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## THE INFLUENCE OF GRAPHITIZATION OF PETROLEUM COKES AND OF GRINDING ON THE SHAPE OF GRAPHITE CRYSTALLITES

UKD [661.666.2:665.63.092.89]:621.926.08:549.212.07

**Abstract:** The structural changes in three different petroleum cokes were examined taking place during heat treatment in the temperature range 1350—2800°C (graphitization). Moreover, the influence of mechanical grinding on the shape of artificial graphite crystallites was investigated. Three stages of growth of the dimensions of crystallites ( $L_a$ ,  $L_c$  and  $L_{112}$ ) were distinguished accompanied by decrease of  $p$  parameter during the graphitization process of petroleum cokes. The most important changes in the dimensions of graphite crystallites, taking place during grinding, occur in the initial 60 minutes of this process.

### INTRODUCTION

The aim of these investigations was to determine the structural changes (i.e. the changes in crystallite size and rearrangement of mutual ordering of adjacent layers in them) taking place during graphitization of three petroleum cokes in the temperature range 1350—2800°C. Moreover, it was intended to examine the destruction process of crystallites during grinding of artificial graphite in a mortar grinder.

Franklin (1951a) proposed a subdivision of high-carbonificated substances, generally called cokes, into soft carbons (graphitizing) — e.g. petroleum cokes — altering into graphite at temperatures above 2200°C, and hard carbons (non graphitizing).

Turbostratic structure of soft carbons is characterized by larger interplanar spacing (3.440 Å) when compared with that of graphite (3.354 Å), small sizes of ordered regions (crystallites) and by the occurrence of disordered phase of carbon atoms. When the heating temperature of soft carbons rises, the size of crystallites also increases whereas  $d_{002}$  spacing diminishes approaching the value characteristic of graphite.

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The examination was carried out in the Institute of Mineralogy and Mineral Deposits, Academy of Mining and Metallurgy in Cracow.

In crystallites consisting of parallel hexagonal carbon layers some part of them shows interplanar spacing 3.440 Å (the layers display mutual random displacement and rotation). The remaining part of layers exhibits interplanar spacing 3.354 Å and these layers are arranged exactly as in graphite. When defining  $p$  as the probability of regular orientation of adjacent layers, following relation between  $p$  and the measured  $d_{002}$  values was proposed by Bacon (1951):

$$d_{002} = 3.440 - 0.086(1-p) - 0.086p(1-p)$$

where  $p$  is called the Franklin's parameter.

The size of crystallites was calculated by means of Scherrer's formula:

$$L_{(hkl)} = \frac{k \cdot R \cdot \lambda}{\Delta B \cdot \cos \Theta_{o(hkl)}}$$

where:  $L_{(hkl)}$  — size of crystallite as measured perpendicularly to the  $hkl$  plane,

$\lambda$  — X-ray radiation wave length,

$R$  — distance between sample and counter in the goniometer,

$\Theta_{o(hkl)}$  — diffraction angle measured for the centre of a band,

$\Delta B = B - B_o$  — difference of half breadths of bands of the standard ( $B_o$ ) and examined substance ( $B$ ).

The value of  $k$  coefficient for the diameter of crystallites ( $L_a$ ) depends on the degree of graphitization of the sample and is determined by the formula proposed by Hirai (1969):

$$k = 0.9 + (1.84 - 0.9)p$$

In the case of the height of crystallites ( $L_c$ ) the value of  $k$  does not depend on the degree of graphitization of a sample and amounts to 0.94. As follows from investigations of Franklin (1951b), Akamatsu et al. (1956), Kuroda (1959), Inagaki and Noda (1962), Fialkow (1965) and others, the petroleum cokes graphitize easily and their behaviour during this process depends on the properties of source material from which they were produced and on the method of their preparation.

Bacon (1957) observed a decrease of crystallite size and Walker and Seeley (1957) a lowering of intensity of diffraction lines during grinding of graphite. In Bailey's opinion (*vide* Walker and Seeley 1957) during the early stage of grinding of natural Ceylon graphite we observe considerable decrease of  $L_a$  and less pronounced changes of  $L_c$ . During longer grinding  $L_a$  varies but slightly, whereas the  $L_c$  value decreases uniformly.

## EXPERIMENTAL CONDITIONS

Graphitization of petroleum cokes was carried out at 1350, 1500, 1650 and 1800°C in the Taman furnace, 12 kVA in power. Nitrogen was passed through the heater tube of the furnace containing crucibles. Graphitiza-

tion of cokes at temperatures 1950, 2200 and 2400°C was carried out in the induction furnace. Crucibles containing coke samples were placed in a large graphite heating crucible filled with powdered graphite. Since there was no possibility of applying protective atmosphere, the crucibles were covered with graphite plates which eliminated the contact of air with coke samples. During all these experiments the time of keeping the cokes at highest temperatures was approximately 20 minutes. The temperature was measured by means of optic pyrometer. At the temperature of 2800°C the cokes were graphitized in the industrial Acheson furnace.

