Influence Of Technological Modes Of Magnetron Spraying On The Structure And Properties Of Coatings Based On Chrome

Saydakhmedov Ravshan, Kutpinisa Kadirbekova

Abstract: The production of chromium-based coatings in vacuum by magnetron sputtering refers to environmentally friendly technologies. The technological capabilities of a magnetron sputtering vacuum system are considered. It was proposed to pre-treat the surface of the substrate with argon ions before applying the chrome plating. For this purpose, a designed ion source and a magnetron sputtering device for the chromium cathode are located in the chamber. Chromium-based nanostructured coatings formed by magnetron sputtering with preliminary treatment of the surface with an ion source are investigated. The thickness, adhesion strength and corrosion resistance of chromium coatings were determined. It was shown that the chemical resistance of samples with chromium-based coatings in solutions of nitric and hydrofluoric acid showed their high corrosion resistance. The effect of the thickness of the chromium-based nanostructured coating on the corrosion resistance is investigated. With an increase in coating thickness, the corrosion resistance of chromium coatings changes several times. For coatings less than 1 micron thick, the number of corrosion points (pores in the coating) was 5-10 times larger than for coatings 2.3-2.5 microns thick. Using electron microscopy, the surface morphology and the size of nanoparticles in the structure of chromium coatings were investigated. It was revealed that, depending on the formation modes, the coatings consist of crystallites with sizes from 45 nm to 200 nm.

Index Terms: coating, nanostructure, chromium, magnetron sputtering, coating thickness, vacuum chamber, adhesive strength, physicochemical properties, composition, structure, technological regimes, electron microscopy and corrosion resistance.

1. INTRODUCTION

Recently, interest in studying materials with a nanocrystall structure has increased, since a decrease in the size of crystals below a certain threshold value leads to a radical change in the physicochemical properties of these materials. The greatest change in the properties of nanomaterials is achieved in the range of crystallite sizes up to 100 nm. The technology for producing thin films and coatings can be attributed to nanotechnology. Thin films and coatings can be obtained by PVD and CVD. Thus, the well-known coatings of titanium carbide and nitride are obtained by ion-plasma deposition, which leads to the formation of nanocrystall structure [1, 2]. Coatings based on chromium and chromium nitride are used in industry as a solid thin film to protect parts and have excellent wear resistance, high hardness, sufficient strength, good adhesion to the base, high corrosion resistance and heat resistance up to 600°C [3-6]. At present, in industry galvanic coatings of chromium on steels and alloys are widely used, which are distinguished by high chemical and mechanical resistance, however, they are obtained by environmentally harmful chemical technology, requiring expensive treatment facilities. During galvanic chromium plating, toxic hexavalent chromium is used, and significant tensile stresses are formed, which lead to the appearance of a network of cracks in the coating immediately after deposition [7, 8].

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Vacuum coating technology does not have these drawbacks. Therefore, in some cases it is advisable to use vacuum methods for the deposition of chromium coatings by magnetron sputtering. Due to the low temperature of coating deposition by magnetron sputtering, it is possible to form them on tools and non-metallic materials, in particular on reflective surfaces and as decorative coatings on various parts of automobiles. Currently, in the automotive industry, aluminium alloys are used to produce reflective and decorative coatings. Coatings based on aluminium do not always meet the requirements for their reflective and corrosive properties. But chromium-based coatings or Al-Cr composite coatings can be successfully used as reflective coatings in the automotive industry. Also coatings based on chromium nitride are hard coatings that can be successfully used as wear-resistant coatings to protect the wearing surfaces of parts and tools. Therefore, the study of chrome vacuum coatings is of interest to both science and industry. In article [9], multilayer coatings based on chromium nitride and chromium carbonitride were studied. Multilayer alternating coating layers based on CrN / CrCN are formed by the PVD (CAD-cathode arc deposition) method. It was experimentally established that the wear resistance of multilayer coatings based on chromium nitride and chromium carbonitride is higher than separately taken CrN and CrCN coatings. As a sublayer, a chromium sublayer with a thickness of 0.1 μm was used. The composition, microstructure and residual stresses, as well as the properties of chromium coatings obtained by the PVD method (Physical Vapor Deposition) were studied in [10, 11]. CrN coatings are obtained on a titanium substrate using physical vapor deposition (PVD) with advanced capabilities. In this work mainly were studied coatings that obtained by the arc deposition method, which is not always acceptable for non-metallic materials due to the high deposition temperature. For the formation of coatings on non-metallic materials with low heat resistance, it is advisable to use magnetron sputtering. Based on the foregoing, it is necessary to note the relevance of the study of the technology of forming coatings based on chromium by magnetron sputtering. The aim of this study is to study the structure, composition and properties of chromium-based coatings formed by magnetron sputtering and also to investigate of the influence of magnetron sputtering regimes on the thickness and structure of coatings.

