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Short communication

Catalytic reduction of magnesia by carbon

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Abstract

Reduction kinetics of magnesia with carbon and transition metal was investigated by thermogravimetry from room temperature to 1973 K. Cu, Co and Ni accelerates the reduction rate. Fe accelerates the reduction rate and decreases the initial reaction temperature. The reaction with Fe addition takes place in three stages with activation energies in the second and third stage of 207 and 295 kJ mol^{-1}.

Keywords: Carbon; Magnesia; Catalytic reduction; Thermodynamic analysis; Reaction mechanism

1. Introduction

Magnesium is the lightest of all metals used for structural alloys. The requirement to reduce the weight of car components as a result in part of the introduction of legislation-limiting emissions has triggered renewed interest in magnesium [1]. Furthermore, magnesium is used in steel-making as a strong deoxidizer or desulfurizer. At steel-making temperatures, magnesium has a very low solubility in liquid iron and a very high vapor pressure [2]. Recently our research group [3,4] developed a new method for desulfurization and deoxidation of molten iron using magnesium vapor produced in situ by carbothermic reduction of magnesia. The kinetics of reduction of magnesia by carbon is a key point in controlling the process of desulfurization and deoxidation, and in finding ways to promote the desulfurization and deoxidation efficiency and rate.

Our previous study [5,6] found that the reduction rate was very slow below 1873 K. The purpose of the present investigation is to understand the reduction kinetics of magnesia and carbon mixtures with added transition metal catalysts.

2. Experimental

2.1. Experimental procedures

The magnesia powders (0.4 μm average diameter, purity higher than 99.99%, High Purity Chemical Institute), graphite powder (fixed carbon 99.12%, ash 0.15%, water 0.4%, average diameter 3.9 μm, Kishida Chemical), Fe powder (150 μm average diameter, purity higher than 99%, Wako Pure Chemical Industries) and Cu, Co, Ni powder (50 μm average diameter, purity higher than 99%, Beijing Chemical

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Reagent) were used in this study. Magnesia, graphite powder and transition metal were mixed in a molar ratio of 1:1:1/2 and the mixture was shaped into a 5 mm diameter pellet at 100 MPa with a cold press. The graphite crucible used in this study was 6.4 mm o.d., 5.8 mm i.d. and 5.5 mm in height.

The reduction experiments were carried out with a thermo-balance (NS95, Sinku-riko, Japan) interfaced to a computer data acquisition and analysis system. The sample was put into the graphite crucible, which was positioned on the top of the thermocouple. The inert atmosphere was maintained with argon at a flow rate of 1.67 $cm^3\,s^{-1}$. After 30 min, the sample was heated from room temperature to 773 K and held at this temperature for 10 min to remove the absorbed gases and water from the sample. Then the temperature was raised to 1973 K at different heating rates. To correct for the effect of the graphite crucible, blank experiments were carried out with blank graphite crucibles. Blank runs were carried out under the same conditions as those used for the samples. The sample phases were analyzed by XRD (Rigaku D/MAX IIIB, Japan).

2.2. Non-isothermal kinetics

During the thermogravimetric reduction experiment, the mass loss of the sample is monitored as a function of time. The reduction ratio α at a given instant is defined as

$$\alpha = \frac{\Delta W}{W_0} \qquad (1)$$

where W_0 represents the initial mass of magnesium in the sample and ΔW is the magnesium mass change to that instant.

For an irreversible reaction, the reaction rate can be expressed as

$$-\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (2)$$

where $f(\alpha)$ is a function of α, the fraction of reaction or reduction ratio, and $k(T)$ is the rate constant, whose relation with the temperature can be given by the Arrhenius equation as

$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

where A is the pre-exponential constant, R the gas constant and E_a is the activation energy.

Combining Eqs. (2) and (3) and taking logarithms, one obtains

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \qquad (4)$$

In Eq. (4), $f(\alpha)$ is determined only by α. When we choose the data of $d\alpha/dt$ and the absolute temperature, T, at the same value of α from experiments at different heating rates, there should be a linear relationship between the chosen $\ln(d\alpha/dt)$ and $1/T$. The slope of the line gives the activation energy E_a. This method is called the multi-heating rate method.

