

Structure and Morphology of Nitride Coating (TiHfZrVNb)N After Thermal Annealing 600°C

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This study reports the influence of thermal annealing 600 °C on the characteristics of the (TiHfZrVNb)N coatings prepared by vacuum arc melting at different deposition conditions. The crystal structures, surface's morphology were characterized by X-ray diffraction and atomic force microscopy. The results indicate that nitride coatings based on high-entropy alloy TiHfZrVNb have *fcc* crystal structure. It is shown that the nitride coatings (TiHfZrVNb)N have a good resistance to oxidation during thermal annealing 600 °C.

Keywords: High-entropy alloys, Thermal annealing, Vacuum arc coating, Nitride, Surface roughness.

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1. INTRODUCTION

One of the major aspects of technical progress is the development of fundamentally new materials with the required distinct physico-chemical properties or the same combination of properties [1-3]. High-entropy alloys (HEAs) are defined as alloys that have at least five principal elements with the concentration between 5 at.% and 35 at.% [4]. Studies have shown that HEAs possess high mixing entropy, lattice distortion, sluggish diffusion and cocktail effect. The new class of metal compounds usually forms simple solid solution structures rather than many complex phases. These alloys have a number of useful properties such as high strength, good resistances of wear, oxidation and others. Based on this concept, nitrides derived from HEAs have a great potential use as protective coatings. Thus the preparation and investigation the structure and properties of nanostructured coatings (TiHfZrVNb)N based on high-entropy alloys is an actual problem of material science [5].

2. EXPERIMENTAL PROCEDURE

The cathodes of the high-entropy alloys TiHfZrVNb was prepared by vacuum arc melting in an atmosphere of high purity Ar. Repeated melting for at least 7 times was carried out to improve chemical homogeneity of the alloys. The (TiHfZrVNb)N nitride coatings were deposited with cathode-vacuum arc method at the "Bulat-6" plant at a substrate bias (-40 – -200) V and the residual gas pressure 0.0066 Pa. The crystal structures of the deposited coatings were characterized by X-ray diffraction (DRON-3M diffractometer and Rigaku RINT – 2500 – MDG Japan) with Cu-K α radiation. Atomic force microscope (AFM, AFM Objective) was used to evaluate the surface morphology and roughness of the coatings.

3. RESULTS AND DISCUSSION

Selection of the constituent elements was based on the properties of individual binary nitride and the crucial role played type of crystal lattice. Ti was selected as constitu-

ent, since TiN have been widely used as a protective coatings due to the excellent physical and mechanical characteristics. To further improve thermal stability, oxidation and corrosion resistance and lower friction coefficient Hf, Zr, Hb and V were incorporated into cubic nitride structure.

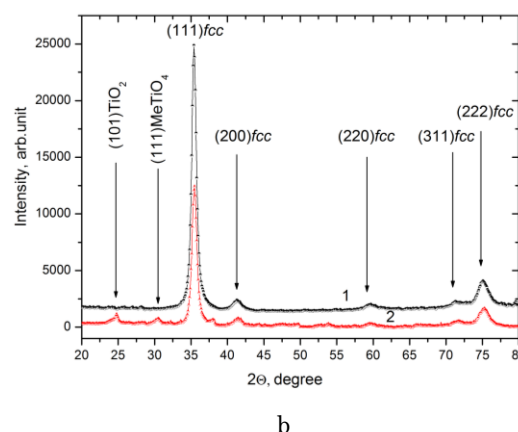
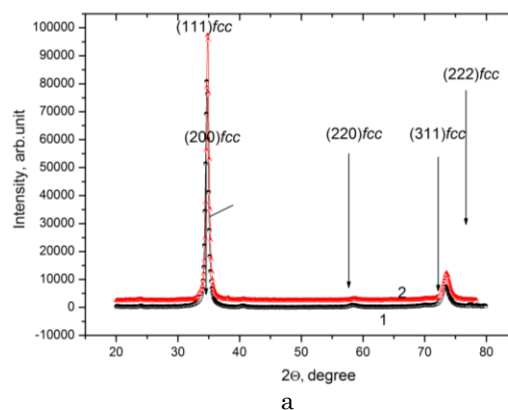


Fig. 1 – X-ray diffraction pattern of the (TiHfZrVNb)N coatings deposited at various conditions: a) $P_N = 0.7$ Pa, $U_b = -200$ V; b) $P_N = 0.1$ Pa, $U_b = -100$ V; 1) before thermal annealing 600°C; 2) after thermal annealing 600°C

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Refractory composites Hf, Zr and Ti in virtue of its high affinity for nitrogen together with stabilizing a bcc lattice V and Nb determine the possibility of creating nitride phase based on high-entropy alloy.

