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Influence of Pulsed Mechanical Activation of Hematite–Graphite–Aluminum Powder Mixtures on the Reduction of Iron Oxides

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Abstract—To decrease the temperature of direct iron reduction by carbon and aluminum, short-term pulsed mechanical activation (PMA) of an $Fe_2O_3 + C_{gr} + Al$ powder mixture is perfumed during sound-frequency shock loading by a flat activating plunger. The PMA efficiency for powders in comparable with mechanical activation in high-energy ball mills in a decrease in the activation time and retaining the chemical purity of a powder composition.

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INTRODUCTION

One of the aspects of improvement of iron production by direct reduction of its oxides with carbon-containing materials is related to searching for optimal ways to decrease the temperatures of reducing reactions, which is promoted, in particular, by an addition of more intensive reducing agents (Al, Ca, Si, Mg) and by mechanical activation of reagents mainly by milling in ball mills over a long period of time [1–3]. When analyzing all previous studies of mechanical activation intended for the reduction of metal oxides with carbon, the authors of [3] used the exothermic effect of aluminothermic reduction in order to decrease the temperature of the endothermic carbothermic reduction of hematite. The influence of aluminum addition (0–10%) on the hematite reduction by graphite was studied on heating to 1100°C after mechanical activation of their mixture in a Fritsch Pulverisette high-energy planetary mill in 2, 5 and 10 h, and the possibility of a significant decrease in the initial temperatures of reducing processes was demonstrated.

In this work, instead of long-term grinding in ball mill, we used short-term pulsed mechanical activation (PMA) of $Fe_2O_3 + C_{gr} + Al$ powder mixtures during impact sound-frequency loading in order to study the possibility of decreasing the temperature of phase transformations in reducing annealing.

EXPERIMENTAL

The Institute of Metallurgy has an installation for processing of powders and liquids by elastic low-frequency vibrations. All previous experiments using this installation were carried out under condition of generation of air flows [4] or liquid flows [5] in the operating space under and around a vibrating plunger. In this work, a new approach was applied to this installation: mechanical activation of powdered reagents by pulsed blows with a flat plunger on the total powder volume. The initial stage of preliminary mixing (PM) of powders with air was performed at the ratio of the plunger bottom-to-powder mixture surface distance to the powder layer height of 1 : 1. The plunger was then lowered onto the powder surface to achieve the maximum possible contact, and the mixture was processed for 5 and 10 min by PMA at a plunger impact frequency of 40 s^{-1}, an acceleration of 240 m/s^2, and a pushing force of 1200 N.

$Fe_2O_3 + C_{gr} + Al$ powder mixtures were prepared in a weight ratio of 8 : 2 : 1. Reagent grade commercial hematite powder was used as initial Fe_2O_3 annealed at 1000°C in a CO + Ar environment and milled to a particle size of ≤50 μm. According to X-ray diffraction data, the reagent after annealing consisted only of Fe_2O_3. Powdered Al was obtained by washing of PAP-2 aluminum powder (GOST Standard 5494–95) from fatty oil in several solvents. High-purity graphite with a maximum particle size of 5 μm was used as C_{gr}.

The mixtures processed by PM and PMA were used for fabrication of 1-g pellets at a pressure of 40 MPa; they were then placed into small graphite crucibles with lids. The small crucibles were placed into a wide graphite crucible, filled with a graphite powder, and heated to 1100°C at a rate of ~10°C/min in a resistance furnace in a constant argon flow. In reducing annealing, the small crucibles were sequentially removed from the furnace starting from 200°C at a step of 100°C. The pellets in the small crucibles were cooled in air and weighed. The phase content was determined by semi-quantitative X-ray diffraction

