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Carbothermal reduction of low-grade pyrolusite by microwave heating

Qianxu Ye [a], Hongbo Zhu [a], Libo Zhang [a], Peng Liu [b], Guo Chen [a, c, *], Jinhui Peng [a, c, **]

[a] *State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, PR China.*

[b] *Changchun Gold Research Institute, Changchun 130012, PR China.*

[c] *Yunnan Mingzu University, Kunming 650500, PR China.*

[*] Corresponding author: Tel: +86 871 65138997; Fax: +86 871 65138997

E-mail address: guochen@kmust.edu.cn

[**] Co-corresponding author:

E-mail addresses: jhpeng@kmust.edu.cn

Abstract

The pyrolusite was carbothermal reduced using coal by microwave heating. The crystal structures and microstructure of the samples were characterized after microwave heating using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), respectively. When the reductants proportion of 10 percent, reduction temperature of 800 °C and holding time of 40 minutes, the reduction ratio of MnO_2 to MnO of 97.2%, Fe_2O_3 transforms to Fe_3O_4 almost completely and there was no Fe (II) produced. It was found that the low-grade pyrolusite was carbothermal reduced using microwave heating with lower temperature and shorter processing time. These results show that the microwave heating can be applied effectively and efficiently to the carbon-thermal reduction processes of low-grade pyrolusite.

Key words: low-grade pyrolusite; microwave heating; coal; carbon-thermal reduction

1. Introduction

With the extensive exploiting and consume of high grade manganese ore (total Mn>35%) [1], people are paying more and more attention to the exploiting and utilization of low grade (total Mn<35%) manganese ore which has low business value [2-3].

Pyrolusite is usually formed by MnO_2 and other oxides such as SiO_2 and Fe_2O_3 [4-5]. It is granular, fibrous or columnar like, which has good properties on absorbing the microwave energy [6]. Pyrolusite is also a significant strategic resource and a key

material to produce MnO_2 and Mn. MnO_2 has many polymorphic forms such as $\alpha-$, $\beta-$, $\gamma-$ and $\varepsilon-$ type [7]. It is widely used in the fields of catalysis, ion sieve, electrode material of Li/MnO_2 and semiconductor [8-14]. Manganese is essential to iron and steel production due to its sulfur-fixing, deoxidizing, and alloying properties. Manganese from these ores can be extracted selectively using hydrometallurgical techniques.

One thing is to pre-reduce pyrolusite at high temperature (1000-1350 °C) [15-18]. The reductants were used as natural gas and methane gas, which contains H_2、CO、CH_4, and carbonaceous material, like coal, wood-charcoal and graphite [19-27]. Firstly, The MnO_2 in the pyrolusite is reduced to MnO, and then leached using hot acid solution, which the Mn^{2+} is obtained from leaching solution. The leaching solution containing Mn^{2+} and Fe^{2+} need to be purified and electrolyzed, and then the high quality electrolytic MnO_2 is acquired. Although this method is mature, it consumes a large quantity of energy and needs a long period (2-4h) [28]. Secondly, the current research hotspot is the directly reductive leaching methods in the water solution. The reductants are oxalic acid [29], pyrite [30], aqueous sulfur dioxide [31], iron powder [32], iron(II) sulfate [33], hydrogen peroxide [34], organic biomass reductants and bio-battery [35-37]. To leach pyrolusite, pyrolusite and another mineral are mixed in the acid solution, and then the leaching solution containing Mn^{2+} and Fe^{2+} is obtained. The advantage of this method is the short process path, low energy-consumption and short processing cycle, but purification of the leaching solution is very difficult because of its complex chemical constituents.

Microwave heating has many characteristics, such as selective, uniform and fast heating, no pollution, low equipment cost, very fast reaction speed and high product yields [38]. It can successfully avoids the disadvantages in traditional heating method, such as large temperature gradient, long processing period, low heating efficiency, high energy-consumption and high pollution industries [39-40].

In this paper, we try to make use of the advantage of microwave heating to solve the current problems (high temperature, high energy consumption and high reductants ratio) in pre-reduction process of pyrolusite. The influence of reaction temperature and holding time on the reduction of pyrolusite were systematically investigated, and the aim is to find the low temperature and the short period process for reduction of pyrolusite.

