NONEQUILIBRIUM PROCESSES AND THEIR APPLICATIONS

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INTRODUCTION

Low-temperature plasma generators are widely used in various branches of industry, and the technological processes developed on their basis have been long applied at numerous enterprises of our Republic. These processes are based on the arc discharge plasma or, as it is often called, thermal plasma, which is characterized by equilibrium distribution of thermal energy over the internal degrees of freedom of a plasma-forming gas. This means that at a given pressure the physical and chemical properties of such a plasma are determined by its temperature which can attain several thousand degrees in modern arc plasmatrons. As a matter of fact, the role of a low-temperature arc plasma generator reduces to rapid heating of a gas up to high temperatures, at which some physicochemical processes are intensified. The latter fact makes plasma technologies very energy-intensive so that the production based on them not always appears efficient from the energy viewpoint.

One of the possible ways of raising the energy efficiency of plasma technologies is the use, where it is possible, a nonequilibrium plasma. The main distinct feature of nonequilibrium plasma systems as compared to equilibrium ones is the substantially nonequilibrium distribution of energy over the internal degrees of freedom of a plasma-forming gas, with the very sense of the notion of temperature in its classical traditional understanding being lost when applied to nonequilibrium systems. Each of the degrees of freedom of the particles composing a plasma-forming gas (translational, rotational, vibrational, and electronic) under nonequilibrium conditions is characterized by its own energy that may differ an order of magnitude from that it could have under equilibrium conditions at the same average plasma energy. A typical example of the device employing a nonequilibrium plasma is the popular daylight lamp, where, under the conditions of a low-pressure glow discharge, excitation of the electron degrees of freedom of the working gas molecules occurs, and the excited molecules lose an excess energy by radiation which we see every time we switch on the lamp. The typical, for the conditions of a glow discharge, distribution of energy over the internal degrees of freedom of the working gas molecules is as follows: the translational and rotational degrees of freedom are characterized by an average energy of an order of 0.03 eV, which in an equilibrium situation could correspond to the temperature close to a room one; the vibrational degrees of freedom have an average energy of about 0.3 eV, which in an equilibrium situation would correspond to a temperature of several thousand degrees; and, finally, the electronic degrees of freedom are characterized by an average energy of the order of several electron-volts, which in the case of equilibrium would correspond to a temperature of several tens of thousands of degrees. Here, the characteristic energy of free electrons and ions may differ from the average energy of the electronic degrees of freedom of the exciting gas molecules and attain tens of electron-volts. Sustainment of a nonequilibrium state as strong as this in the gas is possible only at the expense of an external electric field “warming up” the electrons in a discharge that acquire the energy sufficient for ionization of the gas and provision of its conductivity as well as for exciting the internal degrees of freedom of the working gas atoms and molecules. Another widely known example of application of a nonequilibrium plasma is furnished by molecular gas lasers (the most popular of them are the lasers operating on vibrational-rotational transitions of the carbon dioxide and carbon monoxide molecules), in which the energy of the vibrational degrees of freedom, repopulated as against the equilibrium situation, is emitted in the form of a coherent infrared-range radiation.

1. Physical Principles Underlying Technological Applications of a Nonequilibrium Plasma

The basic idea behind the technological application of a nonequilibrium plasma is to excite precisely those internal degrees of freedom of the gases participating in a technological process that play the key role in implementing some types of physicochemical processes. For example, the majority of exchange reactions involving molecules proceed only due to the break of one or another type of chemical bonds between atoms and formation of new energetically more favorable bonds. The energy of the translational degrees of freedom practically plays no part in this process, since the break of a chemical bond between the atoms in a molecule occurs on excitation of a certain mode of vibrations of the molecule which corresponds precisely to this bond. Under the conditions of an equilibrium plasma, the vibrations of the molecules are excited thermally and the process is accompanied by equilibrium distribution of energy over all the degrees of freedom of reacting molecules. Thus, a possible increase in the energetic efficiency of the process occurring under nonequilibrium conditions as against equilibrium ones must be proportional to the ratio between the energy contained in all the degrees of freedom (under the conditions of an equilibrium plasma this energy is proportional to the heat capacity of the working gas C) and the energy contained only in the vibrations of molecules (under the conditions of a nonequilibrium plasma this energy is proportional only to the vibrational component of the working gas heat capacity C_v). Since in plasma systems energy is supplied only due to the operation of an external source of electric current, the energy consumption in a nonequilibrium process W_{non} is C/C_v times less than in an equilibrium one W_{eq}, which, under typical conditions of a glow discharge in molecular gases, yields a triple decrease in energy consumption during the progress of chemical reactions under nonequilibrium conditions. Schematically the process of stimulation of a chemical reaction in a nonequilibrium plasma is presented in Fig. 1, where the activation barrier of the reaction with an activation energy E_a is surmounted due to the accumulation of energy in the vibrations of molecules-reagents excited by the electrons warmed-up by an external electric field; in this case the value of the energy of the translational degrees of freedom can be close to the equilibrium one corresponding to the room temperature of the gas. Since the quantity of the excited molecules having the vibrational energy corresponding to the energy of the activation barrier of the reaction E_a is proportional to the Boltzmann factor exp $(-E_a/kT_v)$, where T_v is the so-called "vibrational" temperature of the working gas (equilibrium gas temperature at which the equilibrium energy contained in the vibrations of the molecules could be equal to the energy of vibrations of a nonequilibrium gas), the intensity of the nonequilibrium process must be much higher than that of the equilibrium one at the same energy put into the plasma. Since the mechanism of formation of nonequilibrium distributions of molecules over the energy states of different degrees of freedom is based on the kinetic processes of energy exchange between the particles composing the plasma, the systems of the type described are usually called kinetically nonequilibrium as compared to thermally nonequilibrium, which are characterized by an equilibrium distribution of energy over the internal degrees of freedom of molecules-reagents, but have a strongly inhomogeneous spatial temperature distribution in a plasma.

