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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Wear Kinetics of High-Strength Activated Granulated Carbons Based on Peat

A. N. Khomutov, V. N. Klushin, and V. M. Mukhin

Mendeleev Russian University of Chemical Engineering, Moscow, Russia

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Abstract—The wear kinetics of activated carbons made of raw formulations based on peat with furfural and lignin additives was studied in comparison with the wear kinetics of the FAS-3 sample, a top-strength domestic activated carbon.

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The previously developed technology of preparation of high-strength activated carbons based on peat and having developed micropore structure [1] includes preparation of a viscous binder from thermoplastic polyester waste, mixing of a binder with peat, granulation of the obtained paste, carbonization of the prepared granulate, and activation of the carbonizate with stem.

The granulated activated carbons with a 30–40% combustion loss produced by this technology have more than 95% wear resistance. Their total porosity with respect to water is 0.6–0.8 $cm^3 g^{-1}$ and the volume of sorbing pores with respect to benzene, 0.4–0.6 $cm^3 g^{-1}$ [2]. The equilibrium capacity with respect to gold(I) ions in sorption of gold cyanides exceeds the corresponding parameter of domestic activated carbons AG-90 and AG-95 utilized in gold mining in Russia.

The wear resistance of activated carbons is the key parameter of their quality, necessary in gold mining applications, because it determines irreversible loss of the sorbent and the sorption loss of platinum group metals too. A number of methods is available for testing the wear resistance of activated carbons [3, 4]. Among them, the sorbent testing procedure MIS 60-8 is the most common method in Russia. This involves wearing of activated carbons in steel drums (80-mm diameter and length) with smooth inner surface, rotating at a rate of 75 rpm under the action of 1200-g wear rods. The method is based on a single measurement of the residue of coarse carbon fraction after three minutes of treatment [3]. From this result, only wear resistance may be estimated, whereas all complexity of the process cannot be judged.

First, a single test does not contain kinetic data on the sorbent failure. Second, the method is concerned solely with the effects exerted by mechanical loading, with other possible effects disregarded. Third, the effect of adsorption on the decrease of carbon strength is not taken into account.

The wearing, irrespective of the test method, causes failure of the surface layers of sorbent under the action of tangent stresses generated by friction forces between the sorbent granules and the grinding bodies. The main type of failure is wearing. The latter is characterized by the linear and energetic coefficients [$I_h = \Delta V/(A\Delta L)$ and $I_w = \Delta V/W$, respectively, where ΔV is the volume of a worn layer, A, the nominal surface area in contact, ΔL, friction path, and W is friction work].

First of all, the wear intensity is determined by the strength of a material and by tangent stresses, which are equal to a ratio of the friction force to the true surface in contact. The latter, in its turn, is determined by elastic properties of a material and by geometry of its surface profile [5]. The strength and elasticity of carbon materials essentially depend on the structure of their carbonaceous substance [6]. For example, the Van der Waals forces between parallel layers of graphite-like networks are low in comparison with the

C–C bond strength and the elasticity of carbon materials is the larger, the larger the sizes of the aromatic nuclear structure and cross-linking degree.

Increasing elasticity decreases the true surface in contact [5]. The latter, however, is mainly determined by the surface profile formed by open pores of a material. At multiple loading of the contact zones (friction surfaces), not only instant disruption of the intermolecular bonds but mainly fatigue phenomena are responsible for the failure of surface layers.

Sites at which the failure of solids is the most probable are cracks (in carbon, pores). Crack growth occurs in two stages. The first stage proceeds slowly and is the thermal-fluctuation process, whereas the second stage proceeds instantly and is the athermal process.

Thus, the effect exerted by the structure of activated carbon on its wear resistance is ambiguous. On the one side, the structure of carbonaceous substance determines the energy necessary for its failure as a continuous solid. On the other side, the true mechanical energy taken by such material is determined by the above structure and porosity of the material. From the above-said, it is extremely important to monitor (compare) not only the wear resistances of sorbents, as determined by the same method, but also the kinetic curves of wear recorded under the same loading conditions.

The worn granules of the sorbent consist of two fractions: fine (dust) fraction whose size is much lesser than that of granules was separated from their surface by friction, and coarse fraction, granules of the sorbent of decreased size. Depending on the character of wear loading, the gain in mass of fine fraction as a function of time can be expressed by the zero-, first-, or second-order equation of quasi-chemical reaction $dm/d\tau = m^n$, where $n = 0$; 1 or 2 [6]. In practice, the mass of fine fractions after the wear may be determined by sieving a test sorbent through meshes whose size is smaller than the minimal granule size of the sorbent but is larger than the maximal particle size of fine fraction. For worn carbons, the diameter of the sieve mesh is commonly 0.5–1 mm.

The developed method of preparation of activated carbons [1] allows in the stage of paste preparation to introduce various plasticizing (modifying) additives into the raw material. We used in this study furfural and lignin additives, which in a number of studies were used in preparation of activated carbons as modifiers of peat pastes [7–9].

Studying the effect of furfural and lignin additives introduced into the raw compositions at the stage of granulation on the structure and strength of activated carbons prepared by the above technology is of considerable interest. This is because the carbonization of these substances yields cokes with dense network structure, high strength, and developed microporosity [9–11].

