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Carbothermal reduction characteristics of oxidized Mn ore through conventional heating and microwave heating

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Abstract: For the purpose of exploring a potential process to produce FeMn, the effects of microwave heating on the carbothermal reduction characteristics of oxidized Mn ore was investigated. The microwave heating curve of the mixture of oxidized Mn ore and coke was analyzed in association with the characterization of dielectric properties. The comparative experiments were conducted on the carbothermal reductions through conventional and microwave heatings at temperatures ranging from 973 to 1373 K. The thermogravimetric analysis showed that carbothermal reactions under microwave heating proceeded to a greater extent and at a faster pace compared with those under conventional heating. The metal phases were observed in the microstructures only under microwave heating. The carbothermal reduction process under microwave heating was discussed. The electric and magnetic susceptibility differences were introduced into the thermodynamics analysis for the formation of metal Mn. The developed thermodynamics considered that microwave heating could make the reduction of MnO to Mn more accessible and increase the reduction extent.

Keywords: carbothermal reduction; manganese ore; manganese oxides; microwave heating; thermodynamics; electromagnetic fields

1. Introduction

Mn, dominantly consumed in steel industries as FeMn, is an essential element that improves the strength, toughness, and hardness of steels [1]. The primary route for FeMn production is the carbothermal reduction of oxidized Mn ores [2]. The effects of ore composition, particle size, gas atmosphere, and temperature on reduction behavior have been well established in the literatures [3–5]. In oxidized Mn ores, Mn oxides are commonly associated with a certain amount of Fe oxides, but the reduction of Mn oxides is far more difficult than that of Fe oxides. As a transition metal, Mn has various oxidation states to form different types of oxides, mainly including Mn(IV) oxide (MnO_2), Mn(III) oxide (Mn_2O_3), Mn(II, III) oxide (Mn_3O_4), and Mn(II) oxide (MnO) [6]. The transformation process from Mn oxides to metal Mn may be expressed as “ $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO} \rightarrow \text{Mn}$ ” [7–8]. The higher-order Mn oxides are thermally composed or reduced to MnO through solid-state reactions, but the solid-state reduction of MnO is slow and not practically

possible.

For the commercial production of FeMn, MnO is reduced from the molten slag at a smelting temperature range of 1673–1723 K [9]. The reduction process is energy intensive and operated in a blast furnace (BF) or a submerged arc furnace (SAF) [10]. In recent decades, the SAF route largely replaced the BF route to reduce coke consumption. However, a typical operation process for the SAF route needs to consume 2100–3900 kWh of electricity and 250–400 kg of coke per metric ton of FeMn produced [11]. The commercial production of FeMn is still facing serious problems, such as high energy consumption and environmental pollution.

Microwave heating has been adopted as an alternative to current heating technologies due to economic and environmental benefits [12–14]. The heating effect of microwaves results from dielectric polarization, conductive loss, and magnetic loss [15–18]. Thermal energy is directly transferred throughout reaction components due to the volumetric and selective heating characteristics of microwaves [19–20]. The application of microwave energy to metallurgy has been

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widely investigated for several decades [21–22]. The early explorations focused on the high-temperature microwave processing of minerals. After the strong microwave absorption in metal-bearing minerals had been demonstrated, intensive research was conducted on the microwave extraction of metals, such as the reduction of metal oxides [23–25]. Compared with conventional heating, microwave heating can dramatically accelerate the heating rate and reduce the temperature and time required for the reduction processes. Thus, microwave heating may have a potential application to the commercial production of FeMn for the sake of a considerable reduction in energy consumption and pollution.

Although some recent studies have reported the microwave characteristics of Mn compounds and Mn ores, the understanding of its potential application remains insufficient. Su *et al.* [26] adopted three measurement methods to compare the microwave absorption characteristics of several Mn compounds, among which MnO_2 turned out to have the strongest microwave absorption ability. Chen *et al.* [27] assessed the thermodynamic behavior of Mn ores and concluded the effective application of microwave heating to calcination processes. Liu *et al.* [28] investigated the heating characteristics of Mn ore fines containing coal, considering the effects of particle size, basicity, and ore to coal ratio. In general, these studies mostly concentrated on the thermal effect of microwaves but seldom mentioned the nonthermal effect, which has been proposed to explain unusual observa-

tions in microwave chemistry [29–30]. Even though the non-thermal effect of microwaves remains open for debate, increasing evidence has shown that microwaves can change the activation energy and reaction temperature of specific chemical reactions [31–32].

For the purpose of exploring a potential process to produce FeMn, the present work aims to investigate the effects of microwave heating on the carbothermal reduction characteristics of oxidized Mn ore. The comparative experiments were conducted on the carbothermal reductions through conventional and microwave heating. The carbothermal reduction characteristics were discussed from the perspectives of microstructural observation and theoretical thermodynamic analysis.

