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Effect of Cr Dopants on the Structure and Failure Mechanism of TiAlN Multilayered Films

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Structural features and mechanical characteristics of nanocomposite TiAlN multilayered thin films are characterized by electron microscopy, nanoindentation and atomic force microscopy. The films are deposited onto WC–Co substrates using cathodic arc method. As found, Cr dopants have an essential impact on the microstructure of samples, the morphology of cracks, and the mechanical properties of the coatings. It results in an increase in the hardness of the films studied due to disappearance of the wurtzite phase and the formation of a CrN hard f.c.c. phase. Moreover, the formation of the columnar structure and the increase in the number of bilayers, *etc.*, contribute to the additional strengthening of the film. The formation and propagation of indentation-induced cracks are sensitive to both a structure of film and its growth morphology. The primary cracks appear for all films beneath the indenter at the contact site. In columnar films, the morphology of these cracks consists of a network of short, discontinuous, irregular cracks. In fine-grained structures, the straight radial through-thickness cracks are formed. Such modification of crack patterns is attributed to the role of grain boundary sliding which is more pronounced in coarse columnar films than in nanograined materials.

Key words: thin film, cracks morphology, fracture toughness, hardness, transmission electron microscopy.

Методами електронної мікроскопії, наноіндентування та атомно-силової мікроскопії досліджено структурні особливості та механічні характеристики нанокомпозиційних багатошарових тонких плівок на основі TiAlN. Плівки було осаджено на підкладках WC–Co вкуумно-дуговим методом.

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Встановлено, що добавки Cr мають істотний вплив на мікроструктуру зразків, морфологію тріщин та механічні властивості досліджуваних покриттів. Додавання Cr веде до збільшення твердості досліджуваних плівок за рахунок зникнення вюрцитної фази AlN і утворення твердої фази CrN. Крім того, додатковому зміцненню плівки сприяють формування колоноподібної структури та збільшення кількості бішарів у покритті. Формування і поширення індукованих індентацією тріщин виявилися чутливими як до структури досліджуваної плівки, так і до морфології росту її зерен. В усіх покриттях з'являються первинні тріщини в місці контакту з індентором. Морфологія цих тріщин описується системою коротких, розривних, нерегулярних тріщин в покриттях, що мають колоноподібну мікроструктуру. А в плівках з дрібнозернистою структурою формуються прямі радіальні наскрізні тріщини. Зазначені особливості структури тріщин пояснюються ковзанням границь зерен, які є більш вираженими в стовпчастих плівках, ніж у нанокомпозиційному матеріалі.

Ключові слова: тонка плівка, морфологія тріщин, тріщинотсійкіть, твердість, просвічуюча електронна мікроскопія.

Методами электронной микроскопии, наноиндентирования и атомно-силовой микроскопии исследованы структурные особенности и механические характеристики нанокомпозиционных многослойных тонких плёнок на основе TiAlN. Плёнки осаждались на подложки WC–Co вакуумно-дуговым методом. Установлено, что добавки Cr оказывают существенное влияние на микроструктуру образцов, морфологию трещин и механические свойства исследуемых покрытий. Добавление Cr приводит к увеличению твёрдости исследуемых плёнок за счёт исчезновения вюрцитной фазы AlN и образования твёрдой фазы CrN. Кроме того, дополнительный вклад в твёрдость плёнки вносят формирование колонннообразной структуры и увеличение периода бислоя в покрытии. Формирование и распространение индуцированных индентацией трещин оказались чувствительными как к структуре исследуемой плёнки, так и к морфологии роста её зёрен. Во всех покрытиях появляются первичные трещины в месте контакта с индентором. Морфология этих трещин описывается системой коротких, разрывных, нерегулярных трещин в покрытиях, имеющих колонноподобную микроструктуру. В плёнках с мелкозернистой структурой формируются прямые радиальные сквозные трещины. Указанные особенности структуры трещин объясняются скольжением границ зёрен, которые являются более выраженными в столбчатых плёнках, чем в нанокомпозиционном покрытии.

Ключевые слова: тонкая плёнка, морфология трещин, трещиностойкость, твёрдость, просвечивающая электронная микроскопия.

