

INFLUENCE OF HIGH PRESSURE ON TEXTURE OF CARBONACEOUS SUBSTANCES

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The texture changes of carbonaceous substances caused by high pressure (1 500 MPa) have been studied by sorption of N₂ (at 78 K) and CO₂ (at 298 K) and by electron microscopy. The surface increase of cokes is observed in the region of micropores as well as meso- and macropores, whereas that of semicoke is only limited to the region of meso- and macropores. No effect is observed with formed coke and charcoal. Microscopically it has been found that cokes form a layer texture, whereas semicokes show a disconnection of microbreccia character. The surface area increase is ascribed to formation of new surfaces produced by shift and/or deformation of lamellar structures.

Action of pressure forces on coal and cokes causes changes of their internal surface. Pope and Gregg¹ applied a pressure of 420 MPa and found that according to butane isotherm at 273 K the surface area accessible to the adsorbate molecules was gradually decreased for low-rank coals and increased for high-rank coals. Walker and Radamass² submitted an anthracite sample to pressures of 500 and 4 000 MPa and determined its surface area by N₂ (at 78 K) and CO₂ (at 195 K) sorptions. The action of 500 MPa pressure did not change the original surface area values 32 m² g⁻¹ (according to the N₂ isotherm) and 210 m² g⁻¹ (CO₂ isotherm). The compression to 4 000 MPa increased the surface area to 52 m² g⁻¹ according to nitrogen isotherm, whereas the surface area given by CO₂ isotherm remained unchanged. Medek and Baxová³ investigated the influence of high pressure on change of surface of cokes using also CO₂ isotherm (for surface changes in micropore region) and N₂ isotherm (for meso- and macropore regions). The results showed that the changes caused by the pressure of 1 500 MPa are not unambiguous, the surface area increase (by the CO₂ isotherm) being only found with metallurgical cokes, whereas practically no change took place in the case of semicoke and formed coke.

As this ambiguity of high pressure effects on porous structure offers a possibility of broader interpretation, the present communication extends the studies to further samples of carbonization products and to application of electron microscopy to identification of the texture changes.

EXPERIMENTAL

Materials. Three samples of metallurgical coke, one sample of pitch coke, semicoke, formed coke, and charcoal were used. The metallurgical cokes (C1, C2, C3) were industrial products obtained from mixtures of low-volatile coal (35, 20, 20 wt%, resp.) and high-volatile coal (65, 80,

80 wt%, resp.), the final temperatures and coking times being respectively 1 220, 1 270, 1 230 K and 20, 17.5, 18 h. The semicoke (SC) was produced at 790 K from high-volatile coal with added coke dust and pitch. The formed coke (FC) was obtained from briquettes prepared⁴ from a mixture of 50% low-volatile coal and 50% high-volatile coal. The briquettes were cold pressed (59 MPa) and then carbonized in sand bath at 1 020 K for 1.5 h. The pitch coke (PC) was carbonized at 1 120 K and subsequently calcinated at 1 570 K. The charcoal (AC) was produced by carbonization of beech wood at 820 K and subsequent activation with water steam at 1 170 K. A fraction with 60% average burn-off was obtained by air separation. All the samples were ground to less than 0.1 mm grain size and dried to constant weight. Table I gives basic characteristics of the samples.

The pressure treatment was carried out in a steel block in which the powdered material was submitted to a pressure of 1 500 MPa for 15 min. Then the pressure was released and the sample was compressed again at the same pressure for further 15 min. This procedure was repeated three times with each sample. Emptying of the mould gave a compact of slight bond strength so that light grinding produced again a powder without any agglomerates. The compression is accompanied by partial spalling off of projections at the surface of grains, which results in increase of the finest grain fraction³.

