THERMAL INVESTIGATION OF ACTIVE CARBONS IN PRESENCE OF AIR

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Thermal analysis data on the oxidation reaction between air and active carbons obtained during activation by carbon dioxide are presented. The correlation between the modified DTA curves and the TG curves leads to the conclusion that the oxidation of active carbons in the temperature range from 20 to 1000° is a two-step process. It is pointed out that the oxidation reactions in the low-temperature region (450—550°) are governed by the oxygen content of the samples, whereas the reactions in the higher temperature region (550—850°) are controlled by the diffusion process.

Differential thermal analysis and thermogravimetric analysis have been used in many laboratories for determination of the rate of coal oxidation. Several mechanisms relating to the oxidation reaction of carbons have been described in the literature [1−4]. The results presented in these papers show that the oxidation processes depend on many physicochemical properties of active carbons, e.g. degree of carbonization, degree of porosity and porosity spectrum. A very important conclusion from the literature data on differential thermal analysis and thermogravimetric analysis is that the character of the DTA and the TG curves depends on the degree of metamorphism of the carbons. Consequently, this feature makes it is very difficult to compare the results obtained for different types of carbons, e.g. brown coals, cokes and graphites [5, 6].

In this paper thermal data are presented on the oxidation reaction between air and active carbons obtained during activation by carbon dioxide. The modified DTA curves were used to explain the mechanism of the oxidation of active carbons.

Experimental

Active carbon (after activation by steam), produced by the Polish firm, ZEW Racibórz (the trade name of the product is Depolaryt D), was sieved and the fraction of particle size ranging from 75 to 250 μm in diameter was chosen. The active carbon was divided into five groups and activated in a stationary bed by carbon dioxide at different temperatures for 2 hours, as follows:

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sample A: not activated
sample A−6/2:   600°
sample A−7/2:   700°
sample A−9/2:   900°
sample A−10/2:   1000°

The physicochemical properties of the samples are listed in Table 1.

Table 1

Physical and chemical properties of the samples

Sample	Activation temperature, °C	Elementary analysis, %					Ash content, %	Moisture, %	Pores volume with radii cm³/g			Mercury porosity, cm³/g
		C	H	N	S	O diff			V_1 7.5—75 µm	V_2 75—750 µm	V_3 750—7500 µm	
A	—	92.14	0.90	0.90	0.50	5.56	7.92	8.37	0.019	0.032	0.047	0.098
A-6/2	600	91.00	0.94	1.00	0.53	6,53	7.91	2.77	0.020	0.031	0.054	0.105
A-7/2	700	92.62	0.83	0.96	0.60	4.99	7.94	3.23	0.014	0.026	0.049	0.089
A-9/2	900	91.70	0.85	1.00	0.51	2.94	8.66	4.37	0.014	0.030	0.028	0.072
A-10/2	1000	95.90	0.50	0.75	0.46	2.39	8.93	2.32	0.010	0.033	0.046	0.069

The mercury porosity and the volume distribution of the pores in the range from 7.5 to 7500 nm in radius were determined by means of a Carlo-Erba AG−65 mercury porosimeter. For the reasons considered earlier [7, 8], the investigated range of the pores was divided into three groups, involving the following pore radii:

$$7.5 \ nm \le r_1 < 75 \ nm$$
$$75 \ nm \le r_2 < 750 \ nm$$
$$750 \ nm \le r_3 < 7500 \ nm$$

Elemental analysis was performed with a Perkin–Elmer elemental analyzer model 240.

Before the measurements mentioned above, the samples were dried at 105°.

The thermal studies were performed with a MOM OD−102 derivatograph. Vessels consisting of five platinum plates were used for both the samples and a reference substance, which were uniformly distributed on each plate. This ensured a uniform supply of air to the sample particles. The experimental conditions of the analysis were as follows: reference substance: α-Al$_2$O$_3$; weight of sample: 500 mg; TG sensitivity: 500 mg; DTA sensitivity: 1/10; heating rate: 5°/min; T_{max}: 1000°; static atmosphere: air. The $\Delta T = 0$ curve was obtained when the holders for both sample and reference material contained α-Al$_2$O$_3$.

