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The Effect of Constant and High Voltage Pulse Bias Potentials on the Structure and Properties of Vacuum-Arc (TiVZrNbHf)N_x Coatings

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The effect of constant (U_b) and high voltage pulse (U_{ip}) bias potentials supplied to the substrate during condensation, on the structure and properties of vacuum-arc (TiVZrN-Hf)N_x coatings has been studied. It has been determined that the number and size of the drop phase decreases with increasing U_b. The use of U_{ip} promotes a more uniform growth in the coating volume. It is shown that due to the increase of U_b from 0 to 200 V in nitride coatings of high entropy alloys, it is possible to change the growth texture [100] to [111]. This results in increased hardness from 32 GPa to 49 GPa. The supply of high voltage potential in a pulse form leads to a relative decrease in the average size of crystallites and the formation of a bi-texture state.

Conditions and mechanisms of the preferential crystallites orientation (axial texture) of vacuum arc (TiVZrNbHf)N_x coatings and texture influence on mechanical properties have been discussed.

Keywords: Vacuum arc, (TiVZrNbHf)N_x, Structural engineering, Bias potential, Pulse potential, Phase composition, Structure, Hardness.

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1. INTRODUCTION

Presently, structural engineering is the main method for creating materials with high functional properties [1]. This is due to a significant increase in the ability to manage the structural state in nonequilibrium conditions inherent in modern methods of obtaining materials. Based on structural engineering, the highest mechanical properties were achieved for coatings obtained by ion-plasma and vacuum arc methods [2, 3]. To achieve high functional properties in mononitride coatings, two methods are used. The first is based on creating a composite material with a "useful impurity" (to enhance the intergranular (intercrystalline) bond) at grain (crystallites) boundaries [4]. The second is based on modification of the elemental composition and the structural state of the coating crystallites by creating new (nonequilibrium) phases [5], obtaining highly supersaturated solid solutions [1] and composite materials formed by spinodal decomposition [6, 7]. Optimizing properties by changing the elemental composition tends to increase the number of constituent elements. At present, five or more elements have already been used for structural engineering [8, 9]. Such systems based on transition metals are called high entropy alloys [10, 11]. Coatings based on high entropy alloys significantly increase the entire complex of mechanical properties (hardness [12-14], adhesion strength [15], wear resistance [16], resistance to aggressive atmosphere [17], etc.). At the same time, high characteristics were achieved and remained stable up to large (above 1300 °C) temperatures [18]. The highest mechanical characteristics were achieved for vacuum arc coatings based on highentropy alloys nitrides [18]. It was found that one of the determining factors for achieving high properties is the formed texture (preferential orientation of the crystallites). An effective method for controlling the orientation of the crystallites growth using vacuum arc method for obtaining nitride coatings is to supply a bias potential to the substrate [19]. Technological features of the vacuum-arc method for obtaining coatings have two types of potential supply: in constant mode and in high voltage pulse form [20].

It is known that supplying a negative bias potential to a substrate during deposition makes it possible to largely get rid of the main drawback of the vacuum arc method of coating production - the presence of atoms clustering in the form of a drop phase in the material formed [20].

The use of high voltage potentials in pulse form is an effective way of stress relaxation, change in the size and orientation of crystallites [21, 22]. It is shown that such an influence leads to the atoms ordering in the crystal lattice and to decrease in the stress-strain state [22].

The combination of two types of bias potentials in one deposition process is expected to significantly expand the possibilities of structural engineering. To that end, the effect of constant bias potential (U_b) in combination with high voltage pulse potential (U_{ip}) during formation of vacuum-arc nitride coatings based on the highentropy Ti-V-Zr-Nb-Hf alloy has been studied.

