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APPLICATION OF GLOW DISCHARGE PLASMA FOR CLEANING (ACTIVATION) AND MODIFICATION OF METAL SURFACES WHILE WELDING, BRAZING, AND COATING DEPOSITION

As known, the surface phenomena play a crucial role in the formation of strong interatomic bonds while joining dissimilar materials and the deposition of metal films. Thus, the presence of various contaminants, including oxides, on the metal surface reduces drastically the metal surface energy, thereby, preventing the diffusion processes in the contact zone and wetting them with liquid solder and adhesion of condensed films on the substrate surface. As a result, the processes of cleaning (activating) of metal surfaces before welding or coatings' deposition begin to play a significant role. In some cases, metal surfaces have to be modified in order to give them the desired properties. Recently, for activation and modification of surfaces before welding and coatings' deposition, gas-discharge plasma of abnormal glow discharge is widely used. The latter allows treating the surfaces of different configurations, including internal cavities, and various areas from units to tens of thousands of square centimetres. This review contains the results of research on the activation and modification of metal surfaces with low-energy ions (<10 keV) initiated in the plasma of an abnormal glow discharge for welding, brazing, and coatings' deposition. Particularly, we present results of studies of ion treatment with the glow discharge surface of samples, which are made of steels C45 and DC04, a number of active metals and alloys as well as chromium-containing steels 41Cr4, X20Cr13, and X6CrNiTi18-10, which possess the chemically and thermally stable Cr_2O_3 oxides on their surfaces. The decisive influence on the efficiency of purification and modification of metal surfaces with glow discharge by means of such regime parameters as electrode voltage, discharge current density, working chamber pressure, and ion exposure time is indicated. The optimal values of these parameters, in most cases, are determined by the technological conditions of the process and vary in the following ranges: $U_d = 1500–3500$ V, $J_d = 0.4–1$ mA/cm^2, $P = 3.99–7.98$ Pa, $t = 120–300$ s, respectively.

Keywords: glow discharge, plasma, ion bombardment, surface treatment, ion modification, metal and alloy surfaces.

1. Introduction

Surface preparation is the most significant technological operation prior to welding, brazing and coatings deposition that determines the reliability of untouchable joints and formation of complete atomic bonds with the applied coatings. However, the presence of various contaminants on metal surfaces (dust, adsorbed atoms and molecules, chemical compounds, oxide films, *etc.*) complicates significantly the conditions of these processes. For instance, the presence of oxides layer on the surfaces of welded or brazed specimens inhibits the processes of diffusion mass transfer and formation of strong chemical bonds. Instead, the presence of oxides and adsorbed atoms on the substrate surface reduces significantly its surface energy and the adhesion strength of the coatings consequently.

The use of traditional methods of purification such as mechanical, chemical or electrochemical ones does not solve the problem at all. Thus, the use of mechanical methods, such as turning or sandblasting does not appropriate in terms of surface purity, since these processes are closely associated with the presence in air of residues of ultrafine dust, which is deposited subsequently on the samples' surface.

In turn, the chemical cleaning methods (include acidic/alkaline cleaning) is also associated with the significant disadvantages, mainly due to the presence of residues of active detergents on the surface, which are sources of gas in vacuum. On top of that, there is a high probability of harmful chemicals on the surface of the products during chemical cleaning that is definitely threaten to the environment. In this regard, there is a vital to find out a new, more technological and environmental friendly technology and methods for clean and modification of metal surfaces.

Recently, electrophysical methods of purification (activation) and modification, mainly related with the direct action of charged particles on the sample surfaces, have begun to play a significant role. In Ref. [1], it was shown that the use of ion-beam treatment to clean the surface of steel strip samples in terms of speed and quality of processing exceeds greatly the chemical cleaning methods. Thus, according to the technological cycle adopted at the Magnitogorsk Metallurgical Plant, in the process of chemical cleaning for 25 s, contaminants for 1300–1350 mg/m^2 are removed. In the process of plasma associated sputtering of the surface by the heavy ions beams with the energy of 20–50 keV, the same amount of contaminants is removed in 2–5 s [2]. However, the implementation of such a method requires the use of complex high-vacuum and high-voltage equipment.

Among the physical methods of surface preparation, the most promising is the use of glow discharge plasma, which allows to process surfaces of different configurations (including internal cavities) and dif-

ferent areas (from units to tens of thousands of square centimetres). The ability to accurately adjust the parameters of the mode in a wide range, high-energy efficiency and productivity of the process, let alone of environmental friendliness has led to its widespread industrial application. Currently in the literature, the most favourable conditions have developed around the preliminary ion treatment of glass substrates by a glow discharge before coatings deposition and cathode training before ion nitriding. Information about the use of glow discharge plasma for the treatment and modification of metal surfaces before diffusion welding and brazing is limited and contradictory. In addition, it should be noted that there is no any systematic data about the influence of the glow discharge parameters on the results of activation and modification of metal surfaces in mentioned technological processes.

Therefore, the purpose of this review is a detailed analysis of the known experimental works on this issue, which may be useful in elucidating the mechanism of activation and modification of metal surfaces in welding, brazing, and coatings deposition.

2. The Cleaning (Activation) of Metal Surfaces in Plasma of Glow Discharge

The practice of glow discharge (GD) industrial application in various technological processes has shown that among of all the variety of its forms the most suitable for cleaning and modification of metal surfaces is an abnormal GD. The latter normally initiates in the active (nitrogen, hydrogen, hydrocarbons) or inert gases (usually argon) at average pressures of $0.1–100$ kPa. In contrast to the normal GD, where the cathodic potential drop and the current density are constant, in the abnormal GD, a further voltage increase inevitable leads to the growth in the cathodic potential drop and at the same time to an increase in emission from the cathode (treated sample simultaneously).

In a number of works [3–6] dealing with the study of cathode sputtering processes in a glow discharge, it was shown that the sample placed as a cathode in the plasma of abnormal GD will be subjected to an intense ion bombardment. Depending on the energy of ions, the following processes can take place on the cathode surface:

(1) condensation of working gas atoms, which take place at ion energies of $E_i \approx 10–100$ eV, mainly inherent for the processes of coatings deposition;

(2) sputtering of atoms and molecules from the cathode surface as a result of ion bombardment occurs at energies of $E_i \approx 10^2–10^3$ eV, and characterizes the processes of activation of metal surfaces;

(3) bias of the atoms in a crystal lattice and implantation of ions of the working gas in the near-surface layers of the treated sample, is nor-
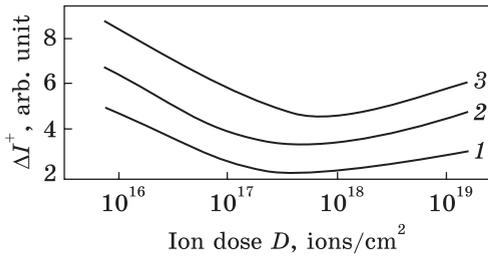
Fig. 1. Ion current from iron sample as a function of Ar$^+$ ion bombardment dose D: (1 keV, 1.2 mA·cm^{-2}), *1* — 300 l; *2* — 3000 l; *3* — 30300 l [11]

mally observed at ion energies of $E_i \geq 10^4$ eV, thus, there is a modification of metal surfaces [7].

Depending on the composition of the working gas and the location of the specimens in the discharge circuit, there are chemical and physical cathode sputterings. In the first case, the parts are placed in the negative glow near the cathode and are under the floating potential. Process of treatment, as a rule, is carried out by low-energy ions of chemically active gases (most often — oxygen). The organic impurities react with the atomic oxygen and are ashed under the formation of a native oxide. The impurities desorb either thermally (thermal desorption) or if bombarded with charge carriers (impact desorption) [8]. During physical sputtering, the treatment is carried out with inert gas ions (normally, it is argon), while the part serves as the cathode of the GD simultaneously. The latter causes a higher productivity of the process, compared with chemical etching, because the ions acquire most of their energy directly in the field of cathodic potential drop.

