Reduction Mechanism of Iron-Manganese Oxide with Carbon

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Reduction mechanism of iron-manganese oxide with carbon was investigated by an effluent gas analysis method. The reaction between carbide formed in this process and the oxide was also studied. EPMA and X-ray diffraction examinations showed the presence of M_3C phase in the reduction products. Effluent gas analysis method was useful and troubleless for studying such reduction process under high temperature and high vapor pressure conditions and also for extremely refractory-attacking materials.

Keywords: effluent gas analysis method, carbon reduction, iron-manganese oxide, iron-manganese carbide, metallurgical reactions, high temperature, reducing atmosphere, high vapor pressure, electron probe micro analysis, x-ray diffraction

II. Experimental Procedure

I. Introduction

The vapor pressure of metallic manganese formed in the reduction process of MnO with carbon is as high as 95Pa at 1473 K. Therefore, the application of the gravimetric technique to study this reduction process seems to be difficult because of the loss through volatilization. Several investigations dealing with the kinetics of the carbothermic reduction of MnO have been carried out by means of the thermogravimetric method; Baukloh and Ziebell⁽¹⁾ studied the reduction of MnO with carbon in vacuum by measuring the amount of manganese lost by volatilization. Singleton *et al.*⁽²⁾ investigated the high-temperature kinetics of the carbothermic reduction of MnO , and determined that the loss of manganese through volatilization was 0.7% at 1573K for 3.6ks and 0.1% at 1373K for 3.6ks.

Mizutani *et al.*⁽³⁾ and Saito *et al.*⁽⁴⁾ studied the thermal decompositions of calcium and lanthanum oxalate by the effluent gas analysis method (EGA). Similar investigation using gas chromatograph was made by Hockings and Jabojskij⁽⁵⁾ on the rate of reduction of hematite with hydrogen and carbon.

In previous papers⁽⁶⁾⁻⁽⁸⁾, the reduction process of MnO_2 to MnO and pre-reduction process of manganese ores with carbon have been investigated by EGA.

Present study is concerned with the mechanism of carbon reduction of iron-manganese oxide, the identification of iron-manganese carbide formed in this reduction process, and the reaction between iron-manganese carbide and its oxide.

1. Specimen

MnO_2 was prepared from a reagent of recrystallized manganese nitrate by heating at 473K in air. This was then reduced to MnO by hydrogen at 1273K for 86.4ks in an electric furnace. Carbon powder as a reducing agent was heated at 1473K under He atmosphere to eliminate any volatile materials.

Iron-manganese oxide ($MnFe_2O_4$, Jacobsite) was fabricated as illustrated in Fig.1; First, the mixture of 5% excess $MnCO_3$ and Fe_2O_3 powders were heated at 773K for 7.2 ks. After grinding in ethanol solution, sample was pressed into a pellet, $1.3 \times 10^{-2}m$ in diameter and $1 \times 10^{-2}m$ in thickness, and heated at 1373K for 43.2ks. This pellet was crushed into powder and extracted for excess MnO with 6N- $(NH_4)_2SO_4$ solution under CO_2 atmosphere.

2. Experiment

The isothermal and non-isothermal reduction processes were studied by EGA. The experimental apparatus is illustrated in Fig.2. Gases adsorbed or evolved by solid sample which was subjected to programmed temperature change, were determined with the aid of thermal conductivity detectors (TCD.1 and TCD.2). A sample container was inserted at the end of a reaction vessel. After apparatus was stabilized in He or mixture gas ($He+O_2$) which ran into the reaction vessel, the sample container was moved to the center of the reaction vessel with a magnet. A horizontal electric furnace can be heated at a constant rate from room temperature to about 1673K by a controller.

In the reduction process, all gases evolved by the reduction of sample were detected by TCD(1), CO_2 was adsorbed by a trap (ASCARITE), and then residual CO gas can be detected by TCD(2).

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Fig.1 Effluent gas analysis method.

TCD : Thermal conductivity detector.

TCD (1) : O₂, CO, CO₂, H₂O, - - -TCD (2) : O₂, COFig.2 Flowchart for preparation of MnFe₂O₄.

Gas evolution was also detected by a gas chromatograph (Type 163, Hitachi Seisakusho, Japan).

In addition, reduction products were identified by X-ray diffraction using Fe-K α radiation and EPMA examinations.

By preliminary experiment, the loss of manganese through volatilization was determined to be 0.08% at 1373K for 18ks and 0.12% at 1473K for 7.2ks. Thus, satisfactory yields of manganese were obtained under these conditions.

Differential thermal gas analysis method (DTGA) using a mixture gas of He and O₂ as a carrier gas seemed to be useful for identifying the sample of manganese, iron-manganese carbides⁽⁹⁾ and the residue of other carbides.

