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ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ
Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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GRAPHEN AND NATURAL FORMATIONS

Abstract. It is well known that a great deal of metallic phases occurs in the ultradispersed state. The extracted phases with a low gross content are scattered over the vast occupied area. Large deposits of Kazakhstan are related to this type of ore-bearing formations.

Studies of the natural objects are complicated manyfold by heterogeneity of substances and the staging of the ongoing processes. In our studies, as reference matter we adopt the solid natural carbon substances, synthetised in various chemical processes running in compliance with strict rules of chemical reactions under given thermodynamic conditions. The natural carbon substance, as a rule, exists in a whole range of probable phases, often having the film-planar structure habit. Rock transformation (squeezing) results in curving film-lamellar carbon-bearing layers, present also within the nanopipes and fullerens; they often break, with obvious formation of a planar structure. Respective alternation of layers may lead to local formation of graphite, which is witnessed in photographies, made using the transmission electron microscopy. Particles, seized by folding, can be trapped in hollows (*a trap trench system*) and start accumulating clusters. The only method so far fixing the newly formed carbon layers is the Raman spectroscopy. It especially concerns the carbon matter, due to various reasons, possessing a small coherent zone. The current paper presents data obtained in the RK MES Institute of Geological Sciences n.-a. K.I. Satpayev, in cooperation with the RK KazNU Institute of Combustion Problems.

Key words: nanoscale, graphene/graphane, graphite.

Introduction. Use of carbon material is associated with large-scale production. One of their sources is natural manifestations. Synthetised substance is programmed for obtaining in a set of designed (pre-calculated) reactions, while a natural substance is formed under unplanned circumstances. At the same time, natural matter exists, i.e., all reactions, leading to its formation and existence under given conditions, are correct.

We find natural carbon matter (geology) in a near-surface zone. That is, in a zone of low temperature and pressure, windy (gases), rainy (atmospheric precipitation), under influence of insulation (sun ray waves). Besides, carbon-containing matter is inseparably integrated with other substances (rocks, minerals, many of which are catalysers not only in respect to carbon matter), under influence of all sorts of nanozones (a nanozone is limited by condition gradients). This predominantly relates to physical and chemical sciences. The realm of formation and existence of nanoparticles is multidisciplinary [1]. Usually, formation energy is sufficient for creating a nanoparticle, and it does not suffice to perform a transit into another state of “large” mass of material. For example, energy produced in tectonic processes is quickly extinguished “to zero”. Natural carbon matter, as a rule, consists of a whole spectrum of probable phases, including those with the film-planar habit. Shall we use all sorts of “new” titles to the natural matter, synthetised and confirmed by some instrumental method, or continue using historically developed old names (graphite and crystalline, fine-crystalline, non-crystalline carbon matter)? How “new substances” look like (not schematically) and relate to “old” definitions?

Nanomineralogy [1] is a multidisciplinary science. Mathematical modelling, physics and chemistry are “reference” disciplines investigating detailed conditions of substance synthesis, properties of obtained materials, suggesting their possible application.

Let us consider graphenes. These theoretically calculated structures, among the first ones, have been developed in the CVD-processes. Recently, increased attention was drawn to them.

In the nature, unidirectional manifestations of graphenes/graphanes are not existent. But manifestations, containing the carbon matter, predominantly with film carbon structures, similar to graphene ones, do exist. In this paper, photographies of transmission electronic microscopy (TEM) are used, and there was no task to discern graphenes from graphanes.

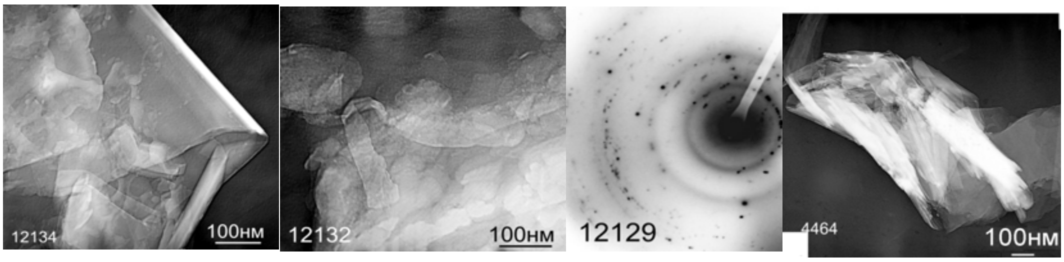
Results and discussion. It follows from the diagramme [2] (figure 1) that grapheme layers can be folded (figure 1a), and the thickened space of the fold can collect admixtures (figure 1b shows fullerene).

