Microwave Carbo-thermal Reduction for Recycling of Cr from Cr-containing Steel Making Wastes

Noboru YOSHIKAWA,1) Ken-ichi MASHIKO,2) You SASAKI,3) Shoji TANIGUCHI,1) and Hidekazu TODOROKI4)

1) Graduate School of Environmental Studies, Tohoku University, 6-6-02, Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan.
2) Graduate Student, Tohoku University, 6-6-02, Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan.
3) Tohoku University, 6-6-02, Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579 Japan.
4) Yakin Kawasaki Co. Ltd. Technical Research Center, 4-2, Kojima, Kawasaki-ku, Kawasaki 210-8558 Japan.

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In this study, Cr-containing steel making slag and pickling sludge were reduced with graphite by microwave (MW) heating. The reduced metal (alloy) particles were obtained and their compositions were determined. Pure Cr$_2$O$_3$ was reduced at lower temperature than expected from thermodynamics.

Fundamental studies on MW heating of Cr$_2$O$_3$ were performed using a multi-mode and a single mode MW applicators in order to investigate the enhanced reaction kinetics. It was demonstrated that heating of Cr$_2$O$_3$ requires incubation period before onset of the sudden temperature rise. Cr$_2$O$_3$ was preferentially heated in the electric ($E$) field of MW and metal pieces were formed.

It was pointed out that the MW heated specimen had inhomogeneous temperature distribution, the temperature could be measured at the localized region and/or it is an average of the temperature distribution in a micro-scale. The reduction might have occurred in the high temperature region, preferentially. In order to account for generation of the inhomogeneous distributions, two possibilities are considered. First, as the enhanced heating behavior in $E$-field, dielectric heating mechanism of Cr$_2$O$_3$ is likely, and its permittivity (loss factor) has large temperature dependence. Therefore, small initial temperature fluctuation was amplified to become the local temperature difference (hot spot). Second, occurrence of local arcing enhanced the kinetics and formation of metal pieces.

KEY WORDS: microwave; slag; sludge; chromium; recycling; reduction.

1. Introduction

Recently, price of alloying elements of steel becomes higher and their effective recycling processes have been pursued. For example, chromium (Cr) needed to be recycled from the slag and sludge in stainless steel production. However, because the reduction temperature of Cr oxide is high, thus the reduction requires the energy consuming processes. We attempted to apply microwave heating for recycling of Cr from these wastes. It is intended to decrease the operating temperature and shorten the process time. In this study, investigation on the fundamental MW heating behavior of Cr oxides and their reduction kinetics is performed.

Details of the Cr-containing slag and sludge states are described first, and then, present recycling processes of the sludge are described.

In stainless steel production, Cr containing slag is produced.1) In order to minimize the loss of Cr into the slag, it is attempted to reduce the Cr oxides with some elements such as ferro-silicon, because Cr is a valuable metal element and also it is needed to meet the requirements of the environmental regulations if they are to be land-filled. Usually in the steel making process, large amount of lime (CaO) is added to increase basicity.2) As a result, dicalcium-silicate is formed and the slags pulverize. If the Cr is not sufficiently removed in the melted state, as mentioned above, Cr-oxides remain in the slag powder.

In the rolling of stainless steel sheets, surface oxide layer (scale) forms, and is required to be removed by acid washing. The wasted acid water contains large amount of the heavy metal ions (Cr, Fe, (Ni)).3) They are neutralized, flocculated and sedimented to form pickling sludge. Some of them are recycled, in which processes, they are dried and pelletized (briquetted) mixing with graphite, and then sintered at relatively high temperature. In this process, heavy metal ions in hydrous or hydroxide states are converted into oxide states, and the partial reduction occurs together with sintering of the pellets having enough strength to be charged in the reduction furnace. These pellets also contain CaO, which is originated in the neutralizing stage of the acid water.