Graphite was grinded in an agate mortar grinder Pulverisette 2. Artificial graphite was preliminarily disintegrated up to the grain size 2—3 mm. Sample were taken from the grinder after 15, 30, 90, 180, 300, 420, 540, 680, and 1000 minutes from the beginning of this process.

Table 1

Measured X-ray reflections of graphites, cokes and tungsten

Sample	Measured reflections	
	Graphite (hkl)	Tungsten (hkl)
Graphites, petroleum cokes at 2200°C, 2400°C, 2800°C	112	
	110	211
	004	200
Petroleum cokes at 1950°C	112	
	110	211
	004	200
	100	110
Petroleum cokes and other below 1950°C	004	200
	100	110

Diffraction measurements were carried out using TUR M-61 X-ray diffractometer (GDR) and  $\text{CuK}_\alpha$  radiation. Basing on diffractometric data half-peak breadths, total and relative intensities of reflections and interplanar spacings  $d_{004} = 1/2 d_{002}$  were measured and are detailed in Table 1. Tungsten standard, approximately 1 micron in grain size, was used.

## RESULTS

### STRUCTURAL CHANGES OF PETROLEUM COKES DURING GRAPHITIZATION PROCESS

The results of measurements of crystallite size and of the values of  $d_{002}$  for several soft coals heated to 1200°C as well as for artificial and