2. Experimental

2.1. Materials

The chemical composition of the low-grade pyrolusite was presented in Table 1, and the compositions of the coal were shown in Tables 2, respectively. The particle size distribution of the pyrolusite and coal used were represented in Fig. 1. All these materials were milled by a ball grinding mill.

2.2. Instruments

A self-made microwave tube furnace, which utilizes a single-mode continuous controllable power was utilized for all experiments and shown in Fig. 2. The

microwave frequency was 2.45 GHz, while the output power was controlled within the maximum of 3000W. The activation temperature was controlled by varying the input microwave power. The activation temperature was measured by nickel chrome-nickel silicon armor type thermocouple which was in contact with the materials. The dimension of the thermocouple were 1000mm in length, 3mm in diameter, with the temperature range of 0-1250 °C, and a measurement with precision up to ±0.5 °C.

2.3. Methods

The pyrolusite powder and the coal were thoroughly mixed in an agate mortar and put into the corundum crucible, which has a temperature test hole at the waist, and the mixed material surface was covered by the layer of coal powder (about 1 g). The reductants proportion was 10%. The mixed materials were placed inside a microwave heating reactor, which the schematic diagram of the microwave reactor was shown Fig. 2. The cavity of microwave heating reactor was filled with nitrogen by the gas cylinder for 10 min. Then the carbon thermal reduction experiments were started according to the process.

Reduction ratios of Mn and valence state of iron were chosen as independent research factors. At the end of the experimental, reduction ratio of Mn was calculated based on the following equation:

$$\text{Degree of reduction} = \eta_{Mn} = \frac{M_2}{M_1} \times 100\% \quad (1)$$

where M_1 is the mass of Mn, M_2 is the mass of Mn(II), and the determination of degree of reduction using ferrous ammonium sulfate as Redox indicators.

2.4. Characterization

After microwave heating, the phase transitions of the pyrolusite were identified using XRD technology (D/Max 2200, Rigaku, Japan). XRD patterns were recorded using Rigaku diffractometer with CuKα radiation and a Ni filter operated at the voltage of 35kV, anode current of 20mA and a scanning rate of 0.25°/min, respectively. The microstructure morphology of the pyrolusite and the microwave heating treated samples were investigated by scanning electron microscope (SEM). The SEM instrument (XL30ESEM-TMP, Philips, Holland) was operated at 20 kV in a low vacuum, while the energy dispersion scanner spectrometer (EDX, USA) attached to the SEM was used for semi-quantitative chemical analysis.

3. Results and discussion

Figure 3 shows the thermodynamics graph of the direct-reduced manganese and iron oxide. The main chemical reductions can be calculated by the following equations,

$$2MnO_2 + C = Mn_2O_3 + CO(g) \quad (2)$$

$$3Mn_2O_3 + C = 2Mn_3O_4 + CO(g) \quad (3)$$

$$Mn_3O_4 + C = 3MnO + CO(g) \quad (4)$$

$$MnO + C = Mn + CO(g) \quad (5)$$

$$2MnO_2 + C = Mn_2O_3 + CO(g) \quad (6)$$

$$3Fe_2O_3 + C = 2Fe_3O_4 + CO(g) \quad (7)$$

$$Fe_3O_4 + C = 3FeO + CO(g) \quad (8)$$

$$FeO + C = Fe + CO(g) \quad (9)$$

It can be seen in Fig. 3 that the reactions of $MnO_2 \longrightarrow Mn_2O_3 \longrightarrow Mn_3O_4$ (equation (2) and (3)) can be done at room temperature and the beginning reduction temperature of the reactions of 289.8-719.74 °C was used in the further research work in order to transform from Mn_xO_y to MnO.

Mainly carbonthermal reductions of the pyrolusite are shown in following equation, which can be observed from the thermodynamic graph of the manganese and iron oxide by indirect reduction, as shown in Fig. 4.

