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# Recent developments of plasma-based technologies for medicine and industry

**Valerii S. Taran,**
**Igor E. Garkusha,**
**Viktor V. Krasnyj,**
**Alina S. Lozina,**
**Renat M. Muratov,**
**Valerii M. Shulaev,**
**Aleksandr I. Timoshenko**

**Abstract.** The paper presents an overview of experimental results of various plasma applications based on atmospheric and vacuum discharges. A multifunctional low-temperature ozone sterilizer with a ultrasonic cavitation and dielectric barrier discharge generated at atmospheric pressure as well as ozonators with a diaphragm for water treatment and disinfection of medical tools have been developed. Particular attention is paid to the investigation of arc, high-frequency and non-self maintained discharges generated in vacuum for coatings application. Some aspects of pulsed plasma treatment, surface modification and hardening due to nitriding, oxidation and carburization are discussed.

**Key words:** discharge • plasma • ozone sterilizer • coating • surface modification

V. S. Taran✉, I. E. Garkusha, V. V. Krasnyj, A. S. Lozina, R. M. Muratov, V. M. Shulaev, A. I. Timoshenko
Institute of Plasma Physics,
National Science Center, "Kharkov Institute of Physics and Technology",
1 Akademicheskaya Str., 61108 Kharkov, Ukraine,
Tel.: +38 057 335 6573, Fax: +38 057 335 2664,
E-mail: vtaran@ipp.kharkov.ua

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## Introduction

Nowadays, various plasma technologies are widely applied in medicine and industry due to their ecological compatibility, relatively low energy consumption, etc. Ozone technologies based on barrier discharges at atmospheric pressure are applied for sterilization and disinfection purposes in medicine, whereas discharges in vacuum are mostly used for coatings deposition [3, 5, 7, 8, 10]. The paper presents overview of experimental results on various plasma applications.

In both cases a promising tendency is to use the combination of several plasma processing schemes to achieve desirable treatment efficiency (for atmospheric discharges) and properties of modified surface layers as well as deposited coatings (for vacuum plasma technologies).

Low-temperature sterilizers based on reactors with dielectric barrier discharge (DBD) and surface discharge (SD) operated in water solution were developed. The combined action of ozone and ultrasonic cavitation in aqueous medium provided effective cleaning of complex-shaped articles with internal cavities as well as inactivation of various microorganisms [6]. Planar DBD with a diaphragm used for water treatment was proposed. The influence of ozone and radicals on the organic impurities and microorganisms was studied.

The expansion of the spheres of the application of ozone initiates new studies directed toward improvements in the characterization of reactors for obtaining ozone. Different methods, connected with preionization in the main discharge, the so-called dual discharges, also attract attention [9]. The ozonizer with superposition of dielectric barrier discharge and surface discharge seems as one of the most perspective. Additional possibilities appear with generation of ultrasonic cavitation in ozonized media.

Surface modification of metal substrates, subjected to ion-plasma treatment with the use of arc, radio frequency (RF) and glow discharges was carried out. The correlation between the modification effect and ion--plasma cleaning of the substrate surface was defined. The effectiveness of nitriding of the inner surfaces of cylindrical specimens made from Ti and SS (stainless steel) has been investigated. The features of surface layers alloyed by gas and metallic plasma as well as previously deposited coating mixing with a steel substrate in the liquid phase have been investigated. In particular, modification of thin, 0.5–2 μm, PVD coatings of MoN, C+W, TiN, TiC, Cr, Cr+CrN during pulsed plasma processing was analyzed. Oxidation and carburization processes in non-self maintained gaseous discharge of SS, HSS (high speed steel) and Ti samples exposed in fluxes of ions $N^+$, $O^+$, and $C_mH_n^+$ have been examined. The microhardness tests after ion-plasma treatment by fluxes of ions in non-self maintained gaseous discharge were carried out.

## Methods and materials

The parameters of discharges operated at atmospheric pressure were measured using: ozone monitor, oscillograph, Rogowski coil and SL40-2-3648USB type spectrometer. The obtained data from these devices were processed by the PC system with a multifunctional plate input-output type L-Card L-783 (3 MHz, 32 channels). The information system modules were based on C++Builder-6.

