Study of the texture and residual stresses in multilayer Nb/Mo coatings obtained by inverted magnetrons

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Abstract. This work is devoted to the study of the formation of the structure, crystallographic texture and residual stresses in multilayer Nb/Mo coatings deposited by inverted magnetrons on a tubular substrate made of a chromium-nickel alloy. Microprobe analysis of the obtained samples did not show the presence of Nb–Mo solid solutions resulting from mutual diffusion, which is most likely caused by low heating of the coating material during deposition. The results of the studies show that in the outer layers of the multilayer coating, residual stresses are characterized by relatively low values. It is likely that the alternation of layers of refractory metals that differ in thermal linear expansion coefficient values leads to mutual compensation of thermal stresses. Thus, the value of the residual stresses of a multilayer coating of any thickness is comparable to a two-layer coating. The texture effect in a multilayer coating is insignificant compared to the effect of solid solution formation, so high-temperature annealing will help to equalize the elastic characteristics and, accordingly, the stress state in the coating.

1. Introduction

Multilayer composite coatings attract more and more attention because of their high service characteristics, such as high hardness, adhesive strength and viscosity, wear resistance, and relatively low residual stress levels [1, 2]. At the same time, magnetron sputtering methods are widely used for their production [3–5]. High quality of these coatings is explained by the deviation of the crack trajectory at the interface of heterogeneous materials with different elastic and strength characteristics, as well as the ability to create favorable gradients of residual stresses, which usually increase with increasing thickness in monolayer coatings. Such capabilities of multilayer coatings make it possible to create layered composite structures of considerable thickness, for example, thin-walled small-sized shells [6, 7]. At the same time, an important role in the formation of the service properties of multilayer coatings is played by the ratio between thermal linear expansion coefficient (TLEC), the values of elastic modules and the crystallographic orientation of each of the layers between themselves and in relation to the substrate. In this paper, we investigated the formation of the structure, crystallographic texture, and residual stresses in multilayer (n = 120) Nb/Mo coatings deposited by inverted magnetrons on a tubular substrate made of chromium-nickel alloy, which was subsequently etched, leaving the composite product clean. The installation and process of applying the layer are presented in [6, 7].
2. Materials and methods of research

Before deposition, the chromium-nickel alloy substrate (a tube with a diameter of 10 mm, a length of 40 mm with a wall thickness of 1 mm) was polished with sandpaper of various degrees of grain to N4 class of surface roughness and wiped with alcohol. Then the substrate was mounted on the rod of the sample transfer mechanism in the chamber moving from the working zone of one magnetron (Nb) to another (Mo) and back, which ensured the formation of a layered structure in this way. The installation chamber was pumped out to a residual pressure of 2\times10^{-4} Pa, then Ar was injected to a pressure of 2\times10^{-2} Pa and the substrate was cleaned in a glow discharge for 30 minutes. The sample formation mode consisted of 120 stages and lasted 40 hours (60 stages of spraying alternately Nb and Mo). The deposition mode is indicated in the table 1. After deposition, the substrate of the obtained sample was etched in a mixture of copper sulfate and NaCl.

Table 1. Parameters of the magnetron sputtering stage.

| Parameter                  | Layer material |
|----------------------------|----------------|
|                            | Nb             | Mo             |
| Voltage on the substrate, V| 200            | 60             |
| Current on the substrate, A| 1              | 1              |
| Substrate temperature, °C  | 550            | –              |
| Voltage on the cathode, V  | 380–260        | 370–250        |
| Current on the cathode, A  | 2              | 2              |
| Argon pressure, Pa         | 0.3            | 0.3            |
| Process duration, min      | 30             | 10             |

Electron microscopic studies were performed using a scanning electron microscope JSM-6610 LV with an Advanced AZtec energy dispersive analyzer. Microstructure studies were performed at magnifications up to ×3000 (possibly up to 100 000 times). Microstructure analysis data are quantitative in the study of thin sections. The analyzer used allows receiving signals only of elements with an atomic number greater than 4. The error for carbon and other light elements is not less than 10 %. The content of elements in the analyzed sample less than 0.1 % was not determined. The results of quantitative analysis are reliable when their size is more than 3 μm. The results of the quantitative analysis of phases for light elements are reliable when the sizes of these phases are more than 5 μm.

