Heat-resistant coatings based on the mo-y-o system deposited from vacuum arc plasma

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Annotation. The possibility of applying an ion-plasma sputtering of continuous coatings based on yttrium molybdates on a composite with a molybdenum matrix is shown. The results of X-ray phase analysis of coatings before and after annealing, as well as microstructure studies are presented.

1. Introduction
One of the most important areas of the Russian economy, ensuring the energy security, is power engineering. Until the 90s of the 20th century, the percentage of Russian power equipment on the world market was 13%, but the political and economic crisis led to its catastrophic decline. Today, due to the development of a large number of space programs, the special relevance is the direction of the development of high-temperature composites with a metal matrix, the use of which will significantly reduce the weight of structures without losing their strength characteristics and thereby increase the competitiveness of domestic products [1].

The special interest from the point of view of high-temperature applications are composites with a molybdenum matrix reinforced with oxide fiber. However, the majority of molybdenum alloys have a low heat resistance due to the fusibility and volatility of molybdenum oxides. A significant increase in resistance to gas corrosion in comparison with the known molybdenum alloys was achieved in the developed alloys, the Mo-Si-B system [2–4].

One of the ways to solve the problem of gas corrosion of the molybdenum alloys is the use of heat-resistant coatings. In [1], the authors achieved an increase in the service life of parts made of molybdenum alloys through the use of protective coatings.

The team of authors [4] found that the formation of the film of yttrium molybdate during oxidation on the surface of a composite sample with a molybdenum matrix reinforced with yttrium-containing fiber served as a protective coating and thus allowed to increase the resistance to gas corrosion. The phase formation temperature of yttrium molybdates exceeds 1,500 degrees, and at such temperatures the molybdenum-based composites are destroyed. Therefore, it is necessary to synthesize a coating based on yttrium molybdates at lower temperatures.

In [5], the authors developed a method for producing coatings based on yttrium molybdates of the required stoichiometric composition by deposition of vacuum-arc plasma deposition. Tests for resistance to the gas corrosion showed that in the process of heating and holding in the gas stream, coatings do not collapse and have high heat-resistant properties. But when the gas flow is turned off and the samples are cooled, the coatings begin to flake off, which is due to the difference in thermal expansion coefficients. In connection with the above, it was decided to develop a method for applying functionally gradient coatings (FGP). FGP is a material characterized by a given distribution of composition, structure, or property by volume. FGP differs from isotropic materials by the presence of a gradient structure and properties: hardness, density, thermal conductivity.
Thus, the purpose of this work is to study the structure, chemical and phase composition of coatings based on yttrium molybdates with a gradient structure obtained by vacuum-arc plasma deposition.

2. Methods of conducting the experiments

As a substrate for coating were used samples of a composite material with a molybdenum matrix reinforced with fiber based on Al₂O₃ oxides and double oxides of Y and Al. The samples were obtained by the method of internal crystallization in the laboratory of reinforced systems at the Institute of Physics and Technology of the Russian Academy of Sciences. For the X-ray phase analysis of the coating, samples of 08X18H10 stainless steel were used as the substrate.

For the deposition of coatings, an ion-plasma sputtering unit NNV–6,6–I1 was used, which makes it possible to apply coatings consisting of both pure metals and chemical compounds (nitrides, carbides, oxides of various metals). The scheme of work and the photo of installation are shown on figure 1.

![Figure 1. Scheme of deposition coatings based on yttrium molybdates on the installation NNV-6,6-11.](image)

For the manufacture of cathodes of yttrium and molybdenum were used rods of commercially available technically pure yttrium and molybdenum brands Itm-5 and MCH, respectively.

Coating on the basis of yttrium molybdates was carried out from two one-component Mo and Y cathodes using the developed technology in the research laboratory “Technologies of coatings and special properties of surfaces” of USATU. The pressure in the chamber was 10⁻³ Pa, the potential on the substrate was 140–200 V and the arc current of the electric arc evaporators was 50–150 A. The deposition of the coatings was carried out with the supply of chemically pure oxygen to the chamber of the reaction gas. The total coating time was 65 minutes. The first adhesive sublayer with low oxygen content was applied within 5 minutes. The second layer, the actual coating, of yttrium molybdates was applied within 60 minutes.

