Influence of the conditions of internal heat exchange on the process of thermal decomposition of carbonates in iron ore raw materials

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This work considers influence of heating rate of iron ore raw materials on chemical and metallurgical processes of thermal dissociation of carbonates, which occur during its high-temperature roasting. The research was conducted for the temperature ranges of the existing roasting and sintering machines, taking into account macro-kinetics of calcination processes. Substantial influence of heating rate of iron ore samples on kinetics of thermal decomposition of carbonates was revealed. The cause of the effect of internal heat exchange conditions in reacting iron ore sample on macro-kinetics of dissociation reaction for carbonates was substantiated scientifically. Influence of non-isothermal properties on precision of thermal analytical investigations, which were conducted using the methods of non-isothermal kinetics with different heating rates of iron ore samples, was studied. The authors suggested the mathematical model, which allows to take into account wide range of variations of the parameters in kinetic equations and volumetric thermal and chemical-metallurgical dissociation processes for carbonates. A series of calculating experiments, aimed on reveal of the relationship between heating rate of iron ore samples and evolution of concentration fields, transformation rates and temperature gradients, was carried out using the suggested model. The obtained results can be used for development of the optimal operating conditions for sintering and roasting machines, which propose optimization of heat treatment processes for iron ore preparation, owing to intensification of heat and mass exchange processes during high-temperature roasting. These conditions are considered as optimal from the point of view of power- and resource efficiency. Forming of the above-mentioned conditions allows to decrease fuel and power expenses for thermal preparation of raw materials at metallurgical production facilities, as well as to lower total economical production charges due to use of thermal decomposition of carbonates.

Key words: iron ore raw materials, iron ore concentration, roasting, dissociation of carbonates, temperature, heat exchange, calcination.
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Introduction

At present time, development of power- and resource-saving technologies and their putting into practice in the Russian metallurgical industry are considered as the most important directions of development of this industry at present time [1-3]. It is evident that these technologies can be applied with maximal efficiency in the industrial branches which are using mineral resources; concentration of iron ore ram materials can be related to such industries [4, 5]. From one side, it is stipulated by strict competition at the iron ore raw material market, which makes metallurgical concentrating works to cut their production expenses and to improve quality of products [6, 7]. Thermal decomposition of carbonates in roasting and sintering machines allows to use non-critical fuel for improvement of metallurgical properties of iron ore raw materials, what promotes lowering of fuel and power expenses during consequent metallurgical technological stages [8, 9]. From other side, elevation of prices for thermal and electric power, which are used for thermal preparation of iron ore raw materials, is considered as an important factor determining necessity of outing into practice the new technologies. In its turn, this elevation of prices leads to total rise of production expenses [10, 11]. Based on this, search of the optimal power- and resource-saving operating procedures for roasting conveyor and sintering machines, which are used for roasting of iron ore raw materials, is rather actual problem. Determination of these conditions is realized via creation of large-scale mathematical models, taking into account the main chemical and metallurgical heat and mass exchange processes, occurring in the dynamic layer of sintering and roasting machines [12-14].

The aim of this work is to research influence of heating rate and the constants of the chemical reaction of carbonates dissociation on macro-kinetics of the process of thermal decarbonization. The obtained results can be used in the future for development of power- and resource-saving procedures for thermal preparation of iron ore raw materials in roasting and sintering machines.

Mathematical model of the process of thermal dissociation of carbonates

Research of mutual determining features of heat exchange and kinetics of heterogeneous transformation in iron ore raw materials was examined during high-temperature roasting via building of a mathematical model, which takes into account the most essential appearances, as well as analysis of taken solutions [15, 16].

The following significant factors were emphasized during building a model describing decarbonization process:

- non-stationary temperature conditions, accompanying chemical-metallurgical processes;
- dependence of thermal physical parameters of iron ore raw materials both on temperature and transformation degree of reacting components.

The following admissions and suggestions were realized in this case:

- diffusion of gas products occurs without restrictions and has no effect on reacting rate of carbonates dissociation;
- temperature relationship of reacting rate is characterized by Arrenius features;
- specific heats of chemical transformations don't depend on temperature.

