Technological Methods of Gradient Composite Coatings Formation in Conditions of Different Plasma Sources Combination in a Common Vacuum Chamber

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Abstract – The research of combined processes of gradient composite coatings synthesis in different kinds of spatial location of electro arc evaporators, magnetron sources and gas plasma generator in a vacuum chamber of NNV6.6-I1 installation was carried out. The optimal scheme of spatial location of different plasma sources was chosen for technological processes realization: two electro arc evaporators, duo magnetron and gas plasma generator. Within this scheme technological methods of graditent composite coatings of different kinds are developed: Ti–C-Mo–S, Ti–C–Mo–S–Cu, Ti–Al–Si–N. Coatings are studied with Auger electron spectrometry method, scratch method, micro hardness measurement method, method of profilometric studies, method of friction coefficient measurement. The basic variants of compositions and macro structures of gradient functional coatings to increase wear resistance of steel and hard-alloy instruments and to decrease friction coefficient of kinematical transmission.

1. Introduction

The efficiency and length of life of every strengthening coating depends primarily on its adhesion (cohesive resistance) with the base of an instrument or components; it is also defined by sufficiently graded junction (gradient) of mechanical-and-physical properties – composition, structure, hardness, thermal coefficient of expansion – from base to functional coating layers. A well-known method to provide the above-mentioned requirements is to construct a multilayer coating structure. Thus, a gradient underlayer Cr/Crc is used in the paper [1], deposited by magnetron sputtering on the base layer before applying the primary antifriction top layer MoS_2–Cr. The use of the gradient underlayer with chemical affinity with regard to the upper functional layer and alloying of molybdenum disulfide (MoS_2) by chrome to become an optimal concentration will provide improvement of adhesion and tribological behavior of the coating as a whole. In the paper [2], a more complicated combined treatment is used to form gradient structure of tribological coating. At first a steel base is nitrified in a special-purpose installation chamber, then the base is extracted from the chamber and the upper nitrified layer is polished by fine abrasive to the depth 0.3 microns. Then the base is placed in the magnetron installation chamber and is cleaned in argon plasma, after that, at the expense of nitrogen flow change, the gradient underlayer $Ti–TiN_{0.2}–TiN_{0.47}–TiN$ is formed. In the last stage of the process the upper functional layer $TiN + MoS_2$ is deposited on the gradient underlayer.

Undoubtedly, such complication of macroscopic structure and methods of gradient coating formation requires developing complete equipment with expanded technological capacities. Previously [3, 4] we already mentioned about combination in the chamber of MIR-2 or NNV 6.6-I1 installations of two magnetrons and gas plasma generator with hot cathode, which provides qualitative cleaning of the base surface, allows to carry out in one vacuum cycle preliminary nitriding of the base and magnetron deposition with positive effect of the gas plasma on the structure and properties of the coating. In [5], the positive impact of assisting influence of gas plasma generator on properties of electro arc coatings is shown. Since both indicated methods – magnetron and electro-arc – have their own specific advantages, it seems to be expedient to unite them in one vacuum cycle with addition of functional capacities of gas plasma generator to expand a range of technological parameters during formation of gradient coatings.

2. Equipment and experimental methods

In order to research possible technological variants of gradient coatings ion-plasma formation under conditions when three types of ion-plasma sources (magnetron, electro-arc and gas-discharge with hot cathode) are united, an experimental sample of complete equipment on the basis of industrial installation NNV 6.6-I1 was developed. The process chamber of this installation (Fig. 1) contains two electro-arc evaporators *3*, is equipped with two planar magnetrons *2* and gas plasma generators *4*, placed on the chamber surface plate with central axis of the gas-charge plasma flow perpendicular to the fixing table surface of workpieces *5*.

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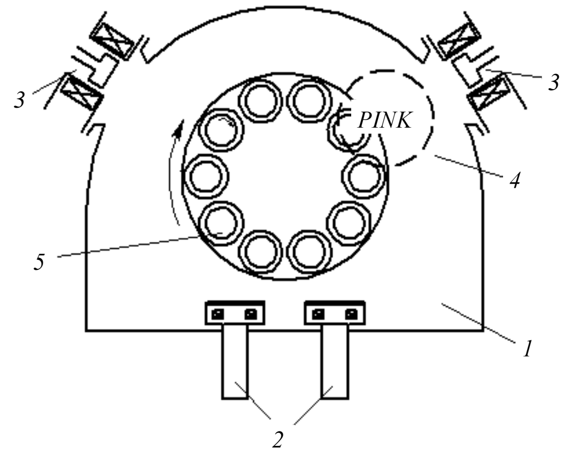

Fig. 1. Basic diagram of the NNV 6.6-I1 installation modernization: *1* – vacuum chamber; *2* – magnetrons; *3* – electro-arc evaporators; *4* – gas plasma generator; *5* – system for product fixation and rotation

Due to availability of two magnetron targets and two cathodes of electro-arc evaporators, which can be produced of different materials and sputtered in different combinations, the technical possibilities to form gradient composite coatings are substantially expanded. In addition, gas plasma generator *4* allows preliminary high-quality ion-plasma stripping of the base surface, to nitrify it if necessary, to heat the base prior to magnetron deposition of the coating up to required temperature, and to assist to the processes of magnetron and electro-arc deposition.

