Combined Vacuum-Arc Deposition of Protective Coatings on Basis of Transition Metals Nitrides Solid Solution[1]

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Abstract – Ti–Zr–N coatings were grown by the method of condensation from a plasma phase in a vacuum with ion bombardment of sample surfaces while combining Ti and Zr plasma flows in a residual nitrogen atmosphere. The coatings were deposited at different arc currents of Ti and Zr cathodes.

XMA studies show that multicomponent systems of different compositions are obtained, and the control of plasma flows gives the possibility to synthesize ternary nitrides of any composition. XRD analysis reveals the formation of ternary Ti–Zr–N solid solutions nitrides with a (111) preferred orientation. A correlation between the lattice parameter and elemental composition of Ti–Zr–N coatings is observed. It is found that the stress-free lattice parameter increases with decreasing Ti arc current. The residual stress is compressive and relatively large (~ 6.5 GPa). The relation between the composition and the stress using the model of formation of ternary solid solution nitrides with combining of plasma flows of Ti and Zr is discussed.

1. Introduction

The multicomponent ternary TiN-based nitrides, such as TiAlN [1], TiCrN [2] or TiZrN [3], are now widely used as protective coatings. They possess advanced physical and mechanical properties, such as high hardness and wear resistance, oxidation and corrosion resistance.

Ternary Ti–Zr–N coatings have been deposited by different methods: reactive sputtering [4], ion-deposition from simultaneous magnetron and arc sources [5] and vacuum arc deposition [6]. In mentioned publications, the ternary nitride coatings were deposited from a TiZr alloy target, which limits the range of structural and compositional variations of the formed coatings. The use of separate Ti and Zr sources, from independently controlled plasma flows, overcome this drawback and provides pathway to fine tune film properties for their use in specific applications. For this purpose, it is important to control accurately the plasma flow density, which is governed by a change in the arc current of the cathode [7, 8]. Recently, we have shown that the method of Cathodic Arc Vapor Deposition (CAVD) using two independent plasma flows was appropriate to synthesize Ti–Zr–N and Ti–Cr–N coatings [7, 8].

This work is devoted to studying the microstructure, elemental and phase composition and their correlation in multicomponent Ti–Zr–N coatings grown by CAVD with variation of the titanium and zirconium plasma flow densities.

2. Experiment

Ti–Zr–N coatings were formed by condensation from a plasma phase in a vacuum with the ion bombardment of the samples surface while combining titanium and zirconium plasma flows in a residual nitrogen atmosphere [8]. Carbon steel St3 (< 0.18 weight % C) and (001) oriented Si were used as substrate material. Prior to the deposition, the surface of the substrate was cleaned and heated by titanium ion bombardment during 1 min with the substrate bias being –1 kV, the arc current of Ti cathode 100 A, the vacuum in the chamber 10^{-3} Pa. This stage prior to deposition resulted in heating the substrate to 450–500 °C. All film depositions were initiated by introducing N_2 gas at a pressure of 10^{-1} Pa into the vacuum chamber and the bias was fixed at –120 V. Ti–Zr–N films were obtained by simultaneous deposition of Ti and Zr (Table I).

Table I. Thickness, element composition and grain cross section size of the Ti–Zr–N coatings with different arc currents of Ti and Zr

Arc current of Ti, A	Arc current of Zr, A	Thickness, µm	Composition, at %		Grain cross section size, nm
			Ti	Zr	
80	80	6	70	30	60
	100	6	65	35	67
	120	7.2	60	40	76
100	80	6	76	24	70
	100	6.8	72	28	77
	120	7	63	37	86
120	80	6	73	27	80
	100	7	71	29	87
	120	7.5	68	32	100

The microstructure of the coatings was studied on cross-sectional samples using a Hitachi S806 Scanning Electron Microscope (SEM). The concentration of the main elements was investigated by the method of X-ray microanalysis using a LEO 1455 VP.

The phase composition and preferred orientation in Ti–Zr–N films were investigated by X-ray diffraction (XRD) using CuK_α characteristic X-ray radiation. The residual stresses were determined using the $\sin^2\psi$ method [9].

