The structure and mechanical properties of multilayer nanocrystalline TiN/ZrN coatings obtained by vacuum-arc deposition

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Abstract

TiN/ZrN multilayered condensates on BK-8 carbide tips substrates (62 HRC) were produced by the vacuum-arc deposition technique, using Ti and Zr plasma flows in reactive nitrogen gas medium with working pressure of $6.6\cdot10^{-1}$ Pa. The TiN/ZrN multilayered condensates consist of TiN and ZrN sublayers, which have a thickness of ~100 nm, controlled by the processing parameters of the used deposition technique. The obtained coatings have hardness of 45 GPa and Young's modulus of 320 GPa. The obtained results show that mechanical properties of such multilayered composites are considerably improved in comparison to those for the single-component coatings, TiN and ZrN. The dependence of hardness and Young's modulus of the composites on sublayer thickness within a range of 100 nm was determined. The investigated structure and improved mechanical properties of the TiN/ZrN multilayered condensates would be very good platform for finding their industrial application, such as hard coatings with different purposes.

Keywords: multilayers, nanohardness, multicomponent coatings, PVD method

I. Introduction

A shortage of tungsten-based materials and their high prices in manufacturing industry were an impetus for researchers to find of alternative materials and technologies, including a hard coating deposition technique. Ceramic coatings, such as refractory nitrides based on transition metals (TiN, ZrN, Mo_2N) [1–3], deposited by an ion-plasma method onto cemented carbide and steel cutting tools have received a wide spread of application in machine-building industry. When deposited by physical vapour deposition (PVD) these compounds are reputed to offer a number of positive properties: i) high hardness, compared with heat-treated high-speed steels, ii) high wear-resistance and low coefficient of friction impart reduced frictional loads in cutting, iii) high resistance to corrosion and good chemical and thermal stability at high temperatures and iv) high thermal conductivity and good adhesion with substrates. However, further improvement of physical-mechanical properties of these nitride coatings is limited. It was a reason for development of multicomponent and multilayered coatings based on nitride compounds with nanocrys-tal-line structures. In this case, improved properties are achieved due to nanosized grains and a large quantity of interlayer boundaries, which is a characteristic feature of multilayered coatings. However, a high degree of dispersion may cause changing in thermodynamic characteristics and lead to displacement of phase fields on constitution diagrams and as a result, the heat operating and heat treatment conditions for the coatings are changed.

This paper presents a study of multilayered TiN/ZrN deposits consisting of nanocrystalline sublayers (with thickness < 100 nm), produced by time controlled vacuum-arc deposition technique, using Ti and Zr plasma flows in reactive nitrogen gas medium onto BK-8 cemented carbide substrates. The deposited TiN/ZrN multilayered coatings are superhard and highly elastic. Thus, these coatings are referred to class of superhard materials (with a hardness > 40 GPa), which allows their wide applications in manufacturing industry. The purpose of the paper is to investigate the structure and mechanical properties of TiN/ZrN multilayered coatings and to compare it with single layered TiN and ZrN deposits.

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II. Experimental Details

The TiN/ZrN multilayered and TiN and ZrN single layered coatings on BK-8 carbide tips were deposited in a modified “Bulat–3T” installation for a vacuum ion-plasma coating deposition. A metallic plasma generation was carried out by means of vacuum arc discharge ignition between consumable electrodes (Ti and Zr cylinder-type 64 mm in diameter cathodes) and non-consumable anode in nitrogen reactive gas flow with a pressure of $6.6\cdot10^{-1}$ Pa (in the working chamber). It is well known that in cathodic arc evaporation three species create the film deposited onto a substrate: i) ions of metal vapour, ii) neutral metal vapour and iii) undesirable microdroplets of various sizes and rounded shapes. The number and sizes of the droplets depend on deposition parameters. According to the literature data [4] the number of droplets on the deposit surface decreases with increasing of the nitrogen partial pressure and reduction of discharge current. An optimum values of these parameters used in this study were $6.6\cdot10^{-1}$ Pa for N_2 pressure and 110 A for the arc current.

A substrate cathode distance was 125 mm and duration of the coatings deposition process was 30 min. The thickness of the obtained TiN and ZrN coatings was 15 µm. The total thickness of the multilayered TiN/ZrN deposits was 13 µm. A sublayer thickness of multilayered coatings was controlled by vacuum discharge power on the cathode (the discharge current I_d = 110 A and operating voltage U_d = 24 V) and by the time of sublayer deposition (10 sec). The sublayer thickness was about 100 nm and a total number of TiN and ZrN sublayers was 140. The sample treatment was made in two stages. The first one was cleaning and heating of the samples by ion bombardment with argon in order to make substrate degreasing and remove other impurities from specimens. In this case the substrate negative bias voltage was equal to –1100 V and the ion current density on the samples was about 3.5 mA/cm^2. Duration of this stage was 5 min. The samples were heated by ion bombardment up to 450°C. At the second stage, argon was substituted by nitrogen and a deposition of TiN/ZrN coating was fulfilled onto 100 V negatively biased substrates. The experimental setup is shown schematically in Fig. 1.

