Proceeding Paper

Extraction of Iron from Russian Red Mud by a Carbothermic Reduction and Magnetic Separation Process [†]

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Abstract: Red mud is a hazardous waste of alumina production. Currently, the total accumulated amount of red mud is over 4 billion tons. The promising method of red mud processing is a carbothermic reduction of iron at 1000–1400 °C into metallic form followed by magnetic separation. In this study, the mechanism of carbothermic solid-phase reduction of red mud was investigated. Based on the experimental data, the two-step mechanism of the first rapid stage of the process was proposed, which leads to almost full iron reduction. The estimated value of activation energy has indicated that solid-phase diffusion is a rate-controlling step for this stage. However, an almost full reduction is necessary, but insufficient factor for successful magnetic separation. The second crucial factor of the process is enlargement of iron grain size, which leads to gangue-grain release during grinding and increases efficiency of the magnetic separation. The prediction model of iron grain growth process during the carbothermic reduction process was suggested. The calculation of average size of iron grains formed during the reduction process that was performed according to the assumption of diffusion-controlled process showed their correlation with experimental data. Various methods were proposed to promote the process of iron grain growth during carbothermic reduction of red mud.

Keywords: red mud; carbothermic reduction; magnetic separation; solid-phase reduction; iron grain growth; reduction

1. Introduction

Red mud is a waste of alumina production from the bauxite ore. The obtaining of 1 ton of alumina generates 0.8–1.5 tons of red mud [1]. Recycling or utilization of red mud is an important current task due to both environmental and economic reasons. Firstly, red mud occupies large areas and causes an adverse environmental impact [2]. Secondly, red mud is a valuable material for extractive metallurgy owing to significant contents of iron, aluminum, titanium, and rare-earth metals [3]. The typical content of Fe_2O_3 in red mud is in the range of 30–60% [4] that enables to consider its treatment to extract iron.

The promising way for iron recovery from red mud is its reduction into metallic form [5]. An implementation of this approach requires creation of physicochemical conditions for iron reduction and development of a technological process for the treatment of significant amounts of red mud. The common reduction process is carbothermic roasting at the range of 1000–1400 °C followed by magnetic separation. This method allows us to use a cheap carbon-containing material as a reducing agent and carry out the treatment in air

without the formation of melts. To obtain iron metallic concentrate, grinding and magnetic separation of the reduced material is needed. The crucial factor of the efficiency of magnetic separation is sufficient iron grain size to release gangue from the metallic part during grinding. Therefore, the physicochemical conditions of the metallization process should provide not only full reduction of iron oxides, but also a certain size of metallic particles above a certain limit.

This study focuses on a mechanism of the carbothermic solid-phase reduction of iron in red mud, as well as prediction model of iron grain growth process. Kinetic parameters of the reduction process were estimated, and the decisions were proposed to promote the process of iron grain growth during carbothermic reduction.

2. Materials and Methods

Ural Aluminum Plant (Russia) provides a red mud sample, which was treated by lime milk at 90 °C for 180 min to lixiviate sodium. The sample has the chemical composition as follows: 25.8% Fe, 17% Ca, 6.3% Al, 4.1% Si, 2.1% Ti, 0.6% Mg, 0.4% P, 0.2% Na, 0.1% S. The main iron-containing phase of the red mud sample was α-Fe_2O_3 (hematite). Experimental carbothermic reduction was carried out the same as in our previous studies [6,7]. Red mud was pressed in tablets and placed into the crucible filled with a considerable excess of finely ground coal to reduce iron; the reduction was carried out in the muffle furnace in the range of 1000–1200 °C.

