

The Analysis of Elemental Composition and Depth Profiles of Nitride Nanostructured Coating Based on the TiHfVNbZr High-entropy Alloy

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The elemental and structural features of the nitride nanostructured coating produced by vacuum arc evaporation from high-entropy cathode TiHfVNbZr were studied. Using of the complementary methods of elemental analysis (RBS, SIMS and GDMS) allowed to carry out a comprehensive analysis of the elemental composition, namely to determine the chemical composition of the surface layer, to establish the characteristics of the distribution of elements in depth and to identify uncontrollable impurities.

Keywords: High-entropy alloy, Nitride coating, Depth profiles, Elemental composition, Ion beam technique.

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1. INTRODUCTION

High-entropy alloys a newly developed alloy system containing at least five principle elements with atomic concentration between 5 % and 35 % for each element. This approach to the formation of alloys is fundamentally new, the first serious studies have been started since 1995 year [1]. These materials have potential as coating system for many applications, for example manufacturing of tools, molds and other mechanical parts [1, 2]. Therefore the preparation of nitride coatings, based on the high-entropy alloys, has received considerable interest as hard coatings owing to their excellent mechanical properties [1-4].

Recent publications suggest that adhesion and mechanical properties of protective coatings depend on both atomic concentration and depth distribution of constituent elements. It is also known, that the light elements, especially hydrogen and oxygen have a great influence on the physical and chemical properties of protective film. Thus the investigation of elemental composition of such coatings requires the application of several methods, which provide a sufficiently high elemental sensitivity and the locality of depth analysis. These requirements are met the RBS, SIMS and GDMS analysis techniques [5-7].

The aim of this work is to analyze distribution of elements and contaminations in the films, using the complementary methods of elemental analysis.

2. EXPERIMENTAL

The cathodes of high-entropy alloy TiHfVNbZr were prepared by vacuum arc melting in an atmosphere of high purity argon. The melting was performed using a nonconsumable tungsten electrode into a copper water-cooled crucible. Repeating melting for at least 7 times with a cooling rate 50 K/s was carried out to improve chemical homogeneity of the alloys [8].

The coating was deposited on steel substrate by cathode-vacuum-arc method in a Bulat-6 setup [8] at a

substrate bias $U_s = 100$ V and the current arc did not exceed 85 A. The substrate was heated to 400 °C before deposition. The deposition rate was set at 1.5 nm/sec.

The elemental composition of the (Ti-Hf-Zr-V-Nb)N coating and surface morphology were determined using a scanning electron microscope with EDS-analysis JEOL-7000F (Japan) and JSM-6010LA InTouchScope. To perform the elemental analysis in the depth of the coating, we employed the Rutherford backscattering (RBS) method with He⁺ ions of 1.7 MeV at normal incidence (the scattering angle was $\theta = 170^\circ$). The energy resolution of ion detector was 17 keV. The dose of helium ions was 5 μ Ci. The standard SIMNRA software [9] was used for processing RBS spectra and obtains profiles of elements distribution in depth of the coating.

One of the effective methods of investigation of depth profile ion sputtering techniques: secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS) [10-14]. For GDMS analysis we used DC 1.8 kV cathode voltage and 0.2 Torr Ar pressure. GDMS analyser SMWJ-01 [15] is equipped with SRS-300 quadrupole mass analyser with 6 mm diameter rods. For SIMS depth profile analysis we used Ar⁺, 3 keV, 1.5 μ A ion beam. SIMS analyser SAJW-05 [16] is equipped with Physical Electronics 06-350E ion gun and QMA-410 Balzers quadrupole mass analyser with 16 mm diameter rods.

3. RESULTS AND DISCUSSION

Fig. 1 shows the result of studies of the surface, which were obtained using SEM. As we can see from Fig. 1 the droplet fraction with a size of 10-15 μ m have been formed on the surface of nitride coating during the deposition process.