The XRD patterns of (TiHfZrVNb)N coatings deposited at various deposition condition, before and after thermal annealing 600°C can be evaluated at Fig. 1.

As we can see from Fig. 1 the (TiHfZrVNb)N coatings have a *fcc* crystal structure. The coatings presented strong (111) and relatively weak (222) orientation. According to X-ray tensometry, the lattice parameter in a relaxed sample cross-section is equal to 0,442 nm and 0,438 nm, respectively [6]. This growth can be attributed to the lattice parameter due to higher working pressure during deposition the coating of the sample 1 and the correspondingly high concentration of nitrogen. The effect of thermal annealing 600°C on the structure of the (TiHfZrVNb)N coatings also show in Fig. 1. In the case of the samples of series 1, no structural phase changes were observed. Thermal annealing is only slightly reduced the stress-strain state of coating from -2.76% to -2.59%. In the case of the samples of series 2,

thermal annealing led to the formation of oxide type TiO_2 , ZrTiO_4 and HfTiO_4 . The driving forces from nitride to oxide are different for different elements. For example, TiN, ZrN and HfN have the relatively strong tendency for oxidation, which means, some elements tend to form oxides such as TiO_2 , ZrTiO_4 and HfTiO_4 [7]. At the same time, there is a decrease of compression strain state from -1.9% to -0.7%.

The AFM images and surface roughness (root-mean-square) of the (TiHfZrVNb)N nitride coatings after thermal annealing 600°C are presented in Fig. 2.

For the description of surface roughness using number of statistical characteristics: maximum vertical drop, the surface roughness (mean square value of height) etc. For the samples of series 1, maximum vertical drop reaches 1.144 μm , roughness $R_{\text{ms}} = 110 \text{ nm}$. For the coating deposited under different deposition parameters (samples of series 2) maximum vertical drop reaches 0.975 μm , roughness $R_{\text{ms}} = 85 \text{ nm}$.

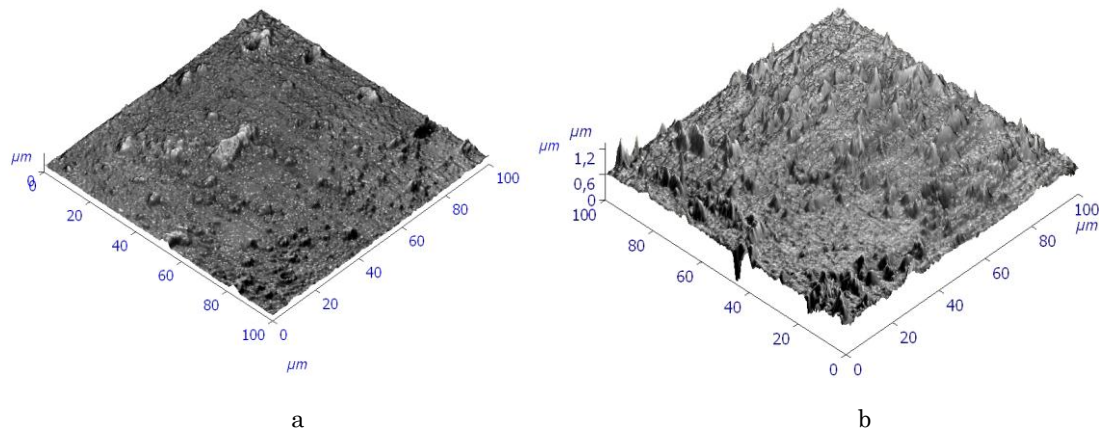


Fig. 2 – Typical AFM images of the (TiHfZrVNb)N coatings after thermal annealing 600°C: a) $P_N = 0.7 \text{ Pa}$, $U_b = -200\text{V}$; b) $P_N = 0.1 \text{ Pa}$, $U_b = -100 \text{ V}$

4. CONCLUSION

In summary the (TiHfZrVNb)N coatings have a simple solid-solution structure that is nanocrystalline. Obviously the greater incorporation of elements with different atomic size in the (TiHfZrVNb)N coatings is believed to result in greater mixing entropy

and severe lattice distortion, which leading to the development of nanosized crystalline grains. Both coatings exhibit good resistance to oxidation. However, the lower nitrogen content and low oxygen diffusion at the 2-d series lead to structural changes in the coating phase.

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