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Phase transformation in reductive roasting of laterite ore with microwave heating

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Abstract: Selective reduction of laterite ores followed by acid leaching is a promising method to recover nickel and cobalt metal, leaving leaching residue as a suitable iron resource. The phase transformation in reduction process with microwave heating was investigated by XRD and the reduction degree of iron was analyzed by chemical method. The results show that the laterite samples mixed with active carbon couple well with microwave and the temperature can reach approximate 1 000 ℃ in 6.5 min. The reduction degree of iron is controlled by both the reductive agent content and the microwave heating time, and the reduction follows Fe_2O_3→Fe_3O_4→FeO→Fe sequence. Sulphuric acid leaching test reveals that the recoveries of nickel and iron increase with the iron reduction degree. By properly controlling the reduction degree of iron at 60% around, the nickel recovery can reach about 90% and iron recovery is less than 30%.

Key words: laterite; microwave; carbothermic reduction

1 Introduction

Laterite ores consist of the majority (65%) of the world's nickel reserves. Although sulfides are still the primary source of nickel and cobalt, increasing underground costs and decreasing the grades of the sulfide ores attract more attention towards the exploitation of laterite ores[1]. One of the major economic factors, which limit the development of the laterite ores, is that the energy costs for processing these ores are 2−3 times higher than that for the sulfide ores[2]. Therefore, in the long term it will be necessary to develop new and more economical processing technologies.

A new technology, which is considered for application in extractive metallurgy, is microwave technology[3−7]. Microwave energy is a nonionizing electromagnetic radiation with frequencies in the range from 300 MHz to 300 GHz. Microwave heating is unique and offers a number of advantages over conventional heating, such as reduction in energy consumption and process duration, rapid and controllable heating, peculiar temperature distribution, and selectivity of energy deposition[8−10].

Selective reduction of laterite ores followed by acid leaching is a promising method to recover nickel and cobalt metal, leaving leaching residue as a suitable iron resource[11]. The iron in leach liquor can be precipitated as goethite, which is also a usable iron resource and has no contamination to the environment. In the present work, the microwave radiation was applied to the carbothermic reduction of limonite laterite ore. The phase transformation in the reduction process and the acid leaching of reduced calcine were investigated.

2 Experimental

2.1 Apparatus

Microwave heating was carried out at a frequency of 2.45 GHz at 800 W power level using WD800B Galanz microwave oven. X-ray diffractometry was utilized to analyze mineral compositions of laterite samples before and after reduction treatment.

2.2 Materials

The limonite laterite ore (＜74 μm) from Philippines used in this work was dried at 90 ℃ for 12 h

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to remove the moist water. The chemical composition of the ore is given in Table 1. The analytically pure grade active carbon was used as reductive agent.

Table 1 Chemical composition of limonite laterite ore (mass fraction, %)

Fe	Ni	Co	Mg	Ca	SiO_2
44.82	0.955	0.146	0.445	0.025	2.47

2.3 Carbothermic reduction with microwave heating

Reduction of iron oxides in a direct reduction system has been known to occur by gaseous phases, for example CO, rather than the solid carbon[12−13]. The reduction reactions are presented as Reaction (1). Fig.1 shows the equilibrium diagram of reduction. The Reaction (2) is the highly endothermic Boudouard reaction. The overall oxide reduction with carbon is shown in Reaction (3).

$$MO+CO{=\!=}M+CO_2 \quad (1)$$

$$CO_2+C{=\!=}2CO \quad (2)$$

$$MO+C{=\!=}M+CO \quad (3)$$

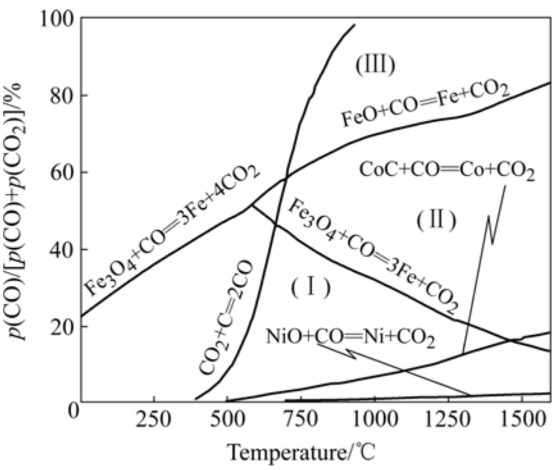

Fig.1 Equilibrium diagram of reduction with CO-CO_2

According to Reactions (4)−(7), the reduction of iron oxide to magnetite (in the reaction region (Ⅰ) of Fig.1) needs 1.9% of carbon, adding the reduction of nickel and cobalt oxide to metallic state. About 5.2% of carbon is needed to completely reduce iron oxide to wustite state (in the reaction region (Ⅱ) of Fig.1). The third series of sample was added with 7.6% carbon, which was 50% carbon excessive to reduce iron to wustite.

$$3Fe_2O_3+C{=\!=}2Fe_3O_4+CO \quad (4)$$

$$Fe_2O_3+C{=\!=}2FeO+CO \quad (5)$$

$$NiO+C{=\!=}Ni+CO \quad (6)$$

$$CoO+C{=\!=}Co+CO \quad (7)$$

Sample mixed with active carbon was put in a covered ceramic crucible which was then heated by microwave for required time. After irradiation, a Chromel-Alumel thermocouple with diameter of 1.0 mm was rapidly inserted to the bottom of the sample to measure the temperature[14].

2.4 Leaching of reduced laterite with sulphuric acid

All the leaching processes were operated at room temperature, with the liquid-to-solid ratio of 20(v/w), sulphuric acid of 0.5 mol/L and stirring speed of 400 r/min for 1.0 h.

Iron content in the solution was determined by the titration method using $K_2Cr_2O_7$. Nickel content was measured by the ICP-AES method. To evaluate the reduction degree of the laterite, the total iron, ferrous iron and metal iron content were analyzed with the standard chemical method[15].

3 Results and discussion

3.1 Microwave heating temperature

The results of microwave heating the laterite ores mixed with different carbon content can be seen in Fig.2. Although laterite ore has poor microwave absorbing ability at low temperature[14], when being mixed with active carbon, the temperature of samples rapidly reaches approximately 1 000 ℃ in 6.5 min. Then the temperature keeps stabilized in the next heating period until the end of 30 min.

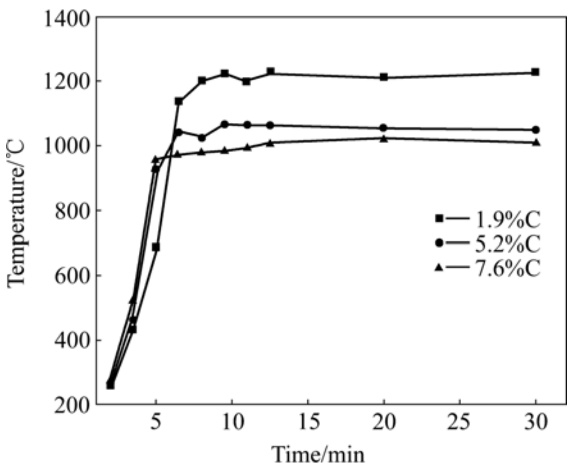

Fig.2 Temperature of laterite with different carbon contents heated by microwave

The fast heating behavior of the sample mixed with carbon may attribute to two factors. Firstly, carbon is an excellent microwave absorber. When it is mixed into other dielectric material, it can facilitate coupling with microwave. This has been proved by PICALES[14]. Secondly, magnetite is similar to the carbon, i.e. a