Taking into account the main requirements and admissions, mathematical formulation of the problem in one-dimensional setting for a flat sample can be expressed as:

$$\begin{cases} \rho C_p(T, \alpha_1, \alpha_2)\dfrac{\partial T}{\partial \tau} = \dfrac{\partial}{\partial x}\left(\lambda(T, \alpha_1, \alpha_2)\dfrac{\partial T}{\partial x}\right) - \\ - C_1^0 Q_1 \dfrac{\partial \alpha_1}{\partial \tau} - C_2^0 Q_2 \dfrac{\partial \alpha_2}{\partial \tau}; \\ \dfrac{\partial \alpha_1}{\partial \tau} = k_{01}\exp\left(-\dfrac{E_1}{RT}\right) f_1(\alpha_1); \\ \dfrac{\partial \alpha_2}{\partial \tau} = k_{02}\exp\left(-\dfrac{E_2}{RT}\right) f_2(\alpha_2). \end{cases} \tag{1}$$

where α – reacting variable, presented as the expression $\alpha = 1 - G(\tau)/G_0$, where G_0 – amount of substance, which participates in the reaction, $G(\tau)$ – amount of non-reacting substance during the time τ; α_1 – transformation degree of $MgCO_3$; α_2 – transformation degree of $CaCO_3$; $\rho C_p(T, \alpha_1, \alpha_2)$, $\lambda(T, \alpha_1, \alpha_2)$ – thermal physical parameters – specific heat capacity and specific heat conductivity, which depends on the temperature and transformation degrees of endothermic reactions of carbonates dissociation: $MgCO_3 \rightarrow MgO + CO_2 - Q_1$ and $CaCO_3 \rightarrow CaO + CO_2 - Q_2$, where $Q_1 = 1.21 \cdot 10^5$J/mol – thermal effect of decomposition reaction $MgCO_3$, $Q_2 = 1.78 \cdot 10^5$J/mol – thermal effect of decomposition reaction $CaCO_3$; C_1^0, C_2^0 – heat capacity values of the substances of the substances of reacted carbonates; E_1, E_2 – activation energy values of carbonates dissociation; k_{01}, k_{02} – pre-exponential multipliers; x – coordinate of plate thickness with semi-thickness X, $x \in [-X; X]$; R – universal gas constant; T – temperature; ρ – density.

Influence on macro-kinetics of thermal decomposition of carbonates was taken into account using widely distributed relationship $f(\alpha) = (1 - \alpha)^n$, where n – a number which is determined experimentally for concrete iron ore raw materials.

The system of equations was solved numerically for the following boundary conditions:

– initial conditions:

$$T(x, 0) = T_0;\ \alpha_1(x, 0) = 0;\ \alpha_2(x, 0) = 0, \tag{2}$$

– boundary conditions of the first genus:

$$T(x, \tau) = T_1(\tau);\ T(-X, \tau) = T_2(\tau) \tag{3}$$

where: T_1, T_2 – temperature on the surfaces of non-limited plate, T_0 – initial temperature of a plate. The presented system of equations was solved via running through according to the implicit finite-difference scheme.

Calculating experiment and analysis of the results

In order to determine temperature gradients in calcinated iron ore samples, depending on the heating conditions and qualitative assessment of the procedure of heterogeneous decomposition reaction for carbonate inclusions, the authors have conducted natural experiments at thermogravimetric unit with simultaneous registration of weight loss and temperature distribution in the samples. Calcination was carried out at linear increase of the temperature of samples surface with different rates b, K·s^{-1}. The temperature gradients through the thickness of a plate were measured by differential thermoelectric pyrometers, weight loss of the samples were fixed. The average transformation degree $\overline{\alpha}$ was determined based on the relationship $\overline{\alpha} = (N_с - N(T_п))/(N_с - N_{от})$, where $N_с$, $N_{от}$ – weights of samples in green and completely roasted states respectively, $N(T_п)$ – current sample weight, which is brought to the surface temperature $T_п = T_п(\tau)$.

