

Onion-like carbon from ultra-disperse diamond

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Abstract

A new material containing macroscopic quantities of onion-like carbon (OLC) particles is produced by heat treatment of ultra-disperse diamond (UDD) powder (2–6 nm). Annealing products (characterized by high-resolution electron microscopy) are presented by: (a) quasi-spherical particles with closed concentric graphite shells, (b) polyhedron particles with closed shells, (c) elongated particles with linked external graphite-like layers and closed quasi-spherical internal shells. The intermediates of UDD transformation have been registered. The structural transformation of UDD begins from the surface of the diamond particles towards a crystal bulk. The transformation rate of (111) diamond planes to graphite-like sheets is higher than that of other planes.

1. Introduction

The discovery of buckminsterfullerenes [1,2], carbon nanotubes [3–6] and onion-like carbon [7] has stimulated the research of non-planar carbon chemistry [8]. All the fullerene-related materials have been usually produced by condensation of carbon vapor in experiments involving transient high-temperature regimes: pulsed laser heating [1], electric arc [2], resistive heating, flame production of soot and high-frequency inductive heating method (see refs. [8,9]). However, Ugarte [10,11] discovered the curling and closure of graphitic networks under electron-beam irradiation onto multiple-shell spheres in the condensed phase. Recently, a new material containing hollow nanometric carbon onions with from 2 to about 8 graphitic shells was produced by the heat treatment of pure carbon soot at 2250–2400°C [12].

In the gas phase the growth of concentric graphitic shell structures (OLC particles) was proposed to

proceed through a spiralling-network mechanism [13]. At the same time the structural fluidity of carbon in the condensed phase induced by electron bombardment was proposed to explain the formation of quasi-spherical shelled particles [10,11]. This idea was used for the creation of OLC by thermally annealing carbon soot [12].

Prospective materials with unusual properties can be obtained from the soot formed under detonation of high explosives with a negative oxygen balance. Under these conditions soot containing high concentrations of ultra-disperse diamonds (UDD) is produced [14–16]. We have found that under some particular experimental conditions the detonation soot, besides UDD, amorphous carbon and graphitic ribbons, contains imperfect quasi-spherical multi-shell particles [17]. The latter are supposed to be the final products of the thermal annealing of the initially formed UDD. This idea led us to investigate UDD annealing and we have shown that UDD can be ther-

mally transformed to particles composed of closed graphitic shells (OLC particles) [17,18].

We report in this Letter further details of the formation of OLC particles upon the UDD thermal annealing. We prepared the intermediates of such a UDD transformation which gave us additional information on the structure and mechanism of OLC formation from UDD.

2. Materials

The detonation soot samples were prepared from 50/50 TNT/RDX (trotyl/cyclotrimethylene-trinitramine) charges fired in a hermetic tank. UDD (with average particle diameter $\bar{d}=4.5$ nm) have been isolated from the detonation soot by the oxidative removal of non-diamond carbon with HClO_4 . The properties of UDD are described elsewhere [19]. The elementary cell parameter of UDD $\alpha=0.3573$ nm (0.35667 nm for bulk diamond). An elemental analysis of UDD has shown a relatively high concentration of hydrogen-, nitrogen- and oxygen-containing groups which could be partially removed from the sample by heating in vacuum, however, a portion of these elements can be included in the annealing products (AP).

UDD annealing was performed in a high-vacuum chamber containing a tantalum cap heated by an electron beam at 1000–1500°C. Temperatures were measured with a tungsten–rhenium thermocouple. The micrographs of UDD and AP were obtained with a transmission electron microscope (TEM) JEM-4000EX.

3. Experiment

Fig. 1 shows TEM micrographs of the original UDD and AP. The UDD sample contains mostly the associates of 3.0–7.0 nm diamonds (Fig. 1a). The dark contrast lines correspond to the diamond crystal planes and the distance between lines corresponds to the (111) lattice parameter of UDD (0.2063 nm calculated from XRD data of UDD [19]; for bulk diamond $d_{111}=0.205$ nm). This distance was used to scale the magnification of the TEM images.

