論 文

Effect of Hydrogen on the Reduction Kinetics of Manganese Oxide at High Temperatures by New EGA Method

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The present study is concerned with the kinetics of carbon reduction of manganese oxide and the effect of hydrogen addition on this reduction process by the new technique, simultaneous measurement of evolved gas analysis (EGA) and the humidity sensor (HS). Water vapor evolved by the reduction with hydrogen was also detected by Humidity sensor. In the reduction process of MnO, manganese carbide was formed at an earlier stage of reduction, and the activation energy of 203 kJ mol^{-1} nearly equal to that for Boudouard's reaction was obtained. As carbon was consumed entirely, the reaction between manganese oxide and it's carbide occurred to yield metallic phase.

It is concluded that the new technique, simultaneous measurement of EGA and HS is useful and trouble less tool for the high temperature reduction processes of active materials such as manganese oxides, as it's high vapor pressure and reactivity with silica tube for reaction vessel in an apparatus may lead to difficulties in measuring the kinetics of reduction processes.

1. Introduction

The system of Mn-Fe-O have so far studied and summarized by several investigators,[1-6] however, the characteristics of high temperature reduction process of manganese oxides with carbon were not clarified sufficiently. The vapor pressure of metallic manganese formed in the reduction process is as high as 890 Pa at 1673 K.[7] Therefore, the application of the gravimetric technique to this reduction process seemed to be difficult because of the loss through volatilization.

Mizutani *et al.*[8] and Saito *et al.*[9] studied the thermal decomposition processes of calcium and lanthanum oxalates by means of the evolved gas analysis (EGA) method. In previous papers,[10-13] MnO_2 or Mn_2O_3 phase in manganese ores continuously converted into lower oxides under a suitable condition of temperature

and oxygen partial pressures. MnO phase was obtained easily in the reduction process up to about 1273 K. The reduction of manganese iron double oxide, $MnFe_2O_4$, which yielded MnO-FeO phase was also investigated.[11]

It is well known that the hydrogen peak area measured by thermal conductivity detector (TCD) as a detector for gaschromatograph is not depend linearly upon the hydrogen concentration using helium as a carrier gas.[14] Though, the carbon reduction process of metal oxides has been investigated by the EGA method,[10-13] it is difficult to study the hydrogen reduction process quantitatively by TCD. The evolution of water vapor can be detected by the humidity sensor (HS) using metal oxidized thin film,[15,16] therefore, the simultaneous measurement of the two techniques of EGA and HS is used to overcome this problem. The humidity sensor can be used as a detector for various gas analyses independently or with combination of gas detector such

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as TCD.

The present study is concerned with the kinetics of carbon reduction of manganese oxide and the effect of hydrogen addition on this reduction process by means of the new technique. The hydrogen reduction process important to obtain the basic data for the reduction kinetics of metal oxides with CH_4 or natural gas, is clarified experimentally.

2. Experimental Procedure

2.1 Specimen

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

2.2 Experimental apparatus

The isothermal and non-isothermal reduction processes were studied with EGA method.[8] In the hydrogen reduction process, H_2O evolved was measured by means of humidity sensor using Tantalum thin film. The experimental apparatus is illustrated in **Fig.1**. Sample is heated at constant rate in a hydrogen-helium 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 when H_2O is evolved from sample, it's concentration is measured by HS sensor individually. After elimination of H_2O by Trap (Ascarite), the decrease of hydrogen concentration in passing through the TCD cell is detected by TCD with high sensitivity. In the case for methane formation, the gas evolved was detected only by gaschromatograph (GC). The gases evolved were calculated in the same way as GC. The application techniques for EGA and HS to reduction process of manganese oxides were described in the previous papers[10,15] in some detail.