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1. INTRODUCTION

TiAlN-based coatings are used to improve tribological behaviour of the surface, in particular, cutting and drilling tools operating in rigid operating conditions [1, 2]. It is known that the coating effectively protects the cutting edge from dissolving and high-temperature abrasive wear and provides a thermal barrier effect between chip and tool [3]. Unfortunately, the strength gained through the application of such thin films could be quickly neutralized by the formation of through thickness microcracks or problems on the boundary between film and substrate, since solid materials (nitride coatings, in particular) cannot maintain significant plastic deformation [4]. One of the possible solutions of this problem is the formation of nanostructures as nanocomposites in them, which will provide better toughness and improve the general mechanical characteristics of such thin films [5, 6]. In particular, experimental studies [7, 8] showed that nanostructured TiAlN nitrides have better functional characteristics and increased thermal and chemical stability compared to monolithic films (single layers) [9–11].

The influence of nanostructures on the mechanisms of deformation and mechanical reinforcement are well described by the known Hall–Petch relations, in which the hardness of the material depends on the grain size [12, 13]. The increase in hardness in multilayer materials is associated with structural barriers and processes controlled by the interface, while the improved crack resistance of the nanocomposite thin film is due to the high yield strength and the ability to withstand large deformation anisotropy [14].

For hard thin films, the issue of destruction is the main thing, since it determines their reliability and durability. In turn, coating nanostructurization can affect the processes of cracks formation in two ways. First, such a structure prevents a sharp transition between film and substrate that provides better interface strength. Second, nanoscaled structures may deviate a crack path or activate other crack modes, which prevent the formation of interlayer through thickness cracks, which are often present in single-layer films.

In this paper, the effect of Cr dopants on mechanical characteristics of the TiAlN based coating has studied. Mechanisms of the formation and propagation of cracks in TiAlCrN thin films have established.

2. EXPERIMENTAL DETAILS

The films were deposited in a commercial batch coater type RCS from Balzers (Liechtenstein) using cathodic arc method. Figure 1 shows a schematic diagram of a coater. The installation uses four targets of Ti/Al (33/66 at.%) and two additional Cr targets placed in opposite positions. The WC–Co substrate is secured to a sample holder for deposition of a nanofilm in a pure nitrogen atmosphere. The pressure during deposition was 2 Pa at a temperature of about 650°C. The substrate bias for all depositions was maintained at 100 V. Deposition rate was approximately 2.6 mm/h, the final thickness of the coating was 4.5

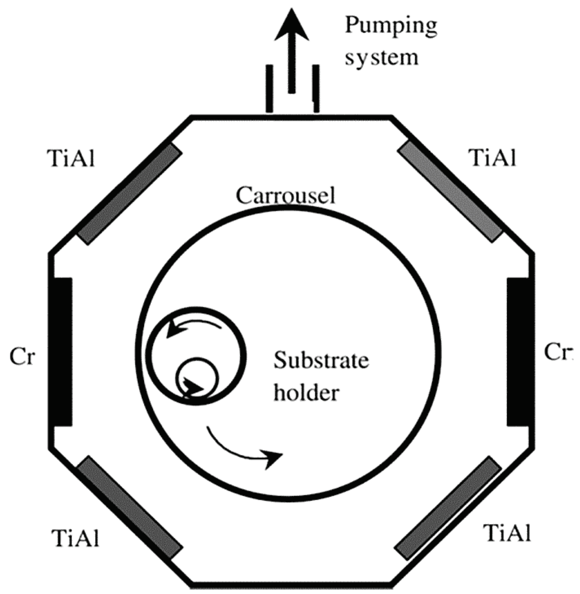


Fig. 1. Scheme of multicathodic arc deposition apparatus.

mm. Rotating the sample holder and periodically interrupting the substrate bias, thin films of different types were deposited:

1) TiAlN film, when only TiAl sources were permanently activated;

2) TiAlN/TiAlCrN multilayer coatings when Cr sources are periodically switched on for 1 minute and 5 minutes while TiAl sources are continuously operating (this sample is called TiAlCrN-I);

3) chemically modulated TiAlN/TiAlCrN films when both the TiAl and Cr sources were always switched on (this sample is called TiAlCrN-II).