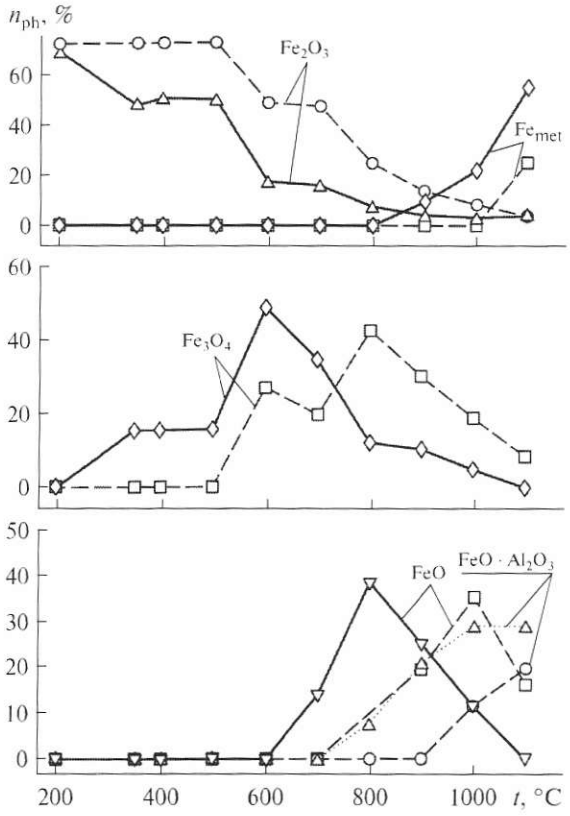

Fig. 1. Influence of reducing annealing temperature t on the phase composition of an $Fe_2O_3 + C_{gr} + Al$ powder mixture after (dashed lines) PM and (solid lines) PMA.

analysis (XRD) using a DRON-3M diffractometer and Cu$K\alpha$ radiation.

RESULTS AND DISCUSSION

The XRD analysis of the specimens demonstrates that, during their annealing, the content of the initial phases decreases and the following new phases are generated: magnetite Fe_3O_4, wüstite FeO, spinel $FeO \cdot Al_2O_3$ and metallic iron Fe_{met}. The XRD data are illustrated in Fig. 1.[1]

Influence of preliminary preparation of a powder mixture on the temperatures of the onset and end of reduction of iron oxides (t_{s1}, t_{s2}, and t_f) and the metallic iron content (Fe_{met}) at 1100°C

Mixture	t_{s1}	t_{s2}	t_f	Fe_{met}, %
	°C			
PM	500–600	900–1000	~900	25
PMA (5 min)	200–350	700–800	~800	55

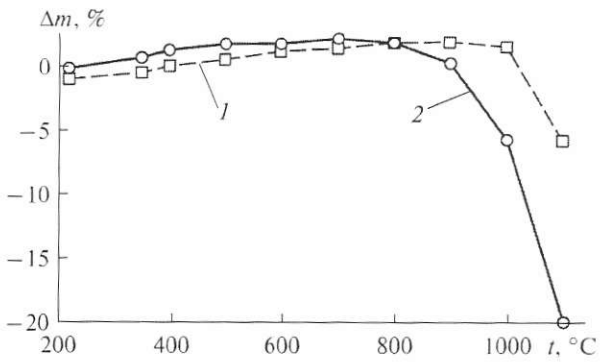

Fig. 2. Variation of the change in the pellet weight Δm for (*1*) PM and (*2*) PMA mixtures as a function of the reducing annealing temperature.

The character of the Fe_2O_3 curves, which describe a gradual decrease in the hematite content during heating for the pellets after PM and PMA, varies equally with the temperature: there are even similar process delay steps at 600–700°C in a PM specimen and at 350–500°C in a PMA specimen. In this case, the magnetite Fe_3O_4 content curves contain delay step, which can be related to an incubation period of structural rearrangements in hematite, in the same temperature range. The hematite content in the PM mixtures (dashed curves) begins to decrease after 500°C, whereas about one-third of Fe_2O_3 is reduced to magnetite in the PMA mixture (solid curves) already at 350°C.