The presence of the droplet fraction is the major disadvantages for the coatings produced by cathodic-vacuum-arc deposition. One of the effective methods to reduce the number and size of macroinclusions is the production of nitride coatings, operating at a sufficiently high nitrogen pressure [17]. Wherein the cathode

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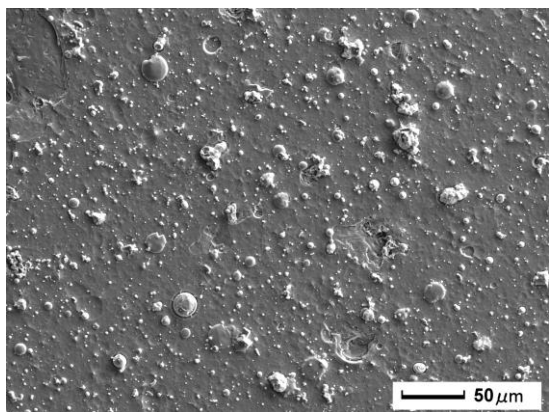


Fig. 1 – SEM image of $(\text{Ti}_{0.25}\text{Hf}_{0.1}\text{V}_{0.04}\text{Nb}_{0.08}\text{Zr}_{0.07})\text{N}_{0.45}$ coating obtained at $P_N = 3 \times 10^{-2}$ Pa, $U_b = 100$ V

surface becomes nitrided, thus forming a surface layer has a high melting point, which reduces the current per cathode spot.

Fig. 2 shows the XRD patterns of $(\text{TiHfVNbZr})\text{N}$ coating deposited at $P_N = 3 \times 10^{-2}$ Pa and $U_b = 100$ V.

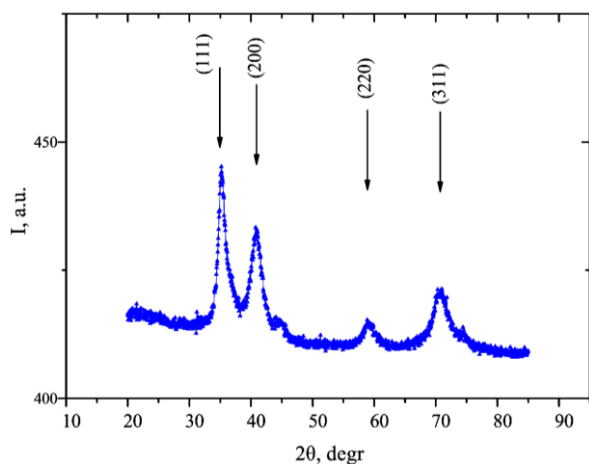


Fig. 2 – XRD spectra of $(\text{Ti}_{0.25}\text{Hf}_{0.1}\text{V}_{0.04}\text{Nb}_{0.08}\text{Zr}_{0.07})\text{N}_{0.45}$ coating obtained at $P_N = 3 \times 10^{-2}$ Pa, $U_b = 100$ V

For nitride coating, only XRD lines belonging to 111, 200, 220 and 311 reflection from fcc lattice (Na-Cl type) are evidenced. It should be noted that, the position of these lines lies between those corresponding to binary nitrides. Also in the present nitride system each binary nitride TiN, HfN, VN, NbN and ZrN have the cubic of sodium chloride (NaCl) phase. As we can see from Fig. 2 the (111) peak position of $(\text{TiHfVNbZr})\text{N}$ coating was measured at 35.8° which matched with the average value of binary nitride TiN, HfN, VN, NbN and ZrN. The lattice constant was calculated as 0.4376 nm which also just matched the average value of mixed nitrides. This finding implying the formation of solid solution from all constituent nitrides is confirming the beneficial effect of high entropy on the random distribution of incorporated components, provided that no strong elastic distortion occurs, as in the case of compounds with similar crystal symmetry and comparable cell sizes [3]. The estimating of the size of nanograins by XRD data, according to the Debye-Scherrer, has shown that the size of nanograins was $(55 \div 60)$ nm.

