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Effect of non-equilibrium atmospheric plasma on the hydrophilicity of metal surfaces

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The comparative effect of non-equilibrium atmospheric pressure plasma on the contact angle of metal surfaces (Cu, stainless steel, Al-Mg alloy) was determined. The plasma was generated using apokampic and nanosecond diffuse discharges in air as well as in an argon jet. Treatment for 15, 30, 60, 120 and 240 sec revealed that a 30–60 sec treatment is sufficient in all cases to achieve maximum hydrophilicity. The apokampic discharge in air and the pulsed discharge in an argon flow, which are simpler in technical implementation, are not inferior to the nanosecond atmospheric discharge in their ability to increase hydrophilicity. Partial preservation of the hydrophilic properties was noted for 24 hours after all three types of treatment.

Keywords: apokampic discharge, vacuum ultraviolet VUV, nanosecond diffuse discharge, non-equilibrium low-temperature plasma, plasma jet.

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Introduction

Atmospheric pressure plasma is a promising agent for controlling the surface properties of various materials (organic, inorganic, metals). In particular, it is known that plasma cleaning and activation of the surface increases the adhesive properties at the "metal–metal" and "metal–polymer" interfaces by approximately 3.4 times [1, 2]. The sources of such plasma are traditionally arc, corona, and barrier discharges, as well as various versions of the so-called atmospheric pressure plasma jets, in which the plasma flow is formed in the discharge gap (excitation is carried out by radio-frequency, corona, glow, or barrier discharge), after which it is ejected through a narrow capillary or slit due to the excess pressure in the discharge zone exceeding atmospheric pressure [3–5].

In the task of controlling the surface wetting angle, polymer and biological materials used in photonics and microelectronics are most often studied [6, 7]. Significantly fewer studies are devoted to controlling the wetting angle of metals, although the advantages of such treatment compared to, for example, plasma activation at reduced pressures are clear: devices for producing plasma jets are mobile and operate under normal conditions, allowing them to act on both smooth and profiled surfaces.

In particular, data have been obtained on the effect of atmospheric plasma on materials such as Al, Cu, Cr, steel (AISI 304L), and galvanized steel (H300LAD) [8–12]. In all these cases, plasma treatment reliably increased the hydrophilicity of the surfaces.

In the present study, to impart hydrophilic properties to the metal surface, we will use three

sources of atmospheric non-equilibrium plasma that have not been used for this purpose before. These are sources based on an apokamp discharge in air [13, 14], a nanosecond diffuse discharge in air [15], and a new source of vacuum ultraviolet (VUV) emission formed in an argon flow [16, 17]. All three sources produce active oxygen and nitrogen species at the boundary of the streamer channel (plasma jet) and the surrounding air or directly in the diffuse discharge. Furthermore, the first and second sources predominantly emit ultraviolet light originating from the second positive system of nitrogen (transitions $C^3\Pi_u-B^3\Pi_g$), while the third emits on the transitions $3s^2P-2p^2P^\circ$ and $3s^2P-2p^2D^\circ$ of atomic nitrogen at 174.3 and 149.3 nm, respectively.

The aim of the work is to assess the ability of these plasma sources to achieve maximum and long-term changes in the hydrophilicity of metallic surfaces (Cu, steel, Al-Mg alloy), considering that they have not been used for this purpose before.

Experimental setups and methods

Objects and methods of treatment. The objects of exposure were metal foils of copper,

stainless steel and aluminum-magnesium alloy (97 % Al, 3 % Mg), with a thickness of 20, 100 and 50 μm , respectively. All these materials are widely used in manufacturing. Rectangular foil samples (15×15 mm) were placed in the path of propagation of an apokamp discharge streamer, an argon plasma jet, or in the area of action of a diffuse discharge at different distances x from the electrode system (Fig. 1).

