UDC 621.793: 548.73

STRUCTURE AND STRESS STATE OF TiN AND $Ti_{0.5-X}Al_{0.5}Y_XN$ COATINGS PREPARED BY THE PIII&D TECHNIQUE FROM FILTERED VACUUM-ARC PLASMA

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The results of investigations of the structure and stress state of TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings deposited from the filtered vacuum-arc plasma under high voltage pulsed bias potential on the substrate are presented. It was found that axial texture [110] is formed in coatings when pulses potential with an amplitude 0.5…2.5 kV are applied. For TiN coatings with increasing amplitude of the potential the perfection of texture is increased and the level of residual compressive stress is decreased. As for $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings with increasing amplitude the stress level is increased. In this case the texture is most strong outlined at the amplitude of 1 kV. With further increase in the amplitude the texture perfection becomes weaker. Differences of structure and stress state may occur due to the possibility of phase transition for multi-component coatings Ti-Al-Y-N associated with the decay of the supersaturated solid solution (Ti,Al)N stimulated by high energy ion bombardment.

INTRODUCTION

The vacuum arc nitride coatings on the base of TiN are widely used for hardening the surface of the parts of machines and cutting tools. Most of the recent studies are now focusing on multicomponent and nanostructured nitride-based coatings. The experimental data available indicate that new types coatings may have unique properties for usage in various branch of industry: high hardness, wear resistant, thermal stability and oxidation resistance and enough low friction coefficient [1, 2]. However the droplet phase of the cathode material in the plasma stream of the vacuum-arc plasma source worsens the quality of the coating deposited. High level of the surface roughness and residual stress restrict essentially the possibilities of usage such coatings for the purpose of hardening the machinery friction pairs [3-5].

The last years were marked by considerable progress in development the vacuum-arc deposition method. Three main techniques should be noted which facilitate the qualitative vacuum-arc nitride coatings deposition: plasma filtration, applying high voltage pulses to the substrate, choice of proper composition of multi-component nanostructured coatings. Plasma immersion ion implantation and deposition (PIII&D) is a technique for the effective combination of these techniques. Generally, in PIII&D vacuum arc source with magnetic filter for plasma is used and negative bias voltages ranging from a few hundred to a few thousand volts are applied to the substrates in a pulsed manner [6-13].

The use of plasma filtration can significantly improve the coatings quality by formation of a more uniform structure with low surface roughness due to a reduction of large macroparticles content in the plasma flow. A high-voltage pulsed bias applied to the substrate permits the deposition of thicker coatings with good adhesion and low residual stresses at low substrate temperature.

There are the data in literature on the effect of pulses amplitude on the level of residual stresses in simple single-phases nitrides (e.g. TiN, AlN) [11-13]. An increase in internal stresses is observed up to -500 V pulse bias voltage, which gradually decrease, with increasing bias voltage magnitude. The observed change in the level of intrinsic stress is explained with the model proposed by Davies [14]. This model is based on the competitive effects that occur during subplantation of ions under the growing surface of the film and its relaxation during the high energy ion bombardment.

In our recent papers we studied the structure and some properties of the coatings $Ti_{0.5}Al_{0.5}N$, alloyed with small additions of Y (up to 1 at.%), which were produced by PIII&D technique. Multi-component nitride coatings had significantly better the oxidation resistance and wear resistance in comparison with titanium nitride [9, 10]. It was found that the dependence of the residual stress on the pulsed voltage potential is non-monotonic with a minimum when the amplitude was of 1 kV.

In this paper, a comparative study of the structure and stress state of $Ti_{0.5-x}Al_{0.5}Y_xN$, and TiN coatings deposited under identical conditions from the filtered vacuum arc plasma under pulsed bias potential on the substrate was carried out.