1. To assess the influence of heating rate b, calculating experiments for the plate with semi-thickness $X = 4 \cdot 10^{-3}$ m were conducted at different heating rates using the computer model which was developed by the authors [17, 18]. This model realizes solution of the system of equations (1), taking into account the boundary conditions (2) and (3). The values of thermal physical parameters for all calculating variants were selected in correspondence with their temperature relationships, which were presented by the authors in the previously published work [19].

Initial data for the calculation variants No. 1 - $b = 0.278$, No. 2 - $b = 1.11$, No. 3 - $b = 2.22$ are as follows: $E_1/R = 25.3 \cdot 10^{-3}$; $E_2/R = 12.6 \cdot 10^{-3}$; $k_{01} = 0.378 \cdot 10^9$, s^{-1}; $k_{02} = 0.124 \cdot 10^{-3}$, s^{-1}; $C_1^0 \cdot Q_1 = 0.00144$, $C_2^0 \cdot Q_2 = 0.00072$; $n = 2/3$.

Calculation results are presented in graphical mode for three values with average transformation degree: $\overline{\alpha} = 0.25$, $\overline{\alpha} = 0.5$, $\overline{\alpha} = 0.75$.

Influence of heating rate of the samples on concentration fields of carbonates $C = C_1 + C_2$, where C_1 – con-

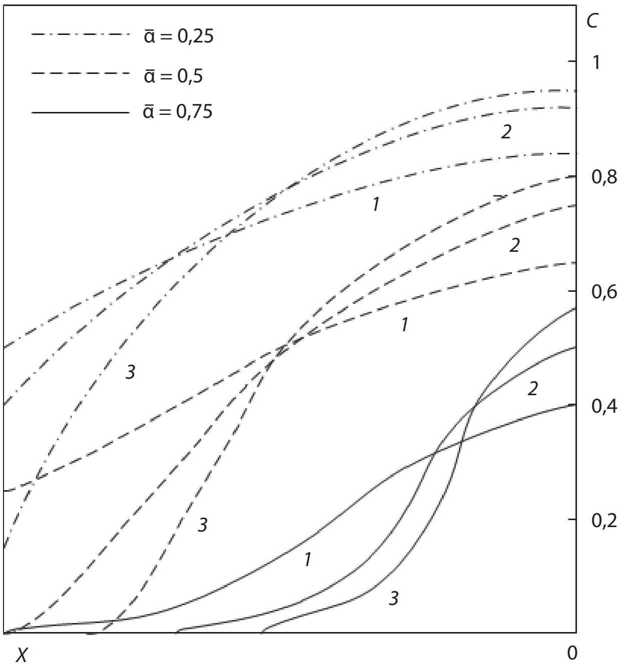

Fig. 1. Influence of heating rate on the field of carbonates concentration. Numbers of curves correspond to numbers of calculation

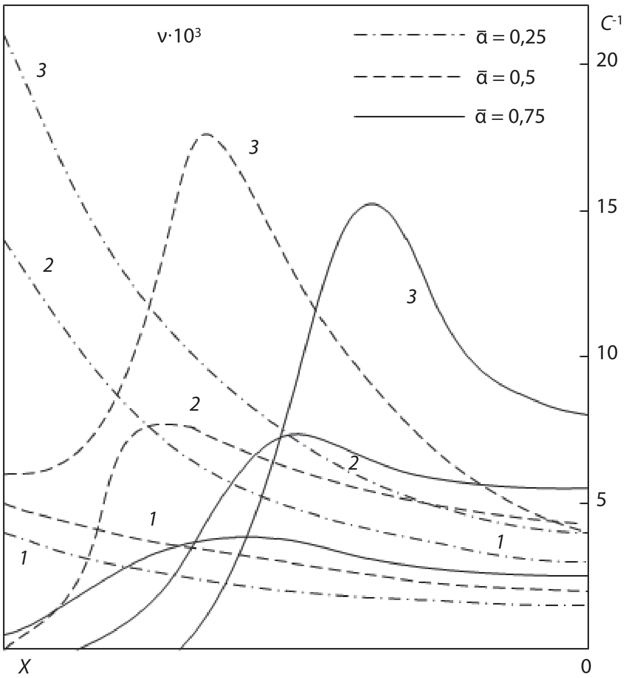

Fig. 2. Influence of heating rate on the field of transformation rates. Numbers of curves correspond to numbers of calculation $[c^{-1} = s^{-1}]$

