Investigation of iron grains growth during solid-phase carbothermic reduction of red mud in the presence of iron metallic particles

A S Zakunov\textsuperscript{1,2}, P I Grudinsky\textsuperscript{1}, D V Zinoveev\textsuperscript{1}, A F Semenov\textsuperscript{1}, M O Panova\textsuperscript{1}, V G Dyubanov\textsuperscript{1} and A L Petelin \textsuperscript{2}

\textsuperscript{1}A.A. Baikov Institute of Metallurgy and Material Science RAS, 49 Leninsky avenue, Moscow, 119334, Russia
\textsuperscript{2}National University of Science and Technology "MISiS", 4 Leninsky avenue, Moscow, 119049, Russia
E-mail: az437@yandex.ru

Abstract – Red mud is a hazardous waste obtained from bauxite ore by the Bayer method. It has a high content of iron. In this study, the iron grain growth process during solid-phase carbothermic reduction of red mud in the presence of added iron metallic particles was investigated. Carbonyl iron, cast iron shots and metallurgical mill scale were used as the additives. The influence of amount and fraction of the additives on size of reduced iron grains obtained after reduction roasting of red mud at 1250-1350°C and 60-180 min duration was studied. It is showed that the best effect on size of iron grains has the addition of carbonyl iron and mill scale. In this way, besides red mud, some other iron-containing wastes can be recycled, e.g. mill scale.

1. Introduction
The production of alumina forms a waste called a bauxite residue. Another common name for this waste is red mud. According to the data of 2018, more than 4.5 billion tons of red mud have already been accumulated worldwide [1]. Moreover, the main problem is open storage of red mud in sludge fields. This waste has a high alkalinity and contains toxic compounds including salts of heavy metals, so it has a potential hazard for soil and groundwater. Also sludge field destruction can be a serious environmental disaster for nearby settlements [2].

Red mud has a high iron content, which can reach 45% [3]. In addition to iron, red mud also contains aluminum, titanium, scandium and other rare-earth metals (REEs) that can be recovered [4–6].

A large number of studies were carried out on the topic of red mud recycling. The valuable elements from red mud can be recovered by hydrometallurgical and pyrometallurgical methods. Pyrometallurgical methods is generally used for recovery of iron at the temperatures over 1000 °C to obtain the slag [7,8] or the tailings [9,10] with high content of valuable elements. Hydrometallurgical methods can be used for recovery of aluminum, titanium and rare-earth metals by leaching using different mineral acids or alkalis [11]. NaOH solutions are applicable for selective recovery of aluminum and sodium from red mud because of low solubility of ferrous minerals in these solutions [12–14]. It is showed that more than 95% of Al and Fe from red mud can be extracted by HCl leaching [15,16]. The best results for Ti [17] and Sc [18] selective extraction were achieved by H\textsubscript{2}SO\textsubscript{4} leaching. The methods were proposed to prevent Fe and Si dissolution and to pass Sc into solution by HCl and H\textsubscript{2}SO\textsubscript{4} leaching, respectively [6,19]. Some researchers studied the extraction of Sc and other REEs from red mud by different methods [20–22]. In [22], a comparative investigation of leaching efficiencies of different acids on solubility of Sc, Y, Nd, La, Ce and Dy showed the best results by application of HCl leaching.

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High iron content makes possible to consider bauxite residue as a potential source for its extraction. Pyrometallurgical methods are the most applicable for iron recovery. Conventionally, they can be divided according to the applied approach. The first and most common method is reductive smelting at temperatures over 1450 °C [23,24]. As a result, valuable components are distributed between the iron ingot and slag. The second popular method is solid-phase reduction at temperatures between 950 and 1400 °C [25] with following magnetic separation of reduced iron [26]. The iron grains obtained are small in size and form intergrowths with an aluminosilicate phase [27] that decrease the efficiency of magnetic separation. To obtain high-quality iron concentrate it is necessary to find a way for enlargement of reduced iron grain and gangue-grain release after grinding. In the process of growth of reduced metal particles the formation of stable nuclei consumes most of energy. In this regard, we suggested that the addition of iron metallic particles to the charge for solid-phase carbothermic reduction can promote iron grain growth of the reduced iron grains. In this paper, the effect of addition of iron metallic particles on the growth of reduced iron particles was studied.

