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Effects of Deuterium Implantation Dose on Hardness and Deuterium Desorption Temperature Range from High Entropy TiVZrNbHf and TiVZrNbHfN Coatings

A.S. Kuprin[1], O.M. Morozov[1*], V.A. Belous[1], S.A. Firstov[2], V.F. Gorban[2], V.D. Ovcharenko[1],
E.N. Reshetnyak[1], G.N. Tolmachova[1], V.I. Zhurba[1], V.O. Progolaieva[1]

[1] *National Science Center "Kharkov Institute of Physics & Technology",1 Akademicheskaya Str., Kharkov, Ukraine*
[2] *I.Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kyiv, Ukraine*

High entropy TiVZrNbHf and TiVZrNbHfN coatings prepared by filtered vacuum arc plasma from a single equiatomic HEA cathode. Similarly were obtained titanium and titanium nitride coatings. The structure of coatings was investigated by X-ray analysis and the changes in nanohardness by nanoindentation method. The effusion of the implanted deuterium was studied by thermal desorption spectroscopy (TDS).

It is shown that the structure of effusion spectrum is a function of deuterium dose. With increasing implantation dose deuterium desorption temperature range from coatings is expanding in the direction of lowering the temperature and the temperature of the peak maximum gas emission gradually shifts to lower temperatures. For nitride coatings deuterium desorption starts at about room temperature and the maximum rate of desorption at a temperature of ~500 K.

When irradiation doses more than 5×10^{17} D/cm^2 hardness of nitride coatings decreased by half. Hardness reduction of coatings is caused by occurrence hydride structural formations in coatings.

Keywords: High-entropy composites, Deuterium, Hardness, Thermal desorption spectroscopy (TDS), Implantation

1. INTRODUCTION

Protective coatings are widely used in various fields of industry for the hardening of cutting tools and machine parts. In order to obtain a high hardness are interesting of multi-component condensates on the basis of high entropy alloys (HEA) containing ≥ 5 elements in equiatomic ratio, a concept which has been proposed in [1]. HEA possess high entropy of mixture and, as consequence, a minimum of Gibbs energy that defines stability of their structure and high operational characteristics. These coatings also can be applied as diffusion barrier for copper metallization [2].

The method of ion implantation can be one of ways change of coatings properties that basis on HEA. A special interest is the study of the stability properties of the single and multicomponent coatings after irradiation. The authors of [3] have not detected change in the hardness of multilayer coatings irradiated with helium ions. In work [4] it is shown that after irradiation by Xe ($E = 360$ keV; 8×10^{14} cm^{-2}) ions has a more stable system TiZrN compared with single-nitride coatings (TiN, ZrN).

In the present work influence of irradiation dose on thermal desorption deuterium from metal coatings of the titanium and TiVZrNbHf, and also their nitrides was investigated. Change of hardness of nitrides after an irradiation was studied.

2. THE METHODICAL ASPECTS

Coatings with the thickness of 5 microns, deposited from the filtered vacuum arc plasma stream [5]. Titanium condensates deposited on molybdenum, copper and stainless steel in vacuum $(P = 5 \times 10^{-4}$ Pa), metal coatings from HEA cathode (25Ti-10V-25Zr-25Nb-15Hf) deposited at argon pressure ~0,05 Pa, and nitride coating at nitrogen pressure ~0,3 Pa.

