

Thickness measurements of coatings formed from metal plasma of a vacuum arc discharge using X-ray radiation

A A Lisenkov¹, S A Martsinukov², V V Chernigovskiy², D K Kostrin²
and E A Smirnov²

¹ Institute of Problems of Mechanical Engineering, Russian Academy of Sciences,
199178, Saint Petersburg, Russia

² Department of electronic instruments and devices, Saint Petersburg Electrotechnical
University "LETI", 197376, Saint Petersburg, Russia

E-mail: lisran@yandex.ru

Abstract. Using vacuum arc plasma sources allows obtaining coatings with broad spectrum of functional properties. The main problem is to control the thickness of a formed coating. This paper shows the possibility of using X-ray radiation to determine the coating thickness.

Currently a wide range of various by composition coatings deposited from metal plasma of a vacuum arc discharge is developed and applied [1, 2]. Universal properties of the formed coatings allow their use in various branches of engineering to improve wear resistance, reduce coefficient of friction and provide protection from corrosion [3, 4]. To meet market requirements the coating must provide a sufficient hardness, low friction coefficient and high thermal stability. The solution to this problem is achieved either by the development of new coating formulations with enhanced performance properties, or by developing new methods of coating deposition to improve the coating quality and increase the speed of its formation. To achieve this goal vacuum arc plasma sources are very widely used [5]. Modifying parameters of a generated flux of metal plasma, the pressure of the reaction gas and the magnitude of the accompanying magnetic field, it is possible to control the properties of condensate and to obtain the necessary coating quality.

In vacuum arc plasma sources with coaxial design of the electrodes the cathode is made in a form of a cylinder or truncated cone, the working surface in this case is the side with the smallest area S_c (figure 1). Section of the cathode opposite to its working surface is cooled with running water. Continuous chaotic movement of cathode spots at a fixed surface of the cathode [6], regardless of the initial distribution, leads to some average equilibrium temperature of the surface, determined by the geometrical dimensions of the cathode: the diameter and length, and conditions of its cooling.

Diameter of the working surface of the cathode may be as much as 200 mm. Geometric dimensions are selected to provide lowest average operating temperature of the cathode. During the work of the source due to erosion of the material the length of the cathode decreases (figure 1) that leads to a decrease in temperature of the cathode and to changes in the conditions of plasma flow formation.

Thus, the temperature of the cathode is the main factor determining modes of generation of the plasma flux, and therefore, even providing the stabilization of the discharge parameters, as the cathode is sputtered, there are significant changes in it leading to deviations of thickness of the formed coatings. In batch deposition of coatings these conditions require adjustments to the process.



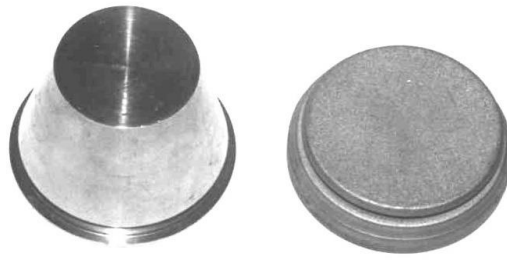


Figure 1. Consumable cathode of a vacuum arc plasma source before (left) and after (right) work cycle.

If the surface receives a flux of ions with energy W_i and the ion current density j_i , from the condition of mass balance, the rate of coating growth is determined by the expression [7]:

$$v_{\text{dep}} = j_i(z) (\chi(W_i) - S(W_i)) / \xi e n_0, \quad (1)$$

where $j_i(z)$ – is the density of ion flow to workpiece; $\chi(W_i)$ – accommodation coefficient (the fraction of the condensed ions); $S(W_i)$ – sputtering rate (fraction of ions leaving the surface layer); ξ – average ion charge in plasma; n_0 – concentration of particles in surface, uncompacted layer with a characteristic thickness, equal to the path of ions.

Average in time and space magnitude of the ion current density at the cathode axis and at a distance z from it is possible to determine, based on the assumption that the supersonic flow of plasma outbound from the cathode area extends in the radial direction with the speed of ion sound:

$$j_i(z) = 4I_i / \pi \left(D_c + 2z \frac{v_{is}}{v_{pl}} \right)^2,$$

where $I_i = 0.08I_{\text{dis}}$ – value of the ion current; D_c – diameter of the cathode.

