

THERMAL TRANSFORMATIONS IN MANGANESE ORES IN THE ZAPADNYI KAMYS DEPOSIT AND IN CHARGE MATERIALS USED TO PRODUCE PELLETS IN AN AIR FLOW UNDER NONISOTHERMAL CONDITIONS

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Results are reported from a study of phase transformations in manganese ores and in charges used to make pellets. The study was performed by the method of differential-thermal analysis (DTA) with continuous heating. The article also presents data obtained by using DTA curves to determine kinetic parameters.

Keywords: manganese pellets, ferroalloy, kinetic parameters, nonisothermal method.

In developing an efficient technology for processing ores, it is important to study the laws that govern the physico-chemical processes which take place during the ores' heating in air under nonisothermal conditions. One of the more complex problems encountered in the kinetics of chemical reactions is calculation of the activation energy. Such determinations are very time-consuming and require a high degree of empirical precision, and increasing use has recently been made of indirect methods for this purpose. One method in particular that is now being used to study the kinetics of reduction under nonisothermal conditions is thermogravimetry [1–3]. The main advantage of this approach (compared to methods employed under isothermal conditions) is that the calculation of kinetic parameters requires much less empirical data. Also, those parameters can be calculated directly for an entire range of temperatures. The nonisothermal approach is more complex in terms of the equipment that is needed and the parameter computations. Kinetic parameters are commonly determined by solving a system of two equations that connect the reaction rate constant k with the temperature T and connect reaction rate v with the degree of transformation α :

$$k = A \exp(-E_{\text{act}}/RT), \quad (1)$$

$$v = kf(\alpha), \quad (2)$$

where E_{act} is the activation energy of the reaction; A is a pre-exponential multiplier which is independent of temperature within a small temperature range; R is the universal gas constant. For the case of the decomposition of solids, reaction rate is expressed by the equation $v = k(1 - \alpha)^n$, where n is the order of the reaction. The activation energy E_{act} is determined from the slope of the relation $\log k = f(1/T)$, which is obtained from Arrhenius' logarithmic equation (1). To determine the reaction

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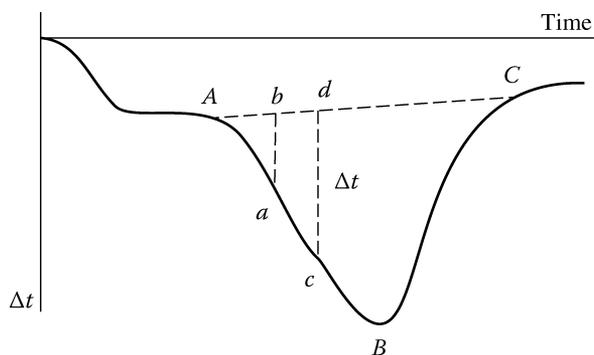


Fig. 1. Thermal effect and its characteristics.

rate constants k , it is necessary to perform a series of experiments under isothermal conditions at different temperatures while continuously recording the loss of mass.

Differential-thermal analysis (DTA), thermogravimetry (TG), and differential thermogravimetry (DTG) are increasingly being employed to study solid-phase reactions based on determination of the apparent activation energy during the heating of substances undergoing reaction at a constant rate. These methods are being widely used to investigate phase transformations, dissociation, reduction, oxidation, dehydration, and other phenomena, i.e., processes connected with changes in the enthalpy and mass of substances. The interest being shown in methods based on nonisothermal kinetics is due to the fact that it is possible to conduct a single experiment and determine all of the kinetic constants (E_{act} , A , and n) appreciably more simply than by the classical gravimetric method used under isothermal conditions. However, since experimental errors can play a significant role, a high degree of measurement accuracy and careful statistical analysis of the data are needed in order to perform a reliable kinetic analysis when there is an additional variable (temperature).

The authors of [4, 5] described methods that can be used to determine the activation energy of reactions after analyzing data from TG or DTA curves. Most of these methods entail choosing among different values of n and require time-consuming computations. In addition, it is impossible to determine the order of reactions that involve chemically impure substances such as natural materials of complex composition (ores, minerals, etc.)

We used the method proposed by Piloyan [4] to determine the activation energy of thermal transformations in the manganese ore of the Zapadnyi Kamys deposit and in charge materials used to produce pellets. This method makes it possible to determine the activation energy of all of the phase transformations which occur during heating by a process that uses a single derivatogram and includes calculation of the area of the DTA peak, an index of the curve's shape, and the order of the reaction. The method is based on an equation that describes the nonisothermal kinetics of solid-phase reactions

$$d\alpha/dT = (A/b)[f(\alpha)]e^{-E/RT}; \quad f(\alpha) = (1 - \alpha)^n. \quad (4)$$

Equation (4) was obtained from the formal kinetic equation for solid-phase reactions $d\alpha/d\tau = k(1 - \alpha)^n$, the temperature dependence of the rate constant (the Arrhenius equation) $k = Ae^{-E/RT}$, and an equation that describes the change in temperature with a constant heating rate $T = T_0 + b\tau$, $dT/d\tau = b$. Here, b is the heating rate.

