1. Introduction

Iron carbide is an important phase in steels and it is also an attractive material for steelmaking. It can be used for magnetic recording medium and electromagnetic shielding materials due to its special magnetic properties. It is produced from iron ore fines in a fluidized bed using a gas mixture of hydrogen and hydrocarbons at a relatively low temperature. However, since iron carbide is metastable at all temperatures compared with graphite and its saturated solution in iron, it is easy to decompose to solid carbon and metallic iron at elevated temperature. The first commercial scale process for producing iron carbides at the Trinidad island did not succeed. This process needs long residence times and a few residual iron oxides leaves in the iron carbide depending on ore type. In recent year many researches were focused on this area to investigate the influences of gas composition, temperature, and additives on the process of iron carbide formation. The yield and the stability of iron carbide have been paid more attention. In 1995, Grabke and Müller-Lorenz found that sulfur has the effect on the stability of iron carbide. In 1997, Hayashi and Iguchi reported the synthesis of iron carbide by reaction of iron ores with H₂–CO gas mixtures bearing traces of sulfur. They confirmed the role of sulfur on the iron carbide synthesis, which inhibits precipitation of carbon and stabilizes iron carbides through allowing substantially carburization into iron bulk. Wang et al. reported that potassium carbonate and calcium chloride can accelerate the iron carbide synthesis. Egashira et al. studied the effect of gangue compositions such as SiO₂, Al₂O₃, MgO and CaO on the behavior of the iron carbide formation. It was recognized that the formation of iron carbide is suppressed by CaO and promoted by Al₂O₃.

In order to clarify the influences of other oxide additives on the production of iron carbide and to improve the production yield of iron carbide, the effect of MnO, Cr₂O₃, TiO₂ and V₂O₅ additives on iron carbide production from iron ore fines was experimentally investigated in present work.

2. Experimental

2.1. Specimen

The Brazilian iron ore was used, and its chemical composition is listed in Table 1. Fine powders with grain size less than 80 mesh were made from this iron ore block and the pellets were made from the mixture of iron ore powder and one kind of reagent grade oxide additives (MnO₂, Cr₂O₃, TiO₂ and V₂O₅), in the ratio of 1, 3, and 5 mass%, respectively. The original grain size of the oxide additives are listed in Table 2. Pellet without oxide addition was prepared for the comparison. The pellets were sintered in air at 1173 K for 15 min and the phases in the sintered pellets were examined by XRD. The diameter of sintered pellets is 7 to 8 mm and their weight is 1.5±0.15 g. MnO₂ can be de-
was then put into the reaction tube. Argon was changed to 20 min. Iron ore pellet contained in a basket with a chain gas were mixed.

2.3. Experimental Procedures

After the reaction tube was heated to 1 023 K, argon gas was flowed into the reaction tube to purge the tube for 20 min. Iron ore pellet contained in a basket with a chain was then put into the reaction tube. Argon was changed to methane and hydrogen mixture of 70%H2–30%CH4 with the flow rate of 1 000 cm3/min after the furnace temperature stabilized again. The weight change of the sample due to reduction and carburization was recorded on line by the balance with computer. When the reaction time attained a certain period and the weighing was stopped, methane and hydrogen mixture gas was changed to argon with a large flow rate. At the same time the quartz reaction tube with sample was pull out from the furnace, keeping the flow of argon gas to quench the sample. The samples were analyzed by X-ray diffraction, Mossbauer spectra and EDX. The X-ray diffraction was carried out by a PANalytical X'Pert PRO diffraction system with Cu Kα radiation. The Mossbauer spectra were recorded at room temperature on a constant acceleration and conventional standard transmission spectrometer (Wissel) with a 57Co(Pd) source. The drive velocity scale was calibrated with a 25 μm thick pure α-Fe foil. All isomer shifts were quoted relative to the center of the α-Fe calibration spectrum. The experimental Fe Mossbauer spectra were fitted by a least-squares regression fitting procedure.

3. Results and Discussion

3.1. The Influences of Oxide Additives on Reduction and Carburization Rates

The weight loss curves of iron ore pellets with or without oxide additions are shown in Figs. 2(a)–2(d), where the weight loss ratio is relative to the original weight of sintered pellet sample in mass percent. Figure 2 shows that the kinds and quantity of oxides addition have different effects on the reduction and carburization processes. From Figs. 2(a) and 2(b), it can be seen that the weight loss curves of samples with Cr2O3 and MnO additions are similar to that without addition. The weight losses of Cr2O3 and MnO added pellets are less than that with no additives until the maximum weight loss was observed and the deviation from the line without oxide additions becomes large with increasing contents of additives. The times of maximum weight loss for pellets with or without oxide additives are almost same. After the turning point the increase of weight shows similar tendency. It can be estimated from these curves that the decrease of maximum weight loss due to Cr2O3 and MnO addition are caused by the difference of the reducibility of oxides, since Cr2O3 and MnO are more difficult to be reduced than FeO. The addition of Cr2O3 and MnO has no big influence on FeO reduction and the carburization of reduced iron. The different behaviors were observed as shown in Figs. 2(c) and 2(d) when V2O5 and TiO2 was added in the pellets. From Fig. 2(c) the maximum weight loss for samples added 1, 3 and 5 mass% V2O5 decreased comparing with that without additive. The important phenomenon is that the weight loss curve with V2O5 addition deviated from that without additive. The tendency of the weight loss curves in Fig. 2(c) means that the V2O5 addition increases the carburization rate of reduced iron. On the other hand, as shown in Fig. 2(d), the addition of TiO2 retards the reduction of iron oxide and the carburization reaction.