$$MnO_2 + CO(g) = MnO + CO_2(g) \quad (10)$$

$$3Mn_2O_3 + CO(g) = 2Mn_3O_4 + CO_2(g) \quad (11)$$

$$Mn_3O_4 + CO(g) = 3MnO + CO_2(g) \quad (12)$$

$$MnO + CO(g) = Mn + CO_2(g) \quad (13)$$

$$3Fe_2O_3 + CO(g) = 2Fe_3O + CO_2(g) \quad (14)$$

$$Fe_3O_4 + CO(g) = 3FeO + CO_2(g) \quad (15)$$

$$FeO + CO(g) = Fe + CO_2(g) \quad (16)$$

$$2C + O_2(g) = 2CO(g) \quad (17)$$

$$C + CO_2(g) = 2CO(g) \quad (18)$$

Quantitative evaluations of the studied reactions from the perspective of thermodynamics are characterized. It can be seen from Fig. 4 that the reactions of $MnO_2 \longrightarrow Mn_2O_3 \longrightarrow Mn_3O_4 \longrightarrow MnO$ (equations (10), (11) and (12)) can be achieved at room temperature. The reactions of $Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO$ can be done at room

temperature under standard conditions, and the temperature should be controlled at 575 °C. According to the thermodynamic analysis of fig. 4, Mn_xO_y can be reduced into MnO and Fe_xO_y is reduced into FeO at room temperature, respectively.

The microwave heating curve of the raw material are characterized, with coal proportion of 10 %, total material of 50 g and microwave power of 200 W, are characterized and the results are illustrated in Fig. 5. It can be seen from Fig. 5 that the mixed materials could be heated to 800 °C from room temperature at 6 min under the low microwave power density (4w/g), which the highest heating rate is 372 °C/min and the average heating rate is 165.2 °C/min. It can be concluded that the mixed pyrolusite powder, which contains coal, has a good characteristic of microwave absorbing.

Figure 6 shows the relationship between the reduction ratio of Mn (η_{Mn}) and the holding time (T), when the reductant proportion of pyrolusite of 10 %, and the holding time of 40min. It can be seen from Fig. 6 that the reduction ratio of pyrolusite increases gradually from 16.56% to 97.2%, with increasing the microwave heating temperature from 400 °C to 800 °C. it can be concluded that with the temperature increasing, the ΔG^{Θ} value of reaction $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ decreases obviously (Fig. 3 and Fig. 4), which means that the thermodynamic condition becomes better, and while the temperature is higher, the dynamic condition is also improved markedly.

The relationship between the reduction ratio of Mn (η_{Mn}) and the holding time (T) of the pyrolusite under microwave heating are obtained, and the results are illustrated

in Fig. 7. It can be seen from Fig. 7 that, the reduction ratio of Mn increases with the extension of the microwave holding time. After holding for 40 minutes, the reduction ratio increases slowly, due to the amount of un-reduced MnO_2 and the remaining reductant are reduced.

The crystal structures of the raw materials after microwave heating are characterized by XRD, and the results are illustrated in Fig. 8. It can be seen that MnO, Fe_3O_4, $MnSiO_4$ and SiO_2 are the major phase composition in the microwave treated samples. In addition, a minor amount of $MnSiO_4$ is also present. The XRD results of microwave reduced product show that the XRD patterns of the reference MnO and all peaks match the standard spectra of MnO well (JCPDS card No. 89-4835), the strongest and second preferential orientation of (2 0 0) and (1 1 1) planes of the reduced MnO are observed at 2θ= 40.577° and 2θ= 34.950°, respectively. It can be seen from Fig. 8 that the total Mn of raw materials completely transforms to MnO, and Fe_2O_3 is reduced to Fe_3O_4. It can be seen from Figs. 6 and Figs. 7 that Fe_2O_3 transforms to Fe_3O_4 almost completely at 800 °C (equations (8) and (15)), and there was no Fe (II) produced.

The results also indicate that the low-grade pyrolusite was carbothermal reduced using microwave heating with lower temperature and shorter processing time. Because of the major advantages of using microwave heating for industrial processing are rapid heat transfer, volumetric and selective heating, compactness of equipment, speed of switching on and off and pollution-free environment.

The pyrolusite before and after microwave reduction at the microwave heating

temperature of 800 °C and the holding time of 40 min are characterized, by SEM and EDAX techniques, and the result as shown in Figs. 9 and Figs. 10, respectively. Compared with the untreated raw materials (Fig 9(a)), From the SEM in Fig. 9(b), the results indicate that the size distribution of the microwave treated samples is wide (0.3-20um), and the product seems to be hard agglomerates, which may have formed by sintering of small particles. EDAX analyses of microwave treated pyrolusite are carried out to estimate the elemental composition of microwave heating prepared MnO, and the results are shown in Figs. 10. It was observed from Fig. 10(a) and Fig. 10(b) that the microwave treated product consists of Mn and Fe, and minor amounts of Si, Au, Ca and Al.

