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Diffraction and absorption of X-rays in a thin-layer system $Ni_{(1-x)}W_x$/TiN

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The foundations of methodology for studying two-layer objects like "substrate-coating" through combination of methods of absorption and diffraction spectroscopy in a single experiment are developed. It is shown that X-ray diffraction and absorption spectra for $Ni_{(1-x)}W_x$/TiN systems based on ferromagnetic $Ni_{0.95}W_{0.05}$ and paramagnetic $Ni_{0.905}W_{0.095}$ alloys are qualitatively different. In the $Ni_{0.95}W_{0.05}$/TiN system, the substrate $Ni_{0.95}W_{0.05}$ has a cubic texture, the degree of perfection of which does not depend on the thickness of the TiN coating. In the $Ni_{0.905}W_{0.095}$/TiN system, an abnormal X-ray optical effect was discovered — an increase in the intensity of the diffraction lines of the substrate $Ni_{0.905}W_{0.095}$ with growing the TiN coating thickness. The nature and mechanism of the detected effect are established.

Keywords: abnormal X-ray optical effect, "substrate-coating" system, Ni–W alloys, titanium nitride, stacking faults.

Развиты основы методологии исследования двухслойных объектов типа "подложка-покрытие" путем сочетания в едином эксперименте методов абсорбционной и дифракционной спектроскопии. Показано, что спектры дифракции и абсорбции рентгеновского излучения для систем $Ni_{0.95}W_{0.05}$/TiN на базе ферромагнитного $Ni_{0.95}W_{0.05}$ и парамагнитного $Ni_{0.905}W_{0.095}$ сплавов носят качественно отличный характер: в системе $Ni_{0.95}W_{0.05}$/TiN подложка обладает кубической текстурой, степень совершенства которой не зависит от толщины покрытия TiN; в системе $Ni_{0.905}W_{0.095}$/TiN обнаружен *аномальный рентгенооптический эффект* — усиление интенсивности дифракционных линий подложки при увеличении толщины покрытия. Установлена природа и механизм обнаруженного эффекта.

Процеси поглинання та розсіювання рентгенівського випромінювання у тонкошаровій системі $Ni_{(1-x)}W_x$/TiN. *В.О.Фінкель, Т.В.Сухарева, М.С.Сунгуров.*

Розвинуто основи методології дослідження двошарових об'єктів типу іпідкладка-покриттяі шляхом поєднання в єдиному експерименті методів абсорбційної та дифракційної спектроскопії. Показано, що спектри дифракції та абсорбції рентгенівського випромінювання для систем $Ni_{0.95}W_{0.05}$/TiN на базі феромагнітного $Ni_{0.95}W_{0.05}$ і парамагнітного $Ni_{0.905}W_{0.095}$ сплавів мають якісно інакший характер: у системі $Ni_{0.95}W_{0.05}$/TiN підкладка має кубічну текстуру, ступінь досконалості якої не залежить від товщини шару покриття TiN; у системі $Ni_{0.905}W_{0.095}$/TiN знайдено аномальний рентгенооптичний ефект і посилення інтенсивності дифракційних ліній від підкладки при збільшенні товщини покриття. Встановлено природу та механізм виявленого ефекту.

1. Introduction

As is known, the subject of X-ray optics is the study of the processes of propagation of X-ray radiation in various media and its interaction with matter. The main interaction channels are the absorption and scattering of X-ray quanta, as well as the emergence of secondary X-ray radiation (fluorescence).

The intensity of an X-ray beam passing through a layer of matter of thickness h is described by the exponential Lambert-Beer equation

$$I_h = I_0 \cdot e^{-\mu h}, \qquad (1)$$

where I_h is the intensity of a beam passing through a layer of matter with effective thickness h; I_0 is the incident beam intensity; μ is the linear absorption coefficient. Coherent scattering occurs when the diffraction conditions described by the system of three Laue equations for single crystals or the Bragg's equation for polycrystalline materials are satisfied. X-ray fluorescence occurs when the wavelength of the incident radiation is less than the wavelength for the edge of the absorption band of the irradiated material.

It should be assumed that the combination of diffraction and absorption spectroscopy methods in a single experiment opens up broad prospects for studying the structure of two-layer objects of the type "massive substrate — thin-layer coating". In this regard, the purpose of this work is to develop a strategy for studying the crystal structure and morphology (the term "morphology" characterizes the dimensions and relative orientation of the components of a two-layer system) of two-layer compositions through the investigation of $Ni_{(1-x)}W_x$/TiN systems.