Table 1. Chemical composition of iron ore (mass%).

<table>
<thead>
<tr>
<th>Composition</th>
<th>T. Fe</th>
<th>FeO</th>
<th>SiO2</th>
<th>CaO</th>
<th>MgO</th>
<th>S</th>
<th>Fe2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>67.05</td>
<td>0.81</td>
<td>1.89</td>
<td>0.89</td>
<td>0.11</td>
<td>0.033</td>
<td>94.89</td>
</tr>
</tbody>
</table>

Table 2. Original grain size of oxide additives (μm).

<table>
<thead>
<tr>
<th>Oxide additives</th>
<th>MnO2</th>
<th>Cr2O3</th>
<th>TiO2</th>
<th>V2O5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size</td>
<td>≤40</td>
<td>≤5</td>
<td>≤5</td>
<td>≤100</td>
</tr>
</tbody>
</table>

Fig. 1. Experimental Apparatus. 1. hydrogen gas cylinder; 2. methane gas cylinder; 3. argon gas cylinder; 4. valve; 5. pressure gauge; 6. dehydration chain; 7. flowmeter; 8. gas mixing bottle; 9. triple valve; 10. balance; 11. quartz tube (gas inlet); 12. computer; 13. stainless steel tube; 14. rubber stopper; 15. thermocouple; 16. mullite furnace tube; 17. quartz reaction tube; 18. FeCrAl chain; 19. sample basket; 20. furnace; 21. thermocouple.
3.2. X-ray Diffraction Analysis for the Quenched Pellets

X-ray diffraction analysis was carried out for the quenched samples reacted for 30 min without additive, 26 min with 1% V$_2$O$_5$ addition, and 30 min with 5% TiO$_2$ addition. The XRD patterns are shown in Fig. 3. It is clear that for the sample without oxide addition the main composition after the reaction of 30 min is iron carbide with a few free carbon and metal iron. However, in the sample with 5% TiO$_2$ addition, more iron remained and it was not completely carburized. For the sample with only 1% V$_2$O$_5$ addition, the main phase after 26 min is iron carbide, and no metallic iron was observed by XRD even though a small quantity of free carbon existed. These finding confirmed that V$_2$O$_5$ addition enhances the carburization reaction and TiO$_2$ retards this reaction.

3.3. Effects of Oxide Additives on the Reduction and Carburization Process

The Mossbauer spectra of samples obtained by iron ore reduction and carburization with 70%H$_2$–30%CH$_4$ gas at 1 023 K for 30 min are shown in Fig. 4. The results are summarized in Table 3. Although the main phases are iron carbide and metallic iron in the three samples, the relative intensities are quite different from each others. As summarized in Table 3, the ratio of iron converted to iron carbide for the sample added with 5% TiO$_2$ is 73.2% but that added with 1% V$_2$O$_5$ is 96.0% at the same condition. From the accurate phase composition obtained by Mossbauer measurement it is confirmed that V$_2$O$_5$ addition can promote the carburization reaction and TiO$_2$ addition retards this reaction.

Iron ore pellets with 1% V$_2$O$_5$ addition and without addition were analyzed by Mossbauer spectra after the reaction with 70%H$_2$–30%CH$_4$ gas mixture at 1 023 K for various
times. The obtained spectra are shown in Fig. 5. For both pellets added 1% V$_2$O$_5$ and without addition, the reduction and carburization sequences are as follows at the present experimental conditions:

\[ \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \rightarrow \text{Fe}_3\text{C} \]

This is in good agreement with that observed by Park et al. using Mossbauer measurement. The phase composition change of these two kinds of pellets with reaction time was quantitatively determined from Mossbauer spectra and plotted in Fig. 6. The reaction of iron oxide reduction and carburization of metallic iron can be separated to three stages: (1) in the initial 10 min, the main reaction was the reduction of iron oxide to magnetite and then to wustite, and the reactions from hematite to magnetite and from wustite to metallic iron were fast. Therefore, the iron ore was quickly reduced to FeO and metallic iron; (2) In the middle stage (10 to 20 min) methane cracked quickly due to the existence of metallic iron and iron carbide was formed, while the remained FeO was reduced to iron. (3) In third stage, since the process of iron carbide formation and decomposition were in steady state, the contents of iron carbide and metallic iron tended to be constant.