Sorption was measured with a volumetric apparatus, CO₂ at 298 K within the absolute pressure interval 0.5 to 120 kPa and N₂ at 78 K within the relative pressure interval 0.05 to 0.35. The sorption time was limited uniformly to 30 min for all the points except for the pressure of 120 kPa, where it was prolonged to 60 min. According to a number of authors⁵⁻⁸ a considerable part of the surface of carbonaceous substances is presumed to be involved in micropores, and, therefore, the adsorption isotherm of CO₂ was interpreted by the potential theory using the Dubinin equation⁹

$$w = w_0 \exp(-A/E)^n, \quad (1)$$

where w and w_0 are the volumes of the adsorption space occupied at the equilibrium fugacity (f) and saturation fugacity (f_s), respectively, $A = RT \ln(f_s/f)$ is differential molar adsorption energy, and E means characteristic energy. Linearization of the isotherm in the coordinates

TABLE I

Basic characteristics of the samples

Sample ^a	Ash ^d wt%	C ^{daf} wt%	H ^{daf} wt%	VM ^{daf} wt%
Coke (C1)	12.8	96	0.6	1.5
Coke (C2)	9.3	98	0.2	0.7
Coke (C3)	9.9	97	0.4	1.2
Pitch coke (PC)	0.5	98	0.1	0.0
Formed coke (FC)	11.2	94	1.0	3.8
Semicoke (SC)	13.8	92	2.6	15.4
Charcoal (AC)	2.2	86	2.1	—

^a VM volatile matter, d dry, daf dry and ash free.

In $w_{DS} (\ln(f_s/f))^n$ and calculation of the optimum values n , w_0 and E were carried out with a computer. The pressures were transformed to fugacities by application of the Berthelot equation¹⁰. Structural characteristics of the micropores were evaluated by the mathematic relations¹¹ derived from the Dubinin equation and taking into account the mechanism of volume filling. Surface area of the micropores^{11,12} is

$$S_{\text{micro}} = 2w_0(E/k)^{1/2} \Gamma((3n + 1)/3n), \quad (2)$$

where Γ means the gamma function, and k is the so called interaction coefficient which has the value of $3 \cdot 145 \text{ kJ nm}^3 \text{ mol}^{-1}$ for CO_2 . The size of micropore is expressed by the equivalent radius (r_e) which is independent of geometrical shape of the pore. Distribution of the micropores according to the equivalent radii is given¹² by

$$dw/dr_e = 3nw_0(k/E)^n r_e^{-(3n+1)} \exp(-(k/E)^n r_e^{-3n}). \quad (3)$$

In contrast to the sorption of CO_2 , that of N_2 in the micropores is strongly limited by activated diffusion, and therefore nitrogen molecules can only penetrate in a slight part of micropores at 78 K, which can be seen in Fig. 1 giving the distribution curves obtained with semicoke. Hence it can be concluded that the surface area calculated from the N_2 isotherm by the standard method according to BET theory will correspond predominantly to the surfaces involved in pores, gaps and fissures wider than 3–5 nm.

The texture changes were followed by means of a scanning electron microscope JEOL JSM-U3 either with a dust specimen prepared from methanolic suspension and coated with C/Au or with a granular specimen prepared by polishing and coating with carbon. The image was formed by means of secondary emission electrons at 25 or 15 kV, respectively.

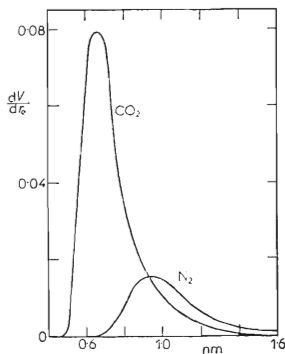


FIG. 1

Distribution of micropores in semicoke according to CO_2 isotherm at 298 K and according to N_2 isotherm at 78 K. The isotherms were measured within the pressure intervals from 0.5 to 120 kPa and evaluated by Eq. (3)