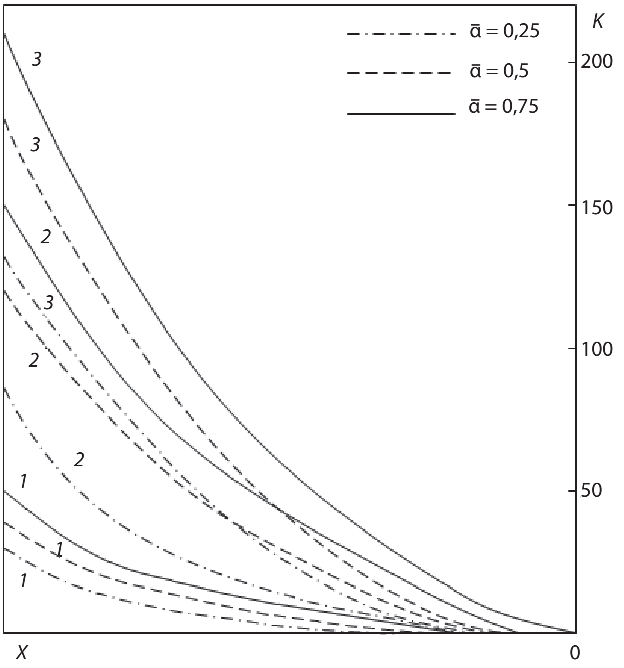

Fig. 3. Influence of heating rate on the temperature gradient. Numbers of curves correspond to numbers of calculation [K/м = K/m]

centration of $MgCO_3$ and C_2 – concentration of $CaCO_3$; on transformation rates $\partial\alpha/\partial\tau$, where $\alpha = C_1\alpha_1 + C_2\alpha_2$; and on temperature gradients $\partial T/\partial x$ are displayed on the **Fig. 1**, **2** and **3**, respectively.

Calculations which were conducted at different heating rates show that increase of the heating rate and, respectively, temperature gradients lead to rise of heterogeneity of reactant concentrations (Fig. 1). Formation of heterogeneous concentration field and presence of temperature gradients in a sample promotes forming of extremal distribution of reaction speed (Fig. 2), its maximal value moves into the sample as soon as endothermic decarbonization reaction passes. It should be noted that the most far is the distance between a corresponding point from the surface, the lower is the maximal value which is crossed by local reaction speed values.

Absolute maximal values of reaction speed increase with rise of the heating rate, what promotes enlargement of temperature gradients in the samples [20, 21].

2. Calculating experiments were conducted at the constant heating rate $b = 0.278$ and at different values n in the function $f(\alpha) = (1 - \alpha)^n$, which determines kinetics of thermal decomposition of carbonates, in order to assess the influence of the function $f(\alpha)$ kind. The initial data for calculation variants No. 1 – $n = 0.1$, No. 2 – $n = 1$, No. 3 – $n = 3$ are presented above.

The results of calculation display that increase of n parameter in the kinetic equation leads to decrease of heterogeneity of concentration of reactant (carbonates) in the sample (**Fig. 4**). The absolute values and heterogeneity of local speeds in dissociation reaction of carbonates also reduce (**Fig. 5**). In its turn, it promotes lowering of the temperature gradients in the samples [22, 23].

The results of investigation of influence of thermal decomposition activation power show that its increase leads

