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Nikolay Iloukha, Zoya Barsova, Irina Cwhanovskaya and Valentina Timofeeva

KINETIC INVESTIGATIONS OF PHASEFORMATION PROCESSES IN THE $BaO-Al_2O_3-Fe_2O_3$ SYSTEM

Ukrainian Engineering Pedagogic Academy
Department of Chemistry, Chemical and Food Technology

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Abstract. The kinetic investigations of phase formation processes in the mixture which contains BaO, Al_2O_3, Fe_2O_3 were carried out. The degree of conversion and the activation energy were calculated, the dependence of the reaction rate and the rate constant on reaction temperature was determined.

Keywords: activation energy, reaction rate, rate constant.

1. Introduction

The $BaO-Al_2O_3-Fe_2O_3$ system finds wide application for synthesis of composite materials with target noninflammable, electro-physical and magnetic properties which are used in industry and medicine. Therefore research of possible ways of compounds synthesis in this system and optimization of phase formation parameters in this system are very important. The research of phase formation processes in the $BaO-Al_2O_3-Fe_2O_3$ system, which take place at its synthesis from initial components allows to reveal technological parameters of products synthesis in this system. Therefore kinetic researches of the $BaO-Al_2O_3-Fe_2O_3$ system are very important and urgent.

At present time kinetic research of the whole $BaO-Al_2O_3-Fe_2O_3$ system is revealed in the literature in general [1]. But kinetic research of compounds formation in the $BaO-Al_2O_3-Fe_2O_3$ system has not been found.

The aim of the present paper is carrying out the kinetic research of phase formation processes in the $BaO-Al_2O_3-Fe_2O_3$ system, optimization of technological parameters of composite materials synthesis with magnetic properties.

2. Experimental

Raw mix produced from primary components such as $BaCO_3$, Al_2O_3, Fe_2O_3 (analytically pure) is taken in strict stoichiometric relation. Depending on the phase structure of the $BaO-Al_2O_3-Fe_2O_3$ system synthesis conditions have been set taking into account that final products must be $BaO{\cdot}6Fe_2O_3$ and the mixture of $BaO{\cdot}6Fe_2O_3$ (50 %) and $BaO{\cdot}Al_2O_3$ (50 %). Burning of samples was made in the temperature interval from 1173 to 1673 K with isothermal endurance of 30, 60, 90 and 180 minutes. In the clinkers received by ethyl-glycerate method [2] the content of a free barium oxide was detected. The presence of the free barium oxide in clinkers indicates that synthesis is not finished yet.

Variable factors of the experiment are the temperature and isothermal endurance at definite temperature.

Conversion degree (*G*) of substances was calculated by following formula:

$$G = \frac{BaO_{total} - BaO_{free}}{BaO_{total}} \cdot 100\%$$

The velocity of components interaction of mixes with BaO was calculated according to Ginstling – Brownstein equation:

$$I = 1 - 2/3G - (1 - G)^{2/3}$$

where *I* - reaction rate, *G* - degree of reagents conversion.

Numerical values of the reaction rate constant for each temperature have been obtained from the graph dependence of reaction rate on temperature and endurance time, and equaled to a slope tangent angle of a straight line to an abscises axis.

The rate constant of the reaction calculated according to Boltsman's law is expressed by the Arrhenius equation:

$$K = Ae^{-Q/RT}$$

where *A* – pre-exponential factor, *Q* – activation energy of a crystal lattice, kJ/mol, *R* - universal gas constant which is equal to 8.314·J/mol·K, *T* - temperature, K.

Having found the logarithm of this equation, we get

$$\lg K = b - \frac{a}{T}$$

where $a=\dfrac{Q}{2.303R}$, $b=\lg A$. From here $Q = a\cdot4.575$. From the graph $\lg K = f(t)$ a is found which is equal to the slope tangent angle of a straight line to an abscise axis and b which is equal to segment value cutting off by a straight line on an ordinate axis. For $BaO\cdot6Fe_2O_3$ $a = 2.50\cdot10^3$, and for the mixture of $BaO\cdot6Fe_2O_3$ and $BaO\cdot Al_2O_3$ $a = 2.67$.