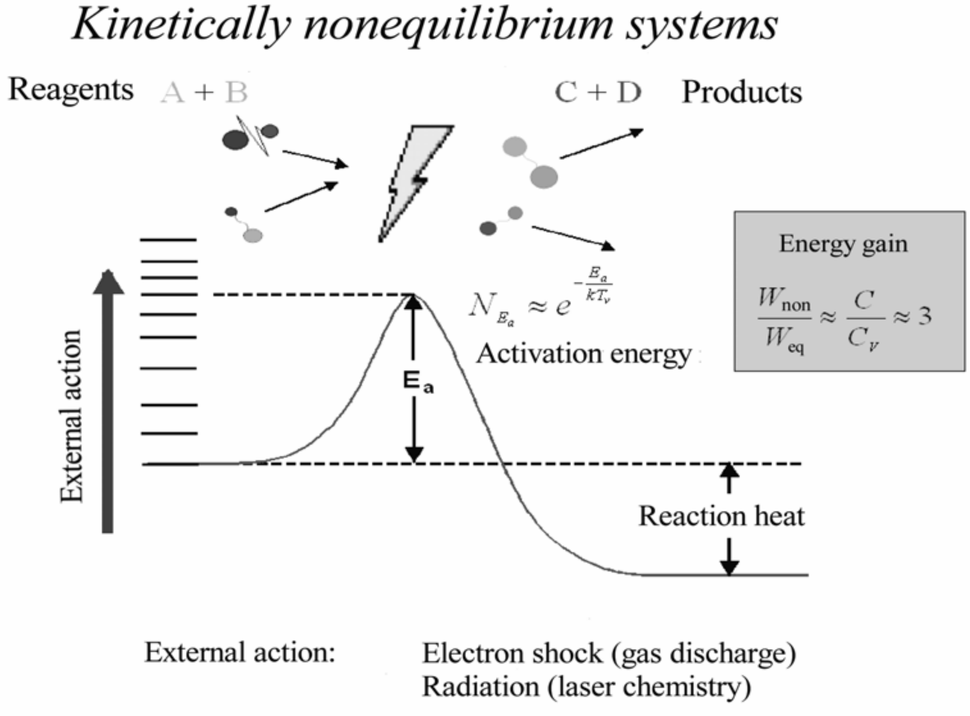

Fig. 1. Schematic representation of a nonequilibrium process

2. Technological Applications of a Nonequilibrium Plasma

As is already noted in Introduction, a low-pressure glow discharge is the most widespread form of gas discharge in which a nonequilibrium plasma is generated. Although it has been rather well studied, such a discharge can be hardly used for solving the majority of applied problems, because its stable sustainment is possible only at low pressures. Of greatest interest, from the viewpoint of practical applications, are atmospheric-pressure electric discharges the realization of which implies special measures of stabilization needed to suppress numerous instabilities that develop in a nonequilibrium plasma at elevated pressures. In the present work, the problem of possible instabilities in atmospheric-pressure gas discharges and the ways of their stabilization are not analyzed, since the problem has been covered in the magnificent monograph of Yu. P. Raizer "Gas-Discharge Physics", Nauka Press, 1987. We only briefly consider some types of atmospheric-pressure electric discharges that have found application in solving specific applied problems that correspond most closely with the professional activity of the present author.

An atmospheric-pressure high-voltage discharge is one of the simplest electric discharges that have found application in various plasmachemical processes. It has been investigated rather in detail and described by some research workers of the Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus (see, e.g., E. M. Vasilieva, S. A. Zhdanok, and L. A. Sergeeva "Investigation of an atmospheric-pressure high-voltage discharge and its use for treating surfaces", Journal of Engineering Physics, Vol. 58, No. 1, 1990). The schematic diagram of the atmospheric-pressure high-voltage discharge (APHVD) and the photo of the discharge gap in which a nonequilibrium plasma is generated are presented in Figs. 2 and 3. The APHVD made it possible to implement such nonequilibrium technological processes as nitrogen fixation, dissociation of carbon dioxide, nitration of metals, conversion of a hydrocarbonic fuel into hydrogen, etc. Of particular interest is the possibility of using the APHVD nonequilibrium plasma for synthesizing carbon nanotubes (CNT) which constitute a very promising material for application in various fields of engineering due to their unique properties.