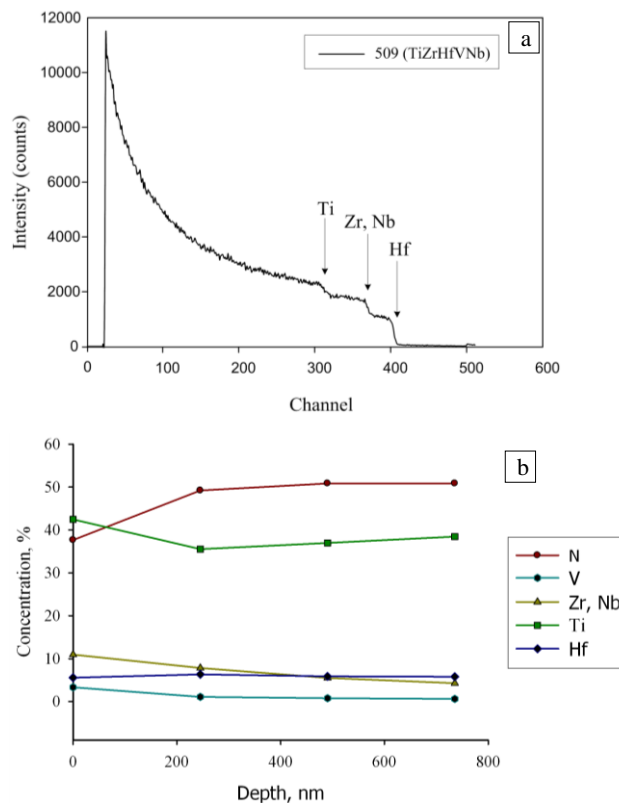


Fig. 3 – RBS spectra (a), depth profile of elements (b) for $(\text{Ti}_{0.25}\text{Hf}_{0.1}\text{V}_{0.04}\text{Nb}_{0.08}\text{Zr}_{0.07})\text{N}_{0.45}$ coating

The results of RBS analysis of the elemental composition of the $(\text{TiHfVNbZr})\text{N}$ nitride coating are given in Fig. 3.

The peaks in this spectrum correspond to the all constituent elements of $(\text{TiHfVNbZr})\text{N}$ coating. The Fig. 3b presents the depth-profiles of coating composition elements. As we can see from these profiles, the elemental composition is homogeneous in the coating and the main constituents are N and Ti, followed by V, Zr, Nb and Hf. It is well known that RBS is a reference method for determining the concentration of large elements as well as for determining the thickness of film. Unfortunately, normally the peaks of light elements (C, N and O), which have a major influence on the properties of thin films, cannot be separated from the background of heavy elements by RBS measurements. Also, as we can see from Fig. 3 the peaks corresponding to the elements with similar atomic radii are difficult to distinguish (for example Ti and V, Zr and Nb).

In the same time ion sputtering techniques is mainly used for depth profile analysis [18-20]. In our work we used secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS) for investigation depth profile. Both methods use argon sputtering, however the ionization mechanisms of the sputtered material are different. In SIMS, the ionization occurs at the bombardment surface, and neighboring atoms influence strongly the ionization process due to the so-called matrix effect, the process. In GDMS, ionization occurs mainly above bombardment surface in glow discharge and the matrix effects are negligible. It should be noted that these methods are destructive. Fig. 4 shows the sample after SIMS and GDMS analyses.

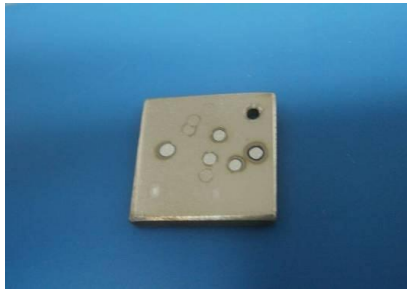


Fig. 4 – The sample surface after SIMS and GDMS analyses

Mass spectra registered with GDMS and SIMS are shown in Fig. 5 and raw data of depth profile analysis are shown in Fig. 6.