2. SAMPLES AND METHODS OF RESEARCHES

Samples were obtained by vacuum-arc evaporation in the "Bulat-6"unit. The ingots from the high entropy alloys of the Ti-V-Zr-Nb-Hf systems were made by vacuum arc melting in high-purity argon atmosphere

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[23]. The melting was carried out by a non-consumable tungsten electrode in a copper water-cooled subcase. The resulting ingots were melted 6-7 times to homogenize the composition. The ingots were cooled at the speed of 50 K/s. Later on, the thread was cut to secure the ingot in the form of a vacuum arc evaporator cathode in the upper part of the ingot with a diameter of 60 mm. The polished plates with dimensions $20 \times 20 \times 3$ mm of stainless steel 12Kh18H9T, as well as copper foil 0.2 mm thick, were used as a substrate. Coatings deposition was carried out without supplying and when a constant negative potential $U_b = -200$ V was supplied to the substrate. The nitrogen pressure during deposition was 0.66 Pa. The deposition rate was about 1.5 nm/s. In addition to the constant negative potential, a high voltage pulse potential of -2000 V with pulse duration of 10 μs and a frequency of 7 kHz was supplied.

The structural-stressed state was studied on a DRON-3M diffractometer in Cu-K_α radiation. To monochromatize the detected radiation, a graphite monochromator was used and installed in a secondary beam (in front of the detector). The study of the phase composition, structure (texture, substructure) was carried out using traditional X-ray diffractometry methods by analyzing the position, intensity and shape of the diffraction reflection profiles. To processing the diffractograms, the tables of the international diffraction data center Powder Diffraction File were used.

Microindentation was carried out at the “Micron-gamma” unit [24] at a load up to $F = 0.5N$ with a Berkovich diamond pyramid with an angle of 65°, with automatic loading and unloading for 30 seconds.

3. RESULTS OF COATINGS STRUCTURE AND PROPERTIES STUDYING

The structure of cathode evaporating from the highentropy alloy is shown in Fig. 1. It can be seen that even after repeated homogenization melts the structure remains dendritic.

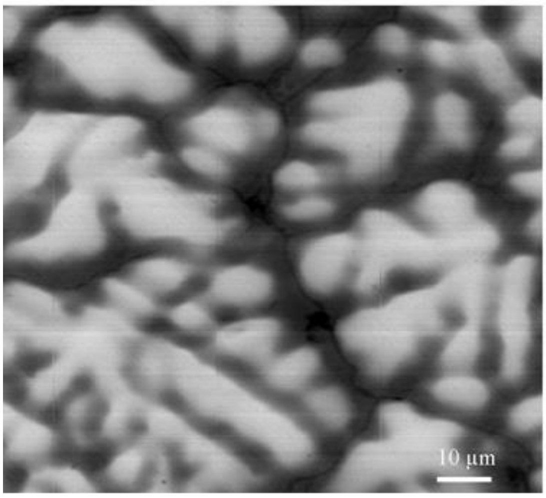
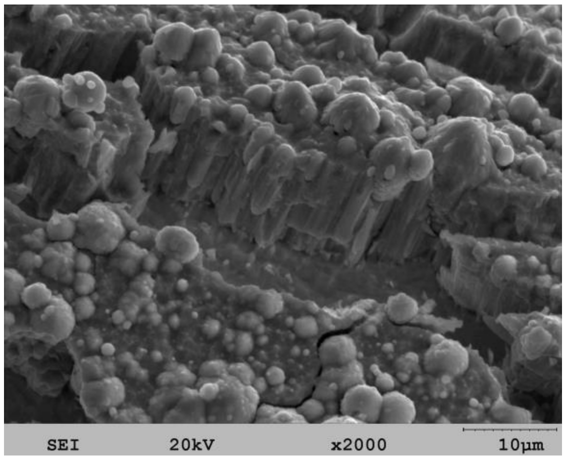
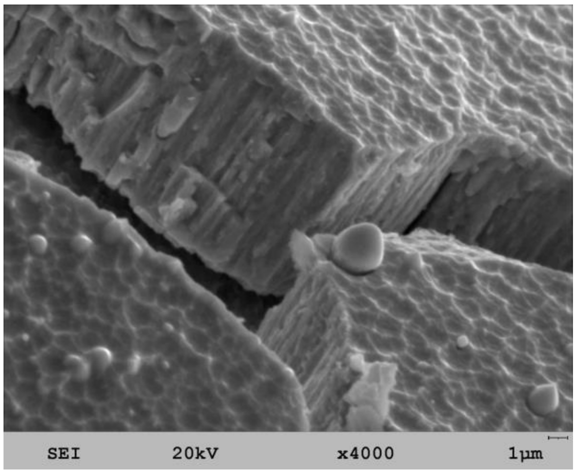


