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Effect of the Degree of Aluminum Doping on the Mechanical and Tribological Characteristics of Titanium–Aluminum Nitride Films

D. A. Golosov[a, *], E. M. Oks[b], V. A. Burdovitsin[b], T. D. Nguyen[a], S. N. Melnikov[a], S. M. Zavadski[a], I. L. Pobol[c], N. A. Kananovich[c], Xiubo Tian[d], and N. N. Lam[a]

[a] *Belarusian State University of Informatics and Radioelectronics, Minsk, 220013 Belarus*

[b] *Tomsk State University of Control Systems and Radioelectronics, Tomsk, 634050 Russia*

[c] *State Scientific Institution "Physical-Technical Institute of National Academy of Sciences of Belarus", Minsk, 220141 Belarus*

[d] *Harbin Institute of Technology, Harbin, Heilongjiang province, 150001 China*

**e-mail: dmgolosov@gmail.com*

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Abstract—The mechanical and tribological characteristics of titanium–aluminum nitride films deposited by the reactive magnetron sputtering of Ti–Al mosaic targets with different aluminum concentrations were studied. The dependences of the elemental composition, microhardness, and friction coefficient on the degree of doping of the films with aluminum and nitrogen concentration in the Ar/N_2 gas mixture during film deposition were obtained. It was found that an increase in the aluminum content in the film results in an increase in film hardness and decrease in the friction coefficient. The optimum nitrogen concentration in the film was achieved at maximum hardness and low values of the friction coefficient. A maximum hardness of 23.5 GPa and a minimum friction coefficient of 0.082 were obtained for films of the composition $Ti_5AlN_{1.33}$, which had a Ti/Al ratio of 5 : 1 and a nitrogen deficiency.

Keywords: thin films, wear-resistant coatings, titanium–aluminum nitride, reactive magnetron sputtering, mosaic target, microhardness, wear resistance

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INTRODUCTION

An effective method for increasing the life of a cutting tool for high-speed cutting without the use of cutting fluids is to apply hardening wear-resistant coatings [1]. Such coatings should have high wear resistance and adhesion, a low friction coefficient, and high resistance to oxidation at elevated temperatures (up to 800°C). Traditionally, titanium nitride (TiN) coatings are used to increase the life of a cutting tool. Titanium nitride has a relatively high hardness (20–30 GPa) and wear resistance. The main disadvantage of titanium nitride is its low thermal stability. TiN coatings oxidize at temperatures of 500–550°C [2]. One way to increase the temperature resistance of binary nitride coatings and improve their characteristics is to add additional alloying elements (Al, Cr, Si, Cu, etc.) to the film composition [3]. Upon doping, a complex multiphase nanocrystalline or amorphous structure is formed in the films, which provides an increase in microhardness, a decrease in the friction coefficient, and an increase in thermal stability and resistance to oxidation at high temperatures.

Significant improvement in the performance characteristics of titanium nitride coatings is achieved by alloying with aluminum. $Ti_xAl_{(1-x)}N_y$ coatings hardly oxidize at all up to a temperature of 800°C [4]. This is because at high temperatures, a thin dense layer of aluminum oxide forms on the coating surface, which acts as a diffusion barrier [5]. Along with increased corrosion resistance, alloying with aluminum increases the hardness and wear resistance of titanium nitride-based coatings.

In most cases, hardening coatings based on multicomponent nitrides are applied by arc evaporation [6] or reactive magnetron sputtering [7]. To obtain a multicomponent composition of the films, cosputtering from individual sources [8] or sputtering of alloy metal targets [7] is used. The cosputtering method has a number of significant drawbacks and limitations. First of all, there are great difficulties in ensuring homogeneous mixing of the components, especially with a large set of components and complex shapes of workpieces. Sputtering of alloy targets yields good results when it is possible to obtain an alloy or solid solutions