3. Results and Discussion

3.1 Isothermal reduction process

The typical reduction process of MnO_2 to MnO in a helium and hydrogen gas stream is shown in **Fig.2**. As the evolution of H_2O is detected clearly by HS corresponding to the decrease of hydrogen measured by TCD, it is thought that HS is responded only to the
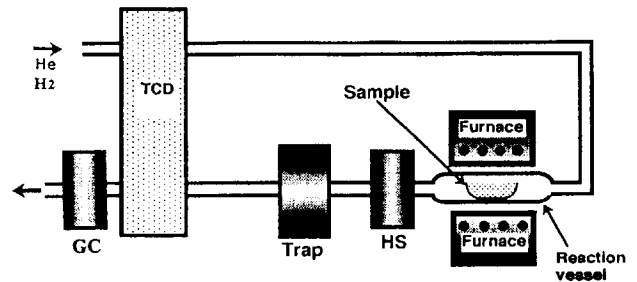

Fig.1 Experimental apparatus for simultaneous measurement of EGA and Humidity sensor.
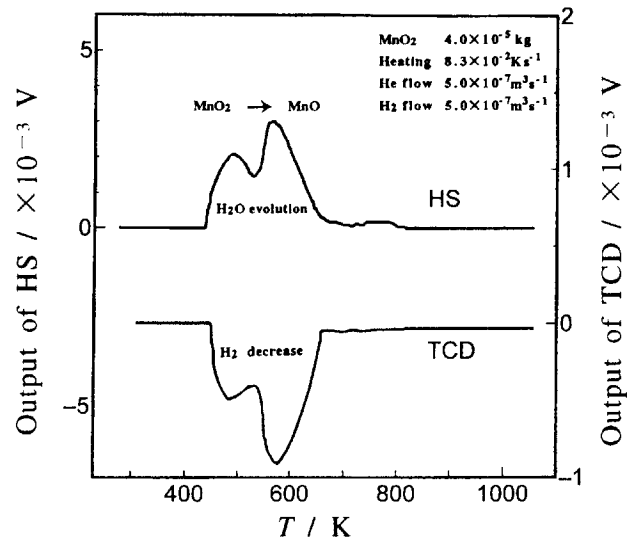

Fig.2 Evolved gas analysis curves for the reduction of MnO_2 with humidity sensor (HS) and thermal conductivity detector (TCD).

water vapor.

In the present study, hydrogen gas was added to the reduction process of MnO, but only CO gas was detected by a gas chromatograph. Then, the CO gas evolved in the reduction process of MnO is detected by TCD. The effect of hydrogen flow rate on the reduction process of MnO with carbon is shown in **Fig.3**, where α is the fraction of reduction in converting MnO to metallic manganese. As shown here, the H_2 flow rate of 2.00×10^{-6} m^3 s^{-1} is sufficient for achieving the critical gas velocity, and the product gas can be removed quickly from the outer side of the sample to the bulk gas. The reduction rates of MnO were measured for several carbon contents and particle sizes of carbon at 1423 K. The result shown in **Fig.4** indicates that the rate increases with decreasing particle size and with increasing carbon content. For the experiment with
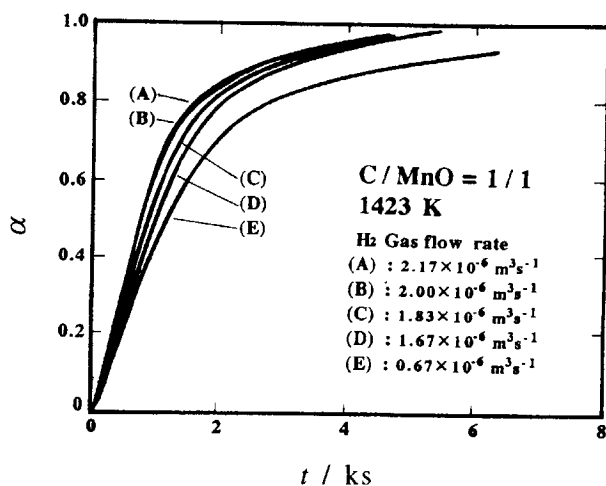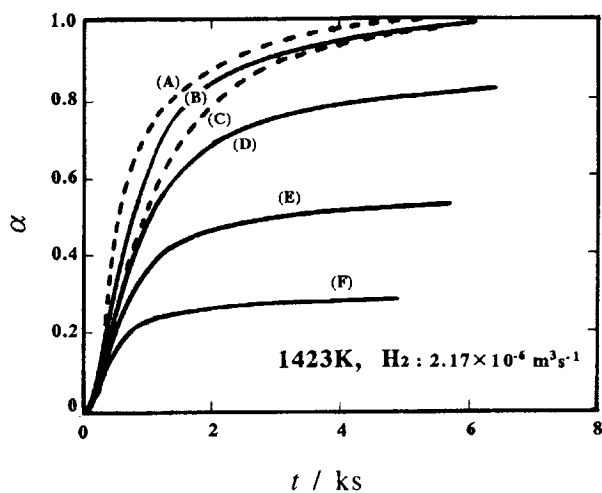
C / MnO = 1 / 1
1423 K

