The X-ray method of structure and phase composition characterization of nanocomposite coatings: Hard carbon-based coatings alloyed with metals

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Abstract. Theory and methodical peculiarities of studying the atomic structure of multiphase nanostructured coatings of arbitrary thickness deposited onto thick substrates with the method of X-ray powder diffractometry, and specific examples of phase composition and nanocomposite structure analyses of transition metal-alloyed hard carbon coatings deposited by reactive and non-reactive magnetron sputtering have been discussed.

1. Introduction
The development of modern technologies in microelectronics, machine manufacturing and instrument making has led to the development of various techniques of thin coatings and modified surface layers production based on the principles of physical and chemical vapor deposition. Traditional radiography of such coatings and layers requires their sufficient thickness or working only with “good” materials having high values of X-ray absorption coefficient otherwise. The solution of the problem sometimes is difficult for instance due to the peculiarities of the deposition technology or the significant level of technologically conditioned internal stresses existing in coatings. The latter factor greatly reduces the possibility of studying the structure of “free-standing” coatings separated from the substrates. In this connection it seems more natural to investigate coatings in their “as deposited” state together with the substrate. In this case the stresses existing in the coating may be equalized by the substrate. Such a technique was proposed for example in [1]. The authors of [1] have noted that the method might be useful for the analysis of amorphous coatings, coatings with short-range order or coatings with nanocomposite structure.

In this paper the method described in [1] that allows taking into account the substrate contribution to the total value of X-ray diffraction intensity of a “coating-on-substrate” composite has been modified to take into account the possibilities of the modern full-profile analysis methods. This made possible to analyze nanostructured multiphase coatings obtained by vacuum deposition under highly non-equilibrium conditions. To illustrate the possibilities of the method some examples of its application to the study of specific types of magnetron-sputtered nanocomposite hard carbon coatings alloyed with transition metals have been presented.
2. Theory

The experimental intensity of X-ray scattering by a semi-infinite flat sample can be written as [2]:

\[ I^{(\text{exp})} = I^{(0)} \cdot (e^2 / mc^2)^2 \cdot \frac{1 + \cos^2 2\theta \cdot \cos^2 2\theta_m \cdot A \cdot I \cdot \Delta V}{1 + \cos^2 2\theta_m}, \]

(1)

where \( I^{(0)} \) – the intensity of the primary X-ray beam; \((e^2 / mc^2)^2\) – the Thomson factor; \(\theta_m\) – the crystal monochromator angle of reflection; \(S^{(0)}\) – the primary beam cross section; \(A\) – the X-ray absorption factor; \(I\) – the intensity scattered by a unit of volume of the material taken in electronic units; \(\Delta V\) – the volume of the reciprocal space involved in X-ray scattering.

Since the explored material is composite and consists of a film of thickness \(t\) deposited on a semi-infinite substrate, the product \(A \cdot I\) contains contributions both from the film and the substrate. From the X-ray absorption factor theory [3] it follows that

\[ A \cdot I = \left( I / 2\mu_i \right) \left( 1 - \exp(-2\mu_i t / \sin \theta) \right) + \left( I / 2\mu_s \right) \exp(-2\mu_s t / \sin \theta), \]

(2)

where \(\mu_i\) and \(\mu_s\) are the linear coefficients of absorption and the intensities scattered by the units of volume of coating \((i = 1)\) and substrate \((i = 2)\) materials, respectively.

The procedure of the intensity reduction to electronic units [2, 4] requires a standard – a reference material whose atoms scatter X-rays independently at high \(\theta\) angles. For \(I_{st}\) – the intensity of scattering by the standard the expression similar to equation (1), which includes \(\mu_{st}\) – the standard’s coefficient of absorption and \(I_{st}^{(calc)}\) – the intensity of standard scattering under a fixed large angle \(\theta_{st}\) where all the atoms of standard scatter independently calculated theoretically. Dividing the expressions for the intensity scattered by the sample with coating and the standard to each other one obtains the expression for \(K\) – the constant of intensity reduction to electronic units. Thus, the expression for the scattering intensity by the coating material reduced to electronic units is equal to

\[ I = \frac{K}{1 + \cos^2 2\theta_m \cdot \cos^2 2\theta} \cdot \frac{I^{(\text{exp})} / I_{st}^{(\text{exp})} - K_1 \exp(-2\mu t / \sin \theta)}{1 - \exp(-2\mu t / \sin \theta)} \cdot I_{st}^{(\text{exp})}, \]

(3)

where \(K = (A_1\mu_i / \rho_1) / (A_2\mu_s / \rho_2)\) \((1 + \cos^2 2\theta_m \cdot \cos^2 2\theta_{st}) \cdot I_{st}^{(calc)}\), \(K_1 = (A_1\mu_i / \rho_1) / (A_2\mu_s / \rho_2)\) and \(I_{st}^{(exp)}\) – the intensity of scattering by the standard experimentally measured at \(\theta_{st}\).

