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Original Research Paper

Effect of microwave heating on the microstructures and kinetics of carbothermal reduction of pyrolusite ore

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ABSTRACT

This article focuses on the development of phase transformation and morphology of low-grade pyrolusite during carbothermal reduction using microwave heating. The XRD, SEM and EDS results show that selective carbothermal reduction of Mn_xO_y and Fe_xO_y in pyrolusite is easy to realize with microwave heating, which can reduce MnO_2 to MnO, and Fe_2O_3 to Fe_3O_4, rather than FeO. It was also observed that the phases of Mn_2O_3, Mn_3O_4 and MnO appear at 300 °C, 450 °C and 500 °C, respectively. The MnO phase, formed by the accumulation of MnO sphere particle with a diameter of 266.75–420.05 nm, is loose and porous. At a temperature of 750 °C, the Mn_2SiO_4 layer of about 316 nm in thickness, tightly wrapping SiO_2 particle is generated at the interface between MnO and SiO_2 embedded with MnO. Above 650 °C, Fe_2O_3 in pyrolusite can be transformed into a very dense Fe_3O_4 phase.

1. Introduction

Manganese is one of the most important strategic resources for any country [1] as it is widely used in several forms of alloys which includes ferromanganese, manganese silicon, electrolytic manganese dioxide (EMD), electrolytic manganese, Mn_3O_4 [2–6] and $MnSO_4$ [7–12]. Additionally it is also utilized as, battery material [13–15], soft ferrite [16–18] and catalyst [19–22], etc. The China's manganese ores reserve was about 215 million tons by the end of 2013 [23]. The oxidized manganese ores and rhodochrosite account for 25% and 56% in the total reserves of manganese ores, respectively. The rich pyrolusite grade is higher than 40% [24]. Conservative estimates indicate that over 95% of manganese resources in China are low-grade with complicated composition and finely disseminated grains, which need to be beneficiated [25]. With the continuing huge consumption, rich oxidized manganese ores and rhodochrosite that are directly leached by sulfuric acid can be expected to run out in the near future. Thus technological development to utilize low-grade pyrolusite is imperative.

At present, two popular methods are adopted for leaching low-grade pyrolusite: reduction roasting followed by sulfuric acid leaching or reductive leaching with water [26]. Reductive leaching of pyrolusite refers to mixing the manganese ore containing Mn^{4+} with the reducing agent that reduce Mn^{4+} to Mn^{2+}, followed by leaching with sulfuric acid solution. In this process, the reduction and leaching happen simultaneously. This method can effectively avoid the high-temperature reduction. The reducing agents for leaching are mainly classified into two groups: more pure reducing agents without inorganic impurities, such as methanol [27,28], oxalic acid [1], cellulose [29–31], cane molasses [32], glucose [33], hydrogen peroxide [34,35], SO_2 solution [36,37] and so on and is reductive ores whose composition is complex, including pyrite [38,39], sphalerite [40], chalcopyrite [41,42], and stone coal vanadium ore [43], etc. The leaching solution obtained by the former is more pure, but the process needs a long period (1.5–2.5 h), high temperature (85–90 °C), and more importantly, very high cost [44,45]. For the later, it inevitably needs tremendous consumption for these ores (30–82% of the weight of pyrolusite), long period of leaching (1.5–10 h), high leaching temperature (90–180 °C), low

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Table 1
Compositions of the pyrolusite (Total manganese 27.51%).

MnO_2	Mn_3O_4	MnO	Fe_2O_3	Fe_3O_4	SiO_2	Al_2O_3	K_2O	CaO	BaO
41.00	1.67	0.51	11.97	1.15	36.73	3.66	0.86	0.82	0.38
P_2O_5	MgO	TiO_2	SO_3	Co_2O_3	NiO	ZnO	SrO	CuO	Y_2O_3
0.38	0.36	0.16	0.11	0.06	0.05	0.05	0.04	0.02	0.01

Table 2
Compositions of the coal (Percentage).

Fixed carbon	Volatile organic matter	H_2O	SiO_2	Al_2O_3	SO_3	Fe_2O_3	TiO_2
67.58	10.89	4.67	7.19	3.55	2.55	1.83	0.76
CaO	K_2O	MgO	MnO	ZrO_2	P_2O_5	Cr_2O_3	SrO
0.63	0.19	0.08	0.02	0.02	0.02	0.01	0.01

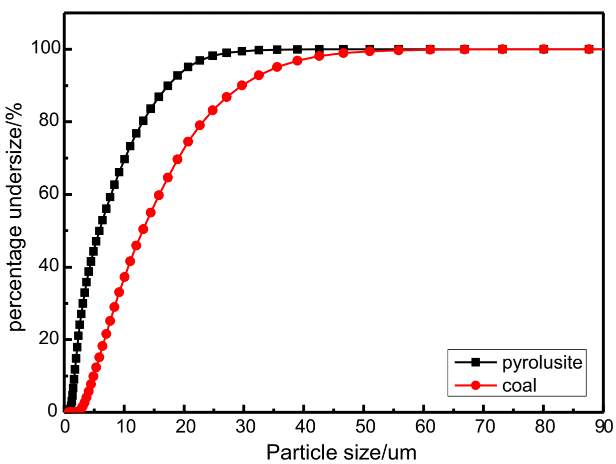

Fig. 1. Particle size distributions of pyrolusite and coal.