This equipment was used to research technological possibilities to form gradient-composition tribological coatings of the TiC:MoS_x system. The composition material TiC + MoS_2, produced by method of self-spreading high-temperature synthesis, was used as sputtered magnetron targets and cathodes of electro arc evaporators, as well as copper for alloying addition. The magnetron sputtering method was used to form underlayer, which provides adhesion (cohesion) of the coating with the base.

All processes of ion-plasma treatment and coating deposition were carried out in the argon medium and with operating pressure $2.66 \cdot 10^{-1}$ Pa. When coating was deposited by each of methods (magnetron or electro arc), the displacement potential on the base amounted to 100 V. The base temperature was maintained within given range of 400–450 °C, by regulating the discharging currents of magnetrons, electro arc evaporators and assisting gas plasma generator.

The heat-treated for temper hardening steel ShH-15 (52-54 HRC) was used as a material of the base.

In order to carry out tribological tests an installation of “Cyclometer”-type was used. This installation is an implementation of test circuit with moving line contact (fixed indentor – rotating disk). Disk rotation velocity was 250 rpm, a linear speed of indentor and disk relative moment was 0.4 m/s. The load on indentor during tests was constant and amounted to 0.5 N. A ball with 3.3 mm diameter made of hardened steel ShH-15 was used as the indentor. The coatings wear-resisting properties were tested by an indirect method – by counting the time when the friction coefficient of the sample with coating comes to the friction coefficient level of the original sample without coating.

The microhardness of the coatings was measured by a microhardness tester PMT-3 with load on diamond pyramid 0.1–0.2 N. In order to estimate the cohesive resistance of the coatings and the base, the Rockwell methods of dent optical study were applied with load on the indentor of 150 kg and diamond pyramid on the PMT-3 installation with load on the indentor 200 g. The coatings cohesive resistance was also researched by scratch-method by means of an acoustic emission signal analysis with help of device MST-S-AX-0000. The analysis of coatings element composition and element distribution within the gradient underlayer is carried out by Auger spectral method using “Shkhuna-2” instrument.

3. Results and discussion

During preliminary experiments, properties of magnetron and electro arc coatings of TiC:MoS_x system were researched separately. It was ascertained that, in spite of identical component composition of the sputtered magnetron targets and electric arc cathodes, the properties of these coatings differed substantially. First, the electro arc coatings contain three times more sulfur than the magnetron coatings. Respectively, phase composition and structure of these coatings also differ. The magnetron coatings build two-level microstructure with grain size up to 1 micron, and the electro arc ones build nanostructure with grain size 2–5 nm.

In our previous researches of the Ti–Si–B–N coatings it was ascertained, that formation of nanocrystalline structure, which differed drastically from base structure, would lead to reduction of binding forces (adhesion) of the coating and the base. Fig. 2 shows Rockwell dents of electro arc coatings TiC:MoS_x.

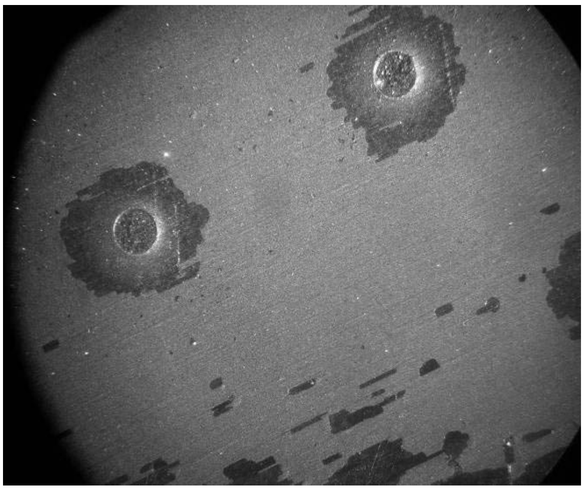

Fig. 2. Surface of electro arc coating TiC:MoS_x on the base made of steel ShH-15 without binding (adhesion) underlayer

One can see that nanostructure electro arc coating is characterized with a very weak adhesion with the base, made of steel ShH-15. This coating is separated from the base even in zones, remote from deformational impact of the Rockwell indentor.

On cannot detect such delaminating on magnetron coating. On the basis of the abovementioned experiment results, it was decided to form the coating binding underlayer by magnetron sputtering method. For this purpose two variants of the underlayer were used: TiC:MoS_x and TiC:MoS_x:Cu. The primary functional layer of the coating was also deposited by the electro arc method in two variants: TiC:MoS_x and TiC:MoS_x:Cu. The layer formation was carried out together with assisting influence of gas plasma generator. By method of Auger-spectrography it was ascertained, that such technique provided alloying of the basis (base) with composition components of the coating to the depth of 200 nm. Relying on well-known facts about adhesion mechanisms, you can suppose, that increasing of chemical affinity of the base and the coating leads to increasing of cohesive resistance, which was confirmed by microindentation methods and scratch-tests of the coatings.

