Chapter from the book *Advances in Induction and Microwave Heating of Mineral and Organic Materials*


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1. Introduction

Metals have been used in human society for thousands of years, and the amount of metal production continuously increased. In modern society, the production of metals has explosively increased, and the use of metals becomes inevitable in our daily life throughout society. However, the source of metals seems to be changed from high concentrations of ores to low concentrations or industrial wastes.

Among the global primary metals production, crude steel shares approximately 90% (Worrell, 2004), and major metallurgical industrial waste comes from iron- and steel-making industries. In 2007, the total production of crude steel reaches 1,351 million tons (Worldsteel Association, 2009), and it is expected to increase continuously. Along with the continuous growth in steel production, the generation of iron- and steel-making industrial wastes such as mill scale, slag, dust, sludge, etc. have increased considerably. Considering that these industrial wastes contain lots of useful resources such as Fe, Zn, etc., many researchers have suggested various processes recycling the valuable metallic elements.

Pyrometallurgical process can be a general solution to recover valuable elements from industrial wastes. However, traditional pyrometallurgical recycling processes (e.g. Waelz process) have some problems inherently (Lee et al., 2008). (1) Industrial wastes are difficult to handle due to their physical characteristics as fine particles: apparent low density and flying. Therefore, recycling processes require pre-treatment such as pelletizing with binders. (2) During the process, erosion of refractory materials easily occurs, because the heating zone temperature is much higher than the reaction zone. Therefore, maintenance cost is a critical barrier, when the process is extended from a pilot plant to a commercial one. (3) After processing, the metallic components mainly iron-based alloys are difficult to be separated from residues (originated from the waste as well as the binders).

Recently, many researchers have paid attentions to the microwave heating process as an alternative recycling method due to its unique characteristics such as fast heating and direct internal heating (Nishioka et al., 2002; Morita et al., 2001; Morita et al., 2002; Saidi & Azari, 2005; Cho & Lee, 2008; Lee et al., 2008; Kim et al., 2009; Lee et al., 2010; Kim et al., 2010; Lee et al., 2010). It is also believed that the microwave heating may provide savings in both time and energy (Kelly & Rowson, 1995; Ishizaki et al., 2006).
2. Microwave heating fundamentals

Details of the microwave heating are precisely described in a reference (Gupta, 2007). Here, a brief explanation of the microwave heating is suggested. Microwaves are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz. Accordingly, the wavelength of microwaves ranges from 1 mm to 1 m, which is much larger than molecular (nm) or crystalline grain size (µm). Therefore, microwave may supply energy on valence electrons, yielding electron fluctuation. Microwave can be transmitted, absorbed, or reflected, depending on the sorts of materials (Fig. 1). When microwave is absorbed in a material, the electron fluctuation is eventually transferred to lattice ions and generates vibrations in matrix, which can be transferred to heat energy. The heating rate depends on the electromagnetic properties of a material (complex permittivity and permeability), and the average power absorbed by a material is the sum of electric loss and magnetic loss.

\[
P_{av} = \omega \varepsilon_0 \varepsilon''_{\text{eff}} E_{\text{rms}}^2 + \omega \mu_0 \mu''_{\text{eff}} H_{\text{rms}}^2
\]

where \( \omega \) is the angular frequency (=2πf), \( \varepsilon_0 \) the permittivity of free space (= 8.854 x 10^{-12} F/m), \( \varepsilon''_{\text{eff}} \) the effective relative dielectric loss factor, \( E_{\text{rms}} \) the root mean square of the electric field, \( \mu_0 \) the permeability of free space (= 2π x 10^{-7} H/m), \( \mu''_{\text{eff}} \) the effective relative magnetic loss factor, \( H_{\text{rms}} \) the root mean square of the magnetic field.

![Microwave penetration, reflection and absorption (Sutton, 1989)](image)

Yoshikawa et al. investigated the heating behaviour of NiO and carbon under electric field and magnetic field respectively using a single mode microwave applicator (Yoshikawa, 2007). They found that NiO was heated only in the electric field, whereas carbon was heated both in the electric and magnetic fields. Typical microwave heating furnaces make use of multi mode applicators. Therefore, it is inherently difficult to distinguish the effect of the
electric field from that of the magnetic field, and vice versa. This unique feature of microwave heating results in so-called “thermal runaway” behaviour. For several ceramic materials, the dielectric constant shows strong temperature dependence, namely, above a critical temperature the dielectric constant rapidly increases with temperature (Birnboim et al., 1998). When the microwave is concentrated on a certain spot, the local temperature becomes higher than neighbours. As the local temperature exceeds a critical value, the heating rate becomes much faster, and results in the acceleration of the heating rate of the neighbours. This thermal runaway behaviour would be very useful to accelerate high temperature reactions and reducing energy consumption.