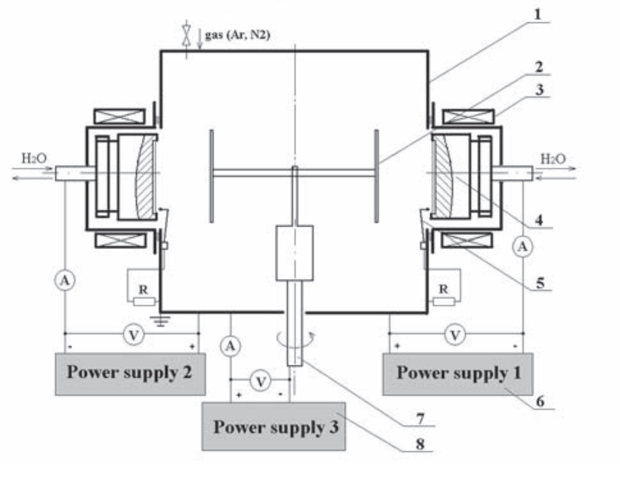


Figure 1. Scheme of the cathode arc coater “Bulat-3T”: 1. vacuum chamber, 2. substrate, 3. stabilizing coil, 4. butt-type cathode, 5. trigger; 6. power supply for the arc discharge, 7. substrate holder rotation mechanism, 8. power supply for substrate holder negative biasing

The structure and thickness of TiN/ZrN multilayered deposits were investigated using scanning electron microscopy (SuperProb 733, JEOL). Phase composition and lattice parameters of the deposits were determined with X-ray diffraction (XRD) analysis from (hkl) lattice spacings in the direction perpendicular to the film surface. X-ray diffraction lines were taken with a goniometer using CuKα; radiation (DRON – 3 unit). The microhardness was measured by hardness testers “PMT 3” and “Micron – Gamma”. The loads within a range 20–200 g were applied both to the top coating surfaces and to the coating cross sections. “Micron – Gamma” use method based on automatically registration loads (*P*) onto indenter and depths of penetration (*h*), in a load diagram form *P=f (h)* (Fig. 2).

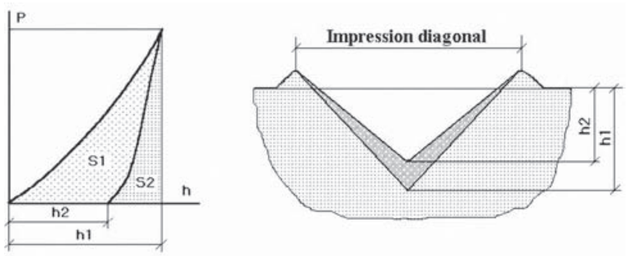


Figure 2. Load diagram and impression cross section: S1 – the area of a load; S2 – the area of an unload; h1 – depth of indenter penetration; h2 – depth of indenter penetration after elastic deformation

III. Results and Discussion

A typical nanostructure of the TiN/ZrN multilayered coating prepared by vacuum arc deposition is shown in Fig. 3. The picture shows that composite deposit has a well-marked layered structure, with the average sublayer thickness of ~ 100 nm. The sublayers have some irregularities because of plasma flow nonuniformities during vapour deposition onto substrates.

Example of the surface topography obtained for the deposited TiN/ZrN coatings is shown in Fig. 4. Presence of microdroplets on the deposit surface is clearly visible on the SEM image. Their average size does not exceed 5–10 µm. The same surface topography structures are observed for the single layered TiN and ZrN deposits.

X-ray analysis has shown that the multilayered TiN/ZrN condensate consists of stoichiometric TiN and ZrN sublayers of cubic structure with preferred (111) orientation of different intensity. The single-layer coatings