This study is concerned with the wear kinetics of the carbonizates and activated carbons with a combustion loss of 30%, obtained from the raw pastes (formulations) with and without furfural and lignin additives introduced in amounts ensuring the maximal wear resistance of the given materials and of the FAS-3 activated carbon, the best domestic carbon adsorbent. Differences in the structures of a carbonaceous substance of the activated material, which, in our opinion, are responsible for different wear behavior of the samples under study, were also evaluated.

EXPERIMENTAL

Samples of carbonizates were prepared in the form of cylindrical granules with the cross-section diameter of 1 mm [1]. Steam activation was run at the consumption of 3g of steam per 1 g of carbon at 840°C in a stainless steel vertical reactor, placed into a SUOL-4 tubular furnace. The wear resistance was estimated according to the MIS 60-8 (sorbent testing procedure) in a rotating cylinder equipped with steel rods, with the treatment time not necessary constant.

Development of the pore structure was monitored by determining the total pore volumes with respect to water V_Σ and the volume of sorbing pores with respect to benzene V_s by standard procedures [3, 12]. The total content of ash A^s (%) was determined by calcin-ing carbon samples in air by the standard procedure [3]. Deashing was performed by treating carbon samples first, in HCL and then, in HF solution by the procedure proposed in [13]. The X-ray phase analysis was done at 25°C [PANalytical X'Pert PRO diffractometer, CuK_α radiation, 40 kV, 30 mA, Bragg angle 2θ = 1.01°–89.99°, scan rate 2/9 deg s^{-1}].

The results of the performed experiments were plotted in the form of graphs of the mass of the fine fraction formed in wear on the treatment time (Fig. 1).

Table 1. Kinetic equations for the dependence of the logarithm of the mass of fine carbon fraction on the wear time

Sample	Stage	Kinetic equation log *m*	Wear constant
Without additives:			
Carbonizate	1	0.08τ + 0.88	0.080
	2	0.018τ + 1.88	0.018
Activated carbon	1	0.083τ + 0.88	0.083
	2	0.02τ + 1.88	0.020
With furfural additive:			
Carbonizate	1	0.08τ + 0. 8	0.080
	2	0.01τ + 1.32	0.010
Activated carbon	1	0.079τ + 0.76	0.079
	2	0.007τ + 1.382	0.007
With lignin additive:			
Carbonizate	1	0.104τ + 1.98	0.104
	2	0.011τ + 3.0	0.011
Activated carbon	1	0.088τ + 2.31	0.088
	2	0.082τ + 3.31	0.082
Activated carbon FAC-3	1	0.075τ + 0.893	0.075
	2	0.013τ + 2.098	0.013

As seen, the wear is a two-stage process for all the samples studied. This indicates that the outer layers of the sorbent are less resistant than their central areas and subject to wear faster. This behavior is typical of a majority of the sorbents and catalysts [6].

Samples of carbonizates prepared from pastes containing varied additives have the high wear resistance, as estimated by MIS 60-8. As seen from Fig. 1, this value is higher than 90% for all the samples studied, which satisfies, in particular, to the gold mining requirements. Steam activation of the carbonizates differently affects their resistance. The carbonizate obtained from lignin-containing paste, like that obtained without additives, is more resistant than the products of its activation and the activated carbon obtained from furfural-containing paste, on the contrary, is more resistant than its carbonizate.

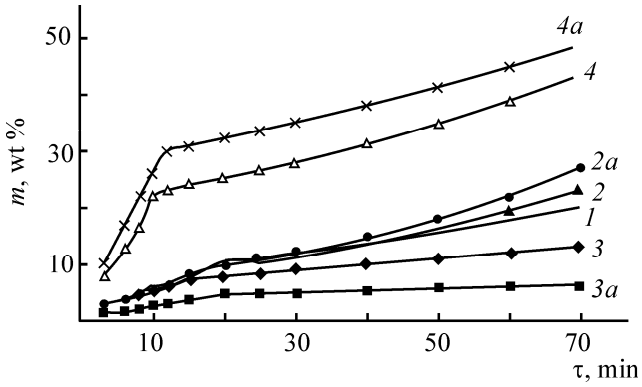

Fig. 1. The mass of fine fraction of carbons *m* vs. the time τ. (*1*) FAC-3; carbonizate and activated carbon: (*2, 2a*) without additives; (*3, 3a*) with furfural additive; (*4, 4a*) with lignin additive.

The amount of the worn carbon made of lignin-containing paste is 30% of the starting mass in the first stage and 45 % in the second stage. Consequently, this carbon cannot be used at prolonged mechanical loading. For carbon sample made of furfural-containing paste, this amount is minimal (4.5 and 5.5%, respectively). The times of the wear stages are different owing to the use of additives. For samples of activated carbons and carbonizate, obtained from paste containing lignin additive, the first wear stage is 15 and 10 min, respectively, for those made without additives, 15 min, for carbonizate obtained from furfural-containing paste, 15 min, and for activated carbon made of the same paste, 20 min (the same as for FAS-3 carbon).

