Cementite Formation in CH₄–H₂–Ar Gas Mixture and Cementite Stability

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Iron ore reduction/cementation by CH₄–H₂–Ar gas (35 vol% CH₄, 55 vol% H₂ and 10 vol% Ar) was examined in a fixed bed reactor in the temperature range of 600–925°C. Iron oxides were first reduced to metallic iron and then iron was carburised to cementite. The rate of iron ore reduction and iron cementation increased with increasing temperature. Iron carbide formed in the reduction/cementation process was unstable and decomposed to metallic iron and carbon. Cementite stability was studied in the temperature range of 500–850°C. At temperature below 600°C and above 750°C, the rate of cementite decomposition increased with the increase in temperature. However, in the range of 600–750°C the rate of cementite decomposition decreased with increasing temperature. Cementite was the most stable at 750°C and least stable at 600°C. At 750°C, iron ore was converted to cementite by gas containing 35 vol% CH₄, 55 vol% H₂ and 10 vol% Ar in 15 min.

KEY WORDS: iron carbide; methane; hydrogen; reduction; cementation; cementite decomposition; methane cracking.

1. Introduction

Iron carbide is an attractive material for steel making.^{1,2)} It is produced from iron ore fines in a fluidized bed using a gas mixture of hydrogen and hydrocarbons at a relatively low temperature (570°C). However, conversion of iron oxides to cementite at low temperatures is very slow. Increasing temperature increases the rate of the iron carbide formation.^{3–5)} However, it also accelerates hydrocarbons cracking and cementite decomposition.

Iron carbide at elevated temperatures decomposes to metallic iron (austenite or ferrite) and solid carbon (soot), causing metal dusting.^{4–8)}

Nakagawa *et al.*³⁾ studied reduction of iron ore using CH₄–H₂ gas mixture in fluidised bed and fixed bed reactors in the temperature range 650–950°C using XRD quantitative analysis and combustion method. The CH₄/H₂ ratio was varied from 20/80 to 45/55, and reaction time was from 10 to 120 min. They found that cementite was most stable at 750°C, and that optimum CH₄/H₂ ratio was 40/60. Effect of temperature on cementite stability was attributed to two factors, affecting cementite formation: 1) methane cracking which was considered as a source of carbon for cementation reaction, and 2) reaction activity of reduced iron in the cementation process. Increasing temperature increases the methane cracking, and decreases iron activity as a result of sintering and decreasing surface area. Reverse effects of temperature on these processes were suggested to be behind the optimal temperature of cementite formation at about 750°C.

This work in addition to cementite formation also examines cementite stability in different gas atmospheres (CH₄–H₂–Ar gas mixture and pure argon), having the aim to establish mechanisms and kinetics of iron carbide formation and decomposition. Study of cementite stability in pure argon was in the temperature range 500–850°C. Experimental arrangement employed in this work allows tracing of free carbon deposition, which plays an important role in cementite stability as was demonstrated by studies of the metal dusting.^{6–8)}

2. Experimental

Cementite formation in the iron carbide process by CH₄–H₂–Ar gas mixture and cementite decomposition in different gas atmospheres were investigated in a vertical tube electric furnace. Experimental set-up is schematically presented in **Fig. 1**. Gas mixture was prepared from purified argon, methane and hydrogen using mass gas controllers. The gases passed through traps filled with 4A molecular sieve to remove moisture before mixing. The total gas flow rate was maintained at 1 000 cm³/min. The extent of iron ore reduction was calculated by measuring H₂O and CO concentrations in the off gas. The content of water vapor in the gas was measured by a dew point sensor (General Eastern Hygro M4/D-2). Concentrations of CH₄, H₂, CO and CO₂ were monitored on-line by the Fisons scanning mass spectrometer.

The composition of iron ore is given in **Table 1**. The ore was sized in the range from 0.35 to 0.5 mm. A sample with

Fig. 1. Schematic of experimental set-up.

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

T.Fe	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	TiO ₂	P	Mn	S
62.7	89.56	4.81	2.61	0.08	0.087	0.04	0.026

Fig. 2. Schematic of experimental reactor.

a mass of 2 g was placed into the inner tube (reactor) with a porous magnesia plug at the bottom (Fig. 2). The sample was heated in argon atmosphere to required temperature. When temperature was stabilized and no oxygen was detected in the reactor, reaction gas was introduced. It flew through the fixed bed of the ore sample and left the reactor through the porous plug. After reduction, a sample was quenched in argon gas atmosphere.