The chemical composition of the thin films obtained is determined by Rutherford backscattering spectroscopy (RBS) and particle induced X-ray emission (PIXE) using 2 MeV proton beam and 2 MeV He^+ beam, respectively.

To prepare specimens for electron microscopy, the coating was initially cut with a diamond disc in parts with a thickness of 500–800 μm. The obtained parts were mechanically polished on diamond substrates to a thickness of ~40 μm, after which ion grinding was performed for final thinness. The microstructure of the films was analyzed by the Philips CM300 high-resolution electron microscope.

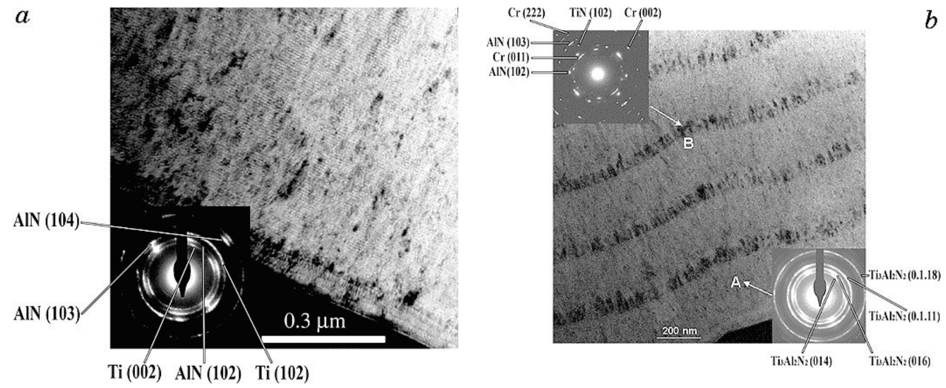
Hardness (H) and elastic modulus (E) for coated systems were measured on the Nanoindenter XP equipped with the Berkovich tip. To obtain the dependence of H and E on the indentation depth, the system worked in a continuous stiffness mode (CSM). A set of nine independent measurements was obtained for each sample, which allowed averaging the obtained values of hardness and elastic modulus. The analysis of nanoindentation data was carried out by Oliver and Farr method [15].

The surface morphology of the film was studied by atomic force microscopy (AFM-Nanoscope III).

3. RESULTS AND DISCUSSION

3.1. Microstructure of Samples

TiAlN films exhibit a modulated structure with a periodicity of about 2.6 nm associated with a rotation of samples during deposition. These films are characterized by a weakly columnar microstructure with a crystallite size of less than 10 nm (Fig. 2, *a*). The formation of such fine crystallites is associated with the presence of about 65–70 at.% Al, which is known to improve the structure of TiN and prevent the formation of highly columnar morphology [9]. When activating the Cr targets and rotating the substrate holder, TiAlCrN (I) and (II) multilayer coatings are formed (Fig. 2, *b*, *c*).



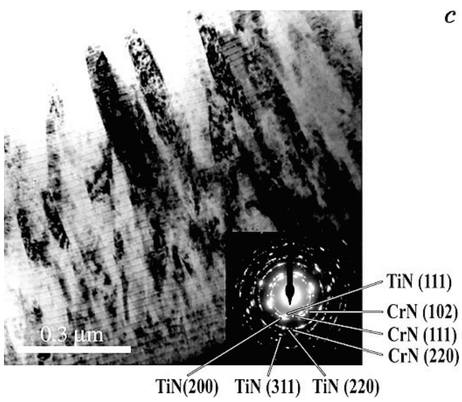


Fig. 2. Cross sectional TEM micrographs showing the microstructure of the samples studied: TiAlN nanolayers, 2.6 nm, obtained due to holder rotation (*a*); TiAlN/TiAlCrN (I) multilayer with bilayer thickness of 400 nm (*b*); TiAlNTiAlCrN (II) multilayer with bilayer thickness of 10 nm (*c*).