In the reaction furnace, Joule heating by electric current is utilized as one of the heat sources by direct insertion of graphite electrode. There are various other methods of heating, such as burning of crude petroleum. These conventional processes require high temperature and prolonged process time, as mentioned before. There are some reports on the sludge reduction by the conventional heating
method.\(^5\)\(^6\)\(^7\)\(^8\)

In this article, an attempt is reported to enhance the reduction reaction of these Cr-containing slags and sludges with an addition of graphite by microwave (MW) heating. Among many oxides present in the slags, gangue minerals such as alkaline-earth oxides (CaO, MgO), silica and silicates (including dicalcium-silicates) are MW-transparent and don’t absorb MW energy well, but the heavy metal oxides of (Ni, Fe, (Cr)) are easier (Cr case will be mentioned, later) and are better heated. Moreover, graphite has much superior MW absorbance.\(^9\) Therefore, it is easier to supply heat for causing these endothermic (reduction) reactions.

The authors reported studies on MW carbo-thermal reduction of NiO as one of the components in the stainless sludge.\(^7\)\(^8\) The possibilities of the shorter time and the lower temperature of the reaction have been demonstrated. The reduced metals can be separated from the mixture, because the metal particles tend to be coagulated and grown under heating conditions of (Ni, Fe, (Cr)) are easier (Cr case will be mentioned, later) and are better heated. Moreover, graphite has much superior MW absorbance.\(^9\) Therefore, it is easier to supply heat for causing these endothermic (reduction) reactions.

In the case of Fe- and Ni-oxides, the reduction reaction occurs lower than 1 000°C. On the other hand, reduction of Cr-oxide (Cr\(_2\)O\(_3\)) requires higher temperature, and the reduction is practically not easy, according to the thermodynamics.\(^1\)\(^2\) Moreover, Fe, Ni-oxides are possibly reduced with CO(g) by gas–solid reaction, while there is no such reactions in Cr\(_2\)O\(_3\) system, as below:

\[
2\text{Cr}_2\text{O}_3(s) + 3\text{C}(s) = 4\text{Cr}(s) + 3\text{CO}_2(g), \quad \Delta G^0(0, T) = 1\,253°C
\]

\[
\text{(1)}
\]

\[
\text{Cr}_2\text{O}_3(s) + 3\text{C}(s) = 2\text{Cr}(s) + 3\text{CO}(g), \quad \Delta G^0(0, T) = 1\,531°C
\]

\[
\text{(2)}
\]

And Cr carbides are readily produced, as the follows:

\[
3\text{Cr}_2\text{O}_3(s) + 13\text{C}(s) = 2\text{Cr}_7\text{C}_3(s) + 9\text{CO}(g)
\]

\[
\text{(3)}
\]

\[
7\text{Cr}_2\text{O}_3(s) + 27\text{C}(s) = 2\text{Cr}_3\text{C}_2(s) + 21\text{CO}(g)
\]

\[
\text{(4)}
\]

It is shown\(^13\)\(^14\) that MW heating behavior of Cr\(_2\)O\(_3\) is different from other oxide ceramics in that frequent occurrence of thermal runaway or sudden temperature rise with absence of heating controllability. In this study, it is attempted to investigate the possibility and the conditions of Cr reduction from the Cr-containing stainless steel making wastes, such as slag and sludge. And it is intended to perform the fundamental study on the reduction reaction kinetics of Cr\(_2\)O\(_3\) under MW irradiation.

2. Experimental

2.1. Specimens

Supplied specimens are Cr containing steel making slag, (in which Cr has not been completely removed, intentionally) and the other is the pickling slag of stainless steel acid washing. On the other hand, commercial grade of Cr\(_2\)O\(_3\) regents (Wako, 3 micron meter) were heated alone or mixed with graphite (Wako, 5 micron meter) with MW heating apparatus described next. The powders were mixed gently in a mortar.