It is known that the thermal curve deviates more and more from the specified position AC as the reaction proceeds in a specimen (Fig. 1). As is shown by the theory in [6], as a first approximation the magnitude of this deviation Δt (the segments ab , cd , etc. in Fig. 1) can be described by the expression

$$\Delta t \approx \Delta S d\alpha/d\tau, \quad (5)$$

where ΔS is the area under the DTA curve when it deviates from the base line and returns to it (the area ABC , see Fig. 1). Here, τ is the duration of the test.

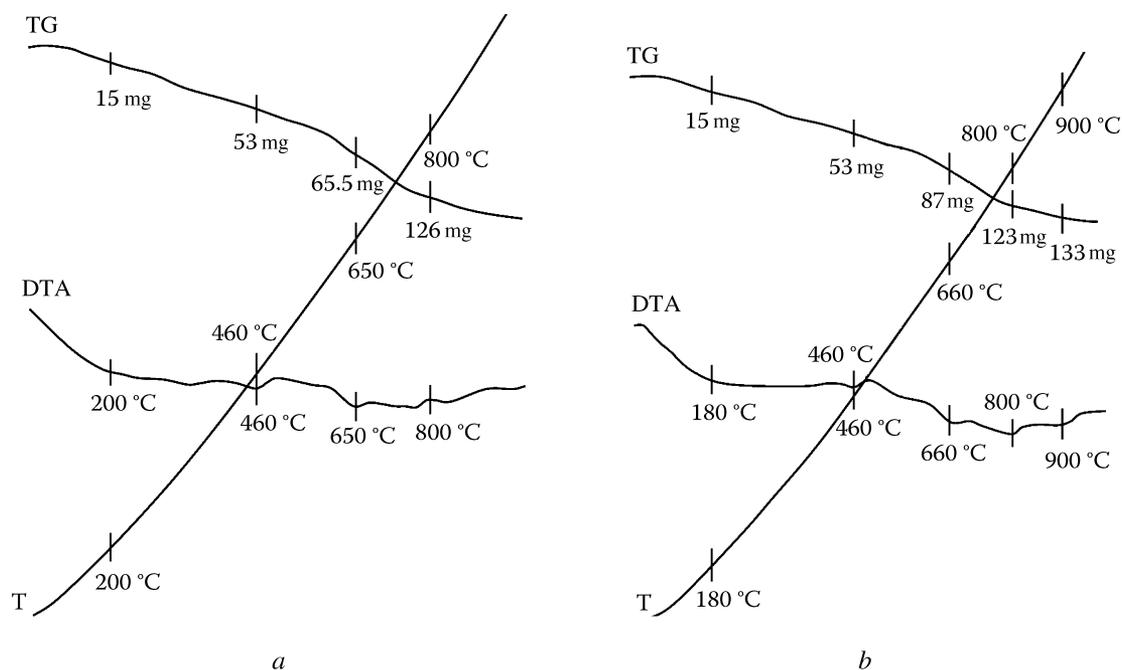


Fig. 2. Derivatograms of the materials studied: *a*) fines of manganese ore; *b*) fines of manganese ore and clay.

With $dT/d\tau = b$, the deviation of the curve from the specified direction Δt is actually determined only by the reaction rate.

If we convert Eq. (5) to logarithmic form with allowance for Eq. (4), we can obtain the following expression:

$$\ln \Delta t = C + n \ln(1 - \alpha) - E_{\text{act}}/RT, \quad (6)$$

where $C = \Delta SA/b$ is a coefficient that combines all of the constant terms in Eqs. (4) and (5). For small values of α , the quantity $n \ln(1 - \alpha)$ can be ignored and Eq. (6) takes the following form:

$$\ln \Delta t = C - E_{\text{act}}/RT. \quad (7)$$

Equation (7), which connects the apparent activation energy with the deviation of the differential recording from the reference value, can be used to calculate E_{act} from the slope of the straight line that describes the deviation from the base line of the DTA curve in the coordinates $\log \Delta t - 1/T$.

Derivatographic studies were conducted with a maximum temperature of 1000°C to investigate the processes that took place during the roasting of fines of manganese ore (sample No. 1) heated at a rate of 25°C/min, a mixture of the ore fines and clay (sample No. 2) heated at the same rate, a mixture of the ore fines, clay, and coke breeze (sample No. 3) heated at a rate of 20°C/min, and a mixture that included the ore fines, clay, coke breeze, and high-ash coal used as a partial replacement for the fines. The last-mentioned mixture was heated at a rate of 20°C/min.

