

## Properties of Coatings Deposited from Filtered Vacuum Arc Plasma with HEA Cathode

V.A. Belous<sup>1</sup>, S.A. Firstov<sup>2</sup>, V.F. Gorban<sup>2</sup>, A.S. Kuprin<sup>1\*</sup>, V.D. Ovcharenko<sup>1</sup>, E.N. Reshetnyak<sup>1</sup>,  
G.N. Tolmachova<sup>1</sup>, M.G. Kholomeev<sup>1</sup>

<sup>1</sup> National Science Center "Kharkov Institute of Physics and Technology", 1, Akademicheskaya Str.,  
Kharkov, Ukraine

<sup>2</sup> I. Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine,  
Kyiv, Ukraine

(Received 27 May 2013; published online 31 August 2013)

Ti-V-Zr-Nb-Hf metallic and nitride films were deposited by filtered vacuum arc plasma from a single equiatomic HEA cathode. The composition, microstructure, mechanical properties, thermal stability and corrosion properties were investigated.

The deposited metallic film has a two-phase structure with bcc and hcp-lattice. The nitride films were found to have only an fcc structure. All coatings have nano-grained structures, with grain sizes 5 nm for metallic and 36 nm for nitride. The nitride coatings have a compressive stress of around  $-12,5$  GPa, high hardness  $\sim 40$  GPa and elastic modulus  $\sim 450$  GPa. After annealing in vacuum in range 400-1200 °C, 3 h for every temperature, hardness decreased to 25 GPa. It was found that both the metallic and nitride coatings exhibited their best corrosion resistance than steel samples in a 3,5 wt. % NaCl solution. The metallic coatings showed better corrosion resistance than the nitride coatings.

**Keywords:** Filtered vacuum arc, High-entropy alloy, Nanostructured coatings, Hardness, Thermal stability, Corrosion.

PACS numbers: 81.15.Cd, 81.15. - z, 81.40.Cd,  
68.60.Dv, 81.65.Kn

## 1. INTRODUCTION

Ion plasma modification techniques commonly used to enhance the processing tool because of increasing the surface hardness, improved thermal stability and corrosion resistance. A coating on the basis of high entropy alloys (HEA) contained  $\geq 5$  elements in equiatomic ratio, which concept was proposed in [1], is one way to further improve the surface properties. HEA have high entropy of mixing, and as a result a minimum of Gibbs energy, which determines the stability of their structure, composition and high performance.

Implementation of this approach applied to the magnetron nitride coatings based on HEA showed that, depending on the partial pressure of nitrogen in an argon-nitrogen mixture can form coatings in an amorphous or single-phase crystal structure, such coatings also have high mechanical properties [2, 3]. These coatings may also be applied as diffusion barrier for copper metallization [4].

So far, the deposition of multi-component coating vacuum-arc method carries out several cathodes [5] or with the aid of a HEA cathode [6] without plasma filtering from the particles generated by the cathode spot.

The purpose of this paper is to study the structure and properties of coatings obtained from filtered vacuum arc plasma flow of one cathode, made from alloy of Ti-V-Zr-Nb-Hf.

## 2. EXPERIMENT

The coatings were deposited by vacuum arc method from filtered plasma flow [7] at substrate of steel 08Cr18Ni10Ti and steel (C: 0.14-0.12; Mn: 0.40-0.65;

Si: 0.12-0.30; S:  $< 0.055$ ; P:  $< 0.050$ , wt. %). The cathode of high entropy alloy system Ti-V-Zr-Nb-Hf was prepared by vacuum arc melting in an atmosphere of high purity argon. Arc current was  $\sim 122$  A, metal coatings were deposited at an argon pressure of 0.05 Pa and a substrate bias voltage  $U_b = -50$  V, nitride – at a nitrogen pressure of 0.3 Pa and a bias voltage of  $U_b = -100$  V.

Composition of the cathode and coatings was determined by EDX method on scanning electron microscope JSM-7001F and by X-ray fluorescence method. Morphology of the coatings investigated by SEM 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. Vacuum annealing at  $1 \cdot 10^{-3}$  Pa for 3 hours at temperatures of 400, 600, 800, 1000 and 1200 °C were proceed by to determine the thermal stability of coatings. Corrosion properties of the coatings were investigated by potentiodynamic method at IPC-Pro potentiostat in 3,5 % NaCl solution.

## 3. RESULTS AND DISCUSSION

### 3.1 Composition and Morphology of the Coatings.

The composition of metal coatings, as shown in Table 1, is somewhat different from the composition of

\* [kuprin@kipt.kharkov.ua](mailto:kuprin@kipt.kharkov.ua)

the cathode: reduced content of heavy elements and increased content of lighter. This is all about the metal plasma flow separation system. Multicomponent nitride is formed with almost equal ratio of metal and nitrogen components after nitrogen flooding into the vacuum chamber during deposition. In the nitride coating metal components ratio is also distinguished from the cathode. In this case, not only a separation of the metal components of the plasma is determine the coating composition, but its scattering by the gas target, as well as changes in the conditions of existence of the cathode spot on the surface of the cathode.