H₂ Gas flow rate
(A) : 2.17×10⁻⁶ m³s⁻¹
(B) : 2.00×10⁻⁶ m³s⁻¹
(C) : 1.83×10⁻⁶ m³s⁻¹
(D) : 1.67×10⁻⁶ m³s⁻¹
(E) : 0.67×10⁻⁶ m³s⁻¹

Fig.3 Effect of hydrogen flow rate on the carbothermic reduction of manganese monoxide.

1423K, H₂ : 2.17×10⁻⁶ m³s⁻¹

carbon size,	carbon content
(A): -1.05×10^{-4} m,	C/MnO = 1
(B): $1.49 - 1.25 \times 10^{-4}$ m,	C/MnO = 1
(C): $1.77 - 1.49 \times 10^{-4}$ m,	C/MnO = 1
(D): $1.49 - 1.25 \times 10^{-4}$ m,	C/MnO = 0.75
(E): $1.49 - 1.25 \times 10^{-4}$ m,	C/MnO = 0.5
(F): $1.49 - 1.25 \times 10^{-4}$ m,	C/MnO = 0.25

Fig.4 Effect of particle size and carbon content on the hydrogen added carbothermic reduction of manganese monoxide.

carbon ratio less than MnO/C = 1/1, residual MnO is detected after the completion of the reduction. At an earlier stage of reduction up to about 40 %, manganese carbide, Mn_7C_3, is formed. When carbon is consumed entirely, the reaction between manganese oxide and it's carbide occurs to yield metallic phase. For the reduction

with excess carbon content, only carbide is formed.

The carbon reduction of MnO occurring at the interface of the solid phase MnO-C are;

$$7MnO + 13CO = Mn_7C_3 + 10CO_2 \tag{1}$$

$$C + CO_2 = 2CO \tag{2}$$
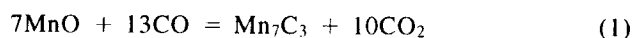
and the overall reaction is,

$$7MnO + 10C = Mn_7C_3 + 7CO \tag{3}$$
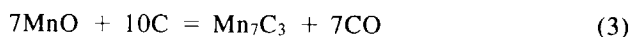
The rate determining reaction seemed to be a chain reaction between $CO-CO_2$ gas phases [10,17] expressed in eq.(2).

Manganese carbide formed during the reduction was also identified by X-ray diffraction using Fe-Kα radiation and EPMA examination. The loss of manganese through volatilization was calculated to be less than 0.12 % at 1473 K.

3.2 formation of methane

The addition of hydrogen to the reduction process of MnO with carbon, results in the formation of methane gas. This methane formation reaction between carbon and hydrogen, proceeds actually at the temperature range of 1000 - 1420 K. The equilibrium constant K is given by [18]

$$\log K = -5.77 + 4765/T \qquad K = P_{CH_4} / P_{H_2}^2 \tag{4}$$

where, T is temperature, P_{CH_4} and P_{H_2} are the partial pressures of CH_4 and H_2, respectively. As the standard free energy of formation at 1423 K under the hydrogen flow rate of 0.33×10^{-6} m³ s⁻¹ is estimated about -7.3 kJ mol⁻¹,[19] the formation reaction of methane seemed to be proceeded. The amount of methane formed from carbon is measured by gaschromatograph, and shown in **Fig.5**. The formation of methane proceeds at about 1073 K, and the maximum peak is observed at 1323 K. At more high temperatures, methane decomposes to yield the formation of nascent carbon, which tends to result in the acceleration of reduction rate with carbon. Furthermore, the addition of nickel powder accelerate the methane formation. In addition, the acceleration for the formation of methane by nickel catalyzer (0.2 mol%) is also shown in **Fig.5**.