MATERIALS AND METHODS

Coatings of Ti-N and Ti-Al-Y-N systems of 6…8 micron thickness were deposited from the filtered vacuum arc plasma at a nitrogen pressure of 0,1 Pa and arc current of 100 A using cathodes made of commercially pure titanium and alloy $Ti_{0.49}Al_{0.5}Y_{0.01}$ respectively. Deposition was carried out on substrates made of tool steel with a diameter of 17 mm and thickness of 3 mm. The negative potential pulses with an amplitude A_U in the range 0…2.5 kV were applied to the substrate with a repetition frequency of 24 kHz. The pulse duration was 5 μs. In the intervals between pulses the substrate was under a self-consistent "floating" potential -(3…15) V.

The elemental composition of the coatings was controlled by X-ray fluorescence analysis at the vacuum scanning crystal-diffraction spectrometer SPRUT.

X-ray diffraction studies, including analysis of the phase composition, determination of residual stresses and the parameters of the crystal structure were carried out in the filtered Cu-K$_\alpha$ radiation on DRON-3 diffractometer. The grain size (coherent scattering zone) in the nitride films was calculated from the (111) or (220) peak broadening, using the Scherrer relation. Determination of residual macroscopic stresses in the films was carried out by X-ray tensometry ($\sin^2\psi$-method modified for textured samples). Stresses were calculated using a-$\sin^2\psi$ plots in approach of quasi-isotropic symmetric biaxial stress state.

RESULTS AND DISCUSSION

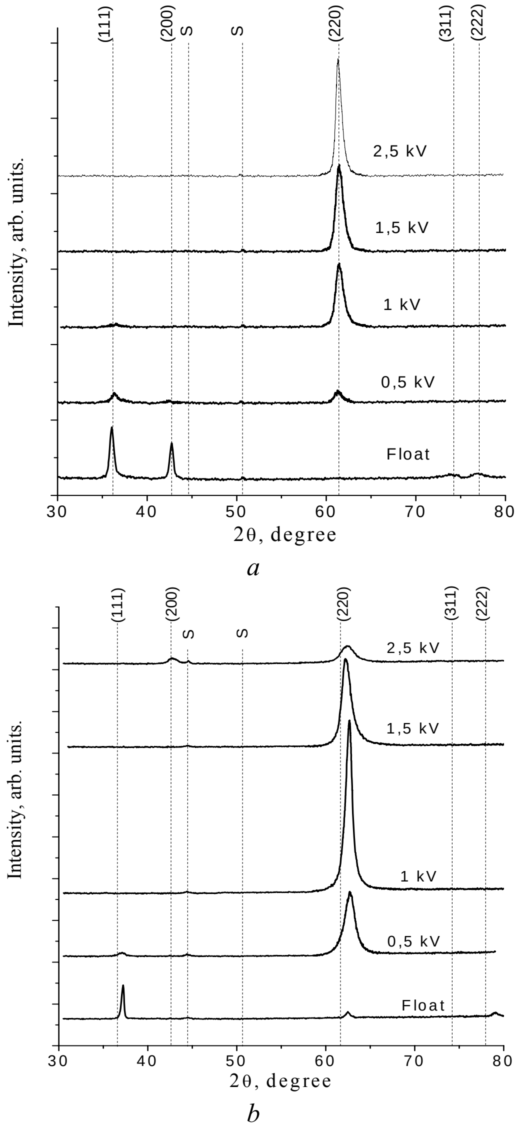
X-ray fluorescence analysis of the elemental composition of the coatings showed that the change in the amplitude of the pulse bias potential on the substrate in the range 0…2.5 kV has no significant effect on the elemental composition of the coatings. The ratio of metal components in a multicomponent cathode is well reproduced in the films.

According to X-ray diffraction data the single crystal phase in the coatings is the cubic nitride with the structure of titanium nitride (structural type NaCl). Diffraction patterns of the investigated coatings are shown in Fig. 1.