Nanohardness was measured on Nanoindenter G200 by Berkovich diamond indenter with radius in top ~230 nm. Hardness measurement spent to depth of introduction indenter 300 nm by CSM method. The phase structure and substructure of coating has been studied by a method X-Ray analysis on DRON-4-07. The concentration of components in coatings was determined by a energy dispersive method: $Ti_{31,5}Zr_{16,6}Nb_{20,1}V_{24,2}Hf_{7,6}$ and $Ti_{24}Zr_{15}Nb_6V_{8,3}Hf_{1,3}N_{45,4}$ (at%). Deuterium desorption temperature range from samples were investigated by a method thermal desorption spectroscopy (TDS) on installation "SKIF" [6]. The temperature was measured by thermocouple WRe5/20 attached to a heater. For the purpose of reduction of influence of the background hydrogen which is available in samples and the chamber of targets, in experiments the hydrogen isotope - deuterium was used. Introduction deuterium in the samples cooled to temperature ~100 K was carried out by a bunch of ions D_2^+ energy 24 keV in the range of doses from 1×10^{16} D/cm^2 to 6×10^{18} D/cm^2. After introduction of the set dose deuterium the bunch was switched off and then heating in which process the temperature of the sample raised to ~1200 K under approximately linear law from time with average speed ~3.5 К/c joined. Allocation deuterium in the measuring chamber were registered by means of a mass spectrometer on $m = 4$ a.u.m. (D_2^+).

3. RESULTS AND DISCUSSION

3.1. Coatings structure

The X-Ray phase analysis of titanium coatings produced from surveys in θ-2θ, has shown that on all thickness of investigated films presence of one phase - **α**-Ti (hcp). Crystallites are focused by planes (100) along a film surface. The lattice constant – 0,2950 nm. Definition of the crystallites sizes in films **α**-Ti was made on broadening diffractional lines of different usages of reflexion (100) and (300). It has been established that the crystallite size $L \sim$ 40-45 nm.

TiN coatings have well generated cubic crystal structure (structural type NaCl) with characteristic columnar coatings axial texture [111] and the crystallite size ≈22 nm. On diffraction pattern this coating intensive and narrow enough lines (111) and (222) are visible.

By results of X-Ray diffractometry coating from alloy TiVZrNbHf, received in atmosphere of argon the basic phase in a coating, is the firm solution with **bcc** structure and a strong axial structure with an axis [100] in a direction of a normal to a covering surface. The average size crystallite in a direction of an axis of the structure, calculated of broadening lines under the Sheerer formula makes 5 nm. Value of the period bcc a crystal lattice makes 0,3333±0,0005 nm. The second is more weak and broad line available in the diffraction pattern neither near 40 degrees, not the detected bcc solid solution nor on the angular position of any width. Most likely, this is the line (011), which belongs to the solid solution with the hcp-lattice. The average crystallite size of this phase makes about 2 nm.

In high entropy coating TiVZrNbHfN received in atmosphere of nitrogen, the structure is formed single-phase texture paint **fcc**. On diffraction pattern coatings are visible narrow enough and very intensive lines of this phase of type (hhh). The curve hunting reflection (111) testifies that in a coating the structure of axial type with an axis [111] in a direction of a normal to a surface of a substrate and a corner of dispersion of structure 10 degrees are formed. Period fcc crystal lattice in a relaxed cross-section is equal to (0,4385±0,0003) nm. The crystallite size of this phase is about 36 nm.

3.2 Deuterium desorption temperature range

In the spectrum of thermal desorption of deuterium from titanium samples deposited on molybdenum there is only one peak at temperature ~910 K (see fig. 1). With increasing dose of implanted deuterium maximum temperature of gas emission peak gradually shifts to lower temperatures. This suggests that the effusion of deuterium occurs at the eutectoid reaction.

For samples high entropy composite TiZrNbVHf (HEA) spectrum evolution (see fig. 2) with dose growth submits basically to the same laws and has appreciable similarity with spectra thermodesorption for samples of the titanium. With growth of a dose implanted deuterium the temperature area deuterium desorption extends in a direction of temperature fall and the temperature of gas evolution a maximum of peak is gradually displaced in area of lower temperatures.
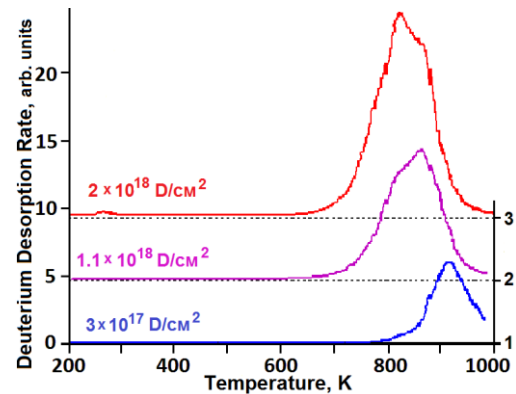

