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Comparative Characteristics of Stress and Structure of TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ Coatings Prepared by Filtered Vacuum-Arc PIIID Method

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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 high voltage pulsed bias potential on the substrate was carried out. It was found that for $Ti_{0.5}Al_{0.5}N$ coatings the dependence of the residual stress on the amplitude of the pulsed voltage potential is non-monotonic with a minimum when the amplitude is of 1 kV. As for TiN films, a monotonic decrease in the level of residual stresses takes place when the amplitude of the potential is increased in the range 0-2.5 kV. Non-monotonic dependence 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.

Keywords: Nitride coatings, Solid solution, Filtered vacuum arc deposition, Pulsed substrate bias, Residual stress.

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1. INTRODUCTION

Multi-component nitride coatings of Ti-Al-Y-N system can significantly improve the wear resistance of parts operating in extreme conditions, in comparison with traditionally used titanium nitride [1]. Deposition with the ion bombardment (when applying high voltage pulsed potential to the substrate) allows apply coatings with good adhesion and low residual stresses at a low substrate temperature [2-4]. 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). In all of the cases reported a monotonic decrease in stress level with increase in amplitude was associated with the relaxation of the material due formation a texture that is thermodynamically stable at low levels of biaxial stress [4].

In our recent paper [1] 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 1at.%), which were produced by plasma immersion ion implantation and deposition (PIII & D) technique using a filtered vacuum arc plasma source. 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.

2. 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 µsec. 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_α radiation on DRON-3 diffractometer. Determination of residual macroscopic stresses in the films was carried out by X-ray tensometry ($\sin^2\psi$ method). Technique based on the crystallite group method (GCM) was applied to investigate the strain/stress state, the approximation of quasi-isotropic symmetric biaxial stress state was used.

3. RESULTS AND DISCUSSION

X-ray 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.

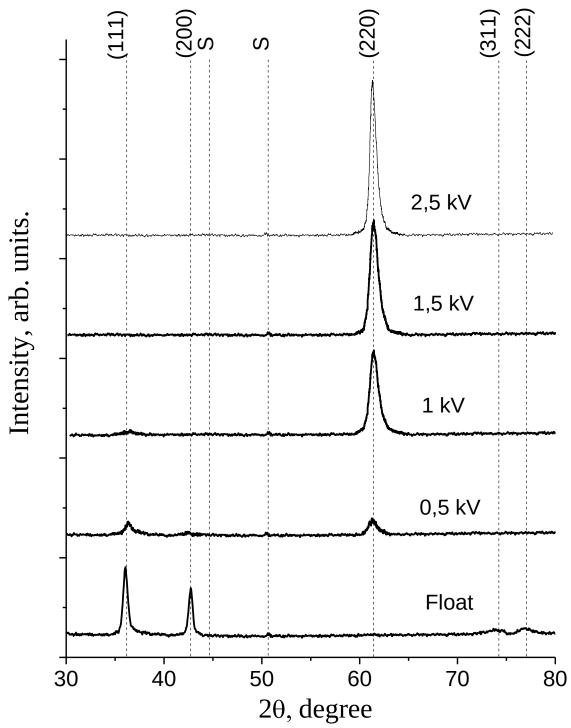
According to X-ray diffraction data the single crystal phase in the coatings is the cubic nitride with the structure of titanium nitride (structural type NaCl). Diffraction patterns of the investigated coatings are shown in Fig.1. The ratio of the intensities of the diffraction peaks differs from the value characteristic to the chaotic orientation of crystallites in which the strongest line is (200), which indicates the presence of texture. 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 (CSR) 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 size of the CSR is in the range 11-14 nm. For $Ti_{0.5-x}Al_{0.5}Y_xN$ 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 size of the CSR decreases from 14 to 7 nm. In the diffractogram of the film $Ti_{0.5-x}Al_{0.5}Y_xN$ 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 lines, which amounted to (0.4209 ± 0.0003) nm and (0.4238 ± 0.0005) nm respectively. We hypothesized that these lines belong to two different nitride phases of various compositions. This hypothesis was indirectly confirmed in further studies.