The phase composition was determined quantitatively by XRD (Siemens D5000) with a copper K α X-ray source. X-ray scans were at a rate of 0.6°/min and step of 0.01°. The morphology of samples was observed by optical microscope (Olympus PMG3). Total carbon content in a sample was determined by combustion method (LECO CS-244 carbon-sulfur detector).

Fig. 3. Degree of iron ore reduction by CH₄-H₂-Ar gas mixture (35 vol% CH₄, 55 vol% H₂ and 10 vol% Ar) at 650, 750 and 850°C.

3. Results

3.1. Cementite Formation and Decomposition in CH₄-H₂-Ar Gas

Iron ore was converted to cementite using CH₄-H₂-Ar gas mixture, containing 35 vol% CH₄ and 55 vol% H₂ in the temperature range 600–925°C. Hematite was first quickly converted to magnetite and then reduced further to wustite and metallic iron. The degree of reduction as a function of reaction time at 650°C, 750°C and 850°C is presented in Fig. 3. Reduction rate increased with increasing temperature. Reduction extent of 95% was achieved in about 15 min at 650°C, 10 min at 750°C and 7 min at 850°C.

As soon as iron ore was reduced to metallic iron, cementite started to form. Figure 4 presents XRD spectra of iron ore subjected to reduction and carburisation at 750°C. After 2 min reduction, hematite was converted mainly to wustite with some amount of magnetite. After 5 min reduction, most of iron ore was reduced to metallic iron. When reaction time increased to 7 min, cementite was formed. Iron ore was completely converted to cementite in 15 min. Cementite started to decompose to metallic iron and carbon after reaction time over 90 min.

Figure 5 shows the cementite fraction, defined as molar fraction of iron in cementite, at different temperatures. Increase in temperature increased the rate of cementite formation at all temperatures. Cementite fraction increased with increasing time, achieved maximum, and decreased with further exposure to CH₄-H₂-Ar gas as a result of cementite decomposition. The rate of cementite decomposition depends on temperature in a more complex way than the rate of cementite formation. As a result of the competing processes of cementite formation and decomposition, a fraction of cementite in the reduced sample is a quite complex function of temperature and reaction time. The rate of cementite formation at 925°C was the fastest in the investigated temperature range. However, at this temperature cementite decomposed also with the fastest rate. As a result, cementite fraction in the sample reduced at 925°C was the largest in the very beginning of the reduction/cementation process, reaching the peak value of 0.7, and then decreased very quickly after 5 min reaction. At low temperature of 600°C, cementite was slowly formed, and cementite fraction started to decline when cementite fraction was only 0.4 after about 1 hr of reaction. At 650°C, cementite fraction reached its peak value of 0.85 after 30 min reaction. Iron

Fig. 4. XRD spectra of iron ore subjected to reduction and cementation by $\text{CH}_4\text{-H}_2\text{-Ar}$ gas (35 vol% CH_4 , 55 vol% H_2) at 750°C .

Fig. 5. Cementite fraction as a function of reaction temperature in the process of iron ore reduction/cementation by $\text{H}_2\text{-CH}_4\text{-Ar}$ gas mixture (55 vol% H_2 and 35 vol% CH_4).

ore was almost completely converted to cementite in about 30 min at 700°C , 15 min at 750°C and 800°C , and 10 min at 850°C . It was found that cementite was most stable at 750°C . Increase in temperature from 750°C to 925°C increased the rate of cementite decomposition. However in the temperature range of $650\text{--}750^\circ\text{C}$, increasing temperature decreased the rate of cementite decomposition. Therefore, the optimum temperature for cementite formation using gas mixture containing 35 vol% CH_4 , 55 vol% H_2

and 10 vol% Ar was 750°C .

Free carbon formed as a result of cementite decomposition ($\text{Fe}_3\text{C} \rightarrow 3\text{Fe} + \text{C}$) and methane cracking ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) was also observed in the reduced sample. Its fraction increased with the reaction temperature and time. Free carbon content was found to increase slowly at the early reduction and carburisation stages. However after about 60 wt% cementite formation, the rate of free carbon formation increased quickly with increasing exposure time. This increase is clearly seen in Fig. 6.