4. Conclusion

The pyrolusite was microwave pre-reduced using coal at varying heating times. The optimum conditions for experiment parameters of microwave pre-reduced pyrolusite were obtained with the proportion of coal of 10%, process temperature of 800 °C, and holding time of 40 min. Under these optimum conditions, the reduction ratio of MnO_2 to MnO in the pyrolusite was 97.2%. Fe_2O_3 transforms to Fe_3O_4 completely and there was no Fe (II) produced from the microwave heating processing. The reduction product was formed by sintering of small particles. Compared with the traditional high temperature (1000 °C-1350 °C) method of pre-reduce pyrolusite, the microwave heating technique was characteristic of short time, low temperature, low consumption and high quality. Based on the mention results, this method can be

applied effectively and efficiently to the carbon thermal reduction processes of low-grade pyrolusite.

Acknowledgements

Financial supports from the Key Projects in the National Science & Technology Pillar Program during the Twelfth Five-year Plan Period (No.: 2015BAB17B00), Specialized Research Fund for the Doctoral Program of Higher Education (No.: 20125314120014) and the Applied Foundation Fund of Yunnan Province of China (No.: 2012FD015), and Yunnan Provincial Science, and Technology Innovation Talents scheme - Technological Leading Talent (No.: 2013HA002) and the award for new academic graduate student of Yunnan province were sincerely acknowledged.

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

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 (mass %).

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

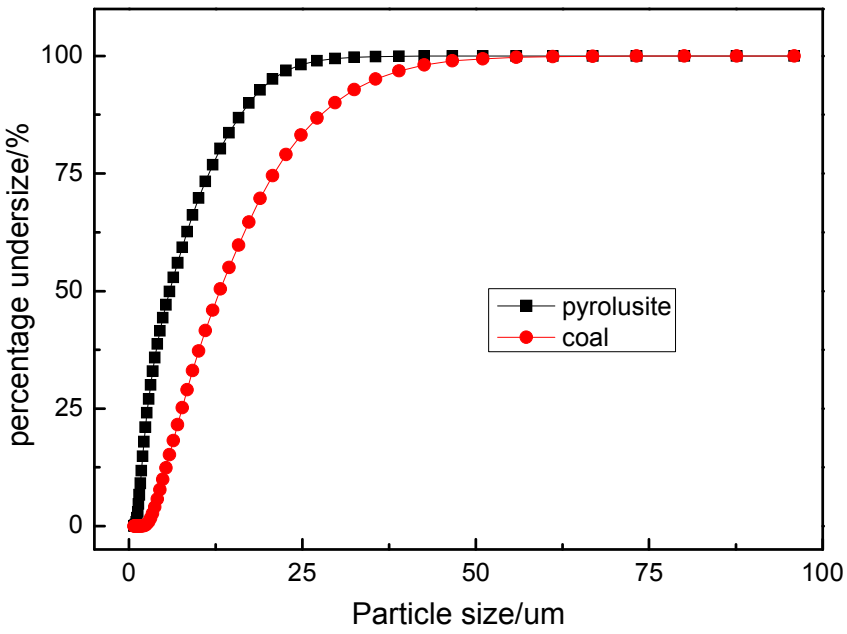


Fig. 1 Particle size distributions of pyrolusite and coal.

