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Mass Spectrometric Study of the Chemical Composition of the Gas Environment in the Zone of Electrospark Alloying

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The article presents the results of mass-spectrometric studies of changes in the composition of the air environment in the restoration area of worn-out working parts' surfaces obtained using a monopole gas mass spectrometer MX7304. The restoration of worn working parts' surfaces was carried out by the traditional method of electric arc welding by surfacing in a protective argon environment on steel 12X18H10T wear-resistant coating with OK61.30 grade electrodes. The electrospark alloying method was also used using the Elitron-52A installation. As a result of the studies, it was found that no toxic gases appear in the composition of the air in the area of electrospark alloying. At the same time, the presence of a large amount of carbon dioxide CO_2 and unstable nitric oxide NO was found in the composition of the air in the area of electric arc welding. Both of these gases are toxic even in small quantities. On the basis of the experimental results obtained, a conclusion was made about the environmental safety of the method of electric spark alloying in the restoration of worn working parts' surfaces in comparison with the traditional method of electric arc welding.

Keywords: Gas mass spectrometry, Air chemistry, Toxic gases.

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1. INTRODUCTION

Industrial enterprises that use pumping equipment, compressor equipment, centrifuges, etc. in their production process are faced with the need to restore the parts' surfaces subjected to various types of abrasive wear. The technology for restoring such parts consists in removing their worn-out areas and replacing them with separate segments made of steel sheets of the same grade. Attaching segments to worn areas in most cases is carried out by various types of welding.

The most commonly used for this is arc electric welding (AEW) with a consumable metal electrode in an inert protective gas. AEW is a source of dangerous and harmful effects on the environment, such as powerful ultraviolet light, the formation of aerosols and toxic gases, etc. Some of the atmospheric air enters the arc zone. When the metal is heated, the gases dissolved in it are also released there. As a result, the synthesis of biologically active gases – O_3, CN, HCN, NO_2, N_2O, CO – is possible in the arc zone. These gases are toxic, they pollute the air of the working area and create a danger of poisoning personnel [1].

In recent years, to improve the quality of surface layers applied to worn parts of machines, the method of electrospark alloying (ESA) has become increasingly popular. ESA is a process of interaction between the material of the anode and the cathode during unipolar transfer from the anode to the cathode, which is a workpiece [2, 3]. The specific features of ESA that attract technologists are the locality of action, low energy costs, the absence of volumetric heating of the material, the strong connection of the applied material with the base, ease of automation and the absence of synthesis of toxic gases.

The article presents the results of a mass spectrometric study of the chemical composition of the gas environment in the area of ESA at the Elitron-52A installation (electrode-tool made of T15K6 hard alloy, discharge energy 3.4 J) and in the area of AEW (wear-resistant coating surfacing in a protective argon environment on steel 12X18H10T with OK61.30 electrodes, welding current $I = 80$ A, arc voltage $U = 20\text{-}25$ V).

2. EXPERIMENTAL METHODOLOGY AND TECHNIQUE

To study the chemical composition of the gaseous environment in the area of ESA and AEW, we used the UVBL-4 vacuum unit manufactured by us (oil-free vacuum laboratory unit), the schematic diagram of which is shown in Fig. 1.

A high vacuum of 10^{-6}-10^{-7} Pa was created in a small vacuum chamber (9) made of X18H10T stainless steel using an NMDO-0.25 magnetic-discharge high-vacuum pump (12). The high vacuum in the chamber was measured with a VMB-14 vacuum gauge with a PMM-32 manometric transducer (10). To analyze the composition of the gaseous environment in the vacuum chamber, an MX7304 monopole mass spectrometer was used, the analyzer (8) of which was built into the chamber.

