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Modification of Native Graphite from Russian and Ukrainian Deposits by Intercalation and Flash-Pyrolysis

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Abstract

The investigation of obtaining thermoexpanded graphite from native graphite samples of four deposits in Russia and Ukraine involving various procedures of intercalation and pyrolysis is described. It is established that the most promising raw material for the production is graphite from Zavalye (Ukraine) and Kyshtym (Russia). Intercalation of these samples with chloric, nitric, acetic acids and chromic anhydride followed by thermal treatment in the steady mode allows obtaining carbon materials with the bulk density about 1 kg/m^3. It is demonstrated that pyrolysis of the same intercalated samples in a flow reactor results in obtaining carbon materials with substantially smaller specific volume, but they possess a number of technological advantages in comparison with those obtained under steady conditions.

INTRODUCTION

Intercalation of native graphite followed by pyrolysis is widely used at present for the production of carbon materials with unique properties for increasing applications in industry and in household activities. High elasticity, good pressing ability and compatibility with most construction materials provide the use of thermally expanded graphite as a material for gaskets, bushings and so on [1–3].

Relative translation of carbon layers possessing mutual attraction and substantial specific surface provides excellent absorption of energy due to internal translation and friction of graphite particles [4–7]. This allows using plates, obtained by pressing thermoexpanded graphite without binders, as a damper against vibrations arising in dangerous natural phenomena (sharp changes in weather, winds, oceanic waves or earthquakes) [8]. Obtaining thin films with high electric conductivity and stability to electric voltage is of interest because of the possibility to use them in television technology [9].

All the indicated applications and many other areas of the use of thermally expanded graphite are based on procedures including the following stages: synthesis of intercalation compounds of graphite (ICG), pyrolysis of ICG in order to obtain thermally expanded graphite as flakes or “worms”, and compression of the obtained material for the purpose of obtaining products of the necessary shape and strength.

Diversity of requirements to different kinds of carbon products obtained from thermally expanded graphite, and permanently growing need for them explain urgency of search for cheap sources of graphite raw material and for new methods of chemical and thermal modification of native graphite.

In the present paper we describe the results of investigations of native graphite samples from four deposits in Russia and Ukraine for the purpose of obtaining thermally expanded graphite using various intercalation and thermal treatment procedures.

EXPERIMENTAL

We used native graphite samples substantially differing from each other in their characteristics. The graphite from the Zavalye Graphite Plant (Ukraine) is a large-scaly natural graphite subjected to chemical decalcination under industrial conditions. The Kyshtym large-scaly graphite (the Tayginka deposit, East Ural region, Russia) is an industrial concentrate with ash content of 16.2 %. Graphite samples from the Kureyka deposit (Krasnoyarsk Territory, Russia) are represented by a bedded sample. They have fine-grained structure and contain substantial amount of dispersed inclusions of the layered character (mica and chloride) and rounded shape (pyrite and calcite) with particle length of 20–40 μm and 2–4 μm wide. Averaged ash content of this graphite is about 10 %. Graphite samples from the Noginskiy deposit (Kranoyarsk Territory, Russia) are represented by a bedded sample. Mean ash content of the graphite is about 16.5 %.

The Kureyka and Noginskiy graphite samples were crushed with a jaw crusher till particle size of –5 mm, then treated in a vibrational rod mill SVU-2 for 20 min. Additional grinding of all the samples was performed in agate mortar. Particles smaller than 200 μm were used for further treatment. The material of rods (St3) wears out during mill operation, so the ground sample was subjected to double magnetic separation in order to remove the rasped and oxidized iron. At the first stage, ferromagnetic constituent of the sample was removed (metal iron and magnetite), then the sample was heated to 100 °C in order to transform the diamagnetic constituent (goethite, hydrogoethite, haematite) into ferromagnetic one, and separation was repeated. The mass of the treated sample after separation was about 97–98 % of the initial portion.