2. Materials and methods

The oxidized Mn ore lump and coke powder used in this work were collected from a ferroalloy plant. Their chemical compositions are shown in Table 1. The ore lump, which consists mostly of MnO_2 , was ground to powder and then passed over a 100-mesh screen to obtain the desired particle size of 150 μm . The coke powder with a particle size of 180 μm was used as the reductant. Ore and coke powders were dried at 373 K for 24 h before being used. The sample of carbothermal reduction experiments was prepared by mixing the ore and coke powders in a C/O molar ratio of 1:1.3.

Table 1. Chemical compositions of the Mn ore lump and the coke powder

Material	TMn	TFe	SiO_2	CaO	MgO	Al_2O_3	P	S	C	Ash
Ore	38.8	4.68	6.13	1.9	0.37	0.84	0.022	0.027	—	—
Coke	—	—	—	—	—	—	0.024	1.43	81.87	15.6

Note: TMn and TFe stand for total Mn and total Fe in the material, respectively.

The dielectric properties of the sample were characterized using the cavity perturbation technique. The testing system adopted in this work has previously been described in detail [33]. The experiments were conducted at temperature intervals of 50 K in the range between room temperature and 1273 K. The real part ϵ' and the imaginary part ϵ'' of complex dielectric permittivity ϵ were obtained in accordance with the Nicholson–Ross–Weir model. The measurement error is 2% at room temperature and 4% at high temperatures.

The carbothermal reduction experiments were conducted at temperatures of 973, 1173, and 1373 K through conventional and microwave heating. A 500 g sample was used in each experiment. After the heating process, the reacted sample was naturally cooled down to room temperature, embedded in cold resins, and polished. The phase component was determined using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

The experiments using conventional heating were per-

formed in a Si–Mo bar resistance furnace rated at 380 V and 12 kW. Fig. 1 shows the schematic of the experimental resistance furnace. The thermocouple is connected to the temperature controller and inserted into the flat-temperature zone of the furnace from the bottom. An alumina crucible is fixed

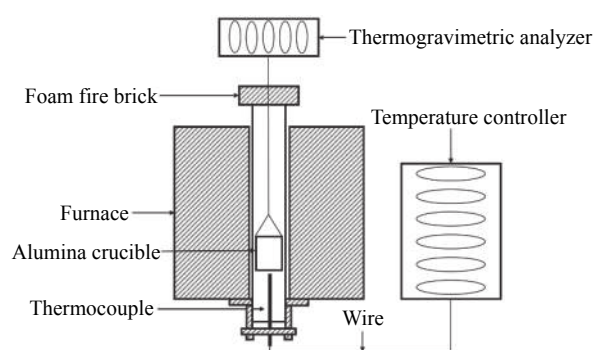


Fig. 1. Schematic of the Si–Mo bar resistance furnace.

to a hanging basket made of Fe–Cr–Al alloy. The top end of the hanging basket is connected to a thermogravimetric analyzer. A typical run is started by heating up the experimental resistance furnace from room temperature to the desired temperature. After the furnace has reached the desired temperature, the alumina crucible with the sample was placed into the flat-temperature zone of the furnace and then was held at the desired temperature until the mass measured by the thermogravimetric analyzer tended to remain relatively stable.

The experiments using microwave heating were performed in a metallurgical microwave heating furnace with the maximum power of 4 kW. Fig. 2 shows the schematic of the experimental microwave furnace. Four microwave magnetrons are respectively installed at both sides of the furnace to increase the penetration depth of microwaves into materials. A quartz crucible is placed in an insulation bucket and supported by three sensors that are connected to a thermogra-

vimetric analyzer. The insulation bucket is made of ZrO_2 and quartz. These materials are non-microwave absorbable, so that microwaves can penetrate the wall of the insulation bucket and be mostly absorbed by the sample in the quartz crucible. The exterior of the insulation bucket is wrapped in cotton to hinder heat loss. A thermocouple is connected to a temperature controller and inserted into the sample. To start a typical run, a transformer boosts the 220 V alternating current to the high voltage, under which magnetrons could produce microwaves with a frequency of 2.45 GHz. The sample was heated up from room temperature to the desired temperature with a constant microwave power of 4 kW. After the sample had reached the desired temperature, the temperature controller automatically adjusted the power output to maintain the sample being held at the desired temperature until the mass measured by the thermogravimetric analyzer tended to remain relatively stable.

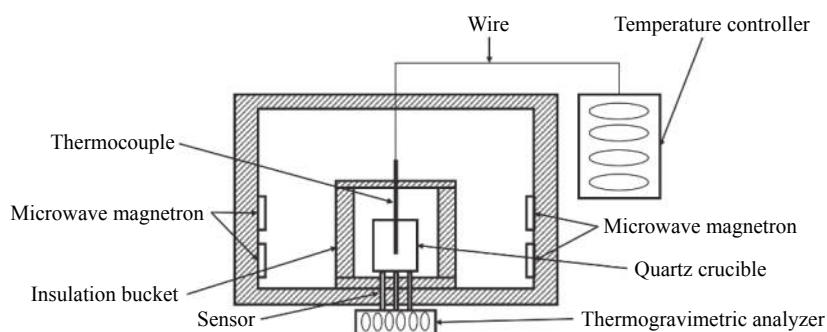


Fig. 2. Schematic of the metallurgical microwave heating furnace.

