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Influence of Deuterium Ion Implantation on the Structure and Hardness of Nanocrystalline Films

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Titanium nitride based coatings are very attractive for protection of materials in extreme conditions. However, their behavior under different kinds of irradiation is not entirely well understood. In this work, the influence of ion-implanted deuterium on changes of the structure and mechanical properties TiZrN, TiAlSiN, TiAlYN films were investigated. Films were deposited by filtered vacuum arc plasma technique. After deposition all films were irradiated at room temperature with 12 keV D^+ ions to dose ~1×10^{18} D/cm^2. Composition, structure and nanohardness of the coatings were determined by X-ray fluorescence method, X-ray diffraction and nanoindentation. The effusion of the implanted deuterium was studied by thermal desorption spectroscopy.

It is shown that irradiation by deuterium ions does not make structural changes in multicomponent films. Deuterium thermal desorption spectrum of various coatings are substantially different. Nanohardness of all investigated coatings after irradiation and thermal desorption are decreased.

Keywords: Vacuum arc, Nanostructured coatings, Hardness, Implantation, Deuterium, Thermal desorption.

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1. INTRODUCTION

Multicomponent nanostructured coatings based on titanium nitride with the addition of the elements Zr, Al, Si, B, Cr, Y have a high hardness, corrosion resistance and thermal stability [1]. The study of the stability properties of nitride coatings with various types of radiation is an actual problem [2,3]. This paper presents the results of a study of hardness, structure and temperature ranges of desorption ion-implanted deuterium from multicomponent coatings based on TiN.

2. EXPERIMENT

TiN based coatings, with different concentration of alloying elements were deposited onto stainless steel substrates by filtered cathodic vacuum arc evaporation system from the $Ti_{80}Zr_{20}$, $Ti_{78}Al_{16}Si_{06}$, $Ti_{67}Al_{28}Y_{05}$ cathodes [4]. In all cases, a pure nitrogen atmosphere was used to deposit the coatings. The pressure during deposition was in the range of 0.04 – 0.8 Pa and the substrates were held at a bias of –100 V. The thickness of all the samples was approximately 3 μm.

Composition of the coatings was determined by X-ray fluorescence method. The phase composition and substructure of coatings were studied by X-ray analysis on a DRON-3 diffractometer in the filtered radiation from a copper anode. The processing of diffraction patterns produced by a computer program New_Profile. The crystallite size was determined from the broadening of the lines from the Selyakov-Scherrer relation. The hardness measurements were carried out on coatings using a Nanoindenter G200 equipped with a Berkovich diamond tip to penetration depth 300 nm by CSM method. Implantation of deuterium and thermal desorption spectroscopy measurements were performed in the experimental apparatus "SKIF", described in detail in [5]. Irradiation was carried by ions D^+ energy of 12 keV, at dose of ~1×10^{18} D/cm^2 at room temperature. The studies of thermal desorption spectrum of ion-implanted deuterium from coatings aged for 50 days at room temperature. The heating was carried out at an average rate ~7 K/s to a temperature of 1500 K, with simultaneous recording of the spectrum of desorption D (4 amu). Temperature measurement was carried out tungsten-rhenium thermocouples WRe5/20 attached to the heater.

3. RESULTS AND DISCUSSION

After deposition, depending on the nitrogen pressure the samples had different elemental and phase composition. Fig. 1 shows the diffractograms of the coatings.

In all diffraction patterns, in addition to the lines of the substrate, revealed a single line of the crystalline phase - nitride with fcc structure characteristic of TiN (structural type NaCl). It is seen that the number of detected lines of this phase, their intensity, position and width depend strongly on the composition of the cathode and the pressure of nitrogen. This demonstrates the significant differences in the structure of the films: the number of the crystalline phase, crystallite size, lattice parameter and texture. Displacement of the diffraction lines of nitrides relative positions of the lines of TiN due to the formation solid solutions and residual stresses in the films.

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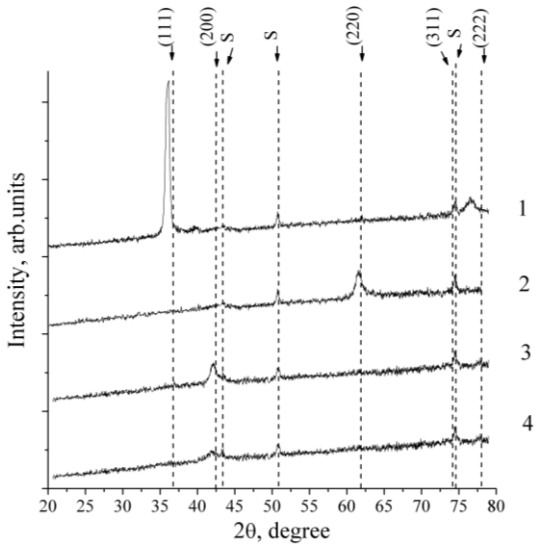

Fig. 1 – X-ray diffraction patterns of vacuum arc nitride coatings: S-substrate, 1 – $Ti_{99}Zr_1N$; 2 – $Ti_{59}Al_{37}Si_4N$; 3 – $Ti_{75}Al_{21}Si_4N$; 4 – $Ti_{50}Al_{48}Y_2N$

Coating $Ti_{99}Zr_1N$ has a well-formed crystalline structure with a characteristic columnar coatings axial texture [111] and the crystallite size ≈ 22nm. In the films, which include the aluminum content of the crystalline phase is much lower, and the size of the crystallites ≤ 10 nm. Depending on the composition of these coatings are characterized by amorphous or amorphous-crystalline structure. The composition, characteristics of the substructure and hardness of the films are shown in Table 1.