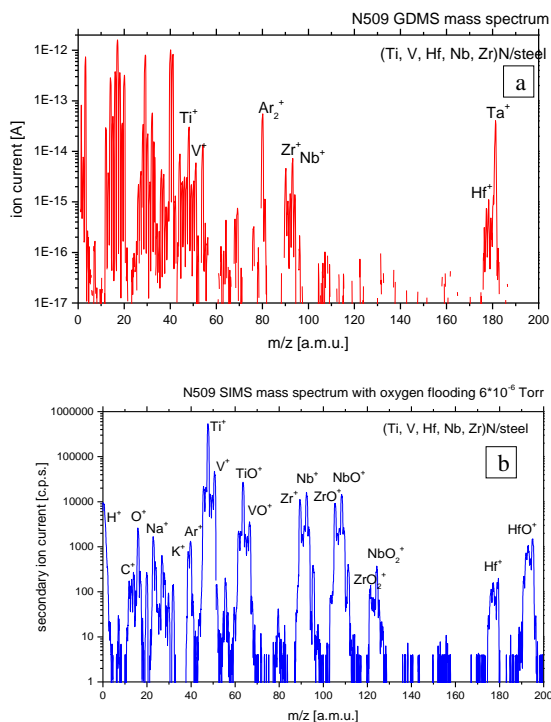


Fig. 5 – SIMS and GDMS mass spectra for the sample registered in range up to 200 a.m.u.

Sputtering conditions in the two methods differed very much. Sputtering rate in GDMS analysis was 5.7 nm/s, while in SIMS sputtering rate was 0.046 nm/s i.e. 2.8 nm/min. As we can see from Fig. 5 the surface of nitride coating is covered with a thin oxide film, as detected species are ZrO, NbO, HfO and ZrO₂ ions and also contains the high concentration of titanium and vanadium. The presence of uncontrolled impurities (H, C and O) is obviously connected with the residual gases in the working chamber.

Ions currents are shown versus sputtering time in seconds. Raw data of GDMS show strong signal of mass 14 (N⁺). This signal remains strong after sputtering the interface between nitride and the substrate. So it means that this signal is background affected. Namely in GDMS we detect strong so called plasma noise of mass 14. Also as we can see from Fig. 6 in SIMS technique the ion current decreases with sputtering time, obvious due to the sputtering of surface layer, which include the oxygen. In the other hand, we can see the

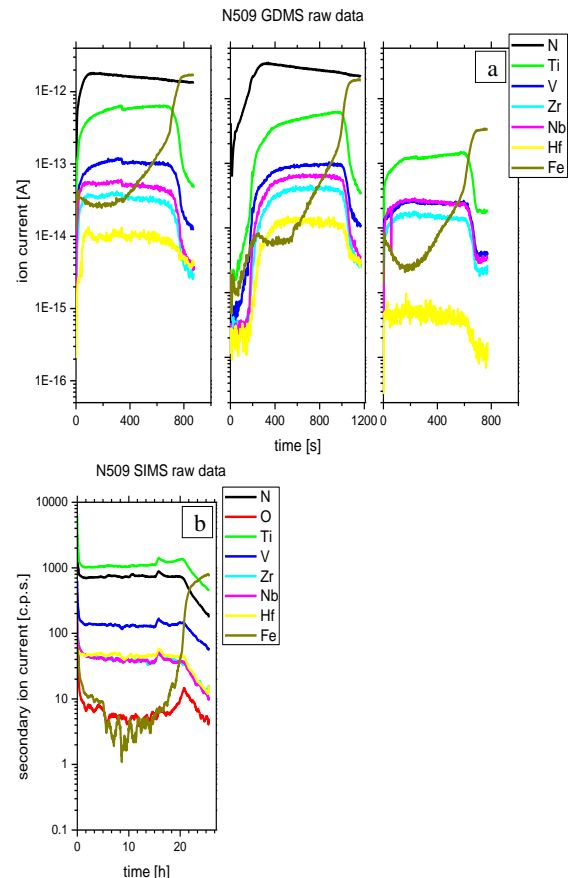


Fig. 6 – Depth profile analysis. Raw data of GDMS (three analysed spots (a)) and SIMS (one crater (b))

initial rise of ion current data in GDMS technique due to the development of direct current glow discharge condition.