Using the dosing valve (7) into the chamber, directly into the area of the open ion source of the analyzer of the mass spectrometer MX7304, it is possible to inject small amounts of reference gas from the cylinder (5) to calibrate the mass spectrometer. When researching air, the cylinder with the reference gas is replaced by a container with the investigated air. The dosing valve is an integral part of the SNA-1 automatic gas inlet system and allows for adjustable gas inlet. The dosing valve is controlled by the electronic control unit CNA-1. The evacuation of the gas inlet channel to 10^{-1} Pa was carried out using a mechanical pre-vacuum pump (1).

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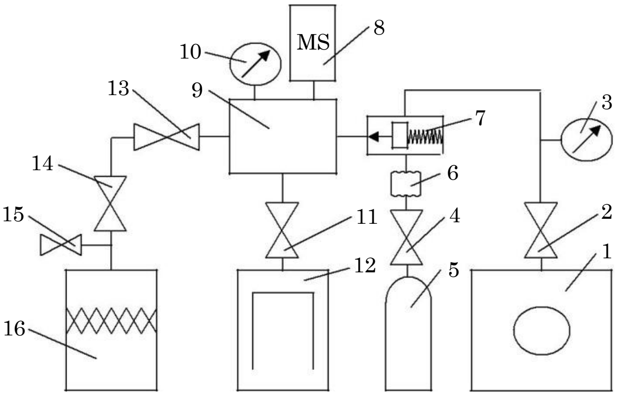

Fig. 1 – Schematic diagram of the UVBL-4 vacuum unit: 1 – mechanical pre-vacuum pump; 2, 4 – shut-off valves; 3 – manometric transducer PMT-4M; 5 – cylinder with reference gas; 6 – bypass cylinder; 7 – dosing valve; 8 – analyzer of mass spectrometer MX7304; 9 – vacuum chamber; 10 – manometric transducer PMM-32; 11 – high vacuum valve DU-50; 12 – magnetic discharge pump NMDO-0.25; 13, 14 – shut-off valve DU-12;
15 – safety valve; 16 – adsorption coal pump

The test gas was taken directly from the ESA zone or the AEW zone using an electromechanical air pump into a clean sealed PET bottle with a capacity of 1.5 L, which was attached to the vacuum chamber (9) instead of the cylinder (5).

Mass spectrometer MX7304 is a gas dynamic mass spectrometer with a monopole mass analyzer and is designed for chemical analysis of gases in the range of mass numbers 1-200 a.m.u. and the range of partial pressures 10^{-3}-10^{-10} Pa.

With the MX7304 mass spectrometer, both qualitative and quantitative gas analysis can be spent. The essence of a qualitative mass spectrometric analysis of a gas is to establish its chemical composition (chemical formula) as a result of measurements of the masses of atoms or molecules of the gas under study. So, for example, a hydrogen molecule H_2 has a molecular weight of 2 a.m.u., a water vapor molecule H_2O has a molecular weight of 18 a.m.u., a nitrogen molecule N_2 has a molecular weight of 28 a.m.u., an oxygen molecule O_2 – 32 a.m.u., Ar atom Ar – 40 a.m.u., carbon dioxide molecule CO_2 – 44 a.m.u. etc. Having determined the mass of an unknown gas molecule using a mass spectrometer, it is thus possible to answer the question of what kind of gas it is, that is, spend a qualitative analysis.

The mass of the ion is responsible for the chemical composition of the substance. The amount of this substance in the mixture is determined by the number of ions of a given mass, that is, the value of the ion current created by ions of a given mass in the electrical circuit of the ion receiver. This is the essence of quantitative analysis.

Neutral atoms and molecules of a substance in the ion source of the mass spectrometer are converted into positive ions (ionized). At the exit from the ion source, they are formed into a beam, which is directed to the mass analyzer. The MX7304 mass spectrometer has an open source of ions with electron impact ionization. The ion source, together with a monopole mass analyzer, is placed in the vacuum chamber (9) of the UVBL-4 vacuum unit and is pumped out to a high (10^{-5}-10^{-7} Pa) vacuum.