Figure 2, *b* shows the typical microstructure of the TiAlCrN-I sample, which is a multilayered film formed of TiAlCrN layers (a thickness of about 100 nm) and TiAlN layers (about 300 nm in thickness). In Cr-containing layer, a tendency of columnar growth of grains is observed. The analysis of the selected area of diffraction in the TiAlCrN layer reveals the presence of discrete diffraction spots, indicating a larger size of the grains in this layer. On the contrary, the TiAlN layer exhibits a continuous diffraction ring, which is characteristic of the fine crystals. In addition, the TiAlN/TiAlCrN interface is not sharp, which is confirmed by the data of local chemical analysis. The phase analysis performed in the selected diffraction area showed the coexistence of the f.c.c.-TiN phase, the AlN hexagonal and the b.c.c.-Cr phases.

The microstructure of the TiAlCrN-II sample, in which all the TiAl and Cr targets have been continuously switched on, are shown in Fig. 2, *c*. This sample is a multilayered coating with a bilayer period λ of approximately 10 nm. As shown in Fig. 2, *c* this coating is characterized by a pronounced columnar structure. The width of the columns is about 80 nm, these columns consist of nanocrystallites with the size of 10–200 nm. The phase analysis performed in the selected diffraction area showed that there are two cubic phases in the TiAlCrN-II sample, namely, the f.c.c. TiN and f.c.c. CrN.

3.2. Mechanical Characteristics

The mechanical characteristics (hardness and elastic modulus) of the samples at relative indentation depth of 0.15, on which the effect of the substrate WC-Co is considered insignificant are listed in Table 1. For single layer TiAlN, the measured hardness is 29.3 GPa, and for multilayer TiAlCrN-I coating is 32.9 GPa. Such an increase in hardness may be due to the introduction of a large number of boundaries between TiAlN and TiAlCrN layers. However, the highest hardness (38.4 GPa) is inherent to the chemically modulated TiAlCrN-II coating. This sample is characterized by a structure that is significantly different from the TiAlCrN-I multilayer sample. In TiAlCrN-II coating the bilayer period decreases in 40 times, increasing the effect of the interface on the hardness value [16, 17]. Also, in this sample a solid CrN phase is formed, the hardness of which reaches 11 GPa. In addition, pronounced columnar structures appear in TiAlCrN-II coatings.

Thus, the addition of Cr to the basic TiAlN coating is accompanied by the appearance of a hard f.c.c. CrN phase and the disappearance of the wurtsite AlN, which is known to have low hardness. Therefore, an increase in the hardness of TiAlCrN thin films can be explained by two factors, in particular, the modification of the microstructure, including a decrease in the bilayer thickness, the formation of a columnar structure, and the formation of a hard f.c.c. CrN phase with the simul-

TABLE 1. Microstructure and mechanical characteristics of the films studied.

Sample	Sample's structure	Chemical composition	H, GPa	E, GPa	H/E	H^3/E^2	Crack morphology
TiAlN	Single layer	$Ti_{19}Al_{32}N_{49}$	29.3	500	0.059	1.717	Cracks are straight and parallel to the contact area between indenter and film surface.
TiAlCrN-I	Multilayer with bilayer thickness of 400 nm	$Ti_{18}Al_{22}Cr_{25}N_{35}$	32.9	350	0.094	3.092	Edge cracks are accompanied by local delamination at the interface between layers resulting in bulged areas.
TiAlCrN-II	Multilayer with bilayer thickness of 10 nm	$Ti_{19}Al_{16}Cr_{16}N_{49}$	38.4	323	0.118	4.565	Irregular cracks are formed; radial cracks originating from the corners of the indenter are extended.

taneous disappearance of the wurtzite AlN phase.

Besides, as it is well known from the literature, the superlattice effect (significant hardness enhancement) produced by multilayered films arrangement is dependent on the thickness of the multilayers. Evolution of the hardness as a function of the bilayer thickness (modulation period λ) shows a characteristic behaviour, with maximum hardness values typically obtained for λ between 2 and 10 nm [18, 19]. The high hardness reported to be caused by the blocking dislocations motion at the layer interfaces due to differences on the shear moduli of the individual layers of materials and by coherency strain causing periodical strain-stress fields in the case of lattice mismatched multilayered films. Further increase of the period thickness led to a progressive decrease of the coating hardness up to the moment that remains fairly constant due to the total loss of the superlattice effect. At this point, multilayers start to behave as individual layers and the hardness of the films starts to be represented by the weighted average of the hardness of the individual layers. Thus, the lower hardness and Young's modulus of TiAlCrN-I coating could be interpreted by the high period thickness of the multilayers structure, which avoids the establishment of the superlattice effect.

