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DEVELOPMENT OF THE CONDITIONAL ACTIVATION CRITERION TO EVALUATE GRAPHITE ACTIVITY

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ABSTRACT

This paper is aimed at developing an integrated criterion used to evaluate not only the quality of materials, but also the effect of the material preparation method on the activity of the particles. We studied cryptocrystalline graphite in natural and mechanically activated states from the Kureisckoe deposit. Graphite was activated in a planetary centrifugal mill at Mamina Laboratory of Disperse and Nanostructured, Solid, Viscous and Colloid Materials of Siberian Federal University. In the course of the studies, the authors proposed an empirical criterion based on differential scanning calorimetry to evaluate the energy saturation of filling components for non-stick coatings based on activated cryptocrystalline graphite — the conditional activation criterion. The calculated dependence of this criterion on the activation time proved data earlier obtained: the most optimum graphite activation time in the planetary centrifugal mill is 20 minutes.

Introduction

In view of current requirements for the quality of original molding materials, mixtures and coatings, we need a comprehensive analysis of their properties, including combined analysis techniques used to make a quantitative evaluation of transformations occurred when they are processed and activated at various large-scale levels.

At present, filling components for non-stick coatings may be materials, including cryptocrystalline graphite, in their natural [1, 2], beneficiated [3] or activated [4–6] states.

The quantity of energy "stored" by substances during its activation, namely an indicator of activity of material particles in chemical and physical and mechanical reactions, when manufacturing relevant products, depends on the nature and the rate of external effects during preliminary preparation and activation [7, 8].

At present, there are a lot of various criteria, which are, as a rule, aimed at solving bottleneck problems. When taking such approach, the activity coefficient of materials allows us to make an indicative evaluation, what fold increase we achieved in the quality of materials, exclusive of its energy state [9–13].

The Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) prepared recommendations on obtaining kinetic data which are relevant to actual kinetics of various processes, including thermal decomposition of inorganic solids; thermal and thermo-oxidative degradation of polymers and organic substances; reactions between solids and gases; polymerization and crossing; crystallization of polymers and inorganic substances; hazardous processes. The recommendations are focused on kinetic measurements performed using thermal analysis techniques, such as thermogravimetric analysis, differential scanning calorimetry (DSC) and differential thermal analysis. The objective of such recommendations is to help experts to collect accurate kinetic data by correctly selecting samples and measurement conditions [16–25]. Paper [24] showed that the thermal analysis opened up great opportunities to evaluate technological properties of natural and activated graphite.

This paper is aimed at developing an integrated criterion used to evaluate not only the quality of materials, but also the effect of the material preparation method on the activity of the particles.

Experimental technique

To make a qualitative evaluation of the energy saturation of products obtained after mechanical activation of natural cryptocrystalline graphite, we used results of differential scanning calorimetry (DSC). The thermal-oxidative degradation of graphite was performed in air, using thermal analyzer SDT Q600 in a dynamic mode in air at a heating rate of 10 °C/min up to 1000 °C. To analyze DSC curves, we applied currently available approaches: by initial melting temperature and by crossing of a line tangent to the measured curve and a basic line.

When performing the analysis, we determined the following parameters: ΔH, υ, calculated using Universal Analysis 2000 software, V. 4,5A, ΔE_a were calculated by the Arrhenius equation. ΔT_{ox} was calculated using thermocouple Pt/Pt-Rh (R type) installed in the device.

We studied cryptocrystalline graphite from the Kureisckoe deposit, containing a mineral constituent (ash content is up to 20–25 %), also undergoing changes during the activation process and contributing to the energy saturation of finished products [3–6].

Graphite was activated in the planetary centrifugal mill within 10–30 minutes.