2. Materials and methods

2.1 Raw materials
Red mud of the Ural Aluminum Plant (Kamensk-Uralsky, Russian Federation) was the main raw material in the study. Long-flame coal containing 15 % of ash and 18 % of moisture was used as a reducing agent. Cast iron shot with a size of 0.3 mm, carbonyl iron and mill scale from AO “OMK-stal” (Vyksa, Russian Federation) were used as additives. Alkali components was preliminary leached from red mud by lime milk at 90°C for 3 hours [28]. Table 1 shows the composition of neutralized red mud.

| Fe₂O₃ | SiO₂ | Al₂O₃ | TiO₂ | CaO | MgO | MnO | Na₂O | P₂O₅ | S | Sc | LOI |
|------|------|-------|------|-----|-----|-----|------|------|---|----|-----|
| 36.9 | 8.71 | 11.8  | 3.54 | 23.8| 1.01| 0.95| 0.27 | 0.42 | 0.14| 0.008| 12.46 |

2.2 Reduction roasting
For the experiments red mud and the reducing agent were preliminarily ground and sieved up to the particle size of less than 0.2 mm. Red mud was dried at 110 °C for 4 hours. Cast-iron shot was 0.3 mm in size, the other additives were ground and sieved up to the required size of 0.1, 0.063 and 0.05 mm.

Red mud with the additives was mixed in a V-shell blender for 24 hours. Then the mixtures were pressed into tablets on hand-held hydraulic press Nordberg N3630A (China) with a pressure of 215 MPa. The weight of the tablets was 1 g, they were 17 mm in diameter and 2.5 mm in height.

The tablets were placed in a small corundum crucible of 62 mm in height and 45 mm in diameter. 10 tablets were mixed with charcoal so as to prevent their touching each other. The small crucible was filled by coal and then was turned over and placed in a large corundum crucible of 68 mm in height and 58 mm in diameter. The large crucible was half-filled with coal. This layout of the crucibles provides the reducing atmosphere inside.

The experiment was carried out in a muffle furnace at temperature range of 1250–1350 °C for 60–180 min. The temperature in the furnace was set using a platinum-rhodium thermocouple connected to an automatic programmable controller. The samples were placed in a preheated furnace. After roasting, the samples were quenched in liquid nitrogen to avoid reverse oxidation of reduced iron. After cooling, the roasted tablets were ground and sieved up to the particle size of less than 0.4 mm for further preparation of polished section and calculation of iron grain size

2.3 Calculation of the size of iron grains
The polished sections were investigated using a METAM LV-34 optical microscope (Russia) in reflected light with a magnification of x250. For each sample 16 microphotographs were combined
into one for further calculation. Full range of dimensional characteristics of all iron grains were obtained by Image Pro Plus software (USA). The Feret diameter was chosen as the main analyzed parameter which is the distance between two parallel straight lines tangent to the grain boundaries in a certain direction. The relative area of iron grains with mean Feret diameter in a certain range was taken as an argument in the obtained dependences.

3. Results
Figure 1 shows the influence of addition of cast iron shots on iron grains growth process during carbothermic reduction of red mud at 1200 °C.

![Figure 1. Effect of cast iron shots addition at 1200 °C on relative area of iron grains of different fractions after 60 min (a) and 120 min (b) of the roasting.](image)

The addition of cast iron shots during carbothermic roasting of red mud at 60 minutes has no positive effect on size of iron grains (Figure 1(a)). Iron particles are mainly distributed between small fractions of 1-20 µm. Moreover, after the roasting there were no iron grains with size above 40 µm. An increase of roasting time from 60 to 120 min led to decreasing the amount of iron grains less 1 µm from 17 % to 9 % and to increasing the amount of iron grains above 40 µm from 0 % to 8 % at 10 % of cast iron shot addition (Figure 1(b)). Also amount of iron grains with size of 20-40 µm at 5 % and 10 % of cast iron addition was increased compared with the sample without additions. However, the influence of cast iron addition on iron grain growth is insignificant. It is likely due to the fact that a size of the added particles of cast iron shot was too large compared with a size of reduced iron grains. Figure 2 clearly demonstrates a lack of influence of cast-iron shot at 1200 °C.
Figure 2. Microstructure of the samples after the roasting at 1200 °C with cast iron shots: (a) addition of 5 %, 60 min of roasting; (b) addition of 5 %, 120 min of roasting; (c) addition of 10 %, 60 min of roasting; (d) addition of 10 %, 120 min of roasting.

Figure 3 shows the influence of cast iron addition on iron grain growth process during carbothermic reduction of red mud at 1250 °C.
Figure 3. Effect of cast iron addition at 1250 °C on relative area of iron grains of different fractions after 60 min (a), 120 min (b) and 180 min (c) of the roasting.

An increase of roasting temperature from 1200 °C to 1250 °C led to increase the influence of cast iron shot additions on iron grain growth process (Figure 3). It is showed that there is appreciable growth of the iron grains with size of 5-20 µm at 60 and 120 min of the roasting. An increase of roasting time to 180 min led to increasing the amount of iron grains of 5-20 µm from 15% to 47% and to increasing the amount of iron grains above 40 µm from 3% to 12% compared with the sample without additions. It should be noted that the amount of iron grains less 2 µm was also considerably decreased by addition of cast iron shots.