The paper deals with an experimental study of two fundamentally different systems of $Ni_{(1-x)}W_x$/TiN:

— $Ni_{0.95}W_{0.05}$/TiN system based on the ferromagnetic $Ni_{0.95}W_{0.05}$ alloy [1, 2] with high stacking fault energy E_{sf} [3] and sharp cubic texture <100>(001) [4] (further: system F).

— $Ni_{0.905}W_{0.095}$/TiN system based on the paramagnetic $_{0.905}W_{0.095}$ alloy [1,], with low E_{sf} [5] and rather weak cubic texture [6] (system P).

The choice of the systems for the research is determined by the following circumstances:

– The presence of heavy elements (Ni, W) in one of the components of the two-layer system provides a high intensity of X-ray diffraction.

– The presence of light elements (Ti, N) in another component of the system makes it sufficiently transparent for X-rays.

– The presence of cubic symmetry in the TiN coating excludes the possibility of anisotropy of the absorption coefficient [7, 8].

– The wavelength corresponding to the absorption edge of Ni is less than the wavelength of both components of the CuKα-radiation used in this work (λ^*_{Ni} = 1.488 Å, $\lambda_{CuK\alpha 1}$ = 1.5405 Å, $\lambda_{CuK\alpha 2}$ = 1.5444 Å). This ensures the absence of secondary fluorescence radiation in the X-ray region of the spectrum.

2. Experimental

This section deals with two issues: obtaining the research objects and considering the features of X-ray studies of two-layer systems.

Creation of the objects under study, namely, $Ni_{(1-x)}W_x$/TiN compositions, includes three stages: the synthesis of $Ni_{(1-x)}W_x$ alloys by powder metallurgy methods in high vacuum [2], the preparation of a metallic ribbons (it should be noted that the macroscopic density of the ribbons of $Ni_{(1-x)}W_x$ alloys corresponds to the x-ray density within the measurement error) of $Ni_{(1-x)}W_x$ alloys up to 100 cm long, about 10 mm wide, and up to 100 μm thick by cold rolling and subsequent high-temperature (1000–1200°C) annealing [9, 10, 12, 13] in a reducing medium Ar + 4 % H_2 [9, 11], deposition of a thin coating (up to ≈ 6 μm thick) based on titanium nitride with a NaCl type structure [12, 13].

To deposit a TiN layer on the surface of ribbons made of $Ni_{(1-x)}W_x$ alloys, we used the method of ion-plasma sputtering of titanium in an atmosphere of rarefied nitrogen [14]. The parameters of the deposition processes varied in a wide range : pressure of N_2 ($1.2 \cdot 10^{-2} \le p_{N2} \le 6.2 \cdot 10^{-2}$ Torr) and deposition time ($0 \le \tau_{TiN} \le 15$ min) (the arc current (I_{arc} = 80 A) and the bias potential on the substrate (U_{bias} = – 300 V) were fixed). Each TiN deposition session involved samples of both compositions. A layer of titanium nitride was deposited on the "shadow" side of the substrates, i.e. the side located outside the direct line of sight of the cathode spot. The choice of this geometry of the experiment is characterized by the following advantages: a decrease in the coating deposition rate and the absence of macroscopic defects (in particular, a metal drop phase) [15].

Study of the architecture of two-layer $Ni_{(1-x)}W_x$/TiN systems.

The idea of a joint study of the absorption and diffraction of X-ray quanta is based on the possibility of simultaneously recording a diffraction pattern from both components of a two-layer substrate-coating composition and the degree of absorption of

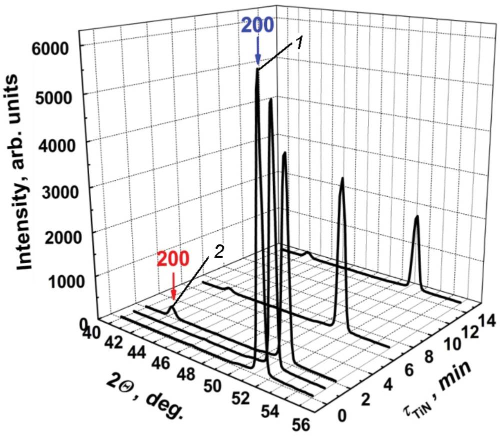

Fig. 1. X-ray diffraction $\theta - 2\theta$ scans for $Ni_{0.95}W_{0.05}$/TiN samples prepared at different coating deposition times. Diffraction indices of the $Ni_{0.95}W_{0.05}$ subsystem are marked in the blue(1), indices of TiN indicated in the red(2).