The image in the scanning microscope was obtained in secondary electrons, which exhibit mainly the contrast of the relief formed on the surface of the sample, and in reflected electrons, which exhibit mainly the contrast of the atomic number value.

X-ray phase analysis, determination of texture and residual macrostresses were performed on a DRON-4 X-ray diffractometer in filtered CuKα radiation with wavelengths λKα = 1.54178 Å. Inverse pole figures (IPF) were obtained by taking radiographs in the angle range 2θ = 30…150°. The pole density of 6 independent hkl reflexes on a stereographic triangle: 001, 011, 013, 111, 112, 123, were determined from the ratio:

$$P_{hkl} = \frac{n \left( I_{hkl}^{\text{tex}} / I_{hkl}^{\text{ref}} \right)}{\sum \left( I_{hkl}^{\text{tex}} / I_{hkl}^{\text{ref}} \right)},$$  \hspace{1cm} (1)

where $I_{hkl}^{\text{tex}} / I_{hkl}^{\text{ref}}$ – integral intensities of hkl reflexes for a textured and non-textured (reference) sample, respectively; $n$ – number of independent hkl reflexes ($n = 6$).

For metals with a cubic lattice, the value of the elastic modulus is determined by the following relation:

$$1 / E_{s} = S_{11} - 2J \cdot \Gamma,$$  \hspace{1cm} (2)
where $J = S_{11} - S_{12} - 0.5S_{44}$ – anisotropy parameter ($J > 0$ – positive anisotropy, $J < 0$ – negative anisotropy); $\Gamma = \left( h^2k^2 + h^2l^2 + k^2l^2 \right) / \left( h^2 + k^2 + l^2 \right)$ – orientation factor; $S_{11}, S_{12}, S_{44}$ – single-crystal compliance constants.

Table 2 shows the values of the Young’s modulus calculated from (2) for Nb and Mo, and the values of the Young’s modulus averaged in these directions, which correspond to the non-textured material. The value of the Young’s modulus for any direction ($X$) of the textured material is found by summing the products of the normalized pole densities ($P_{hkl}^X$) on the Young’s modulus for a given crystallographic orientation $i = hkl$ of a particular metal ($E_{hkl}^{Nb(Mo)}$ from table 2):

$$E_X = \frac{1}{n} \sum_{hkl} \left( P_{hkl}^X \times E_{hkl}^{Nb(Mo)} \right).$$

The values of residual stresses were evaluated by the X-ray method “$\sin^2 \psi$”. In the method “$\sin^2 \psi$” we measured the position of the reflex (321) at the angles $2\theta \approx 122^\circ$ and $2\theta \approx 132^\circ$, respectively, for Nb and Mo with the symmetric position of the sample ($\psi = 0^\circ$) and asymmetrical position ($\psi = -20^\circ$ and $-40^\circ$). From these data, the lattice parameters were calculated and the dependences $a_0$ on $\sin^2 \psi$ were obtained. The slope of the straight line $\tan \alpha$ was determined by the method of least squares, and the value of the residual stress was calculated from the ratio:

$$\sigma = \tan \alpha \left[ E / (1 + \nu) \right]_{hkl} / a_0,$$

where $\nu$ – Poisson’s ratio.

Values of the X-ray elastic constant for the reflex (321) [$E / (1 + \nu)$]$_{321}$ for Nb and Mo are given in table 2. The value of the lattice parameter ($a_0$) adjusted for the value of residual stresses was determined from the ratio:

$$a_0 = a_{0-0} / \left[ 1 + (\sigma_1 + \sigma_2) (\nu / E)_{hkl} \right].$$

Values $(\nu / E)_{hkl} = -S_{11} - G(S_{11} - S_{12} - 0.5S_{44})$ calculated for the reflex (321) for Nb and Mo are given in table 2.

| $hkl$ | $E_{hkl}^{Nb(Mo)}$, GPa | $a_0$ | $a_{0-0}$ | $[1 + (\sigma_1 + \sigma_2) (\nu / E)_{hkl}]$ |
|------|-----------------|------|---------|----------------------------------|
| 110  | 92              | 105  | 0.445   | 0.102                            |
| 200  | 152             | 316  | 1.528   | 0.431                            |

3. Experimental results and their discussion
Figure 1 shows the cross-section of the coating in the secondary electrons. The thickness of the multilayer coating is 796 μm, the layered nature of the coating is clearly visible.
Figure 1. Structure of the cross-section of the coating, image in secondary electrons.