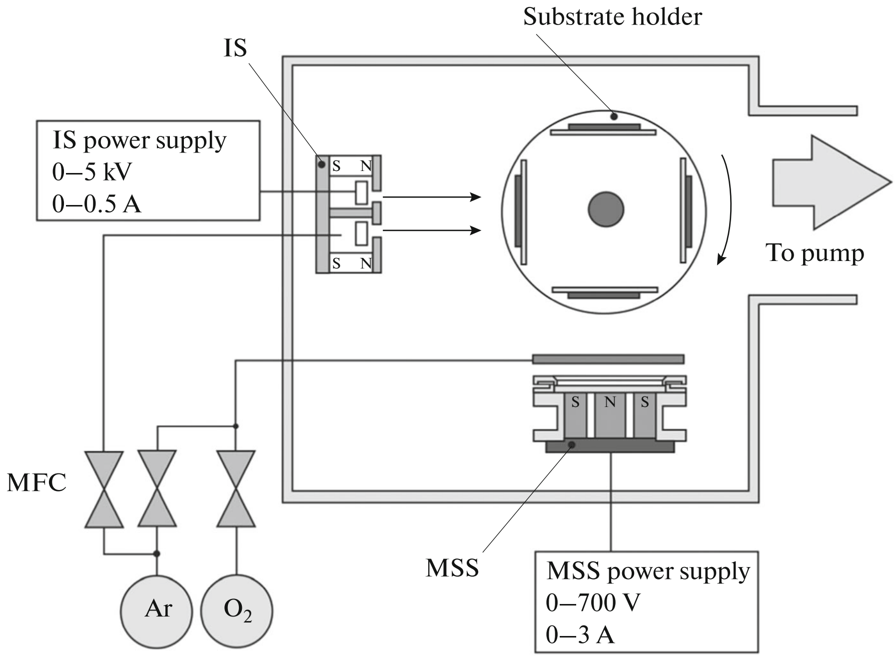

Fig. 1. Diagram of experimental setup for deposition of titanium–aluminum nitride layers by reactive magnetron sputtering.

with the necessary elements. However, in some cases, the composition of the deposited layers includes dissimilar materials with low mutual solubility or vastly different melting points.

One of the latest trends in developing methods for multicomponent wear-resistant coatings is to use thin films, so-called composite or "mosaic" targets, i.e., targets consisting of a matrix with one metal embedded with other metals [9]. This makes it possible to obtain multicomponent films with an arbitrary amount and content of elements using a single magnetron. In this case, the material is sputtered from one target under the same conditions. The advantage of the method is especially manifested in cases when it is necessary to obtain films that include elements with low mutual solubility or greatly different melting points. However, despite the obvious scientific and practical interest, there is practically no information on this method for applying titanium–aluminum nitride films and the relationship of the concentration of nitrogen and aluminum alloying additives with the mechanical and tribological characteristics of the applied layers.

Objective—to study of the features of reactive magnetron deposition of titanium–aluminum nitride films in the sputtering of Ti–Al mosaic targets and the influence of the deposition process parameters and degree of alloying with aluminum on the composition and mechanical and tribological characteristics of the films.

MATERIALS AND METHODS

Figure 1 shows a diagram of the experimental setup for deposition $Ti_xAl_{(1-x)}N_y$ films by reactive magnetron sputtering. The vacuum chamber was equipped with a MAC-80 magnetron sputtering system (MSS) with a target ∅80 mm and an ion source (IS) based on Hall current accelerator. For sputtering, composite mosaic Ti–Al targets and a VT1-00 titanium target (99.5% purity) with ∅80 mm and a thickness of 5 mm were used. The mosaic targets were a Ti base ∅80 mm and 5 mm thick into which four cylindrical Al inserts are pressed. The ∅6 mm or ∅8 mm inserts are evenly distributed over a diameter of 46 mm. In this case, the calculated Al/Ti ratios in the deposited films should have been 1 : 9 (TiAl-10) and 2 : 8, respectively (TiAl-20). $Ti_xAl_{(1-x)}N$ films were applied to polished AISI321 steel substrates.