Further demineralization of graphite samples was performed by treatment at first with hydrochloric acid at graphite : HCl : H_2O ratio of 1 : 3 : 3 by boiling for 12 h, then with hydrofluoric acid (with the concentration of 38.2 %) at the graphite : HF ratio 1 : 2 under mixing for 24 h. The sample thoroughly washed with distilled water was then dried at the temperature of 105 °C till constant mass. After such a treatment, the residual ash content of graphite samples from the Zavalye Plant was 0.1 %, 1.9 % in the Kureyka graphite, 2.4 % in the Noginskiy graphite and 0.1 % in the Kyshtym one.

Several reagents were used for intercalation of the demineralized samples: chloric acid, chromic anhydride, sulphuric, nitric and acetic acids. According to the first procedure, the sample of demineralized graphite was subjected to stepwise treatment with chloric acid (graphite : $HClO_4$ = 1 : 5) within the temperature range of 120–150 °C, and the final stage, the sample was exposed for 1.5 h at the boiling point of $HClO_4$ (160 °C). According to the second procedure, graphite was at first treated with an aqueous solution of chromic anhydride with the density of 1.5 g/cm^3, then by concentrated sulphuric acid (95.5 %). The product was dried at 105 °C till constant mass. The third procedure included the treatment of graphite with fuming nitric acid with the density of 1.5 g/cm^3, followed by the addition of glacial acetic acid. Then the contents of the reactor were filtered with Schott filter in the vacuum of water-jet pump. In all cases, intercalated products were washed with distilled water; the final product was dried at 105 °C till constant mass.

Pyrolysis of intercalated samples was performed in steady and flow reactors. The pyrolysis under steady conditions was performed according to the generally accepted procedure. A cuvette made of stainless steel 150 cm^3 in volume with lapped cap was placed in a muffle furnace heated preliminarily to the required temperature. According to one of the versions of this procedure, a sample of intercalated graphite with the mass of 0.1–0.3 g was placed in a cool cuvette; the cuvette was placed in the muffler thus performing the slow heating mode. According to the second version, an empty cuvette was at first heated to the required temperature, then it was rapidly taken out of the muffler, and the sample was put into it; then it was again placed into the muffler. The flash pyrolysis mode was thus realized. In both cases the cuvette with the sample was kept in the muffler for 3 min. After that, the cuvette with thermally expanded graphite was taken out of the muffler and cooled in air.

Thermal treatment of the intercalated graphite in a flow reactor was performed in the flash pyrolysis mode. It was demonstrated previously that rather high intensity of thermal treatment can be reached by passing a dust-like raw material in the gas flow through a layer of larger particles of oxidation catalyst or thermally stable slag [10, 11]. The rate of heating the raw material reaches 10^4 °C/s; as a rule, the duration of the process does not exceed 1 s. Since an increase in heating rate helps more intensive thermal expansion of graphite, it seemed reasonable to use this procedure for thermal treatment of intercalated graphite samples.

Before loading into a flow metal reactor, particles of thermally stable open-hearth slag were sieved (a fraction with 2–5 mm particle size was taken) and rolled in a drum mill for 24 h in order to remove unstable slag particles and various ledges on them which could get destroyed during experiments with graphite and contaminate the product. Particles of the open-hearth slag play the role of heat accumulator. Thanks to their relatively large mass, temperature in reactor changes insignificantly when the reacting material is fed in. In addition, graphite particles move between larger slag particles along curved trajectories, which increases the duration of their staying in reactor and heat exchange coefficients.

At the beginning of operation, the reactor was driven to the working mode in which the temperature inside the reactor was (800 ± 5) °C. Graphite dosage into the reactor was performed periodically by switching to the line with the batcher of gas flow transporting graphite (argon was used), with the help of a six-way tap. Batcher is a set of tubes in which graphite samples are loaded preliminarily, each of them being weighed to the accuracy of thousandth decimal position. During the movement of argon through the batcher, the weighed portion of graphite is carried with gas flow into the reactor. Then the particles of thermally treated graphite get into the product collector, at the exit of which a multilayered metal filter is placed to prevent fine graphite particles from being carried away.