In the reduction process of several sorts of iron ores by the reformed natural gas, it was reported[20] that the reducing action of natural gas was weak, but it was found that, when gas was decomposed, the
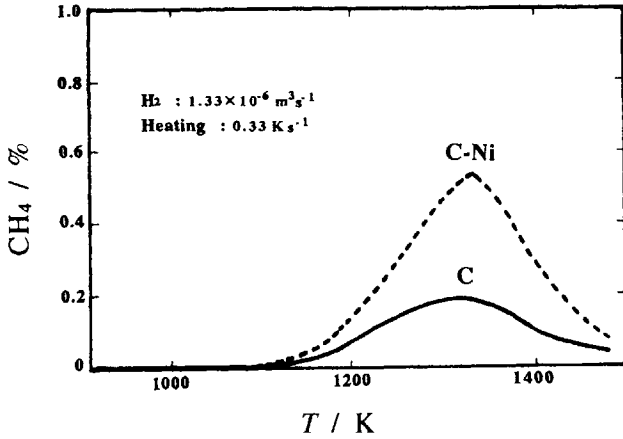
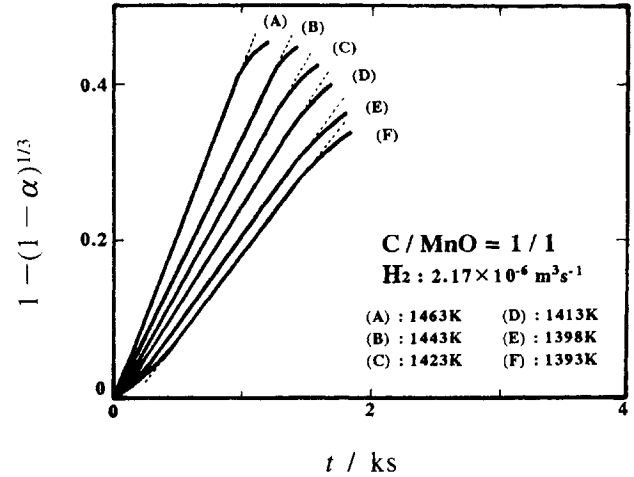Fig.5 The methane amount formed from carbon, and catalyzed by nickel powder.

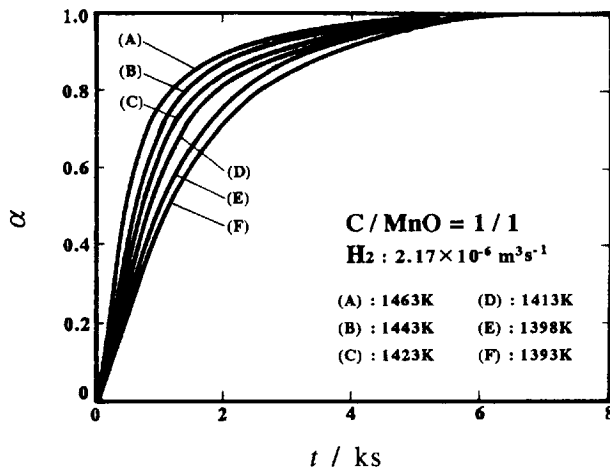Fig.6 Effect of temperature on the hydrogen added carbothermic reduction rate of manganese monoxide.

Fig.7 Relation between time and $1-(1-\alpha)^{1/3}$ in the rate equation for an interfacial reaction.
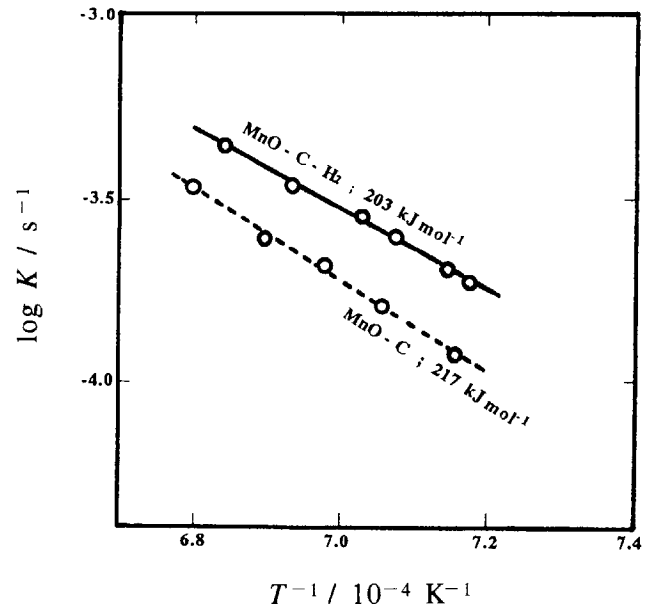

Fig.8 Arrhenius plots for the hydrogen added carbothermic reduction of iron-manganese oxides.