III. Results and Discussion

1. Nonisothermal reduction process

The reduction process of MnFe₂O₄ was measured by EGA, and the results are presented in Fig.3. The reduction of MnFe₂O₄ started at about 1163K, which yielded the compound, (Mn, Fe)O. The ratio of Mn/Fe is taken to be 1/2. Then, rapid reduction of this compound to MnO and metallic iron followed at 1273K, evolving CO₂.

When carbon was consumed entirely on the reduction process, the reaction between MnO and Fe-Mn carbide occurred with evolving CO gas. The phase of this carbide will be described later.

Fig.3 EGA curves for the non-isothermal reduction of MnFe₂O₄ with carbon.

2. Isothermal reduction process

An example of typical effects of temperature on the reduction of MnFe₂O₄ is illustrated in Fig.4. The reaction rate increases as the temperature increases.

For the earlier stage of the reduction of MnO, Fe-Mn carbide was formed, and a rate equation for interfacial reaction control was applied. Time versus $[1-(1-\alpha')^{1/3}]$ plots showed a straight line in the range of α' up to about 0.7. Where α' corresponds to the fraction of reduction of MnO in MnFe₂O₄. The activation energy of about 205 kJmol⁻¹ was obtained. This value is nearly equal to that for the carbon solution reaction, and hence the indirect gaseous reactions seemed to be predominant, similar to the reduction of chromium oxide and other oxides⁽¹⁰⁾.

3. Reduction products

The isothermal reduction products at 1433K were identified to be a compound with C/MnFe₂O₄ = 4/1.

Fig.4 Effect of temperature on the reduction of MnFe_2O_4 with carbon.

X-ray diffraction patterns of the samples quenched from the points corresponding to $\alpha' = 0, 0.4, 0.7, 1.0$ were illustrated in Fig.5.

In this figure, it is clear that reduction of iron oxide in MnFe_2O_4 is completed at $\alpha' = 0$. MnO , metallic iron and carbon was observed. At $\alpha' = 0.4$, MnO , C , Fe_3C and Fe-Mn carbide were formed. As seen in Fig.5(C), carbon was consumed entirely at $\alpha' = 0.7$, then MnO , Fe-Mn carbide (M_3C) and Fe_3C were formed.

At a later stage of carbon reduction, the reaction between MnO and Fe-Mn carbide to yield metallic iron-manganese occurred.

Fig.5 X-ray diffraction patterns of the products during the reduction of MnFe_2O_4 with carbon at 1433K.

4. Reaction between Fe-Mn oxide and carbide

To study the mechanism of this stage, experiment on the reaction between Fe-Mn Oxide (MnO-FeO) and carbide (M_3C) was carried out.

The dried powders of Fe-Mn Oxide and carbide were separately ground and formed into compacts by die pressing at 10 MPa for 300s, respectively. Then these compacts were pressed into a joined compact. The size of the joined compact was $1.3 \times 10^{-3}\text{m}$ in diameter and $3.5 \times 10^{-3}\text{m}$ in thickness. Next, the joined compacts were heated at 1273K and 1373K for 3.6ks in He atmosphere.

Fig.6 shows the optical photographs of the joined compact measured by micro hi-scope system (HIROX Co. LTD). The reaction between Fe-Mn oxide and carbide did not proceed appreciably at 1273K, whereas it proceeded entirely at 1373K. A porous structure caused by the gas evolution in the carbide phase is observed.

Fig.6 Micro hi-scope photographs of joined compact reacted at 1273K(A) and 1373K(B) for 3.6ks in Helium.

The change of Fe, Mn, O and C contents in the joined compact at 1373K was determined by EPMA examination. It is clear from Fig.7 that Mn and O contents increased in the vicinity of the original joined line. On the contrary, Fe content increased in the carbide phase. Variation of the observed data made it difficult to identify the phase formed, although it is considered to be iron-manganese. The joined compact was porous and difficult to detect oxygen and carbon by EPMA in itself.

Fig.7 Change of contents of Fe(●, ○), Mn(■, □), O(▼, ▽) and C(▲, △) in joined compact reacted at 1373K for 18ks and 54ks, with the distance from the surface of oxide.

Therefore, much amount of oxygen is considered to exist in the joined compact, and the oxygen partial pressure was not so low as expected in the carbon reduction process mentioned before.

IV. Conclusions

Thermal reduction process of iron-manganese oxide was measured by EGA. The results obtained were summarized as follows:

- (1) At an earlier stage of the isothermal reduction of MnO, manganese carbide was formed and carbon solution reaction process was thought to be the rate determining step.
- (2) When carbon was consumed entirely for the low carbon mixture, the reaction between manganese oxide and carbide occurred to yield ferro-manganese.
- (3) In the present study, iron-manganese carbide was identified to be M_{23}C phase by means of X-ray diffraction and EPMA methods.

(4) EGA was useful and troubleless for studying such reduction process under high temperature and high vapor pressure conditions and also for extremely refractory-attacking materials.

Acknowledgement

The authors are grateful to Drs. N. Mizutani and M. Kato of Tokyo Institute of Technology for helpful discussions concerning effluent gas analysis method.

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