Fig. 1 – Highentropy alloy ingot used as a cathode

High-resolution scanning electron microscopic images show that without the supply of constant and high-voltage pulse potentials, a large amount of a drop phase (mainly from low-melting-point metals) is observed in the coating (Fig. 2a).



a



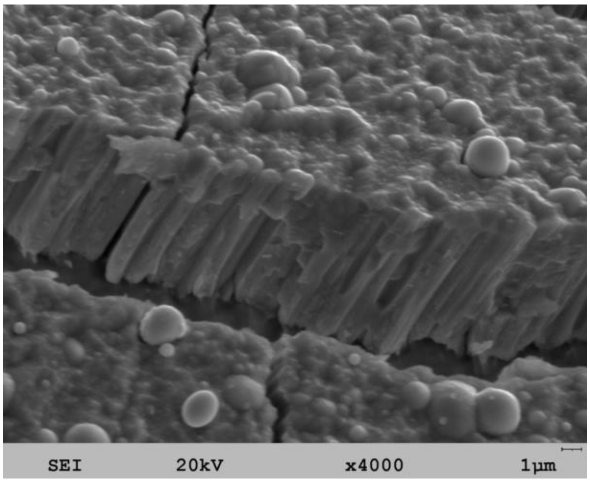
b

Fig. 2 – Scanning electron microscopic images of surface morphology and lateral cross-section of coatings obtained without a constant bias potential (a) and at $U_b = -200$ V (b)

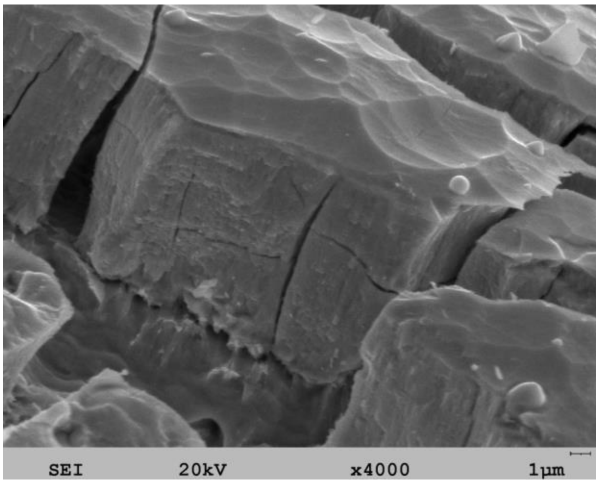
The drop phase is both on the surface of the coating and in its volume. The supply of a constant potential $U_b = -200$ V to the substrate during deposition significantly reduces the drop phase content, both in the volume and on the coating surface (Fig. 2b). This reduces both the average amount and the average size of the drop phase. Thus, uniformity (distribution efficiency) of the composition and structure of the coating increases at $U_b = -200$ V.

The supply of U_{ip} without U_b leads to good uniformity in the coating volume, but to a large drop phase content on the surface (Fig. 3a). Coatings are practically formed without drops when U_{ip} and $U_b = -200$ V are combined (Fig. 3b).

Thus, the influence of constant potential on the coating morphology is the determining factor. The use of U_{ip} contributes to a more uniform morphology of growth in the coating volume.



a



b

Fig. 3 – Scanning electron microscopic images of surface morphology and lateral cross-section of coatings obtained at U_{ip} = – 2000 V without constant bias potential (a) and at U_b = – 200 V (b)

Analysis of the phase composition, structure and substructure of the formed coatings was carried out on the basis of XRD studies results. Figure 4 shows the diffraction spectra of the coatings obtained at $U_b = 0$ and U_b = – 200 V, and Figure 5 shows the same U_b, but under U_{ip}

As can be seen from the spectra obtained at $U_b = 0$ (without U_{ip}), coatings with a predominant orientation {100} are formed (Fig. 4, spectrum 1). The supply of U_b leads to the appearance of the second type of crystallite orientation with the texture axis [110] (Fig. 5, spectrum 1). The supply of U_b = – 200 V in both cases leads to the formation of crystallites preferential orientation with the axis [111] (Figures 4 and 5, spectra 2). The increase in the width of diffraction reflexes is a feature of coatings structure with supplying U_{ip}. This change is associated with a decrease in the crystallites average size.