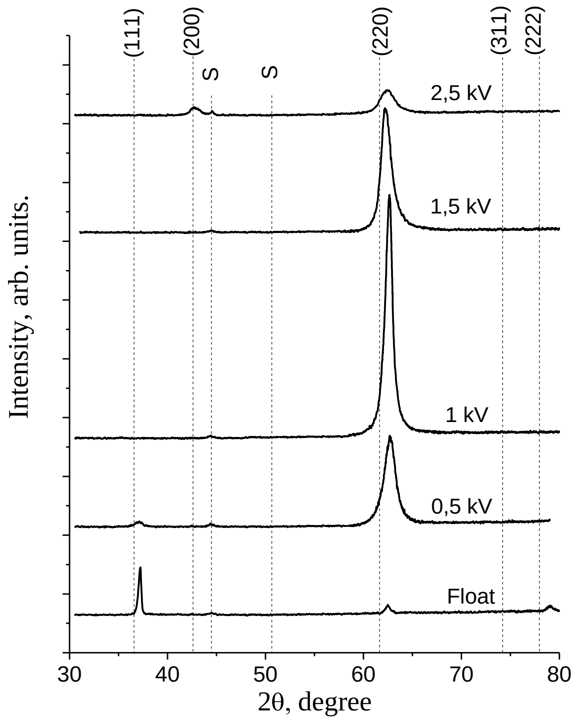
Figure 2a shows the crystal lattice period value of the textured nitrides in the direction normal to the coatings surface $a_\perp$, calculated from the θ-2θ diffraction patterns, which significantly affect the residual stresses. GCM method was applied to investigate the strain/stress state which has allowed determine the level of residual stresses and the period a_0 of the crystal lattice of textured nitride in the unstressed state. The results of calculation are shown in Fig. 2. It is seen that the 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 $Ti_{0.5-x}Al_{0.5}Y_xN$ 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 [5].

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 stress on the amplitude of the pulsed potential for TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings shown in Fig.2b. For TiN the well-known decrease in stress level is observed when the

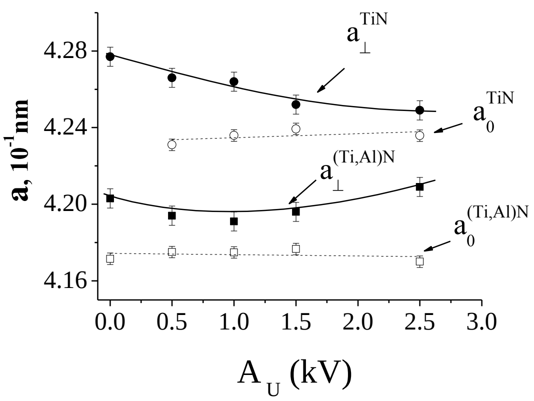


a)

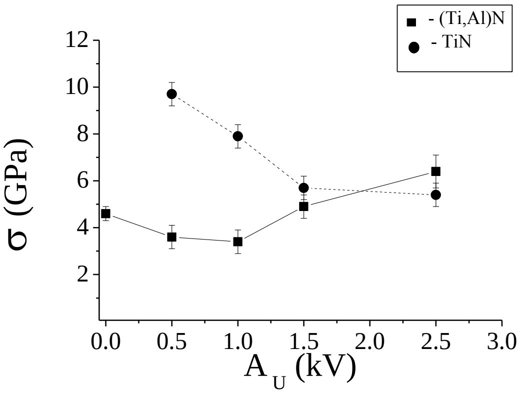


b)

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_α, dashed lines show the position of peaks of TiN (PDF № 38-1420), "S" indicates the line of the substrate): **a** - coating TiN; **b** - coating $Ti_{0.5-x}Al_{0.5}Y_xN$



a)



b)

Fig. 2 – Influence of the amplitude of the pulsed bias potential on the characteristics of the stress state of TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings (on the results of X-ray tensometry): **a** - the period of the crystal lattice, and **b** - the level of residual stresses

amplitude is increased. For $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings the dependence is non-monotonic, and 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.

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 [6]. 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 [1]. 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" hexagonal AlN phase.

4. CONCLUSIONS

Thus, the differences in the stress state of TiN and $Ti_{0.5-x}Al_{0.5}Y_xN$ coatings deposited from a filtered vacuum-arc plasma under pulsed substrate bias potential were revealed. For TiN films, a monotonic decrease in the residual stress level takes place when the amplitude of the potential is increased in the range 0-2.5 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. It is shown that the non-monotonic dependence for multi-component coatings Ti-Al-Y-N may occur due to the possibility of phase transition associated with the of the supersaturated solid solution (Ti,Al)N stimulated by high energy ion bombardment.

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