Ion treatment of metal surfaces in oxygen plasma of abnormal GD mostly inherent for the processes of aluminium coatings deposition, where the role of oxides on the substrate surface is decisive in terms of better adhesion of the condensed phase [9, 10].

However, the authors of the review [11] have noted that some adsorption of oxygen on the surfaces of transition metals (Cu, Ni, Fe) can be observed under the treatment by low-energy Ar$^+$ ions. In order to study the oxygen adsorption kinetics, the treated samples were subjected to the ion irradiation with an argon ions energy of Ar$^+ \approx 8$ keV at a current density of $1.5 \cdot 10^{-3}$ A·cm^{-2}. The pressure in the working chamber was set up so that the residual oxygen pressure did not exceed $2 \cdot 10^{-8}$ Torr. The irradiation dose varied from 10^{-16} to 10^{-19} ion·cm^{-2}. Immediately after ion treatment, the partial pressure of oxygen in the chamber varied in the range of 10^{-7}, 10^{-6}, and 10^{-5} Torr and was maintained steadily for some time to obtain a dose of oxygen of $3 \cdot 10^2$, $3 \cdot 10^3$, and $3 \cdot 10^4$ l, respectively. Then, the chamber was evacuated again, and the bombarding process was repeated. Analysis of the obtained kinetic curves (Fig. 1) shows the presence of oxidation of the iron surface under the treatment by low energy argon ions.

Here, $\Delta I^+ = I_1^+ - I_0^+$ values are plotted as function of the bombardment doses D, where I^+ is the height of the initial current peak (corresponding the initial oxide layer), and I_0^+ is the current corresponding to dynamic equilibrium (approximately it corresponds to the surface oxygen concentrations less than one monolayer) [11]. As follows from the above curves, the initial ion irradiation doses of $D \sim 10^{16}$ are insufficient to remove the oxide layer from the cathode surface. The minimum value of $\Delta I^+(D)$, which corresponds to the minimum concentration of oxides on the surface of iron, was obtained at doses of $2 \cdot 10^{17}-3 \cdot 10^{17}$. With a further growing in the number of ions bombarding the cathode surface, there is a re-increase of the oxides on the iron surface. The authors explain such kinetics of iron surface oxidation under the action of ion bombardment as follows. A small amount of Ar^+ falling on the cathode surface is not enough to remove the primary oxide layer. Instead, the saturation of the oxide film with the argon atoms is observed, which later becomes as a kind of diffusion barrier between the metal and oxygen atoms. The oxidation rate is slowed down, and even there is some removal of oxides from the surface of the iron. A further growth of the oxide layer may be the result of an increase in the number of defects of the macro and micro relief of the surface because of increasing of ion irradiation dose.

The authors of Ref. [8], investigating the mechanisms of removal of adsorbed hydrocarbon and natural oxide layers from the surface of aluminium by the oxygen and argon plasma of abnormal GD, have also indicated a significant role, along with the cathode sputtering, chemical reactions of the adsorbed layer with the oxygen radicals. The following important processes take place here: first, chemical interaction of oxygen radicals formed because of dissociation of O_2 molecules in the region of negative glow with the adsorbed layer of hydrocarbons; second, chemical sputtering of the cathode surface layer as a result of its intensive bombardment with the O_2^+ and O^+ ions; third, physical sputtering of the cathode material, in particular the hydrocarbon layer (CH_xO_y), oxides (Al_xO_y) and, directly, Al itself by low-energy Ar^+ ions. The first two processes allow removing hydrocarbons layers. For spraying of aluminium oxides, where the work function is much greater than for pure metal, the process is carried out in argon plasma of abnormal GD [12].

The surface of the aluminium samples with dimensions of 8×15 cm^2 was treated in abnormal GD and, for comparison, in glow discharge with the hollow cathode effect (HCGD). The main treatment parameters varied within the following limits: discharge current $I_d = 40-120$ mA, voltage at the electrodes $U_d = 500-1200$ V, while the discharge power varied within the $20-140$ W. The gas pressure in the discharge chamber $P = 10-20$ Pa, the treatment time varied within $1-15$ min while the substrate temperature does not exceed $293-423$ K. Purification in abnor-
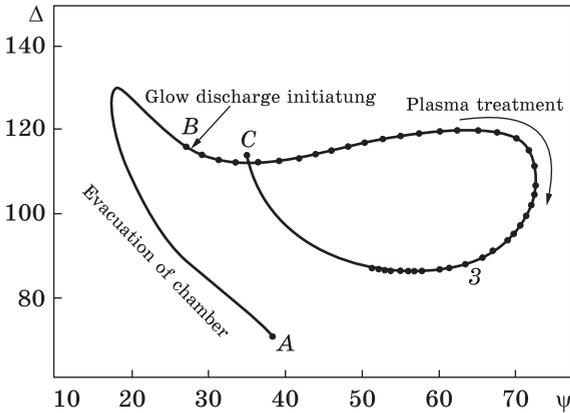
Fig. 2. The $\psi-\Delta$-plot during evacuation and plasma surface treatment [8]

mal GD was implemented according to the diode circuit in which the workpiece serves as the cathode of the discharge, the vacuum chamber acted as the anode. Purification in the HCGD was carried out under the condition of the 'floating' potential of the substrate. The efficiency of the purification process was determined by e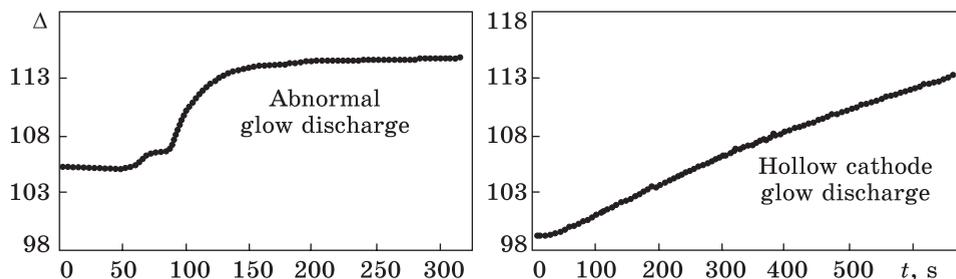llipsometric measurements at the wavelength of the He−Ne laser of $\lambda = 0.6328$ μm. For this method, the change in the time values of the polarization angles ψ and Δ is responsible for the characteristics of the surface state in the cleaning process. The typical dependences of ψ and Δ obtained in the course of ellipsometric studies are shown in Fig. 2.

The authors notice a certain reduction in the layer of oil film adsorbed on the surface of the products at the beginning of the process of evacuation (pumping out) of the chamber to the working pressure (point *A*) due to its high vapour pressure. Volatile impurities at the pumping out stage are removed only to a certain extent, as evidenced by the first critical point *B*. The elimination of oil residues and the hydrocarbon layer was noticed, which manifested by a certain increase in $\psi-\Delta$ (point *C*). The authors have also reported that is impossible to achieve the removal of aluminium oxides from its surface in oxygen GD plasma. It was noted even a certain increase in the oxide layer on the surface of aluminium during prolonged exposure to oxygen plasma, which is correlated with previous studies.

Comparison of the results of ellipsometric measurements after plasma treatment by abnormal glow discharge with a discharge initiated in a hollow cathode showed that the latter provides the same purification level of the aluminium surface, but for a longer time interval. Figure 3 shows the dependences of Δ on the form of the glow discharge.

The low productivity of the process under the condition of the floating potential of the aluminium workpiece during treatment with a HCGD can be explained by a decrease in the effect of low-energy plasma ions on the surface of the treated sample. At this arrangement of the sample, a significant part of the plasma ions falling into a strong electric field and headed to the cathode surface and only a small amount of ions falls direct on the workpiece. This purification process is only chemical and requires additional ion bombardment. In this regard, the authors con-

Fig. 3. Time dependence of Δ for abnormal GD and hollow cathode GD treatment, respectively [8]

clude that the efficiency of plasma treatment by glow discharge increases due to the ionic component.

