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Conference paper

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Surface chemistry of structural materials subjected to corrosion

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Abstract: The article describes a comprehensive mass spectrometric approach to the study of surfaces of structural materials. The combined use of thermal desorption mass spectrometry, gas and liquid chromatography, and laser desorption/ionization mass spectrometry (LDI) to provide information about the surface and surface layers of materials is proposed. The suggested method allows one to determine the thermodynamic characteristics of compounds and surface contaminants adsorbed on surfaces, as well as surface layers, to determine the composition of volatile and non-volatile contaminants on the surface, and to determine the nature of the distribution over the surface of these compounds. The method allows to obtain the most complete information about the surface condition and can be used to predict the life of structural materials.

Keywords: aluminium alloys; copper; corrosion; laser desorption ionization (LDI); mass spectrometry; Mendeleev-21; steel; surface; zinc.

Introduction

Corrosion, biocorrosion, and aging of structural materials are complex physicochemical processes that occur in all environments. Gas corrosion, corrosion in a liquid, and corrosion upon contact of various materials are known. In the process of corrosion complex chemical, electrochemical and catalytic reactions proceed with the formation of numerous intermediate products, often in micro quantities. It makes the study of corrosion processes an extremely difficult problem.

The set of physicochemical methods used to study corrosion includes almost all known methods. At the same time, the complexity of corrosion processes makes it necessary to use the simplest methods to obtain primary information and a total assessment of corrosion effects. Therefore, the integrated use of modern physicochemical methods is of considerable interest.

In the present work, we used a complex of mass spectrometric methods, including thermal desorption mass spectrometry, chromato-mass spectrometry, Matrix and Surface-Activated Laser Desorption/Ionization (MALDI/SALDI) [1–3].

Various structural materials (Ad-0, AMg-6, St-3, n/s 12X18H10T, copper, zinc) subjected to atmospheric corrosion, high-temperature corrosion, and corrosion in aggressive environments have been studied. The prospects of using the developed complex of mass spectrometric methods in the study of various types of corrosion are shown. It was found that the use of a complex of methods allows not only to identify corrosion

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lesions, but also to predict the development of corrosion processes. Prediction is based on a study of the chemistry of surface compounds, that is, the determination of corrosive products, both final and intermediate. A surface morphology is also being studied to determine the development of corrosion lesions and their morphology.

The authors carried out many studies on the surfaces of various materials using SALDI/MALDI [1, 2]. It has been shown that the formation of clusters of silver, lead, and other transition metal salts depends on the morphology and chemical state of the surfaces under study, which can be represented by studying the surface morphology of aluminum alloys and identifying the qualitative composition [3].

The authors developed a program for automatic data collection during mass spectrometric study of surfaces, which can "visualize" the test surface and presents the results in a visual form [4]. This method of processing a large amount of information is widely used in the study of samples of small thickness (living tissues, sections of organs of animals and plants, films). It is shown that the proposed method adequately reflects the actual state of the surface, as confirmed by other independent studies [5].

This article presents new results on the study of structural materials used in various conditions.

Experimental

Materials

Samples of metallic materials from steel grade 3, zinc, aluminum and copper were used for research. All samples were exposed to atmospheric corrosion for one year [6].

Thermal desorption mass spectrometry

A layer-by-layer analysis of the surfaces of the samples was carried out on a JEOL GMS-3000 mass spectrometer with a thermal desorption attachment [7, 8]. The removal of the layer from the sample was carried out at 10 μm with control. The selection was made on an area of 1 cm^2 to a depth of 100 μm. The resulting chips were placed in a thermal desorber of the device and heated according to a given program.

Gas chromatography – mass spectrometry

GC-MS Shimadzu GS-MS TQ8040 was used. Flushing from the surface of the samples was carried out from an area of 100 cm^2. [9, 10]. Chloroform and acetonitrile were used as volatile solvents. Flushing from all the studied samples were carried out identically. The liquid after flushing was injected directly into the injector of the chromatograph.