Results and discussion

The characters of the derivatographic curves of all of the studied samples are similar, which results from their high degree of carbonization. Figure 1 shows the representative DTA and TG curves. The exothermic peak associated with water evaporation was recorded in the DTA curves at 100°. This reaction is accom-
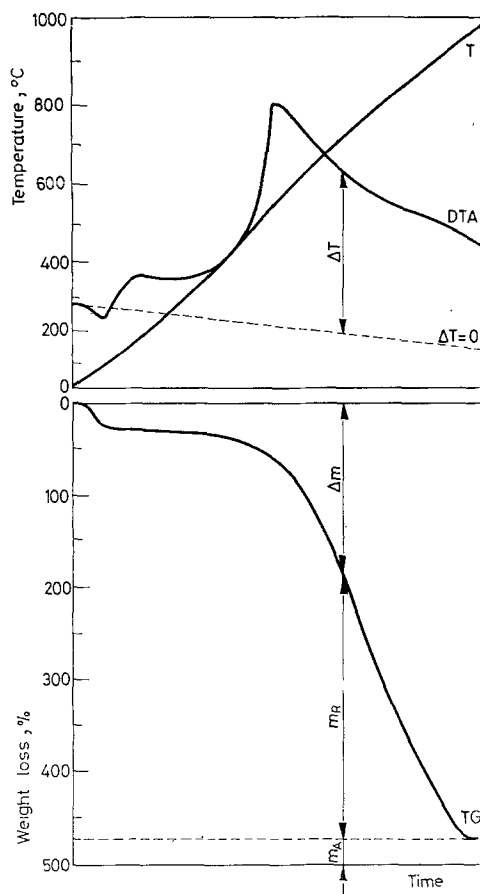

Fig. 1. TG and DTA curves of the sample A-7/2 as a representative of thermal curve

panied by a distinct weight loss in the TG curves. In the temperature range from 200 to 400° the DTA curves exhibit a broad exotherm of low height. In this range the weight loss in the TG curves is slight, too. Between 400 and 550° there is an inflexion in the TG curves. Simultaneously, a sharp exotherm is recorded in the DTA curves. The maximum of this exotherm lies at 550°. With further increase in temperature, the exotherm decreases, although the weight loss reflected in the

TG curves begins to occur very rapidly. The decrease of the exothermic effect at a temperature higher than 550° may be attributed to the rapid decrease in reactive mass of the oxidized carbon. The amount of ash within the samples becomes higher and higher. Because of this, for the interpretation of the mechanism of oxidation of active carbons it is more useful to take into consideration the changes of the parameter T/m_R as a function of temperature [9]. In Fig. 1 the following parameters are illustrated:

ΔT = difference in temperature between the sample and a reference substance;

m_R = mass of the sample reacting with air at the given temperature;

m_A = mass of ash remaining after complete combustion of the sample;

Δm = weight loss of the sample at the given temperature.

Accordingly, the mass of the sample taken for analysis is:

$$m = \Delta m + m_R + m_A$$

whereas $\Delta T/m_R$ denotes the temperature difference relating to the reacting mass of sample. Much interesting information was obtained from the correlation between the $\Delta T/m_R$ and the TG curves. Figure 2 shows that the parameter $\Delta T/m_R$ increases in the temperature range from 400 to 500° (region I). This region corresponds to an inflexion in the TG curve (Fig. 1). The $\Delta T/m_R$ curves (Fig. 2) exhibit an inflexion at a temperature of about 550°. It is accompanied by a rapid loss of weight, as indicated in the TG curves. At 550° the second region of these curves starts.
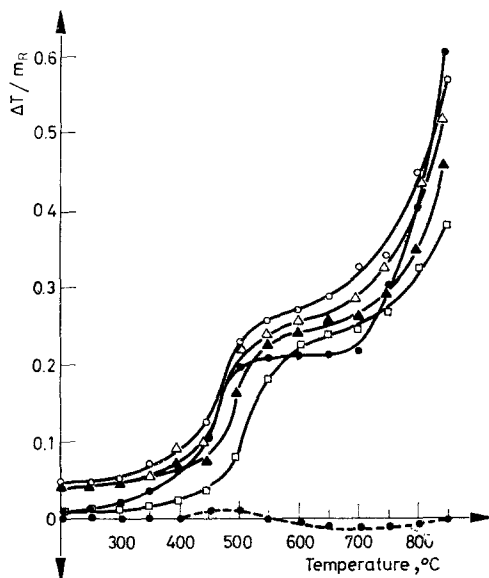

Fig. 2. The variation of the $\Delta T/m_R$ parameter with oxidation temperature: — ● — sample A; — ○ — sample A-6/2; — ▼ — sample A-7/2; — ▽ — sample A-9/2; — □ — sample A-10/2; ---●--- sample A-7/2 in argon

Initially, the rise of the curves is lower than in the first region. However, from 750° the $\Delta T/m_R$ curves increase very rapidly. These two regions correspond to different mechanisms of the oxidation reactions. At temperatures lower than 400° (200−400°) desorption of carbon oxygen complexes occurs simultaneously with chemisorption of oxygen by the carbon surface. However, when the temperature is raised the oxidation of the sample surface occurs more and more rapidly. Therefore, heat released by the reacting mass of carbon in region I is accompanied by a weight loss of the sample (Fig. 1). It was found that the weight loss increased in parallel with the increase of the oxygen content of the sample (Fig. 3). As things now stand, it may therefore be suggested that the weight loss is associated, among others, with desorption of oxygen from the sample surface in the form of carbon dioxide. Examination of the same samples in argon provided evidence confirming the above interpretation. In this case a small, but detectable weight loss in the temperature range 400 to 550° (region I) was also recorded [8]. However, in the considered region, a no less significant reason for the increase of $\Delta T/m_R$
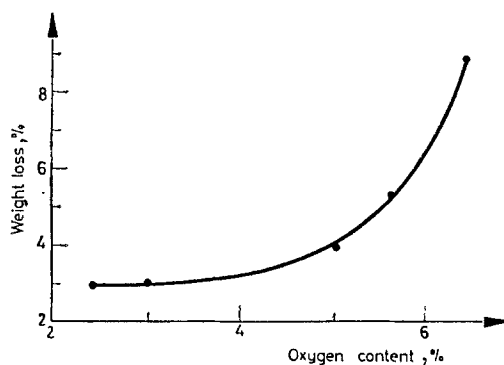