Reduction of metallic component from oxide mixtures was firstly investigated by Standish and Worner (Standish & Worner, 1990). Standish and Huang recovered metallic component from iron ore (magnetite and hematite) using the microwave heating and reported that the microwave heating was 5 times faster than the conventional heating (Standish & Huang, 1991). Mourao et al. investigated the effects of carbonaceous materials on the reduction behaviour of hematite iron ore (Mourao et al., 2001). Ishizaki et al. also obtained pig iron from magnetite ore-coal composite pellets by microwave heating (Ishizaki et al., 2006). Chen et al. investigated the effect of the microwave power on the heating rate of self-fluxing pellets containing coal, and found the heating rate was increased 8 times by increasing the microwave power from 5 kW to 15 kW (Chen et al., 2003). Most of these works have focused on the reduction of iron ore as an alternative iron-making process. Iron- and steel-making industrial wastes generally contain lots of iron oxide, so that similar reduction behaviour can be expected.

3. Recovery of metallic elements from industrial waste

3.1 Recovery of metallic elements from slag

Table 1 shows typical industrial slag compositions (Sano, 1977). Not only copper and lead blast furnace slag but also converter slag of iron shows high Fe content. Morita et al. firstly investigated the recovery of metallic iron from the converter steelmaking slag (Morita, 2001, 2002, 2009). Fig. 2 shows a typical experimental setup of the lab scale microwave heating experiments, and reduced metal droplets (Kim et al., 2010). Morita et al. examined the effect of the ionic status of Fe in synthetic slags on the heating rate, and found that the heating rate strongly depends on Fe\textsuperscript{3+}/Fe\textsubscript{total} fraction. The maximum heating rate was obtained when the Fe\textsuperscript{3+}/Fe\textsubscript{total} fraction equals approximately 0.15~0.16 (Morita et al., 2001). This behavior could be explained by the existence of CaFe\textsubscript{3}O\textsubscript{5} phase, whose dielectric loss was as high as that of Fe\textsubscript{3}O\textsubscript{4} (Morita et al., 2001). They also found that the heating rate increased with increasing the amount of carbon, which implied that carbon was used as the reducant as well as the microwave absorber.

Based on the experimental results with synthetic slags, Morita et al. investigated the reduction behavior of industrial steel-making slag (Morita et al., 2002). Industrial steel-making slag contained relatively high concentration of phosphorus (approximately 4.0 wt%). Accordingly, the reduced iron also contained high content of phosphorus, which should be removed before recycling the reduced iron. Morita et al. suggested a novel steel-making slag recycling process shown in Fig. 3 (Morita et al., 2002). They suggested a process through which Fe-P-C alloy was obtained by using the microwave heating, and phosphorus was removed further with K\textsubscript{2}CO\textsubscript{3} flux. Reduced K\textsubscript{3}PO\textsubscript{4} was supplied as a fertilizer, and Fe-C alloy was recharged to the steel-making process stream. In the reduction of industrial
Chemical composition (wt%)  | Others
---|---
SiO$_2$ | CaO | FeO | Al$_2$O$_3$ | MgO | Zn,S,Cu | Zn, Pb, S | MnO | MnO, P$_2$O$_5$, CaF$_2$ | CaF$_2$
Blast furnace slag (Cu) | 30-40 | 5-15 | 35-50 | 5-10 | 1-3 | 5-10 | - | - | - | -
Blast furnace slag (Pb) | 25-40 | 10-25 | 30-40 | 5-10 | - | - | Zn, Pb, S | - | - | - | -
Blast furnace slag (Fe) | 30-40 | 35-45 | - | 5-10 | - | - | MnO | - | - | - | -
Converter steelmaking slag (Fe) | 10-20 | 40-50 | 10-25 | - | 4-10 | MnO, P$_2$O$_5$, CaF$_2$ | - | - | - | -
Electric furnace slag (Fe) (reduced period) | 15-20 | 65-65 | <1.0 | <3.0 | 5-10 | CaF$_2$ | - | - | - | -

Table 1. Typical composition of industrial slag (Sano, 1997)