Morphologies of samples subjected to reduction and cementation at 750°C are presented in Fig. 7. Figure 7(a) shows that metallic iron (white color) nucleated uniformly in the interior of iron ore in about 5 min of reaction. After 10 min of reaction, no oxide phase (gray color) was detected (Fig. 7(b)). A sample subjected to reaction with $\text{CH}_4\text{-H}_2\text{-Ar}$ gas for 120 min was colored in gray color (Fig. 7(c)), which is related to free carbon deposition on cementite surface. Under optical microscope iron and iron carbide have the same color. To examine different phases formed in the process of cementite decomposition, samples were etched in the boiling solution of alkaline sodium picrate, which makes cementite dark while iron remains bright. Morphologies of etched samples obtained at 750°C are shown in Fig. 8. Nucleation of iron in the interior of cementite phase is seen after 90 min reaction (Fig. 8(a)). Iron fraction increases further with increasing reaction time to

120 min (Fig. 8(b)).

Experimental results on cementite formation and stability in carburising $\text{CH}_4\text{-H}_2\text{-Ar}$ gas atmosphere are similar to those obtained by Nakagawa *et al.*³⁾ in $\text{CH}_4\text{-H}_2$ gas, although processes of iron ore reduction and iron cementation in this work were much faster. For example, it took about 30 min to convert iron oxide to cementite at 750°C in work³⁾ and only 15 min in this work. It may be caused by different reactor design and sample mass (10 g in work,³⁾ and 2 g in this work).

3.2. Decomposition of Cementite in Argon Gas

Decomposition of cementite in the reducing/carburising atmosphere of $\text{CH}_4\text{-H}_2\text{-Ar}$ gas as mentioned above exhibits a complex behavior. To further investigate cementite decomposition two series of experiments were performed in argon atmosphere.

Fig. 6. The content of free carbon formed in the process of iron ore reduction/cementation at different temperatures by $\text{H}_2\text{-CH}_4\text{-Ar}$ gas mixture (55 vol% H_2 and 35 vol% CH_4).

In the first series, cementite was prepared at different temperatures using 35 vol% CH_4 , 55 vol% H_2 and 10 vol% Ar. Exposure time in the reducing/carburising atmosphere was 10 min at 850°C, 15 min at 750°C and 800°C, and 30 min at 650°C and 700°C. Afterwards the reducing/carburising gas atmosphere was switched to pure argon at the same experimental temperature. Cementite fraction at different temperatures is presented in Fig. 9. In general, effect of temperature on cementite decomposition in argon is similar to that in $\text{CH}_4\text{-H}_2\text{-Ar}$ gas. Cementite was also most stable at 750°C. Increase in temperature from 750°C to 800°C and further to 850°C accelerated cementite decomposition. However, the rate of cementite decomposition also increased with the decrease in temperature in the temperature range 750–650°C.

In the second experimental series, iron ore was reduced to cementite by $\text{CH}_4\text{-H}_2\text{-Ar}$ gas at 750°C for 15 min. Then temperature was changed to another value in the interval of 500–850°C, and the gas atmosphere was switched to argon. Cementite fraction as a function of the decomposition time at different temperatures is shown in Fig. 10. It should be mentioned that a temperature change from 750°C to other values in the interval 500–850°C took about 15 min. Therefore, during those 15 min experimental conditions were non-isothermal. It is seen in Fig. 10 that the rate of cementite decomposition increased with increasing temperature from 500 to 600°C, and decreased with further increase in temperature to 730–750°C. Cementite was relatively stable at these temperatures. At temperatures above 750°C, the rate of cementite decomposition increased with increasing temperature. Figure 10 shows that cementite was most stable at about 750°C, and least stable at 600°C.

The morphology of cross sections of samples with cementite decomposed in argon is shown in Fig. 11. Generally, iron formed as a result of cementite decomposi-

Fig. 7. Morphologies of sectioned samples subjected to reduction/cementation by the $\text{CH}_4\text{-H}_2\text{-Ar}$ gas (35 vol% CH_4 , 55 vol% H_2 and 10 vol% Ar) at 750°C with reaction time of a) 5 min, b) 10 min, and c) 120 min.

Fig. 8. Morphologies of sectioned samples of iron ore subjected to reduction/cementation by the $\text{CH}_4\text{-H}_2\text{-Ar}$ gas (35 vol% CH_4 , 55 vol% H_2 and 10 vol% Ar) at 750°C with reaction time of a) 90 min and b) 120 min (samples were etched in the boiling solution of alkaline sodium picrate).

tion was distributed uniformly in the interior of the cementite phase.

4. Discussion

Process of cementite formation includes the following stages:

- (1) Adsorption of methane on the iron surface and its decomposition with the formation of adsorbed carbon and hydrogen.
- (2) Diffusion of carbon into metallic iron and formation of supersaturated solution of carbon in iron.
- (3) Formation of cementite by reaction of iron with dis-

solved carbon.