3. Results

Figure 1 gives the kinetic dependence of iron metallization degree at various temperatures.
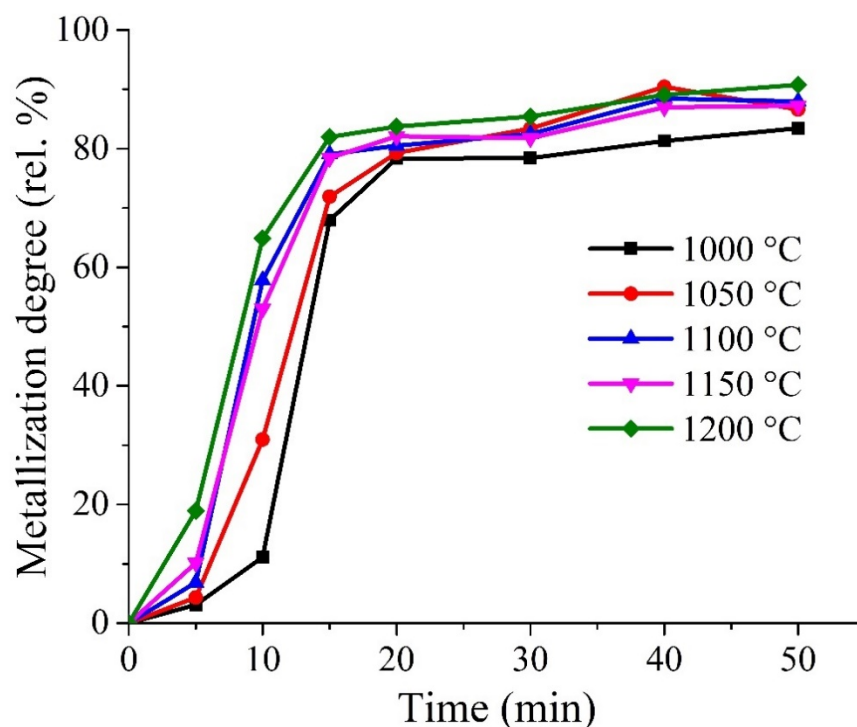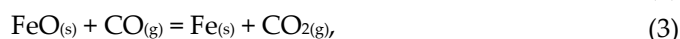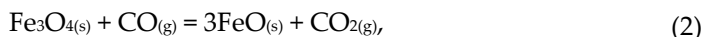

Figure 1. Effect of temperature and reduction time on iron metallization degree.

As can be seen, the process consists of two sectors including a sharp increasing of metallization rate up to 15–20 min and then its moderating growth. The maximum degrees of metallization at all the temperatures are no more than 80–90%, although the thermodynamic potential of the reducing agent is sufficient for full reduction because of its excess. Hence, the incomplete reduction is probably due to a kinetic mechanism of the process.

In any case, the rate of the first stage of the process depends on the surface area of iron oxides available for interaction with the reducing agent. It is clear that the contact of oxide-carbon surfaces in the powder mixture of red mud and solid carbon can be mostly pointwise, especially at the initial stage of the process, while diffusion sintering of the powder particles is not essential. Therefore, there is a point reduction of iron oxides in the first moments of the treatment with a generation of gaseous carbon oxides. Obviously, the carbothermic reduction of iron oxides occurs after an appearance of carbon oxides according the following reactions:

$$3Fe_2O_{3(s)} + CO_{(g)} = 2Fe_3O_{4(s)} + CO_{2(g)}, \qquad (1)$$

$$Fe_3O_{4(s)} + CO_{(g)} = 3FeO_{(s)} + CO_{2(g)}, \qquad (2)$$

$$FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}, \qquad (3)$$

$$CO_{2(g)} + C_{(s)} = 2CO_{(g)}. \qquad (4)$$

Evidently, Equations (1) and (2) go rapidly, so the total reaction can be written as a sum of the Equations (3) and (4):

$$FeO_{(s)} + C_{(s)} = Fe_{(s)} + CO_{(g)}. \qquad (5)$$

In our case, assuming the gas diffusion is not a rate-controlling step, and the auto-catalytic Equation (4) also occurs rather quickly at the temperatures of the experiments, the reduction degree at this stage can be limited by a surface area of the iron oxides available for gas reduction in the red mud samples. To increase the rate of the initial stage of the metallization process, an increase in the outer surface of the iron oxides is needed that can be achieved by an additional grinding of red mud.