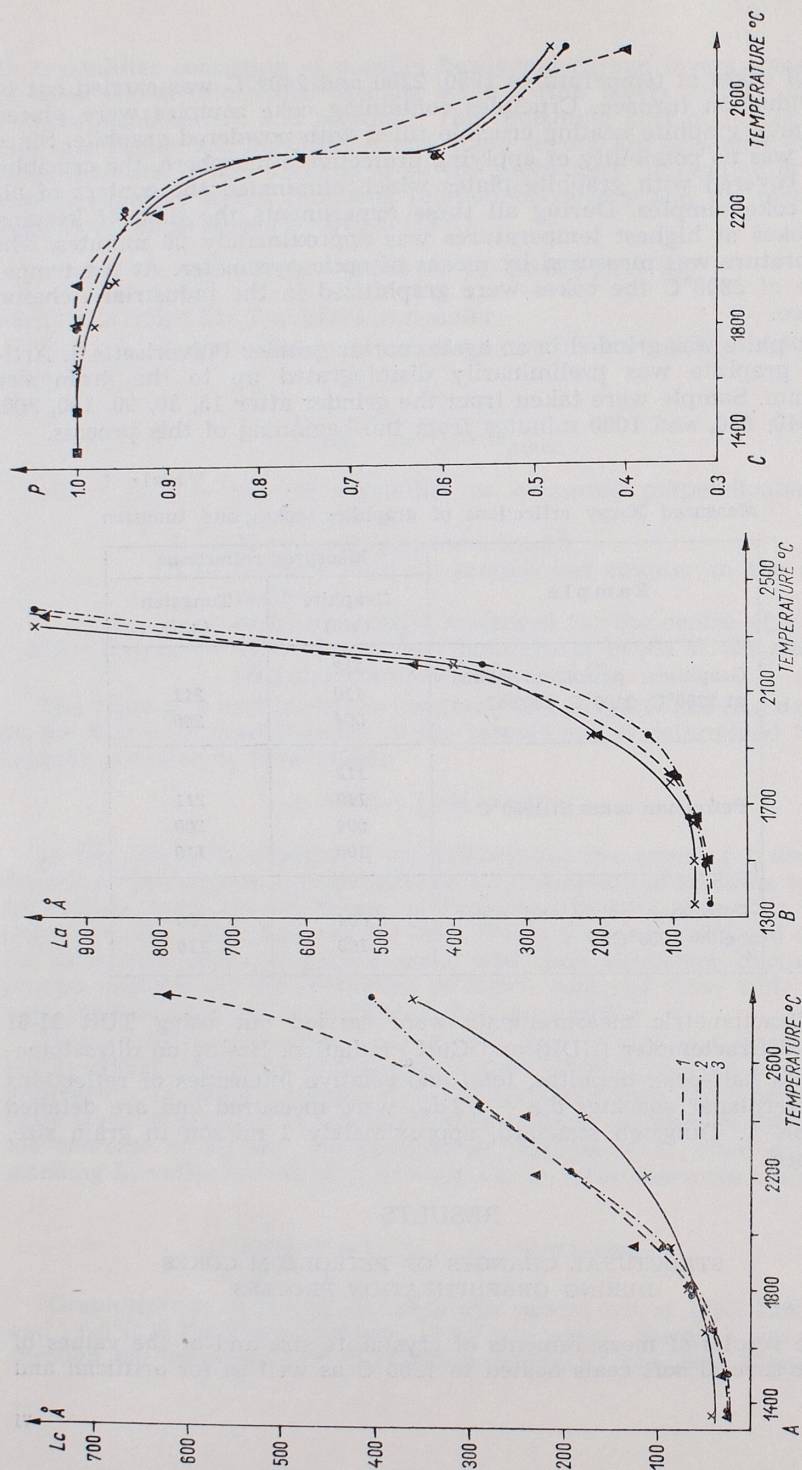


Fig. 1. Changes of crystallite sizes and of  $p$  parameters during heating of petroleum cokes A, B and C  
 A — changes of crystallite height  $L_c$ ; B — changes of crystallite diameter  $L_a$ ; C — changes of Franklin's  $p$  parameter; 1 — coke A, 2 — coke B, 3 — coke C

natural graphites are presented in Table 2. As follows from these data, the size of crystallites of soft coals formed under these conditions are small when compared with those of graphite. The crystallites of petroleum cokes are generally similar in size. Anthracite crystallites display the smallest height and the largest diameter, being thus the most platy in habit.

Table 2  
 A comparison of crystallite size and interplanar spacings  $d_{002}$  in selected soft coals and graphites

Coals and graphites	$L_c$	$L_a$	$L_{112}$	$d_{002}$
Ceylon nat. graphite	2200.0	$> 10^4$	2120.0	3.354
Artificial graphite	914.0	$> 10^4$	360.0	3.372
Petroleum coke A *	24.0	70.1	0	3.440
Petroleum coke B*	26.0	54.1	0	3.440
Petroleum coke C*	40.1	68.7	0	3.440
Pitch coke *	18.4	57.0	0	3.440
Anthracite *	12.7	73.4	0	3.440

\* Calculated at 1200°C.

The changes of crystallite sizes and of  $p$  parameter taking place during graphitization process of petroleum cokes A, B, and C are presented in Fig. 1 and Table 3. Petroleum cokes were obtained from raw materials of various properties and different geological origin. Moreover, they were produced by means of various technological processes. Coke A was obtained by cracking whereas those B and C were produced by hampered coking. Coke C contains more sulphur when compared with cokes A and B (3.7 and 0.5 wt. per cent respectively).

Basing on the results of these experiments following stages of graphitization process can be distinguished:

- Stage I — structural changes in the range 1350—1700°C
- Stage II — structural changes in the range 1700—2400°C
- Stage III — structural changes in the range 2400—2800°C

The most important data concerning the changes in size of  $L_a$ ,  $L_c$ ,  $L_{112}$  and  $p$  taking place during the above distinguished graphitization stages are presented in Table 4.

At temperatures above 2200°C the diameter of crystallites increases considerably exceeding the value measurable on the ground of reflections broadening ( $L_a > 3000$  Å).

The appearance of the 112 reflection on diffractometer patterns indicates that the layers in crystallites display already mutual ordering i.e. the individual layers are stacked as in the graphite structure. As follows from these results (Tab. 4), the process of spatial ordering starts already

Table 3

Interdependence of crystallite size  $L_{112}$  and heating temperature of petroleum cokes

Temperature, °C	Coke A	Coke B	Coke C
	Å		
1950	0	0	45.6
2200	28.5	36.8	75.2
2400	71.7	74.6	107.1
2800	338.0	297.0	378.2

between 1700 and 1950°C for coke C whereas for cokes A and B it occurs at more elevated temperatures (1950—2200°C).

Measurements have shown that the crystallites of coke C display the largest diameter when compared with those of other cokes.

#### INFLUENCE OF GRINDING TIME ON THE SHAPE OF GRAPHITE CRYSTALLITES

The results of measurements of structural parameters of artificial graphite ground in an agate mortar grinder are presented in Fig. 2 a—c.

Basing on Fig. 2a, illustrating the influence of grinding time ( $t_g$ ) on  $L_c$  and  $L_{112}$ , we may conclude that there exist some stages in the change of crystallite shape. The corresponding variation curve can be subdivided into three parts. Considerable decrease of crystallite height (by approximately 300 Å) is observed during the initial 60 minutes. Further decrease of  $L_c$  (by 320 Å) takes place during the next 200 minutes whereas only slight changes of this parameter were observed if grinding was still continued.

Similarly the essential changes of  $L_{112}$  take place during the initial 60 minutes whereas beginning from 180 min. the decrease of this parameter is slow and linear.