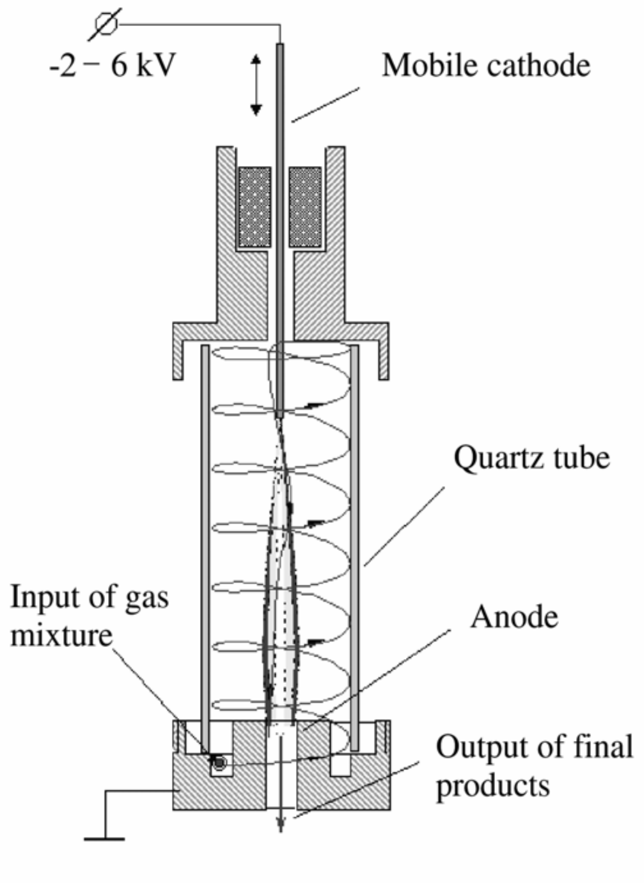

Fig. 2. Schematic diagram of an APHVD

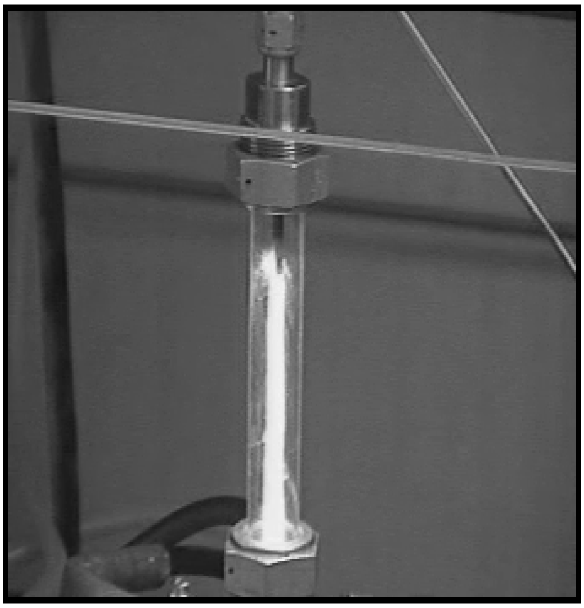

Fig. 3. Photograph of the discharge zone of an operating APHVD

Carbon nanotubes were discovered in 1991 by Japanese researcher Sumio Iijima and since continue to attract an ever increasing attention of both scientists and diverse practitioners. Carbon nanotubes possess a number of unique properties that set them off from all the earlier known materials. With the availability of the technology of mass production they are capable of revolutionizing the whole branches of economy and become a base for forming a fundamentally new technological organization of the society in general.

Among the most important properties of the carbon nanotubes we may single out the following:

- the mechanical strength exceeds the strength of steel 100 times,
- the ratio of the mechanical strength to weight is 500 times higher than in aluminum,
- the electroconductance is as in copper,
- the thermal conductivity is as in diamond.

The uniqueness of the properties of the carbon nanotubes determines the areas of their potential application which today are as follows:

- carbon nanotubes-based composite materials,
- molecular engineering,
- nano-sized robots, devices, sensors,
- energy storage systems and transformers,
- nanoelectronics and computer engineering,
- vacuum microelectronic devices,
- hydrogen accumulators,
- bionics.

According to the NASA specialists, application of carbon nanotubes-based composite materials in space technology will make it possible to create systems of repeated launchings whose weight will be 20% less than those available and to devise conceptually novel specimens of aircraft whose effective range will be 25% larger with a 30% decrease in specific consumption of material and a 20% decrease in hazardous ejections. Application of carbon nanotubes as facilities of autoelectronic emission will allow one to create plane TV and display screens, revolutionize microelectronics and related areas of production.

The main problem on the way of a wide application of carbon nanotubes is their exceptionally high cost (at the present time there are only several firms on the American market such as, e.g., “CARBOLEX”, that offer carbon nanotubes in small quantities at the cost of 100 $/gram) and the absence of a large-scale production technology.