3. Results

3.1. Dielectric properties

Fig. 3 shows ϵ' and ϵ'' of the sample with varying temperatures at a frequency of 2.45 GHz. The variations of ϵ' and ϵ'' versus temperature have a similar trend. Particularly, ϵ' increases from 7.87 to 9.90 as temperature increases until 1023 K where ϵ' then falls back to 8.75 at 1273 K; ϵ'' increases from 0.13 to 1.22 as temperature increases until 1073 K where ϵ'' then falls back to 0.69 at 1273 K. The ratio of ϵ'' to ϵ' is defined as the dielectric loss tangent $\tan\delta$, which can represent the microwave absorption capacity of the sample. Fig. 4 shows $\tan\delta$ of the sample with varying temperatures. Similarly, $\tan\delta$ increases from 0.02 to 0.13 as temperature increases until 1073 K where $\tan\delta$ then falls back to 0.08 at 1273 K. The microwave absorption capacity of the sample strongly depends on the temperature and has a maximum at 1073 K.

3.2. Microwave heating curve

Fig. 5 shows the microwave heating curve of the sample in air at a frequency of 2.45 GHz and a constant power of 4 kW. As time proceeds, the sample temperature increases rapidly

above 1000 K with 150 s and then slows down. After 600 s, the sample temperature can reach above 1600 K, at an average heating rate of 2.7 K/s. It spends approximately 146, 228, and 350 s for the sample to reach the desired temperatures of 973, 1173, and 1373 K, respectively.

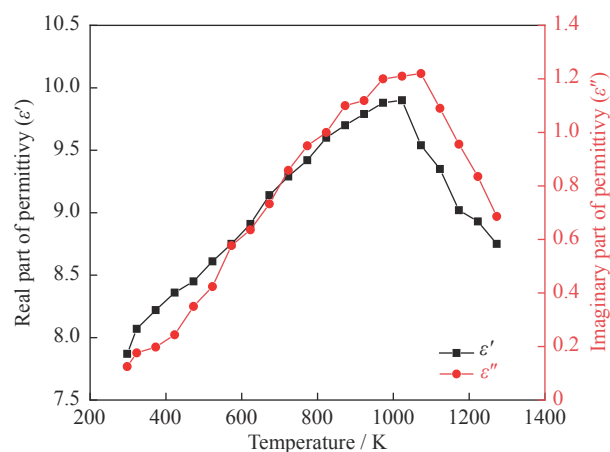


Fig. 3. Permittivity of the sample with varying temperatures at a frequency of 2.45 GHz.

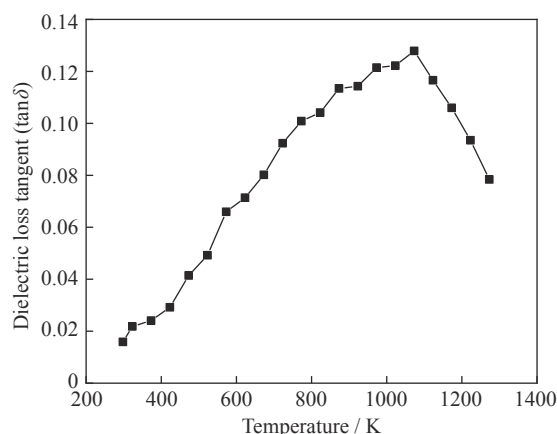


Fig. 4. Dielectric loss tangent of the sample with varying temperatures at a frequency of 2.45 GHz.

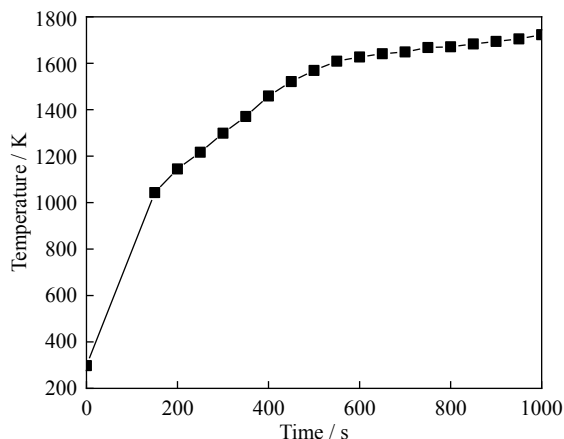


Fig. 5. Microwave heating curve of the sample in air at a frequency of 2.45 GHz and a constant power of 4 kW.

3.3. Thermogravimetric analysis

The mass-loss rate is considered an index to reflect the extent of carbothermal reactions as the reduction of oxides and the gasification of coke are related to the loss of mass. The mass-loss rate is calculated from the following equation:

$$\Delta w = \frac{w_0 - w_t}{w_0} \times 100\% \quad (1)$$

where Δw is the mass-loss rate, w_0 is the mass of samples before reaction, and w_t is the mass of samples after reaction. Fig. 6 shows the mass-loss rate of sample as a function of time at 973, 1173, and 1373 K using conventional and microwave heating. In general, the mass-loss rate increases continuously to a relatively stable level as the heating time proceeds. The mass-loss rate using microwave heating, though, climbs faster than that using conventional heating. The mass-loss rate of former after 20 min can even exceed the latter after 50 min at the same temperature. Therefore, compared with conventional heating, microwave heating can not only accelerate the reaction process but also enhance the reaction extent.