2.2. MW Heating Apparatus

The MW heating was performed both in a multi-mode (Shikoku Keisoku, max power 0.67 kW) applicator and in a single mode apparatus (Nikkoh, max power 1.5 kW) both operated at 2.45 GHz, as schematically illustrated in Fig. 1. In the multi-mode applicator, electric (E-) and magnetic (H-) field exist, while, separated E- and H-field heating is possible by placing the specimen in different positions in the microwave applicator. The specimens are small enough not to disturb the distributions of E- and H-fields. The detailed descriptions are provided in the previous reports.\(^15\)

Temperature measurement in the multi-mode applicator was performed with a thermocouple (K-type sheath). And the heating was performed either with the temperature control or with application of certain power level.

Temperature measured with thermocouple was calibrated with boiling point of water and the melting temperature of pure Al, and confirmed its accordance within 10 degree. On the other hand, optical temperature measurement system (Luxtron, PhotoniX) was applied for the single mode apparatus. Sapphire rod was utilized as the light-guiding pipe. This temperature reading has been also calibrated with thermocouple without MW field. The sufficient accordance within in 10 degree were also obtained.

All the heated specimens were in a powder state and were filled in a container without pressing. The container is made of vitreous silica having different dimension (multi-mode: 15 mm in diameter, 30 mm in length, single-mode: 7 mm in diameter, 10 mm in length). In both cases, the specimen container or the holder were thermally insulated and the heating experiments were conducted in N\(_2\) gas stream of 100 ml/min.

2.3. Observation

The MW-heated specimens were observed by means of an optical microscope (OM, Olympus BX60) and SEM/EDX (Hitachi S-6501). The phase identification and deter-
mination of the reduction fraction was carried out using XRD (Rad-C, Rigaku) peaks. Reduction fraction was defined using the largest XRD intensities of Cr(110) with respected to Cr$_2$O$_3$(104) by $I_{Cr}(U_{Cr}+I_{Cr,O})$. This method of phase fraction determination is only semi-quantitative, but it is considered possible to discuss the progress of the reduction reaction.

### 3. Results

#### 3.1. MW Reduction of Real Wastes Containing Cr

It was not possible to heat the real sludge and the slag powder above 200°C without graphite addition. This is because of the fact that fractions of heavy metal oxides are lower with respect to the gangue components such as CaO, SiO$_2$, and these silicates. Mixture of either slag or sludge with sufficient amount of graphite was successfully heated by MW and the reduced Cr-containing alloys were obtained.

SEM/EDX photographs of the reduced specimens are shown in Fig. 2. The Fig. 2(a) illustrates the Cr-containing slag specimen heated at 1000°C for 10 min., with graphite addition of 5 wt%. The bright areas correspond to the reduced metal (alloy). Composition of the reduced alloy was determined and listed in Table 1. The obtained Cr concentration values differed with different positions, probably because of the original segregation of Cr in the oxide states. The similar result obtained for the reduced sludge is shown in Fig. 2(b), and the compositional analysis datum is also listed in Table 1. In these reduction experiments using the real wasted matters, the reduction occurred from the complex oxides to the alloy, such as Fe–Cr oxide to Fe–Cr alloy and Fe–Cr–Ni oxide to Fe–Cr–Ni alloy. The reduction temperature of Cr has to be discussed with consideration of the Cr activities in the complex oxide and that in the alloy. However, because the compositions and the complex oxide phases are not completely determined in the present stage, it is difficult to discuss the detailed thermodynamics and the reduction kinetics.

#### 3.2. MW Reduction of Pure Cr$_2$O$_3$

In order to investigate the basic kinetics of MW carbothermal reduction, pure Cr$_2$O$_3$ regents were mixed with graphite. They were heated by MW at different temperature for various holding times. Photograph of the reduced metal is shown in Figs. 3(a), 3(b), and the example of XRD profiles at carbon equivalent ($C_{eq}$: carbon moles required for reduction of 1 mol of Cr$_2$O$_3$) 1 and 3 are shown in Fig. 4. These profiles were obtained in the single mode, H-field region. Not only a peak from the reduced Cr, but also peaks from Cr carbides are present. (Cr$_3$C$_2$ has a similar peak to Cr(110), and which is sometimes difficult to separate from each other.) The reduction fraction obtained in a multi-mode applicator was determined by XRD and the values are listed in Table 2.

