Identification of Mn and Fe-Mn Carbide Phases by Effluent Gas Analysis*

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The form of the compounds of Mn and Fe-Mn carbides produced by the carbon thermic reduction of their oxides is determined by the effluent gas analysis (EGA) method using He-O₂ gas mixture. The obtained results are as follows:

(1) The oxidation of Mn carbide to Mn₂O₃ starts at 789 K and that of Fe-Mn carbide occurs from 730 K, resulting in a mixture of Mn₂O₃ and Fe₂O₃.

(2) By the isothermal EGA method at 953 and 903 K, Mn and Fe-Mn carbides are identified to be Mn₇C₃ and (Fe, Mn)₇C₃ phases, respectively.

These observations are supported by the results of EPMA and X-ray diffraction examinations. Thus, it is concluded that the EGA method is useful tool for a state analysis of carbides.

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I. Introduction

The vapour pressure of metallic manganese formed in the reduction process of MnO with carbon is high, and it reaches 95 Pa⁽¹⁾ at 1473 K, and hence the application of the thermogravimetric technique for this process seems to be incorrect because of the loss through volatilization.

The kinetics of the carbon thermic reduction of manganese oxides (MnO₂, Mn₂O₃, Mn₃O₄ and MnO) was studied by means of the effluent gas analysis method⁽²⁾⁻⁽⁴⁾. It was felt that a state analysis of Mn and Fe-Mn carbides produced by the carbon thermic reduction of their oxides would contribute to the study of the reduction process of manganese ore with carbon. Only a few studies⁽⁵⁾⁽⁶⁾ have been reported about the determination of carbide in steel.

The present study is concerned with the phase analysis of Mn carbide and Fe-Mn carbide formed in the reduction process of MnO and MnFe₂O₄ with carbon⁽³⁾⁽⁴⁾ by the effluent gas analysis method using a He-O₂ mixture.

II. Experimental Procedure

1. Specimen

MnO₂ was prepared by heating a reagent of manganese nitrate at 473 K. Then MnO was prepared by heating MnO₂ at 1273 K under a H₂ atmosphere for 86.4 ks. A mixture of MnO and a reagent of ferric oxide was heated in an electrical resistant furnace under an Argon atmosphere for 43.2 ks. These oxide samples obtained had chemical composition of MnO and MnFe₂O₄. Mn and Fe-Mn carbide samples were prepared by the isothermal reduction of the mixture of MnO/C=1/1.5 (molar ratio) at 1423 K and MnFe₂O₄/C=1/4.95 at 1433 K under a He atmosphere⁽³⁾⁽⁴⁾. Carbon powder was heated at 1473 K under a He atmosphere, and iron carbide was prepared by the thermal decomposition of Prussian blue at 1173 K⁽⁷⁾.

2. Effluent gas analysis (EGA) method

The effluent gas analysis method which is employed in the present study has been developed by Mizutani *et al.*⁽⁸⁾ to study the solid-state reactions involving absorption or evolution of gases. An experimental apparatus used in the present study was illustrated in Fig. 1. A sample container (6) was inserted at the end of a reaction vessel (5). After this apparatus

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Fig. 1 Experimental apparatus.

was stabilized in a mixed gas stream of He and O₂, which ran into the reaction vessel, the sample container was moved to the center of the reaction vessel with a magnet (10). A horizontal electric furnace (11) can be heated at a constant rate of ascending temperature from room temperature to about 1673 K by a temperature controller (13).

CO₂ gas evolved by the oxidation of sample was absorbed by a trap (7) and the consumption of oxygen was detected by a thermal conductivity detector (TCD), (8), before and after the oxidation of carbide samples.

The samples of Mn and Fe-Mn carbides prepared by the carbon thermic reduction of MnO and MnFe₂O₄⁽³⁾⁽⁴⁾, as well as the residue of this Fe-Mn carbide after analysed by the effluent gas analysis method were also identified by the X-ray diffraction method using Fe-K α radiation. The results are illustrated in Fig. 2.

Fig. 2 X-ray diffraction patterns from the reduction products and the residue of Fe-Mn carbide in the He+28.6%O₂ mixture at 953 K.