The AP are presented by:

(a) quasi-spherical particles with closed concentric graphite shells (Fig. 1b, marked O);

(b) polyhedron particles with closed shells (Fig. 1c, marked P);

(c) elongated particles with linked external graphite-like layers and closed quasi-spherical internal shells (Fig. 1b, marked E).

Varying the temperature and the time of UDD annealing we have succeeded in preparing samples containing intermediates of the UDD transformation (Fig. 2). Fig. 2a demonstrates the transformation of few surface UDD layers to the graphite-like sheets. The particle SS of Fig. 2b, which looks as if it is composed of semi-spherical shells enclosed one in another, has a core composed of five diamond (111) planes. Particles S (Figs. 2b and 2c) have no diamond layers and look like quasi-spiral carbon shells. Fig. 2d represents the final imperfect OLC particle with a periodic contrast within each shell.

4. Discussion

One can see that the structural rearrangement of UDD under annealing conditions begins from the surface towards a crystal bulk (see Figs. 2a and 2b). It appears that the transformation rate of the (111) diamond plane is higher than that of other index planes. One can see that particle A in Fig. 2a has four transformed (111) planes (one plane is partially transformed) and only two defective graphite-like sheets were formed from the high index plane of diamond. The edges of just exfoliated graphite-like sheets merge to the upper untransformed diamond plane. The distance between the inner graphite-like sheet and upper untransformed diamond layer does not exceed 0.35 nm, so we can assume these layers to interact.

The higher rate of (111) plane transformation can be explained by the structural similarity of (111) diamond planes and (001) graphite planes (see Fig. 3). It is easy to visualize these diamond planes collapsing into more stable graphite planes at high temperature. Fig. 3 demonstrates the scheme of UDD transformation to quasi-spherical particles with closed graphite shells. The closure of graphite sheets could be achieved by the formation of twelve pentagons [20]. Fig. 3a shows the bending of two planar graphite sheets to a bowl-like carbon network due to the