Laser desorption/ionization mass spectrometry (LDI-MS)

Mass spectrometric studies of the surfaces of structural materials were carried out on a Bruker Ultraflex II surface-activated laser desorption/ionization mass spectrometer equipped with a nitrogen laser operating with 337 nm wavelength. Ionization from the studied surface was carried out with a pulse frequency of 5–20 Hz and a quantity of 1–200. Energy was ranged from 0 to 110 μJ/pulse. For each type of sample mode is selected individually by experiment. After selecting the regime, the surface was studied by recording the ionization mass spectra at each point in increments of 50–100 μm. The surface area studied was varied from 1 mm^2 to 1 cm^2. As a result, sets of ionization mass spectra were obtained at each studied point of the alloy [11–13]. Using the software developed in the laboratory, the results were translated into graphical form. The distribution diagrams of the compounds located on the surface are constructed. To determine the relative amount of chlorine on the surface of the material after its study, a solution of sodium chloride was applied to the surface and the mass spectrometric experiment was carried out again. The change in signal was determined by m/z 35 and 37 Da (chlorine) depending on the concentration. Using the additive method, the initial amount of chlorine on the surface of the material was determined.

Results and discussion

Thermal desorption mass spectrometry (TDMS)

TDMS is widely used to establish the presence of adsorbed chemisorbed molecules on the surfaces and in the surface layers of the investigated material. The method was used by the authors to assess the state of the surface of the fuel tanks of rocket carriers made from Ad-0 and AMg-6 aluminum alloys.

The main components during desorption directly from the surface are the decomposition products of the oxidizer of rocket fuel nitrogen tetroxide, namely nitrogen oxides (Fig. 1). Moreover, monoxide exists on the surface in two forms: physically adsorbed (green line in Fig. 1) and chemically sorbed form (in much larger quantities as a decomposition product of nitrogen dioxide) [14].

Energy characteristics of desorption and sublimation from the surface are shown in Table 1. It is noted that the unsorbed part of the molecules on the surface is removed even at a temperature of 70 °C. The average energy of physical desorption is 120 kJ/mol. In this case, two types of chemisorbed molecules with different desorption energies can be clearly distinguished. This fact indicates the presence of contaminants and the exist of compounds in various states with respect to the surface. To determine near-surface contamination, small layers were successively removed from the surface and a thermal desorption experiment was performed. It was found that the main components of the near-surface layers are nitrogen monoxide and carbon dioxide, as well as small amounts of saturated and unsaturated hydrocarbons and esters [15].

According to Fig. 2, the bulk of contaminants is on the surface. At the same time, a high content of hydrocarbons and their derivatives was noted in the layer at a depth of 30–40 µm, which indicates the achievement of the lower edge of the oxide film of the material, under which there are technological impurities in the form of lubricant components and plasticizers used in the production of the material. The method allows determining the qualitative and quantitative composition of the surface layers of the material, determining the activation and desorption energies of the components, assessing the degree of surface damage, and establishing the depth of corrosion penetration into the surface layers. Thus, thermal desorption mass spectrometry is an important tool in the study of surface processes and is a source of additional information in the visualization of mass spectrometric data.

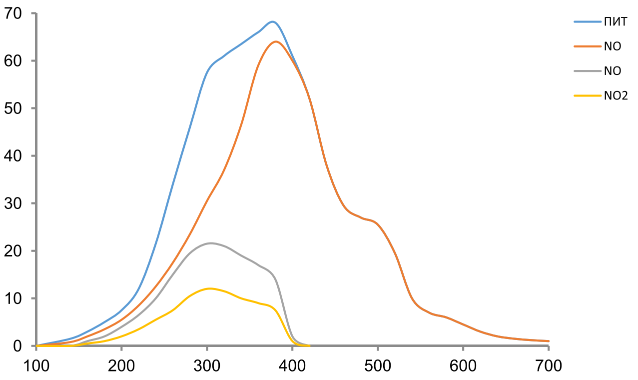

Fig. 1: Thermal desorption curves for the total ion current, nitric oxide and nitrogen dioxide from the fuel tank after storage of nitrogen tetroxide.

Table 1: Thermodynamic characteristics of sublimation and desorption of compounds from the surface of a fuel tank containing nitrogen tetroxide.