As seen in Fig. 2(C), the residue is identified to be a mixture of Mn₂O₃ and Fe₂O₃.

For the oxidation of Mn and Fe-Mn carbides, the following reaction is given:

where MC_x (M=Fe, Mn) represents Mn carbide and Fe-Mn carbide. The oxygen consumption detected by a TCD was estimated according to the procedure of calculation⁽⁴⁾ for gaschromatograph. The content, *x*, of carbon in carbide (MC_x) was determined by the following equation:

$$\left(\frac{3}{4} + x\right)(\text{sample weight})/(\text{molecular weight of } MC_x) = (\text{oxygen consumption}). \quad (2)$$

In the present study, CO gas was not detected by the preliminary experiment using gaschromatograph (Type 163, Hitachi Seisakusho Co., Japan).

Furthermore, these carbide samples were decomposed by means of the potentiostatic elec-

trolytic method⁽⁹⁾⁽¹⁰⁾. Ammoniumpersulfate- and o - Phenanthroline - spectrophotometries were used to determine the amounts of manganese and iron, respectively.

III. Results and Discussion

1. Non-isothermal oxidation process

Mn carbide was prepared by the isothermal reduction of MnO with carbon ($\text{MnO}/\text{C}=1/1.5$) at 1423 K. The EGA curves for this Mn carbide, Mn_7C_3 made in the same way reported by McCabe *et al.*⁽¹¹⁾ and elemental carbon as a reducing agent under $\text{He} + 28.6\% \text{O}_2$ mixture are illustrated in Fig. 3(A)–(C), respectively. Figure 3(D) summarizes these EGA curves to clear the difference in starting temperature of the oxidation reactions. The oxidation of Mn carbide to Mn_2O_3 starts at about 789 K and the maximum peak in an EGA curve is at about 893 K. The thermal decomposition of this Mn_2O_3 to Mn_3O_4 follows at elevated temperatures. The oxidation of Mn_7C_3 occurs from 789 K, and the CO_2 evolution by the oxidation of elemental carbon starts at about 853 K.

For the state analysis of Fe–Mn carbide, a sample was prepared by the isothermal reduc-

Fig. 3 Effluent gas analysis curves for Mn carbide (A), Mn_7C_3 (B) and free carbon (C), where (D) summarizes these EGA curves. ($\text{He} + 28.6\% \text{O}_2$: $2.13 \times 10^{-6} \text{ m}^3/\text{s}$, 0.03 K/s)

Fig. 4 Effluent gas analysis curves for Fe–Mn carbide (A), Fe_3C (B), Mn_7C_3 (C) and free carbon (D), where (E) summarizes these EGA curves. ($\text{He} + 28.6\% \text{O}_2$: $2.13 \times 10^{-6} \text{ m}^3/\text{s}$)

tion of MnFe_2O_4 with carbon under a fixed condition ($\text{MnFe}_2\text{O}_4/\text{C}=1/4.95$, 1433 K). The EGA curves of Fe–Mn carbide, Fe_3C , Mn_7C_3 and elemental carbon are illustrated in Fig. 4(A)–(D), respectively. The oxidation of Fe–Mn carbide to Mn_2O_3 and Fe_2O_3 begins at about 730 K, and the oxidation of Fe_3C starts from 910 K.

2. State analysis of carbide at the isothermal EGA

The isothermal EGA curves at 953 K for Mn carbide are illustrated in Fig. 5. Mn carbide is obtained by the complete reduction of MnO at 1423 K with different carbon content ((A): $\text{MnO}/\text{C}=1/1$, (B): $\text{MnO}/\text{C}=1/2$, and α is the fraction of reduction of MnO. For the oxidation of the sample containing with excess carbon ($\text{MnO}/\text{C}=1/2$), CO_2 evolution in the EGA curve occurs gradually over a long period of time. Therefore, a clear distinction can be observed between the oxidation of Mn carbide and that of elemental carbon.

Fig. 5 Effluent gas analysis curves for the Mn carbide obtained by the reduction of MnO with carbon. (condition of EGA; 953 K, He+28.6%O₂: 2.13×10^{-6} m³/s)

Table 1 Results of state analysis for Mn and Fe-Mn carbides by effluent gas analysis method at 953 K and 903 K.