The crystallites size (determined from the data on the width change of the diffraction reflections) without U_{ip} supply was about 55 nm (at $U_b = 0$) and 80 nm (at

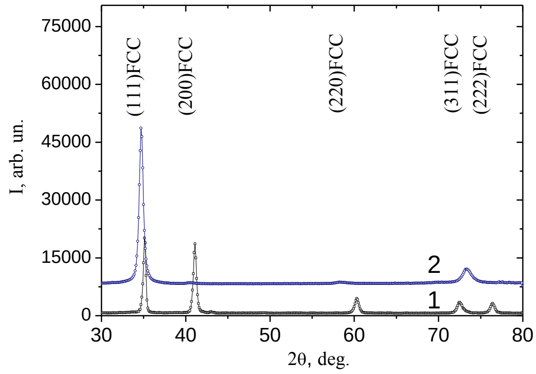


Fig. 4 – XRD patterns of coatings of highentropy alloys nitrides obtained without a constant bias potential (1) and at U_b = – 200 V (2)

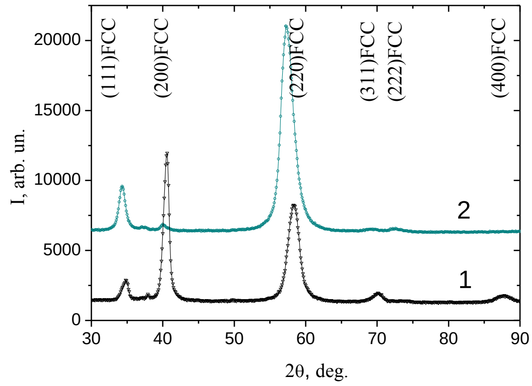


Fig. 5 – XRD patterns of coatings of highentropy alloys nitrides obtained by pulse action with U_{ip} = – 2000 V: 1 – without a constant bias potential, 2 – at U_b = – 200 V

U_b = – 200 V). At the same time microstrain value was 0.6-0.65 % for all U_b.

When U_{ip} was used, the average crystallite size decreased to 16 nm (at $U_b = 0$) and 34 nm (at U_b = – 200 V).

Macrostrain value in the coatings obtained without U_{ip} was – 1.15 % (at $U_b = 0$) and – 2.67 % (at U_b = – 200 V) and was determined by the crystalline groups method [25]. The minus sign showed that the strain had a compression type [2]. In this case, the lattice period in the unstressed section ($\sin^2\psi_0 = 2\mu/(1 + \mu) \approx 0.4$, where μ is the Poisson coefficient of the coating material) increased from 0.434 nm to 0.4426 nm with increasing U_b (without U_{ip}).

The supply of U_{ip} leads to higher values of macrostrain: – 1.47 % (at $U_b = 0$) and – 3.6 % (at U_b = – 200 V). In this case, the lattice period in the unstressed section increased from 0.443 nm to 0.447 nm. The relatively large values of the lattice period were obtained, which cannot be explained only by a composition change (since the composition remained fairly close for all types of coatings obtained, but with a large Hf content, about 44 % by volume). Therefore, the lattice period increase in the unstressed section can be explained by implantation processes. A very large macrostrain of compression (reaching, as noted above, – 3.6 %) is also due to the implantation of accelerated particles during coating formation [15].

The study of physical and mechanical

characteristics of coatings was carried out by the microindentation method. The results of the hardness measurements showed that without U_{ip} and U_b supply, the coatings hardness is relatively small. The average hardness value is 31 GPa. At the same time, a wide range of results is observed, which can be related to the large coatings uniform due to the drop phase. The supply of $U_b = -200$ V and texture formation with the axis [111] leads to an increase in the coating hardness to 49 GPa.