3. Results and discussion

The samples characteristics of Ti–Zr–N coatings deposited by CAVD with different ratio of I_{Ti} and I_{Zr} arc currents are reported in Table I. Fig. 1 shows typical SEM micrographs of Ti–Zr–N coatings grown on silicon substrate at different densities of Ti and Zr plasma flows. One can see that the as-grown coatings are characterized by a columnar microstructure. Columnar grains are closely packed, aligned along the substrate normal, without leaving voids or gaps in between.
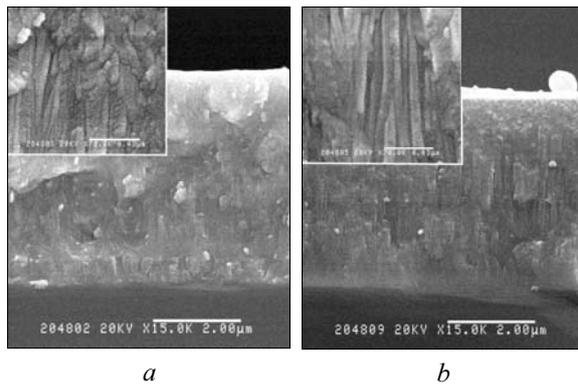

Fig. 1. SEM micrographs of Ti–Zr–N coating deposited at $I_{Ti} = I_{Zr} = 80$ (*a*) and 120 A (*b*)

This is attributed to the directed grain growth. The direction of grain growth coincides here with the direction of the plasma flow, even with increasing coating thickness. Generally, preferred orientation is governed by the "evolutionary selection rule", where the grains with the highest growth-rate plane parallel to the substrate develop at the expense of the others. In our case, the greatest speed coincides with the direction of plasma flow. Thus, the columnar structure is obtained as a result of coating growth. The average cross-section size of columnar grains is ~ 60–80 nm (Fig. 1, *a*) at the small density of plasma flows ($I_{Ti} = I_{Zr} = 80$ A) and the coating thickness is ~ 6 µm (see Table I). A rise in the plasma flows density ($I_{Ti} = I_{Zr} = 120$ A) leads to an increase in the coating thickness to 7.5 µm. SEM investigations of the microstructure of Ti–Zr–N coatings, deposited with different ratio of cathodes arc currents, show that an increase in the total plasma flow density ($I_{Ti} + I_{Zr}$) leads to an increase in the cross section columnar grains size, which amounts to 100 nm (see Fig. 1, *b*, Table I).

As a comparison, the use of one plasma flow of titanium leads to the formation of TiN coatings with typical columnar grain sizes of 30 nm [10].

The CAVD method is characterized by the formation of energetic and highly ionized flows of low-temperature plasma. During the deposition process, an ionic bombardment of the growing film surface occurs. The energy of bombarding species, Ti and Zr ions produced from the metallic cathodes, is partially transferred to the film, leading to a temperature increase in the zone of formation of the coating. This enhances the adatoms surface mobility and may promote activation of the chemical reactions between condensate and components of the reactive gas mixture, therefore increasing the number of nucleation centres [11]. These processes lead to the formation of continuous dense coatings with the fine-grained structure. An increase in the total plasma flow density, and therefore in temperature, may favor relaxation processes, such as annealing of defects, recrystallization or partial stress relief. All these processes contribute to the formation of dense columnar grains.

The content of metallic components in the coating samples was investigated by the XMA technique. A correlation between the cathode arc currents and the concentration of equivalent elements in the coatings is established. Fig. 2 shows the evolution of the titanium and zirconium concentration in the Ti–Zr–N coating with the ratio of the Ti and Zr arc currents.
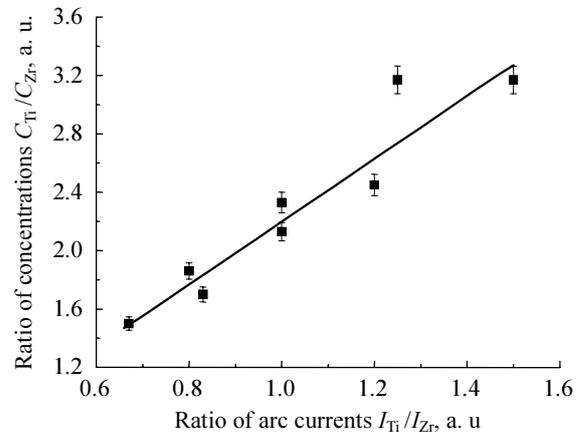