The nanosecond discharge [15] was formed in a point-to-plane gap located inside a coaxial discharge chamber (Fig. 1a). Voltage pulses of negative polarity with an amplitude of -25 kV and a duration of 4 ns were applied to an electrode 6 mm in diameter made of stainless steel, the end of which had a conical shape with an angle of 60 degrees. The voltage pulse repetition rate was 100 Hz. The grounded counter electrode had the shape of a cylinder with a diameter of 20 mm. The distance between the electrodes was 6 mm. Samples of metal foils exposed to the plasma of the nanosecond discharge were placed on the end face of the grounded electrode. Air was pumped along the axis of the discharge gap using a diaphragm pump and a special nozzle placed on the high-voltage electrode. The pumping rate did not exceed 5 L/min.

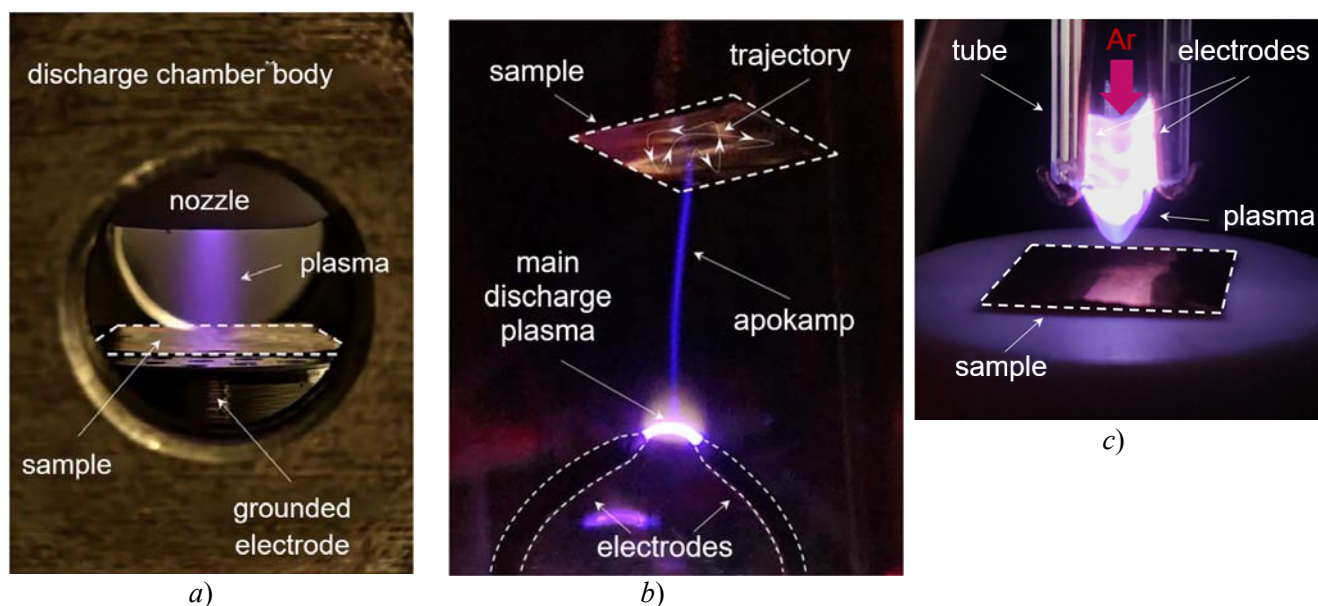


Fig. 1. Photographs of the discharge systems during the treatment of copper samples (15×15 mm):
(a) nanosecond discharge in air at atmospheric pressure with a pulse repetition rate of 100 Hz, exposure 1/90 sec,
(b) apokamp in air at atmospheric pressure, exposure 1/30 sec, **(c)** pulsed discharge in an argon flow with VUV emission, exposure 1/30 sec.