Fig. 3. The variation of the % weight loss on the oxygen content of the samples (in the temperature range 450−550°)

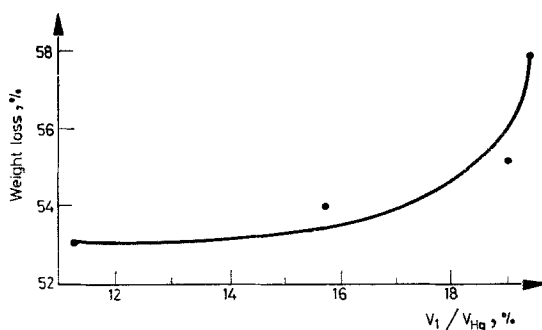
Fig. 4. The variation of the % weight loss on the ratio of the pores volume V_1/V_2 (in the temperature range 550−850°)

and the weight loss of the samples is the chemical reaction between the sample surface and air. At a temperature of about 550° the whole surface of carbon is already oxidized, while inside the carbon mass the endothermic pyrolysis process begins to occur more strongly. Hence, the penetration of oxygen into the carbon mass is restricted by desorption of the oxygen complexes (compare the $\Delta T/m_R$ curve for sample a − 7/2 pyrolyzed in argon, Fig. 2). Consequently, the quantity of escaping heat is decreased and the $\Delta T/m_R$ curves demonstrate the area of an inflexion and the flattened-out region. With further increase in temperature up to 550°, the rate of oxygen diffusion into small pores of the carbon particles increases. Hence, the oxidation processes occurring inside the pores cause a continuous rise of the $\Delta T/m_R$ curves (Fig. 2) and a continuous loss of the sample weight (Fig. 1). Since heat escapes least readily from the inside of the pores, this part rises rapidly in temperature, and internal combustion occurs. Figure 4 shows that the weight loss in the diffusion region of the reaction (550 to 850°) increases when the ratio of the pore volume in the range 7.5 to 75 μm in radius to total pore volume estimated by the mercury method also increases. The conclusion formulated in this paper, that the reaction occurring in region I is governed by the chemical reactivity of the sample, whereas the reaction occurring in region II is controlled by gaseous diffusion of oxygen into the carbon pores, is in agreement with the findings presented in the papers [10, 11].

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RÉSUMÉ — On présente les résultats de l'étude par analyse thermique de la réaction d'oxydation des charbons actifs par l'air qui a lieu lors de l'activation par l'anhydride carbonique. La corrélation entre les courbes ATD modifiées et les courbes TG conduit à la conclusion que l'oxydation des charbons actifs s'effectue entre 20 et 1000°, suivant un processus en deux étapes. Dans l'intervalle des températures faibles (450 à 550°) les réactions d'oxydation sont gouvernées par la teneur en oxygène des échantillons tandis qu'aux températures plus élevées (550 à 850°) elles le sont par le processus de diffusion.

ZUSAMMENFASSUNG — Die thermoanalytischen Ergebnisse über die während der Aktivierung durch Kohlendioxid stattfindende Oxidationsreaktion zwischen Luft und Aktivkohlen werden vorgestellt. Die Korrelation zwischen den modifizierten DTA-Kurven und den TG-Kurven führte zur Schlußfolgerung, daß die Oxidation der Aktivkohlen im Temperaturbereich von 20 bis 1000° ein Zweistufen-Vorgang ist. Es wird betont, daß die Oxidationsreaktion im niedrigen Temperaturbereich (450 bis 550°) durch den Sauerstoffgehalt der Proben gesteuert wird, während er im Bereich der höheren Temperaturen (550 bis 850°) durch Diffusionsvorgänge geregelt wird.

Резюме — Представлены данные термического анализа реакции окисления между воздухом и активным углем, получаемым во время процесса активации посредством двуокиси углерода. Корреляция между модифицированными кривыми ДТА и кривыми ТГ приводит к заключению, что окисление активных углеродов в области температур от 20 до 1000° является двухступенчатым процессом. Отмечено, что реакция окисления в низкотемпературной области (450—550°) зависит от содержания кислорода в образцах, в то время как в высокотемпературной области (550—850°) реакции определяются диффузионным процессом.