The ratio of the intensities of the diffraction peaks differs from the value characteristic to the chaotic orientation of crystallites in which the strongest line is (200), which indicates the presence of texture. Three reflections: (111), (200) and (220) were taken into account when texture coefficients T$_C$ were calculated. The texture coefficient was defined as [13]: $T_C = \left[nI_m^{(hkl)} / I_0^{(hkl)} \right] / \left[\sum I_m^{(hkl)} / I_0^{(hkl)} \right]$, where $I_m^{(hkl)}$ is the measured intensity of (hkl) reflection; $I_0^{(hkl)}$ is the theoretical relative intensity of (hkl) reflection for powder material with random-orientation and n is the total number of observed reflections ($n = 3$). The results of the calculations are presented in Fig. 2.

When substrate bias potential is floating, the crystallites of nitride are orientated with (111) plane parallel to the surface of the coating. The average size of coherent scattering regions in the coatings is 20 nm. When high-voltage pulses of potential with an amplitude 0.5…2.5 kV are applied to the substrate a change in preferred orientation occurs with the formation of a strong axial texture [110]. The only detectable line in the diffraction patterns is (220). Analysis of the diffraction patterns and rocking curves have shown that with increasing amplitude of the pulse potential the degree of perfection of TiN coatings texture increases and the grain size is in the range 11…14 nm.

For Ti$_{0.5\text{-}x}$Al$_{0.5}$Y$_x$N coatings the texture is most strong outlined at the amplitude of 1 kV. With further increase in the amplitude the texture perfection becomes weaker and the grain size decreases from 14 to 7 nm. In the diffractogram of the film Ti$_{0.5\text{-}x}$Al$_{0.5}$Y$_x$N deposited with the amplitude of the pulses of 2.5 kV the intensity of the (220) line is significantly reduced and one more, weak line appeared, which can be identified as (200). However, a closer examination revealed a large difference in the values of the nitride lattice period, calculated on the positions of these diffraction lines, which amounted to (0.4209 ± 0.0003) nm and (0.4238 ± 0.0005) nm respectively. One could assume that these lines belong to two different cubic nitride phases of various compositions. This hypothesis was indirectly confirmed in further studies.

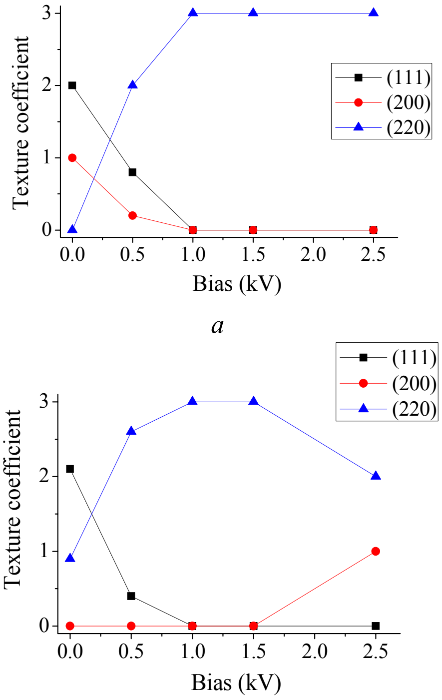


a

b

Fig. 1. X-ray diffraction patterns of vacuum-arc coatings deposited from the filtered plasma at different amplitude pulsed substrate bias potential (emission of Cu-K$_\alpha$, dashed lines show the position of peaks of TiN, "S" indicates the line of the substrate): a – coating TiN; b – coating Ti$_{0.5\text{-}x}$Al$_{0.5}$Y$_x$N

X-ray tensometry method was applied to investigate the strain/stress state which has allowed determine the level of residual stresses and the period a$_0$ of the crystal lattice of textured nitride in the unstressed state. Values of a$_0$ periods for both the considered systems are not varied with the amplitude of the pulse substrate bias potential. In the TiN films the value of the period is closed to 0.424 nm, characteristic of the unstressed nitride of stoichiometric composition. The period of the crystal lattice in the coatings Ti$_{0.5\text{-}x}$Al$_{0.5}$Y$_x$N is slightly smaller than 0.418 nm, calculated according to Vegard's law for the lattice of the solid solution of cubic TiN (a_{TiN} = 0.424 nm) and AlN (a_{AlN} = 0.412 nm) with an equal content of Ti and Al atoms. The presence of yttrium in solid solution is improbable because of the large difference in periods of nitrides (a_{YN} = 0.489 nm). Some authors think that in the films of such composition a solid solution (Ti, Al)N is formed with halfway replacement of Ti atoms in the cubic structure of TiN with smaller atoms Al, and Y is not dissolved in the lattice and involved in the process of grain boundaries formation [15, 16].