Experimental results

As it is shown in [25], the thermal analysis may be used as an express method of the qualitative evaluation

of a state of mineral components. However, to characterize the energy saturation of materials with a complicated phase composition activated in processes of joint chemical and mechanical effect, as it is the case in cryptocrystalline graphite, getting reliable phenomenological models for real applications presents serious difficulty [26, 27]. Therefore, in this paper we propose a conditional integrated criterion, which was formed as a physically meaningless combination of thermochemical and kinetic values of the oxidation process of activated cryptocrystalline graphite.

The DSC curves activated within various periods are given in **Fig. 1–3**.

The analysis of the DSC curves for all the graphite under study within a temperature range of 0–100 °C showed that weight losses are attributed to moisture removal.

At 481 °C graphite GLS-2(K) began to oxidize, and the most intense oxidation is within a temperature range of 700 to 800 °C, which, probably, may be explained as follows: "free" graphite, i.e. the particles that are not related to impurity phases.

During the high-temperature calcination process a share of impurities is dissolved (pyrite is oxidized to iron oxide (III) in a range of 450–500 °C, calcite is dissolved to calcium oxide in a range of 800–1,000 °C, etc.), breaking locked particles and releasing graphite particles for its further oxidation.

In 10 minutes of graphite activation the DSC curve shows two expressed peaks. This may be explained as follows: graphite particles are broken according to the available defects; consequently, impurities are released from graphite locked particles. Thus, the first peak is related to oxidation of graphite itself, and the second peak — to oxidation of released impurities.

Graphite activation within 20 minutes results in a further division of peaks.

An increase in activation time till 30 minutes again will result in a "platform" on the DSC curve. The reason is that after 30 minutes of activation particles are aggregated preventing the oxidation of impurities.

One of core qualitative parameters of the reactive capacity of substances calculated by DSC is the energy of activation calculated by the Arrhenius equation. As according to the Arrhenius equation the chemical reaction rate constant is exponential on the value of activation energy, the decrease of the latter results in an increase in the graphite oxidation rate constant.

However, to evaluate an integrated state of the substance, we need a criterion, which may be considered as an aggregate qualitative thermodynamic characteristic.

Table. **Calculation of the conditional activation criterion**

Activation time, min	Thermodynamic parameters of graphite evaluated by the DSC curve						
	ΔH, kJ/g	υ, °C·min/mg	ΔT_{ox}, °C	Analysis by oxidation onset temperature		Analysis by the temperature resulted when crossing a line tangent to the measured curve and a basic line	
				ΔE_a, kJ/mol	K	ΔE_a, kJ/mol	K
GLS-2(K)	15.14	12.1	734	46.31	1.00	57.07	1.00
10	14.93	11.9	688	43.73	1.17	50.99	1.23
20	14.45	11.5	662	43.28	1.29	47.87	1.44
30	14.90	11.9	737	43.97	1.10	57.37	1.03

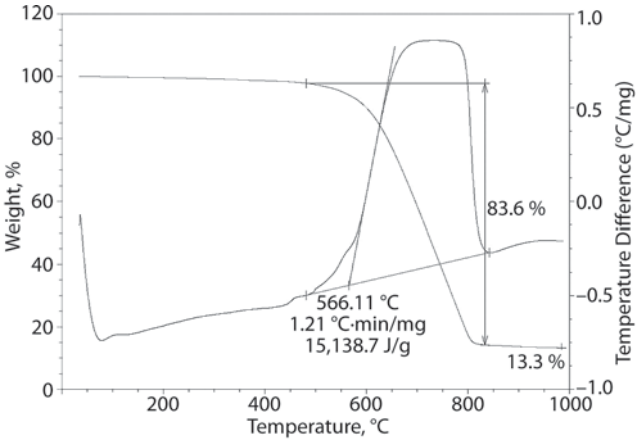

Fig. 1. DSC curve of natural graphite GLS-2 (K)

