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FROM MATERIALS OF ALL-RUSSIAN CONFERENCE “CHEMISTRY OF SURFACE AND NANOTECHNOLOGY”

Specific Features of Chemical Deposition of Polytetrafluoroethylene Films from Hexafluoropropylene Oxide

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Abstract—Influence of the main process parameters on the hot wire chemical vapor deposition (HW-CVD) of polytetraethylene (PTFE) films in the hexafluoropropylene (HFPO)–argon system at low pressure as well as the gas flow structure in the reactor and its effect on the precursor conversion was evaluated. It was found out that that the conversion reaches ~90% at the hot wire temperature above 800°C, increases ~5.5 times with the increase in pressure from 7.5 to 35 Pa and decreases twice with the increase of precursor flow from 8 to 33 ml min^{-1}. It was shown that the process parameters affect significantly the gas residence time and average temperature, and also the intensity of gas flow recirculation in the reactor.

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In the last years increasing interest to the technologies of formation of thin films on the surface of articles having complex form is observed. Such films must be chemically passive, thermostable, biologically compatible, and also have high electrotechnical characteristics. One of the most promising materials possessing this complex of physiciochemical proper-ties is polytetrafluoroethylene (ftoroplast-4, Teflon®) [1].

Traditional methods of obtaining of polytetrafluoroethylene films (application from water dispersions with the subsequent thermal treatment [2]) and some alternative methods such as plasmochemical and also physical deposition from the gas phase [3–6] as a rule do not permit to obtain thin conformal films of stoichiometric polytetrafluoroethylene on the surface of articles having complex form. One of the most promising methods is the creation of such coatings by means of chemical deposition from the gas phase based on decomposition of hexafluoropropylene oxide C_3F_6O in the reactor with the array of hot wires with the subsequent polymerization of obtained difluorocarbene on the surface of cooled substrates. Chemical reactions taking place under these conditions may be described as follows [7]:

$$C_3F_6O \rightarrow CF_2{:} + C_2F_4O,$$
$$2n CF_2{:} \rightarrow –(CF_2–CF_2)_n–.$$

Despite such advantages as comparative ease of the control of the process, the purity of obtained layers, high perfection of molecular structure of the polymer formed, and comparatively low temperatures of substrates, the rules of chemical deposition from the gas phase are studied insufficiently. For example, the effect of technological parameters of the process on the conversion of the precursor is not practically considered. The published data describe only the effect of temperature on the conversion. They are either obtained under the conditions far from that of the processes of chemical deposition from the gas phase at reduced pressure [8], or do not consider the character of gas flow in the reactor with the array of hot wires [9]. Rules of gas flow in such reactors are not studied at all.

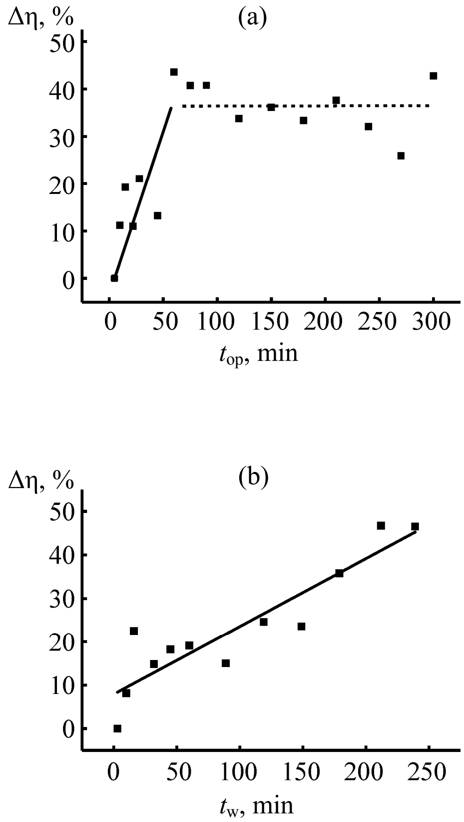

Fig. 1. Change in the conversion of precursor in the course of operating time of the hot wires in the active medium: (a) $T_t = 795°C$ and (b) $T_t = 600°C$.

