Research of the influence of bias voltage on structure and residual stresses in W-coatings deposited on a copper substrate by inverted magnetron

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Abstract. The paper presents the results of a study of the effect of bias voltage on a substrate made of a copper tube on the structure and residual stresses of W-coatings deposited by an inverted magnetron. It is shown that the critical process temperature at which residual compressive stresses of \(-1000\) MPa (which lead to the beginning of the coating delamination process) are formed corresponds to \(-200^\circ\)C and a substrate voltage of \(-100\) V. At a bias voltage below \(-100\) V, the coatings have a columnar structure.

1. Introduction

Thin films and tungsten coatings are of considerable interest for applications in various areas: microelectronics [1] (including spintronics [2, 3]), thermal photovoltaic converters in the power industry, high-temperature nanophotonics [4], etc. Another possible area of application W coatings are thermal barrier coatings for parts of future thermonuclear reactors, such as ITER [5, 6], which will be subjected to extreme thermal loads and ion bombardment, as well as to other thermally loaded products, such as combustion measures of rocket engines. The key problems for such coatings are thermomechanical stability with respect to delamination, oxide formation and diffusion at high operating temperatures and achieving long-term high-temperature grain stability [4].

In this article, we explore the refractory coatings W in the aspect of their suitability for high-temperature layered composite systems. For deposition of W, pulsed laser deposition, atomic layer deposition and sputtering of dc planar magnetrons are usually used. In [7, 8], we showed that to create thin-walled small-sized axisymmetric shell structures made of laminated composites, for example, tubular products with different surface profiles, the system of consecutively inverted magnetrons and one conventional cylindrical magnetron used to clean substrates is very effective. The system allows the formation of layered composite shells by spraying various layers onto a mandrel (for example, from copper), which is subsequently etched. In this paper, we study the process of applying W coatings on Cu substrates using inverted magnetrons, the difficulties of which are manifested already in the course of deposition.

It is known that the deposition of W coatings on Cu substrates [5], which have a significantly higher thermal expansion coefficient (TEC), lead to huge residual stresses, reaching \(-5\) GPa. The magnitude of these stresses in addition to the difference in the values of the thermal expansion coefficient and the Young modulus depend on the temperature of the coating process, which is determined by the energy parameters of the deposition process, primarily the magnitude of the bias
voltage. In this regard, in this paper, we investigated the effect of bias voltage on the residual stresses, as well as on the morphology, texture, and distortions of the crystal lattice of the coatings.

2. Materials and methods
The deposition was carried out on a specialized installation MRM-1, described in [7]. Argon with a purity not lower than 99.9% was used as a working gas. Cathode material – W purity \( \approx 99.9\% \), inner diameter and length cathode were of 37 mm and 24 mm. A copper tube M-1 with a diameter of 10 mm and length 20 mm was used as the substrate. Before spraying the tube was polished and degreased. The substrate was placed on the rod of vertical movement of samples in the chamber; the substrate undergoes reciprocating movements along the cathode axis and periodically completely leaves the cathode area, alternately completely going beyond its ends. Then, the vacuum chamber was evacuated to a residual pressure of \( 10^{-3} \) Pa. Before spraying, a glow discharge plasma was cleaned for 30 minutes at an argon pressure of 5 Pa and a voltage of 1100 V. The substrate was then sprayed with tungsten at different bias voltages on the substrate according to the modes presented in table 1.

### Table 1. Modes of tungsten deposition on a copper substrate.

| No. | \(-U_b\) V | \(I_{\text{cathode}}\) A | \(\tau_{\text{deposition}}\) h | \(t_{\text{deposition}}\) °C | \(P_{\text{Ar}}\) Pa |
|-----|------------|------------------|-----------------|----------------|-------------|
| 1   | 0          | 1                | 3               | 470            | 0,2         |
| 2   | 50         | 1                | 3               | 461            | 0,2         |
| 3   | 100        | 1                | 3               | 430            | 0,2         |
| 4   | 150        | 1                | 3               | 460            | 0,2         |
| 5   | 200        | 1                | 3               | 500            | 0,2         |
| 6   | 250        | 1                | 3               | 560            | 0,2         |
| 7   | 300        | 1                | 3               | 580            | 0,2         |

3. Results and discussion
The magnitudes of the residual stresses were estimated by an X-ray “\( \sin^2\psi \)” method on a DRON-4 diffractometer in filtered CuK\(_\alpha\) radiation. In the “\( \sin^2\psi \)” method, the position of the reflex (321) was measured at angles \( 2\theta \approx 131^\circ \), while the X-ray was taken at the symmetric position of the sample (\( \psi = 0^\circ \)) and asymmetrical (\( \psi = 10^\circ \) and \( 40^\circ \)). The position of the line was measured, the lattice parameters were calculated, and the dependences of \( \sin^2\psi \) on \( \sin^2\psi \) were obtained. The least squares method was used to determine the slope of the straight line, \( \tan\alpha \), and calculate the residual stress value using the relation:

\[
\sigma_\psi = \tan\alpha \left[ \frac{E}{1+\nu}\right]_{hkl} / a_0
\]

Since W is an elastically isotropic metal, for it the value \( [(1+\nu)/E]_{hkl} \) is the same for any (hkl) and we used the values \( E = 390 \) GPa and \( \nu = 0.3 \) [9].