Fig. 1 – Thermal desorption spectra of deuterium implanted into a Ti. The deuterium irradiation doses were: (1) ~3×10^{17} D/cm²; (2) ~1.1×10^{18} D/cm²; (3) ~2×10^{18} D/cm²

Fig. 3 shows the thermal desorption spectra of deuterium implanted in samples of nitride TiN coating at the irradiation temperature of ~100 K for the different doses. As can be seen from the figure, the structure of the TDS spectrum is a function of implantation dose. At doses of irradiation (1÷3) ×10^{16} D/cm² in a spectrum is observed only one peak of deuterium desorption evolution with maximum at temperature ~1060 K. Increasing the dose to 1×10^{17} D/cm² increases the amplitude of the peak and the appearance of the low-temperature region of deuterium effusion. The further increase in a dose to 1×10^{17} D/cm² is accompanied by occurrence of additional temperature area deuterium desorption with the center of gravity in the range of temperatures 800-850 K. With a further increase in the dose trend continues to expand the temperature range desorption of deuterium in the direction of lowering the temperature and the formation of an additional peak with a maximum at a temperature ~650 K (see fig. 3, curves 6, 7).
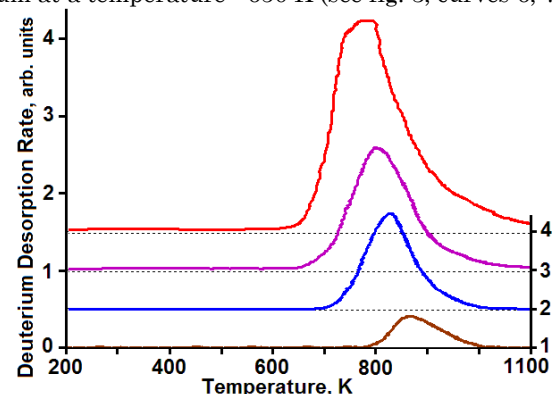

Fig. 2 – Thermal desorption spectra of deuterium implanted into high entropy composite TiZrNbVHf. The deuterium irradiation doses were: (1) – 1.6×10^{17} D/cm²; (2) –5.7×10^{17} D/cm²; (3) – 1.1×10^{18} D/cm²; (4) – 3.3×10^{18} D/cm²

Given the sequence of appearance of peaks with increasing implantation dose, the position of the maxima on the temperature scale, we came to the conclusion that the effusion of deuterium at the peak with a maximum temperature of ~ 1060 K due to the decomposition of the solid solution in the TiN under the influence of deuterium. The appearance of low-temperature peaks in the thermal desorption spectrum of deuterium due apparently structural changes, primarily due to the formation of titanium hydride.
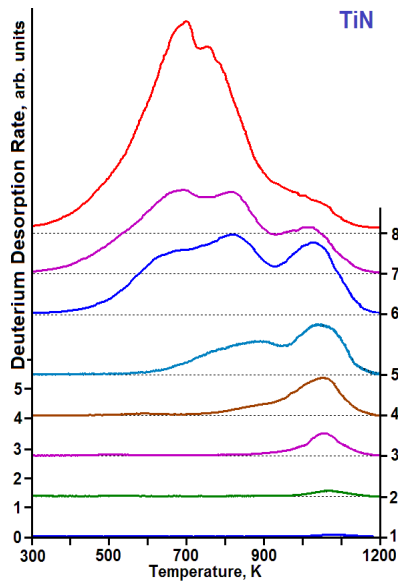
Fig. 3 – Thermal desorption spectra of deuterium implanted into TiN. The deuterium irradiation doses were:
(1) – 1×10^{16} D/cm²; (2) – 3×10^{16} D/cm²; (3) – 1×10^{17} D/cm²;
(4) – 2×10^{17} D/cm²; (5) – 3×10^{17} D/cm²; (6) – 8×10^{17} D/cm²;
(7) – 1.2×10^{18} D/cm²; (8) – 6×10^{18} D/cm²