However, a HCGD can be an effective tool for cleaning and modification of metal surfaces, as long as the workpiece will be under a negative potential, *i.e.* serve as a cathode. In this case, there are no any problems with the charge of the sample surface with the stream of bombarding ions. The method becomes extremely useful in treatment processes of the long metal tubes internal cavities.

In Ref. [13], the results of studies of the HCGD energy characteristics regarding to the conditions of cleaning the small diameter long tubes inner surfaces before deposition of plasma coatings are presented. In these experiments, the cathode was made of steel X6CrNiTi18-10 length of 500 mm, diameter 13.5 mm, thus the ratio of the length and diameter is ≈ 37 mm. The parameters of the mode: discharge current $I_d = 0.24$ A, voltage at the electrodes $U_d = 345$ V, the pressure of the working gas (Argon) in the chamber varied within $P = 10-100$ Pa. The obtained results are shown in Fig. 4.

The research results show a sharp inhomogeneity of plasma distribution within the cathode cavity. The obtained curves shows a rapid decrease in the discharge current density from $J \approx 2.5-3$ mA/cm² to $J \approx 0.1-0.4$ mA/cm² at a distancing from the cathode end, which is placed near the anode. Apparently, such plasma distribution inside the cavity will not provide a uniform cathode sputtering. Thus, the ion bombardment intensity of the remote from the anode–cathode sections decreases dramatically. This inevitably leads to the deterioration of the efficiency of glow discharge cleaning action.

In Ref. [14], a solution for the emission problem at the remote cathode sections where $L = 10d_{in}$ was proposed by introducing into the electrode system an additional anode from the other end of the cathode cavity. The probe measurements of ionic current along the length of the aluminium cathode with a diameter of 10 mm and a length of 110 mm in a double anode system are shown in Fig. 5.
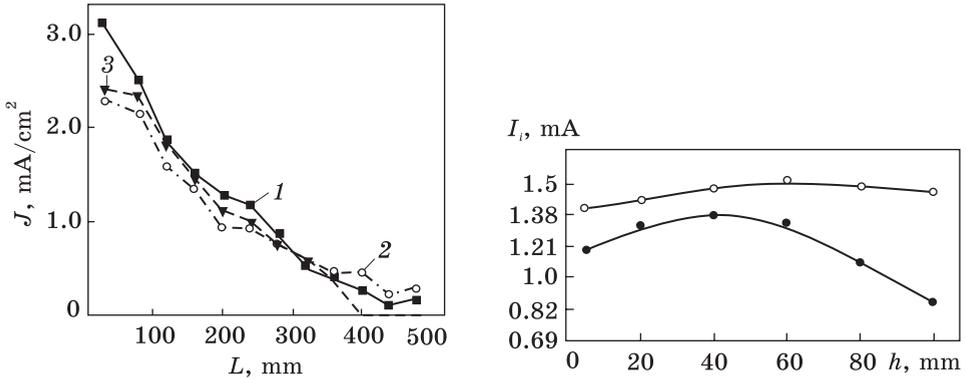
Fig. 4. The distribution of the discharge current density J along the length of the cathode cavity L when: (*1*) $P = 10$ Pa; (*2*) $P = 53$ Pa; (*3*) $P = 100$ Pa [13]

Fig. 5. The results of ion current measurements along the cathode cavity height h: open circles (○) — with an additional anode; solid circles (●) — without an additional anode in the discharge gap [14]

Experimentally obtained probe curves shows a certain redistribution of plasma inside the cathode with a character close to linear when the additional anode in the opposite side of the tube was placed, since the placement of the second anode from the opposite cathode end initiates the appearance of emission processes with the corresponding increasing in the number of ions bombarding the surface. However, the hollow cathode effect for surfaces purification is rather a special case and is rarely used in practice. Instead, the HCGD ended up as extremely effective heating source and found a widespread use in the processes of sintering and doping of metal surfaces, and for the joining of metals as well [15–17].

In Ref. [18], the efficiency of cleaning the surfaces of steel specimens in the plasma of abnormal glow discharge prior to coatings deposition was investigated. Purification of samples made of steel C45 was also carried out with the diode scheme (sample–discharge cathode) in argon. The gas pressure in the working chamber was varied within the 1–11 Pa. Under condition of physical sputtering, such a pressures range is absolutely justified, since, as shown in Ref. [19], the energy dispersion coefficient of particles, coming to the cathode, decreases at 13.3 Pa and above. The latter is associated with the formation on the samples surface of dense adsorbed layers, which prevent sputtering of the surface material. The lower pressure is due to the limit of the glow discharge existence. The treatment time was varied from 30–600 s. The voltage at the electrodes varied in the range of 500–5000 V, and the current density ranged across 0.2–1.5 mA/cm². Thus, the specific power of GD varied from 1 to 5 W/cm². As shown in Ref. [20], this volt-
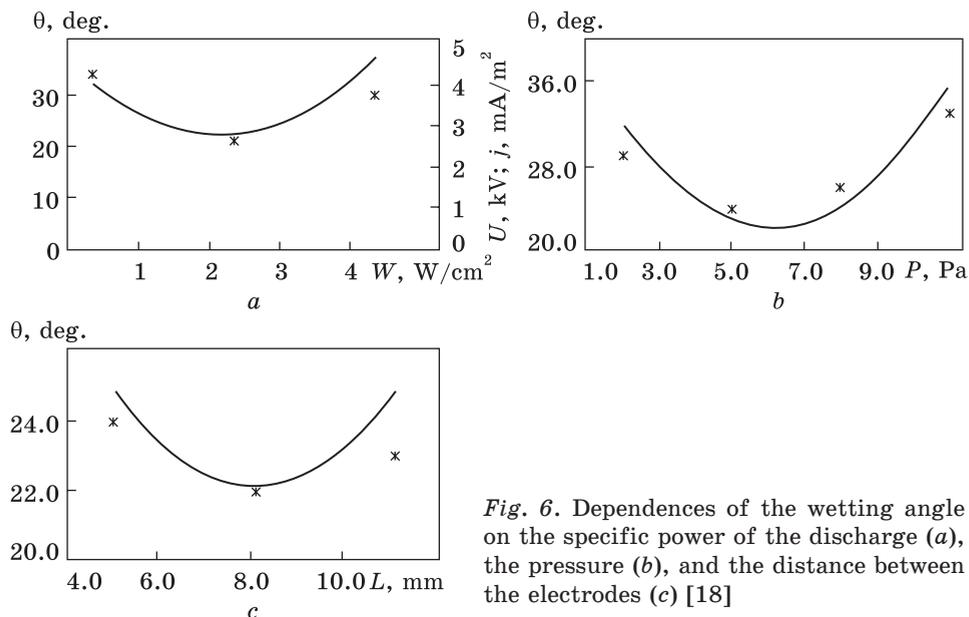
Fig. 6. Dependences of the wetting angle on the specific power of the discharge (*a*), the pressure (*b*), and the distance between the electrodes (*c*) [18]

ages range is the most effective in terms of ion surface treatment, since when the voltage at the electrodes is less than 500 V, the ion energy is not sufficient to knock out the particles off the metal surface. Increasing the voltage above 5000 V is not effective due to the violation of glow discharge stability and its transition into an electric arc. However, in our experiments [21], the appearance of cathode spots of the arc was observed at 2500–3000 V. It is known that the increase in voltage at the electrodes leads to a growth in the glow discharge current density. Nevertheless, in abnormal form of GD, when the entire cathode is covered with a glow, such an increase leads to the rise in electric field strength in the discharge gap. In this context, the presence on the cathode of various cracks and gaps (including those caused by peeling oxides from the cathode surface) or micro- and macroroughness leads to a microarc breakdowns and the violation of the cleaning mode consequently [22].

The efficiency of surface cleaning by a glow discharge was evaluated with the contact angle of wetting the surface (θ) by distilled water. The measurement results are shown in Fig. 6.

