Magnetron sputtered coatings of $AlN–TiCrB_2$ system

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Wear and corrosion resistant coatings have been obtained by HF magnetron sputtering of an $AlN–TiCrB_2$ target (prepared by powder metallurgy technique) on Si, Al_2O_3 and GaAs single crystals. The coatings are characterized by ultra dispersed structure and a considerable high-temperature oxidation resistance caused by the formation of solid solutions in the $Al_2O_3–TiO_2–Cr_2O_3$ and $Al_2O_3–B_2O_3$ systems. The target material mass gain at 1300°C is 1.4 mg/cm^2. After the high-temperature oxidation, a reinforced disperse structure is formed in the coating as tangled Al_2O_3 fibers. The $(AlN–TiCrB_2)Al_2O_3$ and $(AlN–TiCrB_2)$–GaAs coatings are thermally stable up to 900°C and show high microhardness ($H\mu$ = 30 GPa) and fracture strength (K_{1c} = 3.3–4.7 MN/m$^{3/2}$). As the annealing temperature rises ($T > 1000$°C), the coating mechanical properties deteriorate but its adhesion strength becomes improved. The target material $AlN–TiCrB_2$ can be recommended to prepare wear and corrosion resistant coating on tools as well as on vital parts being operated in extreme conditions.

Получены износо- и коррозионностойкие покрытия радиочастотным магнетронным распылением мишени $AlN–TiCrB_2$, изготовленной методами порошковой металлургии, на монокристаллах Si, Al_2O_3 и GaAs. Покрытия характеризуются ультрадисперсной структурой и значительным сопротивлением высокотемпературному окислению благодаря образованию твердых растворов в системах $Al_2O_3–TiO_2–Cr_2O_3$ и $Al_2O_3–B_2O_3$. После высокотемпературного окисления формируется армированная дисперсная структура покрытия в виде переплетающихся волокон Al_2O_3. Покрытия $(AlN–TiCrB_2)–Al_2O_3$ и $(AlN–TiCrB_2)$–GaAs термостабильны до 900°C и имеют высокие значения микротвердости ($H\mu$ = 30 ГПа) и трещиностойкости (K_{1c} = 4.7–3.3 МН/м$^{3/2}$). С ростом температуры отжига ($T > 1000$°C) механические свойства покрытий ухудшаются, но при этом их адгезионная прочность возрастает. Материал мишени $AlN–TiCrB_2$ может быть рекомендован для получения износо- и коррозионностойких покрытий на инструменте, а также на ответственных деталях, работающих в экстремальных условиях.

Magnetron sputtering is used widely for coating cutting and punching tools, that requires to use wear and corrosion resistant materials with high working temperature (700°C) and sufficient thermal conduction for heat removal from the treatment zone. TiAlN coatings obtained by multisectional (Al and Ti blocks) target sputtering are used widely for these purposes [1–3].

As a rule, composite materials containing three and more components meet such requirements to the coatings. But multisectional target application both limits the use of new multiphase materials which provide variation of the coating properties in a wide range, and does not provide obtaining the coating composition corresponding to the target one. That is why, it is more appropriate to use low-porosity composite single-sectional targets prepared by the powder metallurgy methods.

High corrosion resistance and thermal conduction of aluminum nitride in combination with high hardness and electrical conduction of transition metal borides allow to consider the aluminum nitride/refractory boride ceramics as a new generation of targets materials for sputtering of wear, corrosion resistant coatings as well as barrier layers deposited by target sputtering. The aim of this work is to investigate the structure, composition, mechanical properties and high-temperature corrosion resistance of multilayered films obtained by magnetron sputtering of $AlN–TiCrB_2$ ceramics. The binary titanium-chromium boride is a TiB_2 + 20 % CrB_2 solid solution that has higher wear and corrosion resistance than titanium boride. The $AlN–TiCrB_2$ ceramics distinctive feature is the formation of high-temperature corrosion resistant compounds, β-tialite ($\beta–Al_2TiO_5$), $(Al,Cr)_2O_3$, and aluminum borates at high temperature oxidation. Herewith, β-tialite can play the role of a solid lubricant in dry friction conditions like $FeAl_2O_4$ and $FeAlO_3$ compounds [4].