2 METHODS OF RESEARCH

For chromium-based coatings, the method of magnetron sputtering with preliminary surface treatment by an ion source was used. The relative arrangement of devices for processing products in a vacuum chamber is shown in Figure 1. In a vacuum chamber with standard means of pumping and measuring vacuum, the flanges have a device for ion surface treatment and a magnetron sputter cathode. Also, a rotary mechanism is installed in the chamber, which allows changing the position of the workpiece in the technological cycle. These devices can simultaneously or sequentially process the surface of a rotating tool with samples. In this case, an adjustable negative voltage can be supplied to the tool. After loading the sample into the vacuum chamber, the pumping process continues until the pressure is reached. Then the ion source is turned on. The surface of the sample is treated with argon ions. Ion treatment was used to improve the adhesion strength of chromium coatings with a base. Next, the sample rotates relative to the target and occupies a perpendicular position. The next step is coating.

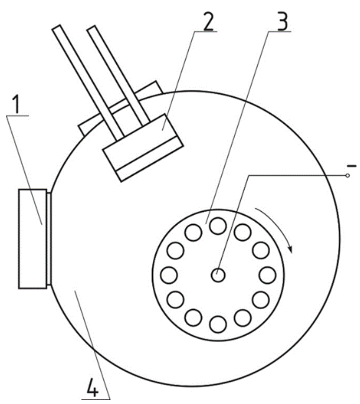

Fig. 1. *Relative arrangement of devices in a vacuum chamber:*
1- cold cathode ion source, 2- magnetron sputtering device, 3- rotating equipment, 4- vacuum chamber.

Figure 2 shows the design of one of the options for a cold cathode ion source. The ion source includes a ring anode in the discharge chamber, at the output of which there is an annular gap (diaphragm) into which the plasma stream is extracted. The UNDK alloy permanent magnet and magnetic core provide a magnetic field in the gap.

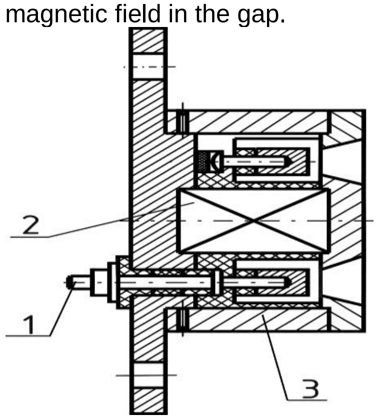

Fig. 2*. Design of a cold cathode ion source:*
1 - high-voltage input connected to a ring anode, 2- permanent magnet, 3- magnetic circuit with a slit diaphragm.

Figure 3 shows the design of a magnetron sputtering device for a cathode made of chromium or other non-magnetic materials.

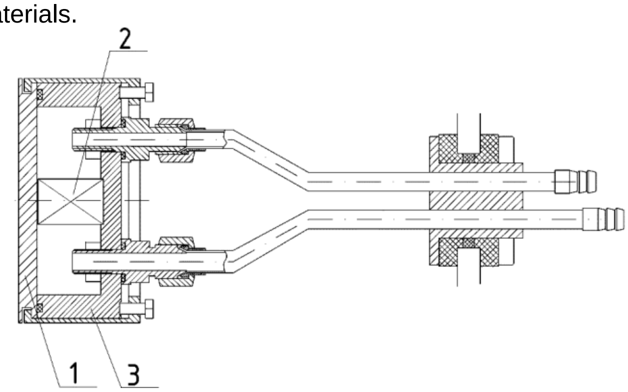

Fig. 3. *Design of the magnetron sputtering device:*
1- atomized target cathode, 2- permanent magnet, 3- magnetic circuit with water cooled and insulated tubes.

