing sulphur content in gas also strongly retarded the rate of free carbon deposition. Figure 3 shows that at 850°C total carbon content was 41.9 wt% in the sulphur-free gas atmosphere after 60 min of reaction but it decreased to 14.6 wt% with addition of 50 ppm H2S and decreased further to 3.3 wt% with the increase in H2S to 100 ppm. Similar effect of sulphur was also observed at 925°C.

All experimental data presented above show that sulphur strongly retards the process of cementite formation even at low sulphur concentrations in reducing/carburising gas. However, the effect of sulphur on iron ore reduction is not as significant as that on cementation process. This is consistent with the fact that sulphur segregates more strongly on the surface of metallic iron than that on the iron oxide surface.7

Sulphur adsorption on metallic iron is very strong, which effectively retards the carburisation process. Grabke et al.1-3 reported that the iron carburisation reaction rate began to decrease at sulphur activities \( \alpha_s > 10^{-4} \), or at \( P_{\text{H}_2}/P_{\text{H}_2} \) > 10\(^{-2} \) and a bulk concentration of dissolved sulphur of about 0.01 ppm at 800 and 850°C. When \( P_{\text{H}_2}/P_{\text{H}_2} \) reached \( 10^{-5} \) or a bulk concentration of dissolved sulphur was about 1 ppm, the initial rate of carburisation was less than 0.1 ppm C/sec.

The rate of reaction \( \text{CH}_4 \rightarrow \cdots \rightarrow \text{C (ad)} + 2\text{H}_2 \), can be presented as:

\[
R = kAf(P_{\text{CH}_4}, P_{\text{H}_2})(1 - \theta)
\]

where \( k \) is the reaction rate constant; \( A \) is the iron surface area; \( f(P_{\text{CH}_4}, P_{\text{H}_2}) \) is a function of partial pressures of methane and hydrogen; \( \theta \) is the fraction of the iron surface occupied by sulphur. Iron surface coverage by sulphur is described by the Langmuir adsorption:

\[
\theta = \frac{K\alpha_s}{1 + K\alpha_s}
\]

where \( K \) is the sulphur adsorption coefficient. Thus, the effect of sulphur on the rate of carbon adsorption can be described by the equation:

\[
R = kAf(P_{\text{CH}_4}, P_{\text{H}_2}) \left( \frac{1}{1 + K\alpha_s} \right)
\]

When \( Ka_s \gg 1 \), the rate of iron cementation is inversely proportional to sulphur activity in iron.

The fraction of iron surface covered by sulphur can be calculated using data reported by Grabke et al.1-3 Calculated results are shown in Fig. 4. The degree of surface coverage by sulphur was above 97.5% in all experiments with sulphur-containing gases. According to Eq. (1) the rate of cementation would be very slow because of the blockage of iron surface for carbon adsorption. Hayashi and Iguchi3,4 suggested that because carbon radius is smaller than sulphur radius, carbon atoms could pierce the sulphur ad-layer to transfer into bulk iron. As a result, carburising and cementation process could take place under the iron surface covered by sulphur. In this case the following equation can be used for the rate of iron cementation5

\[
R = Af(P_{\text{CH}_4}, P_{\text{H}_2}) \left( \frac{k_1}{1 + K\alpha_s} + \frac{k_2K\alpha_s}{1 + K\alpha_s} \right)
\]

where \( k_1 \) represents a rate constant for the reaction occurring on the surface covered by sulphur, which is much smaller than \( k \). The rate of cementation is very slow after iron surface is covered by sulphur especially at low temperature, e.g. 750°C. Increasing temperature accelerates cementation process.

Sulfur also strongly affects the free carbon deposition. Retarding effect of sulphur on the free carbon deposition is stronger than that on the cementation process. A nucleation of the solid carbon phase requires a number of carbon atoms to be adsorbed on the neighbouring sites on the iron surface. Sulphur adsorption strongly decreases the number...
of such sites, and retards the solid carbon deposition and cementite decomposition.

3.3. Effect of Sulphur on Cementite Decomposition

Sulphur effect on cementite decomposition was investigated in the experimental series shown in Fig. 5.

In series 1, iron ore was reduced and carburised by CH₄–H₂–Ar gas mixture (35 vol% CH₄, 55 vol% H₂) with and without H₂S at 850°C. It took 10 min to prepare cementite in sulphur-free gas and 75 min in the gas with 50 ppm H₂S. Then reaction gases were switched to argon atmosphere. As a result, cementite was decomposed. It was found that cementite formed by gas with sulphur was more stable than that by reacting with sulphur-free gas (Fig. 6).

Series 2 and 3 were designed to investigate the effect of sulphur in the gas atmosphere on cementite stability. Cementite was prepared with sulphur in series 2 and without sulphur in series 3. Results are shown in Figs. 6 and 7. It is seen from these figures that sulphur being added to gas after completing the cementation process had no significant effect on cementite stability.

Retarding effect of sulphur on iron cementation is obviously stronger than its cementite stabilising effect. This supports a suggestion that the rate of iron cementation is controlled by methane adsorption/cracking reactions, while the rate of cementite decomposition is predominantly controlled by carbon diffusion in iron. Effect of sulphur on the rate of interfacial reactions is obviously stronger than that on the carbon diffusivity.

However, the thermodynamic condition for cementite formation is high carbon activity in the gas phase and super-saturation of iron-carbon solution. Cementite decomposition in the CH₄–H₂–Ar gas is triggered by deposited carbon, which blocks an access of carburising gas to a sample, and lowers carbon activity down to unity, what makes cementite thermodynamically unstable. The rate of carbon deposition depends strongly on the catalytic iron on the sample surface. When sulphur was introduced to the reacting gas in the processes of iron ore reduction/iron cementation, its adsorption on iron had a retarding effect on methane adsorption/cracking, which stabilised cementite.

Mossbauer analysis showed that some amount of iron, up to 3 wt%, was always present in a sample, although it was not detected by the XRD. It can be suggested that this iron played a significant role in cementite decomposition. In the case when cementite was formed by reacting with CH₄–H₂–H₂S–Ar gas, this iron was covered by adsorbed sulphur, which deactivated its catalysing effect on methane cracking.

4. Conclusions

Effects of sulphur on iron ore reduction and iron cementation using CH₄–H₂–H₂S–Ar gas, and cementite stability can be summarised as follows:

(1) Sulphur slightly decreased the rate of iron ore reduction by hydrogen at 750°C, but had a negligible effect at 850°C.

(2) Sulphur strongly retarded iron cementation. At 750°C the conversion of iron ore to cementite was not completed when gas contained more than 11 ppm H₂S. At 850°C this iron was covered by adsorbed sulphur, which deactivated its catalysing effect on methane cracking.
850°C, cementite was formed in 10 min using sulphur-free gas, 100 min when gas contained 50 ppm H₂S and 180 min when H₂S was in the amount of 100 ppm. Further increase in temperature to 925°C increased the rate of cementite formation. At this temperature, conversion of iron oxide to cementite was completed in 30 min when gas contained 160 ppm H₂S and 40 min with gas containing 270 ppm H₂S.

(3) Sulphur being introduced to the reducing/carburising gas strongly retarded free carbon deposition and stabilised cementite. However sulphur had no significant effect on the rate of cementite decomposition when it was introduced to the gas atmosphere after the completion of the cementation process.

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