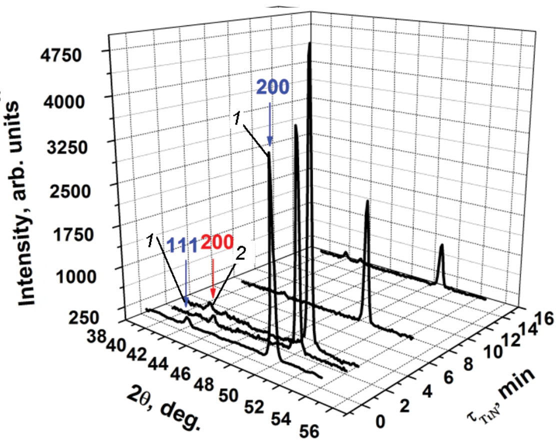

Fig. 2. X-ray diffraction $\theta - 2\theta$ scans for $Ni_{0.905}W_{0.095}$/TiN samples prepared at different coating deposition times. Diffraction indices of the $Ni_{0.905}W_{0.095}$ subsystem are marked in the blue(1), indices of TiN indicated in the red (2).

monochromatic X-ray radiation transmitted through the outer layer of the system (coating) in the experiment. The X-ray studies were performed on a DRONE UM-1 diffractometer with Bragg-Brentano focusing ($\theta - 2\theta$ scan mode) in filtered CuKα radiation. The following slit systems were used in the experiments: 1) S1 = 6 mm, S2 = 1 mm, S3 = 0.1 mm; and 2) S1 = 6 mm, S2 = 0.5 mm, S3 = 0.05 mm. The first set of the slits is focused on measuring the intensities of diffraction lines in the range of $40 < 2\theta < 60$ deg; the second is used to determine the lattice parameters in the angle range of $118 < 2\theta < 125$ deg.

The lattice parameters of the $Ni_{(1-x)}W_x$ substrates were determined from reflections (400) at $2\theta \approx 120$ deg. The diffraction lines (400) were approximated in the form of a convolution of two Gauss functions. The lattice parameters of the $Ni_{(1-x)}W_x$ substrates were determined from the positions of the maxima of the Gauss function for $CuK_{\alpha1}$ and $CuK_{\alpha2}$ radiation and coincided with an accuracy of $1 \cdot 10^{-4}$ Å.

To determine the thickness of the coating, we used a method based on measuring the intensity of X-ray diffraction from the planes of the crystal lattice of the substrate when the beam passes through a coating layer of thickness h [16]. The prerequisite for the effective implementation of this approach is the use of test objects in experiments. The test objects should possess a texture the degree of which does not substantially depend on the coating thickness (see below).

3. Results and discussiom

The strongest dependence of the intensities and positions of diffraction lines of the $Ni_{(1-x)}W_x$ substrates on the time of deposition of a TiN layer in the range of $0 \le \tau_{TiN} \le 15$ min was experimentally observed at a nitrogen pressure of $p_{N2} \approx 1.8 \cdot 10^{-2}$ Torr. In this regard, only a part of the results related to this pressure value is given below.

System $Ni_{0.95}W_{0.05}$/TiN

The results of $\theta - 2\theta$ scanning of two-layer $Ni_{0.95}W_{0.05}$/TiN samples (system F) are set out in the Fig. 1. As seen in the figure, there are no qualitative changes in the diffraction spectra of the system F. Only diffraction lines $(200)_{NiW}$[3] (at larger diffraction angles, second-order reflections (400) from substrates $Ni_{0.95}W_{0.05}$ and $Ni_{0.905}W_{0.095}$ are observed, see below). are observed, the intensity of which naturally decreases with increasing deposition time τ_{TiN}. At $\tau_{TiN} > 1$ min, $(200)_{TiN}$ reflections from the coating appear. The intensity of the diffraction peaks from TiN, the external component of the two-layer system which includes atoms with low scattering power, is significantly lower than that from the Ni–W substrate.

