Investigation of the plasma processability of natural carbon bearing formations

V P Molchanov
Far East Geological Institute FEB RAS, 159 Prospekt 100-letiya
Vladivostok, Vladivostok, Russia, 690022
E-mail: vpmol@mail.ru

Abstract. In the south of the Russian Far East, a new perspective source of minerals was pioneered, which is the metal-bearing high carbon rocks of the Ruzhinskaya square. The rocks are rich in crystalline graphite, gold, platinum and carbon nanostructures (fullerene, nanotubes and diamond-like carbon). The technique of extraction of ultrapure (99.98%) crystalline graphite from these rocks has been developed using hydrometallurgical methods. The obtained graphite was used as a raw material for plasma-chemical tests succeeded in the separation of nanodimensional carbon structures, part of which could be inherited from the natural graphite-bearing rocks. The results of investigation will be used in the development of resource-saving technology of minerals extraction.

1. Introduction
A new perspective source of minerals has been discovered in the south of the Russian Far East [1, 2]. The high carbonaceous rocks of the Ruzhinskaya square incorporate enormous resources of as crystalline graphite as carbon nanostructures, gold, platinum and rare earths. The quantity and quality of useful components concentrated in the graphite rocks of this area indicate that in the nearest future they will determine prospects of the Russian Far East mineral raw material base development.

The main task of the investigation was to study effects of various factors on a graphite-bearing rock in order to devise physicochemical principles of profitable and environmentally acceptable technology of mineral extraction. As is known, graphite of the Ruzhinskaya square represents several varieties [3] depending on formation conditions. The first variety is a result of gas-condensate crystallization from a deep reducing fluid and is characterized by the presence of diamond-like carbon. The second variety is a product of metamorphic recrystallization of sedimentary protolith and is distinguished by the presence of fullerenes and nanotubes. The plasma experiments for synthesis of carbon nanoindividuals from the high-clean graphite extracted from ore formations of the Ruzhinskaya square were carried out having regard to these facts.

2. Methodology of experiment
Commonly, the initial material for plasma chemical synthesis of carbon nanostructures is crystalline graphite [4]. This carbon modification corresponds to a condition of thermodynamic equilibrium, therefore production of the thermodynamically non-equilibrium (unstable) carbon modifications is possible only in conditions of substantial departure from the thermodynamic equilibrium. Such conditions are easily created under intensive energy supply causing sputtering and atomization of the condensed carbon. Subsequent dispersion of carbon vapor in the space of buffer gas goes with the vapor cooling that leads to occurrence of chemically unstable state of the carbon vapor in which content of free carbon atoms many times exceeds the equilibrium value defined by a value of gas temperature. The further condensation of carbon vapor in the buffer gas under the considered non-equilibrium conditions can bring into formation of the thermodynamically equilibrium graphite structure and multiple carbon nanostructures as well.
3. Results of experiment and their discussion

The initial material for the experiment was a sample of high carbon rock from the Ruzhinskaya square with gold content 0.1-0.2 g/t and the total REE concentration up to 100 g/t. The sample was separated into silicate and graphite components by flotation, with the pine oil as a foaming agent, the terpene alcohols as a basic reagent and the long-chain amines as a collector. During the flotation, a bulk of graphite as well as compounds of rare earth elements, silicon, aluminum, iron, magnesium, calcium, sodium, and titanium were concentrated in the foam, whereas ore minerals (gold, platinum) – in the slime [5]. According to X-ray fluorescent analysis, the flotation yielded industrial graphite with the ash content of 4-7 % that corresponds to 829-73 State Standard (the graphite available for making lubricants, coats of current-conducting rubber of the increased hardness, and so on.). However, graphite used in plasma chemistry as the initial raw material is required to have the lesser ach content. To lower the ach content, graphite is usually subjected to acid treatment or alloying with soda. In our case, the high ash content of the graphite is conditioned essentially by the presence of rare earths, silicon, aluminum, iron, magnesium, and calcium. In this connection, the treatment of the foam with ammonium hydrogen difluoride and subsequent acid leaching of the fluorinated product seemed to be the most appropriate decision for picking impurities. The physicochemical basis of fluoridation with ammonium hydrogen difluoride is in the ability of oxygen-containing compounds of the transition and many non-transition elements to form easy-to-process ammonium fluometallates when interacting with NH4HF (Fig.1).

![Diagram of graphite purification](image)

**Figure 1.** Scheme of graphite purification.

In the fluorination, 25 g of the graphite concentrate was mixed with 5 g of NH4HF2, dissolved in 5 ml of water. The dense paste was being slowly heated to 190-200oC; the temperature was then raised 400°C and remained for 2 hours. As a result of this standing, 2.8 g of (NH4)2SiF6 was desublimated in the nickel condenser and 0.8 g of a mixture of NH4HF2 and NH4F in the fluoroplastic one. The NH4HF2 - NH4F mixture can be further recycled. The sublimated ammonium fluorosilicate had high purity. The admixtures content did not exceed 10-4 mass. %. The non-volatile residue in the reaction container was remixed with 5 g of NH4HF2 dissolved in 5 ml of water. The obtained paste was heated to a temperature of 190-200°C and hold at this temperature for 2 hours. The weight of the fluorinated product was 24.7 g.