Fig. 2. Composition of Ti–Zr–N coatings as function of arc currents of Ti and Zr

A direct dependence is observed between the relative content of elements (C_{Ti}/C_{Zr}) in the coating and the ratio of the Ti and Zr plasma flows (I_{Ti}/I_{Zr}). A linear fit to the data of Fig. 2 gives a slope of ~2.2, which means that the Ti concentration is 2.2 times higher than the Zr one for identical values of Ti and Zr arc currents. This is related to the distinct deposition rates of Ti and Zr plasma flows. The elemental ratio in the coating is determined by the content of titanium and zirconium in the growing coating surface, where the plasma-chemical reactions of the formation of condensates occur, i.e., it depends on the deposition rate

of metallic components. For magnetron sputtering, the deposition rate is relatively low, and the Zr concentration exceeds by several times that of Ti, due to the larger scattering of Ti ions (lighter element) in a nitrogen atmosphere [12]. For CAVD, the deposition rate is large, so the Ti concentration is higher than the Zr one, due to their mass difference. So, changing the cathode arc currents makes it possible to tune the ratio of metal concentrations in Ti–Zr–N coatings.

In Ti–Zr–N multicomponent systems, the formation of different phases may be obtained: metallic or nitride phases, single-phase ternary solid solutions or bi-phase structures. To investigate the phase formation under the present growth conditions, XRD measurements were carried out on the coatings and the XRD scans compared with powder diffraction standard data for Ti–Zr–N system. Fig. 3 shows typical XRD scans of Ti–Zr–N coatings grown at different total plasma flow densities. No Bragg peaks corresponding to metallic Ti or Zr phase, nor reflections from pure TiN and ZrN phases were found. In all cases, only one NaCl-type face-centred cubic structure was detected with the Bragg reflections of the coatings lying between that of the corresponding TiN and ZrN mononitrides. The peaks position is found to vary with a change in the arc currents ratio, but remains between that of the corresponding monotrides.
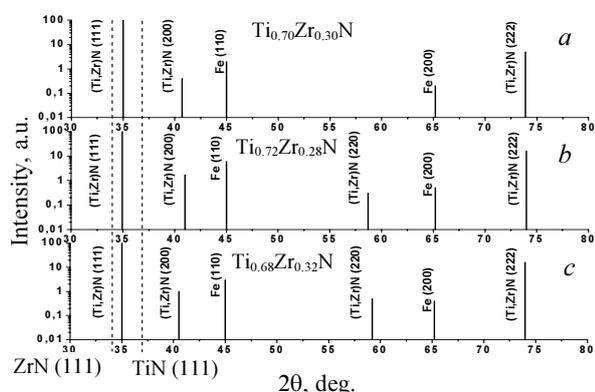

Fig. 3. XRD spectra of Ti–Zr–N coatings deposited at different density of plasma flows: $a - I_{Ti} = I_{Zr} = 80$; b – 100; c – 120 A

These results clearly attest to the formation of $Ti_xZr_{1-x}N$ solid solutions coatings with complete solid solubility ($0.60 < x < 0.76$) and with different ratio of metallic components (x). The nitrogen concentration is about 50 at. % and depends on the N_2 pressure during deposition [12, 13].

The high intensity of the (Ti, Zr)N (111) Bragg peak , as compared to the theoretical values, indicates that the (Ti, Zr)N grains grow with the (111) preferred orientation. This is in agreement with the data of SEM studies about the formation of columnar grains (see Fig. 1). Other studies have reported the formation of single-phase ternary nitrides with a (111) oriented columnar structure [7, 14] for a wide range of Ti and Zr ratios [14]. In our study, beside preferred orientation of (111) grains, the presence of (200) and (220) grains was also observed.

Their intensity is very small in comparison with that of the (111) peak, and an increase in the arc current of cathodes leads to a small increase in the intensity of these peaks. Columnar grains with a strong preferred (111) orientation were also observed for TiN and ZrN coatings [15].

For transition metal nitrides, the development of preferred orientation with film thickness is usually explained by thermodynamics and kinetics arguments [16, 17]. In the absence of kinetics constraints, the development of a (111) texture in Ti–Zr–N coatings may be due to minimization of the overall free energy of the coating, which includes surface and strain energy contributions.

