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NON-DESTRUCTIVE CONTROL OF PVD COATING SURFACE DEFECTS

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Nanostructured ZrN coatings were deposited by the vacuum arc method with partial separation of the plasma flow from macroparticles using a curvilinear magnetic filter. With the proposed deposition parameters, a ZrN coating with an fcc lattice and (111) texture is formed. Theoretical studies are carried out to assess the defects of the surface layer in the presence of an adsorbed impurity of an fcc lattice with the surface orientation plane (111), and the characteristics of surface waves in the ZrN coating are considered. Equations are obtained for the dispersion laws and parameters of the splitting off of the surface wave from the zone of bulk vibrations in the nearest-neighbor approximation.

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INTRODUCTION

Increasing requirements for the quality of parts contributed to the development and creation of various protective layers on their surface. Ion-plasma technologies with the formation of thin coatings on the working surfaces are relevant and promising in this direction. Zirconium nitride films are used as protective coatings in industry for hardening cutting tools [1] and bioinert layers in medicine (including implants) [2-6]. Nanostructured films of the Fe-ZrN system are used for highly sensitive magnetic field sensors and magnetic recording systems. Thin films of zirconium nitride, due to their high reflectivity in the infrared, can be used as thermal mirrors for solar cells [7]. In this case, the optical and electrical properties strongly depend on the stoichiometry of nitrogen [8]. Various production methods and parameters of the technology for coating zirconium nitride can lead to the formation of a protective layer with different stoichiometry, to a change in the amount of impurities, such as oxygen and carbon, as well as the amount of vacancies that are located at the sites of the nitrogen lattice. In this case, it is necessary to control and minimize structural defects in the form of pore formation and adsorbed molecules, which can significantly affect the properties of protective films [9, 10].

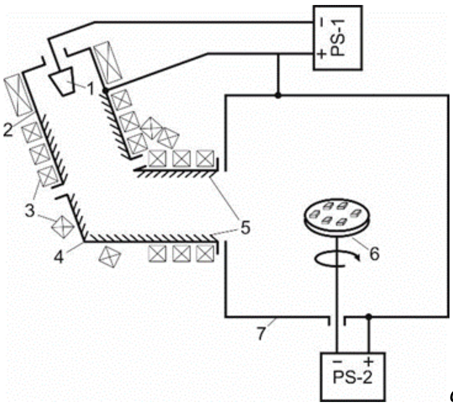
Various experimental and theoretical methods of non-destructive testing make it possible to apply them with high accuracy and efficiency to solve certain previously unsolved problems, as well as compare the results. For the timely detection of defects in the structure of parts, the magnetic method of non-destructive testing for the anisotropy of properties with the measurement of the coercive force is used. A common method for detecting defects and determining the properties of a thin surface layer is ultrasonic testing using ultrasonic surface waves.

Existing computational methods are used to describe both the lattice dynamics of a bulk crystal and surface states, taking into account translational invariance; for considering both isotropic and highly anisotropic crystals and much more. The authors in [11] proposed a method for calculating the pore formation of thin films, based on the calculations of molecular - dynamic modeling of the process of their growth. In [12], the dependence of the pore formation of such films on the conditions of their deposition was theoretically investigated. Despite the variety of existing experimental and theoretical methods [11-14], the list of unsolved problems associated with the presence and influence of defects on the characteristics of nanomaterials is very wide. An unsolved and urgent task is to carry out research and check impurities using the characteristics of pure shear surface waves split off from the continuous spectrum of bulk vibrations.

The aim of the work is to carry out non-destructive control, to study the structure and surface defects of the surface layer of the nanostructured ZrN coating.