The technique of production of carbon nanotubes in a nonequilibrium plasma is based on the idea of effectuating a reaction of disproportionation of carbon oxide with participation of vibrationally excited CO molecules under strongly nonequilibrium conditions at relatively low temperatures of the order of 500°C at atmospheric pressure, with the activation barrier of the reaction (~5.5 eV) being surmounted at the expense of the energy of the vibrational degrees of freedom of CO molecules excited by an electron shock in an APHVD. Figure 4 shows specimens of the carbon nanotubes synthesized in an APHVD.

The above-described method of synthesis of carbon nanotubes in a nonequilibrium plasma has made it possible to carry out scaling of the process and, using inexpensive and easily attainable raw material, to begin mass production of carbon nanotubes for the needs of the domestic market and exporting to other countries.

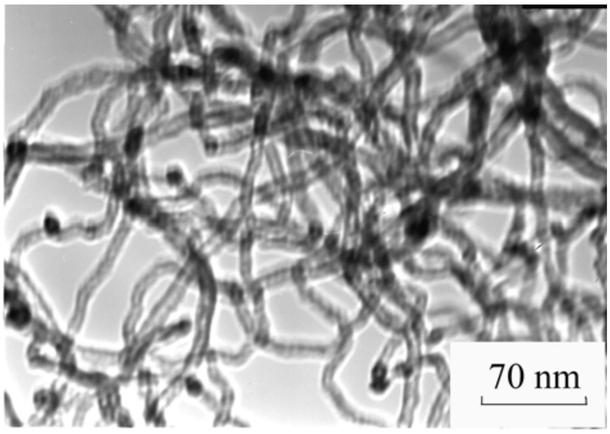

Fig. 4. Microphotograph of carbon nanotubes synthesized in an APHVD

Another discharge, simple to realize and effective in creating a nonequlibrium plasma, is the so-called barrier discharge that has been well studied and described in scientific literature (see, e.g., V. G. Samoilovich, V. I. Gibalov, and K. V. Kozlov "Physical Chemistry of the Barrier Discharge", MGU Press, Moscow, 1989). This electric discharge consists of a set of microscopic streamer discharges propagating in the gap between two electrodes, one or both of which are dielectrics. On supply of an alternating voltage to these electrodes, there occurs alternative charging and discharging of the capacitor formed by these electrodes, and these processes are accompanied by a virtually homogeneous filling of the interelectrode space by a vast number of streamers. One of the most important nonequlibrium processes realized under the conditions of the barrier discharge is synthesis of ozone from atmospheric oxygen. In this process, in the zone of the electric discharge dissociation of oxygen molecules occurs at a low temperature of the translational and rotational degrees of freedom and at a high energy of the electronic degrees of freedom and the resulting oxygen atoms form ozone molecules while interacting with molecular oxygen. The ozone generators, based on the barrier discharge with a special electrode system and an optimized power supply, have been developed at the Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus and successfully tested at some of the enterprises of the Republic of Belarus on systems of water treatment and also in ozone-therapy apparatuses on order of the Ministry of Health of the Republic of Belarus. One of the specimens of such a generator together with the electrode system is presented in Fig. 5.

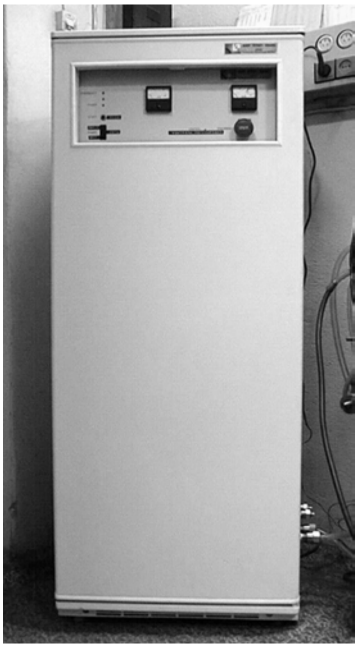 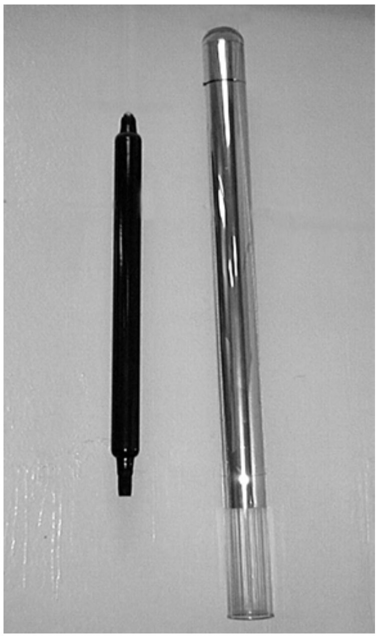

Fig. 5. External view of the ozone generator based on a barrier discharge (on the left) and of its original electrode system (on the right) — both developed at the A. V. Luikov Heat and Mass Transfer Institute