The diameter of crystallites cannot be measured using the applied method because of its very high value ( $L_a > 3000$  Å). Only after  $t_g = 1000$  min.  $L_a$  decreases down to a measurable value (1018 Å). Nevertheless, judging from the variation curves of  $L_{112}$  and  $L_c$ , we may conclude on the character of changes of  $L_a$ . The changes of  $L_{112}$  are the resultant of those of the height and diameter of crystallites. The largest changes of  $L_c$  and  $L_{112}$  take place during the initial 60 minutes, whereby the

slope of the corresponding curves is not constant. In the range of  $t_g$  between 60 and 230 minutes, the difference of slope is approximately constant but with more prolonged grinding  $L_c$  nearly does not change whereas  $L_{112}$  displays further (linear) variation. It is thus concluded that the changes of  $L_a$  are linear in character for the applied grinding times except of the initial 60 minutes.

This conclusion is confirmed by the results presented in Fig. 2 b and 2 c. The variations of total intensity of 110 reflection as well as of relative one are linear except of initial 60 minutes. The character of changes of both total and relative intensities of 112, 110 and 004 reflections confirms the above conclusions deduced from the analysis of changes of  $L_c$  and  $L_{112}$ .

The changes of total intensity ratio of 112 and 110 reflections are presented in Fig. 2b. This ratio is very sensible to structural changes taking place during grinding (Fialkow 1965). The curve illustrating the variation of the ratio  $I_{112} : I_{110}$  with grinding time ( $t_g$ ) displays a characteristic change of slope, confirming the conclusion concerning the change of shape of graphite crystallites during grinding. These changes, however, are not a simple functions of grinding time.

The variation of  $d_{002}$  with grinding time were shown to be irregular and negligible. Maximal mean deviation of results (mean value of  $d_{002} = 3.372$  Å) amounts to  $\pm 4\%$  when accepting as 100% the difference between  $d_{002}$  of turbostratic structure and the value of this parameter of natural Ceylon graphite.

#### CONCLUSIONS

In the graphitization process of petroleum cokes three stages can be distinguished differing in the rate of variation of crystallite size and of  $p$  parameter.

Stage I (temperature range 1350—1700°C) is characterized by very slow increase of crystallite size displaying turbostratic structures. During the stage II (temperature range 1700—2400°C) there begins the process of spatial ordering, starting at lowest temperature in coke C. Consequently, during this stage we observe considerable decrease of the fraction  $p$  of disordered layers (particularly in cokes B and C at temperatures 2250—2350°C). In the temperature range 2400—2800°C (stage III) further decrease of  $p$  parameter (being the largest in coke A) is accompanied by considerable increase of crystallite height (the largest in coke A) and of their diameter (the largest in coke C).

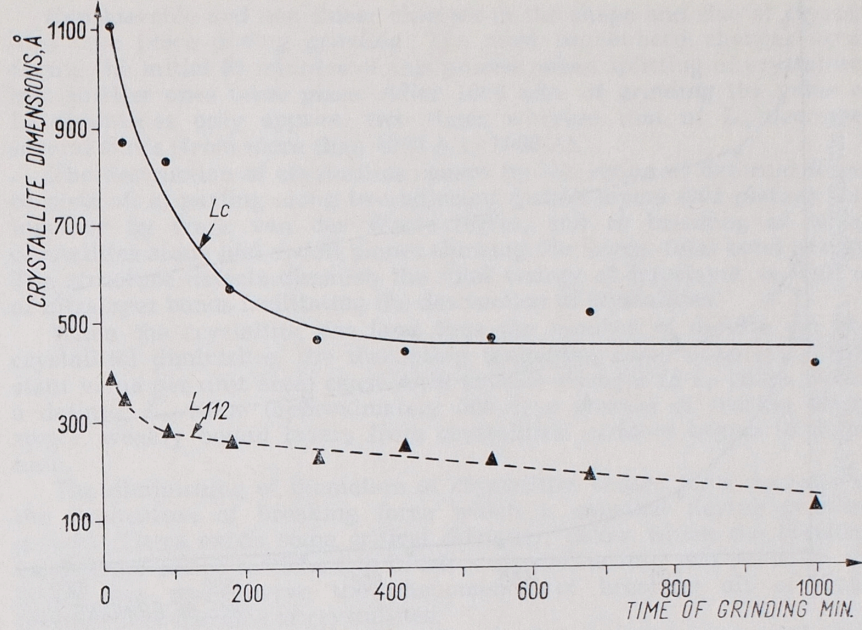
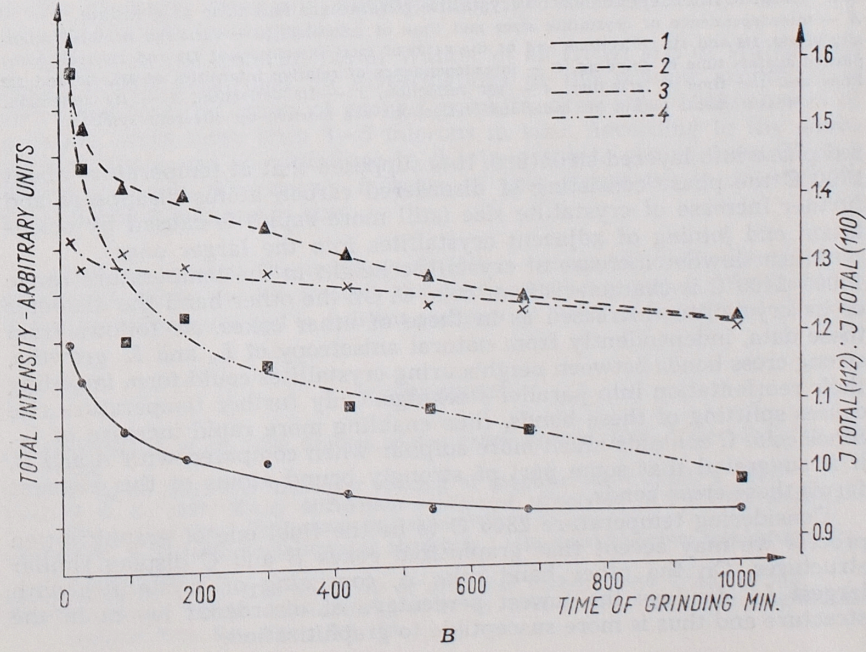
Heating of cokes at temperatures up to 2800°C resulted in a distinct change of crystallite shape. There developed a flaky structure of crystallites, being most pronounced in those of coke C where the increase of diameter was considerably greater than that of the height.