Was found that irradiation of deuterium ions does not lead to significant changes in the structure of coatings. On the diffractograms of the samples after irradiation, no changes were detected. The exception is the coating $Ti_{99}Zr_1N$ the diffraction lines is shifted toward smaller angles. Estimates show that the period of the crystal lattice nitride grown from 0,4309 ± 0,0003 to 0,4321 ± 0,0003 nm. This may be due to the dissolution of the deuterium in the nitride lattice. This is confirmed by thermal desorption of deuterium form the spectrum (Fig. 2, curve 1).

Table 1 – The composition, characteristics of the substructure and hardness of coatings

Coatings composition, at%	Pressure, Pa	Texture axis	Crystallite size, nm	H, GPa as deposited	H, GPa irradiated	H, GPa after thermal desorption
$Ti_{99}Zr_1N$	0,04	[111]	22	30	26	20
$Ti_{59}Al_{37}Si_4N$	0,04	[110]	10	40	15	15
$Ti_{75}Al_{21}Si_4N$	0,8	—	10	25	23	18
$Ti_{31}Al_{68}Y_1N$	0,04	amorphous	—	23	15	13
$Ti_{50}Al_{48}Y_2N$	0,8	—	7	26	11	8

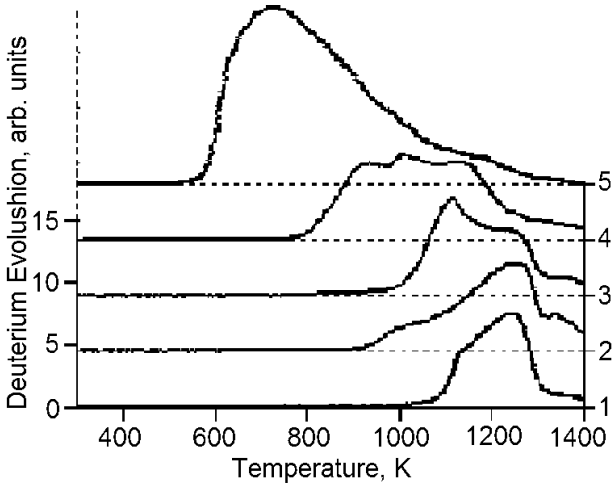

Fig. 2 – Thermal desorption spectroscopy of D_2 ion implanted in coatings: 1 – $Ti_{99}Zr_1N$; 2 – $Ti_{50}Al_{48}Y_2N$; 3 – $Ti_{31}Al_{68}Y_1N$; 4 – $Ti_{59}Al_{37}Si_4N$; 5 – $Ti_{75}Al_{21}Si_4N$

Implanted deuterium forms a phase state of solid solution of deuterium in titanium and titanium nitride that is shown in the spectrum as two peaks with maximum temperatures of ~1100 K and ~1250 K. According to literature data low temperature peak almost exactly coincides with the temperature of a solid solution of deuterium in titanium [6], therefore high temperature peak due to the presence of the phase state of solid solution of deuterium in titanium nitride.

Thermal desorption spectra of samples with a large number of components is much broader, more difficult, but the beginning of the deuterium yield is shifted towards lower temperatures. Especially strongly decreases the temperature started out to cating $Ti_{75}Al_{21}Si_4N$ and is ≈ 600 K. It appears that deuterium interacts with the amorphous component of the condensate, and its output is a multistep process with different activation energies.

In contrast to the crystalline structure, hardness of the coating after irradiation is not retained (see Table. 1). Hardness of the coating $Ti_{99}Zr_1N$ decreases from 30 GPa to 26 GPa after irradiation and up to 20 GPa after thermal desorption. For multicomponent coatings reducing the hardness is significant.

4. CONCLUSIONS

Deuterium ion irradiation dose of ~1×10^{18} D/cm^2 no significant structural changes in multicomponent films, a slight increase in the period observed in the crystal lattice $Ti_{99}Zr_1N$.

High dose implantation of deuterium leads to a decrease in the hardness of coating, which remains relatively high (26 – 23 GPa) for coatings $Ti_{99}Zr_1N$, $Ti_{75}Al_{21}Si_4N$.

The structure of the thermal desorption spectrums of deuterium from the nitride coatings depends strongly on the composition of the component and indicates the presence of significant structural differences in the obtained coatings.

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