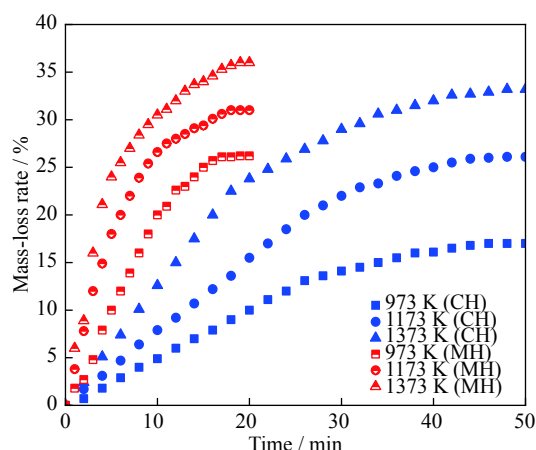


Fig. 6. Mass-loss rate as a function of time for sample under conventional heating (CH) and microwave heating (MH) at different temperatures.

3.4. Microstructures

Fig. 7 shows the microstructures of reacted samples after 50 min of conventional heating at 973, 1173, and 1373 K. In accordance with EDS analysis, these microstructures are mainly composed of oxide phases, of which the typical compositions are shown in Table 2. The oxide phases are dominated by Mn oxides. The Mn content in the oxide phases is higher than that in the sample before the carbothermal reaction due to the reduction of high-order Mn oxides during the heating process. The mole ratio of Mn to O increases with the increase in temperature, demonstrating that high temperatures can expand the extent of the reduction process. MnO is inferred as the major component of the oxide phases at 1173 and 1373 K because the Mn/O molar ratios at the two temperatures are nearly 1:1. However, no metal Mn is observed in the microstructures despite the 50 min heating processes at 1373 K. The result indicates that the studied temperature is likely too low to achieve the complete reduction of MnO_2 to Mn via conventional heating.

Fig. 8 shows the microstructures of reacted samples after 20 min of microwave heating at 973, 1173, and 1373 K. The microstructures have smooth- and rough-surface phases. In accordance with EDS analysis, the smooth-surface areas are identified as metal phases, of which typical compositions are shown in Table 3. The metal phase consists mostly of FeMn and a certain amount of C. The area of the metal phase expands as temperature increases, demonstrating that high temperatures are beneficial to the formation of the metal phase. Compared with the microstructures after conventional heating, the appearance of the metal phase in the microstructures after microwave heating indicates that microwaves can reduce the temperature at which Mn oxides are reduced to metal Mn. This indication agrees with the above-obtained finding that microwaves can enhance the reaction extent.

In addition, a detailed morphology of rough-surface

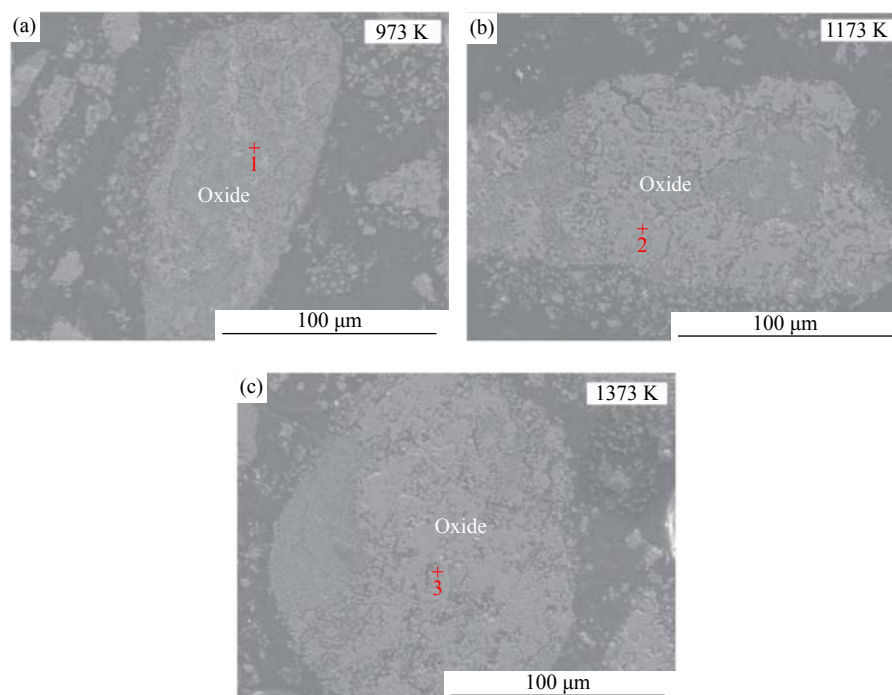


Fig. 7. Microstructures of reacted samples through conventional heating: (a) 973 K; (b) 1173 K; (c) 1373 K. The dark region is the resin material.