The X-ray diffraction data showed that the admixtures in the doubly fluorinated product represented water-soluble fluoammonium salts of aluminum, titanium, and iron and insoluble fluorite. The leaching process consisted in double dissolving of the fluorinated product in water at the liquid-to-solid ratio of 1:10, settling of the suspension and discharging of the transparent solution. The remained portion was filtered and the resulting filtrate was evaporated to dry salts. The mass of the yielded product was 1.44 g. According to the X-ray diffraction data, the product was a mixture of complex aluminum, iron and titanium fluoammonium salts. The ash-content of the graphite purified in this way was 0.56%.

The graphite purity can be raised by acid leaching because in this case the main admixtures are insoluble calcium and magnesium fluorides. The graphite obtained at this stage was subjected to water leaching and then treated with the 10% hydrochloric acid solution at the liquid-to-solid ratio of 1:8 or with the 15% nitric acid solution at the liquid-to-solid ratio of 1:5 for an hour at 700°C. The mixture was filtered, washed with water and dried. The purity of graphite in this case comprises 99.98% [6].
There is an assumption that the REE enter into the structure of natural graphite at nanolevel [5]. In this connection it was important to determine the composition of solution of the acid leaching of fluorinated product. For this purpose nitric solution was evaporated to dryness. In the residue obtained there have been discovered high concentrations of REE (Tab. 1) that clearly confirms our conclusions about the close bonds between the rare-earth components and natural graphite.

| Element | Content (g/t) | Element | Content (g/t) |
|---------|--------------|---------|--------------|
| Y       | 67.2         | Gd      | 18.2         |
| La      | 640.2        | Tb      | 2.3          |
| Ce      | 263.4        | Dy      | 12.6         |
| Pr      | 33.2         | Ho      | 2.5          |
| Nd      | 102.4        | Er      | 7.0          |
| Sm      | 16.8         | Tm      | 0.9          |
| E       | 3.75         | Yb      | 5.3          |

Extra pure graphite can find a wide application as a constructive material in atomic power and heat engineering, as well as a starting material for preparing colloid graphite, graphitic oxide and extended graphite for use in microelectronics (production of electronic components), aircraft construction and automobile industry (fuel system parts, fuel pipes), defense industry.

The extra pure graphite was taken for making rods and a charge which were later used for producing the electric-arc plasma. The charge is a mixture of graphite powder and a collector looking like shavings of low carbon steel.

For experimental use, a plasma chamber was built. The hermetic right-angled chamber with internal dimensions 1000x800x80 mm is equipped with feed and evacuation system for buffer (and cooling, if necessary) gas, quartz windows for optical observations and measurements, and built-in thermo inlets for voltage supply on the plasmatron located inside the chamber. This laminar plasmatron worked as a generator of low temperature plasma. Coefficient of the plasma-generating gas (argon) compression consisted n=0.5-0.8. For electrodes, graphite rods of natural material were used. Electric arcing caused the charge melting.

Plasma chemical method application allowed obtaining the dispersive materials, which then have been studied with the help of Dron equipment, microprobe analyzer, atomic-force and scanning electron microscopes. The results of the study showed that the powder contained high amounts of fullerenes, carbon nano-tubes and diamond-like graphite.

The comparison of native carbon nanotubes discovered in the Ruzhinsky graphite (Fig. 2) and the synthetic nanoforms synthesized from the same material exhibits their great outward and inward resemblance. This similarity may be because of some carbon nano individuals (first of all diamond-like carbon) which could pass from the native graphite-bearing rocks. It seems that the study of native and synthetic carbon nano-objects generation should develop in two complementary ways. The developed technology for obtaining carbon nanomaterials with desired features will be in demand in various fields of science and technology. The designing of new techniques for the mass production of diamond-like carbon and carbonaceous nanotubes to be used, for example, in composite material [7], or nanotubes with given parameters for electronics and metrology [8] becomes perspective.

Figure 2. The image of carbonaceous nanostructure on native graphite – a, the enlarged image of the laminated carbonaceous nanotube with fullerite-like structures – b.
The fulfilled investigations made it possible to create a brand new integrated technology for a useful components extraction. At its first stage, flotation methods are needed to have noble metals and industrial graphite extracted. At the second stage the industrial graphite is treated by ammonium hydrofluoride to remove impurities, first of all rare earths. Then the obtained ultrapure graphite is subjected to plasma chemical procedure with the object of separating out the carbonaceous nanostructures (fullerenes, nanotubes, diamond-like carbon).

4. Conclusion
The fulfilled investigations made it possible to create a brand new integrated technology for a useful components extraction. At its first stage, flotation methods are needed to have noble metals and industrial graphite extracted. At the second stage the industrial graphite

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