Fig. 2. Typical example of a setup of the microwave heating experiments and reduced iron (Kim et al., 2010)

Fig. 3. Steel-making slag recycling process suggested by Morita et al. (Morita et al., 2002)
Fig. 4. Effect of SiO$_2$ addition on the change in the composition of (a) FeO and P$_2$O$_5$ in slag and (b) P in metal at 2073K by the carbothermic reduction. Initial slag weight is assumed to be 100g, and ΔC is the amount of carbon consumption. (Lee et al., 2010)

Steel-making slag, the formation of 2CaO·SiO$_2$ would decrease the reduction rate by decreasing the fluidity of slag. They reported that the reduction rates of Fe and P could be increased by adding extra 10 wt% SiO$_2$ (Morita et al., 2002). Although the recovery rate of Fe slightly increased, that of P considerably increased in their experiments. Therefore, there seems to be another reason except the increase of fluidity. Morita et al. supposed that the change of activity coefficient of P$_2$O$_5$ would increase the reduction rate (Morita et al., 2002). Recently, Lee et al. reproduced the Morita’s experimental results using thermodynamic calculations based on recently developed thermodynamic database with FactSage (Fig. 4), and confirmed that the addition of 10 wt% SiO$_2$ considerably increased the reduction rate of P due to the increase of the activity coefficient of P$_2$O$_5$ (Lee et al., 2010).

Morita and Guo also examined the recovery of Fe and Cr from stainless steel-making slag (Morita & Guo, 2009). They investigated the heating rate of slag before and after Fe-Si reduction. Although the slag after the Fe-Si reduction contained very small amount of Fe and Cr, the heating rate was not so much different from that before reduction. Accordingly, carbon was considered dominant microwave absorber in their stainless steel-making slag reduction.

3.2 Recovery of metallic elements from mill scale

Mill scale is very attractive industrial waste due to high contents of iron (more than 70 wt%). However, generation of mill scale is relatively small, and economical benefit is hard to be expected when conventional pyrometallurgical methods are applied. In the whole world, 13.5 M tons of mill scales are generated annually, and among them only 500 K tons from Korea (Cho & Lee, 2008). Moreover, when a conventional heating method is applied, 180 min is required to obtain 100% metallization at 1373-1473 K (Kim et al., 1986). Therefore, most of them are currently used as coolants in steel-making process or additives in sintering process.

Microwave process seems to be very suitable for the recovery of metallic elements from mill scale, because the reaction rate is much faster and the process facilities are much smaller than the conventional ones. In addition, pre- and post-treatments such as pelletizing and crushing are not required. Moreover, gas burner and related facilities can be eliminated from the recycling process. Cho and Lee suggested a novel process recovering metallic elements from mill scale (Cho & Lee, 2008). The unique feature of this process was the
minimization of the secondary waste emission. Since the reduced metallic particles were coagulated due to the microwave-induced vibration, self-assembled particles (1-5 mm in diameter) were easily separated from the residues (Fig. 5). Most of the residues were carbon particles, which could be re-charged in the process stream. Moreover, this process was successfully applied to stainless steel mill scale. Stainless steel mill scale contains environmentally harmful elements such as chromium and nickel, which could be recovered as metallic particles. Therefore, microwave processing is very useful not only to recover valuable metallic elements from mill scale but to prevent the effluence of environmentally harmful elements from stainless steel mill scale.

3.3 Recovery of metallic elements from dust

Several commercialized processes for recovery of metallic elements from dust from iron-making and steel-making processes have been developed based on Wealz process. Most of these processes pay attention to the recovery of Zn from the electric arc furnace dust (EAF dust), which generally contains 25 wt% Fe and 20 wt% Zn (Kim et al., 2009). However, EAF dust is categorized as hazardous waste in many countries, and the conventional process yields elution of Pb and Cr from clinker. Moreover, the total amount of waste generation cannot be reduced by using additives such as binder and flux. Therefore, environmentally-kindly alternative processes like plasma process, flame reactor process, top submerged lance process have been developed. However, these methods still have some economical, environmental or technical problems.