This indicates Cr$_2$O$_3$ was reduced to Cr at lower tempera-
ture than expected from thermodynamics.\(^{12}\)

### 3.3. MW Heating Behavior of Cr\(_2\)O\(_3\) in a Multi-mode Applicator

MW heating behavior of Cr\(_2\)O\(_3\) was investigated by measuring its heating curves (time–temperature relationship) in a multi-mode applicator and compared with that of graphite and NiO. They were measured under the same input power of 670 W (maximum), and the plots are shown in Fig. 5.

Graphite can be heated very well, and temperature rose up to 1000°C within 2 min. On the other hand, NiO and Cr\(_2\)O\(_3\) had incubation time before onset of the rapid temperature increase. Although the incubation time periods of Cr\(_2\)O\(_3\) is similar to NiO, temperature of NiO saturated at 900°C, but temperature of Cr\(_2\)O\(_3\) still increased. In this case, power was switched off in order to avoid damaging the thermo-couple.

### 3.4. MW Heating Behavior of Cr\(_2\)O\(_3\) in a Single-mode Applicator

Cr\(_2\)O\(_3\) powders were heated in a single-mode MW applicator, where separated \(E\)- and \(H\)-field heating is possible and provides information to discuss the MW heating mechanisms.\(^{15-17}\) The heating curves are plotted in Fig. 6*.

(* NiO heating curve in \(H\)-field differed from the report,\(^{7,8}\) because of the grain size difference.) Although there was an incubation time before onset of the temperature rise, \(E\)-field MW irradiation enabled high temperature heating, while \(H\)-field application was not successful to heat it above the detection limit of the pyrometer. Although there might exist better matching conditions of stub tuning, which could give rise the higher temperature heating, it was not possible to find them. Usually, no better conditions cannot be found, according to our experience in such cases, so far. These facts show that the dielectric heating mechanism is important in heating of Cr\(_2\)O\(_3\), other than the magnetic and the ohmic loss mechanisms.

Cr\(_2\)O\(_3\) powder was mixed with graphite and heated by MW. Photographs of the reduced powder states are shown in Figs. 3(c), 3(d). A distinct difference was observed that metallic pieces appeared more in \(E\)-field irradiation. On the other hand, in \(H\)-field, the mixed powder state such as their grain size remain unchanged. As shown in Fig. 4, a peak from the reduced Cr is present, and Cr-carbide (Cr\(_3\)C\(_2\)) increased at the larger carbon equivalent \(C_{\text{eq}} = 3\).

### 4. Discussion

Not only the Cr-containing oxides’ waste but also pure Cr\(_2\)O\(_3\) were reduced at lower temperature than the expected value from thermodynamics. There are three possibilities to account for this fact. First, in these experimental settings, the temperature is measured from the localized area in the specimen. Namely, some finite area on the surface temperature is measurable by an optical method (2 mm in the optical rod diameter), and a thermocouple sheath in the inside of the powder (having diameter of 3 mm). This means there

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**Table 2.** Reduction fraction Cr (%) at various conditions in a multi mode applicator (\(C_{\text{eq}} = 2\)).

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>0</th>
<th>5</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>15.0</td>
<td>8.3</td>
<td>46.5</td>
</tr>
<tr>
<td>1100</td>
<td>8.1</td>
<td>32.2</td>
<td>26.6</td>
</tr>
<tr>
<td>1000</td>
<td>12</td>
<td>5.3</td>
<td>10</td>
</tr>
</tbody>
</table>

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**Fig. 4.** XRD profiles from the MW heated powder mixture at 800°C for 5 min in \(H\)-field, (a) at carbon equivalent 1 (\(C_{\text{eq}} = 1\)) and (b) \(C_{\text{eq}} = 3\).

**Fig. 5.** Heating curves of graphite (C), NiO and Cr\(_2\)O\(_3\) powders in a multi-mode applicator at maximum power input.

**Fig. 6.** Heating curves of graphite (C), NiO and Cr\(_2\)O\(_3\) powders in a single-mode applicator at input power of 200 W, (a) in \(E\)-field and (b) in \(H\)-field.