Among the most interesting nonequilibrium technological processes realized under the conditions of a barrier discharge is plasma-induced modification of the surface of polymeric materials. The physics of the process is as follows: at high values of the energy of the electronic degrees of freedom in a plasma-forming gas in the region of the discharge adjacent to the surface of a polymeric material, a partial dissociation of molecules occurs as well as formation of free radicals OH, O, N, etc. having a high reactivity. These radicals interact with the carbon atoms and form new bonds on the polymer surface modifying it and imparting new properties to it, with the temperature of the translational degrees of freedom remaining close to a room one, which allows avoidance of fusion of the surface treated. Thus, the Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus has accomplished nonequlibrium process of modification of polyethylene, polypropylene, Teflon, and of other polymeric materials that allowed us to considerably increase the adhesive properties and wettability of their surface, which is extremely important for application of these materials in the printing and packing industries. Figure 6 presents a photograph of the experimental setup based on a nonequilibrium plasma of the barrier discharge for modification of the surface of polymers. The setup has been developed at the Heat and Mass Transfer Institute as a result of many-years investigations of the physics and chemistry of nonequilibrium systems.

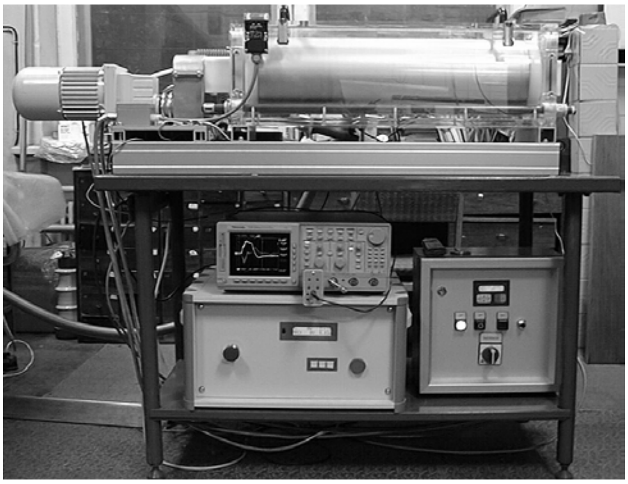

Fig. 6. Experimental setup for modification of the surface of polymers, based on the nonequlibrium plasma of a barrier discharge

An interesting application of a nonequlibrium plasma is for purifying gas ejections by industrial enterprises and vehicles from organic impurities, nitric oxides, and soot. The mechanism underlying stimulation of redox reactions in gas flows excited by an electric discharge is the same as in the case of modification of polymeric surfaces: “warming-up” of the electronic and vibrational degrees of freedom of the molecules composing a gas and, as a consequence, formation of the OH, O, N, H radicals, precisely which accelerate the progress of chemical reactions in the gas being purified. The degree of purification may attain 99% at relatively modest loss of electric energy. Figure 7 shows the photographs of purification facilities based on the nonequilibrium plasma of a barrier discharge. They have been developed at the Heat and Mass Transfer Institute and installed in one of the shops of the Minsk Refrigeration Equipment Factory.

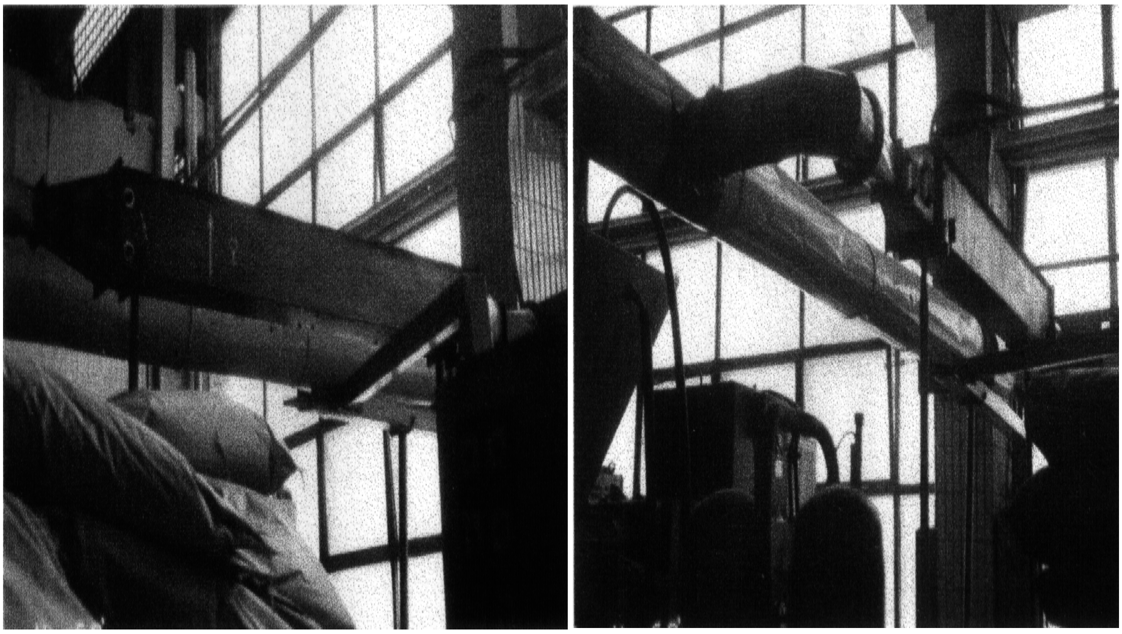

Fig. 7. Nonequilibrium plasma-based purification systems installed in the shops of the Minsk Refrigeration Equipment Factory