The apokamp discharge was formed between pointed rods 2 mm in diameter made of stainless steel, which were oriented towards each other (Fig. 1b). The distance between them was 4 mm. Voltage pulses of positive polarity with an amplitude of 10 kV and a duration of 1 μ s were applied to one of the electrodes, and the pulse repetition rate was 27 kHz. The opposite electrode was connected to one plate of a capacitor with a capacitance of 10 pF, the other plate of which was grounded. This electrical circuit is of fundamental importance for the formation of an apokamp discharge [18]. During the voltage rise stage (0.5 μ s), a breakdown of the gap (over tens of ns) occurred between the rods, forming a discharge channel with a characteristic dark space near the cathode and an extended positive column. As the voltage increased, the capacitor charged almost to the open-circuit voltage of the generator (considering the voltage drop in the plasma channel, as across an active load). From the bend of the discharge channel, which had a positive potential, a positive streamer started in a direction perpendicular to the axis of the discharge gap. Thus, an apokamp with a length of 2–3 cm was formed, visually resembling a so-called plasma jet (Fig. 1b). Samples of metal foils were placed in the path of the apokamp propagation at a distance of 2 cm from the electrodes. Exposure to the apokamp plasma was carried out upon direct contact of its tip, chaotically moving over the surface of the samples.

The pulsed discharge in an argon flow was ignited between parallel wires inside a quartz tube 50 mm long and with an inner diameter of 6 mm (Fig. 1c). Argon (99.99 % purity) was pumped through the quartz tube at a rate of 2 L/min. One of the wires was grounded. The second wire was connected to the high-voltage output of a pulse generator (amplitude 10 kV, duration 1 μ s, pulse repetition rate 27 kHz) through a capacitor with a capacitance of 10 pF. As a result, a discharge channel formed between the wires, sliding along the wires in the direction of the argon flow. At the final stage, the discharge channel "emerged" from the end of the tube to a distance of 5–7 mm and broke off, after which the process was repeated. It is recalled that it was previously shown that VUV emission (174.3 and 149.3 nm) is generated in the plasma of such a

discharge at the transitions of atomic nitrogen ($3s^2P - 2p^2P^0$ and $3s^2P - 2p^2D^0$) [17], formed during the dissociation of molecular nitrogen contained in the argon cylinder as an impurity, as well as when the discharge channel is pushed out from the end of the quartz tube into the atmosphere. Samples of metal foils were placed at a distance of 8–10 mm from the end of the tube so that the plasma channel did not touch their surface (Fig. 1c). However, VUV emission could reach the surface of the samples due to the displacement of air by the argon flow, which is transparent to VUV emission.

The samples were treated with plasma for 15, 30, 60, 120, and 240 seconds. There were 15 samples of each metal in total. The wetting angle was measured immediately after treatment and after 24 hours.

The wetting angle (θ) of the metal sample surface was measured using the sessile drop technique [19] with distilled water as the test liquid.

The measurement bench was assembled to ensure high accuracy in recording the droplet profile. For this purpose, the sample under study was placed on a three-coordinate stage with micrometer screws for precise positioning. A syringe with distilled water was fixed directly above the sample.

The droplet application procedure consisted of forming a droplet of distilled water with a diameter of 1.25 mm ($V \approx 1 \mu$ L) at the tip of the needle, after which the stage was smoothly moved upward until gentle contact was made and the droplet was transferred to the treated (central) part of the sample surface, minimizing dynamic effects. The droplet diameter was monitored using a pre-calibrated digital on-screen ruler.

Illumination was provided by diffuse emission from a semiconductor laser diode ($\lambda = 652$ nm) without a collimator, passed through ground glass, which ensured a uniform and contrasting background for clearly defining the droplet profile.

The profile of the droplet resting on the sample surface was photographed from the side using a full-frame digital camera EOS R (Canon Ltd, Japan) with a K2 DistaMax long-distance microscope fitted with a CentriTel focuser and a CF-3 objective lens (Infinity Photo-Optical Company, USA), which has high (up to 1.7 μ m)

spatial resolution. This ensured the necessary detail of the "droplet-air-sample" interfaces. The image from the camera was transmitted to a computer in real-time via a Wi-Fi channel.