Before starting to study the composition of air samples, the vacuum chamber (9) together with the analyzer of the mass spectrometer (8) (Fig. 1) was degassed by heating to 250-300 °C for 8-10 hours pumping down to rarefaction
(2-5) $\cdot 10^{-6}$ Pa. The mass spectrum of the residual atmosphere of the degassed cooled vacuum chamber is shown in Fig. 2.

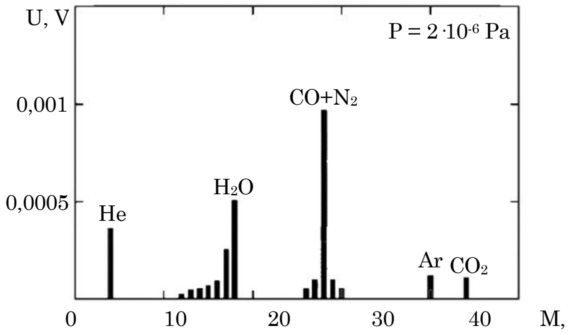

Fig. 2 – Mass spectrum of the residual atmosphere of the vacuum chamber at a rarefaction in it of 2 10^{-6} Pa

Such a mass spectrum of the residual atmosphere is typical for vacuum units with oil-free pumping using magnetic discharge vacuum pumps [4]. The main mass spectrometric peaks in the mass spectrogram of the residual atmosphere of the vacuum chamber are the peaks of the inert gas ions He^+ and Ar^+, which are poorly pumped out by such pumps. The mass spectrogram of the residual atmosphere also contains peaks of H_2O^+ water vapor ions, CO_2^+ carbon dioxide, and CO^++N_2^+ doublet. They appear in the composition of the residual atmosphere of the vacuum chamber due to the desorption of these gases from its walls. The MX7304 mass spectrometer is an instrument with a low resolution $R = 1$M, where M is the rounded mass number of the ion. Therefore, on the mass spectrogram, the peaks of the CO^+ and N_2^+ doublet are not separated (the exact value of the mass number for N_2^+ is 28.00615 a.m.u., and for CO^+ $M = 27.99491$ a.m.u.) [5].

The intensity (height) of a peak is proportional to the number of molecules or atoms (partial pressure) of the respective gas. The height of the peak is usually represented by the magnitude of the electrical signal in volts or amperes, which is created by ions of the corresponding mass in the electrical circuit of the ion receiver of the mass spectrometer. It can be seen from the mass spectrogram that the heights of the peaks of the gases that make up the residual atmosphere at a pressure
$P = 2 \cdot 10^{-6}$ Pa do not exceed 0.001 V.

3. RESULTS AND DISCUSSION

To carry out mass spectrometric analysis, the air under study from the AEW area and the ESA area was let into the UVBL-4 vacuum chamber up to a pressure of $5 \cdot 10^{-4}$ Pa.

To identify changes in the composition of the gaseous environment in the area of the AEW or ESA, a mass spectrometric analysis of a sample of clean atmospheric air as a reference gas was preliminarily carried out. To do this, clean atmospheric air was let into the vacuum chamber up to a pressure of $5 \cdot 10^{-4}$ Pa, that is, 250 times greater than the residual pressure in it. Fig. 3 shows the mass spectrum of clean air, which, on the whole, fully corresponds to the literature data [5, 6]. There are seven main peaks in the air mass spectrum. Peaks with masses of 28, 32, 14, 16 and 40 a.m.u. belong to the N_2^+, O_2^+, N^+, O^+, and Ar^+ ions, respectively. Peaks with masses of 18 and 17 a.m.u. belong to H_2O^+ and HO^+ ions, respectively. The most intense mass spectrometric peaks are the peaks of molecular nitrogen ions N_2 and the peaks of molecular oxygen ions O_2. In the insert of Fig. 3 shows the peaks that belong to the C^+, H_2O^+, HO^+, Ar^{++} ions with a much lower intensity than the intensity of the peaks of the ions of molecular nitrogen N_2 and molecular oxygen O_2. HO^+ and C^+ ions are formed in the ion source of the mass spectrometer as a result of the decomposition of H_2O and CO_2 molecules during their ionization by electron impact. Ar^{++} ions with a mass of 20 a.m.u. are doubly ionized Ar atoms. They are also formed in the ion source of the mass spectrometer as a result of ionization of Ar atoms by electron impact [7, 8].