Plasma treatment was carried out applying a negative shift of potential 1000 V and an arc current of 90 A at a pressure of $5 \times 10^{-3}$ Pa. Cathode was made of titanium of VT1-0 type. The substrates were made of stainless steel of 12X18H10T type and oxygen-free cooper. The surface structure was investigated with a scanning electron microscope JEOL JSM-840 as well as with an optical interferometer Micron-alpha. Chemical composition of the exposed surfaces was examined by energy-dispersive analyzer EDS-1. Microhardness was tested with a Micron--gamma device.

RF-metallic plasma source was used for coatings application in a gaseous discharge into the inner parts of tubes made of titanium, stainless steel and glass exceeded 20 mm in diameter. Low-temperature nitriding of the inner parts of tubes made of a Ti alloy VT1-0 and stainless steel of Cr18Ni10Ti type have been carried out. Nitriding took place by nitrogen ions in RF plasma at a pressure of $P_N = 10^{-2}$ Pa and voltage of 1.5 kV during 60 min.

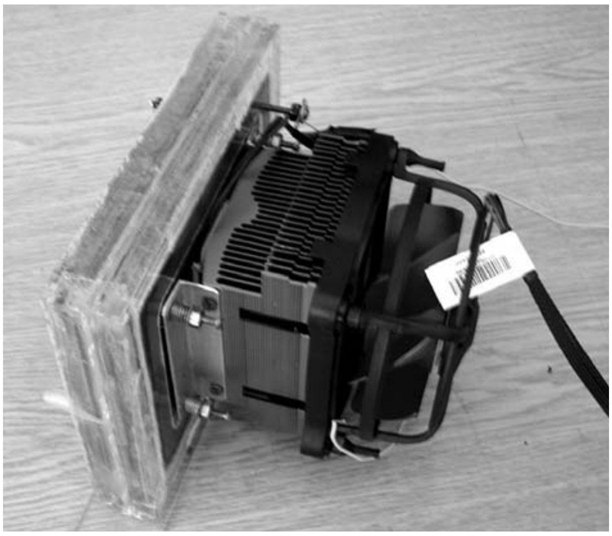

**Fig. 1.** Ozone barrier reactor module with air cooler.

## Results and discussion

### Discharges at atmospheric pressure

The ozone barrier reactor module with an air cooling system is shown in Fig. 1. The discharge is generated between two 180 × 100 mm flat electrodes cooled either with water or air. Both electrodes were coated with a dielectric material. Two types of dielectrics were used: the glass plates of 2 mm thick, and glass-ceramic – 0.2 mm in thickness. Dry air has been served as a working gas. The performed experiments allowed to determine the required power and flow range taking into consideration the ozone concentration and yielding rates. It was found that the ozone concentration rate was increased by 3.5÷4 times at identical energy consumption when operating with oxygen.

The ozone reactor with superposition of dielectric barrier and surface discharges has been used for ozone generation. The scheme of such a combined discharge operated at atmospheric pressure is shown in Fig. 2. Dielectric barrier discharge was generated between two flat metallic electrodes coated with glass-ceramic. The first electrode for the surface discharge was made from 2 mm steel strips placed on a glass-ceramic surface of the lower electrode. The dielectric barrier and surface discharges have been excited by ac voltages of 8 and 4 kV, respectively. The phase shift between applied voltages is varied between 0° and 180°. Discharges were generated in dry air fed through a 2.5 mm gap.

The ozone output concentration was measured for each of the three possible regimes: 1) surface discharge; 2) dielectric barrier discharge, and 3) the superposition