The product was unloaded from the collector after treatment of each sample. The resulting product was weighed to the accuracy of thousandth decimal position. In addition, the volume of initial graphite and of the resulting product was measured for each sample.

The X-ray diffraction patterns of powdered samples were recorded with DRON-3 diffractometer using CuK_α radiation. Electron microscopic photographs were taken with a scanning electron microscope REMMA-202M in the mode of secondary electrons.

RESULTS AND DISCUSSION

Analysis of the diffraction patterns of the Kureyka and Noginskiy graphites brings about definite difficulties because of smear and dissymmetry of reflections in the angle region under investigation $2\theta = 5...80°$. The asymmetry of (002) reflection from the side of small angles is usually explained by the contribution from a set of γ-patterns arising as a result of X-ray scattering on less ordered fragments of the structure. The character of interplanar spacing distribution (d) is unknown in the general case [12].

Comparison of the diffraction patterns of initial raw material revealed that the Kureyka and Noginskiy graphites have similar structure with some differences. A similar conclusion can be made for the structures of the Zavalye and Kyshtym graphites. The diffraction patterns of initial graphite samples from the Noginskiy and Zavalye deposits are shown in Fig. 1, *a*. It follows from the data obtained that the Zavalye graphite possesses a substantially better ordered structure than the Noginskiy one.

The investigated samples of graphite from four different deposits can be divided into two groups. The first one will include the samples of the Zavalye and Kyshtym graphites in which

