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Multilayered vacuum-arc nanocomposite TiN/ZrN coatings before and after annealing: Structure, properties, first-principles calculations

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ABSTRACT

Nanoscale multilayered TiN/ZrN films were deposited using sequential vacuum-arc deposition of Ti and Zr targets in a nitrogen atmosphere. Studies of film's properties were carried out using various modern methods of analysis, such as XRD, STEM, HRTEM, SIMS combined with results of nanoindentation and tribological tests. To interpret the mechanical properties of the deposited multilayer films first-principles calculations of TiN(111), ZrN(111) structures and TiN(111)/ZrN(111) multilayer were carried out. To study the influence of thermal annealing, several samples were annealed in air at the temperature 700 °C. All deposited samples were highly polycrystalline with quite large 20–25 nm crystals. The crystalline planes were very ordinated and demonstrated an excellent coordinated growth. The nanohardness and elastic modulus of non-annealed coatings reached 42 GPa and 348 GPa, respectively. Annealing in air at the temperature 700 °C led to partial oxidation of the multilayered coatings, however hardness of the non-oxidized part of the coatings remained as high, as for initial coatings. All deposited coatings demonstrate good wear resistance.

1. Introduction

Physical-mechanical and tribological properties of the traditional materials, being used in high-temperature aggressive medium, are relatively unsatisfactory in many applications, which leads to necessity of developing new materials with enhanced wear and corrosion resistance as well as high temperatures influence resistance, etc. Intensive studies devoted to the development of composite materials based on nitrides of refractory metals, are carried out intensively nowadays. Such compounds can be used as matrix or as reinforcing filler in the form of fibers or plates. These composite materials are characterized by low specific mass, durability and wear resistance, and demonstrate possibility of complex shapes details formation. Because of high strength and heat resistance, they can be used in aero and space industry as high-temperature construction materials, for gas turbines, petrol engines, heat exchangers production, etc.

Multilayer nanoscale coatings on the base of nitrides of transition metals are well-known for their unique physical-mechanical properties, as well as good corrosion resistance [1–4]. Vacuum-arc evaporation of cathode is a promising deposition method, which allows fabrication of multilayered coatings on the base of nitrides and carbides of transition metals [5–8]. A varying the deposition conditions, such as gas pressure in the deposition chamber, bias potential, bilayer thickness, etc. allows to fabricate coatings with very high hardness [9–11], good wear coefficient and resistance to wear, oxidation [12–17] and to corrosion [18,19] as well as with good electrical properties [20,21]. As it was reported in the previous papers [22,23], coatings on the (Ti,Zr)N base have high hardness 42–48 GPa, as well as resistance to oxidation under the influence of high temperatures 1170 °C [24–28]. It is also known, that nanoscale multilayer coatings on the base of TiN, CrN, ZrN, and MoN have higher hardness in comparison with single-layer ones with the hardness equal to 24–38 GPa [25,29–31].

The main purpose of the present work was to study multilayer nanoscale TiN/ZrN coatings, their physical-mechanical properties, as well

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as their microstructure before and after annealing at 700 °C in air. First-principles investigations were performed to interpret the experimental results. Such combination of experimental studies and computational modeling has been never provided before.

2. Experimental Procedure

The multilayer TiN/ZrN coatings were deposited using vacuum-arc evaporation method from two targets [23], one of which contained titanium and the second contained zirconium (Fe < 0.12%, C < 0.05%, Si < 0.08%, N < 0.04%, O < 0.1, H < 0.008, concentration of Ti or Zr was in the range 99.5–99.9). Ion-plasma deposition or, in other words, coating's deposition using vacuum arc cathode evaporation is a very promising way of fabrication of protective coatings. The coatings were deposited on the A 570 Grade 36 steel (Ra = 0.09 μm, size was 15 × 15 × 2.5 mm) polished substrates under different deposition modes. Total thickness of the deposited coatings was 19 μm, while bilayer thickness was about 39 nm, thus total number of bilayers was 500. The arc current during deposition was 100 A, the nitrogen pressure in the deposition chamber was 0.4 Pa, the distances from evaporators to substrate were 250 mm, the substrate temperature was 250…350 °C, deposition rate of ZrN and TiN layers was around 3 nm/s and 2 nm/s, respectively. Negative bias potential − 200 V was applied to the substrates, it allowed fabrication of homogeneous coatings with good enough planarity. Thermal annealing of the samples were done in the vacuum chamber, pressure in it was 0.0013 Pa, while the pressure of the incoming oxygen atmosphere was 0.4 Pa. Annealing time was 1 h.