After obtaining a starting vacuum degree of the order of 10^{-2} Pa, rigs with moving samples and a control plate were treated with an ion source in the following modes (table 1).

Table 1. *Modes of ionic surface treatment*

№	Technological modes	Values and units
1	Working gas pressure (argon)	$2{\cdot}10^{-1}$ Pa
2	Discharge voltage	4,5-5,0 кV
3	Ion source of discharge current	80-100 мА
4	Current density on the work surface	Up to 1 мА/см^2
5	Sample surface treatment time	3 minutes

Immediately at the moment of operation of the ion source, the magnetron source was switched on, then the equipment was transferred to the position opposite the spray source. The deposition of chromium coatings was carried out in the following technological modes (table 2).

Table 2. *Modes of vacuum deposition of chromium*

№	Technological modes	Values and units
1	The distance from the cathode to the surface of the samples	120-130 мм
2	Working gas pressure (argon)	$2{\cdot}10^{-1}$ Pa
3	Ion source of discharge current	minus 550 V
4	Spray discharge current	2,0-2,5 A
5	Chrome coating deposition time	5-20 minutes

The temperature of the samples during the deposition of coatings did not exceed 150°C. The thickness of the vacuum-deposited chromium coatings was determined by the control silicon wafer, which was under the same processing conditions as the steel samples. The thickness was measured on a MII-4 type microinterferometer according to a standard technique. The adhesive strength of the coatings was investigated by the method of normal separation from the surface of coatings glued to metal rods. The coated sample was placed in a cassette with 7 vertical rods (the diameter of the glued part was 1 mm), which were glued to the coating and torn off using a tensile testing machine. The chemical stability of samples with chromium-based coatings was studied in a solution of nitric and hydrofluoric acid. Using electron microscopy, we studied the surface morphology and particle sizes in the structure of chromium coatings. Information on the surface topography and size of agglomerates of chromium nanoparticles was obtained using transmission electron microscopy. To study the surface, two-stage Pt/C replicas were obtained [12, 13].

3 RESULTS AND DISCUSSIONS

It should be noted that when negative voltage (bias) is applied to the equipment during magnetron sputtering, the ion current appears only at voltages of minus 20-25 V and increases with increasing voltages of the order of minus 80-100 V, after which it changes slightly. The current level depends on the discharge current of the magnetron and the relative position of the magnetron and equipment, reaching values up to 100-300 mA. The thickness of the coatings, the uniformity of its distribution on the surface of the substrate is important, ensuring the properties of the products. We determined the thickness of coatings on the MII-4 device. According to the measurements, the maximum thickness of the chromium-based coating was about 2.4 microns for a deposition time of 20 minutes. Studies have shown that the thickness of chromium coatings is proportional to the deposition time in the range of 2-20 minutes. An important characteristic of the coating is the fulfillment of its functional purpose - for a certain time not to exfoliate from the surface of the product. This indicator determines the adhesion of the coating to the substrate. Studies have shown that the experimentally determined value of adhesive strength was 70-80 MPa (700 kg/cm^2). The corrosion problem observed in coating materials, as a rule, is the result of penetration of aggressive reagents through coating defects and their contact with the substrate. Coating, especially multilayer coating, improves the corrosion resistance of the material. Coatings based on Cr and CrN with a dense structure and fine crystals make them less permeable to aggressive environments. The absence of direct diffusion channels due to non-columnar structure, as a result of which the rate of oxygen diffusion through coatings is significantly reduced. The corrosion resistance of chromium coatings in a solution of nitric and hydrofluoric acid was determined, which showed their high corrosion resistance. For coatings with a thickness of less than 1 μm, the number of corrosion points (pores in the coating) was 5–10 times greater than for coatings with a thickness of 2.3–2.5 μm. As the experiment shows, with a change in the thickness of the chromium-based nanostructured coating, the corrosion resistance also changes considerably. This implies the existence of through channels or their absence with an increase in the thickness of the coatings. Another important feature of nanostructured chromium coatings are structural components, i.e. sizes of nanoparticles in coatings, which have a significant effect on the corrosion resistance of the coating-substrate system. Chrome coatings were obtained under various conditions of the spraying process. The main parameters of the spraying process are shown in table 2. To study the structure of chromium coatings, electron microscopy was used. Electron-microscopic studies showed that for samples (Figure 4, 5), structures with chromium nanoparticles are observed. It was shown that during the formation of Cr nanostructures with a maximum amount of a chromium-containing phase, they are obtained at a pressure ($P = 3 \times 10^{-2}$ Pa), spherical chromium nanoparticles from 45 nm to 130 nm in size are formed (Figure 4), and