Coefficients χ and S included in the equation (1) depend on the energy of ions bombarding the surface W_i , which consists of the initial energy $W_{i0} = m_i v_{pl}^2 / 2$ and the energy acquired in Debye layer $e\xi U_{\text{bias}}$, adjacent to the substrate, provided that it is set to the accelerating negative potential U_{bias} . Changing the value of U_{bias} allows to adjust the energy of the ions, and, consequently, to control the flow of the process, turning it from a spray mode to the formation of the coating. Thus, the process of coating formation is determined by the energy of the condensing particles, which influence not only on the adhesion of the coating, but also on its structure, composition and presence of defects.

Figure 2 shows dependence of the growth rate of the applied coating from the time of the evaporator operation. The original length of the titanium cathode was equal to $4.5 \cdot 10^{-2}$ m, with a diameter $6.0 \cdot 10^{-2}$ m. Change in the length of the cathode in the process corresponds to a change in its operating temperature in time. Transition of the dependence into the horizontal section coincides with the transition of the temperature for the studied material, through the point of the recrystallization annealing. Cathode spots on the working surface of a titanium cathode at a higher temperature leave clearly delineated melted zones with a depth of several millimeters. At a lower temperature the working surface of the cathode has a fine-grained structure with a metallic luster.

With increasing operating temperature of the cathode in the flow increases the percentage of neutral vapor and droplet formation [8], which is confirmed by the dependency of the growth rate of the applied coating from the negative bias, set on the substrate, obtained when the length of the cathode is $4 \cdot 10^{-2}$ and $2 \cdot 10^{-2}$ m (figure 3) and respectively at different temperature.

When the length of the cathode is $4 \cdot 10^{-2}$ m (curve 1 in figure 3) value of the bias voltage has no effect on the growth rate of the formed coating, since the flow is dominated by the presence of droplet formation. During sputtering of the cathode material, a decrease in its working temperature is observed. At the end, when the length of the cathode decreases, all the power that is released at the cathode is withdrawn by the cooling system. Under these conditions the growth rate is determined by the positively charged component of the plasma flow (dependence 2 in figure 3, length of the cathode is $2 \cdot 10^{-2}$ m). The observed decrease in coating thickness with increase in negative bias is associated with the effect of sputtering caused by bombardment of the surface by high energy ions.

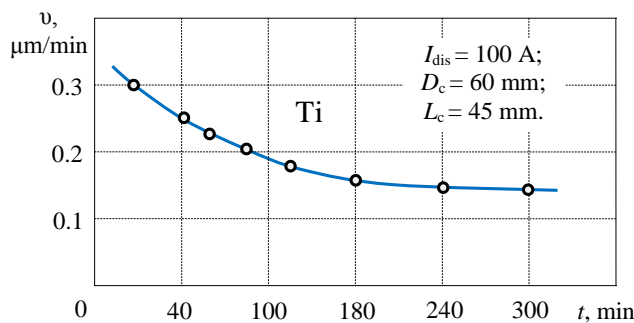


Figure 2. Dependence of the growth rate from the time of the evaporator operation.

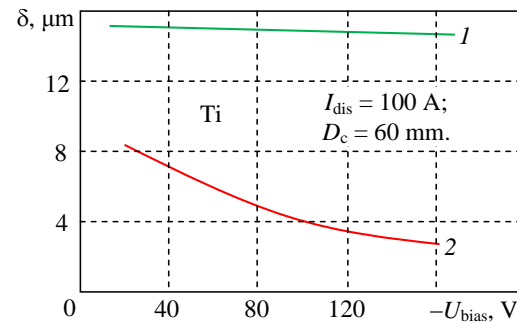


Figure 3. Dependence of the growth rate from the negative bias.

Performed using X-ray diffractometer DRON-3 in CuK_α radiation metallographic investigations showed that the temperature of the cathode depends on the structure of the formed coating. For titanium, at a temperature of the cathode below 880 °C obtained coating had a complex structure. The increase in the magnitude of the negative bias (in absolute value) on the treated substrate leads to the formation of coatings with very distinct components (111), (110) and (012), while at the temperature of the cathode in excess of 880 °C the effect of the orientation was weak and the coating had a loose, rough character. Thus, the temperature of the growing film and the phase composition of the flow have a crucial impact on the properties of the obtained coatings. In this regard, the main problem when using vacuum arc plasma sources is the operational control of the thickness of the formed coating.

