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ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 839−847

Transactions of
Nonferrous Metals
Society of China
www.tnmsc.cn

Kinetics of extracting magnesium from mixture of calcined magnesite and calcined dolomite by vacuum aluminothermic reduction

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Received 5 March 2013; accepted 4 July 2013

Abstract: The vacuum aluminothermic reduction of the mixture of calcined magnesite and calcined dolomite was studied. An isothermal reduction method satisfying the vacuum aluminothermic reduction was proposed. The experiments were carried out at 4 Pa. The results indicate that the reduction rate is increased with increasing temperature, content of aluminum and pellet forming pressure. The XRD patterns of pellets at different reduction stages confirm that the reduction process can be roughly classified into three stages: the formation of $MgAl_2O_4$, and $Ca_{12}Al_{14}O_{33}$ phases; the phase transformation from $MgAl_2O_4$ and $C_{12}A_7$ to $CaAl_2O_4$; the formation of $CaAl_4O_7$ phase. The experimental data were divided into three parts according to the kinetic models. The apparent activation energies of the three parts were determined to be 98.2, 133.0 and 223.3 kJ/mol, respectively.

Key words: magnesium; kinetics; aluminothermic reduction; magnesite; dolomite

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1 Introduction

Magnesium is the lightest metal among the commonly used structured metals, and its wide application in many fields, such as metallurgy, chemistry, automobile industry [1,2], implies the huge demands for magnesium in the world. Magnesium is produced by two principal processes: electrolysis of molten magnesium chloride and thermal reduction of magnesia. The proportion of electrolysis is getting smaller because this process is characterized by high-energy consumption [3] and high cost [4]. The Pidgeon process, which has been in the mature stage [5−7], is widely used in thermal reduction of magnesia. Although this process is better than electrolysis in terms of energy consumption, cost, etc, it is still disadvantaged in these parts [8]. Several works [9,10] proposed the process of carbothermic reduction of magnesia. However, the well-known primary issue with the carbothermal process is the easy reverse reaction. A new vacuum thermal reduction method, by which magnesium is produced through aluminothermic reduction of a mixture of calcined dolomite and calcined magnesite, was proposed by FENG and WANG [11]. Compared with the Pidgeon process, this method can reuse the reduction residue and greatly cut down energy consumption and CO_2 emissions. The optimal parameters of this process were studied by HU [12] et al and WANG et al [13]. However, the kinetics of this process is not well studied.

On the other hand, the kinetics of aluminothermic reduction of magnesia was reported. By use of the isothermal reduction, YANG et al [14] investigated the effects of temperature, carrier gas flow rate, pellet forming pressure on the reduction ratio of MgO. The apparent activation energy of the pellets containing magnesium oxide and aluminum at a molar ratio of 4:2 was calculated and the value was 109 kJ/mol. LAN et al [15] used the non-isothermal reduction method to calculate the apparent activation energy of the pellets containing magnesium oxide and aluminum at a molar ratio of 3:2, which was 151.2 kJ/mol. In addition, they also proved that the lime addition accelerated the reaction. However, the apparent activation energy of the pellets with the lime addition was not calculated in their work.

As for the conventional isothermal reduction methods, such as aluminothermic reduction of titanium

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Foundation item: Project (MYF2011-34) supported by High-tech R&D Plan of Liaoning Province, China; Project (2011221002) supported by Industrial Research Projects of Liaoning Province, China; Project (N100302009) supported by the Fundamental Research Funds for the Central Universities, China

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DOI: 10.1016/S1003-6326(14)63133-2

oxide [16], the reacting substances were preliminarily placed in an alumina crucible and were preheated at a lower temperature. Before starting an experiment, the temperature was increased to the prescribed one as quickly as possible by applying full power of induction furnace. However, this method cannot be applied to a rapid reduction process such as the aluminothermic reduction of magnesium oxide. YANG et al [14] proposed an isothermal aluminothermic reduction method. They promptly inserted a graphite tube charged with the samples into a high-temperature zone to start the experiment and the tube was rapidly lifted up to a low temperature zone to end the experiment. The inert atmosphere was maintained in the furnace by blowing argon gas. However, the method cannot satisfy the vacuum reduction condition.