Process	E, kJ/mol	t,°C
Sublimation	55	70
Desorption of physically adsorbed molecules	120	160
Desorption of chemisorbed molecules	150	250
	180	330

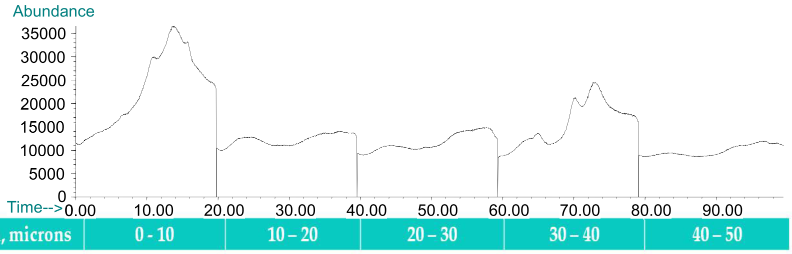

Fig. 2: Thermal desorption curves for the total ion current from the surface layers with a step of 20 µm.

Liquid chromatography mass spectrometry (HPLC-MS)

Gas and liquid chromatography-mass spectrometry are used to compare with the results of thermal desorption mass spectrometry when searching for volatile or labile compounds on surfaces. The method is less applicable when working with samples after atmospheric corrosion due to the low volatility and solubility of corrosion products, therefore, in most cases it is used to study the material after contact with an aggressive environment. A mass chromatogram of non-volatile compounds was obtained when analyzing flushing from the surface of the rocket carrier fuel tank (Fig. 3).

According to mass spectra and library search data, it was determined that components 3 and 8 belong to alkyl phthalates, compounds 1–2 and 4–6 are homologues of alkyl triphenyl phosphate. Both the first and second groups of compounds belong to the class of plasticizers widely used in industry. Peak 7 contains a compound with a molecular weight of 337 Da. When a tandem experiment has been carried out and compared with library data, the molecular ion was identified as dibutyl sebacinate, which is also a plasticizer.

Gas chromatography mass spectrometry (GC-MS)

A GS-MS study of surface flushings was carried out to determine the composition of organic compounds on the surface of the samples. Figure 4 presents the chromatogram of flushing from the surface of sample contacted with fuel. There are no peaks on the chromatogram corresponding to the components of rocket fuel and the products of their transformation. The peaks observed in this chromatogram belong to organosilicon compounds formed by destruction of a stationary liquid phase, impurities in the solvents used for washing, and the

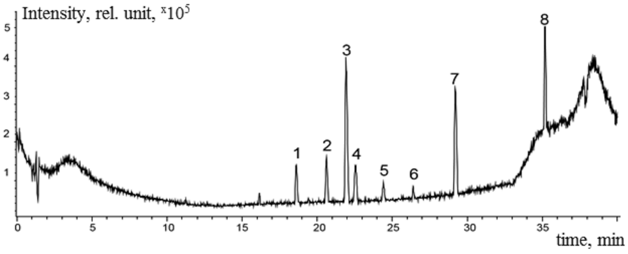

Fig. 3: Mass chromatogram of the total ion current of the acetonitrile flushing from the surface of the fuel tank used in contact with nitrogen tetroxide.

added standard. Mass chromatograms for characteristic ions of saturated hydrocarbons (m/z = 57 Da), column phases (m/z = 73 Da), impurities in the solvent (m/z = 43 Da), phthalates (m/z = 149 Da), and internal standard (m/z = 136 Da - deuteronaphthalene) showed the absence of rocket fuel components and products of their transformation in flushings from samples. Mass chromatograms for the characteristic ions of 1,1-dimethylhydrazine (m/z = 58, 59 Da) and the main products of its transformation (m/z = 83, 97, 74 Da) indicate that the peaks for these ions correspond to isotopic or fragment ions of organic pollutants.

Figure 5 shows the results for the sample Ad-0 contacted with 1,1-dimethylhydrazine. According to the obtained data, as in the case with the sample AMg-6, the chromatogram contains peaks corresponding to the phase of the column, impurities in the solvents used for flushing, and the added standard, and there are no peaks corresponding to 1,1-dimethylhydrazine and its transformation products.

Similar chromatograms were obtained for all samples studied. The presence of saturated and unsaturated hydrocarbons in the flushings be explained by the presence of various lubricants and other process fluids on the surface of the samples under study. At the same time, the presence on the surface of any coatings applied during production, either indelible with solvents, or non-chromatographically, cannot be denied.

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Laser desorption/ionization mass spectrometry (LDI-MS)

In this work, LDI mass spectrometry is used to solve three parallel problems:

(1) Surface monitoring to detect organic contaminants on the surface introduced in the production of structural materials.
(2) The construction of 2D-diagrams of the distribution of a particular compound detected in stage 1 over the entire investigated surface.
(3) Visualization of surface morphology using a marker substance.