The addition of V$_2$O$_5$ increased the ratio of reduced iron to 88.7% comparing with that of 75.9% with no addition in the initial 10 min. The V$_2$O$_5$ existed in the pellet may pro-
mote the cracking of methane to increase the content of hydrogen in the atmosphere and enhanced the reduction of iron ore. The V$_2$O$_5$ addition also accelerates the initial carburization reaction rate significantly larger than that of no addition.

Umemoto and Tsuchiya$^{13}$ calculated the free energy of formation of alloyed iron carbide from graphite and $\alpha$-Fe$_{0.95}$M$_{0.05}$ solid solution in equilibrium with graphite where M represents Ni, Mo, V, Mn, and Cr. Their result of calculation indicated that Mo, V, Mn, and Cr can decrease the free energy of formation of alloyed iron carbide. Therefore, the alloyed iron carbide is more stable than pure iron carbide. However, in present experimental condition, no evidence was found for the formation of alloyed iron carbide. The stable phase diagrams of M–H–O (M = Ni, Mo, V, Mn, Fe) were calculated at 1 000 K using the FactSage software. The result shows that Cr$_2$O$_3$, TiO$_2$ keep no change but V$_2$O$_5$ can be reduced to V$_2$O$_3$ and Mn$_2$O$_3$ (which was decomposed from MnO$_2$ during sintering) can be reduced to MnO during the reduction of iron ore. The EDX analysis confirmed that vanadium and oxygen coexisted with iron carbide in the sample with 1% V$_2$O$_5$ addition reacted for 30 min, as illustrated in Fig. 7. The promotion of reduction and carburization by the addition of V$_2$O$_5$ may be caused by the enhancement of catalytic effect of reduced metallic iron on methane cracking which can enhance both iron ore reduction and carburization. Free carbon found in the sample with 1% V$_2$O$_5$ addition reacted for 26 min also support this mechanism, as shown in Fig. 3, where no free carbon was found in the sample added with TiO$_2$ and very little free carbon was found in the sample without oxide addition. Even though excess carbon was observed in the sample with 1% V$_2$O$_5$ addition, iron carbide was still stable during experimental period.

Methane is thermodynamically unstable and decomposes to carbon and hydrogen at temperature above 823 K and pressure of 10$^5$ Pa. The reaction of methane decomposition is catalyzed by metallic iron. Zhang and Ostrovski$^{14}$ confirmed by experiments that the carburization rate of iron is proportion to the fraction of the iron surface area available for adsorption. They suggested that the rate of iron carbide formation is limited by methane adsorption and cracking. Arabczyk et al.$^{15}$ proposed a mechanism of methane dissociative decomposition involving an active site composed of one uncovered free iron atom and some neighbouring n iron atoms covered with oxygen atoms (1≤n≤3). The carburization process occurs only if n (1 or 2 or 3) hydrogen atoms from this methane molecule are bounded simultaneously to the neighbouring iron atoms covered with oxygen. Their experimental results support this model but the apparent activation energy for iron carbide formation and decarburization does not depend on the chemical composition of oxide additives, because totally 7.85 mass% of oxides such as K, Al, Ca, Si, Mg, Cr, Ni, and V oxides were included in their samples, it is impossible to distinguish the role of each oxides. This mechanism can be used to explain the result of present work as that the surface oxygen with V$_2$O$_5$ addition can promote methane adsorption and cracking on the surface of reduced iron and increased the rate of iron carbide formation. The different effects of V$_2$O$_5$, TiO$_2$, Cr$_2$O$_3$ and MnO additives on iron carbide formation may due to their different electron interaction with iron which results in the different catalytic effects for methane adsorption and cracking. It was also reported that the TiO$_2$ supported Fe catalyst has stronger effect on methane synthesis from CO$_2$ and hydrogen than that of ZrO$_2$, Al$_2$O$_3$ and SiO$_2$ supported ones.$^{16}$ It means that TiO$_2$ supported Fe catalyst does not favor the methane adsorption and cracking. This is in accordance with the present finding that TiO$_2$ addition retards the formation of iron carbide.

### 4. Conclusions

The influences of 1 to 5 mass% MnO, Cr$_2$O$_3$, TiO$_2$ and V$_2$O$_5$ additives on iron carbide formation from iron ore fines reacting with 70%H$_2$:30%CH$_4$ gas mixture at 1 023 K were experimentally investigated by gravimetric measurement. Phases formed in the reaction of iron carbide formation with and without oxide addition were analyzed by XRD, Mossbauer, and EDX technique. The composition change of iron, iron oxides, and iron carbide during reaction were quantitatively determined for samples added with 1% V$_2$O$_5$ and without oxide addition. The addition of Cr$_2$O$_3$ and MnO has no significant effect on the iron carbide formation. The TiO$_2$ addition retards both reduction of iron ore and iron carburization. The V$_2$O$_5$ addition increases the rate of iron carbide formation and also increases the conversion yields from iron ore to iron carbide to 96%. The mechanism for the promotion of reduction and carburization...
tion that the addition of V$_2$O$_5$ may have the catalytic effect for the cracking of methane which can enhance both reduction of iron ore and carburization is proposed.

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