Carbide	Sample weight ($\times 10^{-5}$ kg)	Oxygen consumption ($\times 10^{-3}$ mol)	x (MC _x)
(A) Mn-C	5.19	1.02	0.43
(B) [MnO/C=1/1.5] 1423 K	5.90	1.14	0.41
(C) Fe-Mn-C	4.02	0.78	0.42
(D) [MnFe ₂ O ₄ /C=] 1/4.95, 1433 K	4.47	0.89	0.45

Fig. 6 Effluent gas analysis curves for the Fe-Mn carbide obtained by the reduction of MnFe₂O₄ at 1433 K with carbon. (condition of EGA; 903 K, He+28.6%O₂: 2.13×10^{-6} m³/s)

The results obtained for the oxygen consumption and the content of carbon in carbides are tabulated in Table 1. In the present study, the value of x in MnC _{x} is calculated as about 0.43 from eq. (2), which corresponds to the Mn₇C₃

formed in the reduction process of MnO with carbon⁽³⁾.

The samples quenched from the chosen experimental conditions were identified by means of the X-ray diffraction method and analyzed by the potentiostatic electrolytic method⁽⁹⁾. This sample was confirmed to have the same phase and the same value of x as determined by the EGA method.

The EGA curves using a He-O₂ mixture for Fe-Mn carbide at the constant temperature of 903 K are illustrated in Fig. 6. Fe-Mn carbide is obtained by the complete reduction of MnFe₂O₄ at 1433 K with different carbon contents ((A): MnFe₂O₄/C=1/4.95, (B): MnFe₂O₄/C=1/10)[†]. For the experiment corresponding to excess carbon (MnFe₂O₄/C=1/10), the CO₂ evolution due to the oxidation of elemental carbon is observed (Fig. 6(B)).

The results obtained for the state analysis of Fe-Mn carbide are also tabulated in Table 1(C), (D). The carbon content in Fe-Mn carbide is determined as about 0.44 which corresponds to M₇C₃ (M=Fe, Mn). In addition, the ratios of Fe/Mn/C in Fe-Mn carbide phase are determined as 64.3/26.7/9.0 (mass%) by EPMA examination and the chemical analysis⁽⁴⁾.

In the present study, the Fe-Mn carbide formed in the reduction process of MnFe₂O₄ with carbon has been analyzed to be (Fe, Mn)₇C₃ phase in which the stoichiometric ratio, M/C (M=Fe, Mn), is about 91.5/8.5 (mass%)⁽⁴⁾. This carbide phase corresponds to that reported by Butler *et al.*⁽¹²⁾ and Kuo *et al.*⁽¹³⁾.

IV. Summary

Mn and Fe-Mn carbide phases formed in the reduction process of MnO and MnFe₂O₄ with carbon are determined by the effluent gas analysis method using a He-O₂ mixture. The results are summarized as follows.

[†] The reduction of Fe₂O₃ in MnFe₂O₄ by carbon occurs from 1163 K and that of MnO in MnFe₂O₄ proceeds at 1313 K⁽⁴⁾. A clear distinction between the reduction of MnO and that of Fe₂O₃ in MnFe₂O₄ can be made at the isothermal reduction at 1433 K. Therefore, α presented in Fig. 6 is also the fraction of reduction of MnO in MnFe₂O₄.

(1) The oxidation of Mn carbide to Mn_2O_3 starts at 789 K and that of Fe–Mn carbide occurs from 730 K, resulting in a mixture of Mn_2O_3 and Fe_2O_3 .

(2) By the isothermal effluent gas analysis method at 953 and 903 K, Mn carbide and Fe–Mn carbide are identified to be Mn_7C_3 and $(\text{Fe}, \text{Mn})_7\text{C}_3$ phases, respectively.

(3) EPMA and X-ray diffraction examinations, as well as the chemical analysis show the presence of these carbides in the reduction products of MnO and MnFe_2O_4 with carbon.

It is concluded that the effluent gas analysis method is useful and troubleless tool for a state analysis of carbides.

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