



Non-isothermal kinetics study on carbothermic reduction of nickel laterite ore

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ABSTRACT

In this paper, the non-isothermal reduction kinetics of nickel laterite with graphite was investigated under argon atmosphere. The reduction of nickel laterite was carried out at different heating rates (10, 15 and 20 K/min) and the evolved gas was detected by mass spectrometer in real time. The activation energies were determined by Kissinger-Akahira-Sunose (KAS) method and the reaction kinetics were determined by model-fitting (Coats-Redfern) method. The results showed that the reduction process can be divided into three stages according to the conversion degree (α): $\alpha = 0-0.45$, $\alpha = 0.45-0.75$, and $\alpha = 0.75-1.0$, respectively. In the first stage, the average activation energy was 351.03 kJ/mol and the kinetic model fitted the two-dimensional diffusion function. In the second stage, the model of three-dimensional diffusion function was determined as the kinetic function and the average activation energy was 322.89 kJ/mol. In the third stage, the average activation energy was 341.45 kJ/mol and the kinetic model was in accordance with the chemical reaction function. The phase transformation as well as reaction mechanism during reduction were also analyzed which explained the reduction kinetics of nickel laterite.

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1. Introduction

As an industrial important metal, nickel plays a significant role in modern manufacturing. It is the essential element for stainless steel production, which accounts for 65 wt% of nickel consumption [1]. In recent years, the global annual demand for nickel has increased tremendously due to soaring stainless steel production, particularly in China [2,3]. However, China is short of nickel resource, and has depended on importation for a long period. Nickel sulfide and laterite ores are the two main resources for extracting nickel metal. [4]. Recently, the utilization of low-grade nickel laterite ore has attracted more and more attention due to the growing demand for stainless steel as well as a depletion of sulfide ores [5,6].

The extraction of nickel from laterite ore is relatively difficult because of the low nickel content and isomorphous substitution in goethite or serpentine. Nickel is able to be extracted from laterite using aqueous solution of sulfuric acid. A common problem with direct hydrometallurgical process is, however, low recoveries of nickel and cobalt, as well as the production of iron-bearing waste [7]. Up to now, the pyrometallurgical method, such as the rotary kiln-electric furnace (RKEF) process, has been widely applied to produce ferronickel from the nickel laterite

ore [8]. The RKEF process, which includes calcination and pre-reduction at 800–1000 °C for 4–6 h in a rotary kiln, followed by smelting at 1550–1600 °C for 2–3 h in an electric arc furnace for separating ferronickel from the slag, is characterized by intensive energy consumption. Direct reduction followed by physical separation (magnetic/gravity) has been employed in Japan (Nippon Yakin Kogyo Co., Ltd.) [9]. The ferronickel materials obtained from physical separation can be directly used to manufacture stainless steels. In order to achieve the growth of ferronickel granules, this process still requires a high temperature (1250–1400 °C) during the reduction for partially melting the slag [10]. Nevertheless, to avoid forming a ring against the wall of the kiln, it becomes difficult to enrich and recovery more nickel. An alternative route of direct reduction performed at a relatively lower roasting temperature (1000–1100 °C) and then followed by magnetic separation have also been investigated. Many researchers have studied direct reduction of laterite ore by adding additives (such as Na₂SO₄, CaF₂, CaO, etc.) to improve the reduction and metal-slag magnetic separation [11–13].

Several investigations on the reduction kinetics of nickel or iron-nickel oxides have been carried out. Jankovic et al. studied the non-isothermal reduction kinetics of nickel oxide using hydrogen, the kinetic triplet was obtained as: $E_{\alpha} = 96.4$ kJ/mol; $A = 1.04 \times 10^8$ min⁻¹ and $f(\alpha) = \alpha^{0.63}(1 - \alpha)^{1.39}$ [14,15]. Goro nickel oxide were reduced using hydrogen from 400 to 600 °C in Utigard's study, the results showed that increasing temperature and hydrogen pressure can

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increase the reaction rate. Besides, the activation energy was 90 kJ/mol and the kinetic model fitted the shrinking core model [16].

The previous studies on reduction kinetics were mainly limited to pure nickel oxide and iron-nickel oxide, while few studies focused on reduction kinetics of nickel laterite ore. In this paper, the non-isothermal kinetics of reducing nickel laterite ore with graphite was investigated using a combination of thermogravimetry and mass spectrometer. The evolved gas was detected by mass spectrometer in real time. The activation energies were determined by Kissinger-Akahira-Sunose (KAS) method and the reaction kinetics were determined by model-fitting (Coats-Redfern) method [17].

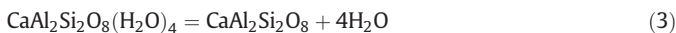
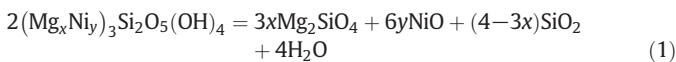
2. Experimental

2.1. Raw materials

The nickel laterite ore sample used in this study was obtained from the Philippines. The main chemical composition of the raw material is shown in Table 1. The content of Ni and total iron grade (TFE) was 1.81 wt% and 17.87 wt%, respectively. It can be observed that the sample has a high content of silica, magnesia, alumina. The mineralogical analysis of the sample was investigated by X-ray diffraction (XRD), and the results in Fig. 1 indicate that the laterite ore is mainly composed of $\text{CaAl}_2\text{Si}_2\text{O}_8(\text{H}_2\text{O})_4$, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, $(\text{Mg,Al})_3(\text{Si,Fe})_2\text{O}_5(\text{OH})_4$ and Fe_2O_3 .