a b

Figure 1 – Graphene folding patterns [2]

As it was said earlier, there are great many planar structures in the nature. Let us, basing on microscopic diffraction images, consider only carbon-containing ones: the two- and three-dimensional [3], graphite-like and graphites [4]. The plural form is used because carbon materials of graphites and graphenes/graphanes containing various admixtures are plentiful. Reflexes belonging to carbon matter, as a rule, are widened. A big role is played by scale: often elements composing the matter are of nanoscales. Usual materials are X-ray amorphous. Electrons (TEM, shorter waves) are often capable of detecting non-amorphousness of the X-ray amorphous phases. Specimens for investigations have been prepared uniformly, by one of the dry preparation methods. It excludes any influences of temperature or solvents.

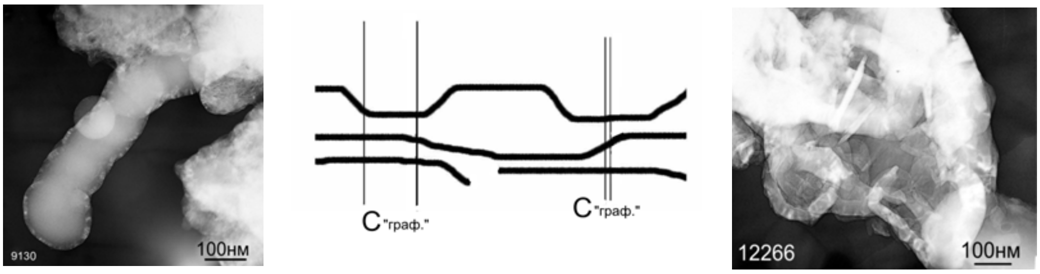
It is seen through microscope that curves of particles have ordinary appearance (figure 2). Folding of *visible* planes (figure 2a) is also not a rare phenomenon. As it was already noticed, carbon substances are present in the nature in unlike phases, for instance (figure 2b), graphites (ribbon particles) and a three-dimensionally ordered matter (the rest of particles' mass). Electrogrammes show them as reflexes grinning through graphite material (more strong dotted reflexes) in the background of widened rings (polycrystallines?) of three-dimensional carbon matter (figure 2c). Figure 2d illustrates a particle (natural too), consisting of "folded" film layers. Its micro-diffraction image relates to graphite.



a b c d

Figure 2 – Morphological images of natural film structure formations:
a, b – the Saryarka field; d – the Nigozero field (Karelia)

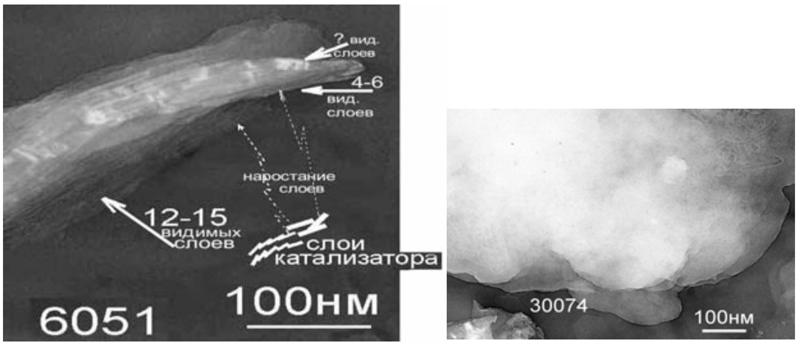
In the figure 3a, a joint existence of graphenes/graphanes and mass has been fixed in a synthetised particle; part of the matter inside the pipe, possibly, is catalytic material for carbon (synthetised matter). Generally, the structure of this tubular formation (figure 3a) is not amorphized. In curves (figure 1b), local graphite gets packed (figure 3b) whih has been described in the work [5]. This matter's micro-diffraction image reveals reflexes of graphites, analogous to those one shown in the figure 2b, in the background of amorphous (structureless) substance. Separating in natural conditions from the central (catalytic) part, the round graphite capsule forms an independent particle, shown in the figure 3c. Its micro-diffraction image corresponds to graphite.