**Table 1** – The composition of the cathode and coatings.

Elements	The concentration of elements <i>at. %</i>		
	cathode	metallic coating	nitride coating
Ti	25	31,5	24
Zr	25	16,6	15
Nb	25	20,1	6
V	10	24,2	8,3
Hf	15	7,6	1,3
N	–	–	45,4

The morphology of the metal and nitride coatings surface according to SEM is characterized by the cellular structure (average cell size is  $\sim 3 \times 3 \mu\text{m}$ ), with a small amount of particulate matter, which is typical for coatings obtained by a stream of filtered vacuum arc plasma.

### 3.2 Coatings Structure

As follows from [6] the cathode is characterized by coarse-grained bcc-structure with a lattice parameter of 0.3358 nm, which is close to the value of 0.3315, calculated by Vegard's rule for solid solution of suitable composition.

Coatings prepared in argon atmosphere, according to the X-ray diffractometer geometry, unlike the cathode is likely not a single-phase. The coating main phase, as a cathode, is bcc solid solution with a strong structure and an axial texture with [100] axis in the direction normal to the coating surface. This phase has the intense and rather broad line (200), located near 55 degrees on the  $\theta$ - $2\theta$  coating diffraction pattern. The average crystallite size in the texture axis direction calculated from the broadening of the line by Scherrer formula is 5 nm. Value of the bcc crystal lattice period is  $0,3333 \pm 0,0005$  nm.

The second, more weak and broad line, available at X-ray diffraction near 40 degrees, dose not corresponds to the detected solid solution bcc not by the angular position nor by 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 is about 2 nm.

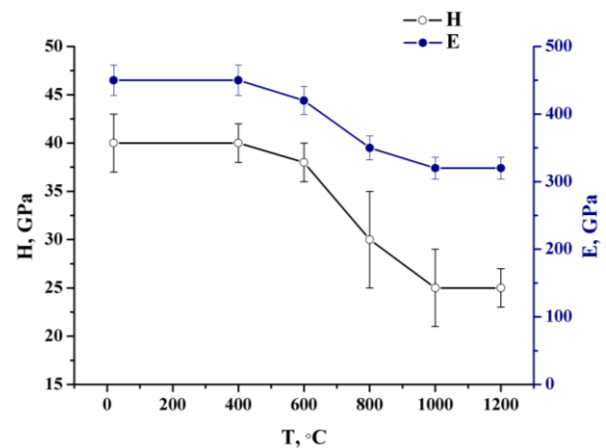
These results differ from the data [6], according to which arc evaporation of high entropy cathode system - Ti-V-Zr-Nb-Hf with bcc-crystal lattice in vacuum (residual atmosphere pressure is 0.0066 Pa), and without separation of the plasma stream, led to the formation of coatings with preserved single-phase, i.e., bcc-lattice and strong texture with the [110] direction.

In the coating, received in a nitrogen atmosphere, formed textured fcc single phase structure. At coating diffraction pattern can be seen a quite narrow and very intense lines of this phase type (hhh). Rocking curve of (111) reflection indicates that the coating is formed with an [111] axis axial texture in the direction normal to the substrate surface, and a texture scattering angle of  $10^\circ$ . An X-ray coating tensometry revealed high compressive residual stress. Stresses calculated for Young's modulus  $E = 450$  GPa (the result of nanoindentation) and Poisson's ratio  $\nu = 0,2$  [8] are 12,5 GPa. In a relaxed cross-section fcc crystal lattice period, equal to  $(0,4385 \pm 0,0003)$  nm within the measurement error, matches on the same value 0.4389 nm calculated by Vegard's rule for a solid solution of the corresponding nitrides. Crystallite size of this phase is about 36 nm.

In the nitride coating annealing process observed recrystallization, wherein the phase composition of the coating is not changed, and the level of residual stress is reduced to  $-1,8$  GPa.

### 3.3 Hardness and Thermal Stability of Coatings

The hardness of the metal coating is  $H = 9$  GPa and Young's modulus  $E = 120$  GPa, which corresponds to the values of bulk high entropy alloys [9] and magnetron coatings obtained in an argon atmosphere [10].



**Fig 1** – Hardness and Young modulus of the coatings as a function of annealing temperature

The coating obtained in a nitrogen atmosphere, has a higher hardness  $\approx 40$  GPa and a Young's modulus  $\approx 450$  GPa, which are usual for titanium nitride and niobium deposited by vacuum-arc method. One of the factors affecting this coating hardness is a high internal compressive stress value. Reduction of hardness and Young's modulus after vacuum annealing begins at temperatures above 600 °C, due to relaxation of internal stresses in the coating and the start of recrystallization.