3. Results and Discussion

We calculated the activation energy according to the above formulas. Activation energy Q is 11.44 kJ/mol for $Ba\cdot6Fe_2O_3$ and 12.20 kJ/mol for the mixture of $BaO\cdot6Fe_2O_3$ and $BaO\cdot Al_2O_3$.

Thus the rate constant of the reaction is expressed by the following formulas:

$$K = 3.16e^{\frac{-11.44}{RT}}$$

for $Ba\cdot6Fe_2O_3$, and for the mixture of $BaO\cdot6Fe_2O_3$ and $BaO\cdot Al_2O_3$

$$K = 2.51e^{\frac{-12.20}{RT}}$$

Graphic dependence of the conversion degree $G = f(t)$ and reaction rates $I = f(t)$ for each temperature and dependence of the decimal logarithm of the rate constant of the reaction $\lg = f(t)$ are given in Figs. 1-6.

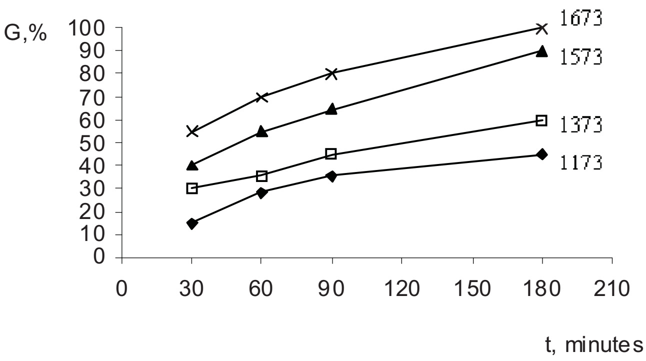

Fig. 1. The dependence of the conversion degree on temperature and endurance time for $Ba\cdot6Fe_2O_3$

Results of researches of solid-phase processes taking place in raw mixes which consist of iron oxide, barium carbonate and aluminium oxide; of iron oxide and barium carbonate in the temperature range from 1173 to 1673 K show, that interaction of barium oxide with iron oxide and aluminium oxide begins with a noticeable velocity already at 1173 K and finishes at 1673 K.

From obtained results we can conclude that BaO completely assimilates at the temperature of 1673 K and endurance time of 3 h both for $BaO\cdot6Fe_2O_3$ and for the mixture of $BaO\cdot6Fe_2O_3$ and $BaO\cdot Al_2O_3$. By this time 45, 60 and 90 wt % of BaO for $BaO\cdot6Fe_2O_3$ and 40, 50, 80 wt % of BaO for the mixture of $BaO\cdot6Fe_2O_3$ and $BaO\cdot Al_2O_3$ react at temperatures 1173, 1373, 1573 K accordingly.

For all temperatures the dependence $I = f(t)$ has a linear character. Since straight lines do not leave the origin of coordinates but cut off definite segments on an ordinate axis, it is possible to conclude that at the initial stage of the process proceeding the velocity is limited by a chemical reaction on the interphase (conversion degree < 0.1). Data linearization on the diffused equations testifies to the further transferring of the reaction in a diffusive mode. The velocity of the process is defined by the diffusive character only after formation of the continuous layer of solid-phase reaction products.

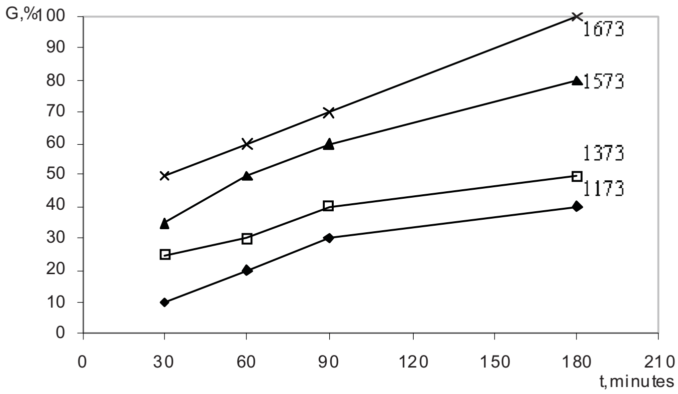

Fig. 2. The dependence of the conversion degree on temperature and endurance time for $Ba\cdot6Fe_2O_3$ and $BaO\cdot Al_2O_3$ mixture

