PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. 1 No 2, 02NFC03(2pp) (2012)

Structural-Strained State and Mechanical Characteristics of Single-Phase Vacuum-Arc Coatings of Multicomponent High Entropy System Ti-V-Zr-Nb-Hf and Nitrides Based On It

O.V. Sobol`[1,*], A. A. Andreev[2,†], V.F. Gorban`[3,‡], N.A. Krapivka[3], V.A. Stolbovoy[2], V.Ye. Fil`chikov[1], S.A. Firstov[3]

[1] *National Technical University "KhPI", 21, Frunze St., 61002, Kharkov, Ukraine*
[2] *National Scientific Centre «KhPTI», 1, Akademicheskaya St., 61108, Kharkov, Ukraine*
[3] *Institute for problems of materials science NAS of Ukraine, 3, Krzhizhanovsky str., 03680, Kyiv, Ukraine*

(Received 13 March 2012; published online16 August 2012)

In this work was shown the high stability of the single-phase structural state of high entropy alloy of Ti-V-Zr-Nb-Hf system in a vacuum-arc method of obtaining of coatings based on it. In the process of deposition single-phase high entropy coatings with bcc-lattice which characterizes the cast state are formed in vacuum, and upon obtaining in a nitrogen atmosphere single-phase nitride superhard coatings based on fcc-metal lattice are formed. Such a stability of structure of multi-element alloy to high temperature evaporation and deposition from high-energy plasma flows allows to use the techniques developed for simple substitution phases in the analysis of their structural-stress state.

Keywords: Vacuum-arc coating, High entropy alloy, Single-phase structural state, Nitride, Superhard.

PACS numbers: 81.07.Bc , 61.05.cf ; 62.25. – g

1. INTRODUCTION

To increase the thermal stability of the material the concept of multi-component high entropy alloys (HEA) (see, eg [1-5]) was proposed and experimentally proved. In this paper, five-element alloy of vaporized cathode consisted two elements (Nb and V) which have *bcc*-lattice at room temperature and form a continuous series of solid solutions, as well as Hf, Zr. and Ti, which also form a continuous solid solutions with each other and have hexagonal (*hcp*) crystal lattice at room temperature, but with *bcc*-lattice at high temperatures. Simultaneously, Hf, Zr, Nb and V are β-stabilizers for titanium.

In such a combination of both stabilizing bcc-lattice V and Nb, and the refractory components of Hf, Zr, and Ti, because of its high affinity to nitrogen [6] define the possibility of formation of nitride phase on the basis of high entropy one-component alloy.

2. METHODS OF SAMPIE MANUFACTURING AND ANALYSIS

The cathodes of the high entropy alloys Ti-V-Zr-Nb-Hf were prepared by vacuum-arc melting in an atmosphere of high purity argon. Preparation of coatings was carried out by vacuum-arc evaporation of the cathode at the "Bulat-6" plant when applying a constant negative bias of the substrate $U_b = (-40 \ldots -200)$ V, arc current 85 A. residual gas pressure of 0.0066 Pa, the pressures of nitrogen (0.04 ... 0.66) Pa. The deposition rate was about 1.5 nm/ s.

The study of structural-stress state was carried out on DRON-3M diffractometer in the emission of Cu-K_α. Microindentation were carried out on the "Micron-Gamma" plant [7] under a load of up to F = 0.5 N Berkovich diamond pyramid with an angle of 65°.

3. RESULTS AND DISCUSSION

Vacuum-arc evaporation of cathodes of high entropy Ti-V-Zr-Nb-Hf bcc-system with content of elements close to the equiatomic in vacuum (residual atmosphere pressure 0.0066 Pa) led to the formation of coatings with preserved single-phase, i.e. with bcc-lattice and a strong texture with the axis [110] parallel to the direction of the fall of film-forming particles. On the X-ray diffraction spectrum (Fig. 1, spectrum 1) in the condition of focusing Bragg-Brentano (θ-2θ -scheme) appear only reflections of two orders of reflection from the {110} planes. The average size of crystallites in the direction of the texture is 80 nm at a thickness of the coating of more than 7 um.

In the case of deposition of coatings in the presence of a nitrogen atmosphere at the lowest of the pressures used in the work $P_N = 0.04$ Pa there is the formation of non-textured polycrystaliine single-phase state (*fcc*-lattice), even when applying high $U_b = -200$ V (see Fig. 1). Size of crystallites vary from 35 nm at $U_b = -100$ V to 50 nm at $U_b = -200$ V.

The increase in pressure ($P_N = 0.11$ Pa) leads to the formation of textured single-phase *fcc*-coatings. When $U_b = -50$ V –100 V there is a transition from a partly textured state with the [111] axis perpendicular to the plane of growth to the state with a nearly uniaxial texture with the axis [111]. When $U_b = -200$ V bitextured state with axes [111] and [110] is formed perpendicular to the plane of growth. The appearance of the latter type of the axis of texture is determined by minimization of the radiation factor influence while the deposition and for pure TiN coatings is usually observed for large values of $U_b > -400$V [8]. The appearance of this type of texture with lesser U_b than for pure TiN can be associated with a high content of Hf (17 ... 25 at.%) in

* sool@kpi.kharkov.ua
† aandreev@kipt.kharkov.ua
‡ gvf@ipms.kiev.ua

the coating. Crystallite size varies from 47 nm to 95 nm with increasing U_b. The hardness of coatings obtained at this pressure is sufficiently high and is (40 ... 50) GPa.