EXPERIMENTAL SET UP

The deposition of the ZrN coating was carried out by the ion-plasma method using "Bulat-6". A curvilinear filter (Fig. 1) was applied for partial separation of the micro-droplet component of the plasma flow [15].



a

b

Fig. 1. Diagram of experimental equipment (a) for coating deposition using a curved filter (b): 1 – cathode; 2 – anode; 3 – electromagnetic coils; 4 – air duct; 5 – partitions; 6 – samples; 7 – vacuum chamber; PS-1 – arc discharge power supply unit; PS-2 – source of pulsed negative bias

The surface was cleaned in an ultrasonic bath with alcohol during 10 min before deposition. Chemically pure zirconium (99.99 %) was used as the cathode material. Pulsed negative bias of 1000 V with a frequency of 50 kHz was applied to the sample holder during 1.5 min for cleaning exposed surface. Zr transition layer of 20 nm-thick was applied (at a potential of -200 V) for improvement the adhesion of the coating to the base. The nitrogen pressure during deposition reached $5.5\cdot10^{-3}$ Torr. The deposition rate was ~ 34 µm/h. Thus, it be possible to obtain a coating with a minimum number of drops and defects, which are typical for layers formed without separation of the plasma flow.

X-ray diffraction (XRD) has been used to study structure, substructure and stress state of deposited samples. ϑ-2ϑ scans were performed using a monochromatic Cu-*K*α radiation within DRON-3M device. Computer processing of the experimental diffraction patterns was performed.

The obtained experimental data were subjected to theoretical analysis: the sample surface has been checked for possible impurities adsorbed on it. The calculation was carried out by the method of finite-difference equations. The given method makes it possible to study at the microscopic level the zones of volume vibrations and the properties of one-component surface waves split off from the continuous spectrum. The surface waves properties have been studied both depending on the surface orientation and on the presence or absence of an adsorbed impurity monolayer. This method has a fairly wide generality and can be used in models close to real systems. The studies of both continuous and discrete spectra of crystal vibrations could be performed. A model of a semi-infinite crystal with an ideal surface was considered for qualitative calculations.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the ZrN coating obtained by the ion-plasma method using a curved filter is shown in Fig. 2. As a result of the X-ray diffraction analysis the as deposited Zr-N coating has a cubic crystal lattice of the NaCl type with a parameter a = 0.4577 nm (according to JCPDS XRD library, card 35-0753). All angles of diffraction peaks with main reflections (111), (222) and (220) were indexed as the ZrN phase. The high intensity of the ZrN (111) Bregg reflection indicates that the ZrN grains grow with a preferred (111) orientation, perpendicular to the growth plane. The X-ray structural analysis data correlate well with the results of transmission electron microscopy, obtained using an EMV-100L microscope at an accelerating voltage of 100 kV. All diffraction lines were indexed as the ZrN phase with a stoichiometric face centered cubic lattice (fcc). No additional phases were found.

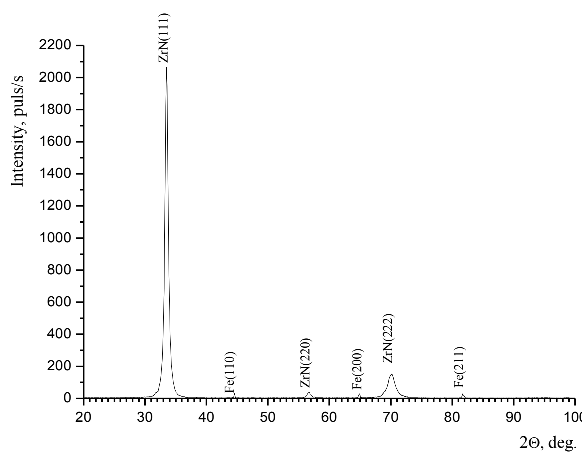


Fig. 2. XRD spectra of the ZrN coating

As experimentally established, the deposition of the ZrN coating by the ion-plasma method results into a surface of face-centered cubic lattice with (111) orientation. Our theoretical analysis has been carried out for such surface type. Oscillations of purely shear surface waves of horizontal polarization were considered. The studies were taken as a basis for the fcc lattice with the surface orientation (001) [15].

When considering the fcc with the orientation plane of the (111) surface, the components of the two-dimensional wave vector χ (k1, k2) with the components k1 and k2 located in the plane of the (111) surface were chosen.

$$\frac{m\omega^2}{\alpha} = 12 - 2\cos(2k_2) - 2\cos(2k_3) - \dots \qquad (1)$$

$$- 8\cos(k_1)\cos(k_2)\cos(k_3).$$

The dispersion law for bulk vibrations has the form (1) in the approximation of nearest neighbors. Here m is the mass of the molecule at the lattice site of the surface layer of the crystal, α is the coefficient of interaction between the nearest neighbors, and ω is the frequency of bulk vibrations.