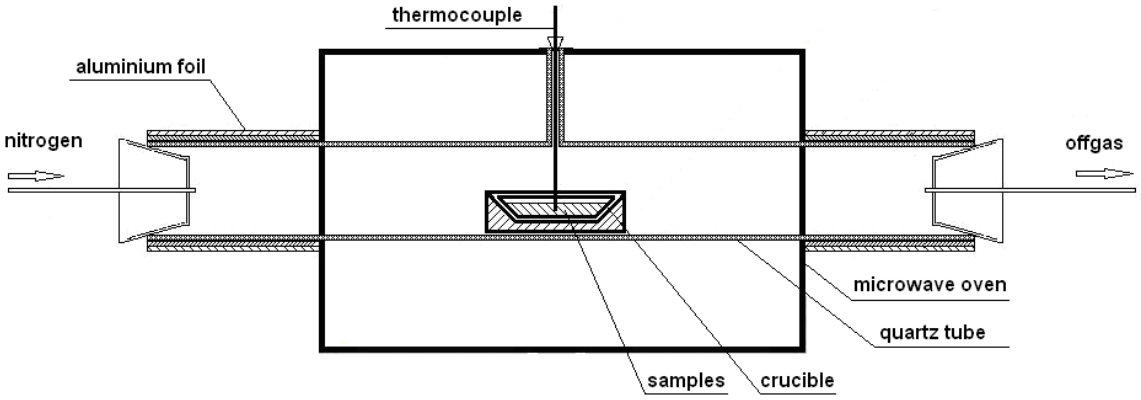


Fig. 2 Diagram of microwave tube furnace.

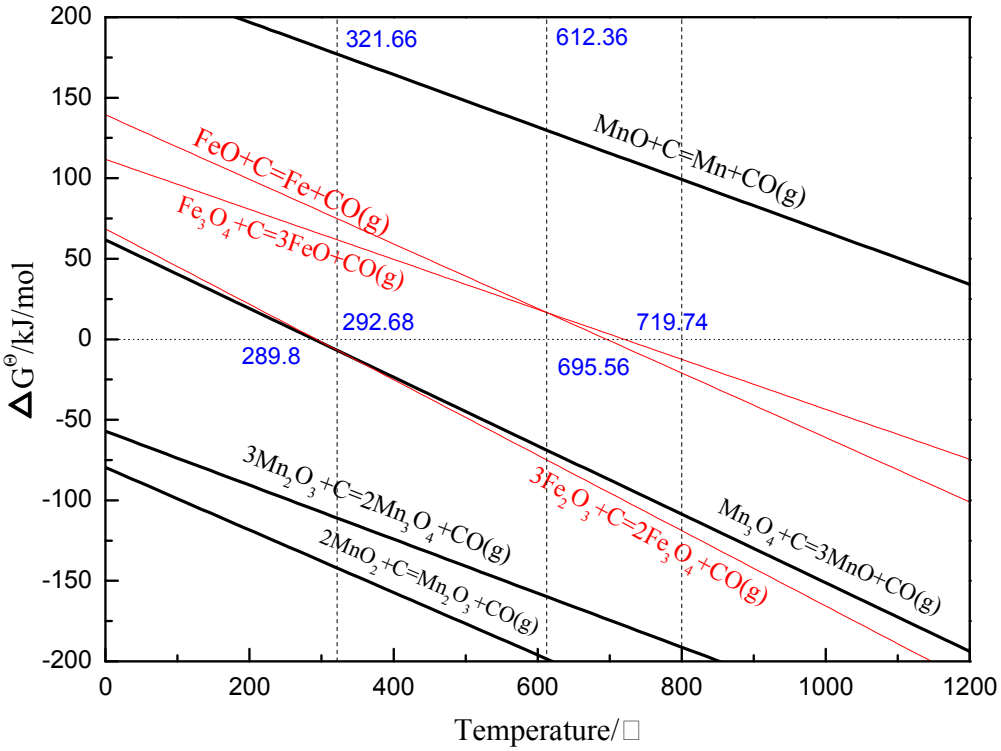


Fig. 3 Thermodynamics graph of direct reducing manganese and iron oxide.