At low film thickness, the influence of surface energy prevails over strain energy, and a (200) orientation is expected since the surface energy is minimum for this plane. With increasing film thickness, the strain energy becomes predominant, especially under the present growth conditions involving energetic plasma flows. In that case, a (111) texture is expected, since for the same strain level, the Young's modulus is the lowest along the <111> direction, resulting in minimization of the strain energy.

Figure 4 shows the evolution of the lattice parameter of (Ti, Zr)N solid solutions (measured from the angular position of the (222) diffraction peak and using the $\sin^2\psi$ method) as a function of the Ti concentration. The corresponding values for pure TiN and ZrN coatings are also reported, being 4.226 and 4.575 Å, respectively, close to the bulk values. A linear variation of the lattice parameter is observed in the 60–76 at % Ti range. However, these values fall far above the Vegard's law.

This is related in part to the presence of compressive stress in the coatings (see below). Small positive deviation from Vegard's law was also observed in sputtered Ti–Zr–N coatings [14]. In order to extract the stress-free lattice parameter, a stress analysis must be performed.
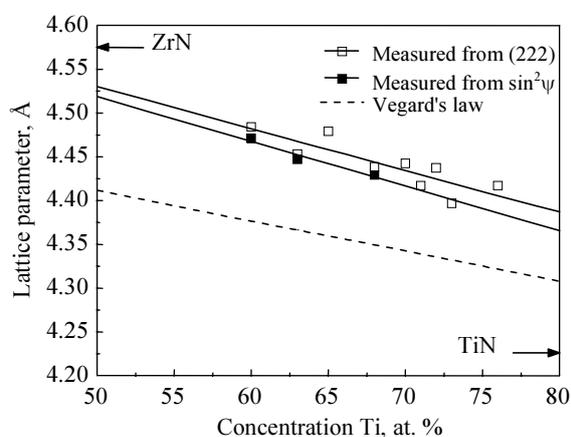

Fig. 4. Lattice parameter of (Ti, Zr)N as function of Ti concentration

The residual stress of Ti–Zr–N coatings was determined using the $\sin^2\psi$ method [9]. The results of investigation show that the stress are largely compressive, (-6.5 ± 0.3) GPa, and independent of the concentration x. This value is in agreement with previous study on Ti–Zr–N coatings [7]. Therefore, the residual stress is essentially accounted for by intrinsic stress developed during the deposition process.

The presence of compressive intrinsic stress is here related to the use of energetic plasma flows.

The a_0 values are reported in Fig. 4 as a function of Ti concentration. These values exceed by ~1.8–2.2% that calculated from Vegard's law. Similar lattice expansion was reported by Donohue et al. [14] for Ti–Zr–N coatings grown by arc-bond sputtering from TiZr alloy target. The origin of this relatively large lattice expansion in Ti–Zr–N coatings may be due to lattice distortions induced by growth-induced point defects (interstitials) or the formation of the substitutional solid solution itself, at the origin of the strong compressive intrinsic stress.

4. Conclusions

Ternary Ti–Zr–N coatings were synthesized by the method of cathodic arc vapour deposition by combining Ti and Zr plasma flows. The as-grown coatings exhibit a complete solid solubility, with the formation of $Ti_xZr_{1-x}N$ $(0.60 < x < 0.76)$ solid solutions with NaCl-type fcc structure and a (111) preferred orientation.

Ti–Zr–N grains are columnar with average cross section size of 60–80 nm, under low plasma flow densities. It is established that a change in the Ti and Zr plasma flows densities leads to an increase in average cross section size of columnar grains to 100 nm. A variation of the arc currents of Ti and Zr cathodes from 80 to 120 A leads to a change in the Ti content of the coating from 60 to 76 at %. Correspondingly, an increase in the Ti plasma flow density leads to a decrease of the lattice parameter of the Ti–Zr–N coatings.

The stress state is found to be largely compressive $(-6.5$ GPa) and the stress-free lattice parameter is expanded by ~ 2.0% with respect to Vegard's law. These results may be explained by the presence of several growth defects introduced in the coating (due to the use of energetic plasma flows) as well as the formation of the substitutional solid solution itself.

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