

Laboratory facility for working with supercritical fluids

A. I. Izotov, G. V. Kilman, R. V. Shalaev, A. M. Prudnikov

Donetsk Institute for Physics and Engineering named after A. A. Galkin,

R. Luxembourg str. 72, 83114, Donetsk, Ukraine

sharos@donfti.ru

DOI 10.17586/2220-8054-2018-9-4-532-536

An apparatus for working with supercritical fluids has been developed, and results have been obtained on purification of the diamond blend by supercritical isopropanol, as well as by selective etching of CN_x films. It is shown that the proposed method for purifying diamond blend in supercritical isopropanol is not only effective, but also quite simple to use.

Keywords: supercritical fluids, diamond blend, carbon nitride.

Received: 14 December 2017

Revised: 24 December 2017

1. Introduction

Supercritical fluid (SCF) is a form of the aggregate state into which many organic and inorganic substances are able to pass when a certain temperature and pressure are reached. The SCF is a phase that exists somewhere between gas and liquid. It can compress like a gas and, at the same time, is capable of dissolving solids, which is not peculiar to gases. In this case, the dissolution capacity of SCF is very sensitive to changes in temperature and pressure, which makes the process completely controllable [1]. A combination of low viscosity and high diffusion coefficient with negligible interfacial tension allows supercritical fluids to penetrate relatively easily into porous media [2]. Not surprisingly, these interesting properties have attracted the attention of a wide range of researchers.

However, supercritical fluids began to be widely used only in the late 1980s, when the general level of industrial development made it possible to make installations for obtaining SCF relatively affordable. Then the intensive development of supercritical technologies began.

The pharmaceutical industry was one of the first to apply the new technology, because SCF allows the most complete extraction of biologically active substances from plant raw materials, keeping their composition unchanged [1,2]. In perfumery and cosmetics, SCF is used to extract essential oils, vitamins, phytoncides from plant and animal products. At the same time, there are no traces of solvent in the extracted substances, and the soft extraction method allows preservation of their biological activity [1]. In the food industry, the new technology makes it possible to extract delicately various flavoring and aromatic components from vegetable raw materials [2]. Radiochemistry uses SCF to solve environmental problems [1]. The previously mentioned property of fluids – to change the dissolving power with increasing pressure – is widely used in polymer chemistry.

Given all of the above, and the fact that SCF-technologies are often cheaper to use than traditional ones, it is not difficult to understand why interest in supercritical fluids has increased over the last few decades. Substances in the supercritical state find new applications, and plants for their production are constantly being improved.

In this paper, we describe the construction and operation principle of a laboratory apparatus for working with SCF that we developed. This apparatus is designed to carry out experiments with relatively small volumes of working substance and is characterized by sufficient accuracy, reliability and safety. Some experimental results for the purification of a diamond blend and processing of thin carbon films, obtained with the help of this device are also presented in the work.

2. Description of the installation and experimental procedure

The scheme of the developed apparatus is shown in Fig. 1. A similar apparatus (with some differences that will be described below) and the method of operating it are also considered in [3].

The apparatus consists of a high-pressure chamber with a heater and thermal insulation. The temperature is monitored and automatically maintained within a given range by the controller 4 (“Termotest-04/2”) having an accuracy of ± 1 °C and a range of 0 – 1000 °C. The pressure is controlled by a MTI type pressure gauge 7 with a range of 0 – 250 kgf/cm².

Preliminary setting of the voltage on the heater is carried out by an adjustable autotransformer 6. The fine adjustment valve serves to relieve the excess pressure 10. The presence of this valve is the main difference of our

