Effect of N\textsubscript{2} and Ar on the properties of multicomponent ion-plasma coatings 12X18H10T+Cu+Al

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Abstract. Currently, more and more attention is paid to the creation of complex coatings on machine parts and mechanisms applied by various methods that can increase hardness, wear resistance, corrosion resistance and heat resistance. Improving the physicochemical and mechanical properties of relatively cheap metal alloys, when applied with such coatings, allows increasing the service life of parts, saving material resources. The purpose of the presented work is to create heat-resistant coatings that are not inferior in their characteristics to expensive heat-resistant steels. In the work, the heat resistance of ion-plasma coatings obtained by the method of cathode-ion bombardment at the same time by three electric arc evaporators (Cu, Al and chromium-nickel alloy) in an atmosphere of argon and nitrogen at a pressure of 0.5 Pa was studied. As a result of the measurements, it was established that the coatings obtained have a hardness and wear resistance greater than the nickel-chromium alloy itself; the heat resistance of the applied coatings, especially those obtained in argon, is uniquely high.

1. Introduction

In heat and power engineering, and especially in nuclear power, many problems arise related to ensuring the reliability of the operation of actuators and protective shields used under extreme conditions - high temperature, intense radiation, high contact loads, etc. One of the ways to solve some problems, in which the main role is played by the surface properties of the parts, is the application of multi-element ion-plasma coatings, allowing significant changes in the physical and physico-mechanical properties of the surface of the parts. Currently, single-phase coatings based on titanium nitrides and some other metals are most widely used [1–7]. At the same time, work has begun on the study of multi-element (high-entropic) coatings, which possess a number of unique properties that cannot be obtained by methods of traditional metallurgy [8–11]. Earlier, the properties of coatings obtained by simultaneously sputtering cathodes from chromium-nickel steel and other metals with high microhardness and heat resistance were studied in [12]. Taking into account the results obtained in [3], we in the present work solved the problem of obtaining coatings with unique heat resistance while simultaneously sputtering cathodes of Cu, Al and steel 12X18H10T in an atmosphere of argon or nitrogen under pressure.

2. Experimental results

Coatings were applied on substrates of steel grade 45. Substrates 5 mm thick were cut from a hexagonal rod with a face length of 14 mm, and then polished and polished on a FORCIPOL 102 polishing grinder. Before installing the substrate into the chamber, they were washed with Nefras C2-
80/120 organic solvent, rubbed with rectified ethyl alcohol and dried at room temperature. At the same time, coatings were applied on 7 substrates.

Coating was carried out on a NNV 6.6-I1 vacuum deposition unit, on which three electric arc evaporators and a heated cathode plasma source (HCPS) were installed, which combined the functions of ion-plasma cleaning and activation of substrates, as well as ion assisting during coating. Thus, three cathodes were installed in NNV 6.6-I1: from Cu, Al and steel 12X18H10T. The substrates were placed on a rotating table with a deposition plane at an angle of 45 degrees to all three evaporators and to the HCPS (Figure 1), which allowed to apply the coating mainly on the polished surface of the substrate, but the reverse sides and faces of the substrates were also covered with a thin, ~ 4 micron film.

The working chamber of the installation was pumped out to a pressure of $P = 0.005$ Pa, then a special frequency argon (99.996) was applied to the chamber using a gas inlet system and a pressure $P = 0.5$ Pa was established. Next, a bias voltage $U = -1000$ V was applied to the substrates, HCPS and a table rotation drive were turned on, after which the surface of the samples was cleaned and activated for $t = 20$ minutes. After cleaning and activation, the bias voltage decreased to $U = -150$ V and all three evaporators turned on simultaneously. The arc current of each cathode during the entire process was maintained at $I = 80$ A.

The coating time was chosen to be $t = 90$ minutes, which made it possible to obtain coatings with a thickness of ~ 12 μm, while minimizing the number and size of microdroplets on substrates due to a relatively small current in the arc.

In a similar mode, the coating was carried out in a nitrogen atmosphere, which also had a high degree of purity – 99.996. As a result, two types of multi-element coatings were formed on the substrates: (12X18H10T-Cu-Al)+Ar (Figure 2, (a)) and (12X18H10T-Cu-Al)+N (Figure 2, (b)), the topography of which is slightly different.