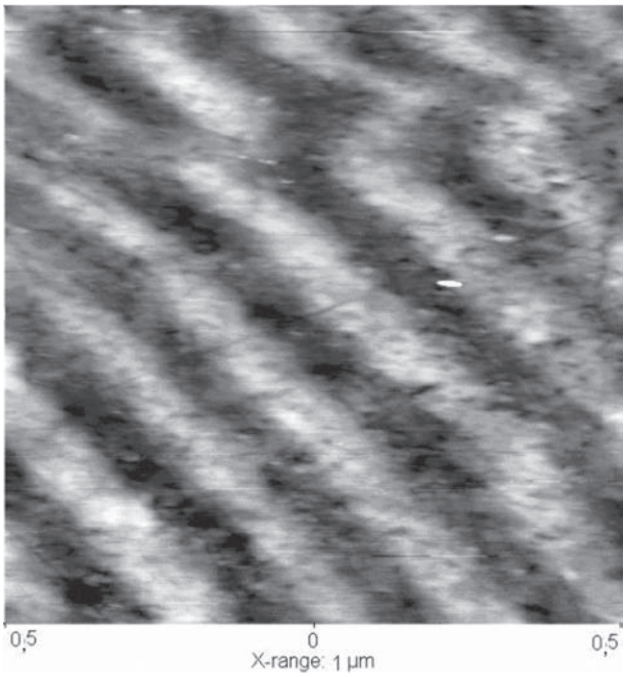
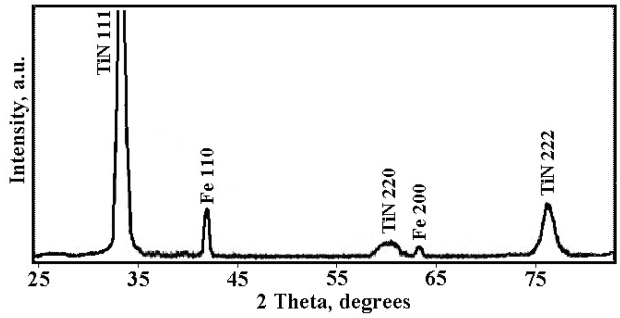
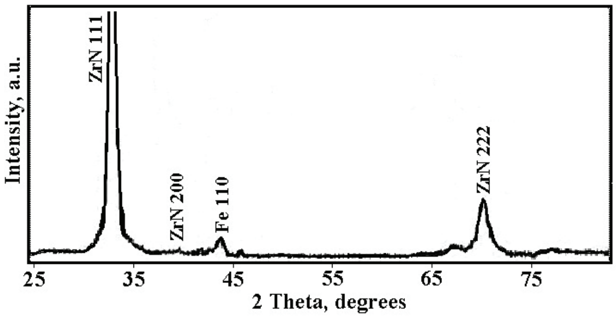


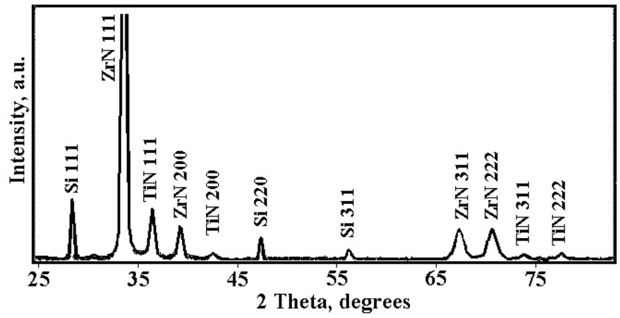
Figure 3. SEM photomicrograph of a cross section of the TiN/ZrN vacuum arc coating



a)



b)

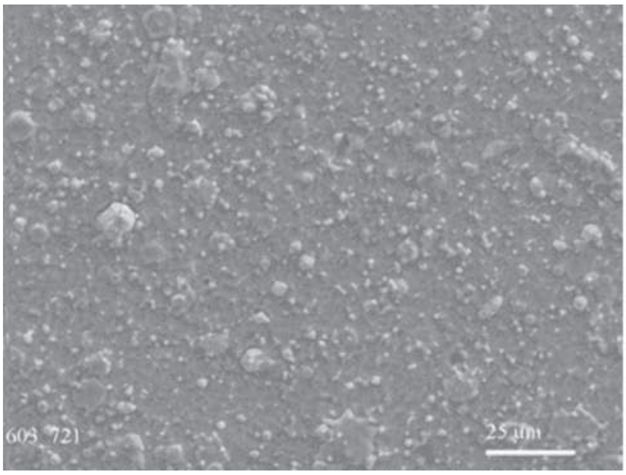


c)

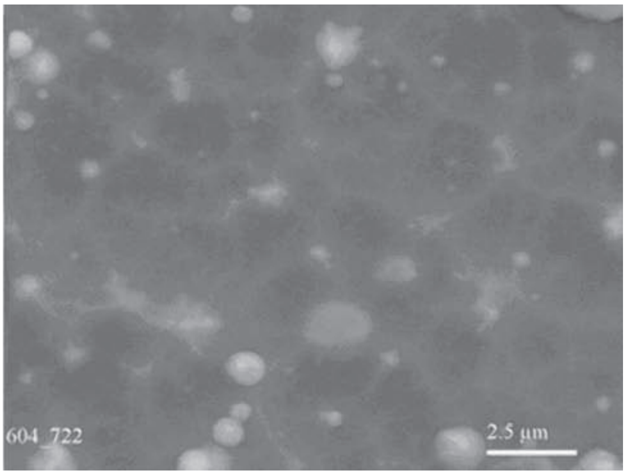
Figure 5. X-ray diffraction patterns of: a) TiN, b) ZrN and c) multilayered TiN/ZrN

TiN and ZrN (Figs. 5 a, b) also have face-centered cubic lattice with preferred (111) orientation. Appearance of crystalline plane can be explained by the ion-peening mechanism involving a superthermal energy particle bombardment of the growing films [5]. Peaks characteristics of the X-ray diffraction pattern (Fig. 5c) indicate dense and fine-grained structure with the average crystallite size of 55–70 nm. The thinning of the peaks responsible for preferred orientation in the crystalline plane (111) explains the absence of large quantity of internal stress.