As can be seen, the obtained curves are almost identical with the minimum of the wetting angle of $\theta = 22°$, which corresponds to the average values of the parameters, namely: specific discharge power $W = 2.35$ W/cm^2, current density $J = 0.7$ mA/cm^2, gas pressure of $P = 5$–6 Pa and the anode–cathode distance of $L = 8$ mm. The increase of θ with the growth of the discharge specific power is explained by authors by means

of the substrate surface heating while ion treatment. The latter leads to the some surface re-oxidation due to $\upsilon_{ox} > \upsilon_{sput}$, where υ_{ox} is the rate of oxide build-up on the metal surface, υ_{sput} is the sputtering rate of particles from the substrate surface. This phenomenon was also observed when the pressure increases by more than 5–6 Pa. This is due to the fact, that in abnormal GD, the discharge current and the current density, accordingly, while the constant voltage, mainly determined by the pressure of the working gas. As the pressure increases, the current density has also goes up approximately in quadratic dependence, and when a certain value is reached, it leads to significant heating with the building up of an oxides on the workpiece surface [23].

Another phenomenon is important herewith, since with increasing of argon pressure in the working chamber the role of gaseous impurities in it (oxygen, moisture, nitrogen, *etc.*) increases. The presence of impurity atoms in the discharge gap reduces the energy of Ar⁺ ions falling on the cathode due to the decline of their free path length. Increasing the interelectrode distance at constant pressure also leads to some decrease in the frequency of ion bombardment of the cathode due to a growth in the number of collisions with atoms of foreign gas impurities.

The authors has also noted the partial loss of GD's stability with the microarcs' appearance on the surface of the sample due to the rapid growth of the oxide film while treatment at voltages above 2500 V. Figure 7 shows the dependence of angle of wetting on exposure time of the sample with argon ions. The results show the highest quality of surface purification (the lowest wetting angle θ) for a minimum processing time of 180 s. These results are totally coincide with the given in Ref. [24] on the study of ion cleaning efficiency of
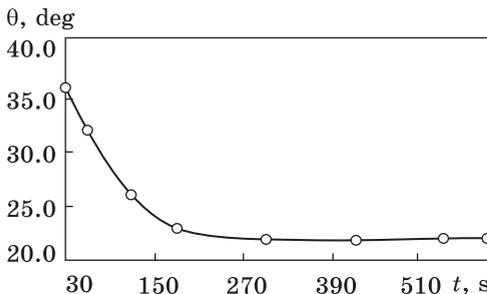

Fig. 7. The dependence of the angle of wetting on the treatment time at $W = 2.15$ W/cm², $L = 9$ mm, $P = 6$ Pa [18]
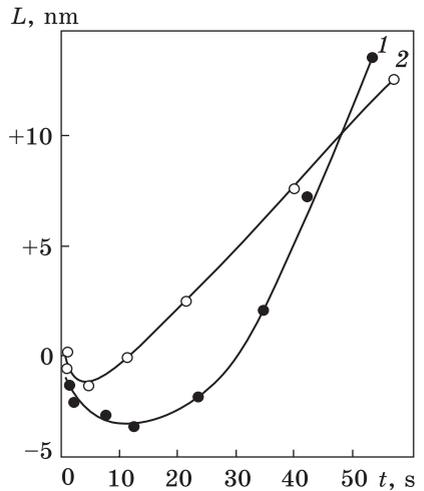
Fig. 8. Dependence of change of surface film thickness on time of ion bombardment in ac glow discharge: *1* — without preliminary cleaning; *2* — pre-electrochemically cleaned surface [24]
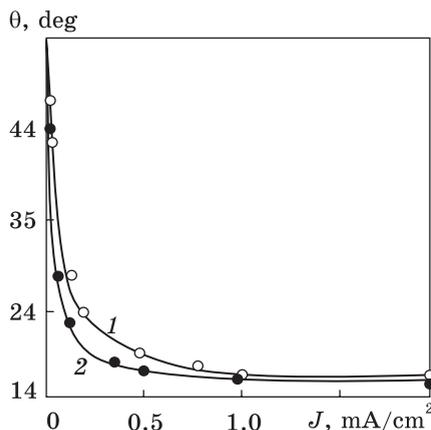
Fig. 9. Dependence of the wetting angle on the discharge current density while ion treatment of steel DC04 in oxygen (*1*) and argon (*2*) plasma of glow discharge [26]
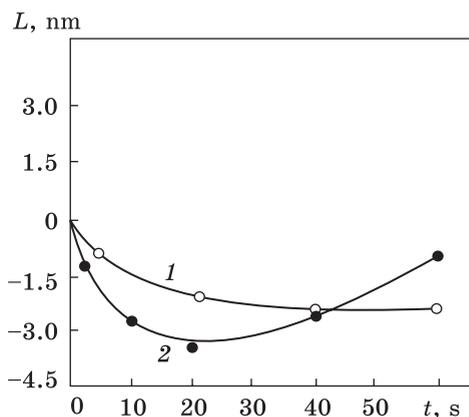
Fig. 10. The dependence of the change in the surface oxide thickness on steel 08kp on treatment time in oxygen (*1*) and argon (*2*) plasma of glow discharge [26]

the surface of steel DC04 in argon at pressures of $P = 0.05–1$ Torr. In these experiments, the voltage at the electrodes was $U_d = 900$ V, current density $J = 0.5$ mA/cm². The authors note that the most of contaminants are removed in the first seconds of the glow discharge action and give the dependences of the change in the metal surface film thickness on the time of argon ions exposure (Fig. 8).

The obtained results have also shown a decrease in the thickness of oxides surface layer in the first seconds of the glow discharge action. With increasing of the treatment time in argon plasma of GD, the some increase in the oxide film thickness was also observed. Moreover, there is a more active build-up of an oxides on the pre-electrochemically cleaned surface is noted. Electrographic study of an oxide layers occurring on the surface of steel DC04 with duration of ion treatment of 360 s have showed the presence of mainly FeO oxide.

At the same time, a number of papers suggests that the glow discharge will be most effective in terms of surface treatment before coatings deposition, namely in an oxygen. For instance, in Ref. [25], it was believed that to improve the adhesion of the aluminium coating on the steel substrate requires an additional oxidation of the surface and have proposed to carry out of periodic oxygen supply to the working chamber during ion treatment.

In Ref. [26], a comparative analysis of the efficiency of ion treatment of the surface of steel DC04 in argon and oxygen plasma of glow discharge was also shown. The results of comparisons are shown in Fig. 9 and 10.
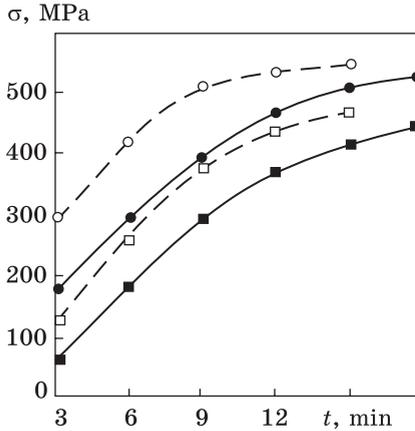
σ, MPa

From the experimental curves, it can be concluded that despite the smaller angle of wetting obtained while treating in argon (Fig. 9), the total intensity of surface films cleaning in an oxygen plasma is a bit higher (Fig. 10). The authors attribute this one to the increase in chemical reactions of surface contaminants with oxygen ions, which in this case lead to an acceleration of the surface cleaning process. However, for the processes of diffusion welding and brazing, the results of these works are not appropriate, since the task of them mainly related with the formation of an oxide layers on the metal surface for the better adhesion of the aluminium coating, since the presence on the metals surface joined by diffusion welding and brazing of an oxides' layer inhibits dramatically the formation of chemical bonds as well as the development of diffusion mass transfer and reduces of metals surface energy [27, 28]. In this regard, the issue of activation (cleaning) of metal surfaces by low-temperature distributed GD plasma before welding and brazing is also relevant and requires of detailed analysis.