Basing on the concentration data obtained by EDX technique (N – 44.7 %, Ti – 25.31 %, V – 4.57 %, Zr – 7.60 %, Nb – 7.99 %, Hf – 9.83 %) we perform normalization of the registered ions currents following formula: $I_x / \sum I_x$, where I_x is the normalized ion current of a given component X and $\sum I_x$ is the sum of the normalized ion currents of all registered components. It should be noted that the sensitivity factors used in SIMS differ up to two orders of magnitude and the ratio $I_x / \sum I_x$ represent the relative concentration of elements if we assume equal matrix effect for all elements. In the other hand, the sensitivity of GDMS are close to 1 and the current ratio $I_x / \sum I_x$ also indicate the relative concentration of analyzed elements since no matrix effect are present in this method [6].

Both methods show element profiles, as we can see the result show the same compositional changes in the analyzed sample. The Hf, Zr, Nb and V profiles are similar in SIMS and GDMS methods, while the titanium profiles are different in two methods. Both techniques show that distribution of metal components across the layer is stable, however titanium concentration slightly increases towards the interface, while the concentrations of Nb, Hf, Zr slightly decrease.

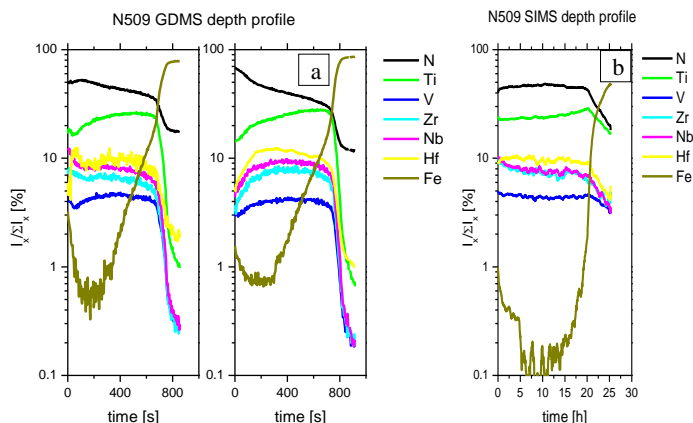


Fig. 7 – Depth profile analysis of the sample (including nitrogen) – left GDMS (a) and right SIMS (b)

4. CONCLUSIONS

New nitride coating based on the TiHfVNbZr high-entropy alloy has been fabricated. The coating exhibits a single cubic (Na-Cl) nitride phase. By combining the results of the RBS and the results obtained with ion sputtering technique (SIMS and GDMS) methods we

received a more realistic picture of the distribution of constituent elements over the depth of the layer. Both analytical methods, SIMS and GDMS give same results. However, the slight deviation in case of nitrogen direction connected with the strong influence of plasma noise.

Анализ элементного состава и профилей распределения нитридного наноструктурного покрытия на основе TiHfVNbZr высокоэнтروпийного сплава

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Изучены элементно-структурные особенности нитридного наноструктурного покрытия, полученного вакуумно-дуговым испарением с высокоэнтропийного катода TiHfVNbZr. Использование взаимодополняющих методик элементного анализа (RBS, SIMS и GDMS) позволило провести комплексный анализ элементного состава, а именно определить химический состав приповерхностного слоя, установить характерные особенности распределения элементов по глубине, а также выявить неконтролируемые примеси.

Ключевые слова: Высокоэнтропийный сплав, Нитридное покрытие, Профили распределения, Элементный состав, Ионно-лучевые методы.

Аналіз елементного складу та профілів розподілу нитридного наноструктурного покриття на основі TiHfVNbZr високоентропійного сплаву

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Досліджено елементно-структурні особливості нитридного наноструктурного покриття, отриманого вакуумно-дуговим випаровуванням з високоентропійного катода TiHfVNbZr. Використання взаємодоповнюючих методик елементного аналізу (RBS, SIMS і GDMS) дало змогу провести комплексний аналіз елементного складу, а саме визначити хімічний склад приповерхневого шару, встановити характерні особливості розподілу елементів по глибині, а також виявити неконтрольовані домішки.

Ключові слова: Высокоэнтропийный сплав, Нитридне покриття, Профіль розподілу, Елементний розподіл, Іонно-променеві методи.

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