$AlN–TiCrB_2$ targets of equimolar composition, of 60 mm in diameter and 2 mm high were prepared by hot pressing. The residual porosity of the targets did not exceed 2 %. Silicon and alumina single crystals with the surface orientation parallel to [1120] and gallium arsenide single crystals of [100] orientation were used as substrates. The coatings were deposited by radio frequency magnetron sputtering in purified argon atmosphere. The deposition was carried out at argon pressure of $6.6 \cdot 10^{-3}$ Pa and discharge current of 0.4 A. Herewith, the deposition rate was 12 nm/min and the thickness scatter from the center to the edges was about 1 %. The coatings were characterized in terms of their structure, composition, and properties using various analytical and measurement techniques, including scanning electron microscopy (SEM), electron probe microanalysis (EPMA), X-Ray diffraction (XRD), Auger spectroscopy. The micromechanical testing (micro-hardness $H\mu$ and toughness coefficient K_{1c}) was carried out by microhardness measuring instrument PMT-3 at 0.1–2 N load. The coating thickness was 0.6 μm. The toughness coefficient was calculated as [5]

$$\beta K_{1c} = PC^{-3/2}, \quad (1)$$

where C is the radial crack length; P, load; $\beta = \pi^{3/2}\mathrm{tg}\theta$, proportionality factor (13.8 for Vickers indenter); θ, slope angle of $C^{-3/2}(P)$ dependence. The $H\mu$ and K_{1c} values were measured both for initial samples and for those annealed up to 1000°C. The high temperature corrosion resistance of materials and coatings were investigated in non-isothermal conditions by thermogravimetry and differential thermal analysis at scanning rate of 20 deg/min up to 1500°C.

In principle, the reactions taking place at high-temperature oxidation of $AlN–TiCrB_2$ magnetron films must coincide with those for the target material oxidation:

$$4AlN + 3O_2 = 2Al_2O_3 + 2N_2, \quad (2)$$

$$2TiB_2 + 5O_2 = 2TiO_2 + 2B_2O_3, \quad (3)$$

$$4CrB_2 + 9O_2 = 2Cr_2O_3 + 4B_2O_3. \quad (4)$$

At high-temperature oxidation, compounds like tialite Al_2TiO_5, $(Al,Cr)_2O_3$, Cr_2TiO_5 and borates are being formed in the target skin. Those seem to play the role of solid lubrication at unlubricated sliding friction. $AlN–TiCrB_2$ oxidation curves (Fig.1), together with the results of EPMA, SEM of the material which have been oxidized at different temperatures [6] confirm this statement. The process has three stages. In the initial one (1000–1120°), double titanium-chromium boride is oxidized resulting in formation of TiO_2, Cr_2O_3 and B_2O_3 oxides. There are elongated TiO_2 grains alloyed with chromium that are situated along the boundaries of oxynitride phase in the structure of this film. In the second stage (1120–1280°), aluminum nitride is oxidized. In the third oxidation stage (1280–1520°), high-temperature corrosion resistant composites like Al_2TiO_5, Cr_2TiO_5 and aluminum borates are formed due to solid-phase interaction in $Al_2O_3–TiO_2$, $Cr_2O_3–TiO_2$ and $Al_2O_3–B_2O_3$ systems, respectively.

The substrate material influences both initial and oxidized film composition. The EPMA results indicate that Ti, Al, Cr, O, and small quantities of Si are present in the composition of the 3–5 μm thick film obtained by $AlN–TiCrB_2$ target sputtering on silicon single crystal in the technical argon atmosphere. The homogeneity of element line intensity and the small peak width along the electron probe scanning, espe-

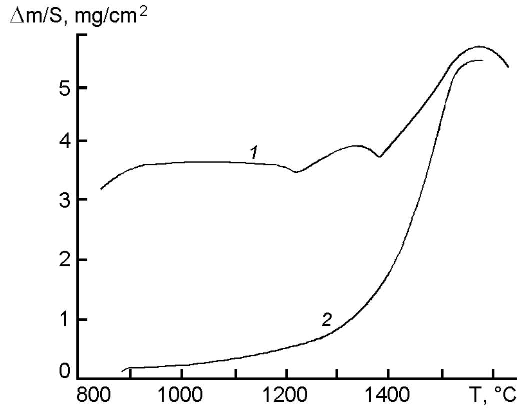

Fig. 1. TG and DTA oxidation curves of AlN–$TiCrB_2$ target material: *1* – DTA; *2* – TG.