System $Ni_{0.905}W_{0.095}$/TiN

Fig. 2 shows the results of $\theta - 2\theta$ scanning of two-layer $Ni_{0.905}W_{0.095}$/TiN objects

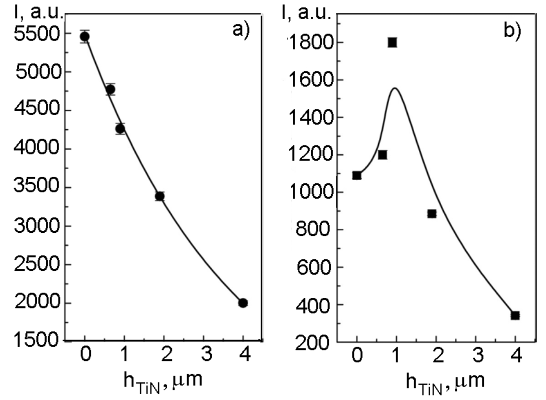

Fig. 3. Dependences of the intensities of $(200)_{NiW}$ diffraction line on the thickness of TiN coating: a) system F; b) system P.

(system P). As seen, the character of evolution of the diffraction pattern in the system P differs significantly from that observed for the system F:

– At $\tau_{TiN} = 0$, in addition to reflections from the cubic plane $(200)_{NiW}$, the diffraction pattern shows a weak reflection from the diagonal plane $(111)_{NiW}$, which indicates a relatively low level of the cubic texture of the substrate in the P system.

– At $\tau_{TiN} = 1$ min, the intensity $I_{(200)NiW}$ increases sharply, while $I_{(111)NiW}$ decreases markedly.

– At $\tau_{TiN} = 2$ min, the trend in increasing of $I_{(200)NiW}$ and decreasing of $I_{(111)NiW}$ continue. In addition, reflections from a cubic plane $(200)_{TiN}$ appear.

– At $\tau_{TiN} \geq 7$ min, the growth of $I_{(200)NiW}$ is followed by the decrease of $I_{(111)NiW}$ to the background level.

Thus, in the X-ray experiments on $\theta - 2\theta$ scanning of the samples under study, we obtained data related to the kinetics of changes in the morphology of the two-layer systems F and P.

To establish the nature and mechanisms of the evolution of the structure of the two-layer "substrate-coating" systems, one should consider the purely kinetic dependences of the intensities and positions of $Ni_{(1-x)}W_x$ diffraction lines on the time of deposition of the TiN coating in order to establish and analyze the dependences of the diffraction intensities I_{NiW} and crystal lattice parameters a_{NiW} on coating thickness h_{TiN}.

As noted above (see Section 3.1), the intensity of diffraction lines from the substrate $Ni_{0.95}W_{0.05}$ in the system F decreases monotonically with increasing TiN coating thickness. This allows using samples of the system $Ni_{0.95}W_{0.05}$/TiN as test objects for

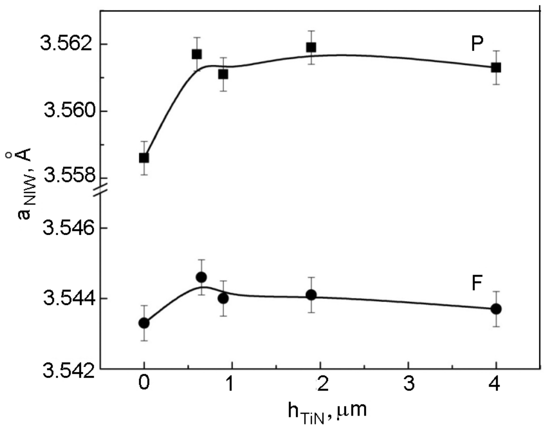

Fig. 4. Dependences of $Ni_{(1-x)}W_x$ lattice constants on the thickness of TiN coating layer for systems F and P.

measuring the coating thickness by the Lambert-Beer equation (1). To determine the thickness of the TiN coating deposited on the $Ni_{(1-x)}W_x$ substrate, equation (1) should be converted to:

$$h_{TiN}(\tau) = -\frac{\sin(2\theta_{NiW}/2)}{2\mu_{TiN}} \cdot \ln\left(\frac{I_h}{I_0}(\tau)\right), \qquad (2)$$

where h_{TiN} is the thickness of TiN layer, $2\theta_{NiW}$ is the diffraction angle for a crystal plane $(200)_{NiW}$, I_h is the intensity of the diffracted X-ray beam from the coated substrate, I_0 is the intensity of the diffracted beam from the substrate without coating, μ_{TiN} is the linear absorption coefficient of titanium nitride [16].