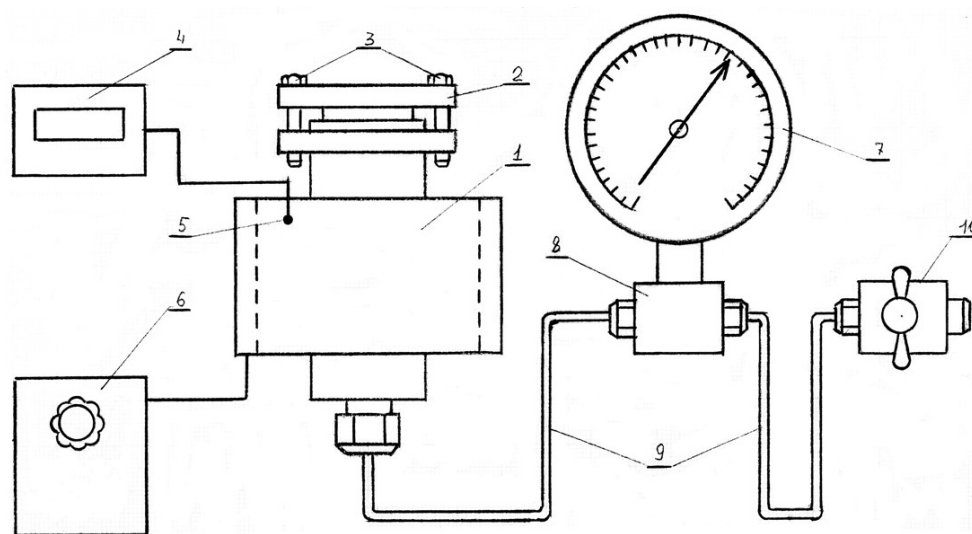


FIG. 1. Scheme of installation for working with supercritical fluids: 1 – high pressure chamber with heater and thermal insulation; 2 – the camera cover; 3 – cover fixing bolts; 4 – temperature controller; 5 – thermocouple; 6 – adjustable autotransformer; 7 – manometer; 8 – T-piece; 9 – high pressure tubes; 10 – fine adjustment valve

apparatus from that described in [3]. It permits more accurate entry into the operating mode, without interrupting the experiment, and maintain the desired pressure value for the entire specified time period.

The high-pressure chamber is shown in detail in Fig. 2.

Chamber 1 is made of heat-resistant stainless steel. On top of the camera is a heater 2 with thermal insulation. A supporting beaker 3 is inserted into the chamber, also made of heat-resistant stainless steel, with a glass tube 4 in which the sample being processed in the experiment. The beaker is designed to preserve the sample in the event of a breakdown of the tube during heating.

The chamber is hermetically sealed with a cover 5. The hermetic integrity of the cover and the outlet tube is provided by copper gaskets 6 and 7.

The method of operating the apparatus is quite simple. The experiment is carried out as follows. A sample to be processed is loaded into the glass tube 4. The tube and chamber 1 are filled with a working substance (we used isopropanol), the amount of which is determined experimentally, in the same way as in [3], but with a small margin, to further be able to more accurately adjust the pressure, dosing it with a fine adjustment valve 10.

Then the chamber is closed by the cover 5 and the heater is turned on. The heating speed is controlled by a step-by-step voltage supply to the heater. With constant pressure monitoring, the temperature is brought to the set value, after which it is automatically supported by the controller 4.

The specified temperature and pressure are maintained for the required period of time; then the heater is turned off and the sample is cooled. After cooling, the cover of the chamber is opened, the tube is removed, and the sample is transferred for further investigation.

The camera allows operation at temperatures up to 300 °C and pressures up to 200 kgf/cm².

3. Results and discussion

The diamond blend with the characteristic nanocrystallite size of about 4 – 5 nm in a glass tube was placed in a high-pressure chamber, as described above. Samples were processed in supercritical isopropanol at the temperature of 240 °C and the pressure of 55 atm for 6 hours.

IR absorption spectra of samples obtained before and after treatment are shown in Fig. 3. The spectra demonstrate the presence of various absorption bands characteristic of the C–H, N–H, O–H bonds, etc., from which the shell of diamond nanocrystallites consists [4,5]. It can be seen from the figure that after treatment with SCF, a noticeable decrease in the intensity of IR absorption bands of oxygen-containing bonds is observed. This indicates an effective etching of the crystallite shell during processing.