cially for Al, indicate the formation of ultra-dispersed film structure (grain size ≤0.1–0.2 μm). After high temperature oxidation of (AlN–$TiCrB_2$)–Si composite up to 1450–1500°C, the dispersed film structure is retained but silicon quantity increases by a factor of 2 in comparison to the initial surface, due to its diffusion from the substrate. The coincidence of Al, Ti, O and Al, O concentration maxima in the EPMA spectra of oxidized surface points to the possible existence of two phases in the film: β-tialite and aluminum oxynitride. Herewith, the film has the structure (Fig. 2) reinforced with Al_2O_3 fibers at the length-to-diameter ratio of 1:10, 1:20 and more. The average grain length is 0.18–0.35 μm. As is well known [7], the solid solution formation in a coating-substrate system increases the adhesion bond strength. Therefore, the solid solution formation in Al_2O_3–TiO_2, Al_2O_3–SiO_2 systems at high temperature oxidation of the film-substrate composite provides high adhesion bond strength of oxide film and silicon. At temperatures exceeding 1350°C, the interaction of these solid solutions takes place with the formation of a dense oxide film, which prevents silicon from penetration into the oxide scale.

The ultra-dispersed film is formed on silicon single crystal also at AlN target sputtering in technical argon atmosphere [8]. According to EPMA data after AlN–Si composite high temperature oxidation up to 1450°C, the Al and O distribution corresponds to alumina; silicon is not observed in the film. Therefore, there is no silicon diffusion across the film. Herewith, the mass gain and heat generation effect are not observed. This testifies to dense alumina film formation being a barrier to oxygen diffusion.

Fig. 2. (AlN–$TiCrB_2$)–Si film microstructure after high temperature oxidation at 1450°C.

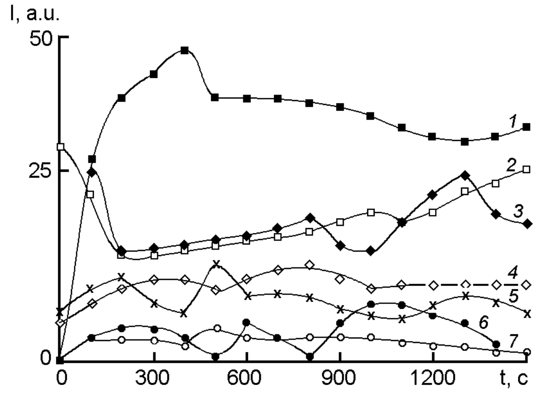

Fig. 3. Auger spectra of (AlN–$TiCrB_2$)–Al_2O_3 (110) film: *1* – O; *2* – B; *3* – Al; *4* – Ti; *5* – N; *6* – Cr; *7* – Si.

The level-to-level Auger spectrum analysis of (AlN–$TiCrB_2$)–Al_2O_3 composite [1120] surface at various ion etching duration *t* testifies the formation of oxide phases in the films, even in purified argon atmosphere (Fig. 3). Aluminum exists in condensate in a combined state — mainly, as oxinitride and possibly as alumina. Herewith, titanium boride and aluminum oxinitride (oxide) coexist along the whole film thickness. However, the oxygen concentration in a thin upper layer that corresponds to $t < 50$ s decreases sharply. This is due to the fact that at target sputtering, oxygen is actively consumed for the formation of aluminum oxinitride (oxide) being deposited on the substrate. This causes both the decreasing of oxygen partial pressure with the time in the working volume and oxygen concentration decrease in the upper layer. Therefore, according to Auger spectrum analysis, the film surface ($t < 50$ sec) contains mainly titanium diboride.

The (AlN–$TiCrB_2$)–Al_2O_3 (110) film in the initial state is amorphous. At annealing