a

b

Fig. 2. Dependence of the texture coefficient for the (111), (200) and (220) reflections on the pulse bias potential: a – coating TiN; b – coating $Ti_{0.5-x}Al_{0.5}Y_xN$

Supersaturated solid solution (Ti,Al)N is metastable, and under certain conditions, the formation of heterophase films is possible due to the partial decomposition of this phase. As the result of such process the nitrides rich in one metal component are formed. Our experiments show the possibility of such phase transition in $Ti_{0.5-x}Al_{0.5}Y_xN$ films deposited at the amplitude of pulsed substrate bias potential over 1 kV. It is likely that (220) peak in the diffraction pattern of the coating deposited at 2.5 kV corresponds to the undecayed component of the solid solution, and the (200) peak belongs to the titanium-enriched nitride. Another product of decomposition, aluminum-rich nitride, can not be detected in the diffraction pattern due to its lower reflectivity.

Such phase transformation may be the reason of differences in the behavior of the dependence of residual compressive stress on the amplitude of the pulsed potential for TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings shown in Fig. 3. For TiN the well-known dependence of the residual stress is non-monotonic with a maximum at 0.5 kV. For $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings the dependence is non-monotonic with a minimum. The level of stress increases when the amplitude exceeds 1 kV. Such an increase can be attributed to an increase in specific volume value which should occur in the film fixed to the substrate as the result of decomposition of metastable supersaturated solid solution (Ti, Al)N on the stable cubic TiN and hexagonal AlN phases. Estimates show that the increase in specific volume can reach 10%, which produce compressive stress 5 GPa.

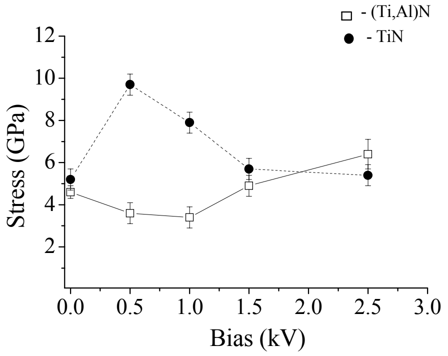


Fig. 3. Influence of the amplitude of the pulsed bias potential on the level of residual compressive stresses on TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings

Another indirect evidence of phase transformation is the hardness of the coatings. The hardness of TiN coatings is 30…35 GPa and practically does not depend on the amplitude of the bias potential on the substrate [17]. Coatings $Ti_{0.5-x}Al_{0.5}Y_xN$ also are characterized by relatively high hardness of 35 GPa regardless the substrate bias potential value in the range 0.5…1.5 kV [10]. The exception is the coating deposited at amplitude of pulse potential 2.5 kV, which hardness is reduced to 25 GPa may be due to the presence of the relatively “soft” AlN phase.

CONCLUSIONS

Thus, the differences in the stress state of TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ (with x~0.01) coatings deposited by the filtered vacuum-arc plasma under pulsed substrate bias potential were revealed. The crystalline phase in the films is a nitride with a cubic NaCl-type structure. In the $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings the atoms of aluminum enter into a solid solution (Ti, Al)N. It was found that axial texture [110] is formed in coatings when pulses potential with an amplitude 0.5…2.5 kV are applied.

For TiN films, the dependence of the residual compressive stress on the amplitude of the pulsed voltage potential is non-monotonic with a maximum at 0.5 kV. Decrease in the residual stress level and increase perfection of texture takes place when the amplitude of the potential is increased in the range 0.5…2.5 kV.