The elastic strain to failure of the coatings is shown in Table 1 through the ratio H/E [20]. There are three general H to E ratios, which influence the wear resistance of a material, either in bulk or in coating form. These are H/E [21, 22], H/E^2 [23] and H^3/E^2 [24]. The first ratio characterizes the resistance of the material to elastic deformation. The second ratio, which is expected to correlate well with abrasive and erosive wear, indicates material's ability to resist permanent damage. Higher H^3/E^2 ratio allows estimating the material's ability to dissipate energy at plastic deformation during loading. However, toughness is the property of material, which relates to its ability to withstand plastic deformation. Thus, it is better to estimate a material's toughness by its H^3/E^2 ratio (Table 1). TiAlN film shows the worst resistance to the plastic deformation. Increasing the Cr content leads to a progressive increase of the H/E and H^3/E^2 ratios revealing the beneficial influence of Cr additions on the toughness of coatings, which can be related with the multilayer arrangement, which allows deflection of cracking, and improving fracture toughness [25].

3.3. Crack Morphology

Study of fracture modes and mechanisms of cracking in thin films requires regulated distribution of well-defined cracks in the film/substrate system or only through the thickness of the film. Despite the fact that nanoindentation technology is a means for creating macrocracks in the nanoscale to study the failure mechanisms of bulk materials, its extension to coated systems is still limited to the specific cases. A pair of coating/substrate is a complex system whose mechanical behaviour depends on the properties of the coating itself, on the characteristics of the substrate, to which the coating is applied and the features of the interface that connects the system together. To find out the fracture modes of hard films shallow indentations were performed to create primary cracks that the behaviour is mainly dominated by film properties where the substrate effects are negligible. Creating cracks requires a certain volume of indentation for which the substrate effect is to some extent always present. This modifies the initiation sequence of indentation cracks known for bulk materials, *i.e.*, cone, radial, median, half penny and lateral. For these reasons, indentations with shallow depths were performed to create primary cracks representative of coating deformation.

Analysis of the indenter's prints shows that the formation of cracks is generally limited to the contact area (Fig. 3). However, the microstructure of a thin film is strongly influenced by the morphology of the crack. One can see that in the TiAlN single layer coating several cracks approximately parallel to the contact area between indenter and film surface are observed (Fig. 3, *a*). The gap between the cracks remained almost constant (about 0.4 mm). Micrographs of the cross-section confirmed that these cracks remain largely superficial and do not apply to the substrate. However, it is established that they propagate deeper into the film at high loads, which correlates with the width of their opening on the surface.

In the TiAlCrN-I sample the cracks are rectilinear and parallel to the boundary of the contact (Fig. 3, *b*). A slight deformation is visible along the cracks, probably due to the destruction of the TiAlN/CrN interfaces. From Figure 3, *b* it was found that the width of the opening of

