Cleaning the surface of products with glow discharge plasma

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Abstract. The paper presents a method for cleaning the surface of products by plasma glow ions. Before applying vacuum-plasma coating methods. The foundations of the evaluation method are formed. Methods of quality control of preparing the treated surface for the coating process based on IR spectra and Raman spectra (Raman spectra) obtained by analytical studies of the surface state of the samples are presented. Based on the analysis of the intensities of the IR and Raman spectra, the dependence of the degree of surface purity of the samples on the cleaning method used is demonstrated.

1. Introduction

The presence on the metal surface of the product of oxide films, adsorbed layers, layers significantly affect the quality of the ion-plasma surface treatment and the application of protective coatings on it. For cleaning, preparation of the treated surface for technological impact, both mechanical impact methods and methods of activation, processing and cleaning with ion, ion-plasma and other vacuum methods are used [1]. Mechanical cleaning is mainly used for processing metal structures of its elements and devices [2], chemical for removing organic layers, ultrasonic treatment, removing organic contaminants, metal particles [3]. Thermal and electrophysical effects, based on which the workpiece surface is heated in a vacuum. Heating the surface of the product allows you to remove the grease present on the surface by evaporation [4].

The plasma generated by electric discharges in a vacuum is quasineutral, with an electron energy of the order of 1-1.2 eV, and a density in the range of $10^9$-$10^{12}$ cm$^{-3}$, and ions of $0.01 \div 0.1$ eV. Plasma concentration in the range of $10^8 \div 10^{11}$ cm$^{-3}$, ionization of $10^6 \div 10^8$, the average ion energy in the range of $0.01 \div 0.1$ eV. The pressure of the residual medium in discharge plasma generation systems is $0.01 \div 0.1$ Pa. The thermal energy of neutral particles is not more than 600K. [3]. As noted in [4], the specified plasma parameters ensure the effective implementation of technological processes of cleaning, activation of the treated surface and deposition of coatings. The ability to regulate the ion energy over a wide range up to several keV allows one to realize a wide range of processes on the surface of products, from cleaning from various contaminants to synthesizing new materials on the surface. According to the results presented in [5], at ion energies up to 1 keV, the adhesion of the applied coatings substantially increases. Thus, the preparation of the treated surface, giving it the necessary purity, is an important step for the implementation of technological processes of coating, modification of properties, effective interaction of the acting flows of atoms of the material, charged particles with the treated surface. Ion bombardment by inert gas ions effectively enough removes contaminants present on the surface 1.1.
1.1 *Surface cleaning by glow discharge plasma.*

A vacuum installation for ionic, processing, and cleaning products is designed to form a vacuum environment, to place a discharge system in which a high-voltage electric gas discharge is implemented, and technical support systems for the parameters of an electric discharge in vacuum, and to control them. The discharge system includes a cathode, on the working surface of which ion-electron emission is generated that generates electrons. The anode is a vacuum chamber housing or an electrode system corresponding to the geometry of the processed products and ensures the placement of the processed products at the optimum interelectrode distance. The technical system for ionic, ion-plasma processing of materials located in a vacuum chamber [6] provides the conditions for: -functioning a glow discharge in the chamber of a vacuum installation; - the formation of a stream of discharge plasma ions in the direction of the workpiece surface; -the implementation of the interaction of the ion flow with the treated surface of the product. The process of cleaning the normal glow discharge by plasma ions involves the following steps, placing the products on the desktop: - evacuating the working chamber to a vacuum of $5 \times 10^{-3}$ Pa; - the formation in the vacuum chamber of the atmosphere of the working gas with a pressure of about $10^{-1}$ Pa gas inlet system. A glow discharge is ignited in the atmosphere of the working gas (inert gases) at a pressure in the chamber of $10^{-1}$- $10^{-1}$ Pa, the ion current density is up to 10 mA / cm$^2$, the voltage on the electrode system is 700 - 1000V.

2. *Basics of quality control of the preparation of the treated surface.*

The choice of a specific method of cleaning the surface of the product is determined taking into account the properties and nature of the contaminants. On products, as a rule, traces of previous processing remain, including various oils, acids, alkalis, as well as pile, dust, etc. Correct determination of the nature of the contaminants helps to obtain the required technical and operational characteristics of the applied coatings. In the process of processing metal parts, various lubricants are used. The variety of lubricants used is due to the presence of various technological processes used in the processing of metal parts. In this case, in each case, to achieve optimal lubrication results, well-defined lubricants are used. Most often, various formulations from a number of organic and inorganic compounds are used as lubricants in the processing of metals. They are mainly represented by liquids based on water and mineral oils. As a rule, the surface of metal products after the manufacturing process is covered with grease and oxide film. The use of chemical and electrochemical processing can significantly reduce the degree of contamination of the surface of products. Degreasing is carried out in alkaline solutions or organic solvents to remove fats of both animal and vegetable origin, as well as various mineral oils. Alkalis contribute to the decomposition of fats with the formation of water-soluble salts of fatty acids and glycerin.

It should be noted that mineral oils are not chemically decomposed by alkalis, but under the influence of surface tension forces the destruction of the oil film and the formation of droplets. In this case, the presence in the solution of surface-active substances with detergent and emulsifying properties is necessary for the complete release of the metal surface from oil. In addition, the movement of the liquid due to heating or mixing the solution also contributes to the course of this process.

Electrochemical degreasing is performed at the cathode or anode in alkali solutions. In this case, the composition used is similar to that of chemical degreasing. The effectiveness of electrochemical degreasing is much higher than chemical degreasing.

One of the stages of the product surface cleaning procedure is ultrasonic cleaning.