Figure 2a shows an enlarged image of the first seven layers, where the points of the microprobe analysis are marked, some of the results of which are shown in figures 2b, c, figure 2d shows the results of layer-by-layer element scanning.

Figure 2. Results of electron probe microanalysis: (a) – spectral survey areas; (b)–(c) – spectra of part of the layers; (d) – distribution of elements in layer-by-layer scanning.

Figure 3 shows a diffractogram obtained from a coated sample with intense Nb reflexes and significantly weaker Mo reflexes. This indicates that the surface layer was Nb, which shielded reflections from the subsurface Mo layer. Microprobe analysis does not provide information about the formation of solid solutions Nb–Mo as a result of mutual diffusion, which could be caused by
heating of the coating material during deposition. In [8], the formation of solid solutions based on Nb and Mo was detected by change in the periods of the solid solution as a result of heating up to 1200 °C during silicification. In this work, when applying coatings, the heating was much weaker – not higher than 550 °C.

The presence of two components in the spectrum in figure 2c is not the proof of solid solution formation, since it could very likely be a consequence of the formation of a mixture of elements at the layer boundary, so only a change in the lattice periods can serve as proof of solid solution formation.

The lattice period of a solid solution depends not only on its composition, but also on the presence of residual stresses. The values of residual stresses calculated from equation (4) are given in table 3, and the values of the lattice periods for Nb and Mo calculated from (5) and adjusted for the value of residual stresses \( \sigma_{\text{res}} \), are given in the same table.

Table 3. Values of residual stresses and lattice periods adjusted for their value for Nb and Mo layers.

|          | \( \sigma_{\text{res}}, \text{MPa} \) | \( a_0 \times 10^\text{nm} \) | Composition of the solid solution |
|----------|--------------------------------------|------------------------------|---------------------------------|
| Nb       | –213                                 | 3.289                        | Nb\(_{0.95}\)Mo\(_{0.05}\)      |
| Mo       | –576                                 | 3.141                        | Mo                              |

The results shown in table 3 demonstrate that in the outer layers of a multilayer coating with a thickness of \( \sim 800 \mu\text{m} \), residual stresses are characterized by relatively low values. The surface Nb layer has compressive stresses of –213 MPa, and in the subsurface Mo layer their value is –576 MPa. It is likely that the alternation of layers of refractory metals differing in TLEC values (\( \alpha_{\text{Nb}} = 5.3 \times 10^{-6} \text{ K}^{-1} \), \( \alpha_{\text{Mo}} = 7.1 \times 10^{-6} \text{ K}^{-1} \)) leads to mutual compensation of thermal stresses. Thus, the first Nb layer deposited on a chromium-nickel substrate experiences compressive stresses (\( \alpha_{\text{Ni-Cr}} = 13 \times 10^{-6} \text{ K}^{-1} \)). The second Mo layer with a lower TLEC value than for the Nb sublayer also experiences compressive stresses, i.e. the total level of compressive stresses increases, but the next Nb layer with a higher TLEC value than for the Mo sublayer already produces tensile stresses. Thus, the value of the residual stresses of a multilayer coating of any thickness is comparable to a two-layer coating. This mechanism demonstrates the measured residual stresses in the outer layers. Compressive stresses in the Mo sublayer (–576 MPa) deposited on the Nb layer with a large TLEC value are largely compensated by tensile stresses in the outer Nb layer and as a result are reduced to –213 MPa. The lattice periods \( a_0 \) adjusted for residual stresses indicate that as a result of technological heating up to 400–500 °C, the

Figure 3. Diffractogram from the coated sample (surface layer – Nb).