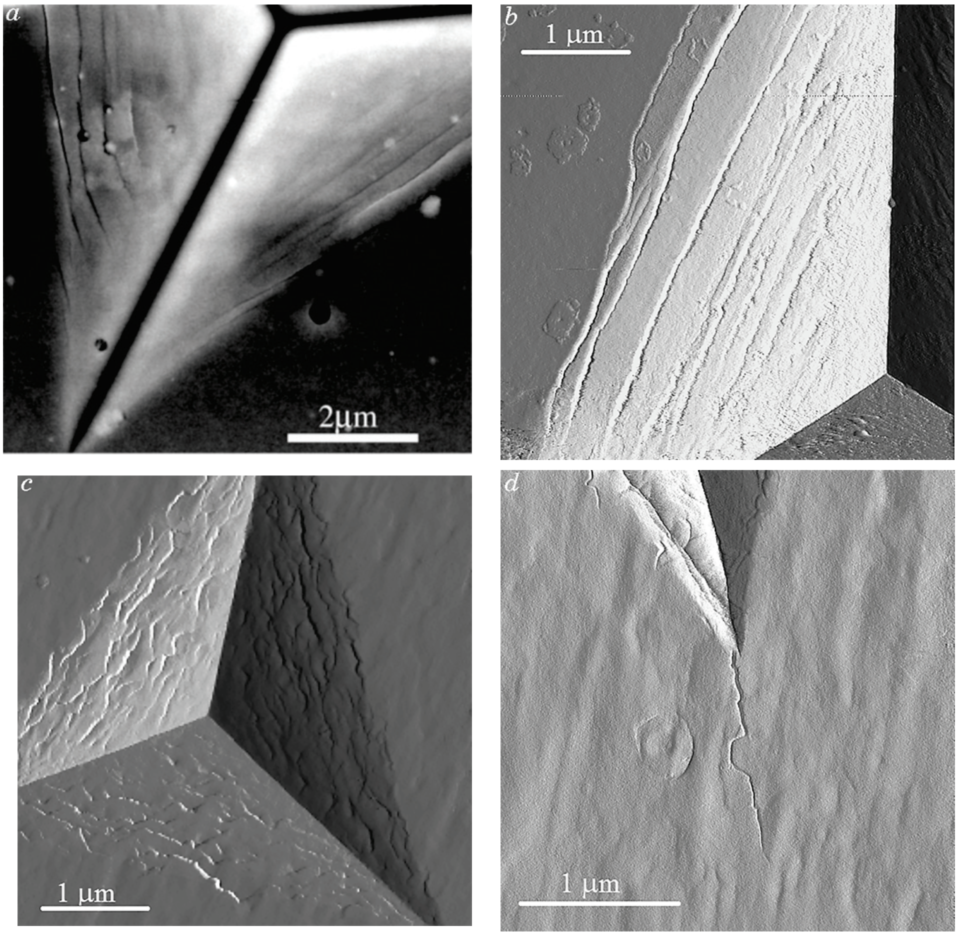


Fig. 3. AFM and SEM micrographs showing crack morphologies on the contact area: TiAlN—cracks are parallel to the contact edge (*a*); TiAlCrN (I)—the edge cracks are accompanied by local delamination at the interface between TiAlN/TiAlCrN layer resulting in bulged areas (*b*); in the TiAlCrN (II) columns boundary sliding result in a network of microcracks (*c*); radial cracks emanating from the indenter corner in TiAlCrN (II) (*d*).

the crack is less than that of TiAlN, which is probably due to the increase in strength (Table 1). Unlike the previous samples, irregular cracks are formed in the TiAlCrN-II sample (Fig. 3, *c*). Such cracks may be associated with a pronounced columnar structure with a larger grain size in this film. In addition, in this sample, unlike the previous films, radial cracks originating from the corners of the indenter are extended (Fig. 3, *d*). It should be noted that radial cracks appear for a relative indentation depth of 0.7.

4. CONCLUSIONS

In this paper, TiAlCrN multilayered thin films have been studied. It was shown that both Cr content and multilayered structure affect the microstructure of samples, the morphology of cracks, and the mechanical properties of the coatings.

Cr dopants result in an increase in the hardness of the films studied due to disappearance of the wurtsite phase and the formation of a hard f.c.c. CrN phase in TiAlCrN-II. Moreover, the formation of the columnar structure and the increase in the number of bilayers, *etc.* contribute to the additional strengthening of the film.

In TiAlCrN multilayer coating with a bilayer thickness of 400 nm (TiAlCrN-I) the columnar growth of grains in the TiAlCrN layer prevents the growth of TiAlN layer, resulting in a nanocrystalline structure. In TiAlCrN-II coating with a bilayer thickness of about 10 nm, the columnar growth of the grains of the TiAlCrN layer is not interrupted by a TiAlN layer, which results in the formation of a pronounced columnar microstructure of the film.

The fracture toughness of coatings obtained was estimated through H^3/E^2 ratio. TiAlN film shows the worst resistance to the plastic deformation. Increasing the Cr content leads to a progressive increase of the H/E and H^3/E^2 ratios revealing the beneficial influence of Cr additions on the toughness of coatings.

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