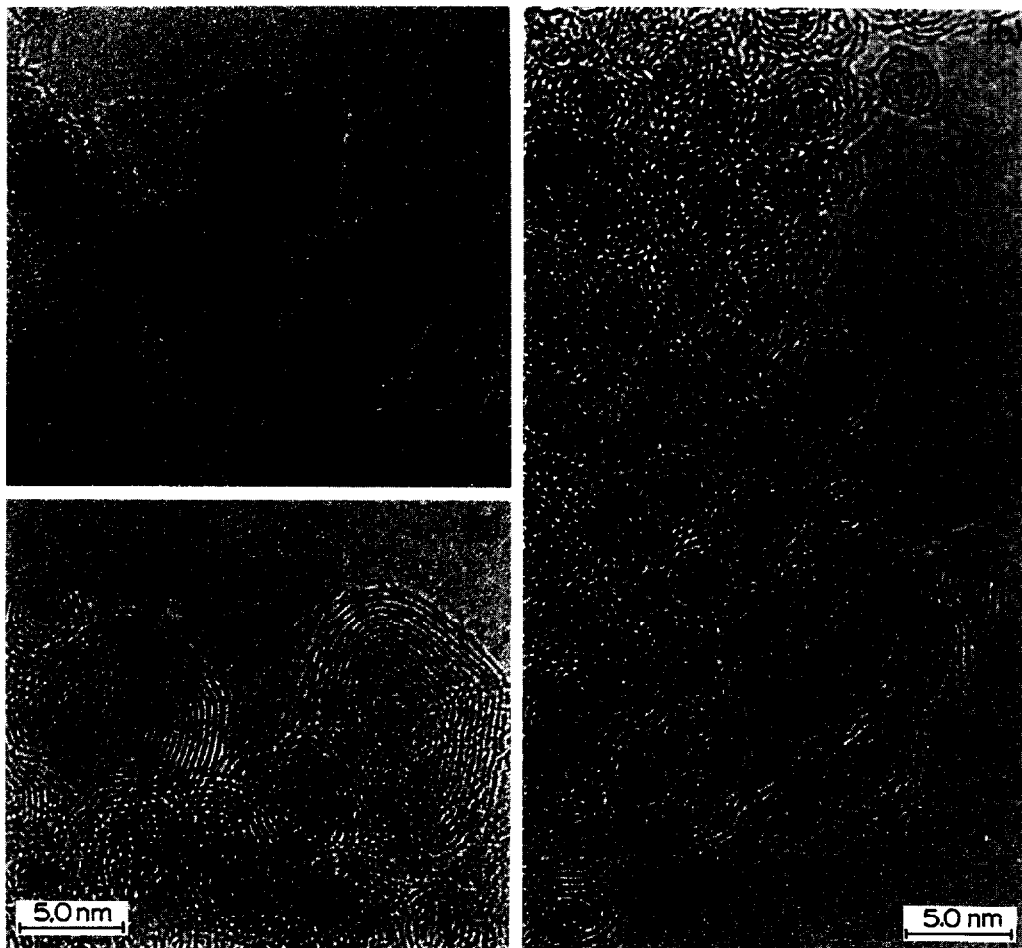


Fig. 1. High-resolution TEM images of original ultra-disperse diamonds (a) and their annealing products ((b), (c) 1500°C). Dark contrast lines (a) and rings ((b), (c)) correspond to diamond crystal planes and graphite-like shells, respectively. The distances between lines correspond to the (111) lattice parameter of ultra-disperse diamond (a) ($d_{111}=0.2063$ nm [19]) and those between rings ((b), (c)) to the distance between the graphite-like shells ~ 0.35 nm ($d_{002}=0.3354$ nm for bulk graphite). Quasi-spherical particles with closed concentric graphite shells (b) are marked O, polyhedron particles with closed shells (c) are marked P, elongated particles with linked external graphite-like layers and closed quasi-spherical internal shells (b) are marked E.

insertion of two pentagons. Small diamond particles were transformed to quasi-spherical particles (Fig. 3b), while the bigger ones transformed to polyhedron particles with closed shells (Fig. 3c). UDD associates could be the source of elongated particles with linked external graphite-like layers and closed quasi-spherical internal shells (Fig. 3d). If enough energy is provided, the transformation of polyhedron particles to spherical ones is likely to proceed. So for each annealing temperature the critical size of polyhedron particles, which could be transformed to spherical

ones, should exist. This proposition is supported by Ugarte's results on the thermal transformation of soot to hollow nanometric carbon onions at 2250–2400°C [12].

Such nanometric graphitic shell curling and closure under the thermal conditions can be interpreted as the difference in surface energy of the basal plane (0.135 J/m²) and the planes formed by the edges of the basal planes, namely (101) and (112) (≈ 4.8 J/m²) [21]. Thus the closure of graphitic shells and elimination of their dangling bonds provide a suffi-