The recovery of metallic elements from EAF dust using the microwave heating was firstly attempted by Nishioka et al. (Nishioka et al., 2002). In their experiments, synthesized dust-carbon composites (38.5 wt% Fe₂O₃, 38.5 wt% C, 19.2 wt% ZnO and 3.8 wt% PbO) were used. They reported that the reduction of ZnO was slower than that of Fe₂O₃. Lee et al. examined the reduction behavior of EAF dust and found that the reduction of ZnO occurred after flaklinate was fully reduced from XRD analysis of the reacted samples: Fe was recovered as fine metallic particles from 1100K and Zn was separated as gas phase from
1200K (Lee et al., 2008) (Fig. 6). Sun et al. carried out similar experiments and successfully recovered metallic iron and metallic zinc (Sun et al., 2009). Saidi and Azari investigated the reduction behavior of zinc oxide concentrate by carbon under microwave irradiation (Saidi & Azari, 2005). They found that the reduction started from the center on the sample with microwave, whereas without microwave the reduction started from the surface. Recently, Kim and Lee studied the reduction kinetics of ZnO with solid carbon at constant temperatures under microwave irradiation (Kim & Lee, 2009). They found that the microwave heating enhanced the reaction rate. When the reaction rates were compared with and without microwave, the reaction rates with microwave showed much higher values. Moreover, when additional microwave power was applied to increase the reaction temperature, the reaction rate became much faster than a expected value (stronger temperature dependence than each elementary reaction).

![XRD analysis results of EAF dust and carbon mixture after microwave irradiation (Lee et al., 2008)](image)

**3.4 Recovery of metallic elements from other industrial wastes**

Morita et al. applied the microwave heating to fly ash treatments (Morita et al., 1992; Nakaoka et al., 1993). Recently, Chou et al. also used the microwave heating and successfully fixed the hazardous elements (Chou et al., 2009). Ma et al. recovered metallic elements from sludge (Ma et al., 2005). In the microwave process with sludge, removal of water is very important (Standish et al., 1988). It is expected that the removal of water can be enhanced by combining vacuum and microwave heating methods. There still have challenges to recover metallic elements from industrial wastes not only from iron- and steel-making plants but also other sectors in many industries. One example is the recovery of Ni from used Ni ion batteries (Yoshikawa et al., 2007). Due to its simplicity and freedom from process limitations, the microwave process is expected to be extensively used in many recycling processes.
4. Prospective

The microwave heating process has gained many attentions from many pyrometallurgy industries, who are searching for an innovative process to reduce carbon dioxide emission. In principle, the microwave heating process generates lower carbon dioxide emission, when the electricity is supplied by a nuclear power plant. Therefore, the use of microwave heating process can be determined based on the social electric power generation system of each country.

In order to commercialize the microwave heating process for the industrial waste treatment, several points should be improved. First, the energy efficiency should be increased from the current status (approximately 10-20%) to a much higher level (at least 30-50%). Second, the capacity and powder of the microwave furnace should be increased. Most of the lab scale experiments have been carried out with 1-2 kW microwave furnaces. Currently, Michigan Institute of Technology and Tokyo Institute of Technology are developing pilot plant type furnaces, Rotary Hearth and Rotary Kiln based furnaces, respectively. Furnace design and process optimization are very time consuming, but should be improved further. Third, more fundamental studies should be carried out. We have very limited knowledge on the electromagnetic properties of materials and related chemical reactions at high temperatures. Extensive works on the microwave treatment of industrial waste have been carried out in the University of Tokyo and Korea University. Nevertheless, there remain many theoretical and technical problems solved.

5. Conclusion

Microwave can penetrate to the core of a target material, and directly heat the inside. Therefore, high energy efficiency can be obtained when heat transfer is a rate-determining step. Microwave heating also reduces the erosion of refractory materials due to internal heating characteristic. Microwave also accelerates agglomeration of the particles, yielding direct contact between oxides and carbonaceous materials. Therefore, fast reaction rates can be expected. Moreover, microwave heating system does not need any gas injection for combustion or reduction, so that fine particles can be directly used without any pretreatment. After the microwave process, recovered metallic components can be easily separated from the remaining materials. Therefore, reduction in process costs can be expected. From the lab scale experiments, it was confirmed that metallic elements were successfully recovered in a very short period of time. In a near future, mass production of recycled metals can be achieved with the microwave heating method.

6. Acknowledgement

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7. References

Application of Microwave Heating to Recover Metallic Elements from Industrial Waste


The book offers comprehensive coverage of the broad range of scientific knowledge in the fields of advances in induction and microwave heating of mineral and organic materials. Beginning with industry application in many areas of practical application to mineral materials and ending with raw materials of agriculture origin the authors, specialists in different scientific area, present their results in the two sections: Section 1-Induction and Microwave Heating of Mineral Materials, and Section 2-Microwave Heating of Organic Materials.

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