Inverse pole figures (IPF) were obtained by taking radiographs in the angle range \( 20 = 30–140^\circ \). The pole density of 6 independent reflections hkl on the stereographic triangle: 001, 011, 013, 111, 112, 123, (figure 1(a)) was determined from the relation:

\[
P_{hkl} = \frac{n \sum_{i=1} (I_{hkl}^{\text{textured}} / I_{hkl}^{\text{reference}})}{n} \]

where \( I_{hkl}^{\text{textured}} \), \( I_{hkl}^{\text{reference}} \) are the integral intensities of the hkl reflections for the textured and non-textured (reference) sample, respectively; \( n \) is the number of independent hkl reflections (\( n = 6 \)).

Figure 1 shows the IPF for W-coatings deposited on a copper substrate at values of bias voltage on the substrate from 0 to –300 V. It can be seen that with an increase in voltage on the substrate, regular changes in the texture of the coating occur, which are non-monotonous. In the voltage range from 0 to
-150 V, the texture of the coating is pronounced and is described by the arrangement of octahedral (111) planes parallel to the substrate (figure 1(b)–(e)). An anomalous character showed a coating deposited on a substrate at -100 V (figure 1(d)), which is characterized by a lower texture intensity (111) compared to coatings applied at lower voltages (figure 1(b), (c)) and at higher voltage (figure 1(e)).

An increase in the voltage on the substrate to -200 V leads to a change in the intensity and type of texture (figure 1(e)), the main component becomes (112), while the pole density of this orientation is almost twice lower than the octahedral texture that coatings have at lower voltages substrate. A further increase in voltage somewhat increases the intensity of the octahedral texture (figure 1(c)), however, it remains significantly weaker than in coatings applied at lower voltages. In figure 2, these results are summarized as the dependence of the pole density (111) on the bias voltage. In figure 3 shows the dependence on the voltage of the half-widths of the diffraction lines (222) and (321). It is seen that with increasing voltage on the substrate, the width of the diffraction lines sharply increases, which is determined by the distortions of the crystal lattice and the grinding of the sub grain structure in the range of 10-100 nm. In figure 4 shows the structure of the surface layer of the coatings.

Figure 1. The standard stereographic triangle of a cubic lattice (a) and IPF for W coatings on a copper substrate, deposited at different values of the bias voltage: \(U_b = 0\) V (b); \(U_b = -50\) V (c); \(U_b = -100\) V (d); \(U_b = -150\) V (e); \(U_b = -200\) V (f); \(U_b = -250\) V (g); \(U_b = -300\) V (h).
Figure 2. The dependence of the pole density for the orientation (111) ($P_{(111)}$) on the bias voltage ($U_b$).

Figure 3. Dependence of half widths of diffraction lines (321) and (222) on the bias voltage ($U_b$).

Figure 4. The structure of the W coatings on the copper substrate applied at different bias voltages:
$U_b = 0\, \text{V}$ (a); $U_b = -100\, \text{V}$ (b); $U_b = -150\, \text{V}$ (c); $U_b = -300\, \text{V}$ (d)

When the bias voltage is below $-100\, \text{V}$, the coatings are columnar. The images indicate the grinding of the microstructure with increasing voltage on the substrate; however, this grinding occurs at the micron level, i.e. in the range of the size of the structure to which the width of the diffraction line is
not sensitive, therefore the more likely cause of line broadening is an increase in the distortion of the tungsten lattice, i.e. increase in dislocation density.

This is also evidenced by a significant amount of residual stresses, which reaches $-2$ GPa at the maximum value of the voltage on the substrate (Figure 5). The reason for this is the increase in the energy of the particles that bombard the growing film as the bias voltage increases on the substrate.

![Figure 5](image_url)

Figure 5. The dependence of the magnitude of the residual voltage from the voltage on the substrate.

For voltages above $-200$ V, peeling of coatings from the substrate occurs, which is caused by high compressive stresses that are excessive for brittle tungsten, despite the fact that ion-plasma nitride and carbonitride coatings withstand compressive residual stresses up to 3–4 GPa. The nature of these stresses is thermal and is due to the difference in the thermal expansion coefficient of tungsten and copper. The magnitude of thermal stresses can be estimated from a simple relationship:

$$\sigma_t = E \Delta T (\alpha_{\text{tungsten}} - \alpha_{\text{copper}})$$

We estimate the voltage for the temperature difference of 100 degrees.

$$\sigma_t = 390 \cdot 100 \cdot (5.5 - 17.2) \cdot 10^{-6} \text{ MPa} = 450 \text{ MPa}$$

4. Conclusion

Based on this estimate, the maximum value of residual stresses ($-2000$ MPa) corresponds to a process temperature above 400 °C, which is close to the actual process temperature. The critical process temperature at which residual compressive stresses of $-1000$ MPa are formed corresponds to $-200$ °C and this temperature is realized at a bias voltage of $-100$ V.

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