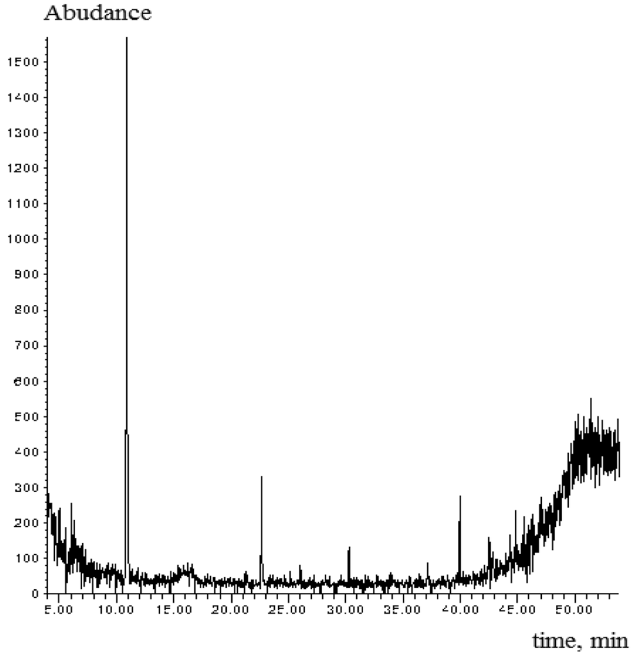

Fig. 4: Chromatogram of the total ion current of flushing from the surface AMg-6 contacted with 1,1-dimethylhydrazine.

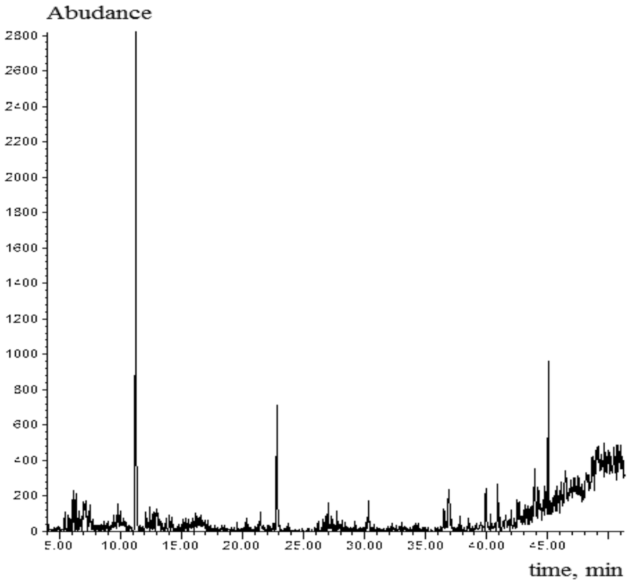

Fig. 5: Chromatogram of the total ion current of flushing from the surface of sample Ad-0 contacted with 1,1-dimethylhydrazine.

Surface monitoring is necessary to obtain an overview mass spectrum containing ions of all compounds present on the surface. So, for example, Fig. 6 shows the mass spectrum of positive ions from the surface of stainless steel grade 3, after exposure to atmospheric corrosion.

Iron is widely used as structural materials in various steel grades, many of which undergo significant corrosion in atmospheric conditions and in contact with aggressive environments. In the study of the initial steel sample, a small amount of corrosion products was discovered, the main of which is a compound of iron hydroxide $Fe(OH)_3 \bullet H_2O^+$. The distribution of this ion over the surface is uniform, and the peak intensities are small (Fig. 6).

It is known that chlorine is the strongest corrosion agent and a lot of work has been devoted to the development of methods for determining the amount of chlorine on surfaces [16]. This article presents a new method for detecting chlorine on large and local areas of steel surfaces.

When studying steel subjected to atmospheric corrosion, a significant difference was found in the surface mass spectra (Fig. 7).