The use of U_{ip} during coating deposition, as noted above, stimulates texture formation with an axis [110]. Thus, at $U_b = 0$ a biaxial texture [100] + [110] is formed, and at $U_b = -200$ V a texture [111] + [110] is formed. The formation of a biaxial texture affects coatings hardness. At $U_b = 0$ the average coatings hardness is 37 GPa, and at $U_b = -200$ V the hardness reaches 47 GPa.

4. RESULTS DISCUSSION

As can be seen from the results obtained, the use of U_b and U_{ip} makes it possible to substantially influence the preferential orientation of crystallite growth. There are two factors for this: energy increase (as well as the kinetic factor [5]) during atoms condensation and displacement cascades formation.

Ions are accelerated in the field of a constant negative bias potential, the magnitude of which is relatively small (up to -200 V) and do not stimulate displacement cascades formation. U_b potential leads to an increase in the ions kinetic energy, sufficient to create energetically favorable structural states on the growth surface and partial implantation in the near-surface layers.

The pulse form of the high voltage potential leads to a relatively short exposure time (with a pulse duration of 10 μs and a frequency of 7 kHz, the exposure time is about 8 % of the total time), which reduces the effectiveness of the effect on the particles surface mobility during their condensation. However, a large energy (for single-charged ions this is an average energy of 2000 eV) leads to displacement cascades formation ("thermal peaks"). The annihilation of defects created in displacements cascades (in the "thermal peaks" areas) leads to the combination of relaxation processes with the formation process of structural imperfections.

The analysis results of the structural state of coatings obtained without U_b and U_{ip} have shown that a texture with an axis [100] appears during the formation of $(TiVZrNbHf)N_x$ condensates. The supply of the bias potential U_b leads to the formation of a preferential orientation of crystallite growth with the axis [111]. And under the influence of high voltage pulses, the predominant growth of crystallites occurs with the texture axis [110].

Figure 6 shows the planes crystallography of the corresponding texture axes. It can be seen that the formation of the texture axis [100] (that is, family of planes {100} parallel to the growth surface) is typical for four atomic nucleation (Figure 6a) with relatively low diffusion mobility of atoms [1]. The formation of such a plane parallel to the growth surface provides the greatest specific density of surface energy per atom [4].

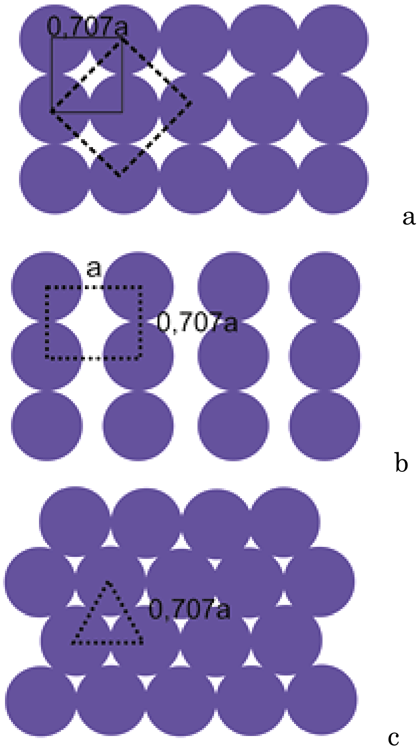


Fig. 6 – Arrangement of atoms for the FCC structure: (a) plane {100}, (b) plane {110}, and (c) plane {111}.

Texture formation with an axis [111] with the highest packing density of atoms (Figure 6c) is typical for the predominant influence (on minimizing the surface energy) of the deformation factor [7]. This determines the appearance of such a texture at the largest $U_b = -200$ V, when ion implantation leads to a large deformation of the crystal lattice.

The texture with the axis [110] (and, correspondingly, with the family of planes {110} parallel to the growth surface (Fig. 6b)) corresponds to the formation of a strong 2-atom bond. This is typical for the formation of crystallites nuclei under the action of relaxation processes in displacements cascades [15].