a b c

Figure 3 – a, c – morphology of particles (outside view); b - the diagramme of (possible) formation of local "graphite" packing; c - curved planes of local graphite packing; a - Synthetised particle; c - the Siyakezen field

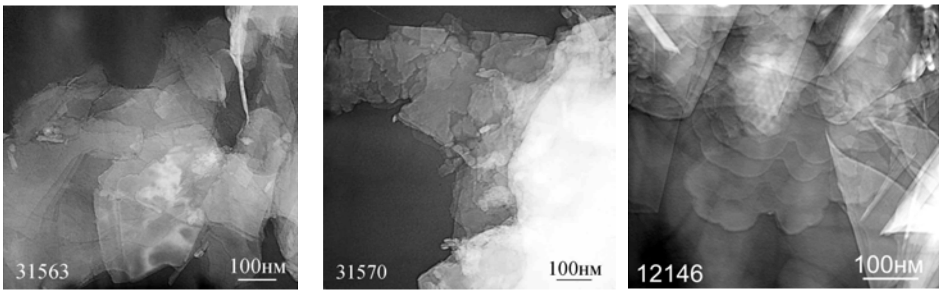
Often encountered are lamellar structures with linear or curved contours of such a locally formed “graphite”. Does it follow that graphites are created locally from graphenes/graphanes? Then, graphene/graphane could be an independent mineral type. It is highly probable that its films have been fixed in carbon compounds (figure 4). Figure 4a shows visible (TEM) layers of basically non-graphite carbon matter. Graphenes/graphanes, as a template, form the first layer, which gradually accumulates carbon mass (figure 4b). This phenomenon is observed both in synthetised and natural formations.



a b

Figure 4 – Graphene layers: a - commercial, b - Koksu

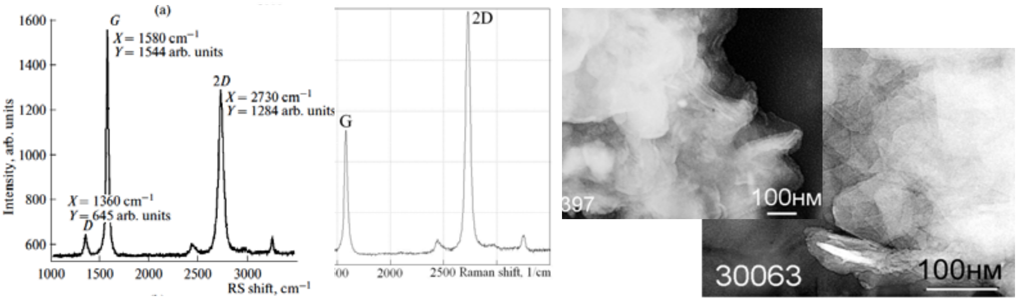
Carbon planar structures (films) can have different scales (figure 5), and this fact may explain the D-peaks discrepancy in the Raman-spectroscopy (figure 6a). Layers of the plain “large” carbon films (up to several nanometers) are shown in figure 5a, small films (first dozens of nanometers) in figure 5b, and a curve carbon layered film packing in figure 5c.



a b c

Figure 5 –Different-scaled natural film particles (the Balta-terek field)

When interconnecting the gauges, it would obviously be possible to tell, what layer thickness and what layer order (in sequence, figure 5) of the Raman-spectra will be obtained (figure 6a). Layers of natural matter would be possible to identify from the relationship between piques I_D/I_G and their relative displacement.



a b c

Figure 6 – The Raman spectra of multilayered (of various discrepancy?) graphenes – a, two-layered particles of natural formation (the Shubarkul field) – b, the trap trench (the Tekeli field) – c

Discrepancy can be connected to quantity of “large and small” surfaces, as well as to presence of various bonds on their endings. TEM is not clear about film thickness. A visible thickness evidently is not atomic. Probably, natural formations contain layers, consisting minimum of two “carbon meshes” (figure 6b). The grapheme film is not a graphene’s layer made only of C-atoms. Rock transformation (squeezing) results in breaking the curved film-lamellar layers, obviously followed by formation of a planar structure (figure 2, 5) and possible local formation of graphite. Particles seized during the folding, also according to the pattern shown in fig. 1b, are singled-out from the trap trench system (figure 6c) for individual development.