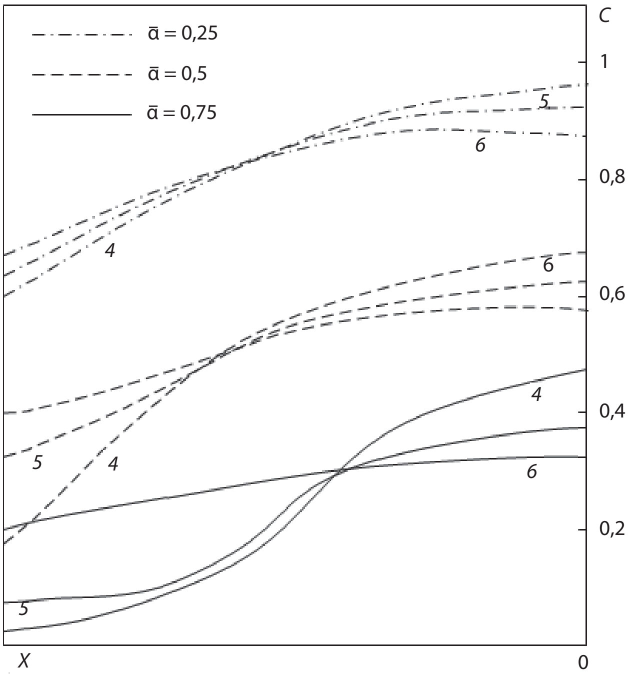

Fig. 4. Influence of the function $f(\alpha)$ kind on the concentration field of carbonates. Numbers of curves correspond to numbers of calculation

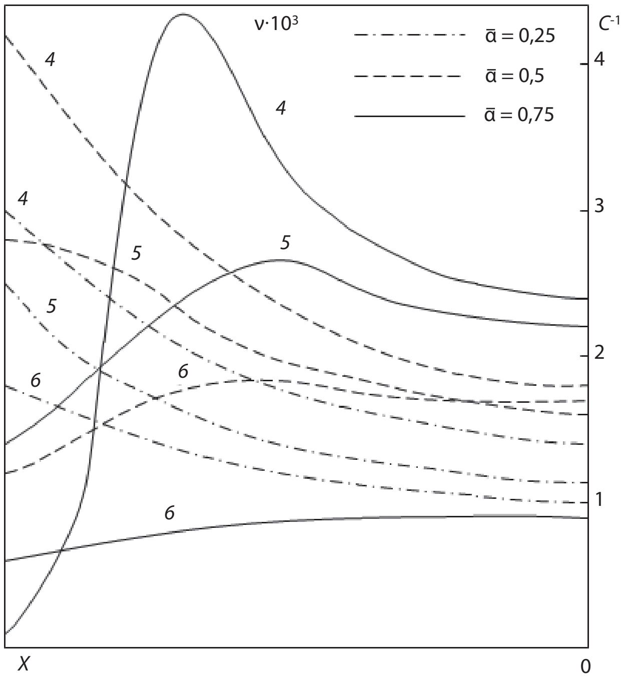

Fig. 5. Influence of the function $f(\alpha)$ kind on the field of transformation rates. Numbers of curves correspond to numbers of calculation [$c^{-1} = s^{-1}$]

to rise of heterogeneity of reactant concentrations, field of speeds and temperatire gradients in the examined iron ore samples [24, 25].

Conclusion

Based on the analysis of the results of calculating experiments, the relationship between heating rate of iron ore raw material and kinetics of thermal decomposition of carbonates was revealed. It should be certainly suggested that in any cases this relationship is connected with influence of the conditions of internal heat exchange in the reacting iron ore sample on macro-kinetics of carbonates dissociation reaction.

In this connection, it is expedient to use the methods of non-isothermal kinetics for determination of influence of examined samples on precision of thermoanalytical examinations: the method of one experiment with preliminary task of $f(\alpha)$ function and the method of series of experiments with different heating rate of the samples.

Calculating experiments using the mathematical model for wide variation range of parameters of kinetic equations and volumetric heats of carbonates dissociation reaction were conducted; this model was developed by the authors. Regularities which allow to create power-efficient conditions of heat treatment for iron ore raw materials via intensification of heat exchange processes during high-temperature roasting, were revealed.

The optimal schemes of roasting conveyor machines for production of iron ore pellets with annual productivity up to 7 mln t are developing in the All-Russian scientific and research institute of metallurgical thermal engineering (VNIIMT). Taking into account that iron ore raw material contains up to 20 % of carbonate components, thermal effect of carbonates dissociation reaction achieves 2.3 GJ per year at one roasting machine.

As soon as annual rise of the costs for energy carriers takes place, increase of power and resource efficiency for metallurgical processes of heat treatment of iron ore raw materials allows to enlarge economical profitability of metallurgical production. CIS

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