All methods of measuring coating thickness can be divided into two large groups based on destructive and nondestructive control methods. In each case the choice of method and equipment depends on the parameters of the controlled sample. To destructive control methods, in particular, may be referred a method of determining coating thickness using a spectrophotometer "Saturn", the principle of which is based on the conversion of the sample into atomic state, with subsequent photometric transformation of the optical density of the atomic vapor into an electrical signal. The thickness of the coating in this case can be determined from the following relationship:

$$\delta = m_s / \rho,$$

where m_s – is the specific surface density of the coating; ρ – bulk density of the coating material.

Information about the concentration of the analyte is obtained as a result of absorption by free atoms of radiation from a spectral source – lamp LSP-1. Test and control samples are processed, whereby the mass is determined using a preset concentration in the control samples. The RMS relative deviation of this method for titanium does not exceed 10 %.

Of special interest are methods of nondestructive testing [9]. Coating thickness can be determined using control sample, which has a step between the film and the substrate (scratch on the surface of the substrate or edge of the film on the open substrate). According to the obtained topography, the thickness is measured with great precision using profilometric methods. Upon reflection from the surfaces of the film and substrate, assuming the existence of the relief are applicable interferometric measurements using microinterferometers MII-4.0, MII-11 or MII-12, and to a certain extent, these measurements can be automated. The resistive method allows estimating the film thickness by its ohmic resistance. To implement this method in a thread, along with the substrates is placed a control dielectric plate, rectangular in shape, which allows applying when of a well-known expression for the resistance of a conductor with a given length and a rectangular cross section.

Capacitive measurement method is only applicable for dielectric films and coatings, and impossible for the metal and semiconductor layers. In addition, this method gives the average value of the coating thickness across the object. Also only for dielectric and semiconductor films can be applied becoming increasingly common spectrometric measurement method [10, 11].

Wide application, due to the high sensitivity (to the deposited mass it is $(10^{-8} \dots 10^{-11}) \text{ g} \cdot \text{cm}^{-2} \cdot \text{Hz}^{-1}$) and the ability to control the weight, thickness and speed of material application, has a method of

quartz resonator. However, its use is hampered due to the temperature drift of frequency of the quartz resonator, which requires additional cooling [7]. Ultrasonic method is applied to coatings with a thickness more than 0.1 mm, the measurement error is 5 %. But the application of this method is limited because of the strong attenuation of ultrasonic waves in thick coating layers, which complicates acquiring of a weak reflected signal due to complex shapes of objects. In addition, when ultrasonic method is used in some cases there can be a detachment of the coating.

The vortex method is based on the analysis of the interaction of electromagnetic field with the electromagnetic field of eddy currents induced by the exciting coil in an electrically conducting test object. Apparatus that implements this method allows to measure thickness from a few micrometers to millimeters, with an accuracy of 2...5 %. The minimum area of the control zone can be increased to 1 mm², which opens the possibility of measuring coating thickness on complex objects. However, this method requires the combination of certain material properties of the coating and the substrate.

All methods of coatings thickness measurement considered above have limitations for practical application. To determine the thickness of the coating from units to tens of microns, provided control efficiency and versatility of the investigated coatings were selected methods based on a quantitative X-ray phase analysis. The coating thickness measurement was performed using diffractometer ADP-2M in two ways relating to the registration of the diffraction pattern of the coating or substrate.

In the first case, the reflected rays leave the crystal from the side of a primary beam and are recorded in front of the crystal. Thus is examined the change in the intensity of the selected diffraction reflection of a coating depending on its thickness. In this case, the calculation of a coating thickness is provided by the following equation [12]:

$$I_{HKL} = I_0 Q S [1 - \exp(-\gamma h / \sin \vartheta)] / 2\gamma, \quad (2)$$

where I_{HKL} – is the intensity of a diffraction reflection with indices H, K, L ; I_0 – intensity of the primary beam; Q – integral reflectivity of the unit; S – area of the cross section of the beam; γ – linear attenuation coefficient of the used characteristic X-ray radiation by the coating material; ϑ – angle of diffraction; h – thickness of the coating.

When conducting the experiment in such way the area of the irradiated surface and the acquisition conditions of the diffraction pattern remain unchanged, thus it is possible to associate the intensity change with changing layer thickness. For a sufficiently thick cover, when $h \rightarrow \infty$ the equation (2) takes the following form:

$$I_{HKL}^M = I_0 Q S / 2\gamma.$$

Table 1 shows how the ratio of the intensities of some diffraction reflections of titanium film and bulk samples is changed during registration in CuK_α radiation.

Table 1. Ratio of the intensities of some diffraction reflections of titanium film and bulk samples I_{HKL} / I_{HKL}^M during registration in CuK_α radiation.

