REDUCTION OF MnFe$_2$O$_4$ WITHOUT AND WITH CARBON
Simultaneous measurements of humidity sensor and evolved gas analysis

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Abstract

We succeeded in studying the mechanism of hydrogen added carbothermic reduction process of iron-manganese oxide by means of the new technique, simultaneous measurement of evolved gas analysis (EGA) and humidity sensor (HS). Water vapor evolved by the reduction with hydrogen can be detected by HS. Other gas was detected by TCD. Without carbon, the hydrogen reduction process was followed to the formation of the intermediate product between MnO and FeO and finally reduction to the mixture of MnO and Fe. With carbon, the intermediate products between MnO and FeO was formed at about 780 K. The methane was formed in higher temperature than 1073 K and the reduction with carbon proceeded mainly. At higher temperatures, methane decomposed to yield nascent carbon that tended to result in the acceleration of the reduction rate with carbon.

The study is concerned with the mechanism of the hydrogen reduction of MnFe$_2$O$_4$ and the effect of without and with carbon on this reduction by means of combining EGA and HS.

Keywords: evolved gas analysis, humidity sensor, iron-manganese oxide, reduction process

Introduction

The iron-manganese double oxide, MnFe$_2$O$_4$, has been studied and summarized by several investigators [1, 2]. However, the characteristics of high temperature carbothermic reduction process of iron-manganese oxide were not clarified sufficiently. The vapor pressure of metallic manganese formed in the reduction process is about 890 Pa at 1673 K. Therefore, the application of the gravimetric technique to this reduction process seemed to be difficult because of the manganese loss through volatilization.

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It is well known that the hydrogen peak area measured by thermal conductivity detector (TCD) of gas chromatograph is not in proportional to the hydrogen concentration using helium as a carrier gas. Therefore, it is difficult to study the hydrogen reduction process quantitatively by TCD alone. As the evolution of water vapor can be detected by HS using metal oxidized thin film, the simultaneous measurement of the two techniques of TCD and HS is carried out to overcome this problem.

The humidity sensor can be used as a detector for various gas analysis independently or in combination with gas detector such as TCD. This useful new method was applied to the reduction process without and with carbon in pyrometallurgy in order to obtain several useful infomations.

Experimental

Specimens

$MnFe_2O_4$ was prepared by heating the mixture of $MnCO_3$ (41–46% purity (as Mn)) and Fe_2O_3 (99% purity) powders. First, this mixture powders were formed into the pellet and inserted into a ceramic tube placed in an electrical resistance furnace. Then, the pellet was heated at 1373 K under a helium atmosphere for 43.2 ks. This reaction product was crushed into $1.05 \cdot 10^{-4}$ m particle size. The product was identified to be single phase of spinel structure by X-ray analysis.

Carbon powder with high purity as a reducing agent was heated at 1473 K under a helium atmosphere to eliminate any volatile materials.

Experimental apparatus

The isothermal and non-isothermal reduction processes were studied with EGA method. In the hydrogen reduction process, H_2O evolved was measured by means of HS. The experimental apparatus is illustrated in Fig. 1.
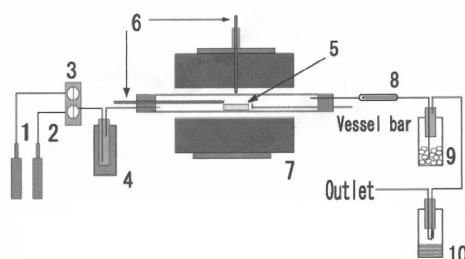
Fig. 1 Evolved gas analysis system: 1 – H_2 gas cylinder; 2 – He gas cylinder; 3 – gas mixer; 4 – deoxidize; 5 – sample; 6 – thermocouple; 7 – reaction furnace; 8 – humidity sensor; 9 – ascarite trap; 10 – TCD