For multi-component coatings $Ti_{0.5-x}Al_{0.5}Y_xN$ the dependence of the residual stress on the amplitude of the pulsed voltage potential is non-monotonic with a minimum at 1 kV. In this case the texture is most strong. With further increase in the amplitude the texture perfection becomes weaker and stress increases. It is shown that the dependence of the residual stress for multi-component coatings Ti-Al-Y-N may occur due to the possibility of phase transition associated with the decay of the supersaturated solid solution (Ti, Al)N stimulated by high energy ion bombardment.

Acknowledgements

The author would like to thank V.V. Vasyliev, A.A. Luchaninov, and V.E. Strel’nitskij for depositing the samples and for helpful discussions.

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Статья поступила в редакцию 02.12.2013 г.

СТРУКТУРА И НАПРЯЖЕННОЕ СОСТОЯНИЕ TiN- И $Ti_{0.5-X}Al_{0.5}Y_XN$-ПОКРЫТИЙ, ПОЛУЧЕННЫХ МЕТОДОМ PIII&D ИЗ ФИЛЬТРОВАННОЙ ВАКУУМНО-ДУГОВОЙ ПЛАЗМЫ

Е.Н. Решетняк

Приведены результаты исследований структуры и напряженного состояния TiN- и $Ti_{0.5-x}Al_{0.5}Y_xN$-покрытий, полученных из фильтрованной вакуумно-дуговой плазмы при подаче высоковольтного импульсного потенциала смещения на подложку. Обнаружено, что при амплитуде импульсного потенциала 0,5…2,5 кВ в покрытиях формируется аксиальная текстура [110]. Для TiN-покрытий с ростом амплитуды степень совершенства текстуры растет, а уровень остаточных напряжений сжатия падает. Для покрытий $Ti_{0.5-x}Al_{0.5}Y_xN$ с ростом амплитуды уровень напряжений увеличивается. При этом наиболее совершенная текстура наблюдается при амплитуде 1 кВ. При дальнейшем увеличении амплитуды степень совершенства текстуры уменьшается. Различия структуры и напряженного состояния покрытий могут быть обусловлены возможностью фазового перехода в многокомпонентных покрытиях Ti-Al-Y-N, связанного с распадом пересыщенного твердого раствора (Ti, Al)N под действием высокоэнергетичной ионной бомбардировки.

СТРУКТУРА І НАПРУЖЕНИЙ СТАН TiN- ТА $Ti_{0.5-X}Al_{0.5}Y_XN$-ПОКРИТТІВ, ОТРИМАНИХ МЕТОДОМ PIII&D З ФІЛЬТРОВАНОЇ ВАКУУМНО-ДУГОВОЇ ПЛАЗМИ

О.М. Решетняк

Наведено результати досліджень структури і напруженого стану TiN- та $Ti_{0.5-x}Al_{0.5}Y_xN$-покриттів, отриманих з фільтрованої вакуумно-дугової плазми при подачі високовольтного імпульсного потенціалу зміщення на підкладку. Виявлено, що при амплітуді імпульсного потенціалу 0,5…2,5 кВ у покриттях формується аксіальна текстура [110]. Для TiN-покриттів із зростанням амплітуди потенціалу ступінь досконалості текстури зростає, а рівень залишкових напружень стиснення падає. Для покриттів $Ti_{0.5-x}Al_{0.5}Y_xN$ із зростанням амплітуди рівень напружень збільшується. При цьому найбільш досконала текстура спостерігається при амплітуді 1 кВ. При подальшому збільшенні амплітуди ступінь досконалості текстури зменшується. Відмінності структури і напруженого стану покриттів можуть бути обумовлені можливістю фазового переходу в багатокомпонентних покриттях Ti-Al-Y-N, пов'язаного з розпадом пересиченого твердого розчину (Ti, Al)N під впливом високоенергетичного іонного бомбардування.