Fig. 3 shows dependences of diffraction lines $(200)_{NiW}$ on the thickness of TiN coating for the two-layer $Ni_{0.95}W_{0.05}$/TiN and $Ni_{0.905}W_{0.095}$/TiN systems. As can be seen, the dependences $I_{(200)NiW}(h_{TiN})$ for the systems F and P differ radically. For the model system F (see Fig. 3a), the dependence $I^F_{(200)NiW}(h_{TiN})$ is adequately described by the exponential equation (1). The correlation coefficient $R^2 = 0.99$ [17]. This means that the dynamics of the change in the character of the diffraction pattern in the F system completely results from the absorption processes of characteristic X-ray radiation in TiN coating layers of different thicknesses.

For the system P (see Fig. 3b), the dependence $I^P_{(200)NiW}(h_{TiN})$ consists of two branches. An abnormal X-ray optical effect is observed on the ascending branch ($0 \leq h_{TiN} \leq \approx 1$ μm); this consists in increasing the intensity of diffraction lines of a $(h00)_{NiW}$ type with increasing coating thickness. On the descending branch ($h_{TiN} > 1$ μm), the curve $I^P{}_{(200)NiW}(h_{TiN})$ acquires a character similar to the behavior of the dependence $I^P{}_{(200)NiW}(h_{TiN})$ for objects of system F in the entire range of coating thicknesses.

We believe that the anomalous behavior of the $I^P{}_{(200)NiW}(h_{TiN})$ dependence is caused by the processes associated with a change in the morphology of the system. First of all, it is talking about the reorientation of $Ni_{0.905}W_{0.095}$ crystallites in the laboratory coordinate system. The driving force of the process of reorient ing the crystalline grains of the substrate in the two-layer system $Ni_{0.905}W_{0.095}$/TiN can be stresses arising at the interface between materials with FCC and NaCl type structures, respectively, and different values of the crystal lattice parameters [18–20].

Fig. 4 shows the obtained lattice parameters a_{NiW} of the Ni–W substrate as a function of thickness of the TiN layer for systems F and P. As can be seen, the dependences $a_{NiW}(h_{TiN})$ for two-layer systems based on a substrate of a ferromagnetic alloy (F) and a substrate of paramagnetic alloy (P) are fundamentally different:

— in the F system, the change in the lattice parameter practically does not go beyond the possible measurement errors ($\Delta a \approx 2\cdot10^{-4}$ Å);

— in the P system, the noticeable increase in the lattice parameter is observed in the range of $0 \le h_{TiN} < \approx 1$ μm. In the range of $1 < h_{TiN} \le 4$ μm, the value a_{NiW} reaches saturation. It is symptomatic that the positions of extreme points in the dependences $a^P_{NiW}(h_{TiN})$ (see, Fig. 4) and $I^P_{(200)_{NiW}}(h_{TiN})$ (see, Fig. 3b) are close to each other.

4. Conclussions

The main outcomes of this work are:

– A methodology for studying the structure of two-layer systems has been developed on the example of the $Ni_{(1-x)}W_x$/TiN system. It is based on the study of the phenomena of diffraction scattering and absorption of X-rays in a single experiment.

– A strategy has been developed to optimize the composition of the researched objects and experimental conditions to study diffraction and absorption of X-rays in two-layer systems: the using test samples for determination of the thickness of the coating, the selection of radiation, the conversion of a "kinetic" parameter — the time of deposition of the coating — into a "structural" one — the thickness of the coating layer, etc.

– For the first time in the two-layer $Ni0_{.905}W_{0.095}$ /TiN system, an abnormal X-ray optical effect was discovered consisting in increasing the intensity of diffraction from the substrate with growing the coating thickness.

– It is established, that the abnormal X-ray optical effect is accompanied by the appearance of non-monotonous dependence of the crystal lattice parameter of substrate material on the thickness of the coating layer.

– The ideas about the nature and mechanisms of the abnormal X-ray optical effect in two-layer systems like "massive substrate — thin-layer coating" are developed.

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