In this work, a method is proposed in order to obtain the isothermal reduction process under the vacuum condition. Effects of temperature, MgO-to-Al mole ratio and pellet forming pressure on the reduction ratio are investigated by the isothermal reduction method. The apparent activation energy is obtained. The reduction mechanism of extracting magnesium from the mixture of dolomite and magnesite is preliminarily analyzed by the X-ray diffraction.

2 Experimental

2.1 Raw materials

The raw materials used in this study were obtained from Dashiqiao in Liaoning Province, China. Table 1 shows the major compositions of magnesite and dolomite. The purity of aluminum power used as reduction agent is 99% in mass fraction.

Table 1 Major chemical composition of raw materials

Ore	*w*/%					Ignition loss/%
	MgO	CaO	SiO_2	Fe_2O_3	Al_2O_3	
Dolomite	21.73	30.62	0.39	0.09	0.08	46.88
Magnesite	47.28	0.56	0.24	0.23	0.08	51.27

2.2 Apparatus

The experimental apparatus is shown in Fig. 1. A resistance furnace with SiC heating elements was used to heat the tube which was made of high-temperature alloyed steel. The temperature was measured with NiCr−NiSi thermocouple.

2.3 Procedures

The dolomite and magnesite were calcined at 1323 K and 1023 K for 90 min, respectively. They were pulverized (10 μm in average diameter) and mixed at a molar ratio of calcined magnesite to calcined dolomite to aluminum to be 5:1:4 since the reaction was expected as follows:

$$CaO\cdot MgO+5MgO+4Al \longrightarrow CaO\cdot 2Al_2O_3+6Mg\uparrow \qquad (1)$$

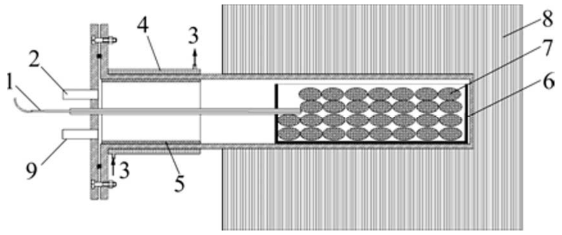

Fig. 1 Schematic of experimental apparatus: 1—Thermocouple; 2—Vacuum tube; 3—Circulating water; 4—Water-cooled jacket; 5—Condenser; 6—Briquettes bucket; 7—Briquettes; 8—Furnace; 9—Atmosphere gas inlet

The mixed powders were compacted into 25 mm-diameter and 23 mm-height cylindrical pellets under a compacting pressure of 90 MPa using a cold isostatic press. The pellet mass was (20±0.2) g before reduction and the change in pellet mass after reduction was measured with an electronic balance with a detection precision of 1 mg. The vacuum thermal reduction experiments were carried out at 4 Pa. The reduction residues at different stages of reduction were qualitatively investigated by XRD (PW3040/60 PANALYICAL B.V, using the Cu K_α target).

The reduction ratio of magnesium oxide (η) is defined as the ratio of magnesium mass loss in the reduction (Δm) to the initial magnesium mass in the pellets (m_0). Since release of the produced magnesium vapor is the only reason of the change in the pellet mass, the change in the pellet mass is taken as the magnesium mass loss.

$$\eta=(\Delta m/m_0)\times 100\% \qquad (2)$$

2.4 Isothermal reduction method

For the isothermal vacuum reduction, if the samples are placed in the vacuum tube at the experimental temperature, the reductant will be oxidized in the operating time for sealing the tube. The other method is that the samples are placed in the tube at the ambient temperature and the atmosphere in the tube is adjusted to the experimental vacuum. The tube is preheated at a lower temperature. Before starting an experiment, the temperature is increased to the prescribed one as quickly as possible by applying full power of the furnace. However, the elapsed time for temperature increasing from the preheated one to the prescribed one is too long to satisfy the isothermal reduction condition for rapid reduction processes such as the aluminothermic reduction.

In the present experiments, two same furnaces were used. The temperature of the first one was kept at 1273 K.