For the fabrication of HS, tantalum wire (99.95% purity) of $1.0 \cdot 10^{-3}$ m in diameter and $1.5 \cdot 10^{-2}$ m in length was mechanically polished to obtain smooth surface. This

wire was cleaned with aceton and oxided at 803 K during 19.8 ks in air. Vacuum evaporation was used for the fabrication of the Au thin film of $1.4 \cdot 10^{-7}$ m in thickness and $1.0 \cdot 10^{-2}$ m in length. Finally, this wire was polished up to remove the Au film for lower electrode and bonded lead wire. The schematic illustration of HS is shown in Fig. 2. This HS belongs to a group of surface sensitive type sensors, which detect the evolution of water vapor by a change in surface electrical conductivity.
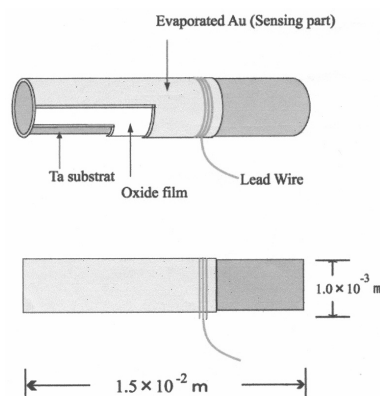
Fig. 2 Schematic illustration of humidity sensor

Sample was heated at a constant heating rate in a helium–hydrogen gas stream as a carrier gas. When interaction such as chemical reaction or adsorption between the carrier gas and sample occurs, the concentration of the hydrogen in the gas stream decreases, and the concentration of H_2O is evolved from sample is measured by HS individually. After elimination of H_2O by trap (Ascarite), the decrease of hydrogen concentration in passing through the TCD cell was detected by TCD with high sensitivity. In the case of methane formation, the gas evolved was detected only by gas chromatograph (GC). The gases evolved were calculated in the same way as GC. The loss of manganese through volatilization was calculated to be less than 0.12% at 1473 K.

Results and discussion

The typical reduction process of $MnFe_2O_4$ in a helium-hydrogen gas stream and the reduction process of $MnFe_2O_4$ with carbon in a helium-hydrogen gas stream are shown in Figs 3 and 4, respectively. As the evolution of H_2O was detected clearly by HS corresponding to the decrease of hydrogen, it was thought that HS responded only to the water vapor. In Fig. 3, the hydrogen reductions proceed in the temperature range of 530–1040 K. The evolution of water vapor in the hydrogen reduction process was followed to the formation of the intermediate product between MnO and FeO and finally reduction to the mixture of MnO and Fe. In Fig. 4, since water vapor was detected by HS at early stage, the reduction with hydrogen proceeded. At higher
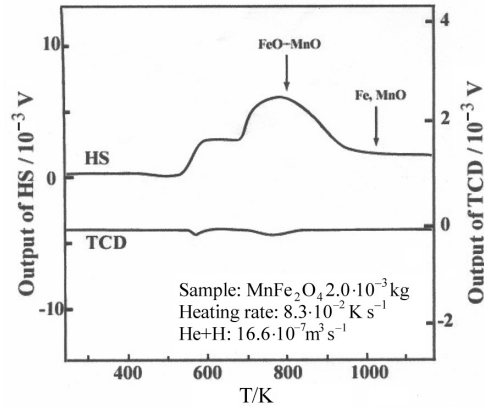
Fig. 3 Evolved gas analysis curves for the reduction of $MnFe_2O_4$ with H_2 and He mixing flow

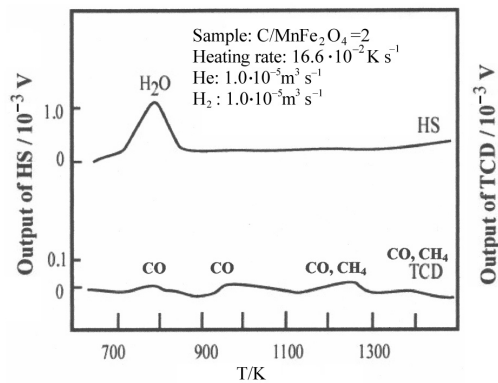**Fig. 4** Evolved gas analysis curves for the carbothermic reduction of $MnFe_2O_4$ with H_2 and He mixing flow

temperature above about 850 K, water vapor wasn't evolved, but CO and CO_2 were detected by TCD. Therefore, the reduction with carbon proceeded mainly at higher temperature of above about 850 K.