The wetting angle was determined based on the obtained images using ImageJ software [20] with the installed Contact Angle plugin [<https://imagej.net/ij/plugins/contact-angle.html>]. This plugin allowed for mathematical approximation of the droplet profile and calculation of the angle between the tangent to the droplet profile at the contact point and the baseline (sample surface). To increase statistical reliability and account for possible surface heterogeneity, the measurement θ was performed 2–4 times on different areas of each sample. The final result was presented as the average value over all measurements, and the random error was also calculated at a confidence probability of 0.95, which made it possible to assess the accuracy and reproducibility of the obtained data. Depending on the method and mode of sample treatment, the relative random error of the wetting angle measurements could range from 10 to 40 %.

Results and Their Discussion

Initially, the wetting angles of the original untreated samples of copper, stainless steel, and the aluminum-magnesium alloy were measured. Thus, the initial values θ_0 for copper, stainless steel, and the aluminum-magnesium alloy were, respectively, $97.0 \pm 3.6^\circ$, $75.5 \pm 3.3^\circ$, $72.9 \pm 3.4^\circ$. The obtained values allow characterizing the initial surface of each sample. Thus, the surface of the copper foil sample can be considered weakly hydrophobic, since the average wetting angle exceeds 90° . As a rule, clean metals are characterized by hydrophilicity. The hydrophobic nature of the copper sample is probably due to the

presence of adsorbed organic contaminants, which reduce the surface energy. The surface of the stainless steel and Al-Mg alloy samples can be characterized as hydrophilic (wetting angle significantly below 90°). These properties are probably determined by the presence of oxide films, the "metal–oxygen" bonds in which are polar and can interact with dipoles – water molecules.

Figure 2 shows the dependences of the wetting angle values of the studied samples immediately after treatment by all methods.

Analysis of the obtained dependences of the wetting angle, measured immediately after treatment, reveals a key pattern common to all samples and treatment methods, namely, the effect of plasma from all three types of discharge (apokamp discharge in air, nanosecond discharge in air, and pulsed discharge in Ar with VUV) leads to a significant decrease in the wetting angle, which indicates an increase in the hydrophilicity of the sample surface.

Let us consider in detail the results for each method of treating the sample surface. When exposing the samples to apokamp plasma, the strongest effect of reducing the wetting angle is observed for the Al-Mg alloy. Thus, the initial value $\theta_0 \approx 73^\circ$ decreased to approximately 20° after just 30 seconds of treatment. Even after 15 seconds of exposure, the wetting angle decreases to 28° . For copper and stainless steel, the reduction in the wetting angle is also significant. Copper demonstrates the largest difference between the initial angle (97°) and that after exposure (32°). The sharpest decrease in θ occurs at short treatment times (15–60 s). Further increase in treatment duration (up to 240 s) leads to a more moderate additional decrease or stabilization of the angle, considering the random measurement error, indicating the achievement of a certain limit of surface modification.