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ГРАФЕН ЖӘНЕ ТАБИҒИ БІЛІМ

Аннотация. Жақсы танымал факт-бұл металл фазалардың көп саны Ультрадисперсті күйде. Жалпы құрамы аз өндірілетін фазалар алып отырған елеулі алаңға себілген. Бұл Кенді типке Қазақстанның ірі кен орындары жатады.

Заттың біртектілігі, ағатын процестердің сатылығы табиғи объектілерді зерттеуді бірнеше рет қиындатады. Қатты табиғи көміртекті заттарды "эталондық" заттарға зерттеу кезінде біз берілген термодинамикалық жағдайларда химиялық реакциялардың қатаң ережелері бойынша өтетін химиялық процестердің әр түрлерінде синтезделген көміртекті заттарды таңдап алдық. Табиғи көміртекті зат, әдетте, пленкалы-пластиналы габитус бар мүмкін фазалардың тұтас спектрінен тұрады. Жыныстардың трансформациясы нәтижесінде құрамында көміртекті иілген пленкалы-пластиналы қабаттар, оның ішінде нанотүбектер мен фуллерен қабырғаларында бар, жиі сынады, және анық жазықтық құрылым пайда болады. Қабаттардың тиісті кезектесуі кезінде жергілікті графит қалыптасуы мүмкін. Растау үшін жарық беретін электрондық микроскопиямен алынған фотосуреттер келтіріледі. Бүктелген кезде басып алынған бөлшектер тереңдете - "науалар - арықтар" жүйесінде бөлініп, содан кейін жиналу пайда болуы мүмкін. Түзілетін көміртекті қабаттарды бекітетін жалғыз әдіс Раман-спектроскопия болып қалады. Әсіресе, бұл көміртекті заттарға қатысты, әртүрлі себептермен когенеренттіліктің шағын аймағы бар. Бұл мақалада ҚР БҒМ Қ. И. Сәтпаевтың Геология ғылымдары институтында алынған және ҚР ҚазҰУ-дың Жану проблемалары институтымен достастықта алынған мәліметтер келтіріледі.

Түйін сөздер: наноразмеры, графен/графан, графит.

Т. А. Шабанова, В. А. Глаголев

Сатпаев Университет, Институт геологических наук им. К. И. Сатпаева, Алматы, Казахстан

ГРАФЕН И ПРИРОДНЫЕ ОБРАЗОВАНИЯ

Аннотация. Хорошо известным фактом является то, что большое количество металлических фаз находятся в ультрадисперсном состоянии. Добываемые фазы с малым валовым содержанием рассеяны на значительной занимаемой площади. К этому рудоносному типу относятся крупные месторождения Казахстана.

Неоднородность вещества, стадийность протекающих процессов многократно усложняют исследования природных объектов. При исследовании твердого природного углеродистого вещества за «эталонные» вещества нами выбраны углеродистые вещества, синтезированные в различных видах химических процессов, протекающих по строгим правилам химических реакций в задаваемых термодинамических условиях. Природное углеродистое вещество, как правило, состоит из целого спектра возможных фаз, часто имеющих пленочно-пластинчатый габитус. В результате трансформации пород изогнутые углеродсодержащие пленочно-пластинчатые слои, имеющиеся, в том числе, в стенках нанотрубок и фуллеренов, часто ломаются, и, очевидно, образуется плоскостная структура. При соответствующем чередовании слоев локально может сформироваться графит. Для подтверждения приводятся фотографии, полученные просвечивающей электронной микроскопией. Частицы, захваченные при сворачивании, могут выделяться в углублениях - в системе «желобков - арычков» и, затем, образовывать скопления. Единственным способом, фиксирующим образующиеся углеродные слои, остается пока Раман-спектроскопия. Особенно это касается углеродистых веществ, по разным причинам обладающих малой зоной когерентности. В этой статье приводятся данные, полученные в институте геологических наук ми К.И. Сатпаева МОН РК и полученные в содружестве с Институтом проблем горения КазНУ РК.

Ключевые слова: наноразмеры, графен/графан, графит.

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