Electron-microscopic studies of the coatings were carried out on a MIRA 3 scanning scanning electron microscope (TESCAN). The elemental composition of the coatings obtained in argon and nitrogen was analyzed by an energy dispersive method also on a MIRA 3 microscope. The results are shown in Table 1, which also shows the chemical composition of nickel-chromium steel from which one of the cathodes was made.
In the first series of experiments, the hardness of the obtained coatings was determined. Vickers hardness was measured on a HVS-1000A microhardness tester. The load on the indenter was chosen to be 0.1 kg, so that the diagonal of the print was 2 times less than the thickness of the coating under investigation. The measurement results are shown in Table 2. As expected, the hardness of coatings formed in a nitrogen atmosphere is significantly higher than in argon. This is due to the formation of...
the nitride phases of the constituent elements, as evidenced by the high nitrogen content of these coatings (see Table 1).

**Table 2. Hardness of coatings received**

| Coatings                                           | Hardness, HV |
|----------------------------------------------------|--------------|
| (12X18H10T-Cu-Al)+Ar                               | 460          |
| (12X18H10T-Cu-Al)+N                                | 1010         |
| Steel 12X18H10T                                    | 240          |

However, it should be noted that the hardness of the coating obtained in argon is also almost twice the hardness of steel 12X18H10T, although metals, Cu and Al, which do not possess high hardness, were added to the coating. It can be assumed that the structure of the coating itself changes significantly, and due to this a change in hardness occurs. In the second series of experiments, the wear resistance of the coatings was determined. To measure this characteristic, the staff of the research center "Ion-plasma technology and modern instrumentation" of Karaganda State University, made a device, a photo of which is shown in Figure 3, (a).

A steel ball (steel grade III15) weighing 262 g, diameter 40 mm, rotated at a constant speed. Somewhat below the center of gravity of the rotating ball was located the sample under study, which touched the rotating ball. To exclude wiping of the coating, the contact time at one point was experimentally selected 60 s, and the number of points — 25 (see Figure 3, (b)). Weighing of samples (before and after testing) was carried out on electronic scales RADWAG AS 60/ 220.R2, allowing weighing with an accuracy of 10 µg. Taking a loss of mass on a sample of steel 12X18H10T (130 µg) per unit of wear resistance, the wear resistance of the coating (12X18H10T-Cu-Al)+Ar (decrease of 70 µg) can be considered equal to 1.86, and for the coating (12X18H10T-Cu-Al)+N) (decrease 40 µg) - 3.25.

![Figure 3](image-url)

**Figure 3.** Photo: (a) the appearance of the device to determine the wear resistance and (b) the sample after the occurrence of holes on the surface

In the third and final series of experiments, the heat resistance of coatings was studied. Heat resistance was estimated by the specific weight gain. Samples (5 samples with coating (12X18H10T-Cu-Al)+Ar and 5 samples with coating (12X18H10T-Cu-Al)+N) were kept in a muffle furnace at a temperature of 650°C, which was maintained in automatic mode with an accuracy of 5°C. Every 40 hours after setting...
the temperature to 650°C, the samples were taken out, cooled to room temperature for an hour, and weighed. The oven did not turn off. Weighing was carried out on electronic scales RADWAG AS 60/220.R2. After weighing, the samples were again placed in the oven, and after 30 minutes from the moment the oven chamber was closed, a report of the next 40 hour interval was switched on. The specific weight gain of the samples (G, g/m²), depending on the time spent in the muffle furnace at 650°C, is shown in Figure 4.

Figure 4. Dynamics of increase in the mass of samples (G, g/m²) depending on the residence time at 650°C.

1 – samples with a coating (12X18H10T-Cu-Al)+Ar,
2 – samples with a coating (12X18H10T-Cu-Al)+N

From Figure 4, it can be seen that throughout the studied time interval for finding samples at 650°C (160 hours), the dependence of the mass increase was linear for both types of coatings. Also from presented on Figure 4 data shows that the oxidation rate of coatings formed in a nitrogen medium (graph 2 in Figure 4) is higher than that deposited in argon (graph 1 in Figure 4). In the first case, the parameter of weight gain was G = 0.092 g/m², in the second - G = 0.067 g/m².