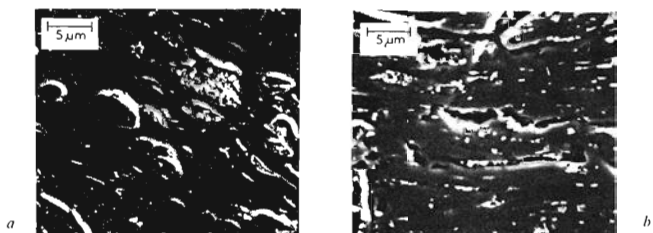


FIG. 2
Macroporous texture of C2 coke: *a* before compression, *b* after compression

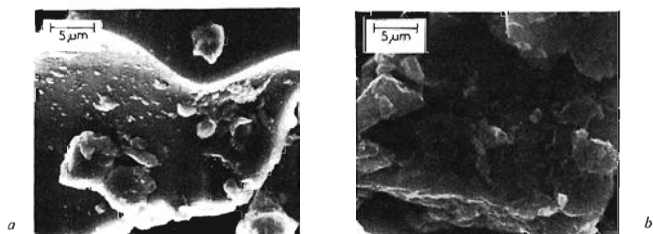


FIG. 3
Macrostructure change of C1 coke; *a* before compression, *b* after compression

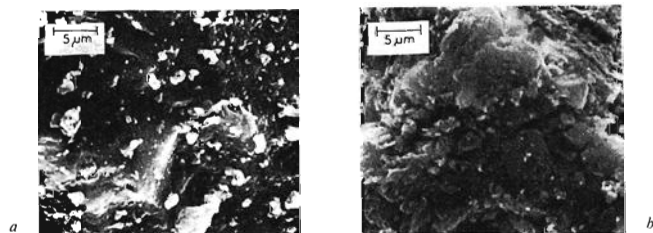


FIG. 4
Macrostructure change of semicoke (SC); *a* before compression, *b* after compression

RESULTS

The results of the sorption measurements are given in Table II. All the samples, except for charcoal, have a developed microporous structure with sieve effect, which is indicated by the $S_{\text{micro}}/S_{\text{BET}}$ ratio. The predominance of microporous structure is also indicated by the value of n exponent close to 2.00, which is presumed by the Dubinin characteristic of porous substances of the first structural type¹³. On the contrary, charcoal exhibits the $S_{\text{micro}}/S_{\text{BET}}$ ratio about 1 : 1 at $n = 1.5$, hence in this case the substance has no clear microporous structure exhibiting the sieve effect.

The samples submitted to the pressure effects show a proved surface area increase (both S_{micro} and S_{BET}) only in the case of cokes, ΔS_{micro} being always greater than ΔS_{BET} . In the case of semicoke, formed coke and charcoal the S_{micro} value remains unchanged, the S_{BET} value being only increased with semicoke (to an about four fold value) and remaining unchanged with the other two samples.

DISCUSSION

The surface area increase can hardly be ascribed to crushing and diminishing of grains during the compression, although the finer powder fractions are increased³. Table III gives an example of changes of grain size classes after compression of the coke C3 and semicoke which exhibit the greatest surface area increases. The change of grain size is accompanied mainly by increase of the external surface area which can be assessed *e.g.* from cubic or spherical model of the grain. If the edge length or diameter of such grain is expressed by the mean value \bar{a}_i of the class i , then relation between volume V^1 and surface S^1 of one grain is $S^1 = 6V^1/\bar{a}_i$. Volume of all grains in 1 g is $1/d$, that in the individual classes is $z_i/100d$, and the total geometrical surface area is

$$S_g = (6 \cdot 10^{-3}/d) \sum_{i=1}^n z_i/\bar{a}_i \quad [\text{m}^2 \text{g}^{-1}], \quad (4)$$

where d is density of the sample, and z_i is the mass proportion (%) in the class i . Within the assessment we can replace the apparent density by the real one (Table II). Comparison of the results given in Tables II and III leads to a conclusion that the calculated difference ΔS_g of the C3 coke is substantially smaller than the experimentally found ΔS_{BET} (0.14 and 4.3 $\text{m}^2 \text{g}^{-1}$, respectively), being even negligible in the case of the semicoke (0.15 and 32.4 $\text{m}^2 \text{g}^{-1}$, respectively). This discrepancy is not changed even if microroughness of surface were taken into account and the calculated values of surface areas were increased *e.g.* ten times.