Targets were sputtered in Ar/N_2 gas mixture at a constant Ar flow rate in all processes of Q_{Ar} = 50 sccm and a constant discharge current of I_t = 1.5 A. The nitrogen flow rate was varied from 0 to 20 sccm using automatic RRG-1 mass flow controllers (MFC). The deposition time varied depending on the deposition rate of 15–25 min. In this case, the thickness of the deposited films was 0.8–1.2 μm.

The thickness of the deposited layers was determined using a POI-08 optical interferometric profilometer [10]. The thickness distribution of the elemental composition of the coatings was studied on a GD Profiler 2 glow emission optical emission spectrometer

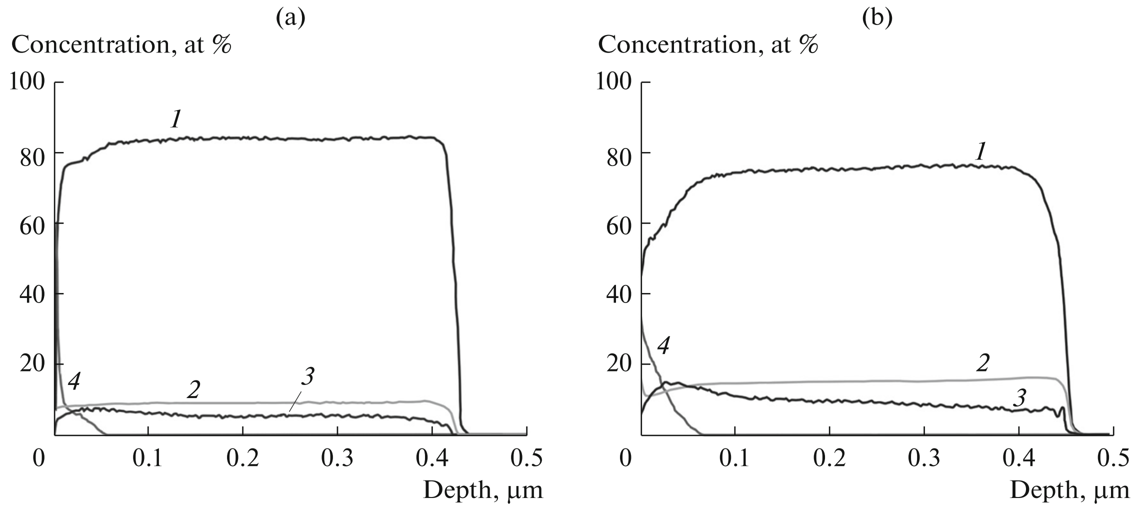

Fig. 2. Distribution of element concentration ((*1*) Ti; (*2*) Al; (*3*) N; (*4*) O) over depth of films deposited by sputtering of TiAl-10 (a) and TiAl-20 (b) targets (Γ_{N_2} = 3.8%).

(HORIBA Jobin Yvon SAS). The hardness of the coatings was measured with a Leika VMHT Mot. For measurements, a Knoop indenter was used. The measurements were carried out with an indenter load of 10 g and a load retention time of 15 s. In measurements, the indenter penetration depth in the film did not exceed 30% of the film thickness, which excluded the influence of substrate deformation. The friction coefficient and volumetric wear of the films were measured on a TAU-1N tribometer using the method of abrasion of the film during reciprocating motion of the counterbody under conditions of dry friction (ball-plane friction system). A ball bearing was used as a counterbody, ∅6.3 mm made of 1.3520 (EN) steel. The indenter load was 500 mN, the sliding speed was 2 mm/s, the length of the double pass was 14 mm, and the number of friction cycles was 1000. Volumetric wear of the coating was calculated based on the width and length of the friction track.