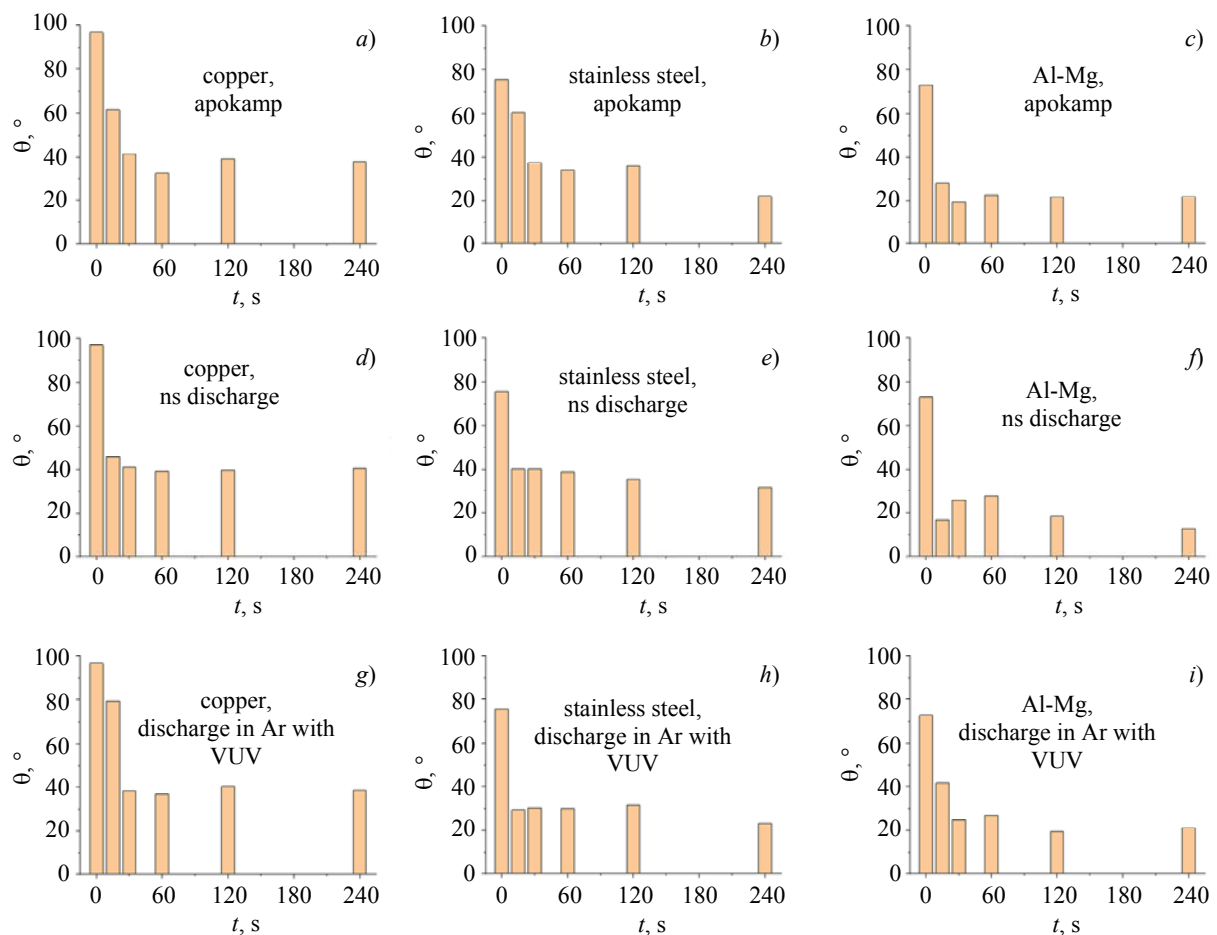


Fig. 2. Dependences of the wetting angle of the sample surface on the duration and method of treatment immediately after treatment: (a–c) apokamp in air at atmospheric pressure, (d–f) nanosecond discharge in air at atmospheric pressure, (g–i) pulsed discharge in an argon flow with VUV emission. Sample material: (a, d, g) copper, (b, e, h) stainless steel, (c, f, i) Al-Mg alloy

When treating samples with nanosecond discharge plasma, maximum (in the entire series of experiments) surface hydrophilization is also achieved. The Al-Mg alloy again shows the lowest values of θ down to 13° . Given the random error (tens of %), the absolute reduction of θ under the influence of the nanosecond discharge plasma is comparable to the results obtained under the influence of the apokamp plasma. For copper and stainless steel, the final values of θ are also comparable to those obtained under the influence of the apokamp plasma. Furthermore, as in the case of the apokamp, the main reduction in the contact angle is achieved within the first 30–60 s, after which stabilization or minor changes are observed.

When treating samples with the pulsed discharge plasma in an argon flow, which also combines the effect of VUV emission, all three

metals also quickly achieve low values of θ ($\approx 20\text{--}30^\circ$) with a treatment time of 30 s or more. Here, stainless steel demonstrates the fastest response to the treatment compared to other metals and discharges: with a treatment duration of 15 s, θ reaches $\approx 30^\circ$. This may indicate a particular sensitivity of the stainless steel oxide film to VUV emission or active species from the argon flow. For comparison, copper after 15 s of exposure shows a reduction in the contact angle only to $\approx 80^\circ$. However, at 30 s or more, a sharp decrease in θ to $36\text{--}40^\circ$ occurs, followed by stabilization. The Al-Mg alloy shows better results. Effective reduction of θ to $\approx 20\text{--}25^\circ$ is achieved after 30 s of exposure.