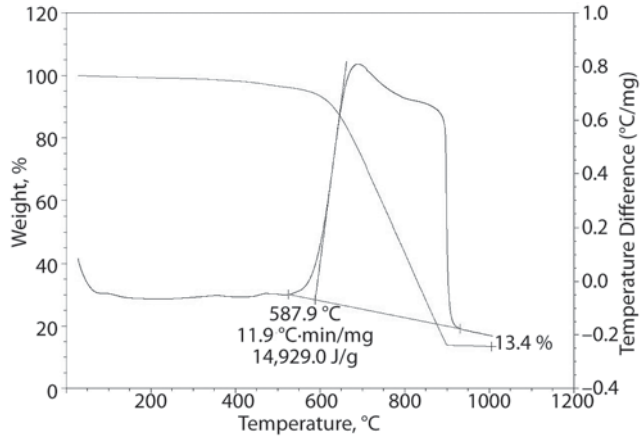

Fig. 2. DSC curve of graphite GLS-2(K) activated within 10 minutes

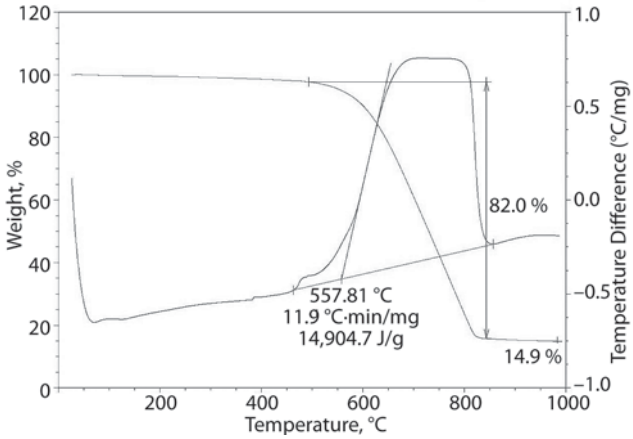

Fig. 3. DSC curve of graphite GLS-2A(K) activated within 30 minutes

Such criterion may be based on the conditional activation criterion, including main thermodynamic characteristics: activation energy of the graphite oxidation process calculated by the Arrhenius equation (ΔE_a); temperature of the maximum oxidation reaction rate, °C (ΔT); υ is a reduced area of the peak of the oxidation thermal effect, as well as a kinetic parameter — heat energy of a graphite oxidation process evaluated by an area of the curve peak (ΔH).

A conditional activation criterion may be calculated as follows:

$$K = k\frac{\Delta E_a}{\Delta E'_a} \cdot l\frac{\Delta H}{\Delta H'} \cdot m\frac{T_{ox}}{\Delta T'_{ox}} \cdot n\frac{\upsilon}{\upsilon'},$$

where ΔE_a, ΔH, ΔT_{ox} and υ are values of activation energy of the graphite oxidation process, heat of the graphite oxidation process, temperature of the maximum oxidation reaction rate and a reduced area of the peak of the oxidation thermal effect before the activation; $\Delta E'_a$, $\Delta H'$, $\Delta T'_{ox}$ and υ′ are values of the same parameters after the activation. As values of these parameters are unknown, in a first approximation they were taken to be equal to one.

This parameter is conditional and has no physical sense, but providing for the decrease in energy barriers, i.e. the rate of achieving the state, and changes in thermodynamic parameters of substances and kinetic characteristics in the activation process.

The dependence between the conditional activation criterion and activation time is given in the **Table**.

The above data show that when increasing activation time to 20 minutes, the conditional criterion increases, and further increase in activation time results in a decrease in such criterion, which is in good agreement with the data earlier obtained. The calculated conditional activation criterion is proved by the results earlier obtained and published in paper [28].

Conclusion

Thus, in the course of the studies the authors proposed an empirical criterion based on differential scanning calorimetry to evaluate the energy saturation of filling components for non-stick coatings based on activated cryptocrystalline graphite — the conditional activation criterion. The calculated dependence of this criterion on the activation time proved data earlier obtained: the most optimum graphite activation time in the planetary centrifugal mill is 20 minutes.

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