The second stage of the overall process begins after the sintering process occludes the through pores for a free penetration of carbon-containing gases. Therefore, CO_2 can't leave the FeO surface fast enough to provide CO an area for the interaction with the oxide, so the reduction process proceeds slowly. The reduction degree increases due to the growth of already formed small iron grains from the surface toward the interior of solid phases. The reducing agent can penetrate through the solid layers as not molecules, but as atoms, so two additional steps can be distinguished during the reduction process, namely, a dissociation of CO or CO_2 molecules to atoms and diffusion of the atoms into the crystal lattice of solid oxides. The diffusion step includes a supply of the reducing agent to the interphase boundary of FeO–Fe and removal of excessive oxygen atoms from this boundary. The value of apparent activation energy (E_A) determines a rate-controlling step.

Based on the Arrhenius equation, E_A was calculated according to the data from Figure 1. The E_A value is in the range of 200–215 kJ/mol within the time interval of 0–10 min, while it is in the range of 5–10 kJ/mol at 10–20 min. The E_A value of 200–215 kJ/mol is approximate to the E_A value of diffusion of oxygen atoms in metal oxides [8]. It can be assumed that the reduction process at this interval is limited by the migration of atoms in the crystal lattice of FeO. The E_A value of further process considerably decreases, so the diffusion is not a rate-controlling step at 10–20 min.

Taking into account diffusion control of the reduction rate at the stage of the rapid increase of the degree of metallization, it is possible to estimate the average size of metallic iron grains using Wagner's theory [9], which allows for calculating the migration rate of the interphase FeO–Fe boundary at any time according to the diffusion characteristics of the system. The distance χ covered by the interphase boundary in a time t can be evaluated as follows:

$$\chi = \sqrt{2 \cdot D_{ox} \cdot t \cdot \frac{C_S - C_1}{C_1 - C_2}} \qquad (6)$$

where C_S is oxygen concentration in FeO (≈0.53 at. %); C_1 is oxygen concentration in the solid solution of FeO in a range of its homogeneity (≈0.05 at. %); C_2 is oxygen concentration

in the solid solution of Fe ($\approx$0.01 at. %); D_{ox}—oxygen diffusion coefficient in solid FeO, m^2/s. It can be accepted that if the iron grains are spheroidal, the covered distance is equal to radius: $\chi \approx r$. According to [8], we accept D_{ox} = 6.2·10^{-8}·exp(−240000/RT).

Table 1 demonstrates the results of the calculation according to Equation (6).

Table 1. The calculation of iron grain size according to the Wagner theory.

Temperature, °C	D_{ox}, m^2/s	r, μm
1000	8.7·10^{-18}	0.5
1100	4.5·10^{-17}	1.1
1200	1.7·10^{-16}	2.2

The calculated sizes of iron grains are consistent with the experimental data obtained in [6,7].

4. Discussion

The analysis of the carbothermic solid-phase reduction of red mud has enabled considering the stages that influence the degree of metallization of the total process. We assume that kinetic mechanisms are similar at all experimental temperatures in the range of 1000–1200 °C. The obtained data indicate that the carbothermic solid-phase process led to a high degree of iron metallization, but the crucial task is an enlargement of the size of reduced iron grains up to the required value for the subsequent magnetic separation. Based on the results of the study, we recommend the following decisions:

- Increasing the fineness of red mud the for reduction process at 1000–1200 °C with a simultaneous increment of the treatment time to decrease the sintering rate that can lead to a promotion of gas reduction stage and an increase of iron growth rate on the surface;
- A rise in the reduction temperature above 1200 °C or an addition to red mud of materials with a low melting point to lower the temperature of the molten phase formation that can lead to the growth of reduced iron particles due to an additional effect of liquid diffusion.

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Conflicts of Interest: The authors declare no conflict of interest.

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