RESULTS AND DISCUSSION

We studied the dependences of the elemental composition of the deposited films on the nitrogen concentration in Ar/N_2 gas mixture during reactive sputtering. Figure 2 shows typical profiles of the element distribution over the thickness of the films obtained by sputtering of TiAl-10 and TiAl-20 targets. The films were deposited under the following conditions: Q_{Ar} = 50 sccm Q_{N_2} = 2 sccm, discharge current I_t = 1.5 A. As can be seen from the figure, regardless of the type of target being sputtered, the distribution of element concentrations over depth was uniform. The presence of oxygen was observed in the surface layers of the films, which is apparently associated with the presence of adsorbed air.

Analysis of the dependences of the elemental composition of the deposited films on the concentration of nitrogen in the Ar/N_2 gas mixture showed that with increasing Γ_{N_2}, regardless of the target used, the nitrogen content in the deposited films increased almost linearly (Fig. 3). When the nitrogen content in Ar/N_2 9% gas mixture, the nitrogen concentration in the deposited films did not exceed 20%; i.e., the films had a nitrogen deficiency. Moreover, during sputtering of TiAl targets, the aluminum content in the film remained approximately constant, and an increase in nitrogen content was achieved due to a decrease in the titanium concentration. This behavior is apparently associated with different chemical reactions rates in the formation of titanium and aluminum nitrides. In reactive magnetron sputtering, small nitrogen concentrations in Ar/N_2 are required to form stoichiometric titanium nitride gas mixture, on the order of 5–8% [11]. At the same time, stoichiometric aluminum nitride forms at nitrogen concentrations of about 30% [12]. Thus, when a mosaic target is at high nitrogen concentrations, titanium nitride and partially nitrided aluminum are sputtered from the target.

The influence of the deposition process parameters on the microhardness and wear resistance of the deposited films were studied. Figure 4 shows the dependence of the microhardness of the deposited films on the nitrogen content in Ar/N_2 gas mixture during deposition. Regardless of the type of target used, the dependences of the microhardness of the films on Γ_{N_2} had a similar character. The hardness of the films initially increased, reached a maximum at a

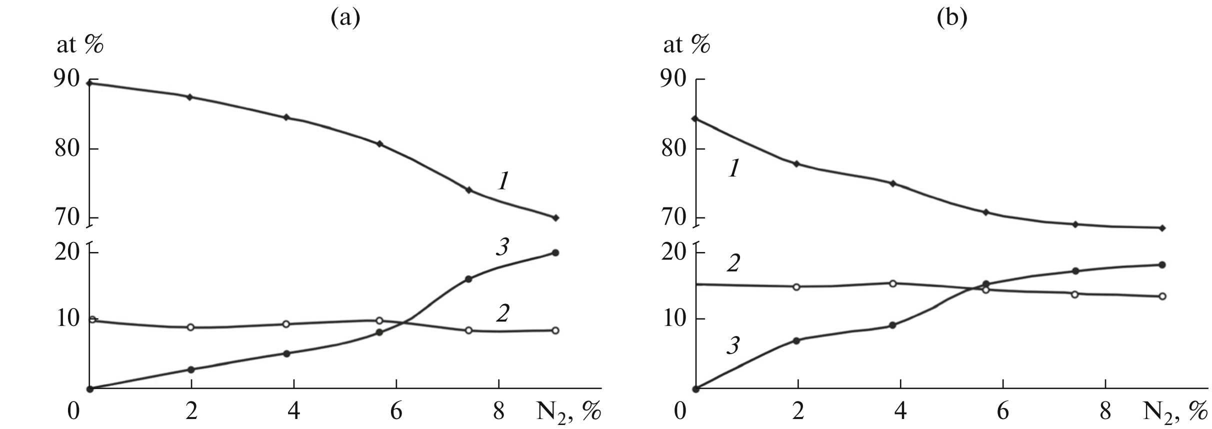

Fig. 3. Dependence of content of elements (*1*, Ti; *2*, Al; *3*, N) in deposited film on nitrogen content in Ar/N_2 gas mixture during sputtering of TiAlN-10 (a) and TiAlN-20 (b) targets.