Values of mechanical characteristics such as hardness (*H*) and elastic modulus (*E*), were determined by means of microhardness testing for the single and the



a)



b)

Figure 4. Surface topography of the TiN/ZrN multilayered deposit

multilayer's condensates (TiN, ZrN, TiN/ZrN), obtained under the same deposition conditions. The shear modulus (G), yield stress (σ_T) and coefficient of resistance to plastic deformation (H^3/E^{*2}); were assessed by means of theoretical calculations using model equations which have been reported previously by other authors.

The shear modulus and yield stress are defined as [6]:

$G = E / 2 \cdot (1+\mu)$ (1)

$\sigma_T = H\mu / 3$ (2)

where E is the elastic modulus [GPa], μ the Poisson ratio and $H\mu$ the microhardness [GPa]. The coefficient of resistance to plastic deformation is defined as H^3/E^{*2} [7], where $E^* = E/ (1-\mu^2)$.

modulus, respectively. The dislocations will be formed only in compound B having the lower shear modulus. Upon applied stress they will be hindered to cross the B/A interface, due to the repelling force of their image in A. The third mechanism, the coherency strain effect, is likely to contribute to the observed excess hardening. Jankowski and Tsakalakos [9] have shown that the increase of the stiffness can arise from different dependencies of the biaxial elastic modulus on the strain of the two materials. In general, the modulus increases and decreases with negative (compressive) and positive (tensile) strain, respectively. If this dependence is stronger for the material, which is under compressive strain than for the material under tensile strain, the total effect of the coherency strain at the interface will be an increase of the elastic modulus of the heterostructure [8–10].

Table 1. Mechanical properties of TiN, ZrN and TiN/ZrN coatings

Sample	H [GPa]	E [GPa]	G [GPa]	σ_T [MPa]	H^3/E^{*2}
TiN	23	370	142	766	0.07
ZrN	21	245	94	700	0.12
TiN/ZrN	45	320	123	1500	0.73

As it can be seen from Table 1, the multilayer coatings have higher hardness (45 GPa), yield stress (1500 GPa) and H^3/E^{*2} coefficient (0.73) than the single-component coatings (TiN and ZrN). As a rule, hardness and elastic modulus correlate in the definite extent. Knowing these data the resistance degree of plastic deformation in coating can be determined. It grows faster with the increase of H^3/E^{*2} relation. This means that for increasing the resistance of plastic deformation of a material having high hardness it is necessary to obtain minimally possible elastic modulus [7].

TiN/ZrN microhardness was examined in two planes relative to the coatings. Determinations got from condensate surface with texture (111) showed the high hardness, 45 GPa, but in cross-section of the coatings the hardness was only 24 GPa. Given data characterize the high coating anisotropy. The elastic modulus of multilayered condensate TiN/ZrN was equal 320 GPa, what is between two elastic modulus of single components, TiN (370 GPa) and ZrN (245 GPa).

A possible mechanism for hardness enhancement could be explained by the blocking of interlaminar layers and dislocations at the interfaces and within the layers. This, in turn, is a result of differences in the shear modulus of the constituents coherency strain present for small periodicity multilayers with a significant lattice mismatch between the layers, the presence of grain boundaries and defects within the layers. Another possible mechanism for hardness enhancement in nanometer-scale multilayers could be explained using the Koehler's model [8]. It is suggested that strength enhancement could be achieved in epitaxial heterostructures consisting of a few nanometer thin layers of two compounds A and B, with a high and low shear elastic

IV. Conclusions

TiN, ZrN and TiN/ZrN condensates with face-centred cubic lattice were successfully prepared with vacuum-arc deposition technique. The coatings have columnar structure with preferred crystallographic (111) orientation. The anisotropic TiN/ZrN multilayered condensate showed the high hardness (45 GPa), in contrast to the single-component coatings, TiN and ZrN, having the hardness of 23 GPa and 21 GPa, respectively. The hardness increase is explained by the presence of large amount of interlayer borders, with increasing of which, the hardness grows by given thickness coatings. In addition, the multilayered coatings showed also the high resistance extent to plastic deformation, whereas the single-component coatings, TiN and ZrN, have low indication of H^3/E^{*2}.

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