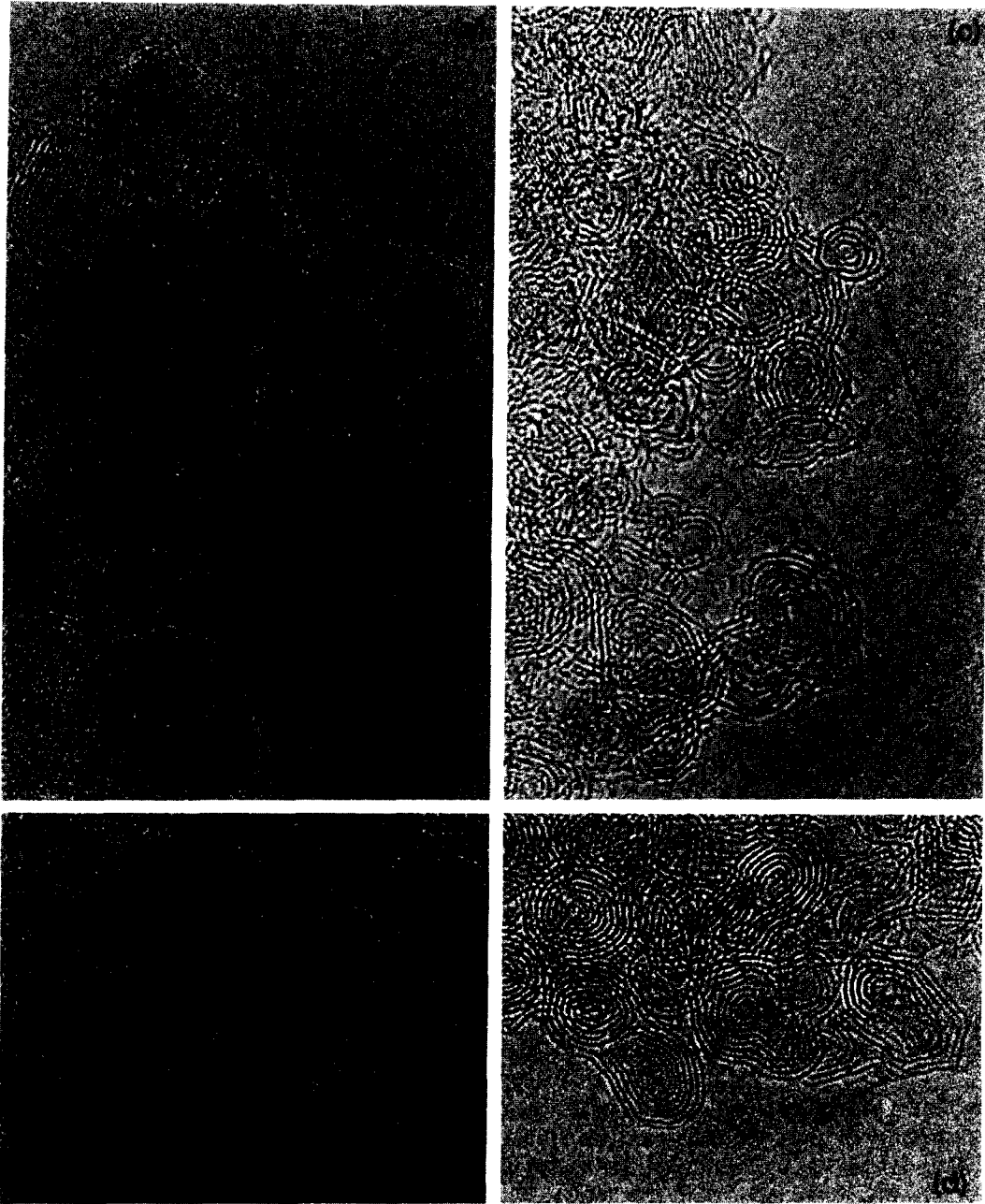


Fig. 2. High-resolution TEM images of UDD annealing products on the different steps of conversion. (a) The diamond particle A has four transformed (111) diamond planes and only two highly defective closed graphite shells; one can see the initial stage (111) plane transformation to graphite sheet which is attached to the neighboring diamond plane. (b) Particle SS composed of semi-spherical shells enclosed one-to-one with the rest of diamond core. Particles S ((b) and (c)) have no diamond layers and look as if they are composed of quasi-spiral carbon shells. (d) The final onion-like carbon particle (O); shells have a periodic radial contrast with a 0.20–0.22 nm spacing which indicates the mutual orientation of graphite-like layers of different shells.