When the carbothermic reduction of $MnFe_2O_4$ proceeded, non-stoichiometric compound was also formed and reduced to metallic Fe and MnO up to 1273 K. At higher temperatures, the manganese carbides such as Mn_3C and Mn_7C_3 were formed. When carbon was consumed entirely, the reaction between Mn carbide and MnO occurred to yield metallic manganese. If carbon was added excessively to the carbothermic reduction process, the rate determining reaction seemed to be a chain reaction between CO and CO_2 gas phases as reported by Maru *et al.* [3].

For the addition of hydrogen to the carbothermic reduction process of $MnFe_2O_4$, this reduction process resulted in the formation of methane gas. This methane forma-

tion reaction between carbon and hydrogen proceeded actually at about 1073 K. It has been mentioned in the previous paper [4] that at higher temperatures methane decomposes to yield the formation of nascent carbon which tended to result in the acceleration of reduction rate with carbon. The rate equation for an interfacial reaction was applicable to this reduction process.

The effect of hydrogen on the hydrogen added carbothermic reduction process of $MnFe_2O_4$ was examined in the temperature range of 843 to 1473 K. In the lower temperature range of 843 to 863 K in Fig. 4, the activation energy for measured by HS was estimated to be about 43.1 kJ mol^{-1}. This value was calculated for interface rate determining process by using the relation of $(1-(1-\alpha)^{1/3})$ *vs.* time, where α is the fraction of the volume that has already reacted. This value is nearly equal to that for the hydrogen reduction of iron oxide, although the former reduction process differs from the latter one. Therefore the interactions between MnO and C were often highly complex, and there was a difference in reaction mechanism. At the higher temperature range of 1373 to 1473 K, the rate equation for an interfacial reaction is applicable to this system of $MnFe_2O_4$. It has been mentioned in the previous paper [4] that the activation energy for this reduction was estimated to be 188 kJ mol^{-1} by TCD. This value is smaller than that for the reduction of MnO with only carbon and nearly equal to that for Boudouard's reaction.

In the reduction process of several sorts of iron ores by the reformed natural gas, it was reported by Kasaoka *et al*. [5]*,* that the reducing action of natural gas was weak, but, when the gas was decomposed the reduction became strong. This strong reducing action would be given by hydrogen and nascent carbon formed by the decomposition of hydrocarbon. Therefore, the fundamental data obtained in this study seems to be useful to develop the direct one step reduction process of iron-manganese ores, and contribute to save the energy of ferroalloy manufacturing industry.

It is concluded that the multi-technique of EGA and HS has made it possible to clarify the hydrogen addition effect that takes place in the reduction process of manganese oxide with carbon.

Conclusions

The kinetics of hydrogen reduction of iron-manganese oxide and the effect of hydrogen addition on the carbothermic reduction of $MnFe_2O_4$ were studied by the new technique, simultaneous measurement of evolved gas analysis method and the humidity sensor. The results are summarized as follows:

1) The activation energy for the reduction of $MnFe_2O_4$ in the hydrogen-helium gas stream was calculated to be 43.1 kJ mol^{-1} by HS in the temperature range of 843 to 863 K. The activation energy for this reduction was estimated to be 188 kJ mol^{-1} by TCD at temperatures of 1373 to 1473 K.

2) The carbothermic reduction process of $MnFe_2O_4$ with hydrogen became clear by TCD and HS. This reaction occurred in the temperature range of 530–1423 K, and the intermediate products between MnO and FeO was formed at about 780 K. The formation

of methane proceeded at about 1073 K, and the maximum peak was observed at 1323 K. At higher temperatures, methane decomposed to yield nascent carbon that tended to result in the acceleration of the reduction rate with carbon.

3) Simultaneous measurement of EGA and HS is useful and trouble-less tool for the high temperature reduction processes of active materials such as manganese oxide, since the vapor pressure of manganese is very high.

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