Also problematic is the idea that the reason consists in opening of the closed pores, which should have made itself felt in the value of real density. If volume of a substance with closed pores is V_a , and its real density is $d_r = 1/V_a$, then opening of the

TABLE II

Texture characteristic of original and compressed samples

Sample	<i>n</i>	w_0 $\text{cm}^3 \text{g}^{-1}$	E kJ mol^{-1}	S_{micro} $\text{m}^2 \text{g}^{-1}$	S_{BET}^b $\text{m}^2 \text{g}^{-1}$	$\frac{S_{\text{micro}}}{S_{\text{BET}}}$	d_r^c g cm^{-3}	
C1	a ^a	2.15	0.0034	11.39	9.7	2.2	4.11	1.87
	b ^a	2.00	0.0054	10.96	15.4	4.5	3.42	1.86
C2	a	2.25	0.0031	12.25	9.1	2.9	3.14	1.92
	b	2.20	0.0043	11.89	12.5	4.9	2.55	1.93
C3	a	2.00	0.024	10.56	66	3.4	19.4	1.93
	b	2.05	0.030	11.08	85	7.7	11.0	1.92
PC	a	2.00	0.0023	12.71	6.8	1.0	6.80	1.98
	b	2.00	0.0025	12.25	7.3	1.1	6.63	1.98
FC	a	2.00	0.129	10.75	360	139	2.59	1.82
	b	2.05	0.130	11.16	370	133	2.78	1.84
SC	a	2.00	0.119	11.06	320	12.1	26.4	1.67
	b	2.00	0.111	11.18	310	44.5	6.7	1.69
AC	a	1.50	0.404	10.11	1 090 ^d	960	1.14	2.02
	b	1.50	0.401	10.64	1 100	940	1.17	2.07

^a a before compression, b after compression; ^b contact area $\sigma_{\text{N}_2} = 0.162 \text{ nm}^2$; ^c pycnometrically in methanol; ^d according to C_6H_6 isotherm at 298 K found $S_{\text{micro}} = 1 030 \text{ m}^2 \text{g}^{-1}$.

TABLE III

Grain size changes of cokes after compression

Size class μm	Mean grain size μm	Distribution in the size classes, z_i			
		C3 coke		semicoke (SC)	
		original %	compressed %	original %	compressed %
100—50	75	14	10	10	5
50—20	35	12	7	18	15
20—10	15	14	11	20	16
10—5	7.5	21	20	22	23
under 5	2.5	39	52	30	41
Geometrical surface area $S_g, \text{m}^2 \text{g}^{-1}$		0.62	0.76	0.61	0.76

pores will change this density to $d'_r = 1/(V_a - V_l)$, where the volume V_l of latent pores can be assessed from the relation

$$V_l = \bar{r}_e S_l / 2. \quad (5)$$

Here \bar{r}_e and S_l stand for mean equivalent radius and surface area of latent pores, respectively.

Assuming that the latent micropores are made accessible, it is possible to put $\bar{r}_e = 0.65$ nm and introduce ΔS_{micro} for S_l . Then the corrected densities d'_r of the cokes are: C1 – 1.88; C2 – 1.92; C3 – 1.95 g cm⁻³. If these values are compared with the experimental ones (Table II; the latter being determined with an accuracy of ± 0.01 g . cm⁻³), then it is obvious that in the region of micropores the opening of the latent cavities within the limits of ΔS_{micro} cannot be proved, because the density change lies within the limits of experimental error. If the latent cavities form meso- and macropores, then the ΔS_{BET} value and 20 nm are introduced for S_l and \bar{r}_e , respectively. In this way we get for the same cokes C1, C2, C3 the d'_r density values 1.95, 2.00, and 2.10 g cm⁻³, respectively; these values are far above the real ones. Therefore, this reason cannot be considered real, too, especially so if the density deviations increase with increasing \bar{r}_e .