When deciphering the obtained peaks, it was shown that they belong to cluster compounds with the general formula $(FeO)_nH^+$. It should be noted that this homological series consists of iron atoms with a charge of 2+, while Fe (III) is also present in the mass spectrum, but the peaks of such cluster ions have a very low intensity. Thus, the method immediately shows the presence of corrosion products on the surface. However, the conclusion about the general state of the surface from several mass spectra is impossible without a general

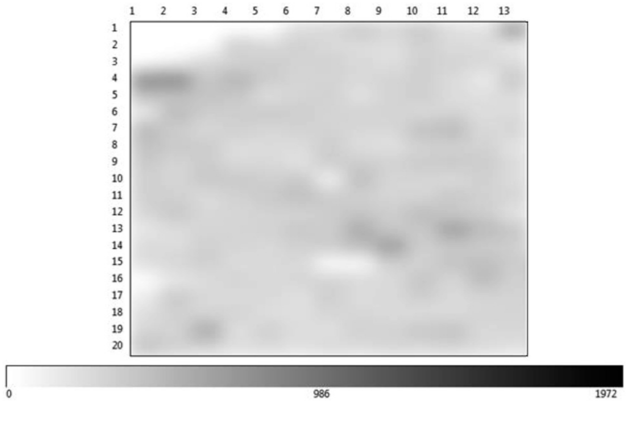

Fig. 6: The distribution of the $Fe(OH)_3 \bullet H_2O^+$ ion over the steel surface (m/z = 124 Da) and the color scale of the integrated intensity of this ion, 20 × 13 pixels with a step of 500 μm.

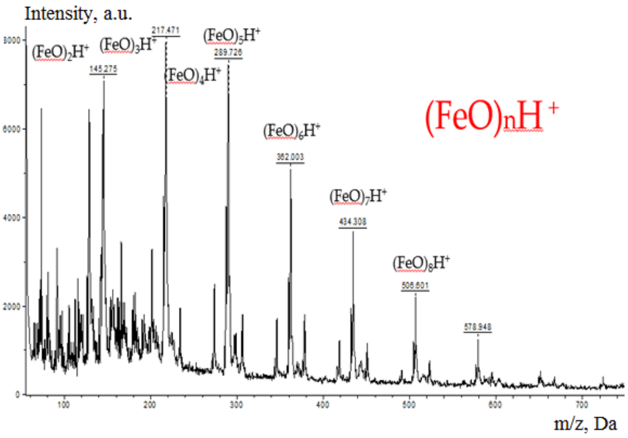

Fig. 7: SALDI positive ion mass spectrum recorded from a stainless steel surface subjected to atmospheric corrosion.

characterization of the surface, which consists in sequentially recording mass spectra over the entire surface under study with a given step.

Figure 8 illustrates the approximately uniform distribution of iron oxide over the entire surface except for the upper left edge, where it is concentrated. Obviously, the entire surface undergoes corrosion almost uniformly, which is characteristic of atmospheric corrosion with low atmospheric aggressiveness. It is possible to estimate the relative amount of oxides at each point using the obtained diagram.

When mass spectra were recorded in the negative ion mode, the presence of chlorine ions on the surface was detected, which is associated with its ingress from the atmosphere during corrosion tests (Fig. 9).

It was found that at a low concentration of chlorine ions over the surface, concentration occurs around a technical hole in the metal due to the presence of chips and microcracks (Fig. 10). Chlorine and its compounds are corrosion activators, therefore, control of their presence is necessary when studying the causes of incipient corrosion. Despite the fact that the amount of chlorine on the surface slightly (~100 ng/cm^2), the local concentration around technical holes may reach 10 g/cm^2.

Research on aluminum structural materials is mainly related to the surface oxide film and the conditions of its stability, as the most important characteristics of the efficiency of inhibition of aluminum surfaces. The first works in this direction appeared back in the 80s of the last century [17–20].

Aluminum alloys are widely used as a material for fuel tanks of modern rocket carriers that come into contact with aggressive components of rocket fuel. That is why, it is important to examine them after operation and washing from toxic components to assess the state of the surface.