The derivatogram of the fines of manganese ore from the Zapadnyi Kamys deposit (sample No. 1) includes three endothermic effects and one exothermic effect (Fig. 2*a*). The derivatogram shows that the first endothermic effect, at 200°C, corresponds to the loss of hygroscopic moisture. The removal of hydrate (structural) moisture takes place smoothly up to 380°C and does not form any distinct peaks. The second endothermic effect, at 460°C, corresponds to the production and decomposition of the α -kurnakite solid solution. A third pyrolytic (endothermic) effect is seen at 650°C, this effect being characterized by the decomposition of pyrolusite, the formation of braunite (β - Mn_2O_3) and oxygen from β -pyrolusite

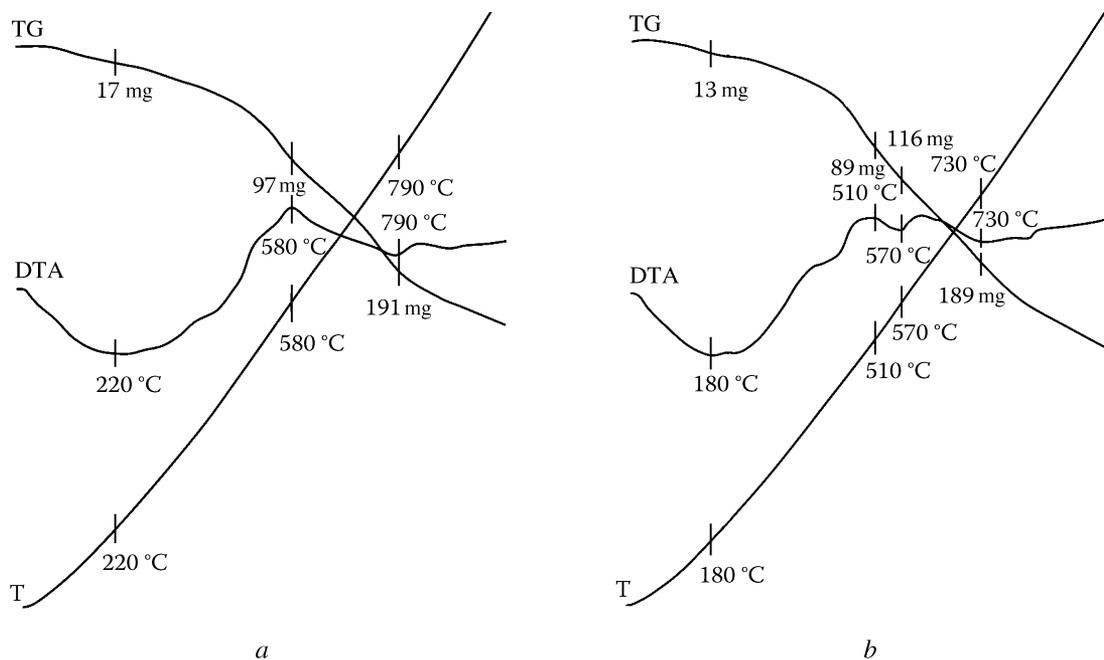


Fig. 3. Derivatograms of the manganese ores that were studied: 1) fines of manganese ore with clay and coke; 2) fines of manganese ore with clay, coke, and coal.

(β - MnO_2), and completion of the decomposition of carbonates of iron and manganese. The fourth effect, at 800°C , corresponds to the decomposition of calcite and the formation of CaO .

The derivatogram of sample No. 2 (fines of manganese ore with clay) includes five endothermic effects (Fig. 2b). The endothermic effect on the DTA curve at 180°C corresponds to the removal of hygroscopic moisture, while the second effect at 480°C corresponds to the formation and decomposition of an α -kurnakite solid solution. The pyrolusite effect is seen at 660°C , where β - MnO_2 dissociates and β - Mn_2O_3 is formed. This event signals the presence of large quantities of minerals which contain manganese in the form Mn_2O_3 . The fourth endothermic effect, at 800°C , is accompanied by a decrease in mass by 123 mg, and it corresponds to the decomposition of calcite and the recrystallization of a small amount of psilomelane. The kurnakite effect seen at 900°C is connected with the conversion of β -kurnakite to β -hausmannite (Mn_3O_4).