A barrier discharge in capillary-porous bodies creates the most interesting systems that vividly manifest the unique properties of the nonequilibrium plasma. Its realization in an operating exhaust system of a diesel has made it possible to decrease ejections of nitric oxides and soot by 60%. Figure 8 represents the photographs of a porous body formed by a packing of Al_2O_3 particles before and after initiation of the barrier discharge in it. It is clearly seen that the plasma fills practically the entire space of the pores which makes it possible to arrange fundamentally new technological processes that combine the advantages of the nonequilibrium plasma and classical catalysis.

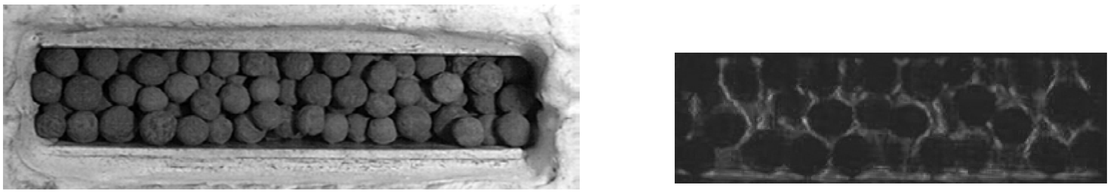

Fig. 8. Porous body formed by a packing of Al_2O_3 small balls of diameter 2 mm before and after initiation of a barrier discharge in it

Figure 9 presents photographs of the elements of a filter in the form of a packing of Al_2O_3 small balls, of different modifications, 2 mm in diameter placed in the exhaust section of a diesel before switching-on of the engine, after its brief operation, and after initiation of a barrier discharge in the packing.

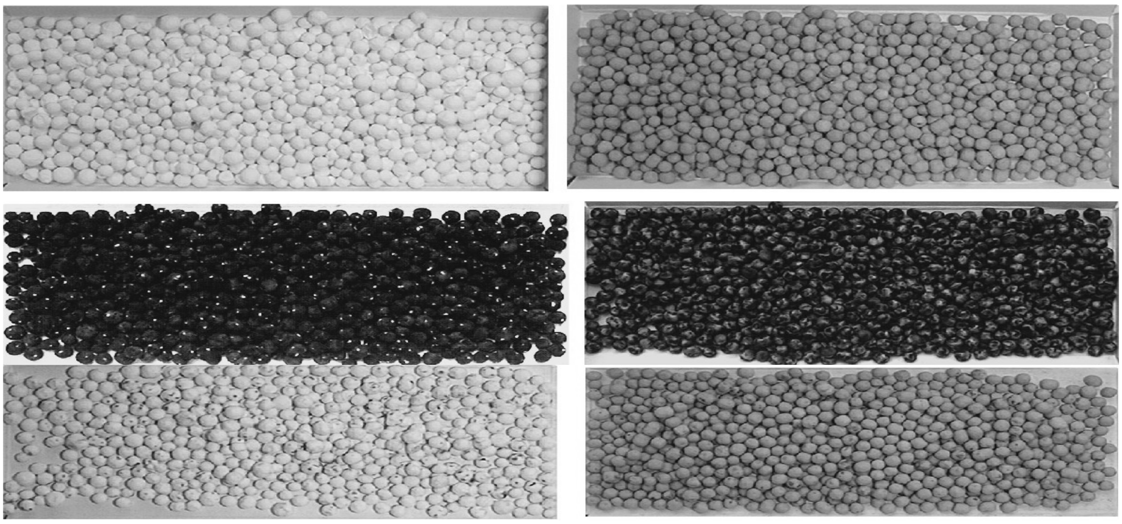

Fig. 9. Elements of the diesel filter based on the barrier-discharge nonequilibrium plasma before and after the start of the engine and also after initiation of the discharge (from above downwards)

As is seen from the photographs, initiation of a barrier discharge in the vapor space of the packing leads to complete filter material regeneration based on stimulation of oxidation reactions under the conditions of a nonequilibrium plasma. The general view of a 2-liter diesel together with a system of nonequilibrium plasma-based purification of exhaust gases is presented in Fig. 10. In the case of 60% purification from nitric oxides and soot particles the filter expends 1 kW from the automobile generator and can be easily installed in its exhaust section.