Thus, it is known the work [29], which presents the results of experimental studies of ion activation of metal surfaces in the glow discharge plasma before diffusion welding. In these experiments, the workpieces with a diameter of 10 mm and a height of 30 mm, made of steel 41Cr4, steel X6CrNiTi18-10 and titanium alloy VT-3-1 were used. Either approximately 24−48 hours before welding, the welded surfaces were finished with the turning and immediately before welding, they were degreased with solvents or ionic treatment in argon plasma of glow discharge was performed. Gas pressure in the working chamber has varied in the range of 5−10 Pa and the voltage at the electrodes of the discharge 2000−2500 V. Treatment time was 300 s.

The workpieces were the cathode of a glow discharge. After treatment, the specimens were brought into the contact with a mechanical compression system and their diffusion welding was carried out. The efficiency of surface preparation before welding was evaluated by mechanical tests of samples welded in homogeneous and heterogeneous combinations in the next mode: welding temperature 1223 K, compression force of samples 10 MPa. The welding time was varied from 6 to 20 minutes.
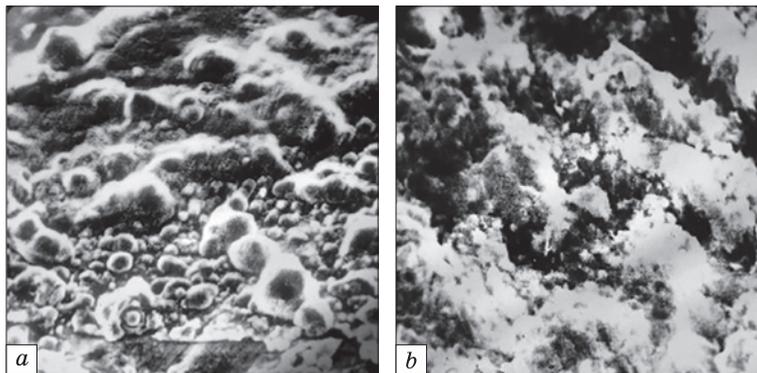
Fig. 12. Relief of steel X6CrNiTi18-10 surface before (*a*) and after (*b*) ion treatment (×5000) [29]

As a result, the authors have found that the effectiveness of the glow discharge as an activating tool of metals surfaces before diffusion welding is primarily in reducing the dissolution time of oxides in the metal and the interatomic bonds establishment. The duration of this period was estimated by the time to achieve the same level of the joints strength during welding with and without of ion activation. The authors note the most noticeable effect in the homogeneous connection of titanium alloys and titanium with stainless steel, where the welding time was reduced in the 28−32% and 22−24%, respectively (Fig. 11).

A much less significant effect of ion treatment was found during the welding of steel 45 samples, where the active surface reducing agent was carbon. Metallographic studies of the surface of steel X6CrNiTi18-10 before and after ion treatment in the glow discharge showed the presence of the globules of contaminants on the samples surfaces before treatment (Fig. 12, *a*), and the open microrelief of steel after bombardment (Fig. 12, *b*).

The study of the wettability of the surface of the same steel with distilled water shows a significant decrease in the wetting angle after ion treatment both in comparison with the original surface and after washing with acetone (Fig. 13).

In Ref. [30], the optimal plasma treatment parameters by abnormal GD of metal surfaces before diffusion welding and brazing were determined. The materials with high oxygen affinity were selected as the investigated, namely, chromium steels 41Cr4, X20Cr13 and X6CrNi-Ti18-10, which possess of chemically and thermally stable Cr_2O_3 oxides on their surface. The presence of the latter complicates dramatically their weldability and ability for brazing as well. Wetting of pre-treated surfaces with liquid solders was chosen as a measure of the effectiveness of the glow discharge. After purification, the samples were re-
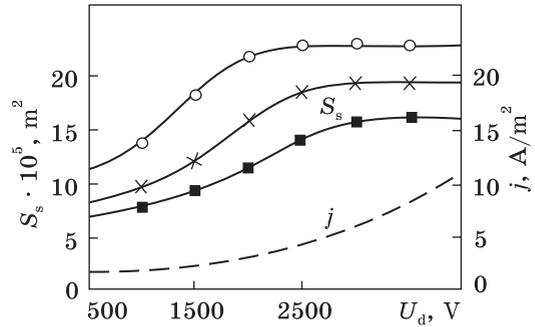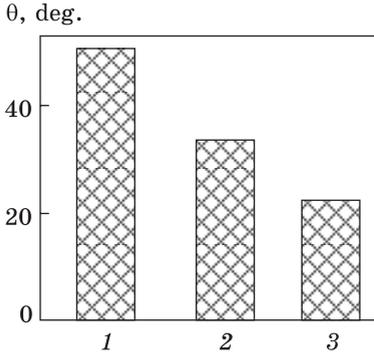
θ, deg.

Fig. 13. Changing the angle of wetting of the steel surface depending on the method of its preparation: *1* — the original surface; *2* — washing the surface with acetone; *3* — ion surface treatment [29]

Fig. 14. The dependence of the solder spreading area S_s on the steel surface from the voltage on the electrodes during treatment in the glow discharge (j — current density on the sample surface, gas pressure 4.65–5.32 Pa): ○ — steel 41Cr4; × — steel X20Cr13; ■ — steel X6CrNiTi18-10 [30]
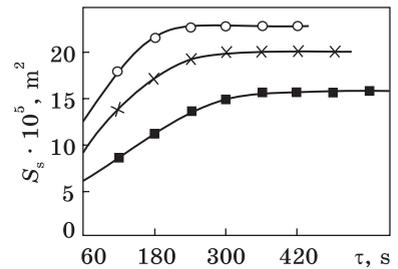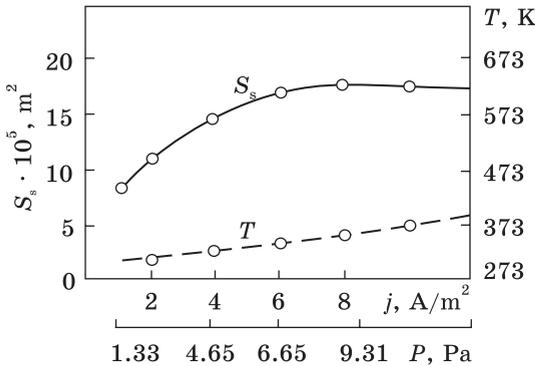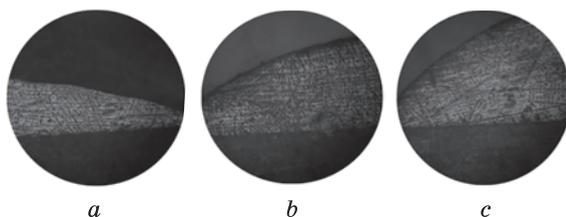

Fig. 15. Dependence of the solder spreading area on the surface of steel X6CrNi-Ti18-10 on current density of the glow discharge while ion treatment and the pressure of the working gas (T — heating temperature of the sample during processing) [30]

Fig. 16. The impact of ion treatment duration of steels on the solder spread area on them: ○ — steel 41Cr4; × — steel X20Cr13; ■ — steel X6CrNiTi18-10 [30]

moved from the discharge chamber and installed in a heater and after evacuation were heated with temperature of 1103 K. The duration between treatment and heating was approximately 15–18 minutes. The treatment was carried out in argon. The experiments were conducted on samples of $30 \times 30 \times 0.2$ mm³. The silver solder (PSr-72) was used. The weight of the solder in all cases was the same — 0.2 g. In accordance with [18], the treatment parameters varied within the following range: voltage at the electrodes $U_d = 500{-}5000$ V, while the magnitude of the

Fig. 17. Spreading of solder PSr-72 on the surface of steels: a — 41Cr4; b — X20Cr13; c — X6CrNiTi18-10 [30]

cathodic potential drop U_c varied from about 300 to 4000 V; gas pressure P = 1.33–16.03 Pa.

Figure 14 shows the obtained dependences of the solder spread area on the steel surface from the voltage at the electrodes while treating in the glow discharge.