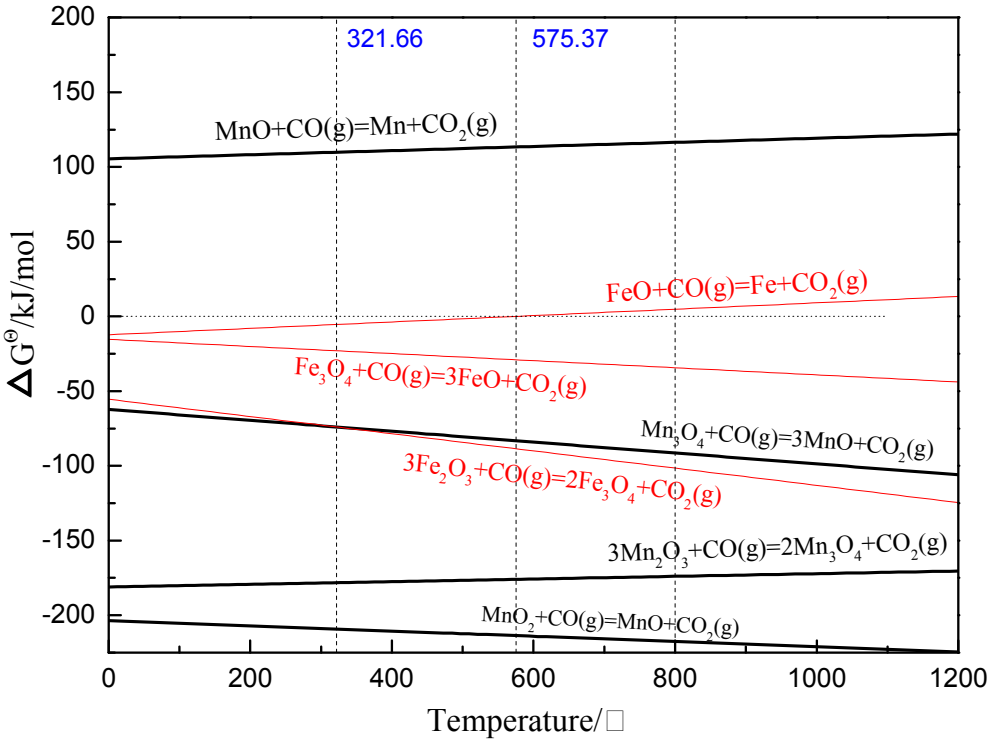


Fig. 4 Thermodynamics graph of reductions of manganese and iron oxide.

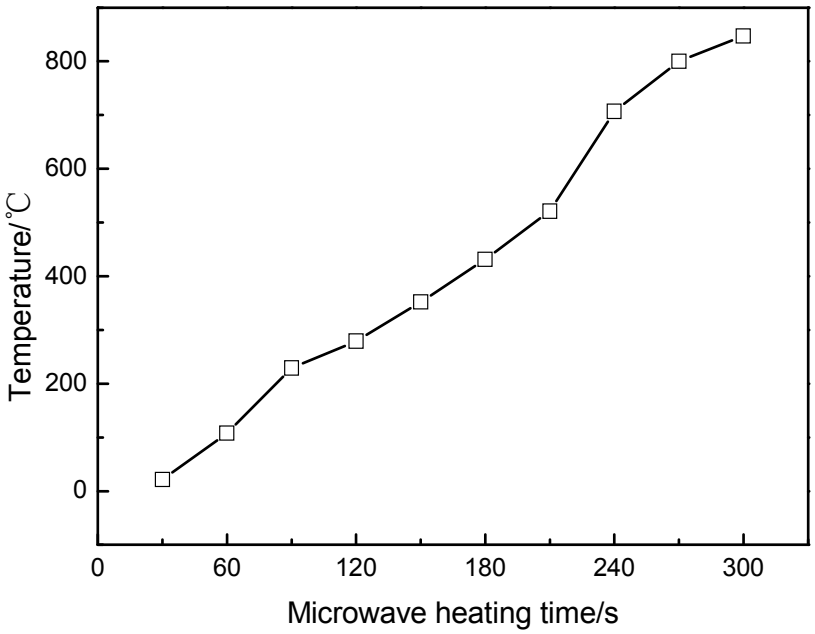


Fig. 5 Microwave heating curve of the raw material with 10% coal.