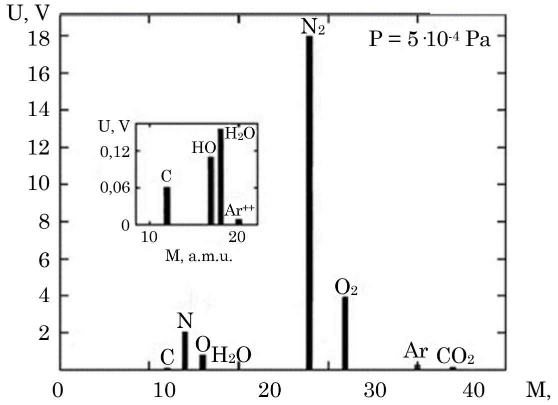

Fig. 3 – Mass spectrum of clean air when it is admitted into a vacuum chamber up to a pressure of $5 \cdot 10^{-4}$ Pa

Comparing the intensities of the mass spectrometric peaks of the residual atmosphere of the vacuum chamber (Fig. 2) and the intensities of the mass spectrometric peaks during the admission of a sample of clean atmospheric air (Fig. 3), we can conclude that when a sample of pure atmospheric air is admitted, the intensities of the mass spectrometric peaks are more than 10,000 times the intensities of the mass spectrometric peaks of the residual atmosphere. Therefore, the effect of the residual atmosphere of the vacuum chamber on the composition of gases when analyzing the composition of both clean air (inlet up to $5 \cdot 10^{-4}$ Pa) and the gaseous environment (with the same inlet) from the area of AEW and ESA can be neglected.

Fig. 4a shows the mass spectrum of the gaseous environment from the area of the AEW when it is admitted into the vacuum chamber up to a pressure of $5 \cdot 10^{-4}$ Pa. As in the mass spectrum of pure air (Fig. 3), the most intense mass spectrometric peaks are the peaks of molecular nitrogen ions N_2 and molecular oxygen ions O_2.

Comparing the mass spectra presented in Fig. 3 and Fig. 4a, we note both quantitative and qualitative differences. So, in the gaseous environment from the AEW zone, a significant amount of carbon dioxide CO_2 is observed (mass spectrometric peak with a mass of 44 a.m.u.), and a mass spectrometric peak with a mass of 30 a.m.u. appears, which corresponds to the unstable nitrogen oxide ion NO^+. Both gases are toxic even in small quantities.