The obtained results indicate an increase in the solder spreading area S_s on the surfaces of the samples after ion treatment with increasing of discharge voltage. The author inferred that the value of the discharge voltage required for the soldier spread on the surface would be determined by the chemical composition of oxide systems. Thus, for steel 41Cr4, the surface of which is covered with the low chromium oxide of spinel type $(FeO)(Cr_2O_3)$, the activating voltage going to be approximately 1200–1800 V. While for steel X6CrNiTi18-10, where quite stable chromium oxides Cr_2O_3 are formed, activating voltage will be 3000–3500 V. As in the case of Ref. [18], the author points to the deterioration of the surface condition after reaching a certain critical voltage and, also, associates this with their oxidation caused by increasing the temperature of the samples, which during ion treatment reached 453 K and more. Increasing the voltage at the electrodes above 2000–3500 V (according to the chromium content in the samples materials) has virtually no effect on the quality of the surfaces cleaning of steel samples.

Investigating the effect of gas pressure on the quality of treatment, the author notes that in the low pressure of 1.33 Pa the surface state of the studied steels after ion bombardment not unlike the untreated ones (Fig. 15).

In author's opinion, this is due to the insufficient concentration of charged particles in the discharge plasma because of low degree of ionization at these pressures. The maximum of solder spread area on the surfaces of the studied steels was obtained at gas pressures of 3.99–7.98 Pa. A further increase in pressure in all cases led to a deterioration in the solder spread. This phenomenon is natural for a glow discharge, because, as was mentioned above, with increasing of pressure, the current density at the cathode has also going up, contributing to the heating of the latter. The most effective results (the largest area of solder spreading) were obtained at current densities of 0.4–1 mA/cm^2.

In Figure 16, the results of experimental studies of the effect of exposure duration of steel surfaces by argon ions are shown. Analysing the obtained dependences, the author concludes that the duration of ion treatment will be determined by the content of easily oxidizable elements in steels, in particular chromium. Thus, achievement of the largest spreading area of PSr-72 solder on the surface of steel 41Cr4 took about 120–150 s, while for steel X6CrNiTi18-10 this parameter has doubled and was about 300–360 s.

Along with the decrease in the solder spread area with increasing of chromium content in the studied steels, a corresponding increase of the wetting angle under other equal conditions was observed (Fig. 17). Thus, the wetting angle of 41Cr4 steel was $\theta = 15$–$18°$, while for steel X6Cr-NiTi18-10 — $\theta = 44$–$52°$.

3. Modification of Metal Surfaces in Glow Discharge Plasma

The ability of joining of dissimilar metals and the strong bonds formation is determined primarily by the joined materials surface properties. However, in practice, the physicochemical properties of most metals are underdeveloped in terms of adhesion, wetting and the strong bonds formation. To obtain the needed surface characteristics of metals, they are normally modified by changing its morphological and physicochemical properties. This is mostly achieved by adjusting its structural–phase composition through the diffusion saturation with appropriate metals or non-metals (nitrogen, boron, carbon) by exposing the samples surface with high-energy ions (10–100 keV). Such ions' energy is normally provided by the use of ion beam technologies [31] or other ion accelerators (discharge with a hollow cathode/anode [32, 33] or immersion plasma ion implantation with the glow discharge [34]). However, for the welding, brazing and coatings deposition conditions the gas saturation of surfaces is undesirable phenomenon. This is because the presence of the gases in the near-surface layers of metals complicates dramatically the diffusion mass transfer processes, thereby degrading of the welded or brazed joints quality and an adhesion of coatings on the substrate respectively. Additionally, the processes of chemical-thermal treatment (nitriding) are normally carried out at the samples temperatures of 823–873 K. As shown from Ref. [35], already at 503 K, there are the related annealing colours on the workpieces surface, which indicates about occurring significant oxidation during processing.

Instead, the effect of penetration of metal atoms from the surface into the microscopic distances at temperatures not exceeding of 493 K while ion bombardment in a glow discharge was established by the scientists of G.V. Kurdyumov Institute for Metal Physics of the National Academy of Sciences of Ukraine [36–38]. Gertsriken and Mazanko showed
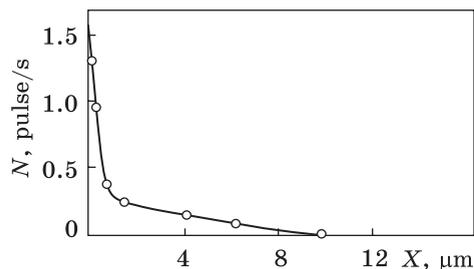
Fig. 18. The distribution of nickel atoms in titanium during treatment in a glow discharge for 10 hours [37]
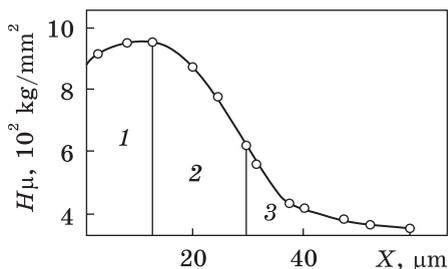
Fig. 19. Changing of microhardness and phase composition along the depth of the diffusion zone after ion treatment [37]

the penetration depth of tens of microns of caesium atoms deposited on the surfaces of nickel and aluminium during ion bombardment in abnormal GD. The diffusion coefficients of caesium atoms in nickel and aluminium were one or two orders higher than similar indicators obtained under isothermal annealing.

In Ref. [37], the results of doping of the titanium surface in glow discharge plasma with nickel atoms galvanically deposited on the titanium are given. The treatment was carried out in nitrogen plasma at gas pressures of 10−1500 Pa. The current density was 0.5−40 mA/cm^2 while the temperature of the samples during ion treatment did not exceed of 473−493 K. The voltage at the electrodes varied in the range of 0.4−2 kV and the duration of ion exposure varied from 1 to 10 hours. In order to increase the intensity of ion bombardment, the process was carried out in a pulsed glow discharge with pulsations of 20−100 μs. The latter allows increasing slightly the magnitude of the discharge current in comparison with the usual glow discharge. The effect of ion bombardment on the redistribution of atoms in the surface layers was studied by the method of radioactive isotopes. In this case, a ^{63}Ni radioisotope deposited on the surface of samples up to 1 μm of thickness was used.

According to this research, the authors have noted the penetration of nitrogen into titanium to a depth of 12−15 microns. However, there is some redistribution and penetration of the surface atoms of treated metal into the distances of $\approx$ 8−10 μm along with the nitrogen ions was observed (Fig. 18). Moreover, the depth of penetration of the doping atoms increases with the growth of ion exposure duration.
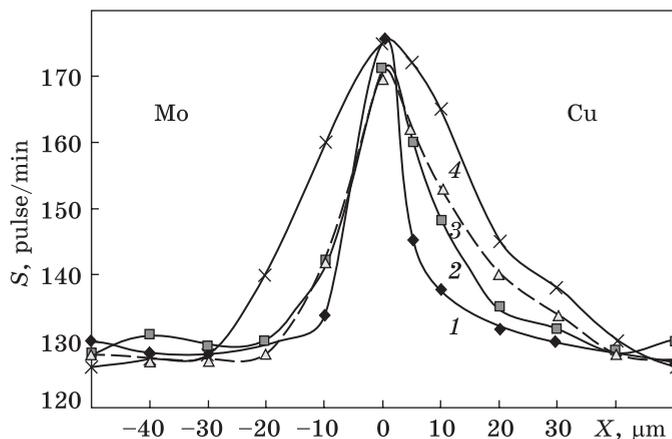
To determine the diffusion coefficient D_{ef} of the radioisotope labelled atoms into the sample, which was treated with a glow discharge for a while, the following equation was used [37]:

$$mN_{n} + \frac{dN_{n}}{dX_{n}} = \frac{\text{const}}{\sqrt{pD_{ef}t}} \exp\left(-\frac{X_{n}^2}{4D_{ef}t}\right), \tag{1}$$

where N_n is the activity of the sample after removal of the layer thickness of X_n, μ is the linear coefficient of the sample material absorption of radiation, and t is the duration of ion treatment. The calculations performed with (1) showed that the diffusion coefficient of nickel in titanium about $3.3{-}10^{-13}$ after treating with the glow discharge. Moreover, nickel and nitrogen forms a solid solution in titanium, the concentration of which in the latter decreases exponentially. The most interestingly, the authors notes the reverse migration of titanium atoms into the nickel layer, which appear even on the surface of the sample in form of titanium nitrides, apparently due to the interaction with nitrogen atoms. Herewith, there is a certain inhomogeneity in the distribution of penetrating atoms on the surface, which is remains at a depth of 2 to 3 μm was observed. The increase of the penetration depth of nickel atoms into titanium to 80–120 μm was achieved through the increase of the discharge energy from 0.9 to 3.14 *J*. Analysing the microhardness distribution along the depth of the diffusion zone (Fig. 19), the authors [37] conclude on the simultaneous saturation of titanium surface with nickel and nitrogen. At that, the following three phases in the interaction zone occur alternately: nickel nitride (zone 1), solid solution of nitrogen and titanium in nickel (zone 2), and solid solution of nickel and nitrogen in titanium (zone 3). The maximum of microhardness of 1000–1200 kg/mm^2 are observed in zone 1, the length of which is approximately 15–18 μm.