certain nitrogen concentration, then decreased. Thus, during sputtering of a Ti target in an Ar medium, the film hardness was about 10 GPa. With increasing nitrogen concentration in an Ar/N_2 gas mixture, the hardness increased, reached a maximum of 17 GPa for Γ_{N_2} of about 2%, then decreased to 5.5 GPa for Γ_{N_2} = 9%. When the TiAl-10 target was sputtered, the maximum hardness of the films reached 21 GPa at a nitrogen concentration of 6.5%, and for the TiAl-20 target, 23.5 GPa for Γ_{N_2} = 9%. For comparison, the microhardness of the initial AISI321 stainless steel substrate was 4.55 GPa. Thus, with an increase in the aluminum concentration in the initial targets, the hardness of the deposited films increased and the maximum hardness was reached at ever higher nitrogen concentrations.

Studies of the tribological characteristics of films under dry friction conditions showed that, regardless of the type of target sputtered, the behavior of all deposited $Ti_xAl_{(1-x)}N_y$ films had a similar character. For example, Fig. 5 shows the dependences of the friction coefficient K_T on the friction track for films obtained by sputtering of a TiAl-10 target. Films deposited with a low nitrogen content (less than 2%) had a relatively high friction coefficient K_T = 0.4–0.6 (Fig. 5, curve *1*). The volumetric wear (*W*) of such films was 10^{-6}–10^{-5} mm^3 for a double pass. With an increase Γ_{N_2}, the friction coefficient decreased to 0.12–0.25 (Fig. 5, curves *2*–*4*). In this case, the volumetric wear of the films also sharply decreased to 10^{-10} mm^3 for a double pass. Such films after the initial running-in had an almost constant K_T in all wear areas, which

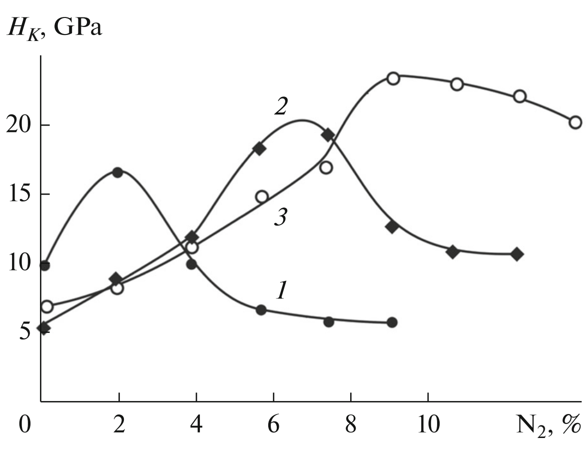

Fig. 4. Dependence of Knoop microhardness H_K of titanium–aluminum nitride films on nitrogen content in Ar/N_2 gas mixture during sputtering of targets with different compositions: (*1*) Ti; (*2*) TiAl-10; (*3*) TiAl-20 (load 10 g).

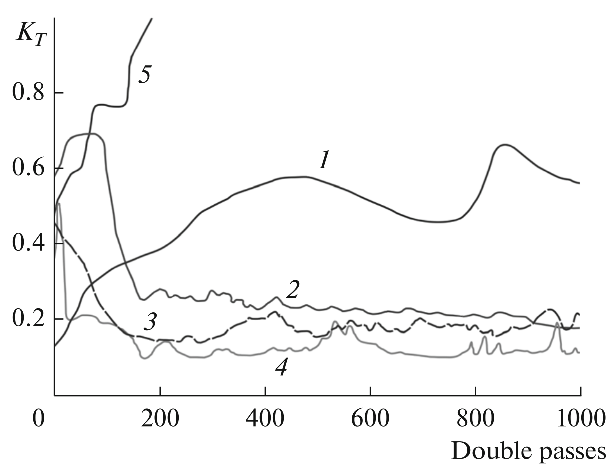

Fig. 5. Dependence of friction coefficient on friction track of titanium–aluminum nitride films deposited at various nitrogen concentrations in Ar/N_2 gas mixture: (*1*) 0; (*2*) 2; (*3*) 3.9; (*4*) 7.4; (*5*) 10.7% (target TiAl-10).