The rate of iron cementation is suggested be controlled by the reaction of methane adsorption and decomposition on the iron surface. Methane mass transfer in the gas phase and carbon diffusion in the iron are relatively fast. This conclusion is consistent with the fact that surface-active sulphur has a significant effect on iron carburisation.^{4,5)} The other evidence to support this suggestion is that the rate of iron cementation increased with increasing temperature in the whole temperature interval investigated. The diffusion coefficient of carbon in iron increases significantly when iron is converted from austenite to ferrite. If carbon diffusion in iron were the rate-controlling step, a jump in the rate of cementation would be expected when austenite is transferred to ferrite, which was not observed experimentally. Fruehan⁹⁾ in his study of the effect of H₂O and H₂S on the rate of carburisation of iron also came to the conclusion that the rate of iron cementation was controlled by interfacial reaction.

At temperatures above 550°C and pressure 1 atm methane is thermodynamically unstable and decomposes to carbon and hydrogen. The reaction of methane decomposition is catalysed by metallic iron. Methane cracking occurs through intermediate hydrocarbons. Overall reaction of methane adsorption and cracking on the iron surface may be presented as:

where C_{ad} is adsorbed carbon.

Then adsorbed carbon dissolves in iron:

Combining reactions (1) and (2), we obtain

On the basis of this reaction, thermodynamic activity of carbon dissolved in iron may be defined as (the standard state for dissolved carbon is graphite)

$$a_{\text{C}} = K(P_{\text{CH}_4}/P_{\text{H}_2}^2) \quad (4)$$

where K is the equilibrium constant of the reaction (5) of methane cracking,

($P_{\text{CH}_4}/P_{\text{H}_2}^2$) ratio in the gas phase which is in equilibrium with graphite is fixed at constant temperature and will be referred to as ($P_{\text{CH}_4}/P_{\text{H}_2}^2$)_{gr}. The Eq. (4) may be re-written in the form:

Fig. 9. Decomposition of cementite at different temperatures in argon atmosphere.

Fig. 10. Decomposition of cementite at different temperatures in argon (in all experiments the original sample of cementite was produced at 750°C).

Fig. 11. Morphologies of a sectioned sample with cementite decomposed in argon at a) 700°C for 1 hr, b) 750°C for 7 hr, and c) 850°C for 1 hr. All samples were etched in the boiling solution of alkaline sodium picrate.

$$a_C = (P_{CH_4}/P_{H_2}^2)/(P_{CH_4}/P_{H_2}^2)_{gr} \dots\dots\dots(6)$$

When $(P_{CH_4}/P_{H_2}^2) > (P_{CH_4}/P_{H_2}^2)_{gr}$, activity of carbon dissolved in iron will be > 1 . This means that the iron-carbon solution in equilibrium with gas with such high $(P_{CH_4}/P_{H_2}^2)$ ratio is super-saturated with carbon, which causes cementite formation.

The key factor in the iron cementation is a high rate of the carburisation reaction (3) in comparison with a rate of reaction (5) of solid carbon deposition. If solid carbon is formed on the iron surface, the $(P_{CH_4}/P_{H_2}^2)$ ratio on the gas/solid interface will be maintained equal to $(P_{CH_4}/P_{H_2}^2)_{gr}$ regardless the high $(P_{CH_4}/P_{H_2}^2)$ ratio in the inlet gas. Under such conditions, cementation of iron is thermodynamically unfeasible.

Rate of chemical reaction (3), R , is proportional to the fraction of the iron surface area available for adsorption, $(1-\theta)$, and is a function of partial pressures of methane P_{CH_4} and hydrogen P_{H_2} :

$$R = kA f(P_{CH_4}, P_{H_2})(1-\theta) \dots\dots\dots(7)$$

Our experiments showed that cementation of iron powder (Aldrich Chemical Company, Inc.) with low surface area ($0.27 \text{ m}^2/\text{g}$) was practically invisible at $600\text{--}925^\circ\text{C}$. High cementation rates in the present work (Fig. 5) were obtained only on freshly reduced iron with high surface area. The effect of the surface area on the rate of iron cementation was illustrated by the following experiments. Iron ore was reduced by H_2 -Ar gas (25 vol% H_2) at 750 , 925 and 1000°C in 30 min, and also at 925 and 1000°C in 120 min. Reduced iron was then cooled down to 750°C in argon atmosphere and carburised by gas, containing 35 vol% CH_4 , 55 vol% H_2 and 10 vol% Ar for 15 min. Cementite fraction in samples obtained at different reduction temperatures is shown in Fig. 12. Increasing reduction temperature and reduction time decreased the surface area of reduced iron. As a result, the rate of cementation decreased according to Eq. (7).