From the established dependences of the percent amount of the coarse carbon fraction on the time of residence of the adsorbate in the drum, approximation equations for the first and second kinetic stages of wear were obtained (Table 1).

The data of Table 1 suggest the following conclusions: (1) activated carbons made from lignin-containing raw formulations have the lowest wear resistance, (2) for carbons under study, the kinetic constants of the first stage of wear differ slightly (0.07–0.1), whereas for the materials prepared from lignin-containing pastes, the time of the first wear stage is twice larger than for those prepared with furfural, (3) the constants of the second stage differ considerably owing to different types of the additives and activation of the material, (4) steam activation of carbons prepared from pastes with varied additives ambiguously affects the strength of target products, i.e., the strength of activated carbons prepared with and without lignin decreases in comparison with that of carbonizates, whereas the strength of activated carbon prepared with furfural additive, on the contrary, increases, (5) carbons prepared from pastes with furfural additive have the highest wear resistance in the second stage and surpass in this property commercial carbon FAC-3. Consequently, the introduction of furfural and lignin into the pastes based on thermoelastic polyester waste and peat essentially affects the wear kinetics of the products of their carbonization and activation.

The technical characteristics of the activated carbons under study cannot give unambiguous explanation for the wear behavior, because with decreasing porosity the carbon strength commonly increases [3, 4, 14], whereas for carbon prepared from lignin-containing paste it, on the contrary, decreases (see Table 2).

Anomalous behavior of the above carbon is accounted for by the structure of its carbonaceous material. The ash content in activated carbons made with and without additives differs slightly (see Table 2). At the same time, according to the X-ray phase analysis of the activated carbons with a 30% combustion loss, deashed by the method described in [13], the structures of activated carbons prepared with different additives are different.

Diffraction patterns of all the samples studied have peaks at 2θ = 24–26 and 2θ = 44–46°, corresponding to (002) and (10) reflections of the crystalline carbon in coals [14, 15] (Fig. 2). At the same time, the Warren's estimate of the height of carbon crystallites does not confirm presence of the above reflections for samples without additive and for those with furfural additive. This is because the number of carbon networks in them does not exceed two, which suggests the amorphous structure of carbonaceous substance. In our opinion, the narrow peaks corresponding to (002) and (10) reflections in the diffraction pattern of the activated carbon made of lignin-containing paste are due to microamounts of crystalline carbon.

Table 2. Technical characteristics of activated carbons

Sample	A^c, %	V_Σ, $cm^3\ g^{-1}$	V_s, $cm^3\ g^{-1}$
Without additive	7.30	0.60	0.40
With furfural additive	5.10	0.73	0.60
With lignin additive	6.00	0.30	0.11
FAS-3	0.01	0.80	0.79

Thus, a carbonaceous substance of the activated carbons made with and without furfural is amorphous, whereas that of the activated carbon made with lignin contains crystalline microinclusions, along with the amorphous phase. Any structural inhomogeneities in solid substances (cracks, pores, voids) and foreign impurities are sites at which the stresses in activated carbons concentrate and,

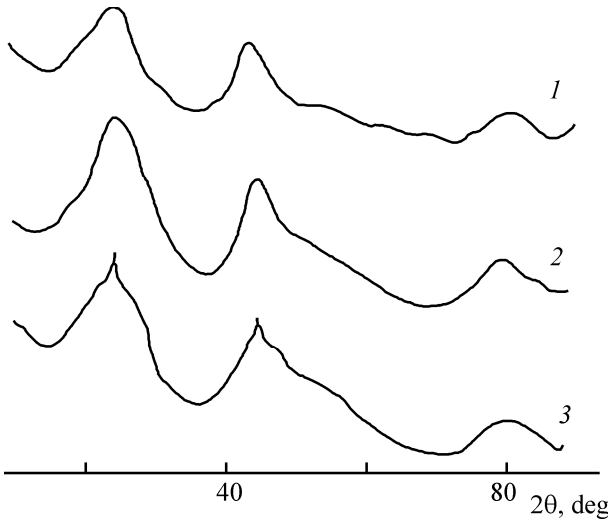

Fig. 2. Diffraction pattern of the activated carbon made from (*1*) pure, (*2*) furfural-containing, and (*3*) lignin-containing paste. (2θ) Bragg angle.

consequently, the failure is the most probable. In all probability, crystalline inclusions observed in carbon prepared with lignin are sites decreasing its strength.

CONCLUSIONS

(1) Modification of pastes with furfural allows fabrication of activated carbons, which are more kinetically stable and resistant to wear than FAC-3 carbon.

(2) The wearing of activated carbons during the first 79 minutes is typical of catalysts and sorbents and proceeds in two stages.

(3) For activated carbons under study, the kinetic constants of the first wear stages are nearly the same, whereas the time of these stages is different.

(4) For different samples, the wear constants of the second stages differ considerably. The highest values have samples prepared from pastes with lignin additive.

(5) The structure of the activated peat carbons under study is amorphous.

(6) The addition of lignin in the starting raw formulation decreases the strength of the final product owing to the formation of crystalline inclusions in the carbon structure.

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