Distinct change in the shape of  $L_a$  curve at temperature approx. 1700°C indicates that the increase of diameter of crystallites at temperatures below 1700°C is caused by other processes than at higher temperatures. In the temperature range below 1700°C (very slow increase of  $L_a$ ) there dominates a process of entering carbon atoms from disorde-

Table 4

Observed changes of crystallite sizes in terms of  $L_c$ ,  $L_a$  and  $L_{112}$  and of  $p$  parameter in individual stages of graphitization of petroleum cokes A, B and C

Temperature range °C	Observed changes				$p$
	$L_c$	$L_a$	$L_{112}$	$p$	
1350—1700	A	increase by 18 Å	no 112 reflection on diffractometer pattern	$p = 1$	most pronounced decrease in the range from 2250 to 2350°C
	B	increase by 35 Å	appearing of 112 reflection at temp. approx. 2200°C	$p < 1$ above 1950°C	
	C	increase by 8 Å	appearing of the reflection at 1950°C	$p < 1$ at temp. 1800°C $p < 1$ at temp. 1700°C	
1700—2400	A	nearly identical increase up to 280 Å at 2400°C	considerable increase from approx. 90 Å at temp. 1700°C up to 3000 Å at temp. 2200°C	increase by 265 Å	linear decrease up to the lowest $p$ value = 0.4 at temp. 2800°C $p = 0.47$ at temp. 2800°C $p = 0.485$ at temp. 2800°C
	B	less pronounced increase up to approximately 180 Å at 2400°C		increase by 225 Å	
	C	$L_c$ increases more than two times i.e. up to 620 Å at 2800°C	No data	increase by 280 Å	
2400—2800	A	less pronounced increase up to 410 Å at 2800°C			no further decrease of $p$
	B	$L_c$ increases two times up to 360 Å at 2800°C			
	C				