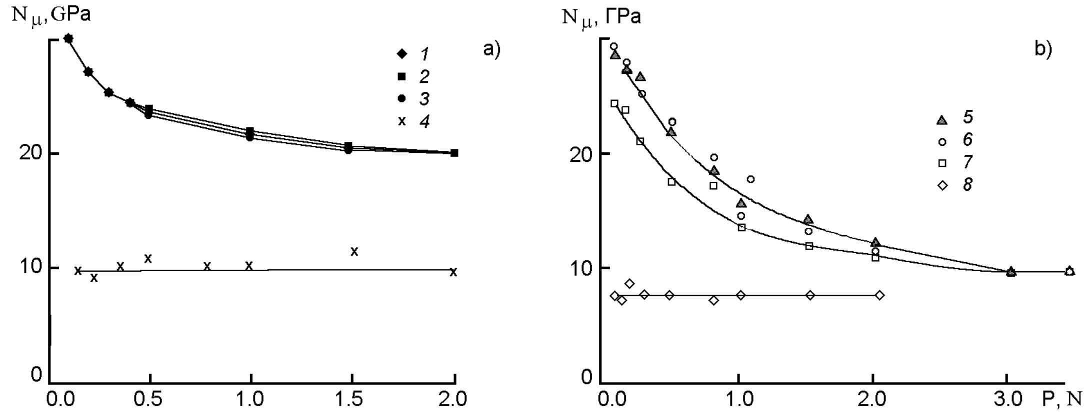

Fig. 4. Nμ(P) dependences for (AlN–TiCrB$_2$)–Al$_2$O$_3$ (110) (a) and (AlN–TiCrB$_2$)–GaAs (100) (b) prior to and after annealing: initial sample (*1*, *6*); samples annealed at temperatures (°C, 0.2 h duration): 600 (*2*); 800 (*3*); 1000 (*4*), GaAs (100) (*5*), 500 (*7*); 900 (*8*).

temperature 600°C, separate crystallization nuclei of the oxide phase of 1–2 μm size appear (Fig. 4). Their quantity and size are growing with the increasing annealing temperature). At 1000°C, a thin oxide layer of crystalline structure is formed (the grain size is no more than 2–3 μm). The EPMA spectra from the annealed condensate surface indicate the presence of alumina and titanium oxides. Herewith, the alumina dispersity is higher. The coincidence of Al, Ti and O concentration maxima in the EPMA spectra on the surface of composite annealed at 1000°C indicates that β-tialite appears in the film at lower temperature in comparison with its temperature formation in stationary conditions (T≈1350°C).

The Nμ(P) dependences for (AlN–TiCrB$_2$)–Al$_2$O$_3$ (110) and (AlN–TiCrB$_2$)–GaAs (100) prior to and after annealing at different temperatures are shown in Fig. 4. The coating microhardness decreases with the increasing indenter load P because of its small thickness (0.6 μm), and aims to the substrate microhardness. At P = 0.1 N and h = 0.1 μm, the film microhardness is rather high and is 30 GPa on both substrates. This value can be assumed to characterize the hardness of the film material. The Al$_2$O$_3$ and GaAs substrate microhardness changes slightly at 0.1 N load and amounts of 21 and 7.5 GPa, respectively. At T_{ann}≤800°C, the Nμ(P) dependence does not change. At T_{ann} = 900°C, the microhardness decreases slightly, probably due to increasing number of oxide phase crystallization nuclei in the coating. At T_{ann} = 1000°C, the microhardness at 0.1–1 N load decreases sharply and

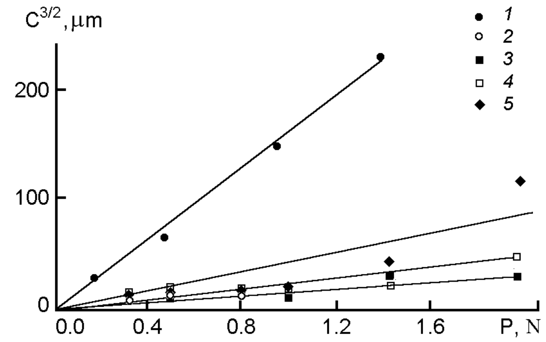

Fig. 5. $C^{3/2}(P)$ dependence for (AlN–TiCrB$_2$)–Al$_2$O$_3$ (110) film prior to and after annealing: GaAs (100) (*1*), initial sample (*2*); annealed at 600°C for 0.2 h (*3*); at 1000°C for 0.75 h (*5*).

equals at about 10 GPa. This testifies to phase and structural change in the film at this temperature which are due to crystallization processes and the beginning of aluminum nitride oxidation. As a result, the film is getting more rough and becomes yellowish.