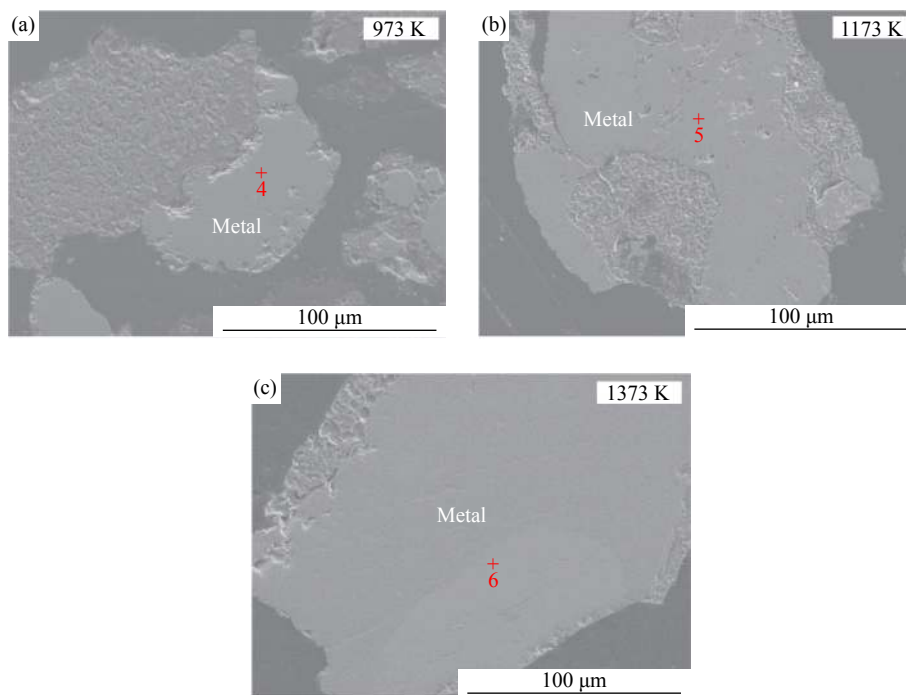


Fig. 8. Microstructures of reacted samples through microwave heating: (a) 973 K; (b) 1173 K; (c) 1373 K. The dark region is the resin material.

phases is shown in Fig. 9. The typical compositions are shown in Table 4 in accordance with EDS analysis. The matrix of the rough-surface phases is composed of oxide and slag phases, and small and rounded metal phases are scattered in the matrix. The scattered particles represent the early mor-

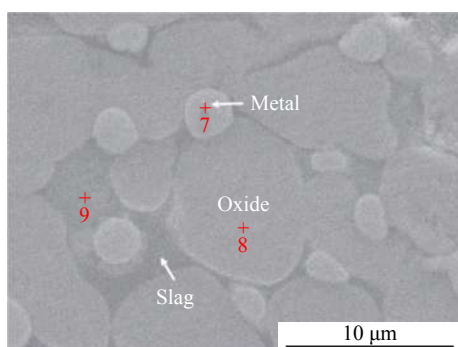
phological type of the metal phase. The reduction of Fe oxides has priority over that of Mn oxides; thus, Fe content is much higher than Mn content in these metal phases. As the carbothermal reaction proceeds, the scattered metal phases continuously grow larger and then connect into a whole one,

Table 2. EDS analysis results of the typical compositions of the oxide phases in the Fig. 7

Spot	Unit	O	Mn	Fe	Mg	Si	Ca
Spot 1	wt%	23.63	64.04	4.07	1.51	0.63	6.11
	at%	50.02	39.48	2.47	2.10	0.77	5.16
Spot 2	wt%	21.61	69.27	5.17	0.29	0.37	3.29
	at%	48.05	44.85	3.29	0.42	0.46	2.92
Spot 3	wt%	19.57	67.18	10.25	0.79	0.38	1.83
	at%	47.99	43.48	5.25	1.17	0.48	1.63

Table 3. EDS analysis results of the typical compositions of the metal phases in Fig. 8

Spot	Unit	Mn	Fe	C	Mg	Ca	O
Spot 4	wt%	70.58	16.71	12.23	0.11	0.04	0.33
	at%	48.94	11.39	38.76	0.07	0.07	0.77
Spot 5	wt%	72.37	15.03	11.78	0.19	0.04	0.59
	at%	50.50	10.31	37.55	0.18	0.04	1.42
Spot 6	wt%	72.10	15.97	11.44	0.13	0.05	0.31
	at%	50.94	11.08	37.15	0.11	0.05	0.67

**Fig. 9.** Detailed morphology of rough-surface phases.

while the gangue in the oxidized phases participates in the formation of slag phases.