Analysis of the microindentation results with load on diamond pyramid 2 N revealed, that there was evident coating breakaway near dent border on the electro arc coating TiC:MoS_x, deposited on the underlayer, containing Cu, i.e., that type of coating was characterized by weak adhesion. Similar breakaway was not detected on the electro arc coating TiC:MoS_x, deposited on magnetron underlayer TiC:MoS_x with affine composition. When copper is added to electro arc coating and the combined coating TiC:MoS_x:Cu is deposited on the underlayer with identical composition, that is, containing copper, the adhesion of the coating also improves.

The scratch-test results of these coatings conform to abovementioned data on microindentation.

By means of Auger-spectrography it was ascertained, that copper content in electro arc coating TiC:MoS_x:Cu amounted to about 10%. Such high concentration of plastic copper in the coating led to reduction of its hardness to 2–2.5 GPa und influenced tribological behavior.

Figure 3 shows results of friction tests of the above-mentioned coatings.

Figure 3 shows, that the coating with high content of copper in the upper arc layer TiC:MoS_x:Cu + + TiC:MoS_x:Cu has the highest friction coefficient, which increases almost linearly within time of tests. The coating TiC:MoS_x:Cu + TiC:MoS_x (curve *2*) has low friction coefficient (less than 0.2) till 15 min of tests. However, after 20 min the friction coefficient of this coating increases sharply and exceeds friction coefficient of the previously considered coating. It seems, that it is conditioned by low adhesion of the coating TiC:MoS_x:Cu + TiC:MoS_x and its relatively high-speed wear. The coating TiC:MoS_x + TiC:MoS_x (curve *3*) is characterized by the highest wear resistance, when quite a low value of friction coefficient (about 0.2) is maintained during the whole period of tests, which is undoubtedly connected with its good adhesion with the base. There are two sectors on the curve *3* (till 10 min, when *f* increases from 0.12 till 0.24, and after 15 min, when *f* is stabilized on the level 0.2), which means, that tribological behavior of combined coating is influenced by a harder magnetron underlayer with low sulfur content, compared to electro arc coating.

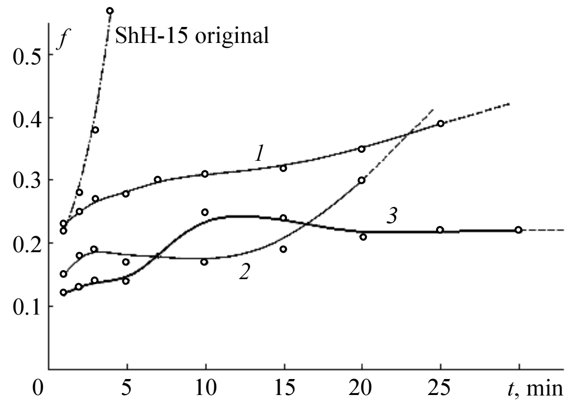

Fig. 3. Dependence of friction coefficient with time of tests with load on indentor 0.5 N: *1* – magnetron-arc coating TiC:MoS_x:Cu + TiC:MoS_x:Cu; *2* – magnetron-arc coating TiC:MoS_x:Cu + TiC:MoS_x; *3* – magnetron-arc coating TiC:MoS_x + TiC:MoS_x

The functional and technological possibilities of developed gradient coating formation scheme were also researched using coatings of Ti–Al–Si–N system. The base component of TiN coating was formed by electro arc sputtering in the nitrogen medium, where alloying additions Al and Si were added. Due to alloying, we received a composition coating with microhardness 42 GPa, which exceeded considerably hardness of titanium nitride TiN.

4. Conclusion

1. As a result of researches, a process flow diagram was developed to form magnetron-arc gradient composite coatings in conditions, when in one vacuum chamber the magnetron sputtering system, the gas plasma generator with hot cathode and two electro arc evaporators were united.

2. The developed scheme was experimentally approved when gradient structures for three variants of coatings were constructed – electro arc TiC:MoS_x with magnetron underlayer TiC:MoS_x, electro arc TiC:MoS_x, alloyed by Cu, and electro arc TiN, alloyed by Al and Si.

3. With account of the research results we are working on processes to apply gradient composite tribological coatings with base component TiC:MoS_x to details of power transmission and hardening coatings Ti–Al–Si–N to metal-processing tools.

References

[1] Y.L. Su and W.H. Kao, Tribology Inter. **36,** 11 (2003).

[2] M. Rahman, Ju. Haider, and D.P. Dowling et al., Surface and Coatings Technology **200**, 1451 (2005).

[3] V. Savostikov, D. Borisov, E. Gromychev, and Yu. Pinzhin, *in Proc.7th Int. Conf. on Modification of Materials with Particle Beams and Plasma Flows,* 2004, pp. 485–488.

[4] V. Savostikov, D. Borisov, S. Sergeev et al., *in Proc.8th Int. Conf. on Modification of Materials with Particle Beams and Plasma Flows,* 2006, pp. 502–507.

[5] V. Savostikov, D. Borisov, V. Kuzmichenko, and Yu. Pinzhin, *in Proc.10th Int. Conf. on Gas Discharge Plasmas and their Technological Applications,* 2007, pp. 424–427.