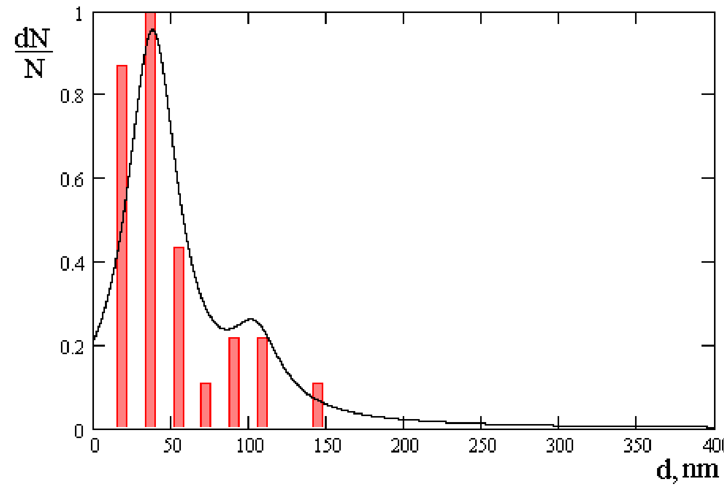

Fig. 4. *Number of nanoparticles: 97% - 45nm, the largest number nanoparticles of sizes 50 nm and 100 nm*

For a sample obtained under pressure ($P = 3 \cdot 10^{-3}$ Pa), larger chromium nanoparticles (66-200 nm) are observed (Figure 5).

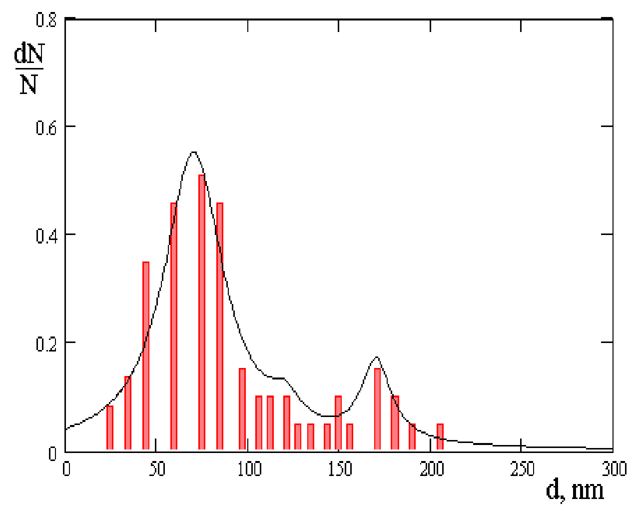

Fig. 5. *Number of nanoparticles: 55% 70 nm; 15% 120 nm; 30% 170 nm*

4 CONCLUSION

In a combined vacuum installation with an ion source and a magnetron sputtering device, nanostructured chromium coatings are obtained. It was found that ion cleaning with argon ions affects the adhesive strength of the chromium coating with the base. It was revealed that by varying the technological conditions of the sputtering process, it is possible to control the size and volume of nanoparticles in chromium coatings, for example, at a pressure in a vacuum chamber of $P = 3 \cdot 10^{-2}$ Pa - the nanoparticle sizes range from 50 to 100 nm, and at a pressure $P = 3\ 10^{-3}$ Pa — the volume content of nanoparticles depending on their size is distributed as follows: nanoparticles with sizes of 70 nm are present in coatings at a level of 55%, with dimensions of 120 nm - 15%, and with dimensions of 170 nm - 30%.It has been established that with increasing thickness the corrosion resistance of chrome coatings changes several times. With an increase in the thickness of coatings from 1 μm to 2.3–2.5 μm, the corrosion resistance increases by 5–10 times.

Based on the studies conducted, it is possible to draw a conclusion about the wide possibilities of using vacuum-deposited magnetron sputtering of chromium coatings instead of galvanic ones.

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