4. Discussion

4.1. Microwave absorption performance

With the heating curve connected with the dielectric properties, $\tan \delta$ of the sample can influence its heating rate under microwave heating because the conversion of electromagnetic energy into heat depends on $\tan \delta$ when microwave absorption occurs. A high value for $\tan \delta$ represents a high ca-

capacity to absorb microwaves, which can lead to the increase in heating rate. According to the dielectric properties of Mn oxides reported in the literature [26], $\tan \delta$ of MnO_2 is much higher than that of other Mn oxides in a wide range of frequencies. Thus, the thermal decomposition of MnO_2 can reduce the microwave absorption ability of the sample. The experimental research shows that MnO_2 can readily thermally decompose to Mn_2O_3 in the range of 673–973 K, and Mn_2O_3 subsequently decomposes to Mn_3O_4 in the range of 1173–1373 K [11]. As shown in Fig. 4, $\tan \delta$ evidently decreases above 1073 K because MnO_2 has largely decomposed to lower-order Mn oxides. The decrease in $\tan \delta$ results in the slowdown of the heating rate. Nevertheless, the sample can still be heated up in a high average heating rate through the volumetric heating of microwaves instead of conventional heat conduction.

4.2. Carbothermal reduction process under microwave heating

The carbothermal reduction of oxidized Mn ore is a complex reaction that consists mainly of direct reduction, indirect reduction, and gasification. The thermogravimetric analysis shows that microwave heating can accelerate the reaction process and enhance the reaction extent. The effects of mi-

Table 4. EDS analysis results of the typical compositions of the phases in the rough-surface area in Fig. 9

Spot	Unit	Mn	Fe	O	C	Ca	Mg	Si	Al
Spot 7	wt%	28.58	60.78	0.66	9.22	0.76	—	—	—
	at%	22.65	43.86	1.67	31.05	0.77	—	—	—
Spot 8	wt%	53.39	3.14	23.41	7.47	5.63	3.94	2.92	—
	at%	29.10	1.56	40.67	17.30	3.91	4.56	2.90	—
Spot 9	wt%	4.60	2.15	33.30	8.78	32.50	3.92	12.71	2.04
	at%	2.03	0.87	46.80	16.45	18.27	3.67	10.21	1.70

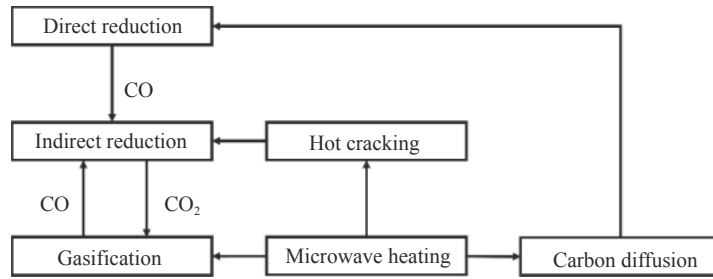


Fig. 10. Schematic of the carbothermal reduction process under microwave heating.

microwave heating on the carbothermal reduction process of oxidized Mn ore are shown in Fig. 10 and further discussed in the subsequent paragraphs.

Under microwave heating, coke particles heat up quickly under microwave heating because they are a strong microwave absorber. The direct reduction process preferentially occurs around the coke particles, and thus the metal phases formed at the early stage are scattered in the matrix (Fig. 9). The composition analysis (Table 4) shows that the metal and slag phases can dissolve a certain amount of C. The dissolution of C can improve the microwave absorption ability of metal phases to keep them at a high temperature. The high temperature is beneficial for the diffusion of C to accelerate the direct reduction process.

The direct reduction process can produce CO, which is further utilized for the indirect reduction process. The gas–solid reaction can significantly enhance the energy efficiency to accelerate the carbothermal reduction process. As shown in Fig. 11, cracks appear in the microstructures after microwave heating. The occurrence of cracking results from the selective heating of microwaves. The ore used in this work contains not only Mn and Fe oxides but also a small amount of gangue, of which the main components are CaO, SiO₂, and Al₂O₃. The microwave absorption ability of gangue is much lower than that of Mn and Fe oxides. The differential expansion of the components contributes to the occurrence of hot cracking due to the uneven heating of the ore. Compared with conventional heating, these cracks are beneficial for the gas flow and thus effectively increase the reaction surface area.

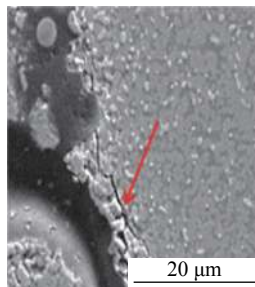


Fig. 11. Hot cracking of reacted samples after microwave heating.

In addition to the direct reduction process, the gasification process can continuously supply the CO required for the indirect reduction process and gradually become the dominant source of CO as the process progresses. This process occurs in the oxide, metal, and slag phases, where C can be dissolved in accordance with the composition analysis (Table 4). C has a strong microwave absorption ability; thus, microwave heating can promote the gasification process and further the indirect reduction process.

4.3. Thermodynamic consideration for the formation of metal Mn

In accordance with the conventional thermodynamic analysis, the high-order Mn oxides can be reduced to MnO by C or CO at relatively low temperatures, whereas MnO may only be reduced by C with a temperature above 1600 K. The formation of metal Mn is thus theoretically impossible at the desired temperatures used in this work. However, based on the microstructural observation, the production of the metal phase after microwave heating reveals that the conventional thermodynamic consideration is less satisfactory for the reactions under microwaves. The effect of external fields should be considered in the thermodynamic analysis of these reactions [34].

