Twenty Years’ Research on Microwave Application to Metal Production and Recycling

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Abstract. Ever since discovery of microwave heating in 1946, its application has been developed in various fields. Our research group has performed intensive studies on microwave heating application to metal production and recycling for these twenty years. In this article, it is intended to introduce our attempts having made for different projects. They are 1. Microwave processing of Ti bearing blast furnace slag, microstructural alteration and comminution. 2. Microwave carbothermic reduction of valuable metals from various oxides. 3. Microwave drying and dehydration of wet wastes. 4. Vapor de-phosphorization by microwave rapid heating. It is to be emphasized that we utilized a single mode microwave applicator for the purpose of clarification on the heating mechanisms of various metallurgical matters and compounds, and it was intended to discuss the reaction kinetics excited by microwave heating.

1. Introduction

Microwave heating has been applied to many fields since the first patent of microwave heating is issued in 1945 [1]. The major application might be the domestic ovens for heating foods [2] and applied to materials processing [3], as well. On the other hand, application of microwave energy to metal production and recycling field [4,5] has been conducted along with the progress in microwave technologies. To the author’s knowledge, its application to iron and steel production fields was first attempted 56 years later in Japan [6].

Microwave heating is suitable for exciting carbothermic reduction reactions of the ores and oxide state wastes, because of its effectivity in heating of carbon and heavy metal oxides. Although it is not possible to replace the current mass production process of the metal production, authors have attempted laboratory-scaled researches on microwave applications for reduction reactions and other processes for metal production and recycling, from an idea that there are growing expectation to apply and utilize the specific characteristics of microwave heating for a small-scale metal production process and for treatment of the by-products occurring in the metal industries.

In our studies, multi-mode microwave applicator was utilized for the heating of large mass in the experimental study, and a single mode microwave applicator was positively utilized for the purpose of fundamental elucidation of the microwave heating processes. Separated electric (\(E\)-) and magnetic (\(H\)-) field heating in the microwave cavity by which it was possible to discuss heating mechanisms of substances and compounds involved in the microwave heating processes. Microwave heating mechanisms (\(P \text{ [W m}^{-3}\text{]: power absorbed by a matter} \) are expressed by Eq. 1, where \(\varepsilon\), \(\mu\) and \(\sigma\) are

\[
\frac{\varepsilon}{\varepsilon_0} + j\frac{\mu}{\mu_0}\frac{1}{\sigma} = \frac{1}{\rho}
\]
imaginary parts of permittivity, magnetic permeability and DC electric conductivity, respectively. And measurement of the permittivity and magnetic permeability were performed at room and high temperature, which were input for simulation of the microwave heating processes. In this article, it is intended to review the authors’ research results presented for these 20 years.

\[
P = \frac{1}{2} (\omega \varepsilon'' |E|^2 + \omega \mu'' |H|^2 + \sigma |E|^2)
\]  

(1)

2. Experimental

Microwave apparatus used in the studies are either multimode or single mode microwave applicator operated at 2.45GHz. Photograph of the former and schematic illustration of the latter are shown in Figure 1 (Fig. 1). Microwave maximum power of multimode applicator was either 800W (domestic microwave oven type) and 6kW (specific microwave furnace). And 1.5kW for the single mode applicator. Temperature measurement was mainly performed by an optical method using a sapphire light pipe. The other detailed apparatus and experimental conditions are described in the references [7]. Numerical simulation was performed using COMSOL Multiphysics ver.5.5.

![Figure 1](image.png)

Figure 1. (1) Photograph of multimode microwave furnace (2.45Hz, 6kW), (2) Schematic illustration of apparatus [7]. (a) Side view of the apparatus, (b) plan view of the wave guide applicator and (c) scale of a specimen container.