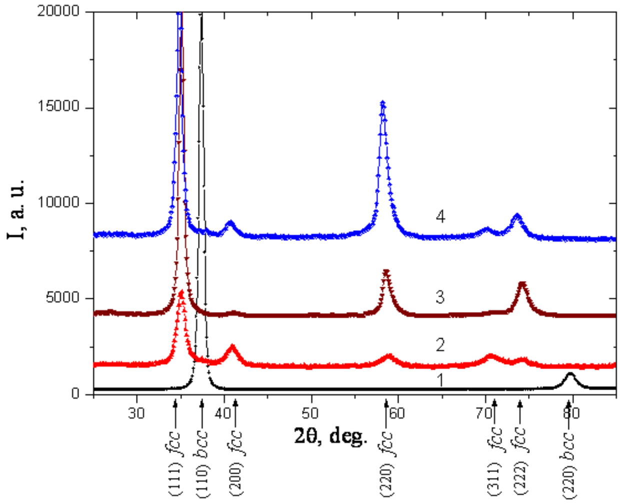

Fig. 1 – Plots of the diffraction spectra of vacuum-arc coating system of high entropy system Ti-V-Zr-Nb-Hf, obtained: 1 - in the absence of atmospheric nitrogen (H = 8.2 GPa, E* = 105 GPa) and P_N = 0.27 Pa and U_b: 2 - –50 V (H = 59 GPa, E* = 401 GPa), 3 - –100 V (H = 64 GPa, E* = 436 GPa) and 4 - –200 V (H = 70 GPa, E* = 429 GPa)

Nitride coatings showed the highest hardness obtained on the basis high entropy alloys under pressure P_N = 0.27 Pa. At this pressure with increasing of U_b structural changes similar to those in coatings deposited at P_N = 0.11 Pa were observed. The appearance of the texture [111] and its growing perfection at U_b = –50 V and U_b = –100 V respectively (Fig. 1), leads to increase in hardness of coating from 59 GPa up to 64 GPa, and the appearance of biaxial texture with axes [111] and [110] at U_b = –200 V leads to the highest hardness of 70 GPa. The size of the crystallites in this case is 57 nm. Note that the coatings generated when U_b = –200 V have a very homogeneous smooth surface.

The analysis of the deformed state of nitride high entropy coatings according to "a - $\sin^2\Psi$»-graphs showed that in the case of biaxial texture, lattice deformation in the crystallites with the texture axis [110] exceed the deformation in the group with the axis [111]. The greatest compression deformation is observed in the crystallites of coatings obtained with the maximum U_b = –200 V, and reaches in the case of P_N = 0.27 Pa value –1.79% and –3.7% for groups of crystallites with the axes [111] and [110], respectively. For a lower P_N = 0.11 Pa the value of deformation is somewhat lower and has a value of –1.7% and –3.45% respectively. In the areas bordering the substrate (at a depth of 1 um from the substrate), there is less deformation (by up to 20%).The reason for this is apparently a partial relaxation of the deformation by means of the substrate (stainless steel 12X18H9T) flow in the border region [9]. In the case of the high brittleness of the substrate (monocrystal Si plate, thickness of 380 um) high stress-strain state of compression in the coating leads to the destruction of the substrate. By lowering the U_b to –50 V the magnitude of the compressive strain of the lattice does not exceed the absolute value of 2%. Thus, when the state of uniaxial texture, the hardness of nitride coatings based on high entropy alloys does not exceed 60 GPa, and the higher the hardness is achieved in the case of formation of biaxial texture with axes [111] and [110], which is observed when U_b = –200 V in alloys with relatively high content of Hf.

REFERENCES

1. V. Dolique, A-L. Thomann, P. Brault, Y. Tessier, P. Gillon, *Mat. Chem. Phys.* **117**, 142 (2009.).
2. V. Dolique, A-L. Thomann, P. Brault, Y. Tessier, P. Gillon, *Surf. Coat. Tech.* **204**, 1989 (2010).
3. M. Tsai, C. Wang, C. Tsai, W. Shen, J. Yeh, J. Gan, W. Wu, *J. Electr. Soc.* **158**, H1161 (2011).
4. S. Ranganathan, *Curr. Sci.* **85**, 1404 (2003).
5. A. Li, X. Zhang, *Acta Metall. Sin.* (*Engl. Lett.*) **22**, 219 (2009).
6. O.V. Sobol, A.A. Andreyev, S.N. Grigoryev, V.F. Gorban, V.A. Stolbovoy, I.V. Serduk, V.E. Filchikov, *West.-Europ. Mag. Tech.*, **6/5(54)**, 4 (2011).
7. E. Aznakayev, *Proceedings of the International Conference "Small Talk*, TP.001, 8 (2003).
8. N.A. Azarenkov, O.V. Sobol, A.D. Pogrebnyak, V.M. Beresnev, *Vacuum-plasma surface ingeneering* (Kharkiv, Karazin KhNU: 2011).
9. O.V. Sobol, A.A. Andreyev, V.A. Stolbovoy, V.E. Filchikov, *Tech. Phys. Lett.* **38**, 26 (2012).