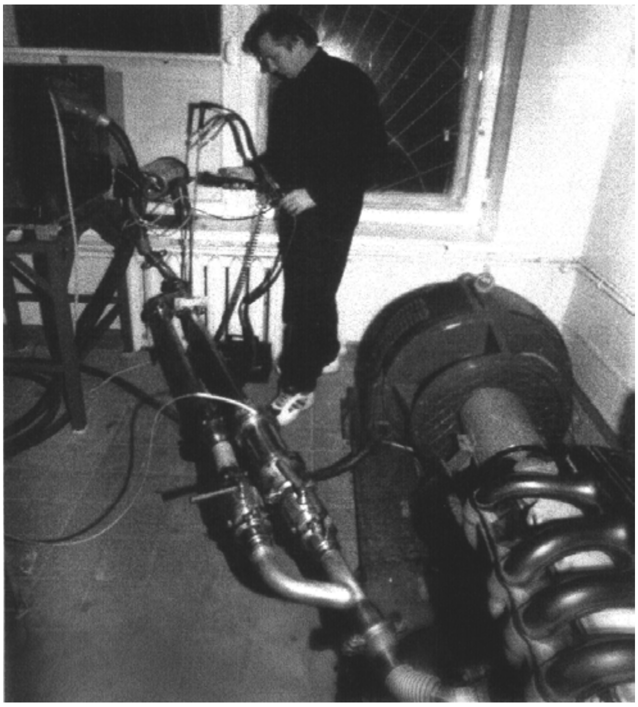

Fig. 10. General view of a diesel with a plasma system of purification of exhaust gases

Another type of a gas discharge characterized by nonequilibrium distribution of energy over the internal degrees of freedom of the atoms and molecules of a plasma-forming gas is a high-current discharge stabilized by a magnetic field. The physical model of such a discharge is shown in Fig. 11.

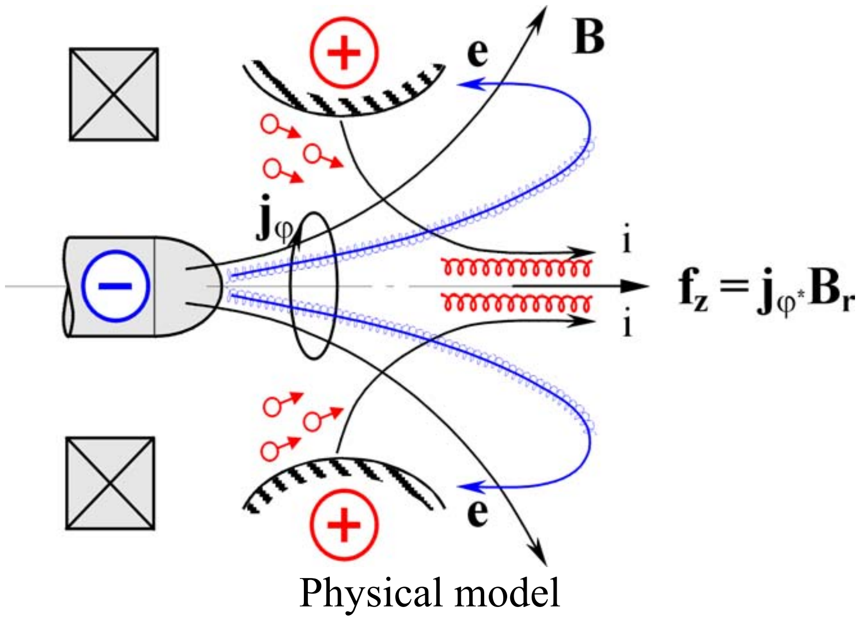

Fig. 11. Schematic representation of a high-current discharge stabilized by a magnetic field

The configuration of the magnetic field *B* in the discharge presented in Fig. 11 causes its interaction with the azimuthal component of the current *j* accompanied by plasma acceleration under the action of the Lorentz force *f* (Hall effect). In this case, the velocity of the plasma flux may attain tens of kilometers per second, which allows one to consider this type of discharge as very promising for creating plasma engines for spaceships. The possibility of attaining high flow velocities and using of gases differing in composition make it possible to use the discharge considered for modeling the entry of spaceships into the atmospheres of the planets of the Solar system. Based on the above scheme, Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus has developed and constructed the so-called Hall plasma accelerator which at the present time is used for testing various regimes of landing of descent modules on the surface of the Earth, Mars, and of other planets. Figures 12 and 13 present the photographs of the general view of the Hall plasma accelerator and of the discharge realized by it in the regime of testing the reentry of the Shuttle-type spaceship into the Earth's atmosphere.