3. Results and Discussion

3.1. Microwave processing of Ti bearing blast furnace slag, microstructural alteration and comminution

In south west China, Ti-bearing blast furnace slag [8,9] occurs because of using iron ores containing titanium which are produced in that area. It was intended to extract Ti- containing phases from the slag and utilize them as one of the TiO₂ resources by microwave treatment. If the slag is slowly cooled, slag contains Ti in a form of CaTiO₃ (perovskite) precipitated in the matrix. On the other hand, if it is rapidly cooled, slag is quenched into a glassy state in which all metal cations are mixed homogeneously in the glass. When microwave is irradiated (in a multimode applicator) to the glassy state slag, we observed their crystallization as shown in Fig. 2. It was illustrated that Ca and Ti are concentrated in the crystallized dendritic area by microwave rapid heating. Next, in order to separate and extract the CaTiO₃ phases in the slowly cooled slags, microwave cyclic heating of the slag was performed to induce some cracks. The introduced cracks can be observed in Fig. 3. Although there are many practical problems, such as the energy costs or the ability in handling large amounts, these attempts on investigation of the microwave irradiation effects were very much meaningful for our understanding microwave processing technologies in the first stage of stating our microwave research.
3.2. Microwave carbo-thermic reduction of valuable metals from various oxides
Attempts on microwave heating application to the oxide reduction reaction have been performed in order to recycle valuable metals by our group. They are mostly for the steel making byproducts such as the Cr containing slag and pickling sludge of stainless steel [7,10,11]. Here, we report the reduction of NiO and Cr₂O₃ mainly, considering their microwave heating characteristics. These oxides were mixed with graphite (C), because C is not only indispensable for the reduction but also play an important role as a very good susceptor (microwave absorber). Reduction of iron oxide will also be shortly mentioned in section 4. Fig. 4 shows the microwave heating curves of NiO, Cr₂O₃ and graphite (C) in a multimode applicator [11]. Comparing with the rapid onset of the graphite heating, the two oxides exhibit an incubation time. It was discussed that this behavior is related with the large temperature dependence of the oxides’ permittivity on temperature. The formation of high temperature area (hot spot) causes acceleration of temperature increase and resulted in the rapid heating after the incubation time.

In these investigations, we introduced a single mode microwave apparatus for the first places in Japan in order to obtain fundamental understanding of microwave heating of matters related with iron and steel production [7,11,12]. By this method, it is also possible to concentrate the microwave power and heat a specimen to high temperature at relatively low power input. The simulated $E^-$- and $H^-$-fields in a single mode microwave cavity is shown in Fig. 5. The maximum positions of the fields differ by a quarter of the wave length, such as 35mm in a wave guide at 2.45GHz. Separated $E^-$- and $H^-$-field heating is possible, by placing a specimen having small enough scale in each position with respect to the field distribution. The heating curves of separated $E^-$- and $H^-$- fields of NiO and graphite are shown in Fig. 6. Graphite can be well heated in both fields, but NiO cannot be heated well in $H^-$-field. This is because NiO is not a ferri-magnetic material nor an electric conductor.
Figure 4. Microwave heating curves C, NiO and Cr$_2$O$_3$ [11].

Figure 5. Simulated distributions of (a) E- and (b) H-field [7].

Figure 6. (1) Photograph of multimode microwave furnace (2.45Hz, 6kW), (2) Schematic illustration of apparatus [7]. (a) Side view of the apparatus, (b) plan view of the wave guide applicator and (c) scale of a specimen container.

It was observed that the reduced states of Ni are different by the reduction in $E$- and $H$-field. As the photographs shown in Fig. 7(a), reduced Ni in H-field maximum position consisted of particles having diameter of several micron meters. On the other hand, a dense and large Ni particle of several millimeter in diameter is formed when reduced in E-field maximum position (Fig. 7(b)). In order to account for the difference, numerical simulation on the static $E$-field distributions around two particles are performed. Assuming the two particles either of ceramics or metals, it was predicted that the degree of the field intensification in the clearance between the particles is different, such that intensified $E$-field is much larger between metal particles than that of ceramics, as demonstrated in Fig. 8. This tendency indicates larger possibility of discharge occurrence upon generation of reduced metals by carbo-thermic reduction. This feature is further related with the better heating tendency of NiO in $E$-field, as well. For a case of graphite and NiO mixture in $E$-field irradiation, first, graphite is preferentially heated at room temperature, then NiO starts absorbing microwave energy as an increase of the ambient temperature, which resulted in the incubation time. If there is some temperature distribution in microscopic scale, it is possible that the hot spot formation or preferential heating occurs, and in this area, metal generation takes place selectively, then occurrence of discharge causes generation of high temperature and melt the metals. On the contrary, in $H$-field, graphite heating only raises the whole temperature. Although measured averaged temperature by an optical pyrometer are the same, it was anticipated the temperature difference have existed in microscopic scales.
3.3. Microwave drying and dehydration of wet wastes