The effect of metal atoms penetration from the surface into the depth with ion bombardment was used in Ref. [38] for development of diffusion welding technology of copper with molybdenum, the joining of which is complicated by a sharp contrast in their physicochemical properties. The lack of mutual solubility of this diffusion pair prevents the formation of a reliable diffusion-welded joint. Therefore, welding was performed through the ion-modified copper layers up to 1 μm of thickness applied to the molybdenum surface by the ion-plasma method. The effect of ion bombardment with the plasma of abnormal GD of the deposited on the molybdenum surface the layer of copper on atoms redistribution and diffusion rates while diffusion welding of molybdenum with copper was investigated. Diffusion processes in the contact zone during welding, as in the previous case, were studied by the method of radioactive isotopes. In addition, the nickel isotope ^{63}Ni was used, which was applied electrolytically to Mo. The thickness of ^{63}Ni layer was about 0.3 μm, the activity was $5{\cdot}10^3$ pulses/min. After welding, the samples were cut and placed on the x-ray film. Exposure time on film was about 100 hours. After that, the film was photometred to obtain the concentration distribution of ^{63}Ni in both Mo and Cu. The efficiency of ion treatment was evaluated by comparing with the base sample, which was not subjected to modification while tensile testing of welded joints. All

Fig. 20. Concentration distribution of [63]Ni in Mo and Cu after welding on the basic mode I and on the modes II, III, IV (see Table 1 in Ref. [38])

the modes was differ from the base and from each other by the duration of treatment with argon (t_{Ar}) and the accelerating voltage of ions (U_{acc}), as shown in Table 1 of Ref. [38].

Analysis of the distribution curves of the radioactive isotope of [63]Ni in Mo and Cu after diffusion welding, shown in Fig. 20 demonstrates a significant penetration of Nickel (tens of microns) in the latter. Moreover, the depth of penetration of [63]Ni into Cu is noticeably greater in comparison with Mo. The authors attribute this to the limited solubility of Ni in Mo, although Ni in Cu diffuses without any restrictions over the entire concentration range.

The influence of the treatment mode (regime) on the penetration depth of [63]Ni in Cu and Mo is illustrated in Fig. 21. The dependences also indicate a greater depth of [63]Ni penetration into the Cu in the whole range of parameters changes that indicates a greater mobility of [63]Ni in Cu. The results of mechanical tests of diffusion-welded joints (Fig. 22) shows the increasing of welded joints strength with increasing of voltage up to 2000 V and the treatment time up to 20 min (mode IV).

In another work [39], the effect of ion bombardment on the penetration of nickel atoms into chromium in order to improve the strength of copper−chromium diffusion-welded joints was investigated. The welding of this pair of metals has the same problems, as for the mentioned previously. Since, as shown in Ref. [40], the solubility of chromium in copper is only about 0.0021% at a temperature of 1173 K. Therefore, the welding was carried out through the nickel layer of 1−2 μm thick, deposited by thermal evaporation on the surface of the chromium alloy VH-2K with the further ion implantation in a glow discharge. The treatment was carried out at a voltage on the electrodes $U_d = 600$ V in argon plasma of GD with pressure of 13.3 Pa. The treatment time was 900 s. Then, the diffusion welding of chromium with copper at a temperatu-
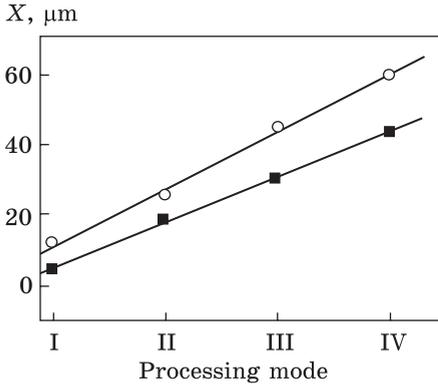
X, μm

Fig. 21. Changing the penetration depth of ^{63}Ni in Cu (●) and Mo (■) depending on the treatment mode (regime) [38]
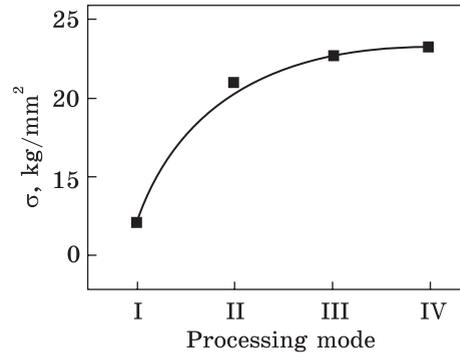
Fig. 22. Dependence of the strength of the welded joints of copper and molybdenum on welding modes [38]

re of 1193 K was performed. The compressive force was of 16 MPa; the welding time — 900 s. As a control, the samples welded through the layer of chromium deposited on the nickel without ion treatment were used.

The results of mechanical tests showed the 162–172 MPa for samples with ion bombardment of the nickel layer vs the 118–120 MPa for the samples without ion modification. The obtained results are explained by the authors based on the analysis of the nature of the diffusion processes in the joint zone of ion-modified samples, and samples welded without ion treatment. Thus, the distribution of elements in the transition zone of the samples without ion bombardment is characterized by a significant inhomogeneity of the distribution of nickel with essential shift towards the copper sample (Fig. 23, *a*). The latter is explained by the greater diffusion coefficient of nickel rather in copper, — $4 \cdot 10^{-14}$ m²/s at $T = 1273$ K, — than in chromium — $6.7 \cdot 10^{-16}$ m²/s at the same temperature. The forced implementation of nickel in the surface layers of chromium changes the pattern of diffusion processes in the weld zone with a character close to homogeneous (Fig. 23, *b*). The latter makes a higher strength of the samples after ion bombardment.