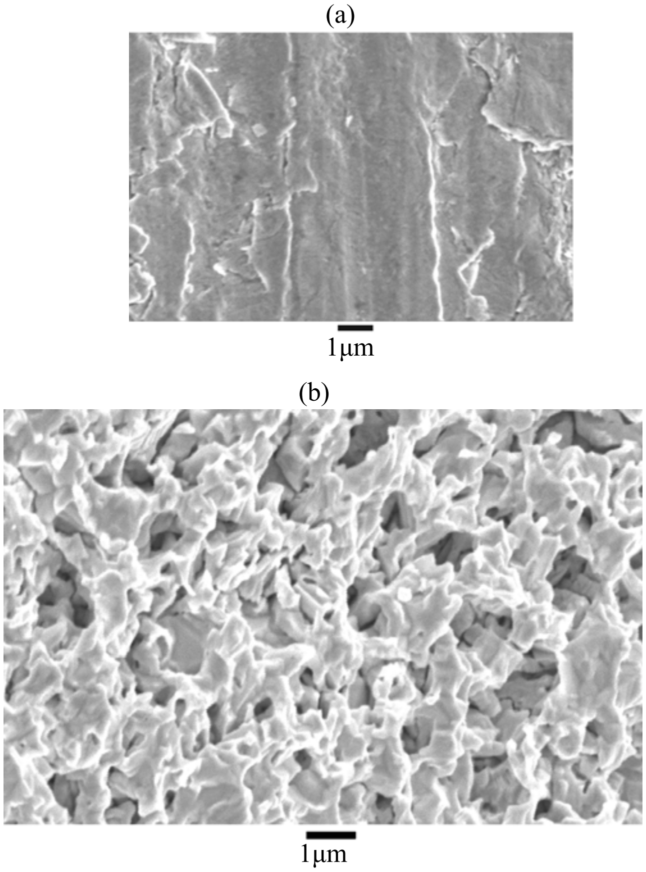

Fig. 2. Image of surface of hot wires: (a) before deposition and (b) after 11 deposition processes.

This study is an extension of the experimental rsearch on the deposition of polytetrafluoroethylene formed from hexafluoropropylene oxide from the gas phase which we have carried out recently [10, 11]. Its aim is the establishing of the effect of main technological parameters of deposition on the conversion of precursor in the hexafluoropropylene oxide–argon system, and also on such parameters of the gas medium as its average temperature and the residence time of gas in the reactor. Also the structure of gas flow in the reactor and its effect on the deposition were studied.

Studies of reproducibility of the results obtained showed that conversion η depends on the operating time of hot wires in the active medium t_w. It increased with t_w and became constant at a level of 140% from the starting one after 60 min at the temperature of threads T_t 795°C. At 600°C the stabilization of conversion was not observed in the course of 250 min (Fig. 1).

The image of the surface of the tungsten threads obtained by scanning electron microscopy before and after use (Fig. 2) showed that etching of the surface of threads took place. Etching was more intense at increased temperature and led to formation of developed contour of surface with the roughnesses about units of microns. The structure formed in such a way provided the increase in the radiation ability of thread surface in the IR range. It was accompanied by the increase in energy transfer by radiation. This effect was confirmed also by the increase in power of glow necessary for support of the given thread temperature. Due to that one of the mechanisms of activation of precursor under the conditions studied may be evidently the absorption of quanta in the IR region analogous to the studied process of decomposition of hexafluoro-propylene oxide under the action of the IR laser irradiation [12]. Another mechanism leading to increase in η may be the increase in the intensity of activation of precursor (for example catalytic) on the surface of threads with the increase in its area.

