

TECHNOLOGICAL EVALUATION OF GRAPHITE AND ITS PROPERTIES

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ANNOTATION

The results of studies of the rate of oxidation of various carbonaceous materials are presented. The possibility of using modern instruments and research methods for the technological assessment of the quality of carbon materials is shown. In addition, detailed information on changes in the physical and chemical properties of carbon during and after the reaction is given. The appearance of reactions based on the oxidation state and oxidation rate of graphite is also a key element of this article.

Keywords: graphite, oxidation state, differential thermal analysis, kinetics, structure.

INTRODUCTION

One of the main trends in the modern market of refractories, both molded and unshaped, is the increase the role of carbon-containing refractories (from 3–5 to 95–98 wt %) [1–4]. This is due to a complex of unique properties of carbon - high refractoriness, thermal conductivity, electrical conductivity, chemical resistance to melts based on most metals, both in oxidized and reduced form, low thermal expansion coefficient, etc. At the same time, carbon in the form of crystalline graphite, carbon black and coke residue of organic binders is part of the refractory material matrix and performs functions as an inhibitor of chemical wear from melts, thermal cracking and bonding. Thus, the properties of carbon-containing refractories are largely determined by the properties of used the graphite. All the above methods for determining the kinetic parameters are based on the so-called isoconversion principle, which consists in the fact that the reaction rate at a constant degree of conversion α is only a function of temperature. These methods make it possible to find the activation energy E (or the dependence of E on α) without knowing the exact form of the dependence $f(\alpha)$. It is assumed that the kinetic parameters are not constant during the reaction. All isoconversion methods are based on determining the temperature corresponding to a certain, arbitrarily chosen value of the degree of conversion α , recorded in experiments carried out, for example, at various heating rates or temperatures.

FRIEDMAN'S DIFFERENTIAL METHOD

Based on the Arrhenius equation, Friedman proposed to apply the well-known expression used in solid-state kinetics, the logarithm of the conversion rate $d\alpha/d\tau$ as a function of the corresponding temperature at any degree of conversion α :

$$\frac{d\alpha}{d\tau} = A_{\alpha} \exp\left(-\frac{E}{RT_{\alpha}}\right) f(\alpha),$$

$$\ln\left(\frac{d\alpha}{d\tau}\right) = \ln\{A_{\alpha} f(\alpha)\} - \frac{E_{\alpha}}{R} \frac{1}{T_{\alpha}},$$

where τ is time; A_{α} is a pre-exponential factor; E is the activation energy; R is the universal gas constant; T_{α} is the thermodynamic temperature.

Since $f(\alpha)$ is a constant in the last term for any fixed value of α , the dependence of the logarithm of the conversion rate $d\alpha/d\tau$ on $1/T_{\alpha}$ is a straight line, the slope of which is $m = E_{\alpha}/R$, and the segment cut off by it on the y-axis is equal to $\ln\{A_{\alpha} f(\alpha)\}$. Thus, by determining m and $\{A_{\alpha} f(\alpha)\}$, one can predict the rate or estimate the activation energy of a reaction using the following expression:

$$\frac{d\alpha}{d\tau_{\alpha}} = \{A_{\alpha} f(\alpha)\} \exp\left(-\frac{E_{\alpha}}{RT_{\alpha}}\right).$$

COMPARISON OF ISOCONVERSION METHODS

A detailed analysis of the differential and integral isoconversion methods for determining the activation energy is given in the article [5]. The coincidence of activation energy values obtained by a differential method, such as the Friedman method, with the values obtained by integral methods when integrating in a small region of the degree of conversion α , follows from the principle of integral and differential calculations. In other words, it can be shown mathematically that the use of isoconversion integral methods can lead to systematic errors in determining activation energies. These errors depend directly on the size of the small conversion ranges $\Delta\alpha$ over which the integration is performed. These errors can be avoided by using an infinitely small range of the degree of conversion $\Delta\alpha$. As a result, the isoconversion integral methods again turn into the differential method previously proposed by Friedman.

The oxidation of carbonaceous materials with air can be described by several parallel reactions [7]:

- 1 $C + O_2 \rightarrow CO_2$,
- 2 $C + O_2 \rightarrow CO$,
- 3 $CO + O_2 \rightarrow CO_2$,
- 4 $CO_2 + C \rightarrow CO$,
- 5 $CO \rightarrow CO_2 + C$,

which can complicate the model and lead to significant errors in estimating the activation energy. But in laboratory experiments, it is possible to create conditions under which, with a high degree of probability, only one reaction 1 will proceed: this is a large excess of air (oxygen) and a high rate of removal of reaction products from the reaction zone. In a real situation of operation of carbon-containing refractories, such conditions are unlikely, but for the problem of comparing carbon-containing materials with each other, they are quite acceptable.

Under such test conditions and the accepted model of carbon oxidation, the chemical oxidation reaction can be described by a simple pair of parameters of the Arrhenius equation - the pre-exponential factor and the activation energy. Although it is possible that the rate of the carbon oxidation reaction will not be a constant value in each specific case, but will depend on the degree of conversion α , which characterizes the course of the reaction. Vyazovkin and Lesnikovich [6] draw attention to the fact that the kinetic parameters calculated from isothermal data are not very dependent on the chosen kinetic model, while the opposite is true for nonisothermal methods. They suggest that this is the reason for determining the kinetic parameters from isometric measurements and the kinetic model from non-isometric measurements. Data for kinetic analysis should be presented either as a set of dynamic measurements at various heating rates, or as a set of isothermal measurements taken at various temperatures. Of course, the programs are able to perform analysis on a data set consisting of both isothermal and dynamic measurements, which allows you to get more complete information about the kinetic system.