For samples high entropy composite TiZrNbVHfN (HEA) spectrum evolution (see fig. 4) with growth dose submits basically to the same laws and has appreciable similarity with thermal desorption spectra for samples TiN. With increasing dose of implanted deuterium desorption temperature range extends in the direction of lowering the temperature and the temperature of the peak maximum gas emission gradually shifts to lower temperatures. At the same time, the desorption temperature range of implanted deuterium has a wide temperature range, deuterium desorption starts at about room temperature and the maximum rate of desorption of deuterium is at a low temperature ~500 K.
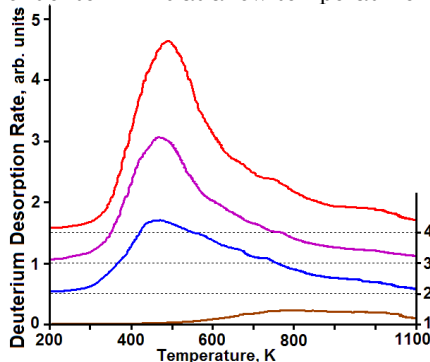

Fig. 4 – Thermal desorption spectra of deuterium implanted into TiZrNbVHfN. The deuterium irradiation doses were:
(1) – 2×10^{17} D/cm²; (2) – 1.2×10^{18} D/cm²; (3) – 1.6×10^{18} D/cm²;
(4) – 4.2×10^{18} D/cm²

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3.3. Hardness of coatings after deuterium implantation

The hardness of the as deposited coatings is similar and is about ~40 GPa. In a dose range of $5 \times 10^{16} \div 5 \times 10^{17}$ D/cm² implanted deuterium hardness decreasing in TiN and TiZrNbVHfN coatings occurs similarly. Dose excess 5×10^{17} D/cm² is accompanied by hardness reduction practically twice. At a dose of an irradiation 1.5×10^{18} D/cm² hardness of the titanium nitride decreases to 20 GPa, and multicomponent coating TiZrNbVHfN to 25 GPa.
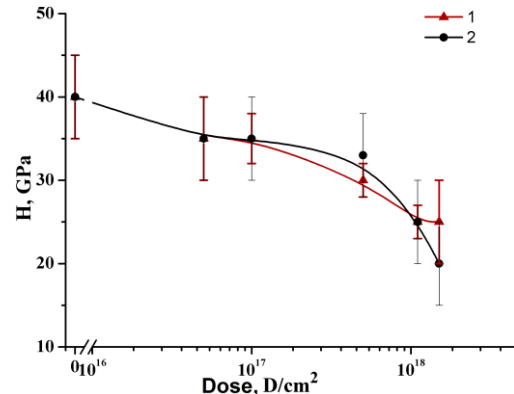

Fig. 5 – Dependence of coating hardness on a deuterium dose: (1) – TiZrNbVHfN and (2) – TiN

On the thermal desorption spectra of deuterium seen structural changes in the form of the appearance of additional peaks in the range of doses (5×10^{17}–1.5×10^{18} D/cm²). Based on these data it can be concluded that the reduction of coatings hardness caused by the appearance of hydride structural formations.

4. CONCLUSIONS

From the filtered vacuum arc plasma were deposited Ti, TiN and high-entropy composite TiVZrNbHf, TiVZrNbHfN coatings.

For all investigated coatings the structure of spectrum TDS is function of deuterium doses. With increasing implantation dose desorption temperature range of deuterium from coatings expands to lower temperatures. The temperature of the maximum peak of deuterium effusion also shifted to lower temperatures.

For nitride coatings temperature range of deuterium desorption wider than for metallic coatings and begins at room temperature with a peak at ~500 K for high entropy TiVZrNbHfN.

The hardness of the nitride coating is reduced to 20 GPa for TiN and 25 GPa for the TiVZrNbHfN at doses above 5×10^{17} D/cm². This is probably due to the formation in the coatings defects and hydride structures.

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