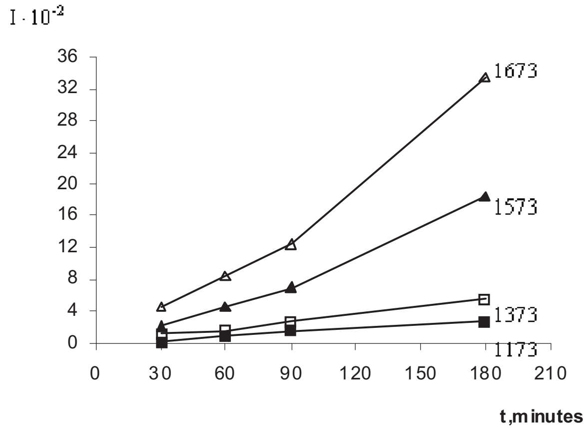

Fig. 3. The dependence of the reaction rate on temperature and endurance time for $BaO\cdot6Fe_2O_3$

4. Conclusions

Phase formation processes are carried out in investigated system due to the solid-phase reactions. Their velocity is satisfactorily described by Ginstling-Brownstein equation.

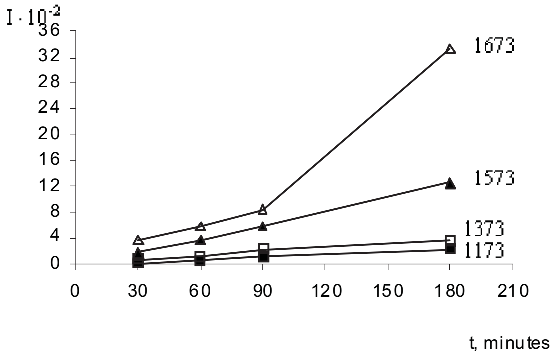

Fig. 4. The dependence of the reaction rate on temperature and endurance time for BaO·6Fe_2O_3 and BaO·Al_2O_3 mixture

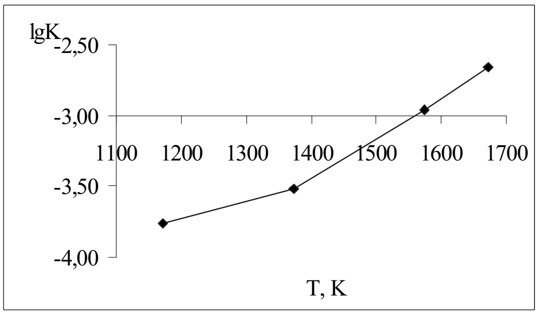

Fig. 5. The dependence of lg*K* on temperature for BaO·6Fe_2O_3

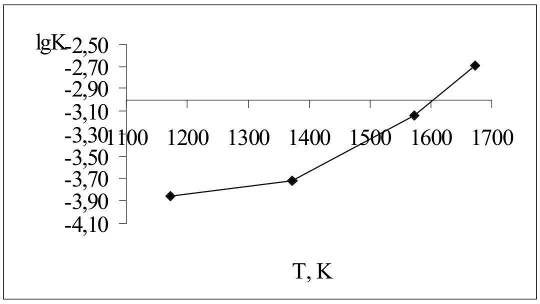

Fig. 6. The dependence of lg*K* on temperature for BaO·6Fe_2O_3 and BaO·Al_2O_3 mixture

Roentgenographic researches confirm the phase formation kinetics in the BaO-Al_2O_3-Fe_2O_3 system.

The carried out researches are important for creation new composite materials with the given magnetic properties. On the basis of kinetic researches composite materials with magnetic properties are obtained which are applied for creation ferromagnetic ceramic materials with high magnetic properties: Curie temperature equals to 560 K and coercetive force equals to 250 E.

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КІНЕТИЧНЕ ДОСЛІДЖЕННЯ ПРОЦЕСІВ ФАЗОУТВОРЕННЯ В СИСТЕМІ BaO-Al_2O_3-Fe_2O_3

Анотація. *Проведено кінетичні дослідження процесів фазоутворення у суміші, що містить BaO, Al_2O_3, Fe_2O_3. Розраховані значення ступеня перетворення, енергії активації, записані рівняння для константи швидкості реакції, отримані залежності швидкості реакції від температури.*

Ключові слова: *енергія активації, швидкість реакції, константа швидкості реакції.*