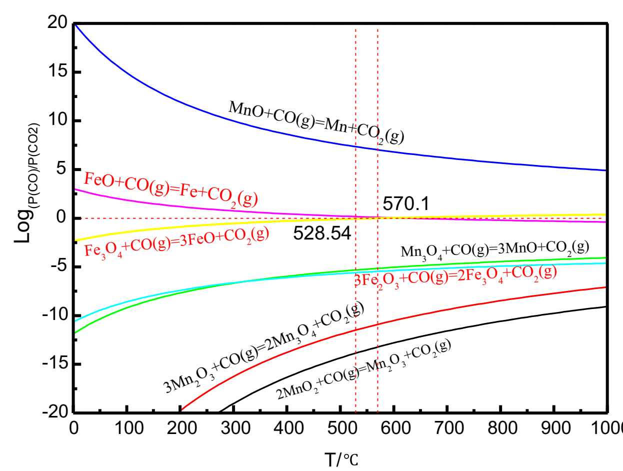

Fig. 4. Thermodynamics graph of reduction of pyrolusite.

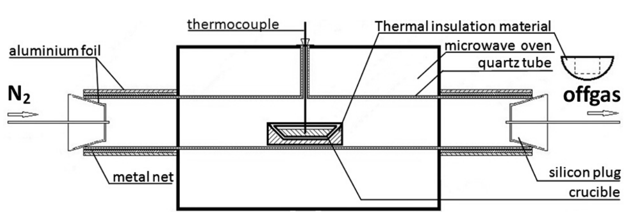

Fig. 2. Diagram of microwave tube furnace.

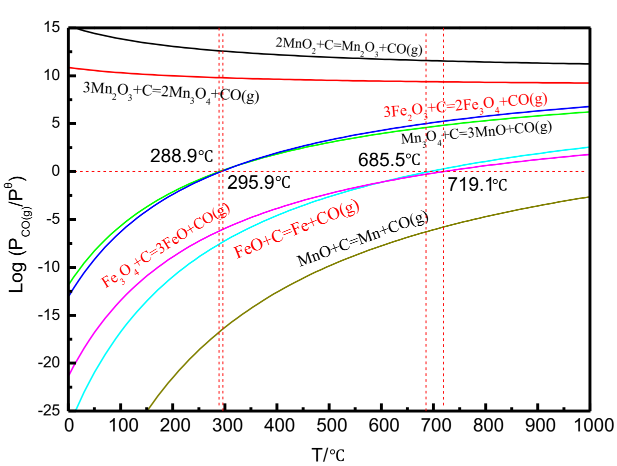

Fig. 3. Thermodynamics graph of direct reducing pyrolusite.

leaching rate, and produces a large number of slag and leaching solution with complex compositions.

Reduction roasting followed by sulfuric acid leaching is a conventional process for low-grade pyrolusite. The mechanism of carbothermal reduction for pyrolusite has been investigated by many researchers, such as А.я. лади [46], Holta and Olsen [47] and Y.X. Hua et al. [48], who have achieved reduction of MnO_2 in pyrolusite to MnO only at temperatures between 780 and 1050 °C. In actual reduction process, however, the temperature is higher. Thus, Fe^{3+} will be reduced to Fe^{2+}, metal Fe, and may be even reduced to Fe_3C or Fe_4C_3 while the MnO_2 is reduced to MnO. The further reduction for Fe_3O_4 will greatly increase the consumption of reductant as well as energy.

Mechanism of heat generation during microwave-material interaction is complex [49–52]. The main mechanisms are as follows: dipolar loss, conduction loss, hysteresis loss, eddy current loss, residual loss and domain wall resonance loss. The transition metal oxides and complex oxides coexisting with variable-valent ions can convert microwave energy into heat energy in the form of electrical conduction loss or dielectric relaxation. The advantages of microwave heating are selective, direct, rapid and volumetric heating. In many instances [53], microwave heating has been proved to dramatically reduce apparent reduction temperature and processing duration, increased product yield, and enhance product purities or material properties compared with conventional process.

This article intends to realize selective reduction for MnO_2 and Fe_2O_3 in low-grade pyrolusite at a low temperature utilizing