After the end of experiments to determine the heat resistance, the surface of the samples subjected to heat for 160 hours, and with periodic heating and cooling, was studied using a metallographic microscope EPIKVANT. The study of coatings at a 600-fold magnification did not reveal the presence of cracks and delaminations on the surface of the samples. The results of photographing using an electron microscope of the coatings before and after thermal exposure were also obtained, which are shown in Figure 5 and Figure 6. From the figures, the appearance of oxides on the surface of microdroplets is especially clearly seen.

Figure 5. Type of coatings before thermal exposure:
(a) - deposited in argon, (b) - deposited in nitrogen
3. Conclusions

From the results of the conducted research, it follows that the coatings obtained have high hardness, resistance to abrasion and heat resistance. The characteristics of the coating, not only are not inferior, but many times higher than the similar parameters of nickel-chrome heat-resistant steel 12Х18Н10Т. This may allow the use of parts made of cheaper steels, coated with them, at high temperatures. In the case of the need for high hardness and wear resistance during operation of products at high temperatures, it is preferable to use coatings obtained by the nitrogen atmosphere.

4. References

[1] Ahlgren M and Blomqvist H 2005 Influence of bias variation on residual stress and texture in TiAIN PVD coatings *Surface and Coatings Technology* vol 200 pp 157-160.
[2] Barshilia H C, Anjana I and Rajam K S 2004 Structure, hardness and thermal stability of nanolayered TiN/CrN multilayer coatings *Vacuum* vol 72 pp 241-248.
[3] Castillejo F E, Marulanda D M, Olaya J J and Alfonso J E 2014 Wear and corrosion resistance of niobium–chromium carbide coatings on AISI D2 produced through TRD *Surface and Coatings Technology* vol 254 pp 104-111.
[4] Eremin E N, Yurov V M, Guchenko S A and Syzdykova A Sh 2015 Structure and properties of steel coatings doped with aluminum *Eurasian Physical Technical journal* vol 12 № 2(24) pp 43-47.
[5] Lee Y J, Lee T H, Kim D Y et. al. 2013 Microstructural and corrosion characteristics of tantalum coatings prepared by molten salt electrodeposition *Surface and Coatings Technology* vol 235 pp 819-826.
[6] Li X, Li C, Zhang Y and other 2010 Tribological properties of the Ti-Al-N thin films with different components fabricated by double-targeted co-sputtering *Applied Surface Science* vol 256 pp 4272-4279.
[7] Liu R, Li X, Hu X, Dong H 2013 Surface modification of a medical grade Co-Cr-Mo alloy by low-temperature plasma surface alloying with nitrogen and carbon *Surface and Coatings Technology* vol 232 pp 906-911.
[8] Martin P J, Bendavid A, Cairney J M and Hoffman M 2005 Nanocomposite Ti-S-N, Zr-S-N, Ti-AlSi-N, Ti-Al-V-Si thin film coatings deposited by vacuum arc deposition *Surface and Coatings Technology* vol 200 pp 131134.
[9] Yeh W, Chen S K, Lin S J, Gan J Y, Chin T S, Shun T T, Tsau C H and Chang S Y 2004 Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes *Advanced Engineering Materials* vol 6 pp 299-303.
[10] Cantor B, Chang L T H, Knight P and Vincent A J B 2004 Microstructural development in equiatomic multicomponent alloys *Materials Science and Engineering A* pp 375-377.
[11] Tsai M H, Yeh J W 2014 High-entropy alloys: a critical review Mater. Res. Lett. vol 2 pp 107-123.

[12] Laurinas V Ch, Syzdykova A Sh, Eremin EN, Guchenko S A and Yurov V M 2015 High temperature strength and corrosion resistance of alloy steel coatings Bulletin of KarSU, ser. Physics 4 (80) pp 24-30.

[13] Yurov V M, Guchenko S A, Platonova E S, Syzdykova A Sh and Lysenko E N 2015 Multiphase composite coatings: structure and properties IOP Conf. Series: Materials Science and Engineering (Electronic Materials vol 81)

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