Reflection indexes HKL	$\vartheta, ^\circ$	Coating thickness, μm					
		0.5	1.0	3.0	5.0	10.0	15.0
(011)	40.2	0.24	0.42	0.80	0.93	0.99	1.00
(021)	77.4	0.14	0.26	0.60	0.76	0.95	0.99
(123)	139.7	0.09	0.16	0.40	0.58	0.82	0.93

Thus, choosing the appropriate reflection for a pattern gives the opportunity to efficiently measure coating thickness in the range from 0.5 to 15 μm . Changing the wavelength of the used characteristic radiation from CrK_α to MoK_α extends the limits for determining thickness by this method to 40 μm .

In the case of thin substrates measurement of coating thickness is possible by the weakening of the direct X-ray beam. The attenuation of the radiation intensity is according to the following law:

$$I_h = I_0 \exp(-\gamma h).$$

Since the attenuation coefficient depends on the wavelength of X-ray radiation it is necessary to use a tube with small energy quanta of radiation. Thus, for this analysis it is necessary to have the X-ray tube with a possible lowest energy of a characteristic radiation. The study of samples was carried out as follows. The sample is placed on the way of direct X-ray radiation. First the intensity of X-ray radiation of the sample without coating is determined and then the measurements are repeated for a coated sample. The obtained data is used to calculate the thickness of the investigated coating according to the following equation:

$$I_h / I_0 = \exp(-\gamma_1 h_1) \exp(-\gamma_2 h_2),$$

where γ_1 – is the linear attenuation coefficient of the used characteristic X-ray radiation by the material of the coating with thickness h_1 ; γ_2 – linear attenuation coefficient of the used characteristic X-ray radiation by the substrate material with thickness h_2 .

The results of measurement of the coating thickness for various samples using a method, based on the X-ray attenuation, are presented in table 2. As the substrate was used aluminum material and copper as a coating. Parallel control of the coating thickness was carried out by weighting method and the study of metallographic sections.

Table 2. Results of the coating thickness measurements for various samples using a method, based on the X-ray attenuation.

Measurement method	Coating thickness, μm				
Weighting	0.78	1.10	1.30	2.10	2.40
X-ray attenuation	0.80	1.10	1.10	1.90	2.10

As follows from the table 2 the proposed X-ray method of measuring the coating thickness gives a satisfactory agreement of data with relatively reliable measurement using weighing of the samples.

Using results of this work were optimized the parameters of a vacuum arc metal plasma source with coaxial design of the electrodes. Also was showed the possibility of rapid measurement of the thickness of the applied coating with a sufficient degree of accuracy by the X-ray methods.

References

- [1] Kostrin D K and Lisenkov A A 2016 *Materials Science Forum* **843** 278–83
- [2] Kostrin D K and Lisenkov A A 2016 *Materials Science Forum* **870** 371–6
- [3] Vetrov N Z, Kostrin D K, Lisenkov A A and Popova M S 2015 *J. Phys.: Conf. Ser.* **652** 012032.
- [4] Vinogradov M L, Kostrin D K, Smelova V V, Trifonov S A and Lisenkov A A 2016 *Proceedings of the 2016 IEEE North West Russia Section Young Researchers in Electrical and Electronic Engineering Conference* 729–30
- [5] Bystrov Yu A, Vetrov N Z, Lisenkov A A and Kostrin D K 2014 *Vakuum in Forschung und Praxis* **5** 19–23
- [6] Bystrov Yu A, Kostrin D K, Lisenkov A A and Vetrov N Z 2015 *Vakuum in Forschung und Praxis* **2** 22–5
- [7] Bystrov Yu A, Kolgin E A and Kotletsov B N 1988 *Technological control of dimensions in microelectronic production* (Moscow: Radio i sviaz)
- [8] Lisenkov A A and Vetrov N Z 2000 *Vacuum arc plasma sources* (Saint Petersburg: Energoatomizdat)
- [9] Martsinukov S A, Kostrin D K, Chernigovskiy V V and Lisenkov A A 2016 *J. Phys.: Conf. Ser.* **735** 012049
- [10] Kostrin D K, Uhov A A and Lisenkov A A 2016 *Vakuum in Forschung und Praxis* **3** 34–7
- [11] Kostrin D K, Lisenkov A A and Uhov A A 2016 *J. Phys.: Conf. Ser.* **735** 012055
- [12] Ivanov S A, Komiak N I and Pavluk E G 1979 *X-ray methods of substances crystal structure research* (Leningrad: Leningrad Electrotechnical institute)