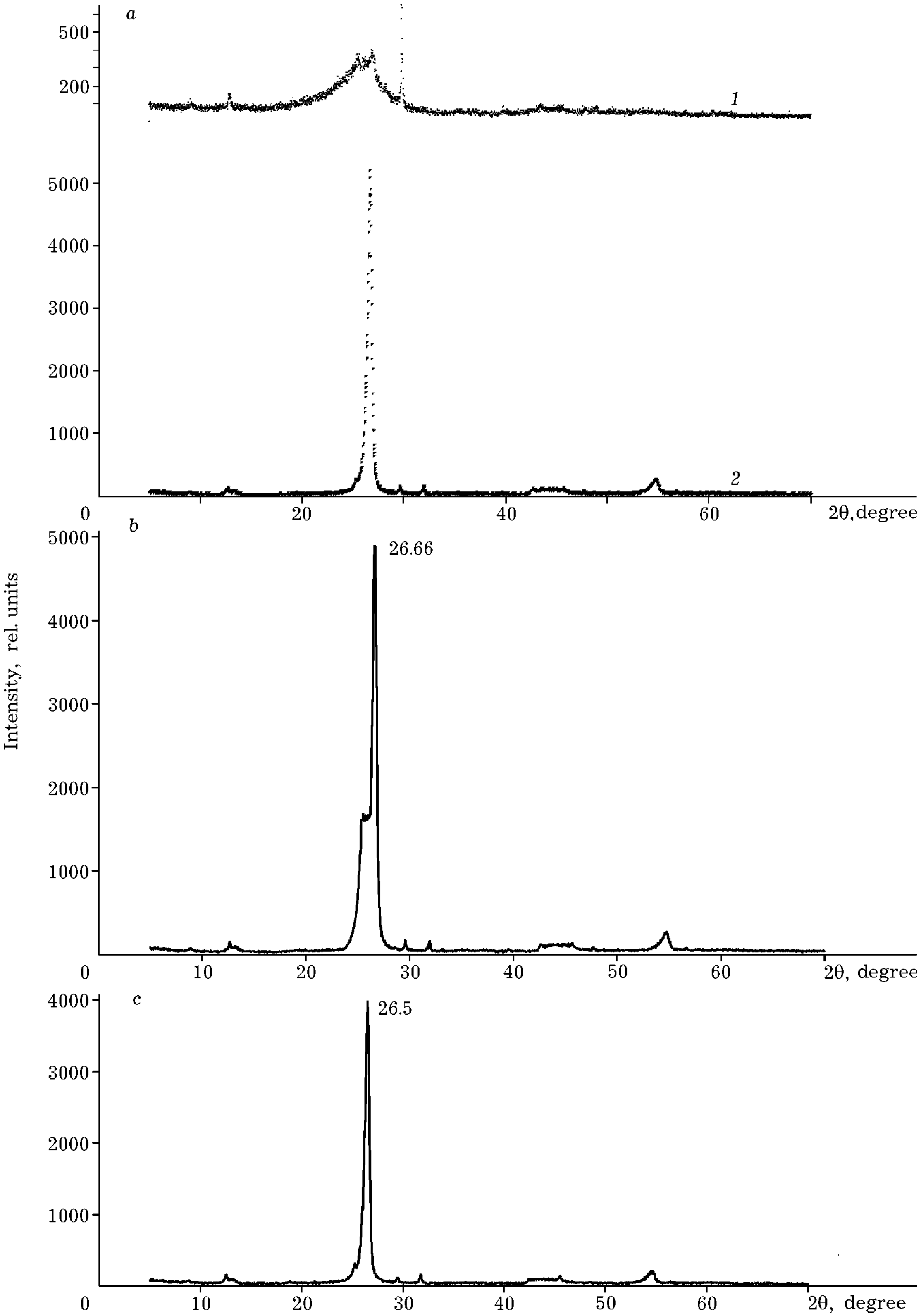

Fig. 1. Diffraction patterns of graphite samples: *a* – graphite from the Noginskiy (*1*) and Zavalye (*2*) deposits; *b* – graphite from the Zavalye deposit after intercalation with nitric and acetic acids; *c* – the same graphite after thermal expansion under steady conditions in the rapid heating mode.

the content of mineral components after chemical decalcification is two orders of magnitude lower and the content of ordered carbon structures is substantially higher than those in the samples of the second group, the Kureyka and Noginskiy graphites.

Comparing diffraction patterns of the initial graphite (see Fig. 1, *a*) and of the same samples after intercalation and thermal treatment (see Fig. 1, *b*) we may conclude that intercalation causes broadening of the main signal corresponding to the ordered carbon structures. According to the literature data [10], the appearance of γ-band from the side of small angles in the diffraction patterns of the intercalated sample, unlike for the initial graphite, should be interpreted as the formation of less ordered carbon crystallites. Judging from some decrease in the intensity of the main peak, we may conclude that this process occurs due to degradation of the initial carbon structures.

For the samples thermally treated in a steady reactor under flash pyrolysis conditions, which causes the removal of intercalate, the diffraction patterns become again similar in shape to the Gaussian (see Fig. 1, *c*). The diffraction patterns contain no γ-band, but the intensity of the main peak decreases even more, and its maximum shifts toward smaller angles.

Most types of carbon raw material, such as native graphite, can be represented as quasi-single crystals which behave similarly to pure graphite with respect to intercalation, though they have some defects and are composed of grains [13].

It is established that if polycrystalline carbon materials with different orientation of carbon layers are used, such as coke, carbon fibres, *etc*., the expansion of carbon crystals along the *c* axis interrupts each other and causes mechanical strain in particles during intercalation. This may lead to disordering of the initial carbon particles; this process occurs only at the grain boundary with the formation of usual intercalation compounds [10].

The results obtained in the present work allow us to make preliminary conclusion that intercalation followed by pyrolysis causes a decrease in the ordering degree of carbon crystallites of the initial graphite. At the intercalation stage, the appearance of γ-band in diffraction patterns is clearly observed; it disappears after pyrolysis.