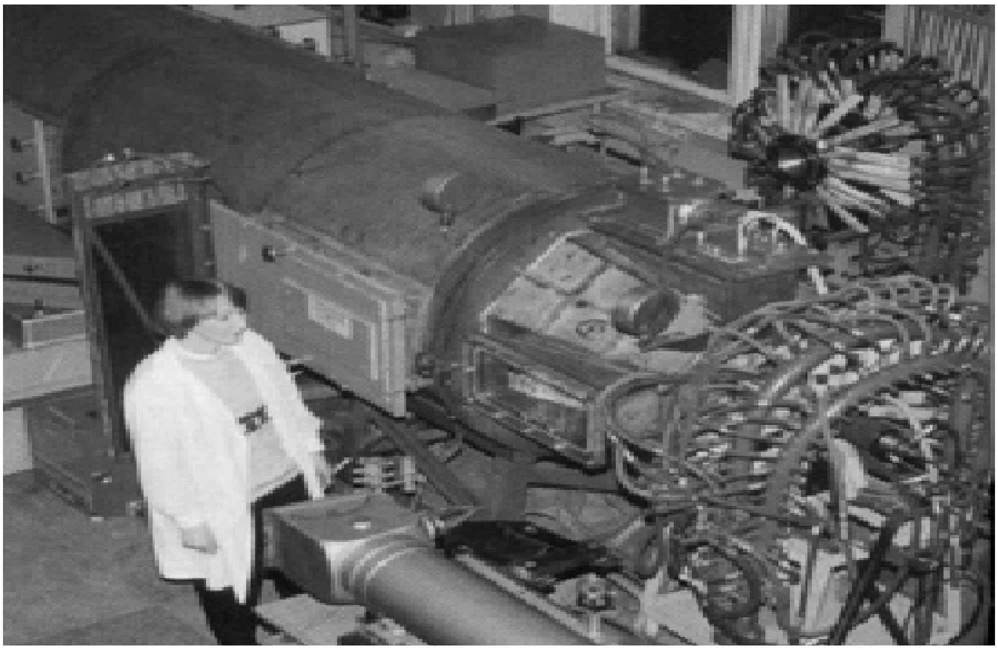

Fig. 12. General view of the Hall plasma accelerator

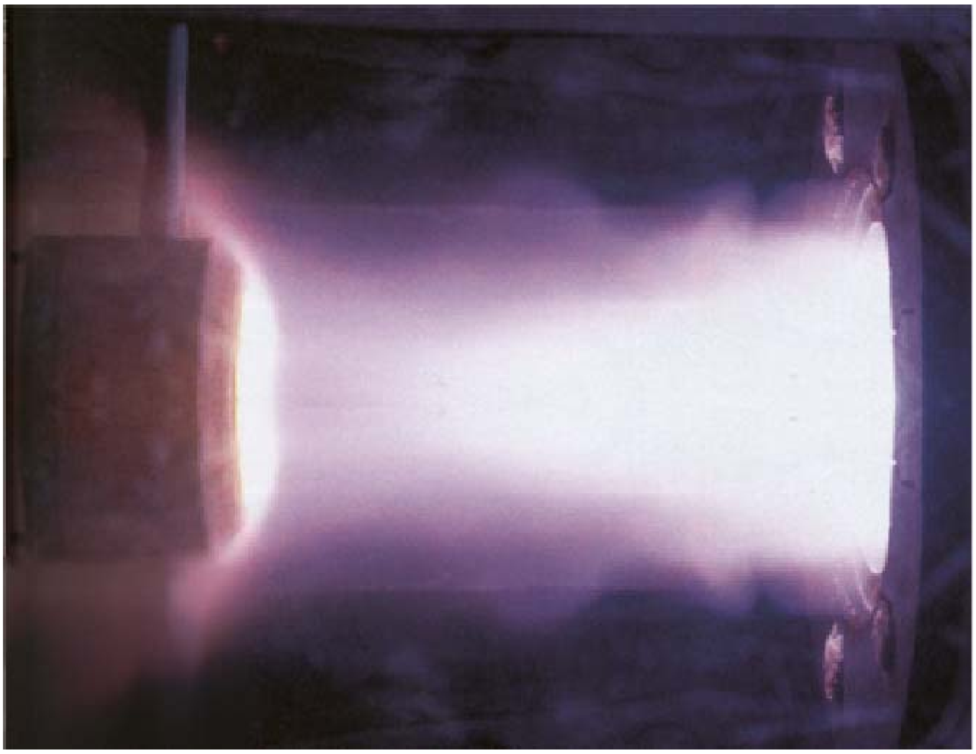

Fig. 13. Application of the magnetic field-stabilized nonequilibrium plasma of a high-current discharge for modeling reentry of space vehicles into the Earth's atmosphere

The strongly nonequilibrium character of the distribution of energy over the internal degrees of freedom of the plasma-forming gas molecules in the Hall plasma accelerator allows using it in accomplishing such processes as synthesis of diamond-like materials under elevated pressures. This allows attainment of high rates of the process and improvement of the quality of the material synthesized.

CONCLUSIONS

The foregoing examples of using various types of atmospheric-pressure gas discharges in accomplishing technological processes are far from exhausting the possibilities provided by the nonequilibrium character of the plasma generated in them. At the present time, the nonequilibrium plasma is widely used in microelectronics, in plasmachemistry for synthesizing new materials, in facilities purifying hazardous emissions at various industries, in special-purpose and domestic devices, and in testing the elements of aviation and rocket-space technology. Its application area is constantly expanding and, for sure, the nearest future will see the appearance of new energy-saving technologies employing the wonderful properties of the nonequilibrium plasma.