Typical Raman spectra of samples in the wave number range 1100 – 1800 cm⁻¹ are shown in Fig. 4. The spectrum consists of at least four components with maxima of approximately 1220 cm⁻¹ (TPA-transpolyacetylene chains), 1322 cm⁻¹ (diamond phase), 1500 cm⁻¹ and 1620 cm⁻¹ (sp²-hybridized carbon), which characterize the

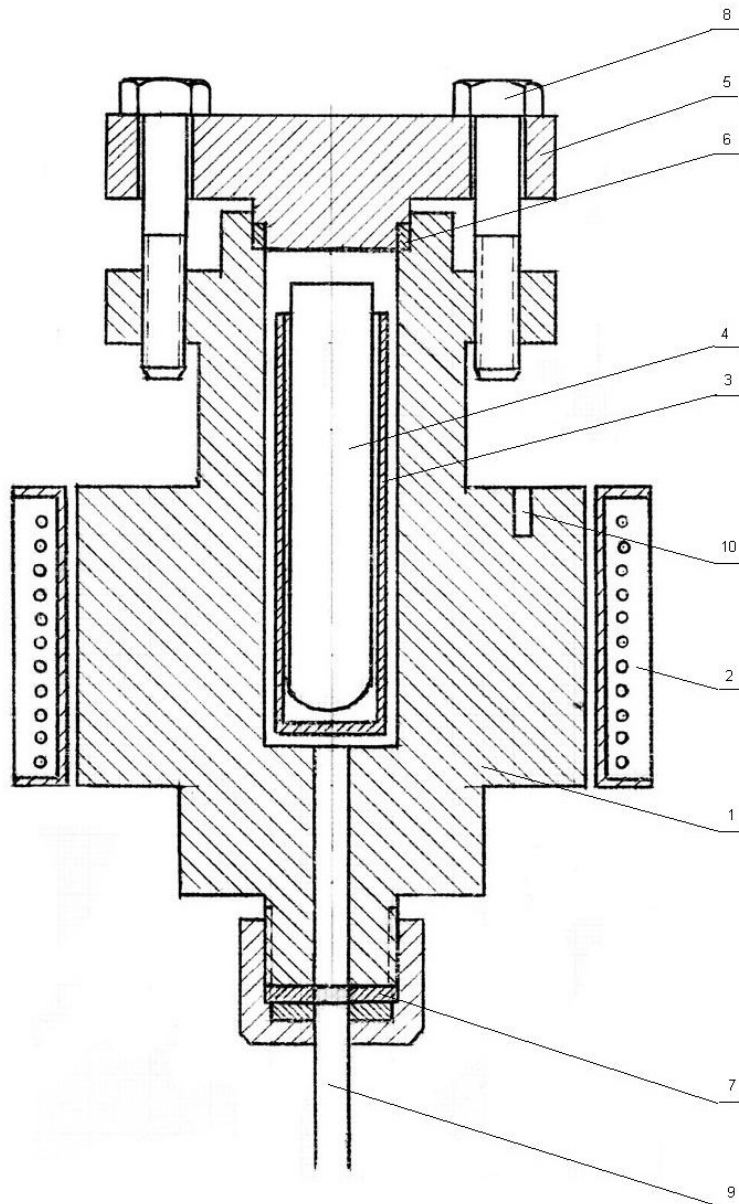


FIG. 2. High pressure chamber: 1 – housing; 2 – heater with thermal insulation; 3 – steel beaker; 4 – glass tube; 5 – cover; 6, 7 – copper gasket; 8 – cover fixing bolts; 9 – outlet tube

volume and surface of diamond crystallites [4,6]. In Fig. 4b, a noticeable increase in the half-width of the diamond line is observed after processing the sample in supercritical isopropanol. This is associated with a decrease in the size of the diamond nanocrystallites by removing the surface defect layer.

Carbon nitride films CN_x were grown by the magnetron sputtering of a graphite target in a nitrogen atmosphere on a cover glass substrate. Films with graphite-like properties were selected for the experiment. They are characterized by low hardness and weak adhesion. The obtained samples were processed in supercritical isopropanol at a temperature of 240 °C and a pressure of 55 atm for 20 min.

The transmittance spectra of the CN_x film studied before and after the treatment are shown in Fig. 5. It can be seen that as a result of the processing, the transparency of the sample as a whole increased, although in the visible region, this increase is not that large. On the spectrum of the sample after treatment, the displacement of the absorption edge toward higher energies is also well marked, which indicates an increase in the optical band gap of the investigated sample. Further calculations carried out graphically showed that the band gap width of the film actually increased by approximately 15 % (from the initial 1.7 eV to 1.95 eV).