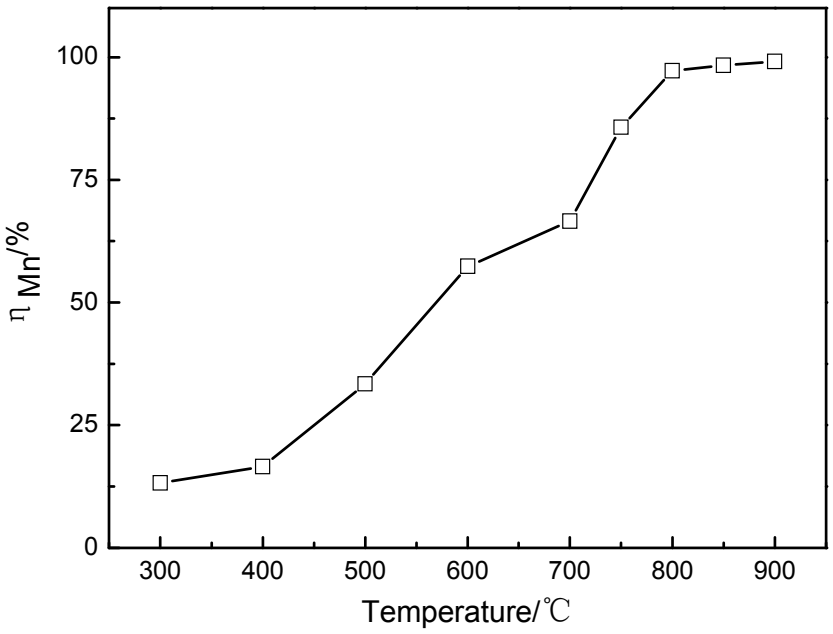


Fig. 6 Influence of reduction temperature on the reduction ratio of pyrolusite.

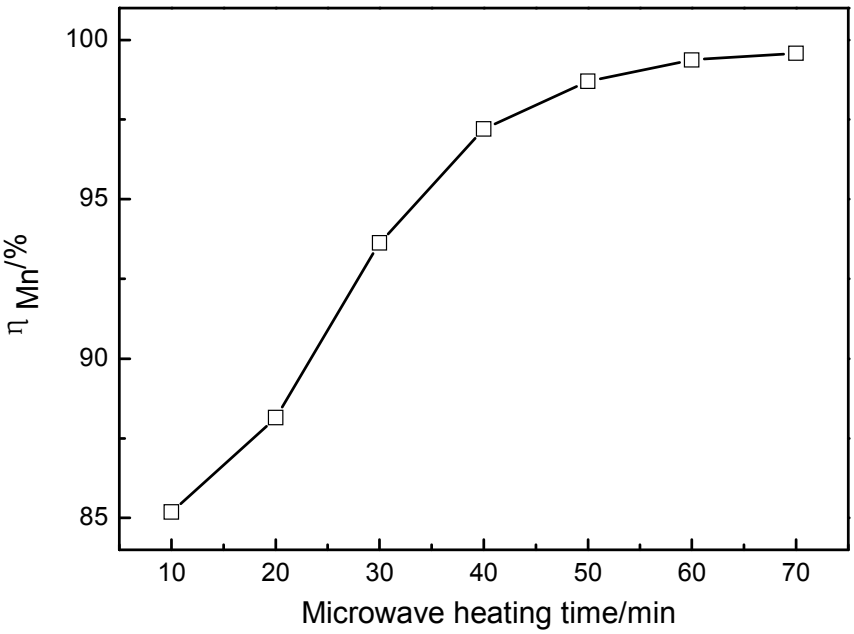


Fig. 7 Influence of holding time on the reduction ratio of pyrolusite.