Microwaves are a type of electromagnetic radiation, and electric and magnetic forces can work on reaction components. The work is presented in the forms of electric and magnetic polarizations and calculated in view of the following assumptions: electric and magnetic field strengths are zero at infinity; reaction components are evenly polarized by electromagnetic fields; the volume variation of reaction components can be ignored. The expressions for the work performed by electric and magnetic forces are:

$$W_E = \frac{V}{\epsilon_0 \chi_E} \int_0^P P dP = \frac{VP^2}{2\epsilon_0 \chi_E} = \frac{V\epsilon_0 \chi_E E^2}{2} \quad (2)$$

$$W_H = \frac{V}{\chi_H} \int_0^M M dM = \frac{VM^2}{2\chi_H} = \frac{V\chi_H H^2}{2} \quad (3)$$

where W_E is the work performed by electric forces, V is the volume of materials, ϵ_0 is the vacuum permittivity, χ_E is the electric susceptibility, P is the electric polarization, E is the electric field strength, W_H is the work performed by magnet-

ic forces, χ_H is the magnetic susceptibility, M is the magnetic polarization, and H is the magnetic field strength.

The “expanded chemical potential $\mu_{(E+H)}$ ” is introduced to replace the conventional chemical potential μ because of the effect of electromagnetic fields, and it is written as:

$$\mu_{(E+H)} = \mu + \frac{\partial(W_E + W_H)}{\partial n} = \mu + \frac{\varepsilon_0 \chi_e E^2}{2} + \frac{\chi_h H^2}{2} \quad (4)$$

where n is the number of moles, χ_e is the molar electric susceptibility, and χ_h is the molar magnetic susceptibility.

For the reaction “ $aA + bB = dD + fF$ ”, the Gibbs free energy change in the presence of electromagnetic fields $\Delta_r G_{(E+H)}$ can be expressed as:

$$\begin{aligned} \Delta_r G_{(E+H)} &= (d\mu_{(E+H), D} + f\mu_{(E+H), F}) - \\ & (a\mu_{(E+H), A} + b\mu_{(E+H), B}) = \Delta_r G^\ominus + RT \ln Q + \\ & \frac{E^2}{2} \varepsilon_0 D_e + \frac{H^2}{2} D_h \end{aligned} \quad (5)$$

where $\Delta_r G^\ominus$ is the conventional standard Gibbs free energy change of the reaction, R is the gas constant, T is the Kelvin temperature, Q is the activity quotient, D_e is the electric susceptibility difference, and D_h is the magnetic susceptibility difference. Here, D_e and D_h are defined as:

$$D_e = d\chi_{e,D} + f\chi_{e,F} - a\chi_{e,A} - b\chi_{e,B} \quad (6)$$

$$D_h = d\chi_{h,D} + f\chi_{h,F} - a\chi_{h,A} - b\chi_{h,B} \quad (7)$$

On the basis of Eq. (5), the standard Gibbs free energy change $\Delta_r G_{(E+H)}^\ominus$ can be expressed as:

$$\Delta_r G_{(E+H)}^\ominus = \Delta_r G^\ominus + \frac{E^2}{2} \varepsilon_0 D_e + \frac{H^2}{2} D_h \quad (8)$$

Although it is $\Delta_r G_{(E+H)}$ rather than $\Delta_r G_{(E+H)}^\ominus$ that serves as a criterion for spontaneous reactions, the latter is more readily available and practical. According to Eq. (8), electromag-

netic fields may be beneficial for the spontaneity of a reaction in the forward direction if the values of D_e and D_h are negative numbers. That is, a reaction is impossible to proceed on the basis of the conventional thermodynamic consideration but may occur in the presence of electromagnetic fields. Furthermore, the standard equilibrium constant in the presence of electromagnetic fields $K_{(E+H)}^\ominus$ is expressed as:

$$\ln K_{(E+H)}^\ominus = -\frac{1}{RT} \Delta_r G_{(E+H)}^\ominus = \ln K^\ominus - \frac{1}{RT} \left(\frac{E^2}{2} \varepsilon_0 D_e + \frac{H^2}{2} D_h \right) \quad (9)$$

The effect of electromagnetic fields on the extent of a reaction is reflected by

$$\ln \frac{K_{(E+H)}^\ominus}{K^\ominus} = -\frac{1}{RT} \left(\frac{E^2}{2} \varepsilon_0 D_e + \frac{H^2}{2} D_h \right) \quad (10)$$

where $K^\ominus$ is the conventional standard equilibrium constant. For a reversible reaction, electromagnetic fields may increase the extent of forwarding reaction when $K_{(E+H)}^\ominus$ is larger than $K^\ominus$, and vice versa.