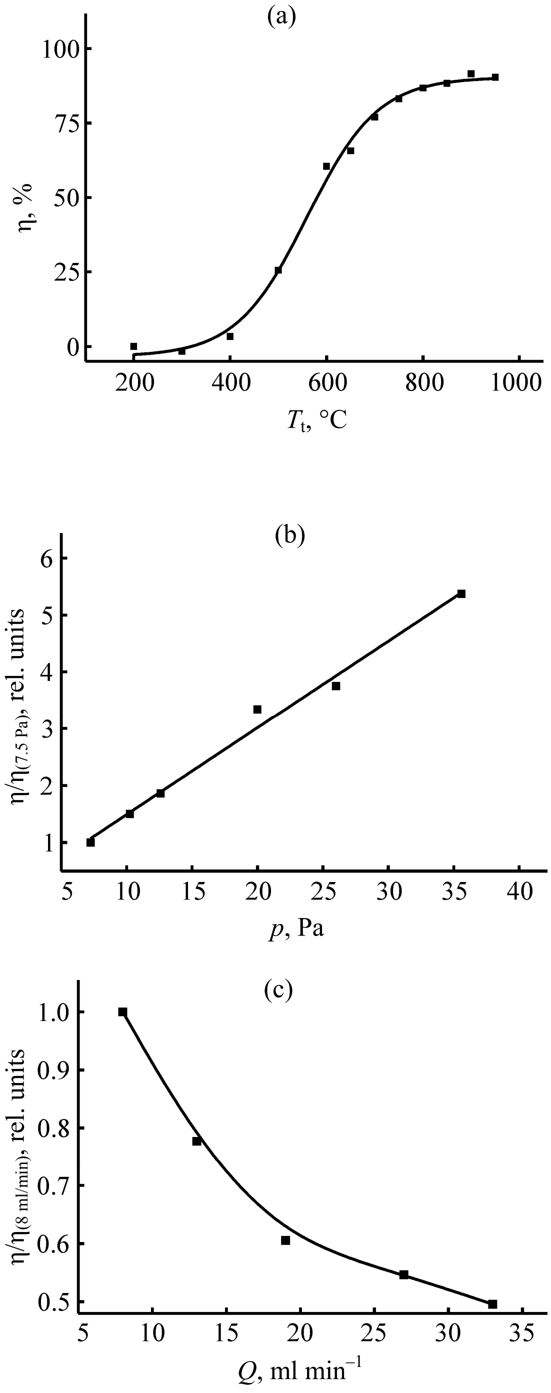

Fig. 3. Dependence of conversion of precursor on the parameters of deposition effect of (a) thread temperature, (b) operating pressure, and (c) flow rate of precursor.

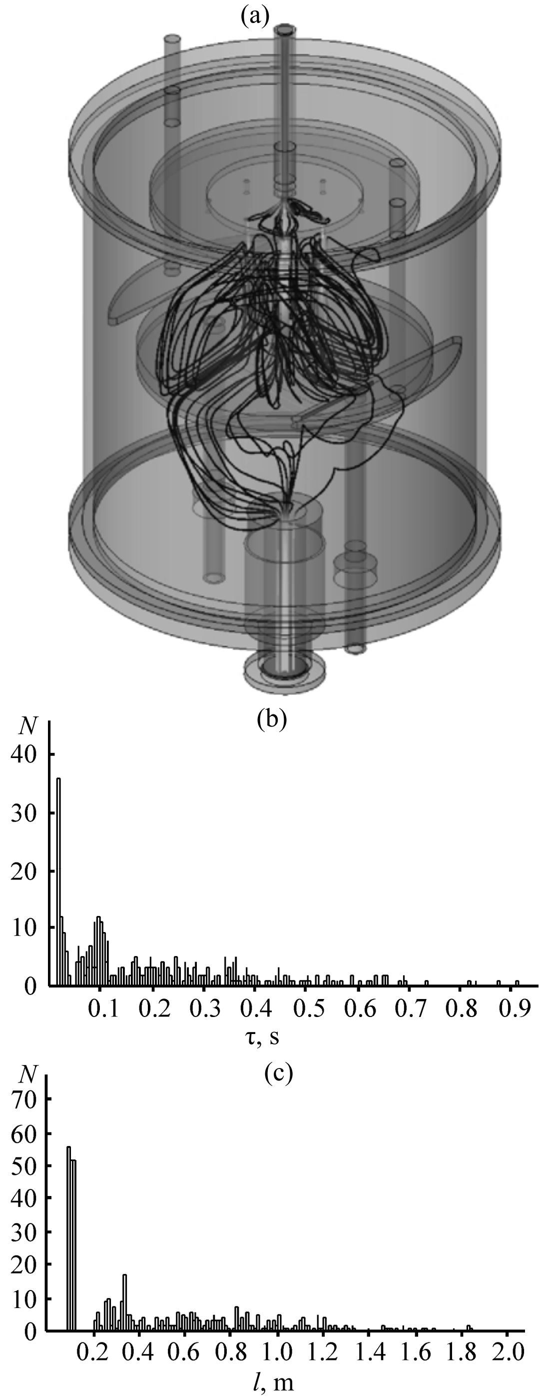

Fig. 4. Characteristics of structure of gas flow in the reactor: (a) image of structure of gas flow; (b) typical distribution of residence times, and (c) lengths of trajectories of movement of gas microvolumes in the reactor.