At the stage of generation of wüstite FeO, the effect of PMA manifests itself also in a decrease in the temperature of onset of the process by ≥200°C. Here, the magnetite and wüstite content curves reach maxima, at 600 and 900°C for a PMA mixture and at 800 and 1000°C for a PM mixture, respectively. Spinel $FeO \cdot Al_2O_3$ forms in the mixtures almost simultaneously with wüstite. Before the termination of the reduction of Fe^{3+} to Fe^{2+}, metallic iron appears starting from temperatures ≥800 and ≥1000°C in PMA and PM mixtures, respectively.

Thus, the activation of PMA mixtures manifests itself in a decrease in the temperature of the onset of hematite reduction by ≥350°C and the temperature of the appearance of metallic iron by 200°C. The influence of powder preparation conditions on the content of metallic iron after reducing heating to 1100°C can be tracked from the data summarized in the table.

The pellet weight variation as a function of the reducing heating temperature is illustrated in Fig. 2. The observed insignificant scattering of the points in

[1] Phase content n_{ph} is given in wt %.

the curves is related to nonideal homogeneity of powder mixing and does not influence the general character of the curves. The increase in the pellet weight by 2–3% at the beginning of reducing heating can be attributed to aluminum oxidation by adsorbed oxygen retained on the particle surfaces of the initial powders.

It can be seen that the weight decrease related to the carbon loss during carbothermic reduction starts in PMA mixtures from 700–800°C, that is, by 200°C earlier than in PM mixtures. For a PMA mixture, the reduction intensity also increases: at 1100°C, the weight loss is 19%, whereas it is no higher than 7.5% for a PM mixture.

The table summarizes the data on the temperatures of the onset of hematite reduction from the beginning of appearance of magnetite (t_{s1}) and from the temperature of beginning a decrease in the pellet weight (t_{s2}). The temperature of the end of aluminothermic reduction (t_f) is determined from the temperature of disappearance of aluminum using XRD data. It follows from a comparison of the data in the table and in Fig. 1 concerning the relative phase content that t_{s1} is the temperature of starting of aluminothermic reduction and t_{s2} is the temperature of starting of carbothermic reduction.

With the aim of revealing the influence of the PMA time, we carried out an additional experiment with an increase in the powder activation time to 10 min. XRD analysis of this powder after reduction heating to 1100°C and holding in 3 min demonstrates that the processes of reduction are completed and iron-containing phases are only present by metallic iron Fe_{met}. In pellets of the same composition obtained after mechanical activation in 10 h after holding at 1100°C in 30 min, there exists non-reduced iron in spinel $FeO \cdot Al_2O_3$ in addition to metallic iron [3].

The higher efficiency of powdered reagents after PMA in comparison with activation in ball mills can be explained by the fact that the kinetic energy of activating plunger is transferred to all particles of the processed material simultaneously, whereas the small (point) contact area between activated powders and milling balls requires a longer time for obtaining a homogenously activated powder volume. The latter results in longer time intervals of all chemical reactions during subsequent heating, as mentioned in [3].

One more important advantage of application of the PMA method is the absence of contact between the activating plunger and the crucible walls, which provides preservation of chemical purity of the activated powders, whereas a common problem of mechanical chemistry is the contamination of processed powders with the materials of the milling bodies (balls) and drum as a consequence of their fracture due to a high force concentration at collisions.

CONCLUSIONS

(1) Our experiments demonstrated that the sequence of phase formation in the Fe_2O_3–C_{gr}–Al system upon reducing heating corresponds to a gradual decrease in the iron valence: $Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow (FeO, FeO \cdot Al_2O_3) \longrightarrow Fe_{met}$.

(2) Short-term (5 min) pulsed mechanical activation (PMA) of powder mixtures by sound-frequency impact loads using a flat activating plunger before reducing annealing decreases the temperatures of the onset and end of all reducing stages by 200–300°C.

(3) The high efficiency of PMA processing is likely to be caused by the large contact area of the contacting surfaces during an impact.

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