A change in the appearance of graphite particles from both groups after intercalation and pyrolysis is shown in Fig. 2. Differences are clearly seen with the samples of initial raw material: the particles of the Zavalye graphite look like flat flakes with rounded edges (see Fig. 2, *a*), while the Kureyka graphite is composed of particles of various shapes mainly with sharp edges (see Fig. 2, *c*). The differences between thermally treated samples are even more substantial. The Zavalye graphite intercalated with chloric acid forms the particles of vermicular shape after thermal treatment (see Fig. 2, *b*). Strongly fragmented (cracked) particles of rounded shape are formed from the Kureyka graphite after thermal treatment (see Fig. 2, *d*).

The degree of sample volume increase under thermal treatment depends on the nature of intercalate, final temperature and heating mode. An increase in the volume for the graphite of the first group was from 100 to 300 times in experiments with the steady set-up; for the graphites of the second group, this parameter did not exceed 10.

In the flow set-up, experiments were performed with two samples (with 10 parallel assays for each): the 1st was graphite from the Zavalye deposit (intercalated with chromium anhydride and sulphuric acid), the 2nd was graphite from the Zavalye deposit intercalated with nitric and acetic acids.

The specific volume of thermally expanded graphite samples is shown in Table 1. It was determined as arithmetic mean of three parallel measurements using equation $K_t = V/m$. Here V is the bulk volume of the sample, cm^3; m is its mass, g. The admissible deviation between parallel determinations of the K_t parameter was 5 %. It follows from the presented data that the specific volume of graphite samples thermally treated in the flow reactor is substantially smaller than for the same samples thermally expanded under steady conditions. The latter differ by very low mechanical strength and decrease in volume when slightly pressed or shaken. Their specific volume (K_t) is determined both by the porosity of particles