Temperature dependence of conversion shows that the decomposition of the precursor begins at thread temperature 400°C (Fig. 3a). The highest conversion (~90%) was achieved at $T_t > 800$°C. At the increase in pressure in the range $p = 7.5$–35 Pa η increased ~5.5 times (Fig. 3b). The increase in the precursor flow Q from 8 to 33 ml min^{-1} led to twofold decrease in η (Fig. 3c). At $T_t > 950$°C and also at $p > 45$ Pa an

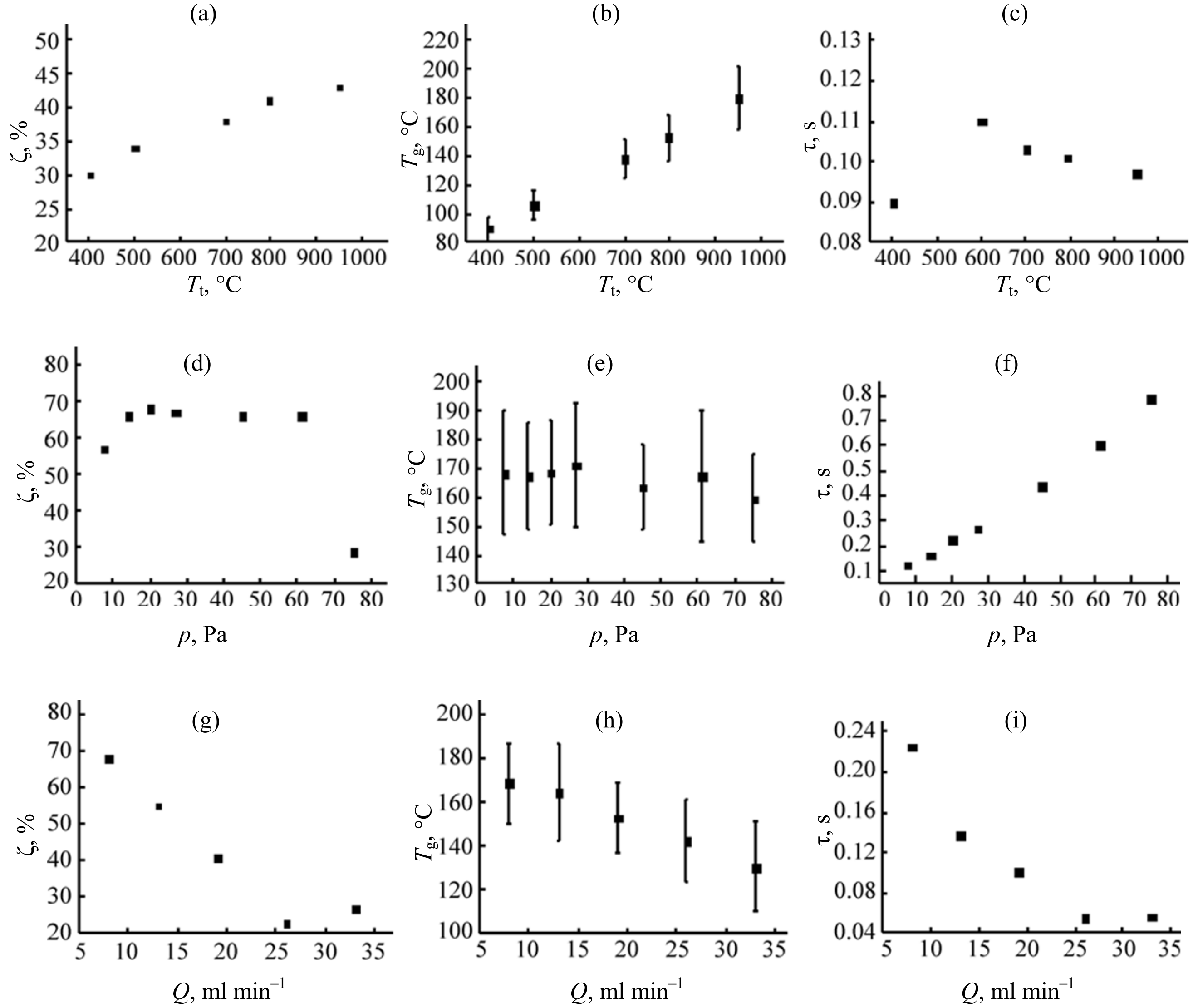

Fig. 5. Effect of parameters of the process on the characteristics of gas flow in the reactor: (a, d, g) part of gas involved in recirculation; (b, e, h) gas temperature; (c, f, i) average residence time

intense formation of powders in the operation zone of the reactor was observed. It did not permit to obtain uniform layers of polytetrafluoroethylene.

