Rapid communication

Iron production from Fe₃O₄ and graphite by applying 915 MHz microwaves

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1. Introduction

The imminent shortage of high-quality iron ore and fossil fuels such as coal and oil has recently been compelling researchers to develop new steel-making methods based on energy transfer processes that do not involve thermal energy generated by high-temperature gases [1–3]. Microwave processing has attracted interest for steel making due to its ability to realize volumetric heating and its high energy efficiency [4,5]. 2450 MHz microwave irradiation has recently been used to reduce, melt, and cast iron ores (magnetite or hematite) in the presence of carbon [4,5]. Ishizaki et al. constructed a high-power (120 kW) continuous microwave furnace and Huang et al. built a 915 MHz, 225 kW microwave furnace to scale up steel production [5,6]. Huang et al. obtained sponge iron, but since they did not reach the melting stage using 915 MHz microwave heating, they employed DC arcing to complete iron ore reduction. If the physical mechanism of the various reactions that occur during microwave heating of a mixture of iron and carbon was determined, a better method could be developed for completing the reduction and melting of iron. In this study, we experimentally investigate the chemical behavior of ore reduction using microwaves.

2. Experimental procedures

The experimental system consists of waveguides with a 915 MHz magnetron oscillator, a three-stub tuner, a plunger, an isolator, and a TE₁₀₂ rectangular waveguide cavity coupled through an iris (Fig. 1). The cavity was tuned to 915 MHz using the plunger at the end of the waveguide. This system provides separation of the electric and magnetic fields inside the cavity [7]. A quartz cylinder was installed in the cavity. It was evacuated by a rotary pump and purged by high-purity (99.9%) N₂ gas. A precursor mixture of iron ore and carbon was placed in a crucible (φ12 mm × 12 mm) and it was insulated by a layer of alumina-silica fiber board. The surface temperature of the reactants was monitored using an infrared radiation pyrometer. In this study, a 89 wt% Fe₂O₃–11 wt% C (10 g; Fe₂O₃–1 μm pass) mixture was placed at an electric field node (where the magnetic field is zero), a magnetic field node (where the electric field is zero), and a location where E and H fields coexist (referred to as the E–H mixed mode), as shown in Fig. 1.

3. Results and discussion

Fig. 2 shows the temporal evolutions of the sample surface temperature for the E-field, the E–H mixed mode, and the H-field, respectively. The E–H mixed mode and the H-field generated temperatures of over 1300 and 1150 °C at 3 min, respectively. In
these experiments, the holding time was fixed at 15 min (for which \( E_{\text{max}} \) and \( H_{\text{max}} \) generated temperatures of 1100 and 1260 °C, respectively). For the \( E-H \) mixed mode, the sample temperature exceeded 1300 and 1360 °C after 3 min and 6 min, respectively. The \( E-H \) mixed mode provided unsteady heating and the temperature gradually increased to 1370 °C in 17 min. This unsteady heating is due to microwave absorption changing as different chemical reactions are promoted. Fig. 3 shows XRD 2θ spectra obtained after processing in the \( E \)-field, the \( E-H \) mixed mode, and the \( H \)-field. The \( H \) field gave lower FeO peaks and higher \( \alpha \)-Fe peaks than the \( E-H \) mixed mode. The \( E-H \) mixed mode gave higher temperature than the \( E \)-field, which indicates that pure \( H \)-field heating enhances ore reduction (FeO = Fe + 1/2O₂).

The maximum temperature obtained using the \( E \)-field did not exceed 1200 °C. The \( E \)-field gave the lowest amount of ore reduction. The reflected microwave power increased suddenly when the microwaves generated plasma in the quartz tube on reducing the temperature. This is because the gas plasma absorbed most of the microwave energy, so that the sample powder was no longer effectively heated. The plasma prevented
direct energy transfer from the microwave to the powder mixture. In the E–H mixed mode, the exhaust gas emitted intense visible light and its XRD spectrum had higher FeO peaks than in the H-field and lower Fe$_3$O$_4$ peaks than in the E-field.

Since 188 kJ/mol (44.9 kcal/mol) of energy is released when FeO is reduced to Fe at 1023 °C and 10 g of the granular sample contains 0.115 mol of Fe, the net energy will be 21.62 kJ [8]. In these experiments, the microwave energy is in the range 300–900 W. A total energy of 412–918 kJ was supplied to the cavity during the holding time between 3 and 18 min. Energy balance estimates that the energy reduction will be less than a few percent of the total microwave energy. About 95% of this energy loss is due to infrared radiation emitted from the sample surface; the remaining 5% is due to conduction and convection losses from the crucible to the thermal insulation. The energy loss to the cavity wall was negligibly small for the present system.