There are two different approaches to the kinetic analysis of thermoanalytical measurements of chemical processes:

- model-independent (non-a priori),
- model (based on kinetic models).

Model-independent analysis can only find activation energies for processes that do not contain parallel or competing steps, but it cannot answer questions about the number of steps, their contribution to the overall effect of the process, or the order of reaction for each step. Model analysis is based on the assumption of a kinetic model of the process, uses a powerful mathematical apparatus to solve the corresponding system of differential equations, performs a statistical comparison of the tested models and therefore can answer all of the above questions. Model-independent analysis includes methods that conduct calculations according to ASTM E698, analyzes according to Friedman and Ozawa.

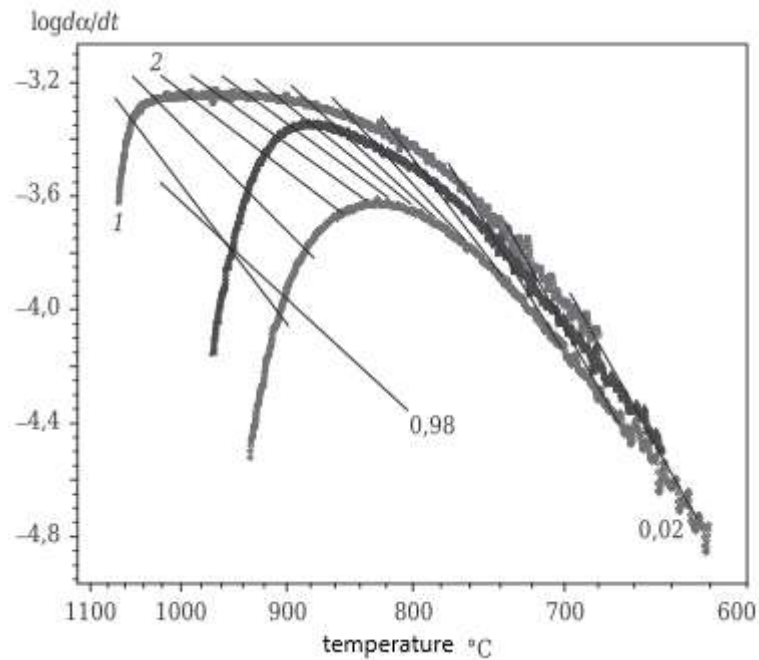


Figure. 1. Dependence of the oxidation rate (according to Friedman) graphite GL-1 on temperature: 1 —experimental curves of the rate of the oxidation reaction; 2 —lines of equal oxidation state (0.1–0.9 with a step of 0.1)

To determine the effect of the degree of crystallinity on the oxidation process, the parameters of the crystal lattice of the studied carbonaceous materials were determined. Shooting diffractometer with a rotating anode "MiniFlex 600" (Cu K α -radiation, $\lambda=1.541862 \text{ \AA}$, shooting interval 3.00–90.00 deg, scanning step 0.02 deg) from Rigaku-Carl Zeiss, Japan, with MiniFlex guidance control and data acquisition software and PDXL Basic data processing package. Diffraction peaks were identified using the JSPDS data bank. The average size of coherent scattering regions (CSR) L was estimated by X-ray method based on harmonic analysis of the profile of diffraction maxima, according to the Selyakov–Scherer formula [8]:

$$L = \frac{\lambda}{\beta \cdot \cos \theta},$$

where λ is the X-ray wavelength, nm; β is the physical broadening, rad.

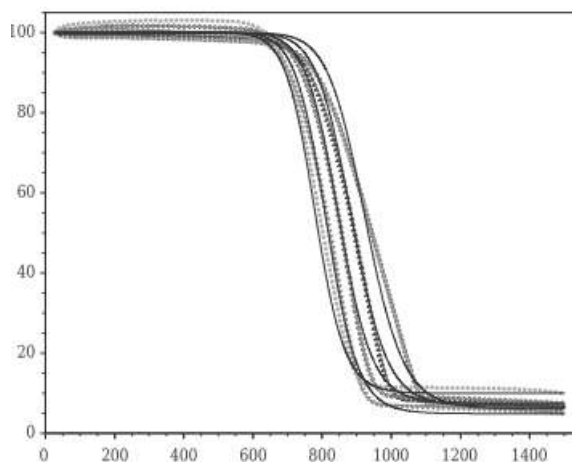


Figure. 2. Dependence of carbon mass loss on temperature by approximation functions on the example of graphite GL-1

CONCLUSION

The rate of oxidation of various carbon-containing materials has been estimated. It is shown that the physicochemical properties of carbonaceous materials and their structure affect the rate of oxidation. The possibility of using modern instruments and methods of conducting experiments for the technological assessment of the quality of carbonaceous materials is shown. The value of the carbon oxidation maximum depends on the effective collisions of gas molecules with the graphite surface; the structure of the surface layer (roughness) in this case contributes to an increase in the number of collisions of gas molecules with the surface. The carbon hexagonal network in graphite can be conditionally considered as a macromolecule [21], in which defects are concentrated at the edges of the network. The stacking density of individual grids is determined by the interplanar distance d , the value of which is 3.354 \AA .

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