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process of mutual diffusion develops insignificantly, ~5 at. % Mo is dissolved in Nb, and Nb is not dissolved in Mo at all.

To estimate the difference in Young’s modulus between layers, it is necessary to take into account the texture effect. Table 4 shows the values of the pole densities for Nb and Mo and the values of Young’s modules for different directions calculated from the ratio:

$$E_{Nb(Mo)}^{N} = \frac{1}{n} \sum_{i=1}^{n} \left( P_{i}^{Nb(Mo)} \times E_{i}^{Nb(Mo)} \right);$$

$$E_{i}^{Nb(Mo),Mo} = 0.05E_{i}^{Mo} + 0.95E_{i}^{Nb}.$$ (6)

Table 4 shows the results of calculations of Young’s modules in the tetragonal direction for solid solutions Nb$_{0.95}$Mo$_{0.05}$ and Mo based on their textures, which is different for these phases and the composition in accordance with the equation (6). The difference of the average values of Young’s modules for non-textured Nb and Mo is 210 GPa, and with the formation of the solid solution Nb$_{0.95}$Mo$_{0.05}$ its value is 200 GPa, and taking into account the texture is 208 GPa, i.e., almost indistinguishable from the values of this difference for non-textured state (210 GPa). This indicates that the texture effect is insignificant compared to the effect of solid solution formation, so high-temperature annealing will help to equalize the elastic characteristics and, accordingly, the stress state in the coating. In the same direction will act the operational heating.

Table 4. Results of calculations of elastic characteristics of Nb and Mo and solid solutions based on them.

| hkl | $E_{hlkl}^{Nb(Mo)}$, GPa | $P_{hlkl}^{Nb(Mo)}$ | $E_{hlkl}^{Nb(Mo)} \times P_{hlkl}^{Nb(Mo)}$, GPa |
|-----|-----------------|-----------------|---------------------------------|
| Nb  | Mo  | Nb$_{0.95}$Mo$_{0.05}$ | Mo  | Nb  | Mo  | Nb  | Mo  |
| 110 | 92  | 304 | 103 | 304 | 0.70 | 0.50 | 64  | 152 |
| 200 | 152 | 357 | 162 | 357 | 0.40 | 0.40 | 61  | 143 |
| 211 | 92  | 304 | 103 | 304 | 1.10 | 0.60 | 101 | 182 |
| 310 | 123 | 336 | 134 | 336 | 0.70 | 0.40 | 86  | 134 |
| 222 | 82  | 290 | 92  | 290 | 2.10 | 2.50 | 172 | 725 |
| 321 | 92  | 304 | 103 | 304 | 1.00 | 1.80 | 92  | 547 |
| $E_{hlkl}^{Nb(Mo)}$ | 106 | 316 | 116 | 316 | 96  | 304 |

4. Conclusions

1. The formation of a multilayer ($n = 120$) composite Nb/Mo tubular shell with a wall thickness of ~0.8 mm was carried out by spraying with inverted magnetrons.

2. Residual stresses of ~576 MPa in the subsurface Mo layer and ~213 MPa in the surface Nb layer are formed in the layered product.

3. Relatively low values of residual stresses for such shell thicknesses are probably associated with mutual compensation of thermal stresses in multilayer coatings, when compressive stresses arising when applying an Nb layer to a Mo sublayer with a smaller TLEC are compensated by tensile stresses when applying the next Mo layer to an Nb sublayer with a larger TLEC value. As a result, the level of residual stresses at any number of layers is comparable to a two-layer coating.

4. It is shown that as a result of technological heating up to 400–500 °C, the process of mutual diffusion develops insignificantly, ~5 at. % Mo is dissolved in Nb, and Nb is not dissolved in Mo at all.

5. The formation of a solid solution Nb$_{0.95}$Mo$_{0.05}$ leads to a convergence of the values of the Young’s modulus at the interface of layers by 10 GPa, and the texture effect is an order of magnitude
smaller, which indicates a greater efficiency of stimulating diffusion processes compared to controlling the texture of layers.

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