In order to obtain yttrium molybdates with different stoichiometric compositions (Y₂Mo₃O₁₂, Y₂MoO₆ and Y₆MoO₁₂), three experimentally selected modes (hereafter modes no. 1–3) were used, each of which differs by the technological parameters of electric arc evaporators and the pressure of the reaction gas.

For the metallographic study of coatings, were prepared slanting sections with an angle of 6° between the plane of the thin section and the surface of the coating. The morphology of the coating section was studied using a JEOL JSM-6390 scanning electron microscope. To obtain the image of the surface of the thin section, the mode of secondary electrons was used. The accelerating voltage was 20 kV. The assessment of the distribution of chemical elements over the coating thickness was carried
out using the system for energy dispersive microanalysis INCA Energy, with which the above-mentioned microscope is equipped.

3. Experimental results
The study of the structure showed that the coatings can be characterized as continuous, without cracks and delaminations. The microstructure of coated samples for all modes has a similar structure. The electronic image of the microstructure of the coating obtained by mode № 1 is shown in figure 2. The "Spectrum from surface of coatings to substrate" dots indicate the areas of local energy dispersive analysis.

![Figure 2](image2.png)

**Figure 2.** The distribution of chemical elements in the secant. The electronic image and the distribution of secant for mode № 1.

The results of energy dispersion analysis show that in spectrum 1, which is located on the surface of the coating, the stoichiometric composition corresponds to the chemical compound of yttrium oxide (Y₂O₃), and the molybdenum content is less than 2%. Analysis of spectrum № 2 from the middle of the coating indicates an increase in the content of molybdenum in this area and the formation of yttrium molybdates. Analysis of spectrum № 3 from the substrate shows the presence of 96% Mo and a small amount of oxygen, which is associated with the formation of an oxide film on the surface of molybdenum during the preparation of the samples.

The thickness of the coatings on samples obtained by the second technology was investigated on the Calotest instrument, the adhesion of the coating – using the installation of CSM Scratchtest (figure 3).

![Figure 3](image3.png)

**Figure 3.** Image of the hole using the CSM Calotest instrument.

Studies of adhesive strength, resistance to scratching and elucidation of the mechanism of destruction of coatings were performed using the CSM Scratchtest (CSM Instruments). Scratches were applied to
the surface of the coating with a Rockwell C-type diamond spherical indenter with a radius of curvature of 200 μm under continuously increasing load. In this case, the applied load (Fn, H) and the depth of penetration of the indenter (Pd, μm) are recorded on the computer. After that, the load is removed and the indenter is moved in the opposite direction, measuring the restored scratch depth (Rd, μm). The tests were carried out under the following conditions: the load on the indenter increased from 0.3 to 30 N, the movement speed of the indenter a was 2 mm/min, the scratch length – 5 mm, the load application rate – 11.88 N / min, the signal discretization frequency – 60 Hz, acoustic emission signal power – 9 dB. As a result of the tests, the minimum (critical) loads of LC were determined – the appearance of the first crack of doped edges. Results of registration the depth of the indenter presented on figure 4.

![Penetration depth graph](image)

**Figure 4.** The results of registration the depth of the indenter under load and after removal of the load.

The results of testing samples with coatings obtained by various technologies showed that the critical load at which microcracks correspond to 10 N in the coating begins to form. These results confirm the good adhesive strength of the coating with a molybdenum base.

4. **Conclusion**

1. According to the results of the conducted research, the possibility of applying continuous coatings based on yttrium molybdates on a composite with a molybdenum matrix by ion-plasma spraying is shown. The thickness of the coatings obtained is about 35 microns.

2. A method of forming coatings based on yttrium molybdates from a vacuum-arc plasma deposition of the required stoichiometric composition has been developed.

3. Immediately after application, the coating material has an amorphous structure, which acquires a crystalline structure after annealing at a temperature of 950 °C for 1 hour in an air atmosphere.

4. Based on the data of X-ray phase analysis, it can be concluded that the most promising, from the point of view of practical application, are the coatings obtained by mode № 1, № 2.

**References**

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