Figure 3 presents the contact angle values of the studied samples, obtained one day after treatment.

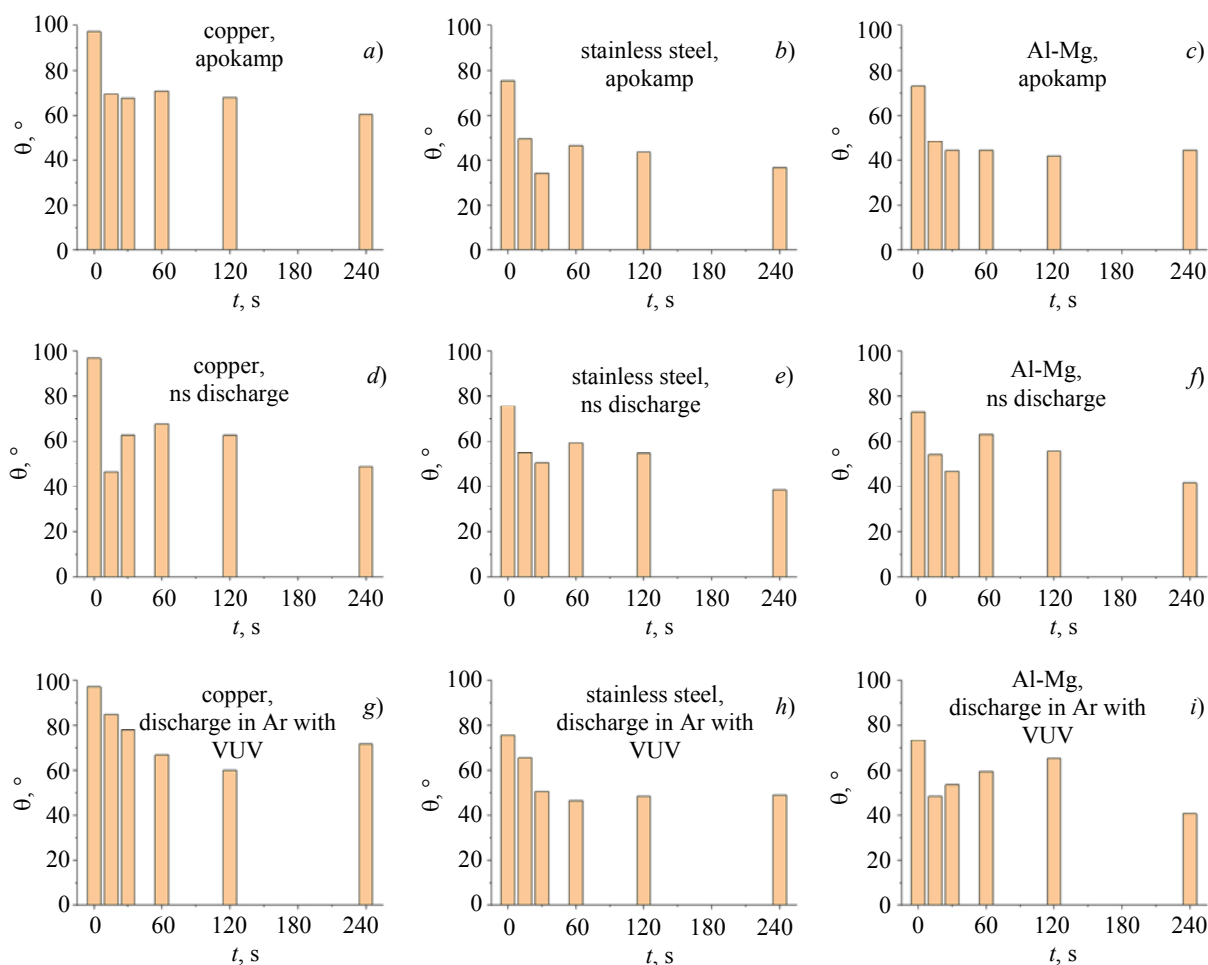


Fig. 3. Contact angles of the sample surface at various treatment durations and methods one day after treatment: (a–c) apokamp in air at atmospheric pressure, (d–f) nanosecond discharge in air at atmospheric pressure, (g–i) pulsed discharge in an argon flow with VUV emission. Sample material: (a, d, g) copper, (b, e, h) stainless steel, (c, f, i) Al-Mg alloy

Measurements taken one day after treatment show a partial recovery of the contact angle, specific to the materials used, which is common for all samples and all treatment methods.