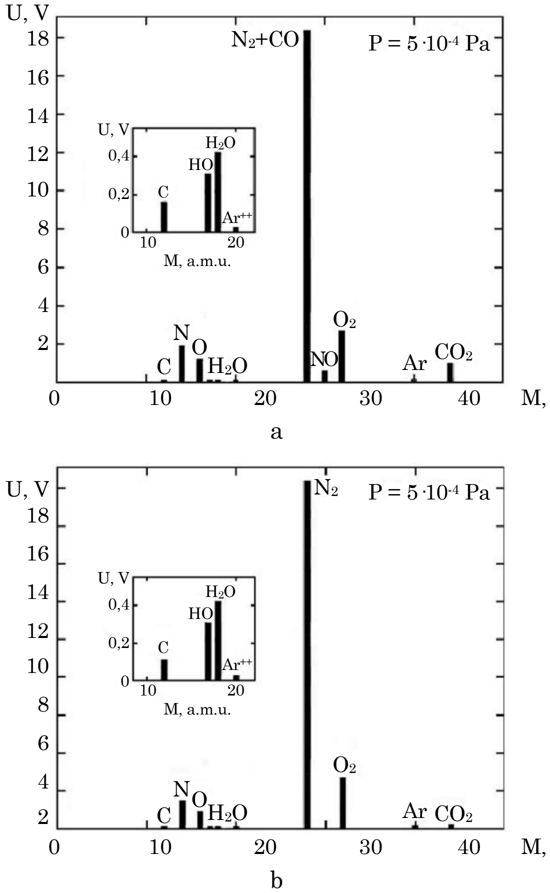

Fig. 4 – Mass spectra of the gaseous environment: from the zones of AEW (a) and ESA (b) when inlet into the vacuum chamber to pressure $5 \cdot 10^{-4}$ Pa

In the inserts in Fig. 4 shows the mass spectrometric peaks of H_2O^+ water vapor ions and fragment ions with intensities less than $U = 0.5$ V (C^+, OH^+, Ar^{++}). The mass spectrometric peaks of N^+ ($M = 14$ a.m.u.) and O^+ ($M = 16$ a.m.u.) ions are not shown in the inserts, because their intensity is much more than 0.5 V. No traces of ozone O_3 were detected using a mass spectrometer.

Fig. 4b shows the mass spectrum of the gaseous medium from the zone of ESA when it is admitted into the vacuum chamber up to a pressure of $5 \cdot 10^{-4}$ Pa. As in the mass spectrum of pure air (Fig. 3), the most intense mass spectrometric peaks are mainly the peaks of molecular nitrogen N_2 and molecular oxygen O_2. In general, the mass spectrum of the gaseous environment from the ESA area is almost identical to the mass spectrum of pure air. Minor differences are observed only in the amount of water vapor, which is most likely due to different air humidity.

4. CONCLUSIONS

1. The study of the influence of welding operations on changes in the air composition showed that in the zone of AEW, when a wear-resistant coating is deposited on steel 12X18H10T with a consumable electrode grade OK61.30, a significant amount of carbon dioxide CO_2 appears (mass spectrometric peak with mass 44 a.m.u.) and unstable nitric oxide ions NO are formed (mass spectrometric peak with a mass of 30 a.m.u.), that is, gases are formed that are toxic even in small quantities. No traces of ozone O_3 were detected by the mass spectrometer.

2. In the study of the chemical composition of the gaseous environment in the area of the ESA at the Elitron-52A installation with a T15K6 hard alloy electrode-tool at a discharge energy of 3.4 J, it was found that the mass spectrum of the gaseous environment is almost identical to the mass spectrum of pure air. Minor differences are observed only in the amount of water vapor, which is most likely due to different air humidity. No traces of toxic gases were found.

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Мас-спектрометричне дослідження хімічного складу газового середовища у зоні проведення електроіскрового легування

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У статті наведено отримані за допомогою монопольного газового мас-спектрометра МХ7304 результати мас-спектрометричних досліджень змін складу повітряного середовища в зоні проведення відновлення зношених робочих поверхонь деталей. Відновлення зношених робочих поверхонь деталей проводилося традиційним методом електродугового зварювання за допомогою наплавлення в захисному аргоновому середовищі на сталь 12Х18Н10Т зносостійкого покриття електродами марки ОК61.30. Також застосовувався метод електроіскрового легування з використанням установки «Елітрон-52А». У результаті проведених досліджень було встановлено, що у складі повітря у зоні проведення електроіскрового легування не спостерігається появи отруйних газів. У той же час, у складі повітря в зоні проведення електродугового зварювання виявлено наявність великої кількості вуглекислого газу CO_2 і нестабільного окису азоту NO. Обидва ці гази є отруйними навіть у малих кількостях. На підставі отриманих експериментальних результатів зроблено висновок про екологічну безпеку методу електроіскрового легування при відновленні зношених робочих поверхонь деталей порівняно з традиційним методом електродугового зварювання.

Ключові слова: Газова мас-спектрометрія, Хімічний склад повітря, Отруйні гази.