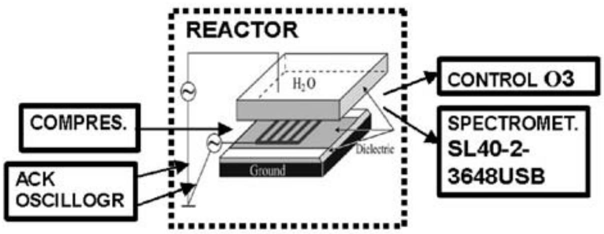


**Fig. 2.** Reactor based on combined discharge.

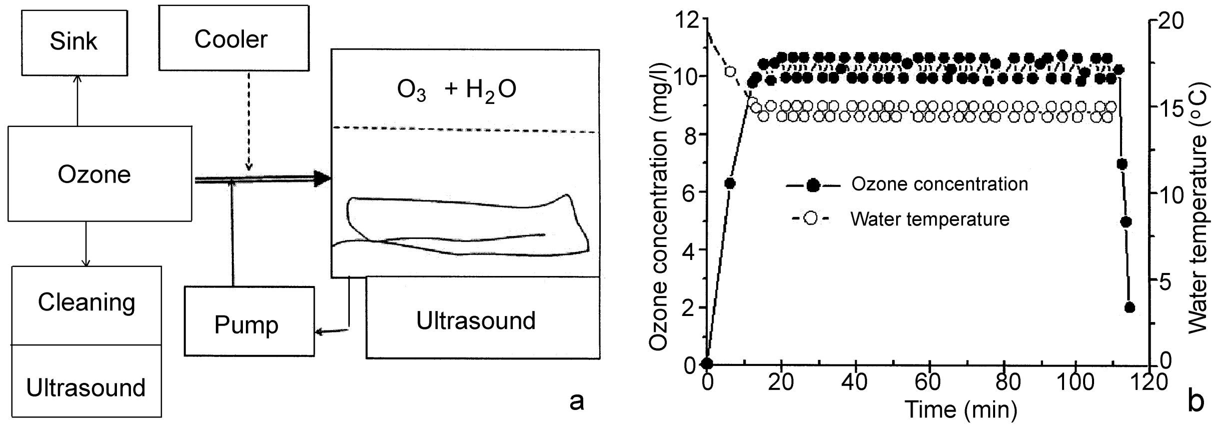


**Fig. 3.** Functional diagram of multifunctional low-temperature medical sterilizer (a) and time dependence of ozone concentration on water temperature (b).

of those discharges. The obtained results have shown that the breakdown voltage required for the dielectric barrier discharge ignition is lower for the combined discharge as compare with the case of barrier discharge only (6 and 8 kV, respectively). In addition, the ozone concentration in combined discharge is approximately 1.5 times greater than that in DBD.

The number of streamers estimated by the Rogowski coil in superposed discharges was greater as compared to either the DBD or surface discharge (SD). The maximal number of streamers was observed under the phase shift of 180° (counter-phase), between the voltages applied to the electrodes of surface discharge and DBD. Spectroscopic measurements had shown that changes of nitrogen concentration depended on the discharges parameters generated in pure air at atmospheric pressure at room temperature. The emission spectra were obtained within the wavelength range of 200–800 nm for the combined DBD and SD under the same phase shift of 180° between the applied voltages. The spectral lines intensity of nitrogen at this phase shift is also maximal that corresponds to the maximum electric field in the discharge gap of the reactor. This is an indication of increased discharge power. The lines intensity in combined discharge is also essentially higher. The growth of ozone concentration is a consequence of the higher intensity of combined discharge as compared to SD and DBD. The output of ozone concentration increases with increasing both discharge power and growing discharge gap from 1.5 to 2.5 mm.

## Low-temperature ozone sterilizer with ultrasonic cavitation

Principal scheme of the multifunctional low-temperature medical sterilizer operated in water medium is shown in Fig. 3a. Multifunctionality in this case is provided by a pre-sterilization process with the following disinfection and sterilization. The high ozone concentration in water solution is achieved due to dielectric barrier discharge generated at the atmospheric pressure using the pulsed power supply scenario. Sterilization camera is equipped with a ultrasound source operated at 50 W. Optimization of the sterilization in water solution was carried out by varying ozone concentration, power of ultrasound source and the water temperature. It was found that the output of ozone concentration exceeded 30 mg/l for the air flow rate of 0.5 l/min and using an additional cooling thermo-electric module.

Figure 3b shows the operating mode of sterilizer in the temperature range 14–15°C. The initial temperature of both water and air was 19°C. The air flow rate through the reactor was kept at a level of 0.2 l/min. The output ozone concentration reached 36 mg/l in air and comprised 10 mg/l in water. Concept-proof-experiments on bacteria inactivation were carried out in distilled water. The following test-cultures of microorganisms seeded on this medium have been studied: *E. coli* 055 K59 no. 3912/41, the *Staphylococci aureus* ATCC no. 25923, *Pseudomonas aeruginoza* 27/99 seeded on meat-peptone broth (MPB), as well as *Cl. oedematiens* 198 and *B. cereus* no. 8035. The control samples were taken from the sterilization bath for the microbiological analysis after 1, 3, 5, 10, 20, 30, 60 and 90 min, correspondingly. During the treatment time, the ozone concentration was increased up to the values indicated in Table 1. The experiments have shown that complete inactivation of *E. coli* and *Staphylococcus aureus* can be achieved at low ozone concentrations and for a quite acceptable time scale, being less than 2 min. The most stable microorganisms were spores of *B. cereus* no. 8035. They were destroyed by successively rising ozone concentration from 0 to 10 mg/l during 15 min in water solution,