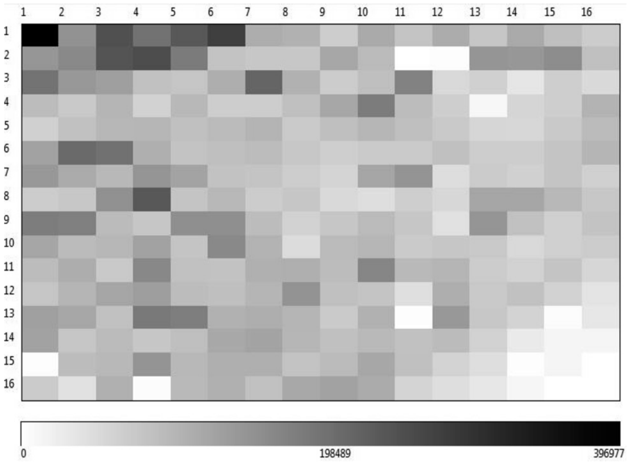

Fig. 8: Distribution of the $(FeO)_3H^+$ ion over the surface of stainless steel and the color scale of the integral intensity of this ion, 20 × 16 pixels with a step of 500 μm.

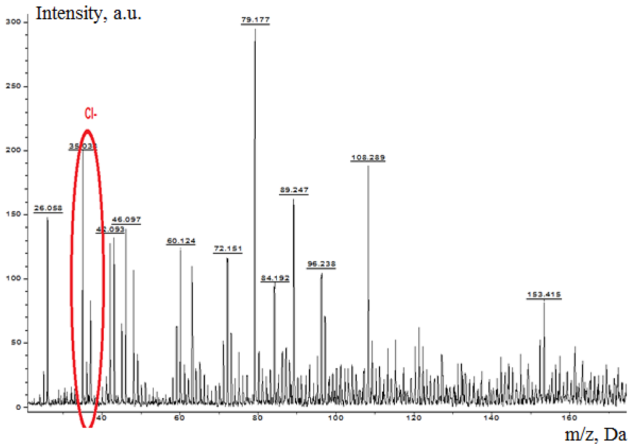

Fig. 9: The LDI mass spectrum of negative ions recorded from the surface of stainless steel, after exposure to atmospheric corrosion.

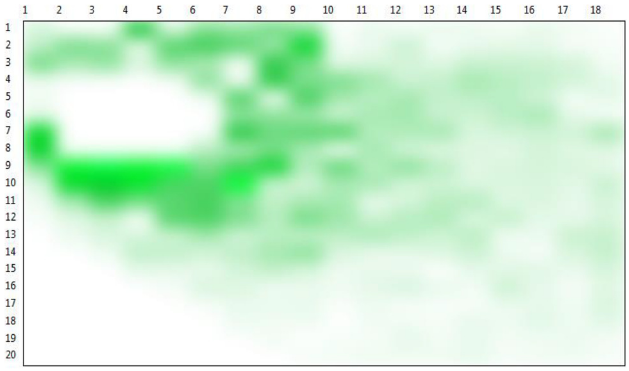

Fig. 10: Chlorine ion distribution over the surface of grade 3 steel, 20 × 18 pixels with a step of 500 μm.

Figure 11 shows the mass spectrum recorded for the surface of the alloy AMg-6. There are ions of hydrocarbons, lower organic acids and esters, as well as phthalic acid esters on the surface. The latter are industrial plasticizers and were probably listed in technological production. In addition, ions corresponding to the components of rocket fuel (nitrates and nitrites) and their transformation products were discovered.

An aqueous suspension of silver bromide was used as a marker substance to assess surface uniformity. The studied fragment of the alloy was placed in a homogenized suspension, then dried in air and the surface was examined by the LDI-MS method. Figure 12 shows the surface distribution of silver bromide. On a clean sample (Fig. 12a), the distribution of the marker substance is uniform and the surface in the photograph obtained with an electron microscope also looks quite uniform, indicating that there is no corrosion damage to the surface. In

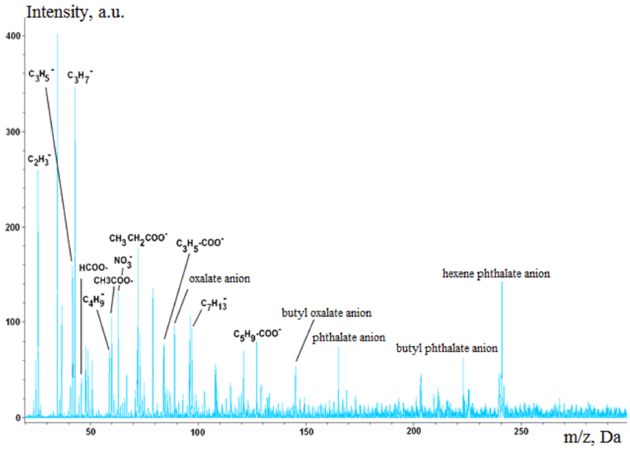

Fig. 11: The LDI mass spectrum of negative ions recorded from the surface of the aluminum alloy AMg-6 after contact with the oxidizer of rocket fuel with nitrogen tetroxide.