The expression (3) differs significantly from the one used in the theory of X-ray diffuse scattering by bulk (indicated by subscript “b”) materials [4]:

\[ I_b = \frac{K'}{1 + \cos^2 2\theta_m \cdot \cos^2 2\theta} \cdot \frac{(I_{b}^{(\text{exp})} / I_{st}^{(\text{exp})})}{1 - \exp(-2\mu t / \sin \theta)}, \]

(4)

where \(K' = (A_1\mu_b / \rho_b) / (A_2\mu_s / \rho_2)\) \((1 + \cos^2 2\theta_m \cdot \cos^2 2\theta_{st}) \cdot I_{st}^{(calc)}\).

This difference is due to both the absorption effects that introduce an additional angular dependence into the intensity and affect its absolute value and to the substrate material contribution. The constant \(K_1\) in (3) is determined by the ratio of atomic weights and mass absorption coefficients of the coating and the substrate substances and does not depend on the characteristics of the standard. The value of \(I_{st}^{(exp)}\) in (3) may be either obtained experimentally by independent measurements of the substrate material or estimated theoretically.

Taking into account equations (3) and (4) the intensity in electronic units scattered by the coating can be written as

\[ I_1 = \frac{C}{1 + \cos^2 2\theta_m \cdot \cos^2 2\theta} \cdot \frac{I^{(\text{exp})} - \exp(-2\mu t / \sin \theta) \cdot I_{st}^{(\text{exp})}}{1 - \exp(-2\mu t / \sin \theta)}, \]

(5)

where \(C = (A_1\mu_i / \rho_1) / (A_2\mu_s / \rho_2)\) \((1 + \cos^2 2\theta_m \cdot \cos^2 2\theta_{st}) \cdot (I_{st}^{(exp)})^{-1}\) = const for the specific standard and coating materials. From (5) it follows that the X-ray intensity in electronic units scattered by the coating is to a large extent determined by the magnitude of the factor \(\exp(-2\mu t / \sin \theta)\) associated with the attenuation of the substrate scattering by the coating material.

The value of attenuation factor \(\exp(-2\mu t / \sin \theta)\) is easy to determine under the assumption that if there is no serious coating and substrate line overlapping the experimental intensity scattered by both the coating and the substrate \(I^{(\text{exp})}\) at angles \(\theta\) close to \(\theta_{st}\) – the positions of the substrate structure
reflections is simply the attenuated value of \( I_i^{(\text{exp})} \) – the intensity of a particular uncoated substrate line:

\[
I_i^{(\text{exp})} (\theta = \theta_2) \approx I_i^{(\text{exp})} (\theta = \theta_2) \cdot \exp(-2\mu t / \sin \theta_2). \tag{6}
\]

Thus, the procedure for estimating the diffuse background of a nanostructured coating consists of two stages: at the first the product of the linear coefficient of adsorption and the coating thickness may be determined for several reflections, and on the second the X-ray intensity scattered by the coating material \( I_i(\theta) \) may be determined.

3. Processing of X-ray intensity profiles and examples

All the X-ray intensity profiles have been of coatings obtained in Cu K\( \alpha \) radiation with an X-ray powder diffractometer equipped with a vertical \( \theta - \theta \) goniometer and a Peltier detector were processed using computer programs Origin 8.5 and Fityk 0.9.4. The initial diffraction spectra were strongly noisy, so the Savitzky-Golay smoothing method that retains the structural features of the experimental X-ray profiles was applied to them. The approximation method was used to describe the shape of substrate and coating lines. Then using equation (6) the value of \( \mu t \) was determined as the average of the five strongest substrate diffraction peak integral intensities and this average value coating intensity \( I_i(\theta) \).