The most probable reasons of the texture changes due to the high pressure effects can be derived from electron microscopy. Fig. 2a* shows porous structure of polished surface of the original C2 coke, Fig. 2b* shows its structure after compression and indicates that the action of pressure force causes collapse of the greatest macropores and formation of new fissures. The dispersed light spots are (according to Si distribution by the EDAX method) agglomerates of mineral components (ash matter). Fig. 3a* shows the original coke grain of about 0.1 nm size with several attached smaller grains and fine coke dust. The particle is limited by smooth surfaces, the newly formed surface shows a conchoidal fracture. Fig. 3b* shows a grain of about the same size after compression, the volume coherence of the grain being retained in spite of considerable crazing and zoning. Formation of layer texture and its flaky disintegration are obvious. Some what different pressure force effects are observed with semicoke, which can be seen in Figs 4a* and 4b* (the original and the compressed grains, respectively). In this case also the grain is disintegrated into very small particles (microbreccia character) which hold together after compression, the layered structure effect being, of course, not observed. With the formed coke and charcoal no changes in grain texture take place on compression, the grain size is reduced only.

The occurrence of layered texture in the compressed cokes is a statistically predominant phenomenon, because this texture can also be observed in the original samples (to a limited extent of course), especially so in small grains which is obviously due to mechanical strain during sample treatment (grinding). The same in the com-

* See insert on the page 32.

pressed samples: some particles remain intact, which can be explained by their favourable position in powder bed in which they were exposed to a lower (*e.g.* only lateral) pressure. This conclusion is also supported by the fact that the intact particles are mostly the smaller ones, whereas the larger ones exhibited the above-described changes. At the perpendicular direction to the lamellar structure this texture could not be proved either on external surface of grains or on polished sections, because the individual layers are so closely adjacent that the fissure width between them exceeds the limits of resolution power of the microscope.

From the results obtained the conclusion can be drawn that the surface area increase (according to both N_2 and CO_2 isotherms) is caused by formation of new surfaces. Metallurgical cokes produced from well-baking coals form, at temperatures above 773 K, a lamellar structure which can only be seen at very high magnification^{14,15}. The interlayer distances are about 0.35 nm (refs^{14,16}), which prevents penetration of the adsorbate molecules. If position of the lamellar system in the force field is favourable, compressive and shearing stress causes disintegration of layers (most probably near some structural defect) and their mutual shifting. Overcoming of interlayer cohesion bonds results in formation of a gap wide enough to enable sorption at the two newly formed surfaces. As the shifting of layers is accompanied obviously also by their deformation, gaps of various dimensions will be formed depending on extent of the deformation, their magnitude corresponding to micropores and, partially, to mesopores, which is indicated by the surface increase according to CO_2 and N_2 sorptions.

The semicoke, having no unambiguous layer arrangement, shows no interlayer shifts but their full disintegration at the sites of minimum cohesion energy. That is why no fissures of micropore magnitude are formed (no change in the surface area according to CO_2 sorption), and the surface area increase is only due to surfaces of the newly formed fissures whose dimensions are comparable with those of meso- and macropores.

No texture changes are observed with formed coke and charcoal. The formed coke produced at 1 000 K from a coal with lower coking properties has no or only very limited oriented arrangement, which is indicated by its vitreous character and considerable mechanical strength. Charcoal is utterly amorphous, its macroporous structure (enabling high compressibility) is not changed on compression. The both materials only show spalling off of projections at the surface of grains on application of high pressure.

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