In the case of a crystal with an ideal fcc lattice, the characteristic equation, taking into account the nearest neighbors, has the form (2):

$$\frac{m\omega_s^2}{\alpha} = 8 - 4\cos(k_1)\cos(k_2) - (\cos(k_1) + \cos(k_2))^2 \quad (2)$$

Fig. 3 shows the zones of bulk vibrations as a function of the two-dimensional wave vector at fixed values, as well as a surface wave splitting off from the bulk spectrum.

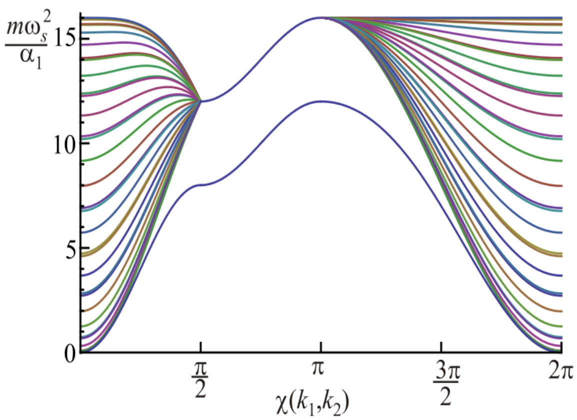


Fig. 3. Zone of bulk vibrations and surface wave in an fcc crystal with the plane (111) surface orientation. The calculations were carried out in the Wolfram Mathematica computer algebra system

From the analysis of Fig. 3, it follows that pure shear surface wave in a crystal with a fcc are split off without taking into account surface distortion even in the case of the same interaction coefficients. As a result of performed studies, it was found that the surface wave splits off from the volume spectrum already in the approach of the nearest neighbors in case of an fcc coating with (111) orientation of the surface plane. The investigated surface waves are one-partial. This significantly simplifies the possibility of surface defects analysis due to the simplicity of theoretical model.

CONCLUSIONS

Nanostructured ZrN coatings deposited by the vacuum-arc method with partial removal of macroparticles from the plasma flow has been investigated. Complex experimental and theoretical studies have been carried out in order to assess the structure and surface defects of the coating. On the base of X-ray diffraction analysis and transmission electron microscopy, it has been established that a coating is formed with an fcc lattice and an orientation plane of the surface (111).

The obtained experimental data are used in theoretical calculations carried out by the method of finite – difference equations to study the surface purity from foreign adsorbed impurities. The theoretical study of the characteristics of surface waves in the ZrN coating are performed. For such a coating, expressions are obtained for the dispersion laws and the parameters of the splitting off of the surface wave from the zone of bulk vibrations. It was found that surface waves appear in a nanostructured ZrN coating having an fcc lattice with the surface orientation plane (111) at the approximation of the first neighbors and are split off from the continuous spectrum of bulk vibrations without taking into account the surface distortion. The obtained theoretical model makes it possible to analyze the surface of ZrN coating for the presence of structural defects.

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НЕРУЙНІВНИЙ КОНТРОЛЬ ДЕФЕКТІВ ПОВЕРХНІ PVD-ПОКРИТТЯ

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Розглянуто параметри осадження наноструктурного покриття ZrN вакуумно-дуговим методом із частковою сепарацією плазмового потоку від макрочасток за допомогою криволінійного магнітного фільтра. При запропонованих параметрах нанесення формується покриття ZrN з ГЦК-ґратками та орієнтаційною площиною поверхні (111). Виконано теоретичні дослідження для оцінки дефектності поверхневого шару в вигляді адсорбованих домішок та розглянуто характеристики поверхневих хвиль у покритті ZrN. Отримано вирази для законів дисперсії та параметрів відщеплення поверхневої хвилі від зони об'ємних коливань при врахуванні найближчих сусідів.