The ultrasonic cleaning method provides quick and high-quality cleaning of products of any, including complex configuration, and also allows you to remove contaminants, sometimes not amenable to removal by other methods. In this case, not toxic organic solvents are used, but significantly cheaper alkaline solutions. In addition, this method allows us to mechanize labor-intensive cleaning operations.

The surface state of the samples, after appropriate mechanical processing, was monitored using both optical instruments such as the MII-4 microscope and the SOLVER NEXT (NT-MDT) scanning probe.
microscope, which makes it possible to assess the degree of surface roughness of the sample. As an example, Fig. 1 (a, b) presents nanoprofilometry data on the morphology of the product surface area.

![Figure 1](image)

**Figure 1.** Nanoprofilometry of the surface area of the sample (a) and the surface profile of the surface of the sample along the cross section (b).

The data obtained using atomic force microscopy make it possible to determine the change in the height of the relief of the investigated section of the product’s surface and, accordingly, the degree of “roughness” of its surface. As can be seen from Figure 1, for a given section of the studied surface, the maximum change in the height of the surface relief is about 9 nm. To obtain objective information about the effectiveness of the types of cleaning used, the surface state of the products was analyzed using an IR Fourier spectrometer before and after each technological cycle: both before cleaning with a plasma glow ion discharge and after cleaning the surface of a product with a glow discharge.

The interpretation of infrared spectra is carried out using the concept of characteristic frequencies. Unlike the simplest diatomic molecules, in polyatomic molecules, vibrations do not refer to only one bond or group of atoms, on the contrary, all atoms of the molecule are in motion, even in the smallest one. However, it was experimentally established that the presence of certain functional groups in the molecule leads to the absorption of radiation of characteristic frequency. The influence of the rest of the molecule usually does not exceed 5%. This observation makes it possible with a high degree of probability to attribute this or that absorption band to a specific functional group present in the molecule [7]. Figures 2 (a, b, c) show the IR spectra of the product surface obtained for the above conditions, respectively. As can be seen from the analysis of the obtained spectra, on the surface of the product there are a number of different contaminants.

According to the literature [8], it can be assumed that the absorption bands in the region of 3400 cm⁻¹, 1400 cm⁻¹ and 400-600 cm⁻¹ are characteristic of Fe₂O₃, the absorption bands in the regions of 3200 cm⁻¹, 2900 cm⁻¹ and 1300-1500 cm⁻¹ mineral oils, absorption bands in the region of 1600 cm⁻¹ are characteristic of aromatic hydrocarbons, absorption bands in the region of 1500 cm⁻¹ are characteristic of petroleum jelly, and absorption bands in the region of 800-1000 cm⁻¹ are characteristic of paraffin.
An analysis of the intensity of the corresponding peaks of the above IR spectra allows us to evaluate the effectiveness of each stage of cleaning the product surface. It should be noted that the degree of purification of the present types of pollution is different. So, if the degree of purification for contaminants corresponding to absorption frequencies in the region of 1300-1500 cm$^{-1}$ has doubled, the degree of purification for contaminants corresponding to absorption frequencies in the region of 800-1000 cm$^{-1}$ has increased nineteen times. The surface condition of the products was also analyzed using a Raman Spectrometer (InVia Raman Spectrometer). Similarly, with studies carried out using an IR Fourier spectrometer, to obtain objective information on the effectiveness of the types of cleaning used, the surface condition of the products was analyzed taking into account the technological cycles carried out: after all the above cleaning procedures, except for cleaning by glow discharge and after cleaning the surface of products by glow discharge. Figures 3, 4 show the Raman spectra of the product surface obtained for the above conditions, respectively.

**Figure 2.** The IR spectrum of the surface of the product, a- the initial sample, b- preliminary cleaning before cleaning by a glow discharge), c- after cleaning by a glow discharge.

**Figure 3.** The spectrum of Raman scattering (Raman scattering) of the surface of the product obtained after preliminary cleaning, except for cleaning by glow discharge.

**Figure 4.** The Raman spectrum of the surface of the product obtained after cleaning the surface of the product by a glow discharge.
As in the case of studies on a Fourier spectrometer, analysis of the obtained Raman spectra indicates the presence on the surface of the product of a number of different contaminants. According to published data [9,10], it can be assumed that in the Raman spectra, frequencies in the 1300 cm\(^{-1}\), 600 cm\(^{-1}\), 400 cm\(^{-1}\), 300 cm\(^{-1}\), 200 cm\(^{-1}\) regions are characteristic of Fe\(_2\)O\(_3\), and frequencies in the 1650 cm\(^{-1}\), 1450 cm\(^{-1}\), 1300 cm\(^{-1}\), 1000 cm\(^{-1}\) and 8200 cm\(^{-1}\) are characteristic of mineral oils.

**Conclusions**

An analysis of the intensity of Raman scattering and IR spectra makes it possible to evaluate the effectiveness of each stage of cleaning the surface of a product, including glow plasma ions. Thus, an analysis of the intensity of the peaks of the IR spectra showed that the degree of purification from contaminants corresponding to absorption frequencies in the region of 1300-1500 cm\(^{-1}\) doubled, while the degree of purification for contaminants corresponding to absorption frequencies in the region of 800-1000 cm\(^{-1}\) increased by nineteen time. An analysis of the intensity of Raman spectra showed that the degree of purification for contaminants corresponding to frequencies in the region of 200-300 cm\(^{-1}\) increased by 10-12 times, and the pollution corresponding to frequencies in the region of 2500 cm\(^{-1}\) increased three times. Thus, in the process of ionic exposure to the surface, it is effectively cleaned of various contaminants, increasing its adhesion properties and, as a consequence, uniformity, and the service life of the applied coatings.

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