**Table 1.** Experimental data on eliminated bacteria

| Test-culture | $O_3$ concentration in water (mg/l) | Water temperature from 0°C | Time-kill assay (min) |
|---|---|---|---|
| *Escherichia coli* | 1.8 | 19 | 2 |
| *Staphylococcus aureus* | 1.8 | 19 | 2 |
| *Pseudomonas aeruginoza* | 6 | 17.5 | 5 |
| *Clostridium oedematiens* no. 198 | 8.5 | 16.25 | 10 |
| *Bacillus cereus* no. 8035 | 10 | 15 | 15 |

which is accompanied by the temperature decrease from 19 to 15°C.

### Dielectric barrier discharge with diaphragm in aqueous media

It was revealed experimentally that the most effective method of water purification from the organic impurities and its disinfection is to provide the discharge generation directly in water-air media. Figure 4 shows the device scheme based on barrier discharge with a diaphragm. In this case, discharge is generated between the upper metallic electrode coated with a dielectric material and the lower water electrode covered by a diaphragm. The distance between the upper electrode and the diaphragm could reach 5 mm. Spectral characteristics of the discharge are presented in Fig. 5. The experimental data on bacteria inactivation in water solution that demonstrate a high efficiency of the applied scheme are summarized in Table 2.

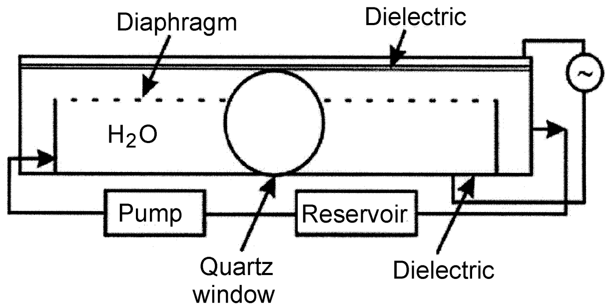


**Fig. 4.** Functional scheme of dielectric barrier discharge with a diaphragm.

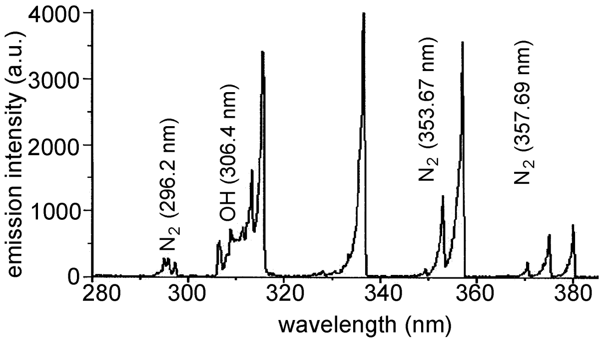


**Fig. 5.** Spectral characteristics of the discharge.

## Plasma technologies based on vacuum discharges

### Cleaning surface treatment

Surface conditioning is one of the most important pretreatment steps forestall different coatings deposition. Therefore, the influence of plasma treatment parameters on the resulting surface modification has to be comprehensively examined. Figure 6 shows the scanning electron images of SS and copper surfaces after treatment with a titanium plasma during 2 min. The substrates have been fixed permanently in the front of titanium plasma. Almost complete melting of the copper substrate has been obtained. Polished surface roughness of the substrate decreased from the initial 13 roughness classes to 8 classes for copper and 9 classes for SS. Microrelief of the surface became changed due to the trapping of titanium microdroplets. Metal film of titanium is easy detected visually on the copper substrate due to the color difference. After the treatment with the titanium plasma for 10 min, the copper substrate

**Table 2.** Experimental data on bacteria inactivation in water solution

| Experimental conditions | Time-kill assay (min) | Amount of living bacteria | (%) | Pressure (*P*) |
|---|---|---|---|---|
| | Initial state | $(8.5 \pm 0.2) \times 10^7$ | 100 | – |
| Ozone + discharge | 10 | $(3.55 \pm 0.3) \times 10^4$ | 0.04 | < 0.05 |
| | 20 | $(1.0 \pm 0.002) \times 10^2$ | 0.000001 | < 0.05 |