The derivatogram obtained for the fines of manganese ore, clay, and coke (sample No. 3) contained two endothermic effects and one exothermic effect (Fig. 3a). An endothermic effect associated with the evaporation of hygroscopic (adsorbed) moisture and having a maximum at 220°C is seen within the first temperature range (20 – 300°C). The complex oxidation-reduction reaction by which MnO_2 is reduced to Mn_3O_4 takes place at a high rate within the range 380 – 620°C . The subsequent endothermic effect at 790°C is characteristic of the dissociation of calcium carbonates and corresponds to completion of the reduction of Mn_3O_4 to MnO . The formation of manganese monoxide under nonisothermal conditions is completed at temperatures ranging to 850°C .

Figure 3b shows the derivatogram of the fines of manganese ore, coke, coal, and clay (sample No. 4). An endothermic effect corresponding to the evaporation of hygroscopic water and having a maximum at 180°C is seen within the first temperature range of 20 – 300°C . The next exothermic effect, occurring within the range 350 – 570°C and having its maximum at 510°C , characterizes complex oxidation-reduction reactions which entail the rapid oxidation of coal and the reduction of MnO_2 (pyrolusite) and Mn_2O_3 (kurnakite) to Mn_3O_4 (hausmannite). As much as 89 mg of mass is lost with these reactions. The overall process of the reduction of manganese oxides takes place with the release of heat, absorption of the heat in the range 510 – 660°C , and a total mass loss of up to 116 mg. The reaction between the ore and the carbon-bearing reducing agents occurs in the range 700 – 900°C and is accompanied by an exothermic effect at 730°C . After we determined the temperature values and the amounts by which the DTA curve deviated from the specified direction, we constructed relations in the coor-

TABLE 1. Values of Apparent Activation Energy

Material	Equation	Correlation coefficient R	E_{act} , kJ/mole	Temperature range, °C
Manganese ore fines (sample No. 1)	$\ln \Delta t = -119.31/T + 3.5$	0.9267	2.284	60–260
	$\ln \Delta t = -768.55/T + 11.1$	0.9524	14.716	400–500
	$\ln \Delta t = -1388.7/T + 15.7$	0.9714	26.590	600–700
	$\ln \Delta t = -4504.4/T + 42.6$	0.9809	86.250	780–840
Manganese ore fines and clay (sample No. 2)	$\ln \Delta t = -221.21/T + 5.7$	0.9630	4.235	100–220
	$\ln \Delta t = -1023.9/T + 14.6$	0.9825	19.605	420–480
	$\ln \Delta t = -1878.8/T + 29.9$	0.9288	35.974	620–700
	$\ln \Delta t = -1887.9/T + 18.3$	0.9757	36.148	750–830
	$\ln \Delta t = -1524/T + 13.8$	0.9553	29.181	850–930
Manganese ore fines, coke, and clay (sample No. 3)	$\ln \Delta t = -91.39/T + 3.1$	0.9008	1.749	60–300
	$\ln \Delta t = -460.61/T + 6.4$	0.9784	8.819	500–660
	$\ln \Delta t = -2180.3/T + 21.1$	0.9818	41.747	750–830
Manganese ore fines, coke, coal, and clay (sample No. 4)	$\ln \Delta t = -117.9/T + 3.3$	0.9957	2.251	100–220
	$\ln \Delta t = -479.57/T + 7.1$	0.9227	9.182	430–520
	$\ln \Delta t = -1189.6/T + 14.8$	0.9281	22.778	510–600
	$\ln \Delta t = -1137.7/T + 12.0$	0.9821	21.784	650–800

ordinates $\log \Delta t - 1/T$ for each thermal effect and used the slope of the linear relation $\log \Delta t - 1/T$ to calculate the values of E_{act} for the reactions corresponding to the peaks on the derivatograms.

Table 1 shows the results obtained by using the method of nonisothermal kinetics to determine the activation energy of reactions that occur during the heat treatment of fines of manganese ore from the Zapadnyi Kamys deposit and in charges employed in the production of silicomanganese. Analysis of the data in the table shows that the thermal processes take place at lower values of apparent activation energy.

Conclusions. The accuracy of the method used in this study and the reliability of the results obtained with it are confirmed by the results' agreement with the literature data for reactions involving the dissociation of oxides and hydroxides of manganese.

The slight disagreement between the values obtained for activation energy is due mainly to the effect of experimental factors on the process of thermal decomposition (factors such as heating rate, the size of the weighed sample, sensitivity in the differential thermocouple circuit, the shape and material of the crucible, the atmosphere of the working space of the furnace, the degree of abrasion of the specimen, etc.).

The data that were obtained served as the basis for the development and introduction of a new technology to obtain pellets from manganese ore at the Taraz Metallurgical Plant. Use of the pellets in a mixture with lump ore has made it possible to make standard ferrosilicomanganese in hermetic RKG-48 MVA ore-roasting furnaces with good performance indices.

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