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 one step direct reduction process of iron manganese ores, and contribute to the save energy of ferroalloy manufacturing industry.

3.3 Effect of H₂ addition

For the reduction process of MnO in the mixture gas stream of hydrogen-helium ($H_2 + He$) gas as a carrier gas, only CO gas was detected by a gas chromatograph. Then, the CO evolution was detected independently by TCD.

The effect of H_2 on the reduction process of MnO with carbon was examined at the temperature range of

1393 K - 1463 K. The results were shown in **Fig.6**. It has been mentioned in the previous paper,[21] that the rate equation for an interfacial reaction is applicable to the cabothermic reduction of MnO. Plots of $[1-(1-\alpha)^{1/3}]$ vs t are shown in **Fig.7**. Since the temperature raising to the desired temperature needed for excess time, a plot of data does not reveal a linear relationship at the first stage of reduction.

From the slope of these straight lines ($\alpha \doteqdot 0.1 -$ 0.7), the activation energy of this reduction was estimated to be about 203 kJ mol^{-1} (**Fig.8**). This value is smaller

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than that for the carbothermic reduction of MnO, nearly equal that for Boudouard's reaction reported by Singleton et al.[22] and Turkdogan et al.[23] Thus, the reduction rate is seemed to be accelerated somewhat by the addition of hydrogen, related to the change of frequency factor for Arrhenius equation.

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.

4. Summary

The kinetics of carbon reduction of manganese oxide and the effect of hydrogen addition on this reduction process were studied by the new technique, simultaneous measurement of evolved gas analysis method and the humidity sensor. The results may be summarized as follows:

(1) In the hydrogen added reduction process of MnO₂, Water vapor evolved was detected by HS and the decrease of hydrogen concentration by TCD, respectively.

(2) For the reduction process of MnO, Water vapor was not detected by gas chromatograph. Then, the reduction process was measured by only TCD.

(3) It became clear by gas chromatograph that the formation of methane proceeded at about 1073 K, and the maximum peak was observed at 1323 K. At more high temperatures, methane decomposed to yield the formation of nascent carbon, which tended to result in the acceleration of reduction rate with carbon.

(4) At an earlier stage of reduction of MnO, manganese carbide was formed, and the activation energy of 203 kJ mol⁻¹ nearly equal to that for Boudouard's reaction was obtained. When carbon was consumed entirely, the reaction between manganese oxide and it's carbide occurred to yield metallic phase.

(5) Simultaneous measurement of EGA and the humidity sensor is useful and trouble less tool for the high temperature reduction processes of active materials such as manganese oxides, it's vapor pressure being very high. The authors would like to thank Prof. N. Mizutani, Department of Inorganic Materials at University of Tokyo Institute of Technology for his able guidance and help rendered during this investigation. The authors wish to thank T.Hashizume who carried out the experiment

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要　旨

発生ガス分析法（EGA）と温度センサ（HS）を併用する新しい同時測定法により，これまで測定できなかったH_2を添加したMn酸化物の炭素熱還元過程について速度論的に検討を行なった。特に，EGA法のキャリヤーガスにHeを使用する場合においても，H_2還元に伴って発生するH_2OをHSで個別に定量することが可能である。また，H_2添加によるCH_4の生成・分解過程についても検討した。MnOの還元過程では最初にMn炭化物が生成し，還元の進行に伴い遊離炭素が消失すると MnOとMn炭化物間の反応により金属Mnが生成する。H_2を添加しない場合と比較して，H_2を添加したMnOの還元過程における見かけの活性化エネルギーの値は少し小さい約$203 \ kJ \ mol^{-1}$が得られた。

本方法は，Mn酸化物の炭素還元過程のような高温・強還元性雰囲気を必要とし，しかも化学的に反応性が高く蒸気圧も高いために従来の測定法が困難な物質に対して，堅牢で維持しやすい非常に有効な測定技術である。