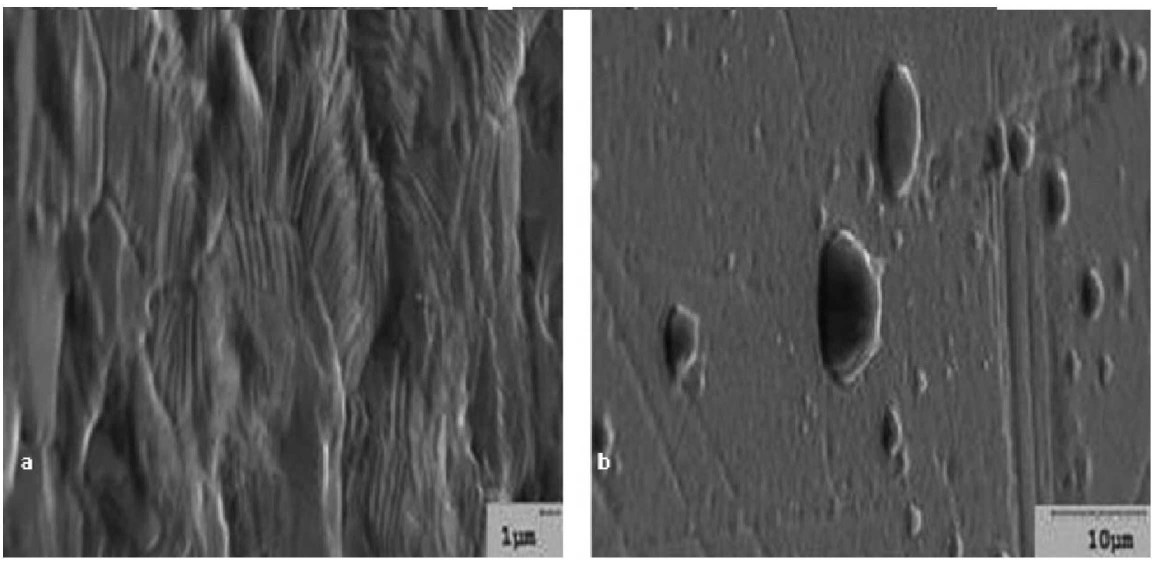


**Fig. 6.** Scanning electron images of the surface after plasma pretreatment during 2 min: (a) – copper substrate, (b) – SS substrate.

**Table 3.** Surface treatment by high-frequency discharge in reactive gaseous media (argon, nitrogen)

| Method of cleaning | HF | arc | HF + arc |
|---|---|---|---|
| $U$ displacement HF (kV) | –1.7 | | –1.7 |
| Pressure $HF_{Ar}$ (Pa) | $2 \times 10^{-1}$ | | $2 \times 10^{-1}$ |
| Pressure $P$ (Pa) | | $2 \times 10^{-3}$ | $2 \times 10^{-3}$ |
| Time $t$ (min) | 30 | 3 | 30 |
| arc current $I_{arc}$ (A) | | 130 | 130 |
| Current of the focusing coil IFC (A) | | 1.1 | 1.1 |
| Current of the solenoid coil ISOL (A) | | 80 | 80 |
| Temperature $T$ (°C) | 50 | 400 | 450 |
| Loss of mass (mg) | 0.45 | 1.7 | 2.25 |

surface undergone a complete melting with the formation of a developed microrelief, which contains a high density of non-porous in the surface layer. The melting zone and the absence of scratch traces extends up to a depth of 1 mm. Thus, one can conclude that the surface microrelief of various substrates is changed noticeably during the plasma treatment by fluxes of titanium ions, manifesting a strong dependence on the process duration. It is discovered that utilization of a high-frequency discharge in reactive gaseous media (argon, nitrogen) could be a competitive method for surface cleaning (see Table 3).

### Coatings deposition and nitriding of inner parts of tubes with high-frequency plasma sources

In these experiments, the plasma density reached quite high values $n > 10^{12}$ cm$^{-3}$ due to the high-frequency generator ($f$ = 5 MHz, $P$ = 3 kW) used in a standard Bulat-6 type device [4]. The device was evacuated to $10^{-5}$ torr with the following working gas inlet to required pressure of $10^{-2}$ Pa. Al, Cu, Ti, and stainless steel were served as materials for a cooled cylindrical cathode of metallic plasma source which had reflective elements at the ends. The cathode was supplied with a mechanism for its longitudinal displacement and it was fixed inside the cylindrical tube made of either stainless steels (SS) or titanium. The cathode temperature did not exceed 350°C. The microhardness of initial samples and after nitriding is shown in Table 4, which clearly demonstrates the possibility of considerable hardening even in the case of SS nitriding.