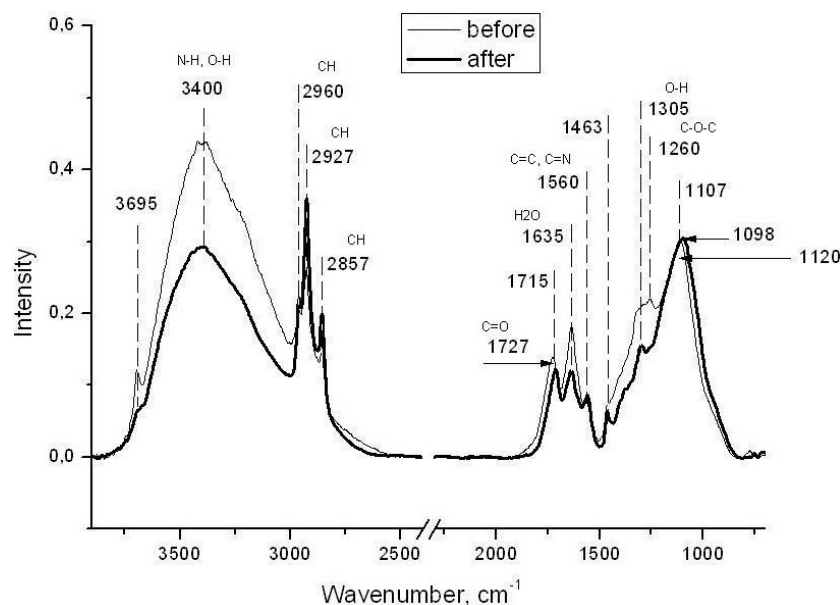


FIG. 3. Infrared absorption spectra of diamond blend before and after treatment

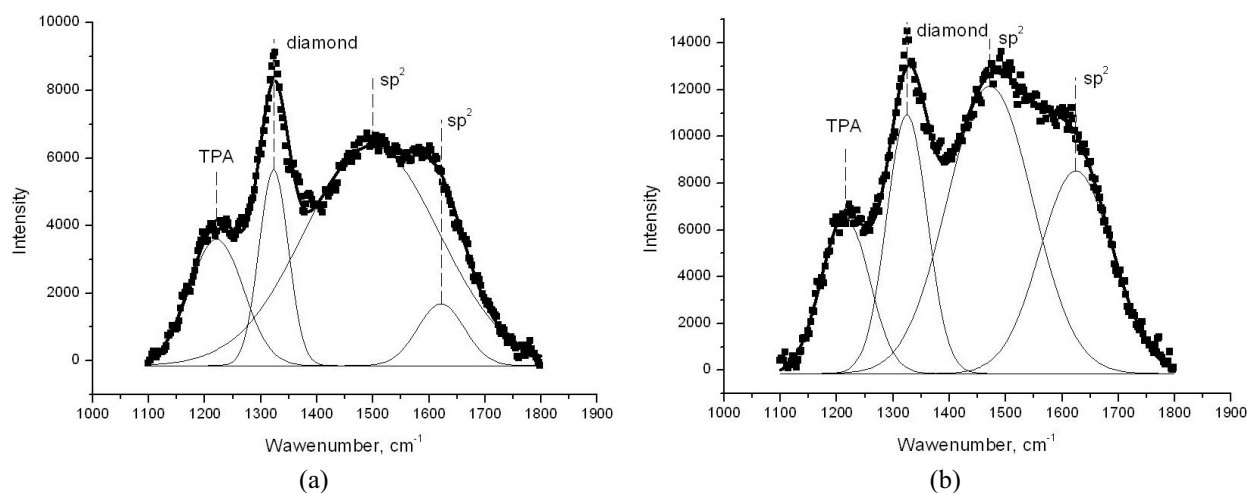


FIG. 4. Raman spectra of diamond blend before treatment (a) and after treatment (b)

It is known that this material is an inhomogeneous metastable structure consisting of two different phases [7]. This structure contains in the amorphous medium elements formed by sp^3 -hybridized C and N atoms, as well as clusters of trigonal sp^2 -hybridized C and N atoms. The physical properties of the resulting film coatings depend, to a considerable extent, on the amount and ratio of the above structural components. In particular, the inverse relationship between the fraction of atoms with sp^2 -hybridization and the band gap width is indicated in [8]. Taking this into account, it can be assumed that an increase in the optical band gap width of carbon nitride films is the result of selective etching of functional groups in the sp^2 state under the influence of supercritical isopropanol.