Structure-phase investigations were done using the DRON-3M and Ultima IV "Rigaku" diffractometers in Cu-K_{α} radiation. Surface morphology and structural properties of the films were studied using JEOL ARM 200F high-resolution transmission electron microscope (200 kV) with an EDX analyzer. The cross sections and lamellas for TEM investigations were prepared by focused ion beam (FIB) processing and observation system JEOL JIB-4000. A broad carbon thin film was deposited on the sample surface to protect the area of interest from damage during the FIB milling and observation with Ga^{+} ion beam. The Ga^{+} ion beam of adjustable acceleration voltage 5–30 kV was used to prepare lamellae down to electron transparency. Secondary ion mass spectroscopy (SIMS) measurements were carried out using SAJW-05 analyzer equipped with Physical Electronics 06-350E ion gun and quadrupole mass analyzer QMA-410 Balzers. An argon ion beam of 1.72 keV was used at 45° incidence angle, digitally scanning over 1 mm × 1 mm area. For depth profile analysis, the positive secondary ion currents emitted from the central part of the scanned area (around 15% electronic gate) were selected. Hardness and elastic modulus of the coatings were measured on HYZITRON TI 950 Tribometer. This device allows performing continuous measurement of the contact stiffness via a superimposed alternating current signal during loading, which provides a continuous measurement of the elastic modulus (E) and hardness (H) as functions of indenter penetration depth (L) during a single loading segment. All indentations were done with a Berkovich diamond tip of a nominal radius equal to ~340 nm. At least ten indentations were made on each sample. The load was continuously increasing to a maximum 10 mN.

3. Computational Aspects

To clarify a role of the interface in the strength enhancement of the deposited TiN/ZrN nanolayered films we performed first principles investigations of TiN(111), ZrN(111) and TiN(111)/ZrN(111) structures. The initial 96 atoms hexagonal supercells with the B1 structure (space group Fm-3m, No. 225) were considered to calculate the total energy and tensile stress-strain relations of these structures. All the supercells consisted of 12 layers aligned perpendicularly to the (111) direction in the B1 lattice. In the case of the TiN(111)/ZrN(111) multilayer, the supercell represented six layers of TiN(111) and six layers of ZrN(111). The motivation of such a choice of the supercells was the fact that the deposited TiN/ZrN nanolayered films had the (111) preferable crystallite orientation.

First-principles calculations were carried out using the Quantum-ESPRESSO code [32] using the periodic boundary conditions. Vanderbilt ultra-soft pseudo-potentials were used to describe the electron-ion interaction [33]. The semi-core states were treated as valence states. To describe exchange-correlation energy, the generalized gradient approximation (GGA) of Perdew et al. [34] was employed. The criterion of convergence for the total energy was 10^{-6} Ry/formula unit. To speed up convergence, each eigenvalue was convoluted with a Gaussian with a width of 0.02 Ry (0.272 eV). The cut-off energy for the plane-wave basis was set to 30 Ry (408 eV). The integration in the Brillouin zone (BZ) was done on special k-points determined according to the Monkhorst-Pack scheme using a mesh (2 2 1). All initial structures were optimized by simultaneously relaxing the supercell basis vectors and the atomic positions inside the supercell using the Broyden–-Fletcher–Goldfarb–Shanno (BFGS) algorithm [35]. The relaxation of the atomic coordinates and of the supercell was considered to be complete when atomic forces were < 1.0 mRy/Bohr (25.7 meV/Å), stresses were smaller than 0.05 GPa, and the total energy during the structural optimization iterative process was changing by < 0.1 mRy (1.36 meV). In the large supercell calculations, the chosen reduced energy cut-off and the mesh of k-points were used in order to spare computing time without compromising accuracy [36]. Such computational conditions were proved to be quite justified [37]. In particular, the calculated lattice parameters for TiN and ZrN were 4.238 Å and 4.579 Å, respectively. These values are very close to the experimental lattice constants of 4.240 Å [PDF 065-0715] and 4.575 Å [PDF 065-0972], respectively.

The tensile stress-strain relations were calculated by: 1) elongating the supercells along the c-axis (the (001)-direction in the hexagonal supercells, or the (111) direction in the B1-lattice) in an incremental step, 2) fixing of the c basis vector and 3) simultaneously relaxing the a- and b-basis cell vectors and the positions of the atoms within the supercell [37,38].

4. Results and Discussion

4.1. Elemental Composition

TEM images of the cross-sections of the TiN/ZrN coatings are presented in the Fig. 1. Studied coatings have rather good planarity of the deposited layers without droplet defects between TiN and ZrN layers and inside them. The layers are clearly visible; they also have clear boundaries and do not intersect.

Compositional analysis for TiN/ZrN coatings before and after annealing is shown in Fig. 2. We should point, that energy-dispersion spectra are typical for all samples (not presented in this article). Stoichiometry of the composition of the TiN/ZrN coatings can be seen from it. Changes of elemental composition in the surface layers of the studied coatings were observed after annealing, see Table 1. SEM was used for studies of changes in the near-surface layers of the annealed coatings. Changes of elemental composition occurred due to annealing, we observed the content of oxygen atoms around 35 at.%. Penetration of oxygen into iterative nitride layers and forming of the titanium and zirconium dioxides in the near-surface layers are responsible for significant structure changes of TiN and ZrN layers due to substitution of nitrogen atoms by oxygen ones.

Increasing of the specific volume of nitrides phases during oxidation led to bending of the layers, their lamination and loss of continuity, see Fig. 3. Main volume changes occurred in TiN layers, while columnar structures were observed in ZrN layers, which led to increasing of fragility of ZrN layers. TiN layers were compressed and compacted due to their high density. Thus, compensating strain appeared in the plane of growth of such layers, and it was responsible for their fragility. The