Microwave is known to have characteristics of internal heating. In drying processes, internal heating is favorable because the temperature inside the objects could become higher than in the surface area, hence the same directions of heat and mass (vapor) transfer are accomplished. Therefore, it was intended to apply microwave heating for the purpose of drying and dehydrating of wet wastes, such as a pickling sludge [10]. We know in advance that the sludge itself can be heated up to 200°C by microwave, but dehydration is not sufficiently accomplished and the moisture still remains. Therefore, we mixed a graphite powder with the sludge and improved the microwave heating characteristics. However, it was found that the too much addition of graphite even reduced the microwave penetration depth, as shown in Fig. 9. Color-changed (dehydrated) regions of the compacted mixture (FeO(OH), graphite (C)) by microwave heating (6kW multimode) are different with the graphite composition [10]. Namely, the larger graphite content (1:2) resulted in heating and dehydration only in the surface area. This behavior was investigated by measurement of the effective permittivity and electric conductivity of the mixture. The electric conductivity of the mixture is plotted as a function of graphite volume fraction in Fig. 10, where rapid increase in the conductivity was observed above 10%. This behavior is known as a phenomenon so called conductivity percolation.

![Figure 7](image1.png)

**Figure 7.** Photographs of (a) reduced Ni in H-field and (b) in E-field at 600°C by heating for 1 min.

![Figure 8](image2.png)

**Figure 8.** E-field distributions around (a) ceramic and (b) metal two particles by simulation.

![Figure 9](image3.png)

**Figure 9.** Appearances of the specimens of FeO(OH)/C heated by microwave. Molar ratios (FeO(OH) : C) (a) 1:1 and (b) 1:2 [13].

![Figure 10](image4.png)

**Figure 10.** Effect of C fraction on electric conductivity of FeO(OH)/C mixture [13].
3.4. Vapor de-phosphorization by Microwave Rapid heating

Phosphorus is an element indispensable for fertilizers or for some chemical products. Because of running short of its natural resources, recycling of steel making slag has been taken into consideration. However, in a process of carbo thermic reduction of a phosphorous containing slag, it has to be taken into consideration that if the slag also contains iron oxides, simultaneous reduction of iron oxide occurs, from the thermodynamic analysis. Especially, when iron is reduced in a liquid state, much phosphorous is expected to be absorbed. The phosphorous cannot be separated from iron. In order to overcome this problem, we took advantage of microwave rapid heating characteristics. It was attempted that the reduced phosphorous is to be removed in a vapor phase immediately by microwave rapid reduction, before the progress in reduction of iron oxide, which causes lowering the iron melting point by an absorption of carbon or phosphorous, leading to further loss of phosphorous. Fig. 11 indicates dependence of the phosphorous removal rate (RR) from TCP (Tri calcium Phosphate) on the heating rate (HR) (a) without and (b) with presence of iron oxide (Fe$_3$O$_4$) [14]. Removal rate is defined as the vaporized amount of phosphorous from TCP divided by the time spent to reach the target temperature. Although the removal rate is lower by one order in the case with presence of iron oxide, same tendency is shown that the removal ratio also increased with the heating.

![Figure 11. Relationship between heating rate and phosphorous (P$_2$O$_5$) removal rates (RR) from TCP with graphite (a) without presence of Fe$_3$O$_4$ and (b) with presence of Fe$_3$O$_4$ [14].](image)

4. Conclusion

In this paper, our attempts of application of microwave heating to various purposes in metal production and recycling processes are reviewed. Here, we payed attention to key materials which absorbs microwave and can be heated well. Examples are perovskite (CaTiO$_3$), carbon (graphite) and the iron oxide (Fe$_3$O$_4$). On the other hand, NiO exhibited a different feature. Carbon is not only a good microwave absorber, but also a reduction regent and very important for metal recycling. It enables rapid heating of the powder mixture, however it was suggested that optimum amount of carbon has to be selected for the microwave treatment by considering the penetration depth, as it varies with the content very much. The studies introduced in this paper emphasized the fundamental aspects in microwave processing, however, the shown knowledge and the information are expected to be very important for the practical or industrial applications, because at present we are facing to the urgent needs to reduce CO$_2$ emission, and electric heating using renewable energy is one of the strategies to cope with this problem.
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