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could be areas having locally much higher temperatures, as schematically illustrated in Fig. 7(a). The reduction occurred at the high temperature regions where the thermodynamic conditions are satisfied. The second possibility is occurrence of arcing (Fig. 7(b)). This needs to be clarified by means of the other intimate experimental techniques to confirm it. The third is due to some special MW effects to enhance the reaction kinetics. Although the so-called “non-thermal effect” has been argued for long time. Its real causes still remain un-clarified. In this study, it is attempted to account for the reduction kinetics from the first and the second standpoints.

4.1. Temperature Dependence of Cr$_2$O$_3$ Permittivity and Its Effect on the Heating Behavior

Heating curve of Cr$_2$O$_3$ in Fig. 5 indicates acceleration of the heating rate as an increase of temperature. If Cr$_2$O$_3$ is heated by a mechanism of MW-dielectric heating,\textsuperscript{18} the absorbed power by the specimen is written as,

$$P = \frac{1}{2} \omega |\varepsilon''| |E|^2 V$$

where $\omega (=2\pi f)$, $f$ is frequency (2.45 GHz), $\varepsilon''$ is the loss factor (imaginary part of the permittivity) $E$ is the MW electric field and $V$ is the volume.

Validity of this assumption of the mechanism is supported by the fact that Cr$_2$O$_3$ was heated better in E-field in the single mode experiment. Thus, it is expected that the permittivity (loss factor, $\varepsilon''$) increased as the increase of temperature. On the other hand, however, behavior of the accelerated heating might be also related with the rapid increase of the DC electric conductivity as the increase of temperature.\textsuperscript{19} If so, other heating mechanisms become important at the elevated temperature, such as the conduction loss mechanism.

It is plausible to assume existence of the local temperature fluctuation at the initial stage of the MW heating, for example, because of the Cr$_2$O$_3$ and graphite grain size distribution or their aggregates’ size in the mixture according to the mixed conditions, although the degree of their difference is not clear. If there are regions with local temperature difference, it is inferred that the high temperature region can be heated preferentially, because of the permittivity increase, and thus the temperature fluctuations are expected to be amplified. Under this circumstance, temperature was measured in some localized regions.

4.2. Possibility of the Enhanced Reduction Kinetics by Arcing

In the experiments of the separated E- and H-fields using a single mode applicator, Cr$_2$O$_3$ heating occurred preferentially in E-field, as demonstrated in Fig. 6. And the reduced metal pieces were obtained more in E-field. Because arcing is often observed through the window of the applicator, obviously, it is inferred that occurrence of arcing might be the another possibility to the enhanced reduction kinetics and/or metal formation.

Occurrence of arcing is induced under a condition of high electric field gradient,\textsuperscript{20} which is more likely to occur in the higher E-field region. There is a simulation report\textsuperscript{21} that the electric field gradient is larger in the locally intruded or bulged regions. However, it is not easy to observe the local arcing and to prove its existence.

Arcing gives rise the locally high temperature regions. Especially, formation of metal pieces in E-field is considered to be related with this phenomenon. However, generation of local plasma by arcing is not necessarily easy to observe. Thus, it is required to prove its existence in the future studies by relating to the spectroscopic observation in light emission.

5. Conclusion

MW carbo-thermal reduction kinetics and MW heating behavior of Cr$_2$O$_3$ were studied and the following results are obtained:

1. Cr containing alloy particles were obtained by reducing the Cr-containing slag and pickling sludge. And Cr
was reduced from pure Cr₂O₃ at the temperature lower than the expected value from the thermodynamics.  
(2) MW heating of Cr₂O₃ has incubation time before onset of the sudden temperature rise, and Cr₂O₃ was heated better in E-field.  
(3) Formation of Cr metal pieces occurred preferentially in E-field.  
(4) Created local difference in temperature and occurrence of local arcing are pointed out for the locally enhanced reduction kinetics and resulted in the lower (average) reduction temperature.

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