Before determining the phase composition of coatings their elemental chemical compositions were established by means energy dispersive X-ray analysis. Further using these results and the ICDD PDF-2 diffraction database all the phases that possibly might be present in coatings have been selected. Then by superimposing a bar chart showing the angular positions of the diffraction peaks for a particular phase from the list of previously selected on the experimental diffraction intensity curve the most likely were selected using the program "Match1.9". The criterion for phase selection was the conformity of its peak positions to the experimental intensity curve peculiarities.

The program "MDI Jade 6.5" functional has allowed synthesizing the total coating intensity curve for the selected set of assumed phases by the sum of specific peaks modeled by pseudo-Voigt functions. This allowed the adjustment of calculated intensities to appropriate experimentally measured diffraction profiles of coatings \( I_i(\theta) \) by the varying intensities, integral widths and specific of Lorentz and Gauss functions to the experimental profiles of pseudo-Voigt functions. The criterion for the success of this adjustment was the minimization of the discrepancy parameter between the experimental and calculated intensities

\[
R_p = \left( \frac{\sum_{i=1}^{N} (I_i^{(\text{exp})} - I_i^{(\text{calc})})}{\sum_{i=1}^{N} I_i^{(\text{exp})}} \right) \cdot 100 \%
\]

To illustrate the technique described above we have presented in table 1 some results on magnetron sputtered metal-carbon coatings that contain nanosized metallic, carbide and nitride inclusions.

| No. | Chemical composition, at.% | Phase composition | Phase proportion | \( R_p \), % | Coherent scattering domain size, nm | Carbides | Nitrides | Metal |
|-----|---------------------------|------------------|------------------|-----------|-----------------------------------|---------|---------|-------|
| 1   | C: 80, N: 4, Me: 15       | Cr\(_2\)C\(_6\), Cr | 1 : 1            | 7.8       | 1.4                              | –       | –       | 8     |
| 2   | C: 64, N: 9, Me: 27       | Cr\(_2\)C\(_6\), Cr | 1 : 3            | 7.5       | 1.6                              | –       | –       | 9     |
| 3   | C: 56, N: 16, Me: 27      | Cr\(_3\)C\(_3\), Cr\(_2\)N, Cr | 1 : 1 : 1       | 3.1       | 3.3                              | 1.7     | 11      |
| 4   | C: 49, N: 18, Me: 32      | Cr\(_2\)C\(_7\), Cr\(_4\)N, Cr | 2 : 1 : 1 | 7.7       | 3.2                              | 2.8     | 11      |
| 5   | C: 27, N: 29, Me: 43      | Cr\(_3\)C\(_2\), Cr\(_4\)N, Cr | 1 : 1 : 1 | 7.2       | 2.7                              | 4.2     | 13      |

| 6   | C: 41, N: 59, Me: 13      | Cr\(_3\)C\(_3\), Cr | 2 : 3            | 9.7       | 14                               | –       | 13      |

\( a \)-C-H:Cr-N\(^a\)

| 7   | C: 75, N: 17, Me: 14      | WC, W\(_2\)C, W | 2 : 4 : 3       | 8         | < 1.0 ("X-ray amorphous")        |         |         |       |

\(^a\)Deposited by reactive magnetron sputtering of chromium in acetylene–nitrogen gas mixtures [5].

\(^b\)Deposited by non-reactive magnetron sputtering of a sintered chromium–nanodiamond target in Ar [6].

\(^c\)Deposited by non-reactive magnetron sputtering of a tungsten-graphite composite ("mosaic") target in Ar [7].
The representative intensity profiles of some coatings with different types of nanocrystalline structure types (diamond-like carbon with nanosized inclusions, nanocrystalline (nc) two-phase and X-ray amorphous) are shown in figure 1. The characteristic sizes of coherent scattering regions of appropriate metallic and interstitial phases are pointed out in table 1. Their values were obtained where it was possible by the Williamson-Hall method and by Scherrer method otherwise.

4. Conclusion
The method of the coating X-ray diffraction intensity pattern evaluation from measurements of coatings deposited on substrate allows one to obtain information about the structure of the coating material, phase composition and the structural parameters of multiphase nanostructured and nanocomposite coatings. This information may help to explain their functional behavior and its peculiarities. In the case of hard carbon coatings this may help to design structures with high wear-resistance and low friction.

References
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