The mathematical simulation of the structure of gas streams in the reactor permitted establishing that the gas entering the reactor divided in two main streams (Fig. 4a). Gas stream entering through the central channel of the gas distribution device moved along the axis of the reactor, reached the base, slipped along it and left the reaction zone. Streams formed from the peripheral channels of gas distributor mainly formed the recirculating whirlpools between the array of threads and the gas distributor. Due to that some part of gas many times passed through the activation area. The distribution of residence times and lengths of trajectories of moving gas microvolumes in the reactor (for typical picture see Figs. 4b, 4c) was characterized by the presence of a narrow group of trajectories quickly leaving the reaction zone having small lengths L and times t and the prolonged group of trajectories with large L and t values.

At the increase in T_t from 400 to 950°C increase in the part of gas involved in circulation ζ occurred (from 30% to 43%, Fig. 5a). The distribution of gas temperatures T_g in the reaction zone broadened and shifted to the range of higher temperatures. Average gas temperatures in the reaction zone T_g increased from 90°C to 180°C (Fig. 5b). Mean residence times $\overline{\tau}$ practically do not alter (~0.1 s, Fig. 5c).

Small effect of T_t on the character of gas flow was confirmed by constant $\overline{\tau}$ values. It permitted a conclusion that in the conditions under study the decomposition of the precursor proceeded mainly due to the thermo- or photoactivation with quanta of the IR range and weakly depends on the gas dynamics conditions in the reactor.

The increase in operation pressure in the range p = 7.5–20 Pa caused the increase in recirculation intensity, ζ value increased from 57 to 68% (Fig. 5d). At p = 45 Pa the structure of gas streams altered. Largest values of trajectories of movement of gas microvolumes increased, and the trajectories of stream making one turn in the reaction zone disappeared. The part of recirculating gas decreased to 66%. Results of calculation of ζ value at p = 75 Pa (29%) confirmed that the change in the gas flow took place in the p range 20–45 Pa. The dependence of $\overline{T}_g = f(p)$ (Fig. 5e) shows the insignificant variation in $\overline{T}_g$ in the range of pressures under study which varied between ~163–168°C.

Results of calculations indicate the decrease in the rate of gas flow at the increase in pressure in the interval under study. Together with the increase in lengths of trajectories of gas microvolumes movement observed at p = 45 Pa the increase in $\overline{\tau}$ from 0.125 to 0.786 s took place (Fig. 5e). Note that the decrease in ζ found at p = 75 Pa did not lead to a decrease in $\overline{\tau}$.

The obtained results permit a conclusion that the increase in the conversion of the precursor at the increase in temperature in the range under study is caused by the increase in the residence time of the precursor in the reaction zone leading to the increase in the probability of its activation.

At the increase of the precursor flow in the range Q = 7.5–26 ml min^{-1} the decrease in ζ from 68 to 23% and of $\overline{\tau}$ from 0.225 to 0.056 (Figs. 5g, 5i) was observed. Further increase in Q to 33 ml min^{-1} led to the increase in ζ to 0.27, while $\overline{\tau}$ changed only slightly (0.057 s). $\overline{T}_g$ practically linearly decreased in all the studied flow range from 169°C to 130°C (Fig. 5e).

Conditions of experiments[a]

Investigated parameter	T_t, °C	p, Pa	Q, ml min^{-1}
t_w	600, 795	20	19
T_t	200–950 (400–950)	20	19
p	795	7.5–35 (7.5–75)	19
Q	795	20	8–33

[a] Values of parameters used in the mathematical simulation are given in brackets.

The comparison of calculated and experimental data permits a conclusion that the conversion of the precursor in the Q range under study is determined mainly by the character of gas flow in the reactor. The decrease in the part of gas involved in recirculation with the increase of the flow causes the decrease in the residence time and the average gas temperature. Combined effect of these factors leads to the decrease in the conversion found in the experiments.

EXPERIMENTAL

Experiments were carried out in the vertical cylindrical reactor (140 mm diameter, 140 mm height) with cold walls designed for the studies of rules of hot wire chemical vapor deposition of polytetraethylene films. The activation of precursor was carried out by means of 18 resistively heated tungsten threads (diameter 0.2 mm) placed inside the reactor at a 9 mm distance from the surface of base. Gas phase consisting of the preliminary mixed precursor (hexafluoropropylene oxide manufactured by OOO "Zavod polimerov Kirovo-Chepetskii khimicheskii kombinat, TU 95-783-80, purity 98.7%) and the traces of argon (High Purity grade) was uniformly injected through the gas distributing shower in the upper part of the reactor. Distance between the gas distributor and the array of threads was 65 mm. For removing the reaction products and maintaining the desired pressure the evacuation by means of the plate rotor vacuum pump from the lower part of the reactor was used. Experimental conditions are listed in the table, argon flow was not varied.