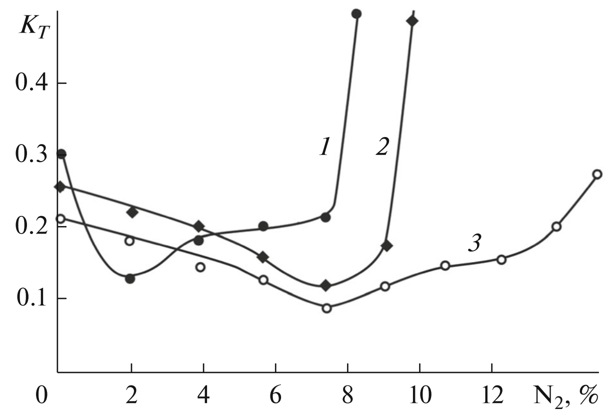

Fig. 6. Dependence of friction coefficient K_T of titanium–aluminum nitride films obtained by sputtering of various targets ((*1*) Ti; (*2*) TiAl-10; (*3*) TiAl-20) on percentage of nitrogen in Ar/N_2 gas mixtures.

indicates the absence of a layered coating structure. At a nitrogen concentration of 7.4%, films with K_T = 0.12–0.13 and $W = 6.3 \times 10^{-11}$ mm^3 were obtained With a further increase in nitrogen concentration (more than 8%), the coefficient began to increase sharply and for $\Gamma_{N_2} > 10\%$ reached 1.0 after 50–150 friction cycles. This behavior is associated with degradation of a film with large internal stresses.

Figure 6 shows the dependences of the friction coefficient of $Ti_xAl_{(1-x)}N_y$ films obtained by sputtering of various targets on the percentage of nitrogen in the Ar/N_2 gas mixture. Analysis of the dependences of the friction coefficient on the nitrogen concentration in the Ar/N_2 gas mixture shows that K_T of the deposited films depends on the nitrogen concentration in the deposition process, and the concentration of aluminum in the film. The smallest friction coefficient K_T = 0.082 was observed in films deposited by sputtering of a TiAl-20 target for Γ_{N_2} = 7.5%. It should be noted that for aluminum-doped films, the maximum hardness and minimum K_T did not coincide.

An analysis of the results shows that the mechanical and tribological characteristics of $Ti_xAl_{(1-x)}N_y$ films depends on both the nitrogen concentration and aluminum concentration in the deposited film. An increase in the aluminum content leads to an increase in the hardness of the films and a decrease in the friction coefficient. For the nitrogen concentration in the film, there is an optimum at which maximum hardness is achieved, as well as low K_T and *W*. The maximum hardness H_K 23.5 GPa and minimum friction coefficient 0.082 were obtained by sputtering of a TiAl-20 target at a nitrogen concentration in the Ar/N_2 gas mixture of about 7–10%. In this Γ_{N_2} range, nitrogen-deficient $Ti_5AlN_{1.33}$ films were formed. The ratio of titanium to aluminum is slightly lower than the calculated one of 5 : 1. Comparison of the mechanical and tribotechnical characteristics of the obtained titanium–aluminum nitride coatings with traditional titanium nitride shows that alloying with aluminum (20%) can increase the wear resistance of coatings and their microhardness by almost 40%. Moreover, it is possible that a further increase in Al concentration in the films can still improve the mechanical and tribological characteristics of $Ti_xAl_{(1-x)}N_y$ films.

CONCLUSIONS

It has been established that reactive magnetron sputtering of a mosaic target is an effective method for forming multicomponent wear-resistant coatings. The method provides homogeneous mixing and formation of films uniform in thickness and substrate area. It has been established that the maximum hardness H_K 23.5 GPa and minimum friction coefficient 0.082 were obtained by sputtering of a TiAl-20 target at a nitrogen concentration in the Ar/N_2 gas mixture of about 7–10%. In this Γ_{N_2} range, nitrogen-deficient films $Ti_5AlN_{1.33}$ were formed.

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