3. Experimental results and discussion

3.1. Effects of Cu, Ni, and Co on the reduction ratio

The effects of Cu, Ni and Co on the reduction ratio as a function of temperature are shown in Fig. 1. The curves show no obvious effect of the transition metals at temperature lower than 1600 K. At temperature higher than 1600 K, the reduction ratio increases with temperature and the catalytic effect of the transition metals is clearly shown. Nickel is most active followed by copper and cobalt.

Cu, Ni and Co accelerate the reaction, but do not decrease the initial reaction temperature. Furthermore, Cu, Ni and Co are also added as impurities when used in the steel-making industry.

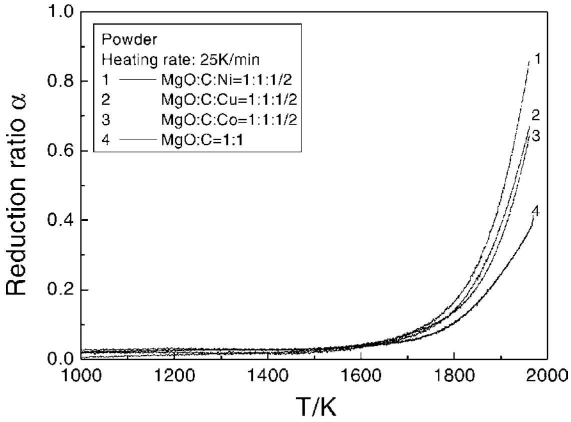

Fig. 1. Effects of Cu, Ni and Co on the reduction ratio.

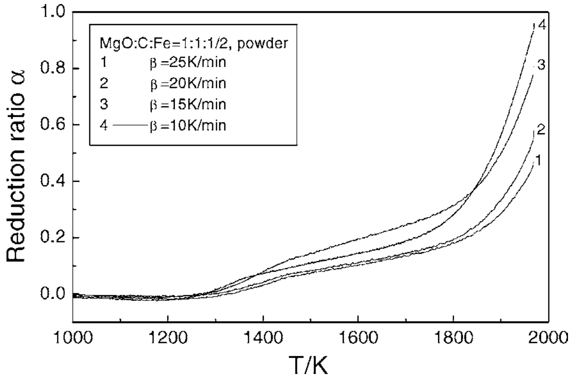

Fig. 2. Effect of Fe on the reduction ratio.

3.2. Effects of Fe and heating rate on the reduction ratio

Fig. 2 shows the effect of Fe addition on the reduction ratio. The initial reaction temperature decreases by 100–200 K, and there are three stages of mass loss with temperature. The first mass loss is about 1–3 wt.% at 1200–1400 K. This part of the mass loss may be due to reduction of the small amount of iron oxide in the Fe powder. The XRD pattern of the sample before the experiment indicates a small amount of FeO. In the second stage, between 1400 and 1750 K, the reduction rate is lower than that of the first stage. The mass loss is about 10–20%. In this stage, the activation energy is 207 kJ mol^{-1} calculated by the multi-heating rate method. This value is similar to the activation energy (208 kJ mol^{-1}) obtained without Fe addition. In our previous work [5], it was found that in the early stage of the reduction of magnesia by carbon without addition of transition metals, the solid phase boundary reaction between magnesia and carbon controls the overall reaction rate. Thus, from the similar activation energy in the case of the addition of Fe metal, it is deduced that the solid phase boundary reaction determines the overall reaction rate. In the third stage, at temperatures higher than 1750 K, the reduction rate increases sharply with temperature. The activation energy was calculated to be 295 kJ mol^{-1}. This value is much lower than the value of 374 kJ mol^{-1} obtained without Fe addition. This indicates that the addition of Fe changes the reduction mechanism.

4. Conclusions

Reduction kinetics of magnesia with carbon and transition metal was investigated by thermogravimetry from room temperature to 1973 K. Cu, Co and Ni accelerates the reduction rate. Fe accelerates the reduction rate and decreases the initial reaction temperature. The reaction with Fe addition takes place in three stages with activation energies in the second and third stage of 207 and 295 kJ mol^{-1}.

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