The concentration of the precursor in the gas phase of the reaction, on the basis of which the conversion was evaluated, was measured by means of the MCX-6 time-of-flight mass spectrometer. Gas samples were taken from the lower part of the reactor near the connection of vacuum line. Due to that the results of measurements reflected mean concentrations of long-living components of the gas medium along the reactor. As the signals of mother molecule ions in the probes ionized by the direct electron impact were absent in the mass spectrum, the concentration of precursor was calculated from the amplitude of the fragment ion $C_2F_5^+$ analogously to [6,7]. Mass spectra were normalized by the value of amplitude of the one-charge argon ion. During the investigation of the effect of precursor flow the normalization was made by the amplitude of $C_3F_3^+$ ion because it remained practically constant while varying technological parameters of the process.

Images of the surface of the hot wires were obtained by means of the JEOL JSM-6510 scanning electron microscope.

The structure of gas streams in the reactor was modeled in the 1/4 of its volume (due to the existence of two symmetry planes in the reactor) by calculation hydrodynamics using SolidWorks Flow Simulation 2010/COSMOS M complex of programs within of k–ε turbulence model. Regular calculation grid was periodically refined in the course of calculations in the ranges of high gradients of velocity of the gas stream, pressure, and density of the medium. It also considered the presence of the array of hot wires and narrow channel in the gas distributing device, as well as the existence of large volume above the base where the accuracy of calculations is not so important, and the net was rarefied. Mean temperature and the residence time of gas in the reactor were calculated on the basis of 500 trajectories of gas microvolume in the reactor. Relative amount of trajectories forming the circulating whirlpools in the reaction area was the expression of part of recycling gas. In the simulation the precursor without the admixture of argon was considered to be the working gas. Due to the lack of data about the thermophysical parameters of precursors adiabatic curve index C_p/C_v was taken equal to 1:1 what corresponds to the value for refrigerant HFC-134a [13]. Chemical reactions in the course of the process were not considered.

REFERENCES

1. Panshin, Yu.A., Malkevich, S.G., and Dunaevskaya, Ts.S., *Ftoroplasty* (Fluoroplastics), Leningrad: Khimiya, 1978.
2. McKeen, L.W., *Fluoronated Coatings and Finishes Handbook*, New York: William Andrew Publishing, 2006.
3. Panneman, C., Diekmann, T., Hilleringmann, U., Schurmann, U., Scharnberg, M., Zaporojchenko, V., and Adelung, R., *Faurel F., Mat. Sci. (Poland),* 2007, vol. 25, p. 95.
4. Oya, T. and Kusano, E., *Vacuum*, 2008, vol. 83, no. 3, p. 564.
5. Schwodiauler, R., Heintz, J., and Arenholz, E., *J. Polym Sci., B*, 1999, vol. 37, no. 16, p. 2115.
6. Liua, D., Gua, J., Feng, Z., Li, D., Niu, J., and Benstetter, G., *Vacuum*, 2010, vol. 85, no. 2, p. 253.
7. Limb, S.J., Labelle, C.B., Gleason, K.K., Edell, D.J., and Gleason, E.F., *Appl. Phys. Lett*., 1996, vol. 68, p. 2810.
8. Safonov, A.I., *J. Appl. Mech. Tech. Phys*., 2011, vol. 52, no. 3, p. 496.
9. Zhou, J., Overmeyer, A., and Wolden, C.A., *Proc. Electrochem. Soc*., 2001, vol. 3, p. 92.
10. Uvarov, A., Uemura, K., Alexandrov, S., Murayama, H., and Soba, R., *Proc. of 10th Int. Conf. "Modification of Materials with Particle Beams and Plasma Flows,"* Tomsk, 2010, p. 500.
11. Uvarov, A.A. and Aleksandrov, S.E., *NTV SPbGPU*, 2011, no. 3, p. 141.
12. Dunyakhin, V.A., Timofeev, V.V., and Zhitnev, Yu.N., *Russ. Chem. Bull*., 1995, vol. 43, no. 11, p. 1816.
13. *Thermodynamic Properties of HFC-134a, [Electronic resource]/ Du Pont, 2004, access regime: http://2.dupont.com/Refrigerants/en_US/assets/downloads, free – English language, call date 10.037.2013.*