4. Conclusions

Thus, the efficiency of the developed installation to work with SCF is shown. It is shown that, as a result of the treatment, the transparency of carbon nitride films has increased, and the band gap width has been increased, presumably as a result of selective etching of sp^2 -hybridized carbon. Also, based on the results of the experiment, it can be concluded that the proposed method for purifying diamond blend in supercritical isopropanol with the help of this apparatus is not only effective but also quite simple to use. Obviously, the described method has obvious advantages in comparison with the use of aggressive hot acid media for prolonged periods [9, 10].

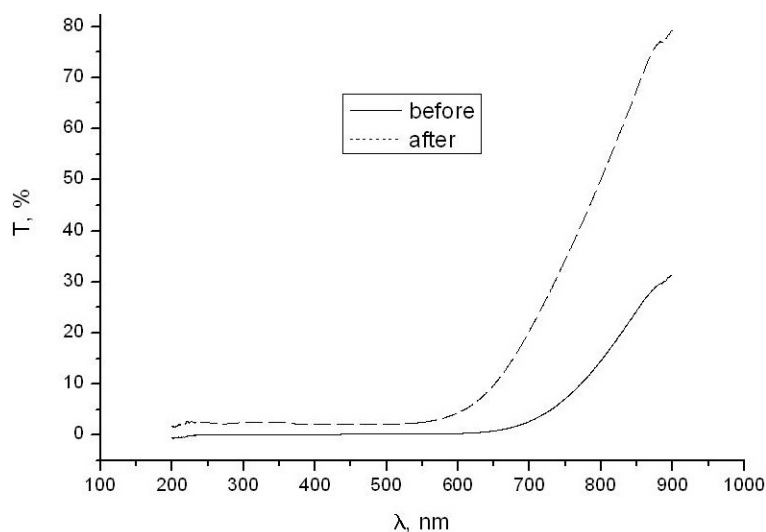


FIG. 5. The transmission spectra of the CN_x film before and after treatment

References

- [1] Beketova A.B., Kasenova Zh.M. State of the art of progress Supercritical fluid technologies. *Bulletin of the L. N. Gumilyov Eurasian National University*, 2012, **4**, P. 249–255.
- [2] Zalepugin D.Yu., Tilkunova N., Chernyshova I.V., Polyakov V.S. Development of technologies based on supercritical fluids. *Supercritical fluids: theory and practice*, 2006, **1** (1), P. 27–51.
- [3] Buslaeva E.Yu., Gubin S.P. Supercritical isopropanol as a reducing agent for inorganic oxides. *Supercritical fluids: theory and practice*, 2009, **4** (4), P. 73–96.
- [4] Uglov V.V., Shimanski V.I., Rusalsky D.P., Samtsov M.P. Spectral analysis of the structure of ultradispersed diamonds. *Journal of Applied Spectroscopy*, 2008, **75** (4), P. 546–549.
- [5] Baidakova M.V., Kukushkina Yu.A., Sitnikova A.A., Yagovkina M.A. et al. Structure of nanodiamonds prepared by laser synthesis. *Physics of the Solid State*, 2013, **55** (8), P. 1747–1753.
- [6] Ferrari A.C., Robertson J. Origin of the 1150 cm^{-1} Raman mode in nanocrystalline diamond. *Phys. Rev. B*, 2001, **63** (12), P. 121405-4.
- [7] Robertson J., O'Reilly E.P. Electronic and atomic structure of amorphous carbon. *Phys. Rev. B*, 1987, **35**, P. 2946–2957.
- [8] Kolpakov A.Ya., Sujanskaya I.V., Galkina M.E., et al. Effect of the degree of nitrogen doping and thickness on the electrical conductivity and morphology of nanoscale carbon coatings on silicon. *Russian nanotechnology*, 2011, **6** (3-4), P. 43–45.
- [9] Dolmatov V.Yu. Detonation-synthesis nanodiamonds: synthesis, structure, properties and applications. *Russ. Chem. Rev.*, 2007, **76** (4), P. 339–360.
- [10] Sushchev V.G., Dolmatov V.Yu., Marchukov V.A., and Veretennikova M.V. Principles of the chemical purification of detonation diamond-containing mixture by nitric acid. *Journal of Superhard Materials*, 2008, **5**, P. 16–25.