Figure 4 shows microstructure of the samples after roasting at 1250 °C and indicates that cast iron shots locate separately from the reduced iron particles and have no effect on the iron growth process. It can be seen that cast iron shots save its original geometric shape and size. This fact was in all experiments with the addition of cast iron shots regardless of roasting duration and temperature.
Figure 4. Microstructure of the roasted samples at 1250 °C with the addition of 5% of cast-iron shots after 60 min (a), 120 min (b) and 180 min (c) of the roasting.

Figure 5 shows the influence of amount and size of carbonyl iron additions on size of iron grains at 1250 °C after 180 min of the roasting.

Figure 5. Effect of amount and size of carbonyl iron addition on relative area of iron grains of different fractions at 1250 °C after 180 min of the roasting.

The bar chart indicates that the main part of iron particles reduced without additives has size less than 5 µm. Taking this into account, the effect of carbonyl iron is clearly visible, namely a decrease of amount of the iron grains less 5 µm and a significant increase of amount of iron grains of 5-20 µm and 40 µm. The largest effect on iron grains growth was obtained with the addition of 10% carbonyl iron with particle size of 50-100 µm. It should be noted that size of the particles of carbonyl iron additions have a more significant effect on size of the reduced iron grains than their amount.

Figure 6 shows a comparison of the effect of carbonyl iron addition with different size on growth of reduced iron grains at 1350 °C after 60 min of the roasting.
Figure 6. Influence of size of 5% carbonyl iron addition on relative area of reduced iron grains of the different fractions at 1350 °C after 60 min of the roasting.

Figure 7 shows microphotographs of the samples obtained after the roasting with the addition of carbonyl iron at different temperatures. It can be clearly seen that the rise of temperature decreases an amount of small particles.

Figure 7. Microphotographs of the samples after the roasting with addition of carbonyl iron 10% of addition 63-100 μm in size at 1250 °C 180 min (a), 10% of addition 63-100 μm in size at 1300 °C 180 min (b) and 5% of addition 50-63 μm in size at 1350 °C 60 min (c).

Figure 8 shows the fraction distribution of metallic iron particles after 180 min of the roasting at 1300 °C depending on the amount and size of mill scale particles.
Figure 8. Effect of mill scale addition of various sizes on relative area of iron grains of different fractions at 1300 °C and after 180 min of roasting.

The bar chart indicates that the addition of mill scale has a positive effect on reduced iron enlargement in the same way with the addition of carbonyl iron. The addition of mill scale 50-63 µm in size led to the best results. The relative area of iron grains larger than 40 µm was 40 % and 65 % with the addition of 5 and 10 % of mill scale of this fraction, respectively. It is important to note that particles with a size of 1-5 µm occupy more significant area at the addition of 5 % mill scale compared with the addition of carbonyl iron of the same size. It also should be noted that the addition of 5 % mill scale with a particle size of less than 50 µm led to the lack of large particles; fractions of 1-5, 5-20, and 20-40 µm were the main part of the area of iron grains in this sample.

Figure 9 shows microphotographs of the samples after roasting with the addition of mill scale.

Figure 9. Microphotographs of the samples after 180 min of the roasting at 1300 °C with mill scale with addition of iron metal particles of different amount and size (a) 5 % of addition, less than 50 µm in size; (b) 5 % of addition, 50-63 µm in size; (c) 10 % of addition, 50-63 µm in size.

As a generalization of the results, it should be noted that the addition of metallic iron particles into the charge for carbothermic reduction of red mud significantly increase a size of reduced iron grains if
the particles have a size in the certain range. The added iron metallic particles should be slightly larger than the size of reduced iron grains obtained under similar conditions without the addition. Furthermore, it is interesting to note that a rise of the roasting temperature significantly increases the size of obtained iron grains. It is most likely due to the partial melting of slag components of the charge that facilitate diffusion of iron grains and promote their aggregation. Hence, the addition of fluxes which can reduce a melting point of red mud, e.g. alkali metal salts, can promote the migration of small grains of reduced iron to the added particles. Evidently, to improve the results it is preferable to use initial red mud in the process of roasting without neutralization stage. Probably, the geometric shape of the added metallic particles also has an impact on the grain growth. The irregular-shaped added particles with defects on the surface can grow easier than particles with regular shape. Figure 10 demonstrates a comparison of the surfaces of the added particles.

Figure 10. Microphotographs of added particles of cast-iron shots (a) and carbonyl iron (b).

4. Conclusions
Thus, the study has found out a positive effect of addition of iron metallic particles during carbothermic reduction of red mud but the effect of such additives is limited. In this way, besides red mud, some other wastes can be recycled, e.g. mill scale.

To improve the process of iron grain growth during carbothermic reduction of red mud it is necessary to add iron metallic particles of slightly larger size than the size of reduced iron grains obtained under similar conditions without the additions. The optimal temperature range of the roasting is appeared to be between solidus and liquidus point with duration of more than 120 min.

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