The dependence of radial crack length on indenter load for the film-GaAs system is shown in Fig. 5. The cracks near the indentations appear at rather low loads (0.2–0.3 N). In $C^{3/2}$–P coordinates, the dependences are linear (except for T_{ann} = 1000°C). This points to the applicability of formula (1) for toughness coefficient (K_{1c}) calculation. The substrate material is characterized by the maximum $C^{3/2}(P)$ curve slope, and, therefore, it has low toughness factor. The curve slope decreases sharply for the film-substrate system and is minimum for the coated unannealed sample. This indicates that the film provides high resistance to

Table. Effect of annealing on coatings toughness factor K_{1c}, $MN/m^{3/2}$

Sample	Annealing conditions, T, °C (t, min)					
	Initial	500 (30)	600 (30)	800 (30)	900 (30)	1000 (45)
$(AlN-TiCrB_2)-Al_2O_3$	4.7	–	3.3	2.9	–	1.6
$(AlN-TiCrB_2)-GaAs$	3.3	3.1	–	–	1.2	–
GaAs	0.5(0.8*)	–	–	–	–	–

crack extension, perhaps because of its lower thermal expansion coefficient as compared to that of the substrate. The latter fact promotes compression stress occurrence in the surface layer. The increasing of $C^{3/2}(P)$ curve slope with rising annealing temperature testifies the decreasing effective crack growth resistance of film-substrate composites. The decrease of calculated K_{1c} with the temperature $T_{ann.}$ increase (see Table), in our opinion, is connected with changes in both phase composition (because of oxidation) and stress state of the subsurface film layer.

The XRD results indicate that after annealing at 900°C, the Al_2O_3 lattice parameter does not change. As for GaAs, it increases, perhaps due to coating components dissolution in gallium arsenide and thermal tension stresses appearing in the substrate, and, consequently, compression ones in the film, that results in the observed changing of toughness factor.

Thus, the coatings obtained on Si, Al_2O_3 and GaAs single crystals by magnetron sputtering of $AlN-TiCrB_2$ target have ultradispersed structure. The coating phase composition can differ from that of the target because of aluminum nitride oxidation due to its dissociation under ion bombardment during deposition. The main coating phases are binary titanium-chromium boride, aluminum nitride (possibly oxynitride), and alumina. After high temperature oxidation up to 1500°C, the coating dispersity and its high adhesion to the substrate are retained. Herewith, the structure comprising reinforcing elongated Al_2O_3 grains as twisted fibers is formed. The $(AlN-TiCrB_2)-Al_2O_3$ and $(AlN-TiCrB_2)-GaAs$ coatings are thermally stable up to 1000°C, have rather high microhardness $N\mu = 30$ GPa and toughness factor $K_{1c} = 3.3-4.7\ MN/m^{3/2}$. At $T_{ann} \geq 1000$°C, structural and phase changes take place. Those are accompanied by worsening of mechanical properties. The high hardness of condensates combined with a high-temperature corrosion resistance make it possible to propose the $AlN-TiCrB_2$ target material for the deposition of wear and corrosion resistant coatings on the tools and articles working at the extreme conditions.

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Зносо- та корозійностійкі магнетронні покриття на основі системи $AlN–TiCrB_2$

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Зносо- та корозійностійкі покриття одержано радіочастотним магнетронним розпиленням мішені $AlN–TiCrB_2$, виготовленої методами порошкової металургії на монокристалах Si, Al_2O_3 та GaAs. Покриття характеризуються ультрадисперсною структурою та значним опором високотемпературному окисненню завдяки утворенню твердих розчинів у системах $Al_2O_3–TiO_2–Cr_2O_3$ та $Al_2O_3–B_2O_3$. Після високотемпературного окиснення формується армована дисперсна структура покриття у вигляді волокон Al_2O_3, що переплітаються. Покриття $(AlN–TiCrB_2)–Al_2O_3$ та $(AlN–TiCrB_2)$–GaAs термостабільні до 900°C та мають високі значення мікротвердості ($H\mu$ = 30 ГПа) та тріщиностійкості (K_{1c} = 4,7–3,3 МН/м$^{3/2}$). З підвищенням температури відпалу (T > 1000°C) механічні властивості покриттів погіршуються, при цьому їх адгезійна міцність зростає. Матеріал мішені $AlN–TiCrB_2$ можна рекомендувати для отримання зносо- та корозійностійких покриттів на інструменті та на деталях, що працюють в екстремальних умовах.