When the annealing temperature is 1000-1200 °C the hardness and Young's modulus are at 25 and 320 GPa, respectively.

### 3.4 Corrosion resistance.

Potentiodynamic tests results are shown in Fig. 2. The graph shows that the corrosion potentials of coated steel is higher than the potential of the original substrate.

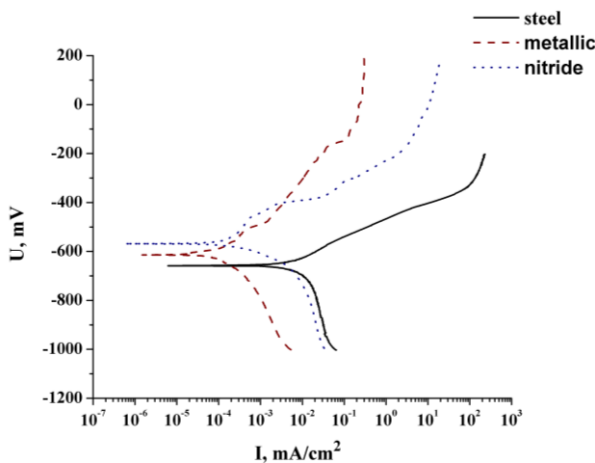


Fig. 2 – Corrosion resistance of coatings in a solution of 3,5 % NaCl

Extrapolation of the potentiodynamic curves cathodic part shows the influence of the type of coating on the steel corrosion rate (Table 2).

Table 2 – Data from polarization corrosion tests

Sample	$U_{corr}$ , mV	$I_{corr}$ , mA/cm <sup>2</sup>
steel	- 658	$1,5 \cdot 10^{-5}$
metallic coating	- 614	$3 \cdot 10^{-7}$
nitride coating	- 568	$6 \cdot 10^{-6}$

Despite the fact that the corrosion potential of a nitride coating above the corrosion potential of the metal coating, the corrosion rate in the last less than an order

of magnitude. This fact suggests that the metal coating is obtained in an argon atmosphere more corrosion-resistant. The reason for the reduced corrosion resistance of nitride coating over the metal can be very high internal stresses which cause accelerated corrosion under stress.

4. CONCLUSIONS

Applying of metal and metal nitride filtering plasma deposition coatings using cathode of high entropy alloy Ti-V-Zr-Nb-Hf significantly improves the surface morphology, but leads to a slight change in the composition of the condensate.

A metallic coating deposited in such conditions is not likely phased. Along with the bcc-structured solid solution a hcp-lattice solid solution is formed therein. In the nitride coatings a single-phase fcc-textured structure with a high compressive residual stress (12,5 GPa) is formed.

The metal coating has typical mechanical properties of such alloys ( $N = 9$  GPa,  $E = 120$  GPa). Nitride coating is characterized by high hardness  $H = 40$  GPa, which remains stable during vacuum annealing up to 600 °C and decreased to 25 GPa at 1200 °C, which is followed from a decrease in internal stress and recrystallization processes.

The metal coating has higher corrosion resistance compared to nitride one and a 1,5-order decrease the corrosion rate of steel in solution 3,5 % NaCl.

REFERENCES

1. Y.Y. Chen, U.T. Hong, J.W. Yeh, H.C. Shih, *Scr. Mater.* **54**, 1997 (2006).
2. Ping-Kang Huang, Jien-Wei Yeh, *Surf. Coat. Technol.* **203**, 1891 (2009).
3. H.W. Chang, P.K. Huang, J.W. Yeh, A. Davison, C.H. Tsau, C.C. Yang, *Surf. Coat. Technol.* **202**, 3360 (2008).
4. S.Y. Chang, M.K. Chen, *Thin Solid Films* **517**, 4961 (2009).
5. I.V. Blinkov, A.O. Volkhonskiy, V.N. Anikin, M.I. Petrjik, D.E. Derevcova, *Phys. Chem. Mater. Treatment* No 4, 37 (2010). [in Russian].
6. O.V. Sobol', A.A. Andreev, V.F. Gorban', N.A. Krapivka, et al., *Tech. Phys. Lett.* **38**, 41 (2012).
7. I.I. Aksenov, V.M. Khoroshikh, *Proc. TATF'98*, 283 (Regensburg, Germany: 1998).
8. G. Abadias, *Surf. Coat Technol.* **202**, 2223 (2008).
9. S.A. Firstov, V.F. Gorban, N.A. Krapivka, et al., *Sovremenny problemy fizicheskogo materialovedenya: Sb. nauchn. tr.* **18**, 140 (K.: IPM NAS Ukraine: 2009). [in Russian].
10. Ming-Hung Tsai, Chia-Han Lai, Jien-Wei Yeh, Jon-Yiew Gan, *J. Phys. D: Appl. Phys.* **41**, (2008).