Pure graphite powder ($\geq 99.9\%$ purity, $< 13 \mu\text{m}$ in particle size) was prepared as the reductant.

Before the thermogravimetric experiments, the raw nickel laterite was pretreated by roasting at 1100°C for 2 h in a muffle furnace to remove the crystal and hydroxy water. The XRD pattern of the roasted nickel laterite ore is shown in Fig. 2. It reveals that the main water-bearing phases of $\text{CaAl}_2\text{Si}_2\text{O}_8(\text{H}_2\text{O})_4$, $(\text{Mg,Al})_3(\text{Si,Fe})_2\text{O}_5(\text{OH})_4$ and $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ were decomposed and disappeared in the XRD pattern. Instead, NiFe_2O_4 was detected in the roasted samples. During the roasting process, the main chemical reactions are shown as follows:



2.2. Methods

Roasted nickel laterite sample was ground to 100% passing 0.074 mm . Then the ground nickel laterite was thoroughly mixed with the graphite powder and the molar ratio of C/O in mixtures was fixed as 1.2, the O content corresponds to the oxygen in the nickel oxides and iron oxides.

The thermogravimetric experiments were conducted by thermogravimetric technique (Setaram Evo TG-DTA 1750) which consisted of a vertical furnace, a gas manometer system for controlling the atmosphere in the reactor, an electronic balance attached to a computer which recorded the mass loss. The samples ($20 \pm 0.5 \text{ mg}$) was added into an alumina crucible ($\Phi 6 \text{ mm} \times 8 \text{ mm}$) and placed into the thermogravimetric apparatus. Then, the TG experiments were carried out under Argon flowing at the rate of $20 \text{ mL} \cdot \text{min}^{-1}$ with three different heating rates of 10, 15, and 20 K/min . The evolved gas engendered

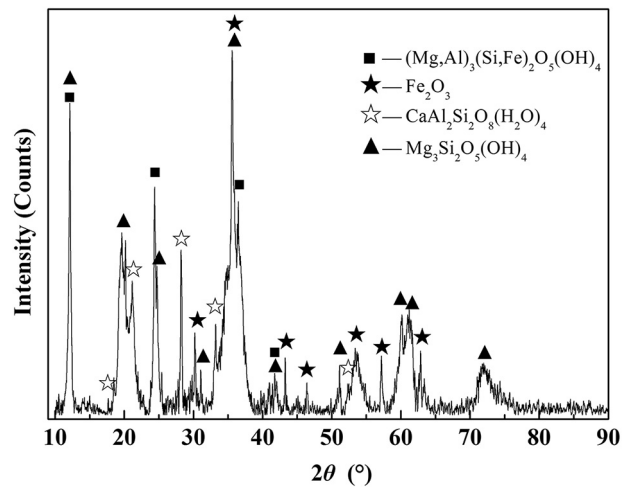


Fig. 1. XRD pattern of nickel laterite ore.

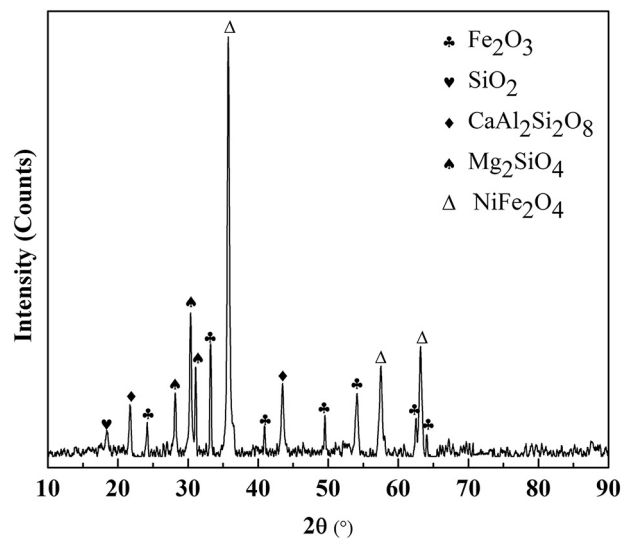


Fig. 2. XRD pattern of nickel laterite after roasting at 1100°C for 2 h.

from the TG experiments was detected in real time by advanced quadrupole mass spectrometer (TILON LC-D200, AMETEK LLC., USA), which indicated that CO and CO_2 were the main gas components of the reduction reaction. Each experiment was repeated three times and the repeatability was excellent.

3. Theoretical basis

Many representative non-isothermal methods have been summarized in previous study [18]. The kinetic equation was expressed as Eq. (4):

$$\frac{d\alpha}{dt} = A e^{-\frac{E_\alpha}{RT}} f(\alpha) \quad (4)$$

where α is the conversion degree, T is Kelvin temperature, R is the gas constant, A is a pre-exponential factor, E_α is the activation energy, and $f(\alpha)$ is the model function.

Under non-isothermal condition in which the sample is heated at a constant heating rate (β), the corresponding value can be expressed as

Table 1

Main chemical composition of nickel laterite ore (wt%).

Ni	TFE	Cr_2O_3	SiO_2	Al_2O_3	CaO	MgO	P	S	LOI*
1.81	17.87	0.51	34.97	4.75	1.54	13.5	0.005	0.064	17.35

LOI*: Loss on ignition.

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