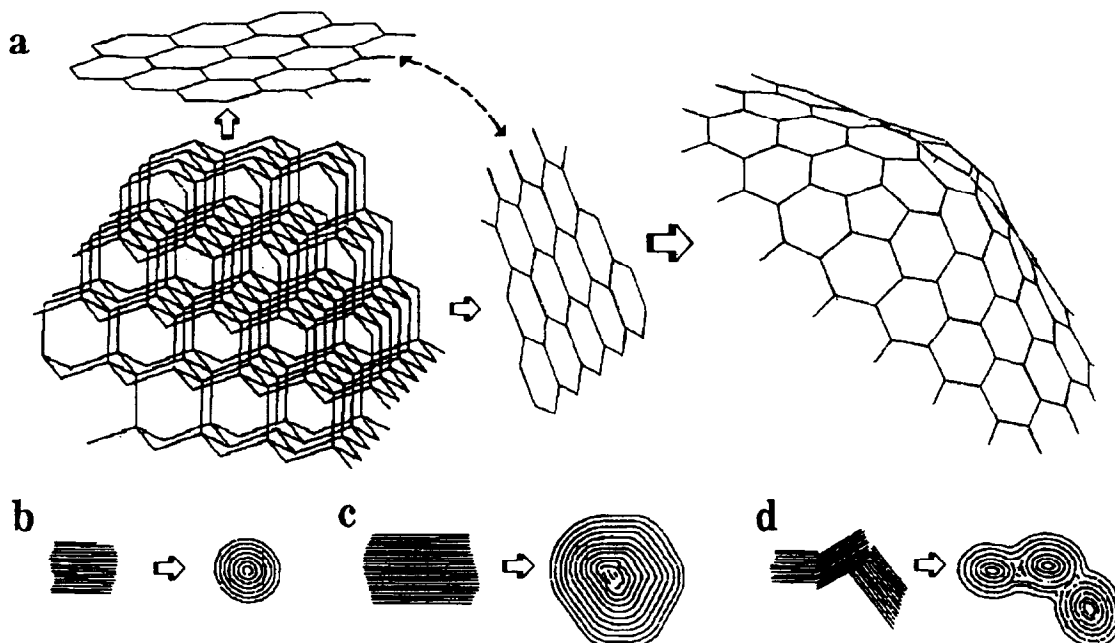


Fig. 3. The scheme of UDD to onion-like carbon transformation. (a) The transformation of two (111) diamond planes to graphite sheets and their curling due to two pentagons formation. (b) The formation of a spherical onion-like particle from a small UDD. (c) The polyhedron particle formation from a large diamond particle. (d) The formation of elongated particles from diamond associates.

cient decrease in the carbon particle surface energy.

The transformation of the (111) diamond plane to the (001) graphite one is accompanied by shrinkage along the graphite network. At the same time UDD to OLC transformation leads to a dramatic increase in particle volume (compare the densities of graphite and diamond, 2.265 and 3.515 g/cm³, respectively). Thus it is clear that the number of surface carbon atoms of the initial diamond particle is not sufficient to form the perfect closed graphite-like sphere.

Thus, the cuboctahedron diamond particle, the most stable form of diamond crystals, composed of 1683 carbon atoms, has 530 surface atoms. The size of such a particle is about 2.14 nm (between $n00$ planes). The cubic diamond particle of the same size, having 1963 carbon atoms, has 434 surface atoms. At the same time, a perfect OLC particle (with size 2.814 nm) composed of four fullerene shells, containing 1800 carbon atoms, has 960 surface atoms. Thus, the lack of carbon atoms needed for the formation of closed carbon shells should be compensated by the capture of carbon atoms from the edges of the inner diamond layers.

The presence of a growing inner core should prevent the closure of outer graphite-like layers and the formation of perfect fullerene-like shells before the UDD particle annealing is completed. At this state the spiral-like carbon shells, which can be formed by one or several carbon layers (particles S), or semi-spherical shells enclosed one-to-one (particle SS) are mostly probable intermediates. The preliminary analysis of the TEM micrographs provides images of both types of intermediates. Intermediates S are presented in Figs. 2c and 2d. Particles SS are likewise presented in Fig. 2b.

While UDD annealing finishes the following closure of quasi-spherical shells can proceed. In accordance with van der Waals interactions the carbon shells should be spaced by the intersheet distance in graphite. Thus it is likely that bonds should break between the imperfect inner and outer shells. If enough energy is provided to the transforming particle this process can progress from the surface to the bulk (as observed by Ugarte [11] for the electron beam annealing of soot to OLC) or from the bulk center to the surface as proposed for the spiral multiple shell

mechanism [13]. We intend to get more information to clarify the detailed mechanism of the observed UDD annealing to OLC.

It is of particular interest that the soot annealing into OLC demands more severe heating conditions, i.e. electron beam [10,11] or thermal heating at 2200–2400°C [12], since initial carbon–carbon nets should be broken. UDD annealing, however, produces onion carbon under milder conditions due to the favorable orientation of carbon layers which could be an appropriate matrix for further transformation. Thus the formation mechanism for the onion-like particles from UDD is different from the mechanism based on the initial formation of spiral multiple shell particles proposed for the gas phase aggregation of carbon vapor [13], the mechanisms being based on the structural fluidity in the condensed phase induced by irradiation or the thermal treatment stimulated graphitization of soot [10,11]. However, these mechanisms can contain some common steps.