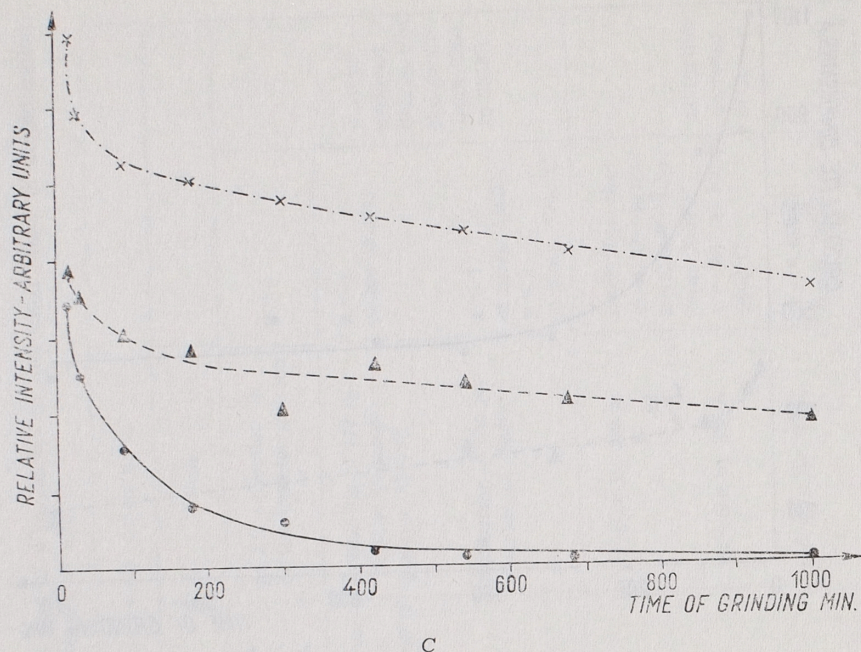


Fig. 2. Interdependence of crystallite parameters and time of grinding  
 A — interdependence of crystallite sizes and time of grinding, B — variation of total intensity of 004, 110 and 112 reflections and of the ratio of total intensities of 112 and 110 reflections plotted against time of grinding, C — interdependence of relative intensities of 004, 110 and 112 lines and the time of grinding; 1 — 004 reflection, 2 — 112 reflection, 3 — 110 reflection. Measurements points for individual reflections are marked by different symbols

red phase into layered structure. It is supposed that at temperature about 1700°C the phase consisting of disordered carbon atoms disappears and further increase of crystallite size (still more rapid) is caused by orientation and joining of adjacent crystallites into the larger ones.

Much slower increase of crystallite height in the temperature range 1700—2400°C is characteristic of coke C. On the other hand the diameter of its crystallites increased as in those of other cokes. As follows from these data, independently from natural anisotropy of  $L_a$  and  $L_c$  growths, strong cross bonds between neighbouring crystallites could form impeding their reorientation into parallel stackings. Only further temperature rise causes splitting of these bonds, thus enabling more rapid increase of  $L_c$ . Since coke C contains much more sulphur when compared with A and B, it is suggested that some part of strongly bound atoms of this element forms these cross bonds.

Considering temperature 2800°C to be the final one of graphitization process we may accept that graphitized cokes B and C display similar structures. On the other hand coke A, consisting of crystallites with largest  $L_c$ , displays the lowest percentage of disordered layers in the structure and thus is more susceptible to graphitization.

Considerable and non-linear changes in the shape and size of crystallites take place during grinding. The most pronounced changes occur during the initial 60 minutes of this process when splitting of crystallites into smaller ones takes place. After 1000 min. of grinding the value of  $L_c$  diminishes only approx. two times whereas that of  $L_a$  decreases several times (from more than 4000 Å to 1000 Å).

The destruction of crystallites caused by the action of external forces consists of: a) parting along two adjacent carbon layers (001 planes) held together by weak van der Waals forces, and b) breaking of whole crystallites along  $hk0$  or  $hkl$  planes showing the lowest total bond energy. The structure defects diminish the total energy of interlayer as well as of intralayer bonds facilitating the destruction of crystallites.

When the crystallite size (and thus the number of defects per one crystallite) diminishes, the disrupting tangential force (displaying constant value per unit area) causes still smaller changes in  $L_c$  value. Below a definite  $L_c$  value (approximately 500 Å) a process of tearing off of single, weakly bound layers from crystallites surfaces begins to dominate.

The diminishing of diameters of crystallites causes some decrease of the momentum of breaking force which is constant during grinding process. There exists some critical diameter, below which the breaking momentum is not sufficient to break a crystallite into two parts. In the latter case we observe the phenomenon of breaking off of small fragments of margins of crystallites.

It should be also taken into account that crystallites are packed in grains of larger sizes and microporosity of the latter influences the process of their disintegration.

Basing on the experiments of Walker et al. (1954) and of Walker and Seeley (1957) confirmed by investigations of the present author, it is concluded that the grains of ground graphite, even after 1000 minutes of grinding, were more than 3—5 microns in size. According to the above authors, there are no variations in  $d_{002}$  in graphite grains from 75 to 5 microns in size, whereas an increase of this parameter is observed in those below 3 microns in size.

*Acknowledgements:* The author would like to express his gratitude to assistant professor J. Kubisz for his constant help and valuable suggestions and discussion during the experiments and to assistant professor W. Żabiński for editorial remarks.

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## WPLYW GRAFITYZACJI KOKSÓW NAFTOWYCH ORAZ EFEKTU MIELENIA NA KSZTAŁT KRYSZTAŁITÓW GRAFITU

### Streszczenie

Badania autora miały na celu określenie zmian struktury trzech różnych koksów naftowych, które zachodzą w czasie ich ogrzewania w temperaturach 1350—2800°C, oraz poznanie wpływu mielenia mechanicznego na strukturę grafitu sztucznego.