The chemical reaction rate constant normally increases with increasing temperature in accordance with the Arrhenius law. However, the rate of cementite decomposition changes with temperature in a more complex way. It decreases with increasing temperature in the temperature interval $600\text{--}750^\circ\text{C}$. It is seen in Fig. 13 that the rate of cementite decomposition is highest at around 600°C . Cementite is the most stable at $730\text{--}750^\circ\text{C}$ in the temperature range $550\text{--}850^\circ\text{C}$.

Cementite decomposition includes two reactions: 1) phase transformation of cementite to super-saturated carbon solution in iron, and 2) carbon precipitation from the super-saturated solution. It is known from the Fe-Fe₃C phase diagram that cementite decomposes to austenite and graphite at temperatures above 727°C , and to ferrite and graphite at temperatures below 727°C . At this temperature the thermodynamic driving force for cementite decomposition to ferrite and graphite is the same as that to austenite and graphite. However, at 727°C the diffusivity of carbon in ferrite is $8.1 \times 10^{-7} \text{ cm}^2/\text{sec}$,¹⁰⁾ which is much higher than that in austenite, $1.45 \times 10^{-8} \text{ cm}^2/\text{sec}$.¹¹⁾ So the rate of cementite decomposition to ferrite and graphite is much higher than that to austenite and graphite at this temperature. Increase

Fig. 12. Iron ore reduced at different temperatures in hydrogen-argon gas mixture (25 vol% H_2) for 30 min and 120 min, and then carburised at 750°C for 15 min in methane-hydrogen-argon gas mixture (35 vol% CH_4 , 55 vol% H_2).

Fig. 13. Rate of cementite decomposition as a function of decomposition temperature in argon atmosphere.

Fig. 14. Arrhenius plot for cementite decomposition rate in argon atmosphere.

in the rate of cementite decomposition as a result of austenite $\rightarrow$ ferrite transformation evidences that the decomposition rate is controlled by carbon diffusion in iron. The austenite $\leftrightarrow$ ferrite transformation occurs not exactly at 727°C , as follows from the phase diagram, but in the temperature interval because of impurities present in the ore. At $600\text{--}750^\circ\text{C}$, iron probably presents as the mixture of ferrite and austenite. This may explain the increase in the rate of cementite decomposition with decreasing temperature in the temperature range $750\text{--}600^\circ\text{C}$. At temperature below 600°C , the apparent activation energy for cementite decomposition was found to be 90.8 kJ/mol (Fig. 14), which is close to the diffusion activation energy for carbon in ferrite, 85.0 kJ/mol , reported by Wert.¹⁰⁾ At temperature above

750°C the activation energy was 92.4 kJ/mol (Fig. 14), close to 96.9 kJ/mol reported by Tibbetts¹¹⁾ for carbon diffusion in austenite (2.11 wt% C). This supports the suggestion that diffusion of carbon in iron is the rate limiting stage in the cementite decomposition process.

5. Conclusions

Iron ore reduction, iron cementation and cementite decomposition were investigated using CH₄-H₂-Ar gas mixture (35 vol% CH₄, 55 vol% H₂ and 10 vol% Ar) in the temperature range from 600°C to 925°C. Hematite was first reduced to metallic iron and then cementation reaction took place. Increase in temperature accelerated both reduction and cementation processes. Extent of reduction of 95% was achieved for about 15 min at 650°C, 10 min at 750°C and 7 min at 850°C. Cementite formation was completed for about 30 min at 700°C, 15 min at 750°C and 800°C, and 10 min at 850°C.

Cementite was unstable and decomposed to iron (ferrite or austenite) and free carbon. In the temperature range 500–850°C, cementite was most stable at about 750°C, and least stable at 600°C. The rate of cementite decomposition increased with increasing temperature at temperature below 600°C and above 750°C. The activation energy for cementite decomposition was found to be 90.8 kJ/mol at temperature below 600°C, and 92.4 kJ/mol at temperature above 750°C. In the temperature range 600–750°C, the rate of ce-

mentite decomposition increased with decreasing temperature. Such behavior was attributed to the fact that at temperatures above 750°C cementite was decomposed to austenite and carbon, while at temperatures below 600°C, cementite was decomposed to ferrite and carbon.

It is suggested that the rate of cementite formation is limited by methane adsorption and cracking. While the limiting stage for cementite decomposition is suggested to be carbon diffusion.

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