Although the conventional thermodynamic considers that Mn may only arise from the reduction of MnO by C, C and CO are involved in the subsequent discussion. The corresponding reactions are expressed as:



In accordance with Eqs. (6) and (7), the values of χ_e and χ_h are required for the calculation of D_e and D_h . Table 5 gives the values of χ_e and χ_h for the reactants and products [26,35]. The values of χ_h are directly collected from the literature, whereas those of χ_e are approximately calculated from Eqs. (13)–(16) as follows:

Table 5. Values of χ_e , χ_h , ε_r , and ρ for the reactants and products

Reactants or products	$\chi_e / (\text{cm}^3 \cdot \text{mol}^{-1})$	$\chi_h / (10^{-6} \text{cm}^3 \cdot \text{mol}^{-1})$	ε_r	$\rho / (\text{g} \cdot \text{cm}^{-3})$
MnO	43.5	4850	4.5	5.39
Mn	27.9	511	5	7.3
C	37.6	−6.0	12	3.513
CO	0.05404	−9.8	1.00065	—
CO ₂	0.07663	−21.0	1.0009217	—

$$\chi_E = \varepsilon_r - 1 \quad (13)$$

$$\chi_e = \frac{\chi_E M}{\rho} \chi_E = \varepsilon_r - 1 \quad (\text{for solid}) \quad (14)$$

$$\chi_e = \chi_E V_m \quad (\text{for gas}) \quad (15)$$

$$V_m = \frac{RT}{p} \quad (\text{for gas}) \quad (16)$$

where ε_r is the relative permittivity, M is the molar mass, ρ is the density, V_m is the molar volume of gas, and p is the pressure. The values of ε_r and ρ are shown in Table 5, and V_m is

calculated at $T = 1000 \text{ K}$ and $p = 100 \text{ kPa}$.

Table 6 shows the values of D_e and D_h calculated from Eqs. (6) and (7), and all calculated results are negative numbers for the two reduction reactions. If the values of D_e and D_h are applied to Eqs. (8) and (10), then $\Delta_r G_{(E+H)}^\ominus$ becomes less than $\Delta_r G^\ominus$, and $K_{(E+H)}^\ominus$ becomes larger than $K^\ominus$. Microwaves are thus supposed to make the two reduction reactions accessible and increase the extent of the reactions. Furthermore, the values of D_h are similar for the two reduction reactions, whereas the absolute value of D_e for the reduction

reaction with C is larger than that with CO. This finding implies that microwaves should have a large beneficial effect on the former reaction. Fig. 12 shows the qualitative comparison of $\Delta_r G_{(E+H)}^\ominus$ and $\Delta_r G^\ominus$ for the two reduction reactions. The production of metal Mn tends to arise from the reduction of MnO by C under microwave heating at a relatively low temperature. The thermodynamic consideration is in good agreement with the experimental results, and the formation of metal Mn under microwave heating is more accessible than that under conventional heating.

Table 6. Calculated results of D_e and D_h for the reactions

Reaction	$D_e /$ ($\text{cm}^3 \cdot \text{mol}^{-1}$)	$D_h /$ ($10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$)
$\text{MnO} + \text{C} = \text{Mn} + \text{CO}$	-53.1	-4342.8
$\text{MnO} + \text{CO} = \text{Mn} + \text{CO}_2$	-15.6	-4350.2

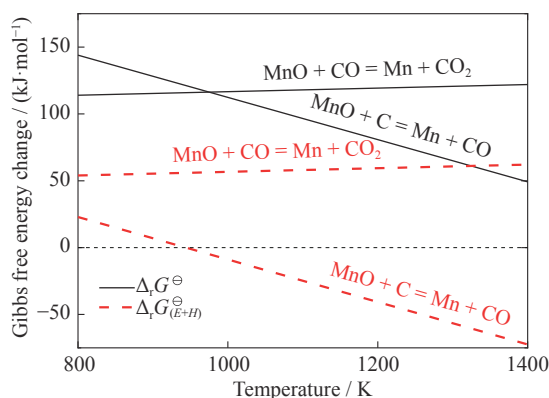


Fig. 12. Qualitative comparison of $\Delta_r G_{(E+H)}^\ominus$ and $\Delta_r G^\ominus$ for the two reduction reactions.

5. Conclusions

The carbothermal reduction characteristics of oxidized Mn ore through conventional heating and microwave heating were comparatively analyzed and discussed in this study. The conclusions are listed as follows:

(1) The mixture of the oxidized Mn ore and coke can be rapidly heated up under microwave heating. The heating rate, which strongly depends on the dielectric properties, varies due to the thermal decomposition of MnO_2 .

(2) Compared with the carbothermal reduction of oxidized Mn ore under conventional heating, microwave heating can accelerate the reaction process and enhance the reaction extent. The hot cracking generated by the uneven microwave heating can effectively increase the reaction surface area. The strong microwave absorption ability of C can promote the gasification process and further the indirect reduction process.

(3) The metal phase is produced at the studied temperat-

ures only under microwave heating. The thermodynamic consideration shows that microwaves can make the reduction of MnO to Mn accessible. The production of metal Mn is most likely to arise from the reduction of MnO by C under microwave heating at a relatively low temperature.

(4) Based on the present work, microwave heating has a potential application to the production of FeMn for the sake of the reduction in energy consumption and pollution.

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