### Nitriding, oxidation and carburization in non-self maintained gaseous discharge

SS, HSS (high speed steel) and Ti samples were exposed to fluxes of $N^+$, $O^+$, and $C_mH_n^+$ ions with a current density of 20÷30 mA/cm$^2$. Ion fluxes with energy of 20÷30 eV were generated from a hollow anode. Vacuum chamber played a role of hollow cathode, where the samples have been placed. The treatment time for all samples was chosen as 20 min. The temperature of samples has been changed by applying negative potential to its fixture and it has been maintained for SS at 700°C, for HSS at 550°C and for Ti at 550, 700 and 1000°C, respectively. Figure 6 demonstrates that under these conditions Ti oxidation is running more quickly, and is followed by nitriding. The microhardness of samples treated by fluxes of ions in non-self maintained gaseous discharge grows from 1.5 for HSS (except the carburization) to 6 times for Ti and SS (see Table 5).

## Application of pulsed plasma streams for surface modification of constructional materials

Mo and W were previously deposited using a planar electron cyclotron resonance (ECR) plasma source with a multipolar magnetic field. The working frequency of ECR source and HF power are 2.45 GHz and 300 W, respectively. The ultimate pressure in the vacuum chamber was about $2 \times 10^{-4}$ Pa. The working pressure ($2 \times 10^{-3}$ Pa) was defined by variation of the working gas (Ar) flow and the pumping speed. The plasma pa-

**Table 4.** Microhardness tests

| No. | Material | Hμ initial (kg/mm$^2$) | Hμ experimental (kg/mm$^2$) |
|---|---|---|---|
| 1 | SS | 150 | 150 |
| 1 | Ti | 200 | 230 |
| 2 | SS | 150 | 265 |
| 2 | Ti | 200 | 280 |
| 3 | SS | 150 | 280 |
| 3 | Ti | 200 | 300 |

**Table 5.** Microhardness of samples treated by fluxes of ions in non-self maintained gaseous discharge

| Material | SS | HSS | Ti |
|---|---|---|---|
| Initial microhardness (GPa) | 2.2 | 9.0 | 1.9 |
| Microhardness (GPa) after: | | | |
| – nitriding | 14.0 | 14.0 | 8.0 |
| – oxidation | 4.5 | 14.0 | 12.0 |
| – carburization | 5.6 | 9.0 | 9.0 |

rameters close to surface of the processed target were as follows: electron density up to 10–11 $cm^{-3}$, electron temperature ~ 12 eV, ion current density to the grounded substrate ~ 3.5 $mA/cm^2$. TiN, Cr, CrN and other coatings were deposited to the samples surfaces by the PVD method in the "Bulat" installation. In particular, modification of thin PVD coatings of MoN, C+W, TiN, TiC, Cr, Cr+CrN and others in result of consecutive pulsed plasma processing [2] have been analyzed. Alloying of surface layer in result of the coating-substrate mixing [1] allows the achievement of desirable chemical composition in surface layers being most loaded in all machine components.

## Conclusions

Low-temperature medical sterilizers with reactors on the basis of DBD have been developed. Combined action of ozone and ultrasonic cavitations in aqueous medium provides effective cleaning of complex-shaped articles including cavities and causes inactivation of various microorganisms. The planar DBD with a diaphragm has been proposed. The influence of the discharge components: $O_3$ and radicals on the organic impurities and microorganisms in treated water has been studied.

Investigations of surface modification effects in metals, subjected to plasma treatment with the use of arc, RF discharges and their combination are carried out. The important correlation between the modification effect and the duration of the plasma cleaning has been identified.

The effectiveness of PVD with additional use of RF discharges for coatings on inner surfaces of metallic and dielectric pipes and nitriding of the inner surfaces is manifested.

Nitriding, oxidation and carburization in non-self maintained gaseous discharge has been investigated in the fluxes of ions $N^+$, $O^+$, and $C_mH_n^+$. The microhardness of samples, treated in non-self maintained gaseous discharge, grows from 1.5 for HSS to 6 times for Ti and SS.

Modification of thin 0.5–2 μm PVD coatings of MoN, C+W, TiN, TiC, Cr, Cr+CrN and others during consecutive pulsed plasma processing has been discussed. Alloying of the surface layer in result of coating-substrate mixing, provides desirable chemical composition of surface layers being most loaded in all machine components. Thus, combined plasma processing was found to be advantageous for modification of piston rings and other machine parts operating in conditions of bearing or dry friction.

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