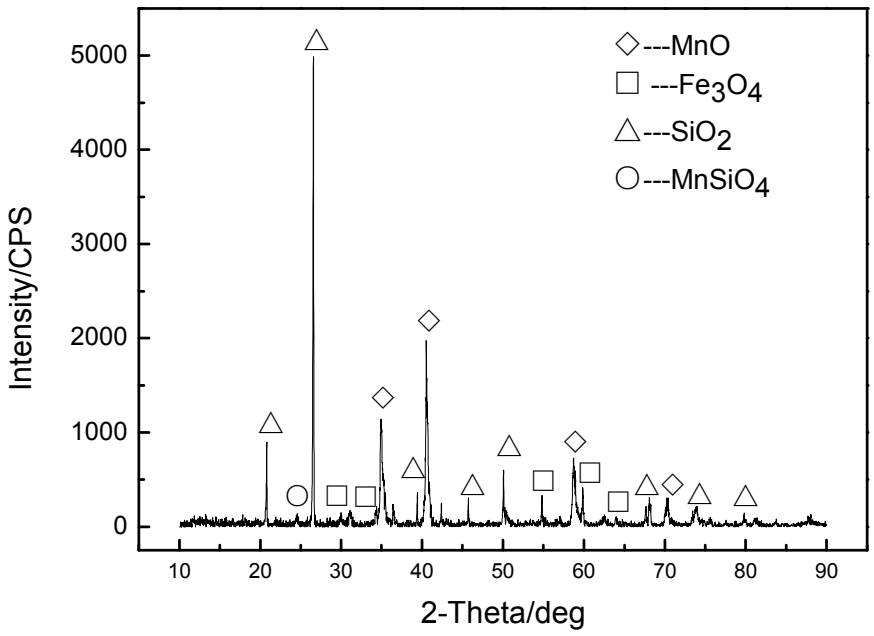
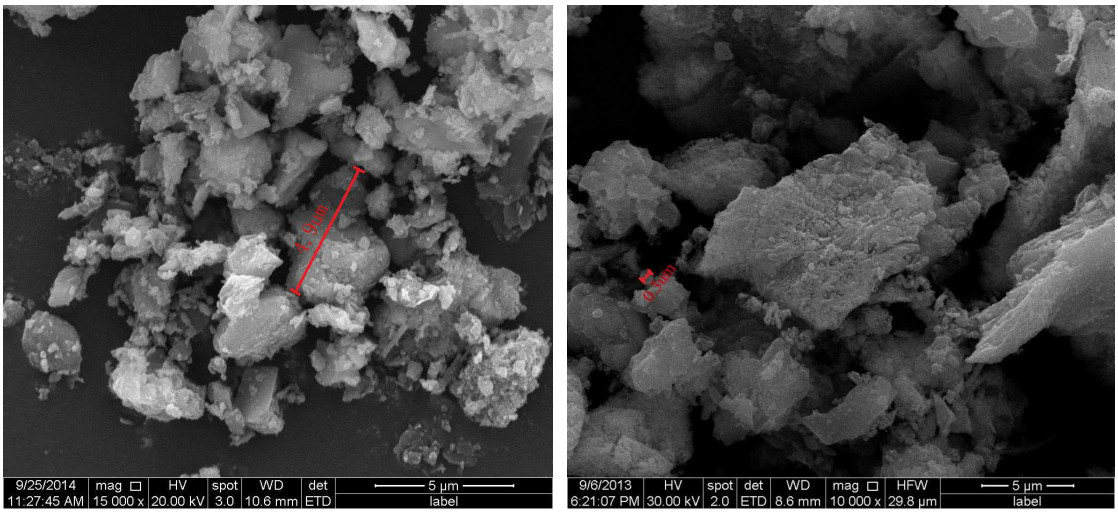
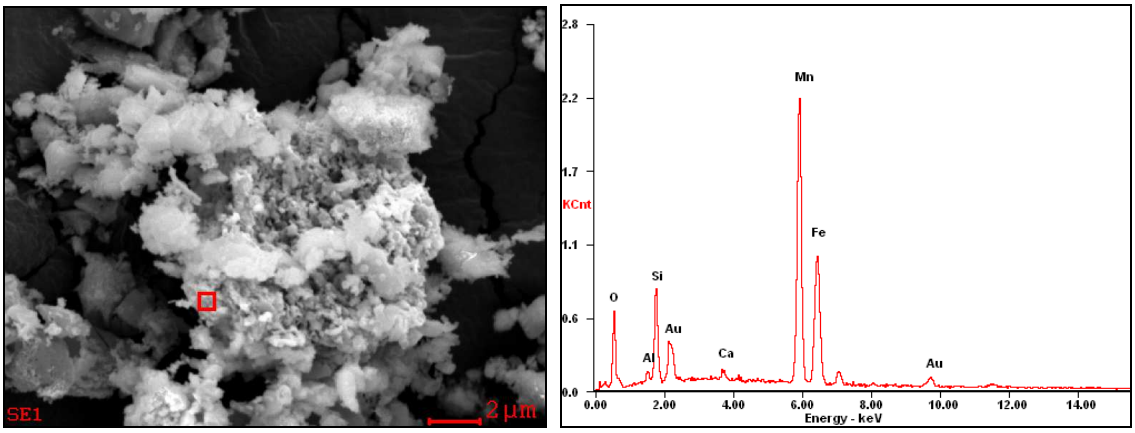


Fig. 8 XRD of the product prepared after microwave heating at 800 °C for 40min.



(a) (b)

Fig. 9 SEM of the raw materials before and after microwave irradiation at 800 °C for 40 min. (a) raw materials; (b) microwave treated samples



(a) (b)

Fig.10 EDS of the product prepared after microwave heating at 800 °C for 40min.

(a) district of EDAX analysis; (b) EDAX analysis results of red area