Thus, the mechanism of activation of the nickel atoms motion deep into chromium during ion bombardment with GD cannot be explained in terms of methods of metal surface modification by diffusion saturation [41] and ion implantation [1]. Firstly, due to the significant ions energy, which, as was mentioned earlier, in these processes, reaches up to 100 keV. While treatment with the glow discharges, the energy of ions is only 0.2–3 keV. In this case, the doping of the surface layer of the sample by recoil atoms (initially displaced atoms) from the predeposited
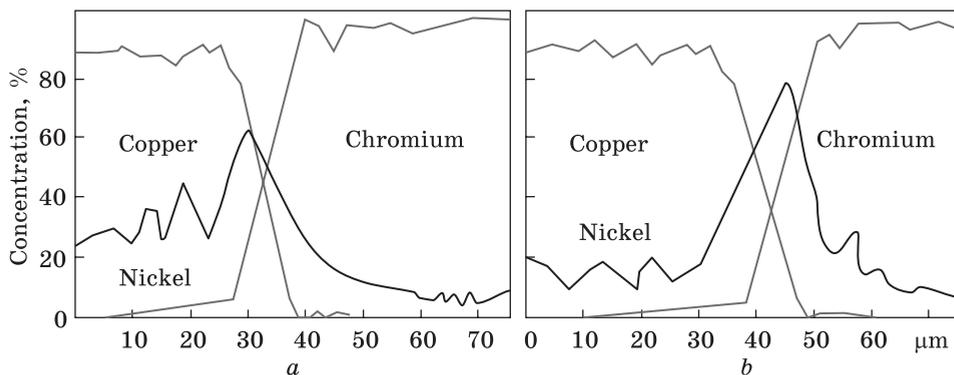
Fig. 23. Distribution of elements in the transition zone of chromium–copper joint through the deposited (*a*) and additionally treated with argon ions (*b*) an intermediate layer of nickel [39]
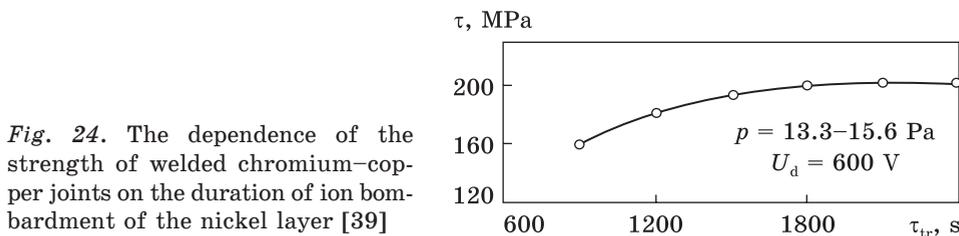

Fig. 24. The dependence of the strength of welded chromium–copper joints on the duration of ion bombardment of the nickel layer [39]

on the sample surface film during ion treatment is more likely [42]. The recoil atoms receive a quite high energy from the accelerated ions and can be moved in a solid body at a distance of several units or tens of nanometers. A similar effect can be observed in the processes of ion implantation at high concentrations of doping atoms in the ionized vapour phase. If the energy transferred by the ion to the initially displaced atom exceeds some threshold energy of the atom displacement, which for the most metals is $T_d = 10-30$ eV, in turn, it can displace the other atoms, and so on. The average number of atoms displaced by the recoil atom is determined by the energy of the initially displaced atom, which in the first approximation can be assumed with correspondence to the voltage drop in the cathode region of the glow discharge. In an abnormal glow discharge at gas pressures $P \ll 133$ Pa, the magnitude of this drop is 0.9–0.95 of voltage at the discharge electrodes [30].

It follows that the unit effect of the accelerated ion on the film's surface atoms leads to a sequential shift in the direction of impact of several tens or hundreds of atoms of the latter. In conditions of small film thickness, this can lead to the implementation of film atoms into the sample. Prolonged dynamic impact on the moving atoms of accelerated ions transmitting energy and momentum to them, promotes the movement of the film atoms deep into the substrate [30].

As was mentioned earlier in Ref. [18], increasing the duration of ion bombardment leads to a certain growth in the depth of penetration of alloying atoms into the depth of the treated sample. The result obtained in this work absolutely correlates with our data, which we have while investigating of the impact of ion treatment time of the nickel film deposited on chromium on strength of the chromium–copper welded joint of [39]. The study was performed at a discharge voltage of 600 V and a gas pressure of 13.3 Pa. The treatment time ranged from 300 to 3600 s. The research results are shown in Fig. 24 and demonstrates the gradually increasing of the welded joints strength with the maximum of 212–223 MPa (in a 2400 s), with the growth of the treatment duration. After that, the welded joints strength did not change.

In the above cases, ensuring the quality of welding was achieved by using intermediate layers of copper or nickel, having solubility with both metals (copper and molybdenum in the first and chromium and copper in the other case). Additional ion bombardment of interlayer served as an acceleration tool for its forced implementation into the surface of the less active metal (molybdenum and chromium, respectively). This is because, for example, the thermal diffusion coefficient of nickel into chromium is two orders of magnitude lower than copper. Thus, implemented into chromium nickel forms 'paths' along which copper, due to its high diffusion coefficient in nickel ($9.58 \cdot 10^{-14}$ m^2/s at 1273 K [43]), penetrates into the chromium, expanding the diffusion zone and, thereby, increasing the strength of the welded joints.

4. Conclusions

An analytical review of the mechanisms of purification (activation) and modification of metal surfaces by low-energy ions (0.2–3 keV) initiated in the plasma of an abnormal glow discharge is performed. The experience of effective application of highly ionized glow discharge plasma for surfaces preparation in welding, brazing, and coatings deposition was shown on the example of steels C45, DC04, a number of active metals and alloys as well as chromium-containing steels 41Cr4, X20Cr13, and X6CrNiTi18-10, which have chemically and thermally stable oxides Cr_2O_3 on their surface. As reported, the presence of such oxides on the surfaces of contacting metals deteriorate dramatically the diffusion mass transfer processes, reduces the surface energy of the metals, thereby preventing the formation of reliable joints and coatings. As shown, while bombardments by argon ions of a glow discharge, the processes of reoxidation of metals surfaces because of their excessive heating can be observed. To prevent this, the optimal values of the treatment regime main parameters, such as voltage at the electrodes, current density, gas pressure, and duration of processing are given; they are as follow: U_d = 1500–3500 V, J_d = 0.4–1 mA/cm^2, P = 3.99–7.98 Pa, and t = 120–300 s, respectively.

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ЗАСТОСУВАННЯ ПЛАЗМИ ЖЕВРІЙНОГО РОЗРЯДУ
ЗАДЛЯ ОЧИЩЕННЯ (АКТИВАЦІЇ) ТА МОДИФІКУВАННЯ
МЕТАЛЕВИХ ПОВЕРХОНЬ ДЛЯ ЗВАРЮВАННЯ,
ЛЮТУВАННЯ ТА НАНЕСЕННЯ ПОКРИТТІВ

Відомо, що поверхневі явища відіграють вирішальну роль у процесах утворення міцних міжатомових зв'язків при з'єднанні різнорідних матеріалів, а також осадженні металевих покриттів. Так, наявність на поверхні металів різного роду забруднень, зокрема шарів оксидів, істотно понижує поверхневу енергію металу, перешкоджаючи таким чином перебігу дифузійних процесів у зоні контакту та змочуванню їх рідкою лютою, а також адгезії конденсованих плівок на поверхні субстрату. У зв'язку з цим істотну роль відіграють процеси очищення (активації) металевих поверхонь перед зварюванням або нанесенням на них шару покриття. У ряді випадків металеві поверхні модифікують задля надання їм необхідних властивостей. Останнім часом з метою активації та модифікування поверхонь перед зварюванням і нанесенням покриттів широкого використання набуває газорозрядна плазма жеврійного розряду. Остання уможливлює здійснення оброблянь поверхонь різної конфіґурації, у тому числі й внутрішніх порожнин, та різної площі — від одиниць до десятків тисяч квадратних сантиметрів. Даний огляд містить результати досліджень стосовно очищення та модифікування металевих поверхонь йонами низької енергії (<10 кеВ), ініційованих у плазмі аномального жеврійного розряду для зварювання, лютування та нанесення покриттів. Зокрема, тут наведено результати досліджень йонного очищення в плазмі жеврійного розряду поверхонь зразків, виконаних з криць 45 і 08кп, ряду активних металів і стопів, а також хромовмісних криць 40Х, 20Х13 та 12Х18Н10Т, що мають на своїй поверхні хемічно та термічно стійкі оксиди Cr_2O_3. Зазначається вирішальний вплив на ефективність очищення та модифікування металевих поверхонь таких параметрів режиму, як напруга на електродах, густина струму розряду, тиск у робочій камері та час йонної експозиції. При цьому оптимальні значення цих параметрів у більшості випадків визначаються технологічними умовами процесу та коливаються в наступних межах: $U_p = 1500-3500$ В, $J_p = 0,4-1$ мА/см², $P = 3,99-7,98$ Па, $t = 120-300$ с відповідно.

Ключові слова: жеврійний розряд, плазма, йонне бомбардування, оброблення поверхні, йонне модифікування, поверхні металу та стопу.