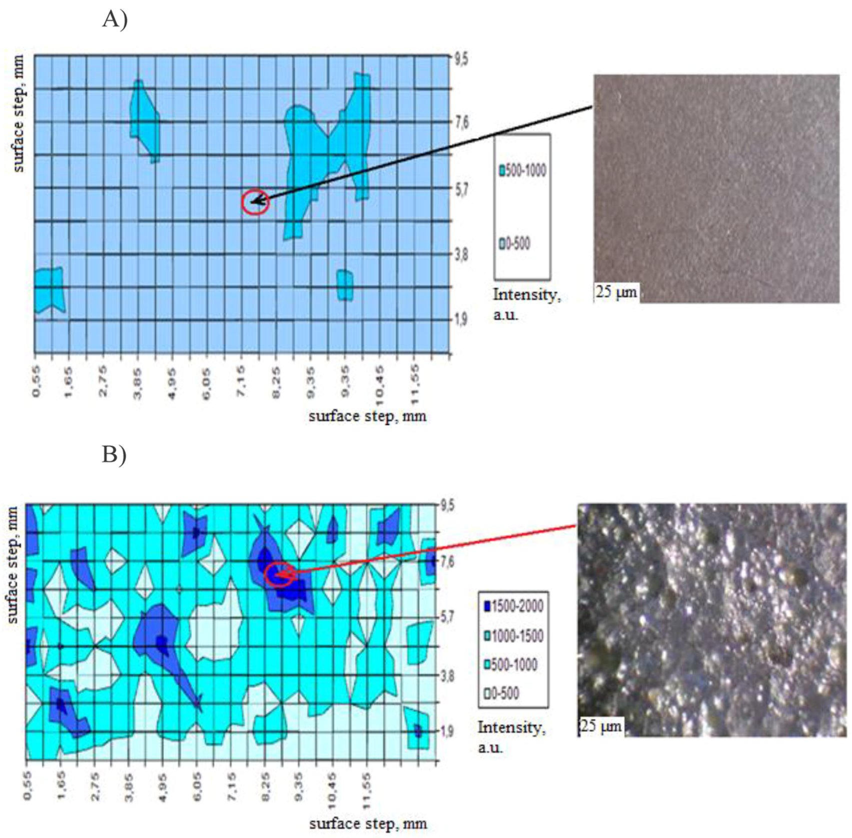

Fig. 12: Distribution of the marker substance (silver bromide) $Ag_3Br_2^+$ on the surface of the aluminum alloy and a micrograph of the indicated region. (A) reference sample, (B) sample after use.

Fig. 12b (alloy after operation), local inhomogeneities are detected. An electron micrograph confirms the presence of foreign formations in these areas that can be attributed to corrosion damage resulting from operation.

It should be noted that the proposed method allows you to immediately cover a relatively large surface area (up to a centimeter) and detect areas affected by corrosion.

Construction materials from copper and its alloys are widely used in various industries. It is often used in contact with aggressive environments of both organic and inorganic substances in a wide pH range. Operation under such conditions leads to corrosion, an increase in the oxide film, a change in the surface morphology, and the penetration of corrosion products deep into the material, which in turn can lead to partial destruction of the surface or the formation of defects.

The surface study of copper products was carried out on plates subjected to corrosion under atmospheric conditions. It should be noted that in the registration mode of negative ions, cluster ions of copper chloride were mainly recorded. In addition, the presence of anion of free chlorine is observed in all mass spectra. The presence of clusters of copper chlorides proves the fact that chlorine interacts with the metal surface, which leads to active surface corrosion. The result of prolonged atmospheric corrosion can be estimated by the presence on the surface of the plate of the corrosion products – copper chlorides (Fig. 13). It should also be noted that the upper left corner of the sample is more susceptible to corrosion, which is explained by damage in this area when preparing the sample for the experiment. As a rule, active corrosion processes occur on chips and cracks. At the same time, the lower right corner did not corrode as it was covered by part of the holder during the experiment.