Structural particularities of OLC could be obtained from detailed examination of the TEM micrographs. The distance between shells is close to 0.35 nm, i.e. typical for bulk graphite ($d_{002} = 0.3354$ nm). Moreover, each shell (up to seventh or eighth from the center) has a periodic contrast change with a 0.2–0.22 nm stem. The contrast changes of various shells form the radially spread structured images. Hence, the closed shells seem to be rigidly oriented towards each other. These data give unique information about the mutual orientation of giant fullerene concentric shells in the OLC described elsewhere [22].

UDD production is well-developed [14] and diamond particles of different dispersion can be prepared [23]. Thus the production of macroscopic quantities of material containing OLC can be elaborated. The further development of onion-carbon preparation techniques and the isolation of fractions with narrow size distributions can provide a new family of carbon materials with unusual properties.

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References

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, *Nature* 318 (1985) 162.
- [2] W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D. Huffman, *Nature* 347 (1990) 354.
- [3] S. Iijima, *Nature* 354 (1991) 56.
- [4] J.W. Mintimire, B.I. Dunlap and C.T. White, *Phys. Rev. Letters* 68 (1992) 631.
- [5] N. Hamada, S. Savada and A. Oshiyama, *Phys. Rev. Letters* 68 (1992) 1579.
- [6] K. Tanaka, K. Okahara, M. Okada and T. Yamade, *Chem. Phys. Letters* 191 (1992) 469.
- [7] S. Iijima, *Cryst. Growth* 5 (1980) 675.
- [8] H. Kroto, guest ed., Special issue on fullerenes, *Carbon* 30, No. 8 (1992).
- [9] D.H. Parker, K. Chatterjee, P. Wurz, K.R. Lykke, M.J. Pellin, L.M. Stock and J.C. Hemminger, *Carbon* 30, No. 8 (1992) 1167.
- [10] D. Ugarte, *Nature* 359 (1992) 707.
- [11] D. Ugarte, *Chem. Phys. Letters* 207 (1993) 473.
- [12] W.A. de Heer and D. Ugarte, *Chem. Phys. Letters* 207 (1993) 480.
- [13] Q.L. Zhang, S.C. O'Brien, J.R. Heath, Y. Liu, R.F. Curl, H.W. Kroto and R.E. Smalley, *J. Phys. Chem.* 90 (1986) 525.
- [14] A.I. Lyamkin, E.A. Petrov, A.P. Ershov, G.V. Sacovich, A.M. Staver and V.M. Titov, *Dokl. Acad. Nauk SSSR* 302 (1988) 611.
- [15] V.M. Titov, V.F. Anisichkin and I.Yu. Mal'kov, *Prepr. Papers 9th Symp. on Detonation – Portland* (1989) p. 175.
- [16] N.R. Greiner, D.S. Phillips, J.D. Johnson and F. Volk, *Nature* 333 (1988) 440.
- [17] V.L. Kuznetsov, I.Yu. Malkov, A.L. Chuvilin, E.M. Moroz, V.N. Kolomiichuk, Sh.K. Shaichutdinov and Yu.V. Butenko, *Carbon*, in press.
- [18] I. Yu. Mal'kov, V.M. Titov, V.L. Kuznetsov and A.L. Chuvilin, *Fiz. Gorenia i Vzryva* (Russian) 30, No. 1 (1994) 130.
- [19] V.L. Kuznetsov, M.N. Aleksandrov, I.V. Zagoruiko, A.L. Chuvilin, E.M. Moroz, V.N. Kolomiichuk, V.A. Licholobov, P.M. Brylyakov and G.V. Sakovitch, *Carbon* 29 (1991) 665.
- [20] H. Terrones and A.L. Mackay, *Carbon* 30 (1992) 1251.
- [21] J. Abrahamson, *Carbon* 11 (1973) 337.
- [22] P.W. Fowler, D.E. Manolopoulos and R.P. Ryan, *Carbon* 30 (1992) 1235.
- [23] I.Yu. Malkov, *Fiz. Gorenia i Vsryva* 27, No. 5 (1991) 136.