Grafityzację koksów naftowych wykonano w piecu Tamana (temperatury 1350, 1500, 1650, 1800°C), w piecu indukcyjnym (1950, 2200, 2400°C) oraz w piecu Achesona (2800°C). Mielenie grafitu wykonano w agatowym młynku moździerzowym, a pomiary dyfraktometryczne na dyfraktometrze TuR M-61.

Wykonano pomiary wysokości ( $L_c$ ), średnicy ( $L_a$ ) kryształitów, wymiaru  $L_{112}$  kryształitów oraz parametru  $p$  dla grafitowanych koksów A, B, C. Na podstawie przedstawionych wyników (fig. 1, tab. 3 i 4) w procesie grafityzacji koksów naftowych wyodrębniono trzy etapy różniące się szybkością zmian wymiarów kryształitów i parametru  $p$ . Etap I (zakres temperatur 1350—1700°C) charakteryzuje się bardzo wolnym wzrostem wielkości kryształitów o turbostratycznej budowie. W etapie II (zakres temperatur 1700—2400°C) rozpoczęty zostaje proces uporządkowania przestrzennego, następuje więc duży spadek ułamka warstw nieorientowanych (parametru  $p$ ). W etapie III (zakres temperatur 2400—2800°C) wraz z dalszym spadkiem wartości  $p$  obserwuje się znaczny wzrost wymiarów kryształitów.

Uważając temperaturę 2800°C za końcową prowadzonego procesu grafityzacji można przyjąć, że zgrafitowane koksy B i C mają zbliżoną do siebie strukturę, natomiast koks A charakteryzuje się lepszą zdolnością do grafityzacji.

Wyraźna zmiana kształtu krzywej  $L_a$  w temperaturze ok. 1700°C wskazuje, że wzrost średnicy kryształitów przy temperaturze do 1700°C spowodowany jest głównie przez proces przyłączania pojedynczych atomów z fazy nieuporządkowanej, natomiast w temperaturach wyższych wzrost  $L_a$  spowodowany jest łączeniem się sąsiednich kryształitów w jeden o znacznie większej średnicy.

Wolniejszy wzrost  $L_c$  dla kryształitów koks C przy zakresie temperatur 1700—2400°C wydaje się być spowodowany istnieniem silnych wiązań poprzecznych uniemożliwiających ustawianie się kryształitów w równoległe stopy.

Z pomiarów  $L_c$  i  $L_{112}$  oraz intensywności refleksów badanych (fig. 2) wyciągnięto wniosek o dużych zmianach kształtu kryształitów zachodzących w czasie mielenia grafitu. Największe zmiany w wymiarach kryształitów następują w początkowych 60 minutach mielenia, kiedy to zachodzi proces rozszczepiania kryształitów na kilka o mniejszych wymiarach. Przy dalszym mieleniu zmiany wymiarów są coraz wolniejsze. Zaobserwowano ponad 2-krotny spadek wartości  $L_c$  i kilkakrotny spadek wartości  $L_a$  po mieleniu grafitu przez 1000 min.

Rozrywanie i łamanie kryształitów spowodowane jest działaniem siły zewnętrznej. Rozrywanie i łamanie nastąpi wzdłuż płaszczyzn i linii o najmniejszej sumarycznej energii wiązań.

Mniejsze zmiany  $L_a$  przy czasach mielenia większych od 60 min. można wytłumaczyć działaniem na kryształit o coraz mniejszej średnicy zmniejszającego się momentu łamiącego siły. Przy zmniejszaniu się wymiarów kryształitów działająca styczna siła rozrywająca powoduje coraz mniejsze zmiany  $L_c$ . Przy wartości  $L_c$  równej ok. 500 Å dominuje już proces odrywania pojedynczych, słabo związanych warstw na powierzchni kryształitów.

Z porównania wyników pomiaru  $d_{002}$  z danymi literaturowymi wynika, że ziarna grafitu po mieleniu przez 1000 min. mają średnicę większą od 3—5  $\mu$ .

### OBJAŚNIENIA FIGUR

Fig. 1. Zmiany wymiarów kryształitów i parametru  $p$  podczas procesu ogrzewania koksów naftowych A, B, C  
A — zmiany wysokości kryształitów  $L_c$ , B — zmiany średnicy kryształitów  $L_a$ , C — zmiany parametru  $p$  Franklin; 1 — koks A, 2 — koks B, 3 — koks C

Fig. 2. Zależność parametrów kryształitów od czasu mielenia  
A — zależność wymiarów kryształitów od czasu mielenia, B — zależność całkowitej intensywności refleksów 004, 110, 112 oraz stosunki intensywności całkowitych linii 112 do linii 110 od czasu mielenia, C — zależność względnej intensywności linii 004, 110, 112 od czasu mielenia; 1 — refleks 004, 2 — refleks 112, 3 — refleks 110. Punkty pomiarowe dla poszczególnych refleksów oznaczone są różnymi znakami

Кишиштоф П. ПАВЛОВСКИ

## ВЛИЯНИЕ ГРАФИТИЗАЦИИ НЕФТЯНЫХ КОКСОВ И ИЗМЕЛЬЧЕНИЯ НА ФОРМУ КРИСТАЛЛИТОВ ГРАФИТА

### Резюме

Целью исследований автора было определение изменений структуры трех видов нефтяных коксов во время прокаливания при температурах 1350—2800°C и изучение воздействия механического измельчения на структуру синтетического графита.