Zinc is a metal widely used in industry and household. This metal is especially appreciated for its relative resistance to atmospheric corrosion in both humid and dry air. Therefore, it is often used as protective coatings on more corrosive metals and alloys. In this case, zinc can be used both in pure form and in alloys (for example, with aluminum).

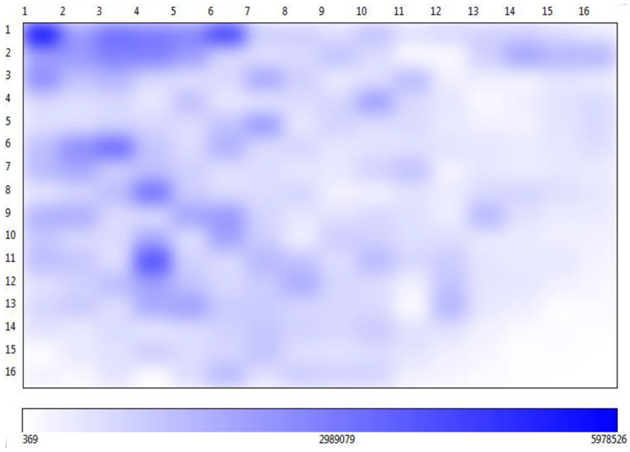

Fig. 13: Distribution of copper chloride ion over the copper surface (m/z = 134 Da) and the color scale of the integrated intensity of this ion, 16 × 16 pixels with a step of 500 μm.

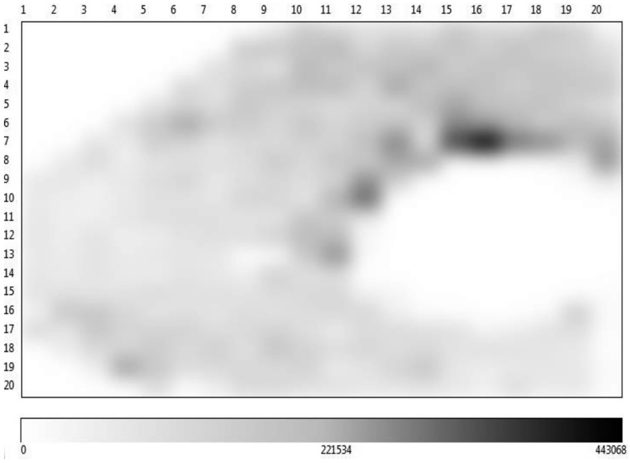

Fig. 14: Distribution of the KNaCl•ZnOH$^+$ ion over the zinc surface (m/z = 177 Da) and the color scale of the integrated intensity of this ion, 20 × 20 pixels with a step of 500 μm.

In the last decade, studies of zinc, in addition to electrochemical methods, have been supplemented by modern methods of X-ray structural analysis, which provide a large amount of additional information.

A study of the surface of zinc after atmospheric corrosion showed the presence of traces of chlorine adsorbed from the atmosphere. However, the absence of zinc chlorides on the surface indicates the surface is inert to chlorine. At the same time, cluster ions of zinc corrosion products, including alkali metal salts of the $Zn(OH)^+$ and KNaCl•ZnOH$^+$ types, were detected in the positive ion registration mode. The distribution of such ions over the surface is shown in Fig. 14.

It should be noted that the test sample was triangular in shape and had a technological hole in the middle. This explains the presence of "empty" points in the diagram. At the same time, the brightest points correspond to the edges of the surface, where there are irregularities on which the formation of corrosion products is most intense. The intensity of the peak ion with a mass of 177 Da on the remaining surface is small, which corresponds to the formation of a thin film on the surface of zinc protecting the metal from further oxidation.

Conclusions

Thus, thermal desorption and chromatography-mass spectrometry are indeed an important tool for determining the chemical composition of the surface and near-surface layers and, when used together, provide additional information for the "visualization" surface mass spectrometry. An integrated mass spectrometric approach to metallic surfaces of materials allows to obtain a unique result:

- determination of the presence of physically and chemically sorbed compounds on the surface and their identification in the near-surface layers;
- to detect centers of corrosion and establish its causes using the mass spectrometric imaging method.

It should also be noted that the proposed innovative method can be used for any type of surface, both in combination with other mass spectrometric methods, and separately from them. The method allows you to quickly and accurately assess the uniformity of the surface, the presence of contaminants and foci of corrosion and determine their cause and source.

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