Comparison of the obtained structural states with the results of mechanical tests shows that the bi-texture state [111] + [110] leads to the highest hardness in the joint action of U_b and U_{ip}. Considering a uniaxial texture, the greatest hardness is achieved when the most densely packed planes with the texture axis [111] are parallel to the surface.

5. CONCLUSION

1. The use of a negative bias potential supplied to the substrate during coating formation makes it possible to control the growth surface morphology, the size and the preferential orientation of the crystallites.

2. With increasing U_b, the number and size of the drop phase decreases. The use of U_{ip} promotes more uniform growth morphology in the coating volume.

3. By increasing the U_b from 0 to 200 V in the nitride coatings of high entropy alloys, the growth texture [100] can be changed to [111]. This leads to an

increase in hardness from 32 GPa to 49 GPa.

4. The supply of a high voltage potential in a pulse form leads to a relative decrease in the crystallites average size and the formation of a bi-texture state.

5. The formation of the bi-texture state under the combined action of U_b and U_{ip} is based on two mechanisms for the formation of predominantly oriented crystallites: 1) the growth texture under the action of a constant potential ([100] or [111], depending on the value of U_b);

6. The texture [110] which is determined by the radiation-stimulated action when bombarded with high-energy ions and displacement cascades formation.

Вплив постійного і високовольтного імпульсного потенціалів зміщення на структуру і властивості вакуумно-дугових (TiVZrNbHf)N_x покриттів

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Досліджено вплив постійного (U_b) і високовольтного імпульсного (U_{ip}) потенціалів зміщення, що подаються на підкладку при конденсації, на структуру і властивості вакуумно-дугових (TiVZrNbHf)N_x покриттів. Встановлено, що зі збільшенням U_b зменшується число і розмір крапельної фази. Використання U_{ip} сприяє однорідної морфології зростання в об'ємі покриття. Показано, що за рахунок збільшення U_b від 0 до 200 В в нітридних покриттях високоентропійних сплавів можна змінити текстуру росту [100] на [111]. Це призводить до збільшення твердості від 32 ГПа до 49 ГПа. Подача високовольтного потенціалу в імпульсній формі призводить до відносного зменшення середнього розміру кристалітів і формуванню бітекстурного стану.

Обговорено умови і механізми формування переважної орієнтації кристалітів (аксіальної текстури) вакуумно-дугових (TiVZrNbHf)N_x покриттів і вплив текстури на механічні властивості.

Ключові слова: Вакуумна дуга, (TiVZrNbHf)N_x, Структурна інженерія, Потенціал зміщення, Імпульсний потенціал, Фазовий склад, Структура, Твердість.

Влияние постоянного и высоковольтного импульсного потенциалов смещения на структуру и свойства вакуумно-дуговых (TiVZrNbHf)N_x покрытий

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Изучено влияние постоянного (U_b) и высоковольтного импульсного (U_{ip}) потенциалов смещения, подаваемых на подложку при конденсации, на структуру и свойства вакуумно-дуговых (TiVZrNbHf)N_x покрытий. Установлено, что с увеличением U_b уменьшается число и размер капельной фазы. Использование U_{ip} способствует однородной морфологии роста в объеме покрытия. Показано, что в результате увеличения U_b от 0 до 200 В в нитридных покрытиях высокоэнтропийных сплавов можно изменить текстуру роста [100] на [111]. Это приводит к увеличению твердости от 32 ГПа до 49 ГПа. Подача высоковольтного потенциала в импульсной форме приводит к относительному уменьшению среднего размера кристаллитов и формированию битекстурного состояния.

Обсуждены условия и механизмы формирования преимущественной ориентации кристаллитов (аксиальной текстуры) вакуумно-дуговых (TiVZrNbHf)N_x покрытий и влияние текстуры на механические свойства.

Ключевые слова: Вакуумная дуга, (TiVZrNbHf)N_x, Структурная инженерия, Потенциал смещения, Импульсный потенциал, Фазовый состав, Структура, Твердость

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