Thus, for the case of apokamp plasma treatment, the fastest recovery of the contact angle is observed for copper samples. The values of θ recover to 60–70° for all treatment durations. For stainless steel and the Al-Mg alloy, the recovery is more moderate. The angles are in the range of 40–50°. It should be noted that there is no clear dependence of the final angle on the treatment duration. Such a dependence might possibly appear when measuring the contact angle minutes to hours after exposure.

In the case of treating samples with nanosecond discharge plasma, the degree of recovery of θ for copper and stainless steel is comparable to that of the apokamp, with final

values of θ in the range of 50–70° for copper and 40–60° for stainless steel. The Al-Mg alloy shows a slightly less pronounced recovery, with values of θ remaining in the range of 40–55°.

The strongest recovery of θ values (up to 70–80°) is observed for copper one day after exposure to the products of the pulsed discharge in an argon flow, which also combines the VUV emission. This may indicate that the increase in surface hydrophilicity is achieved precisely through VUV modification, the effect of which is less stable. For stainless steel and the Al-Mg alloy, recovery of θ is also observed, but the final values of θ remain relatively low ($\approx$ 50–60°).

The obtained data indicate that in our experiments, the change in the wettability of metal samples is the result of a complex impact (of plasma products and VUV emission). Their contribution depends on the type of discharge and the material. In the case of direct exposure of the

sample surface to apokamp and nanosecond discharge plasma in air, highly active plasma species (reactive nitrogen and oxygen species, radicals, and ions) probably effectively destroy and remove loosely bound contaminants from the sample surface. Subsequently, prolonged exposure to open air leads to the readsorption of contaminants/dust by the high-energy surface. Furthermore, upon direct contact of the air plasma with the surface, chemical modification may occur as a result of interaction with the same reactive nitrogen and oxygen species. New polar oxygen-containing functional groups (e.g., oxides) are formed on the metal surface, significantly increasing the surface energy and, consequently, the hydrophilicity.

In the case of exposing samples to the products of a pulsed discharge in an argon flow, which also includes the action of VUV emission, both photochemical reactions on the surface, causing the destruction of contaminants and the formation of radicals, and reactions with metastable particles of argon and nitrogen molecules can occur. These factors can modify the structure or chemical composition of the existing oxide and other films.

Conclusion

Three sources of non-equilibrium atmospheric pressure plasma with different spectral compositions and presumably different quantitative compositions of active components were used for the first time to increase the hydrophilicity of metal surfaces (Cu, stainless steel, Al-Mg alloy). It is shown that the contact angle drops to a minimum within 30–60 seconds,

remaining unchanged at longer exposures considering the measurement error.

Measurements taken one day after treatment show a partial recovery of the contact angle, specific to the materials used, which is common for all samples and all treatment methods. The obtained data are preliminary for the subsequent identification of physical factors affecting the hydrophilicity of metal surfaces.

From the point of view of selecting the source (from those taken for the study) that provides the maximum and long-term change in hydrophilicity, the following can be concluded:

- compared to the nanosecond discharge, the apokampic discharge provides a comparable long-term change in the hydrophilicity of metal surfaces and is technically simpler to implement (no nanosecond pulse generation technique is needed, and no impedance matching of the generator output, transmission line, and load is required);

- the VUV emission source formed in an argon flow allows precise localization of the treatment area compared to the apokampic discharge.

Therefore, in the future, for treating other metal surfaces, particularly those used in medicine, a choice should be made in favor of sources that are relatively simple to operate — the apokampic discharge and the VUV emission source formed in an argon flow.

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