Графитизация нефтяных коксов производилась в печи Тамана (температуры 1350, 1500, 1650, 1800°C), в индукционной печи (1950, 2200, 2400°C) и в печи Ачесона (2800°C). Измельчение графита производилось в агатовой ступке, а дифрактометрические анализы осуществлялись на дифрактометре ТУР М-61.

Производились замеры высоты ( $L_c$ ), диаметра ( $L_a$ ) и размера  $L_{112}$  кристаллитов, в также параметра  $p$  графитизированных коксов А, В, С. На основании полученных данных (фиг. 1, табл. 3 и 4) в процессе графитизации нефтяных коксов отмечены три этапа, характеризующиеся различной скоростью изменений размеров кристаллитов и параметра  $p$ . Этап I (температурный интервал 1350—1700°C) характеризуется очень медленным ростом величины кристаллитов турбоэпитаксиального строения. Во II этапе (температурный интервал 1700—2400°C) начинается процесс пространственной упорядоченности и значительно уменьшается количество неориентированных слоев (параметр  $p$ ). Этап III (температурный интервал 2400—2800°C) характеризуется дальнейшим снижением величины  $p$  и значительным ростом размеров кристаллитов.

Принимая температуру 2800°C в качестве конечной температуры процесса графитизации можно заключить, что графитизированные коксы В и С обладают сходными структурами, а кокс А характеризуется лучшей способностью графитизации.

Отчетливое изменение формы кривой  $L_a$  в температуре около 1700° показывает, что увеличение диаметра кристаллитов при этой температуре вызвано, главным образом, процессом присоединения отдельных атомов из неупорядоченной фазы, а при более высокой температуре увеличение  $L_a$  обусловлено соединением смежных кристаллитов в один кристаллит большого диаметра.

Более медленный рост  $L_c$  кристаллитов кокса С в температурном интервале 1700—2400° вызван, как кажется, более сильными поперечными связями, препятствующими образованию параллельных пачек.

Замеры  $L_c$  и  $L_{112}$ , а также интенсивности рефлексов (фиг. 2) приводят к выводу о значительных изменениях формы кристаллитов в процессе измельчения графита. Наибольшее изменение размеров кристаллитов отмечается в течение начальных 60 минут измельчения. В это время происходит расщепление кристаллитов на более мелкие части. При дальнейшем измельчении изменение размеров происходит все медленнее. Отмечено более чем двухкратное снижение  $L_c$  и многократное снижение  $L_a$  после 1000 минут измельчения графита.

Разрывы и переломы кристаллитов под воздействием внешней силы происходит вдоль плоскостей и линий наименьшей суммарной энергии связей.

Меньшее изменение  $L_a$  после 60 минут измельчения можно объяснить уменьшением ломающего момента силы, действующей на кристаллиты все меньшего диаметра. При уменьшении размеров кристаллитов касательная разрывная сила вызывает все меньшие изменения  $L_c$ . При  $L_c$  равной около 500 Å преобладает уже процесс отрыва отдельных, слабо связанных слоев на поверхности кристаллитов.

Сопоставление данных замера  $d_{002}$  с данными, известными из литературы, следует, что зерна графита после измельчения в течение 1000 минут имеют диаметр больше 3—5 микронов.

Фиг. 1. Изменение размеров кристаллитов и параметра  $p$  в процессе прокалывания нефтяных коксов А, В, С

А — изменение высоты кристаллитов  $L_c$ , В — изменение диаметра кристаллитов  $L_a$ , С — изменение параметра  $p$ ; 1 — кокс А, 2 — кокс В, 3 — кокс С

Фиг. 2. Зависимость параметров кристаллитов от времени измельчения

А — зависимость размеров кристаллитов от времени измельчения, В — зависимость полной интенсивности рефлексов 004, 110, 112 и отношения полной интенсивности линии 112 к линии 110 от времени измельчения, С — зависимость относительной интенсивности линий 004, 110, 112 от времени измельчения; 1 — рефлекс 004, 2 — рефлекс 112, 3 — рефлекс 110. Точки измерений в отдельных рефлексах обозначены разными знаками