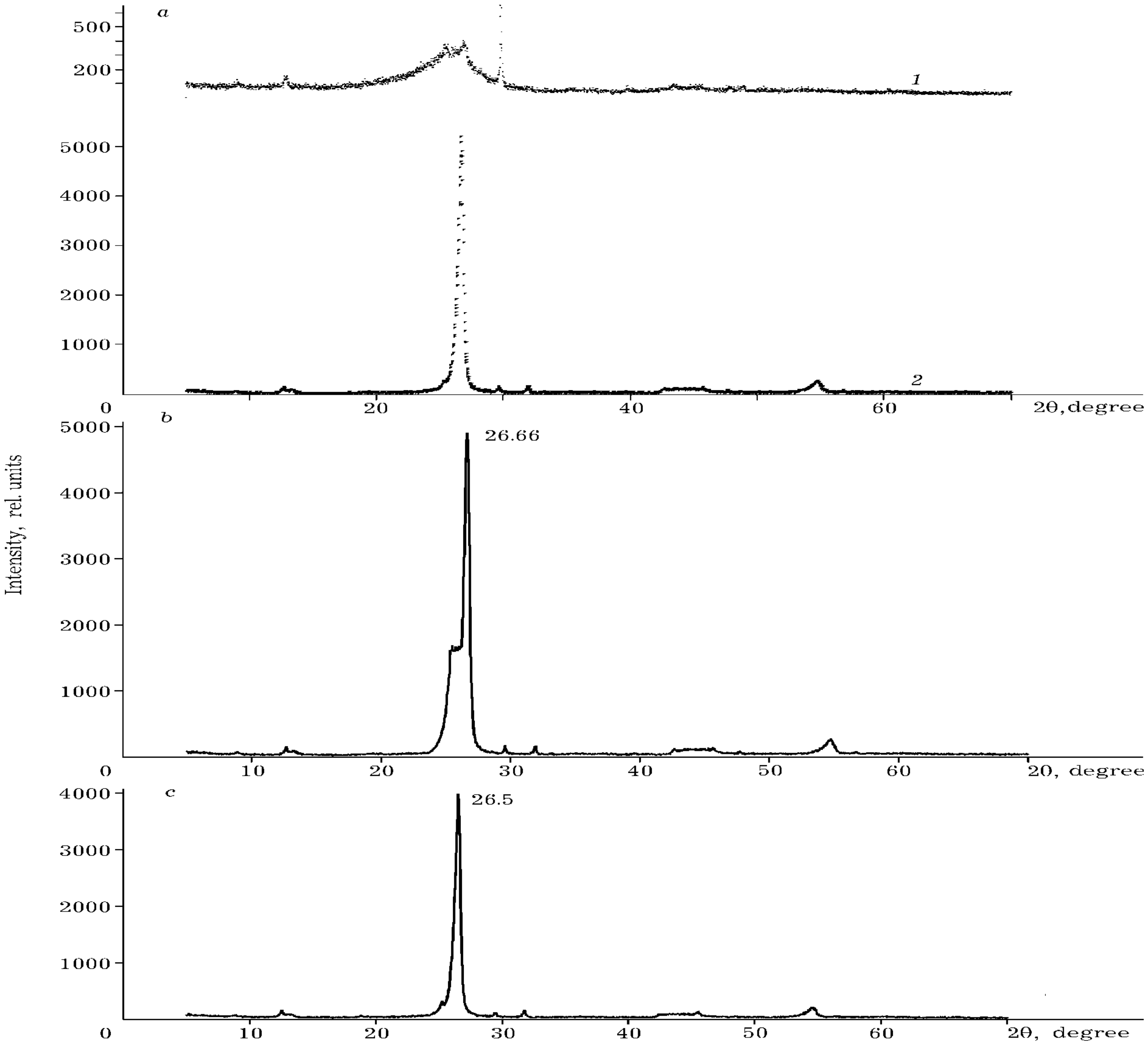

Fig. 2. Electron microscopic images of the initial and thermally expanded graphite samples (×250): *a* – graphite from the Zavalye deposit; *b* – graphite from the Zavalye deposit intercalated with chloric acid and thermally treated in a steady set-up at 900 °C; *c* – graphite from the Kureyka deposit; *d* – graphite from the Kureyka deposit intercalated with chloric acid and thermally treated in a steady set-up at 900 °C.

TABLE 1

Thermal expansion coefficient (K_t) of the intercalated samples of graphite from the Zavalye deposit subjected to different thermal treatment procedures at the temperature of 800 °C

Sample	Thermal expansion coefficient		
	Linear heating mode in a beaker	Collision heating mode in a beaker	Flow set-up
1*	180	301	6.6
2**	207	423	9.6

*Intercalated with chromic anhydride and sulphuric acid.

**Intercalated with nitric and acetic acids.

themselves (that is, by the volume of voids inside the particles) and by fractional void volume (FVV), which is the volume of voids between particles. The latter value can be divided into the FVV of particles in agglomerates and the FVV between agglomerates.

It may be assumed that at first the intercalated graphite expands during thermal treatment in the flow reactor similarly to the steady case, then the particles of thermally expanded graphite survive substantial mechanical load as a result of their collisions with slag particles and with reactor walls. Less strong particles and their agglomerates are destroyed as a result of this load. So, relatively low specific volume of graphites pyrolyzed under flow conditions is due to subsequent degradation of the particles of thermally expanded graphite.

The mode of treatment in the flow set-up has definite technological advantages in comparison with the treatment under steady conditions. That is because materials obtained under steady mode have very small bulk density (about 1 kg/m^3), which hinders their transportation and makes it inefficient from the economic viewpoint.

In order to obtain a molded product from thermally expanded graphite with large specific volume, it should be at first compacted, for example by passing through rolls, otherwise molding process would be inefficient due to low density of the raw material. In the flow set-up, primary compacting occurs as early as during thermal treatment of graphite.

The carbon material obtained in the flow set-up will exhibit more stable properties during further processing, because the weakest particles and agglomerates are already destroyed. Because of this, transportation, mixing and other technological operations will cause less destruction of the remaining particles and agglomerates.

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