These experimental results conflict with the theory of chemical kinetics, which states that the chemical reactivity should increase with increasing temperature and holding time under a low oxygen partial pressure. According to the above-mentioned energy balance, over 95% of the incident energy is coupled to the granular sample and is converted into thermal energy. The coupling mechanism can be explained by an elementary reaction based on the Mie theory. The supplied energy limits reduction in a granular process at about 1000 °C [2,5,9]. In the present experiments, the FeO particles behave as metallic particles in which the absorptions of FeO and Fe$_3$O$_4$ particles differ by three orders of magnitude. When a magnetic moment is induced, metallic particles will have a non-zero magnetization; i.e., a particle effectively behaves as a magnetic particle with a complex magnetic permeability $\mu_r \neq \mu_0$. For $r < \delta$, a simple formula approximately describes the absorption properties in an H-field, $W_{FeO}/W_{Fe_3O_4} = 1.1 \times 10^{-3}$ if $r < \delta$, where $r = 1$ μm, $\sigma_{FeO} = 9.15$ S cm$^{-1}$, $\sigma_{Fe_3O_4} = 1.0 \times 10^{15}$ S cm$^{-1}$, $\mu_{FeO}(r) = 1.7$, $\mu_{Fe_3O_4}(r) = 0.2$, $\delta$, the skin depth [10–12]. This indicates that the ohmic loss will be higher in the wustite phase (FeO–Fe+1/2O$_2$). The heated FeO was in thermal equilibrium, just like in conventional heating. The classical electromagnetic theory can explain the heating mechanism, but it cannot explain why the H-field enhances deoxidation.

This suggests that the reduction process partially involves non-equilibrium energy transfer from the microwave H-field to the electrons in the material. In this explanation, the electronic structure of FeO is given by quantum mechanics. Metal oxides with many unpaired electrons near the Fermi surface exhibit very specific behavior. The microwave photon energy is $10^{-5}$ eV, which is too low to excite valence electrons from their orbitals at low temperatures. However, as they have degenerate bands near the Fermi level at higher temperatures, unpaired electrons could be excited above the Fermi level where unpaired electrons are more unstable, as shown in Fig. 4. The number of electrons in each orbital is given by the product of the density of state and the Fermi distribution. The data in this calculation was taken from Ref. [13]. The small microwave magnetic field (estimated to be of the order of $10^{-4}$ T) causes FeO with these unpaired electrons to fluctuate; this is similar to TiO$_2$–x ($x \approx 1$), which emits a large amount of oxygen on field fluctuation [7,14]. The coupling strengths are different in the lower and upper regions of the Fermi level because itinerant electrons function as solid-state plasmas and the H-field of the microwaves could couple to elementary excitations (spin waves).

Only a small portion of the H-field energy functions in this manner in the reduction process. The microwave photon energy is $10^9$ times lower than the energy required to break bonds between Fe and oxygen. However, if an alternating microwave magnetic field interacts with an unstable state of an unpaired spin system (i.e., the antibonding state), it will vibrate the state at a frequency of over $10^9$ Hz and will irreversibly enhance deoxidation. This implies that the microwave H-field acts as a catalyst rather than a heat source, which is why applying a microwave H-field effectively reduced a metal oxide with unpaired spins in the 3d shell [15].

In conclusion, application of a microwave H-field plays a critical role in the final stage of iron ore reduction; this distinguishes microwave processing from conventional heating.

4. Conclusion

We investigated carbothermal reduction with 915 MHz microwave heating using a system that enables the electric and magnetic fields to be separated inside the cavity. The microwave magnetic field generated a lower temperature than the electric field and the E–H mixed mode at the surface, whereas the magnetic field rapidly heated the center of the powder. Furthermore, the H field generated lower FeO XRD peaks and higher α-Fe XRD peaks than the E–H mixed mode. In previous studies, the microwave energy was considered to perturb electrons in the antibonding state of metal oxides and the oxide in a magnetic field is more unstable than a conventionally heated oxide. In this study, the microwave energy distribution was investigated theoretically. The combined effect of the thermal energy and a portion of the microwave magnetic field is predicted to enhance deoxidation in carbothermal reduction. The proposed theory enables us to qualitatively model the redox or nitration processes that use microwaves and it can be applied to industrial applications that employ microwaves.

References