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PRODUCTION, STRUCTURE, PROPERTIES

Influence of the High-Temperature Annealing on the Structure and Mechanical Properties of Vacuum–Arc Coatings from Mo/(Ti + 6 wt % Si)N

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Abstract—Scanning electron microscopy with energy dispersive element microanalysis, X-ray structural analysis, and microindentation were used to study the effect of the deposition conditions in a reactive nitrogen atmosphere on the growth morphology, phase composition, structure, and microhardness of vacuum–arc multilayer coatings produced by the evaporation of cathodes from Mo and (Ti + 6 wt % Si) both after their deposition and after high-temperature annealing. It has been established that the use of the composite cathode of Ti and Si allows the formation of the structure state inclined to ordering to form a two-phase compound from TiN and Ti_5Si_3 at high-temperature annealing. In this case the coating hardness increases to a value higher than 45 GPa.

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Keywords: multielement coating, concentration of silicon, pressure, phase composition, structure, hardness, annealing.

1. INTRODUCTION

The production of various types of composite coatings based on nitrides of transition metals with silicon is the actively developing direction in the film material science for almost two decades [1–5].

Coatings based on TiN have high mechanical characteristics, but sufficiently low thermal stability [6]. Their mechanical and tribological properties along with the thermal stability may be considerably improved due to the addition of Si [7], which may affect a change of the phase composition, structure (dispersion at a high concentration of Si makes it possible to achieve the amorphous-like state, and preferential orientation of their growth) and functional properties, among them the highest effect is revealed for mechanical characteristics. These changes are the results of the spinodal type decomposition of a solid solution oversaturated with silicon [1, 4] realized by the diffusion of the ascending type [8, 9]. Besides, silicon is an alloying element increasing the stability to oxidation [10, 11]. The hardest materials form at the silicon deposition at the grain boundaries and formation of the SiN_x phase that delimits individual crystallites of titanium nitride or (in the case of the nitrogen low content) crystallites TiN and Ti_5Si_3 [12, 13]. Such nanocomposites have a unique combination of high mechanical properties and the thermal stability, and thus, they are very promising for applications at high-temperature technological conditions. To attain the highest hardness, crystal grains should be separated by a SiN_x interlayer 1–3 monolayers thick, which corresponds to the Si concentration about 1.5–7.0 at % [14].

The formation of coatings with high mechanical characteristics occurs also in the use of the ternary silicon-containing systems like (Ti–Mo–Si)N [15].

To control nanostructured state to a large extent and to improve functional characteristics is possible by projecting multilayer systems with a nanometer modulation period [16, 17]. In these systems the improvement of properties is caused by the combination of dissimilar materials.

Based on the above results, to attain the high mechanical characteristics, is advisable to use a material of the Ti–Si–N system as one of the layers and according to the results reported in [18, 19], as the other layer is promising to use a material based on the Mo–N system.

The aim of the present work was to study the effect of a high-temperature postcondensation annealing on the phase composition, structure, and hardness of nanocomposite nitride coatings produced by the deposition onto substrates rotating in a reactive nitric working atmosphere at the vacuum–arc evaporation from Mo and Ti + 6 wt % Si cathodes.

2. SAMPLES AND RESEARCH TECHNIQUE

The samples were produced by a vacuum–arc method on a modernized Bulat-6 installation [20]. The pressure of the working (nitric) atmosphere at the deposition was $p_N = (0.6–5.0) \times 10^{-3}$ Torr. The coatings deposition was performed from two sources (Mo and Ti + Si) at the continuous rotation of samples fixed on the substrates at the rate of 8 rpm, which allowed us to have an ~ 7 nm thick layer with the total layers number 960 (or 480 bilayer periods) of coatings.

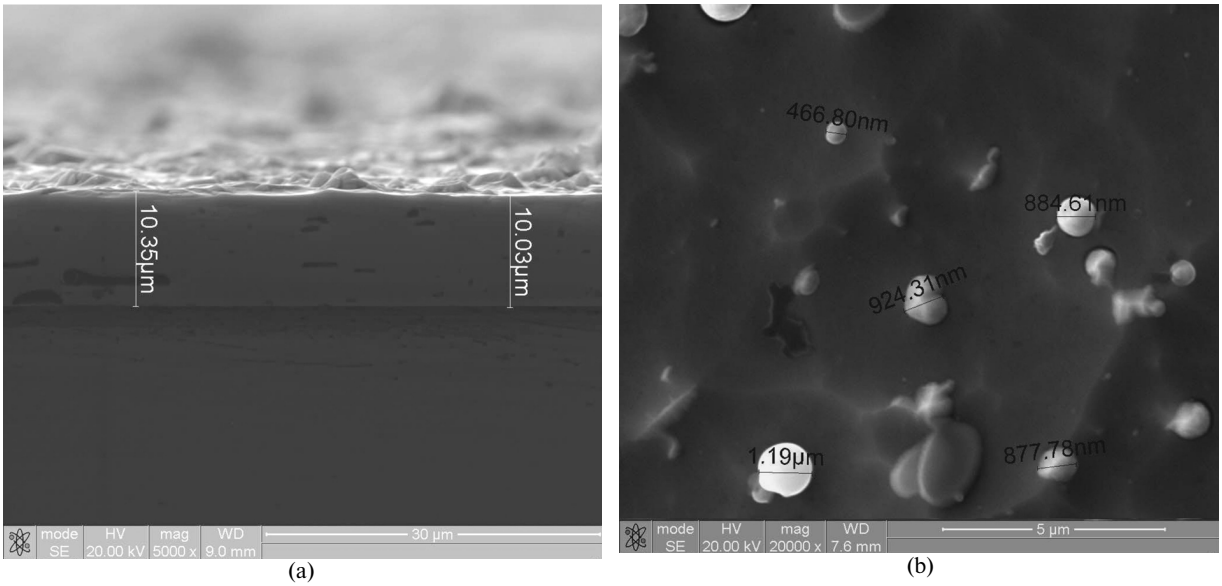
The total time of the coating deposition was about 1 h. In the course of the deposition a constant negative potential $U_{pp} = -100$ and -200 V was supplied on the substrates. High-temperature annealings were performed at the temperature 750°C for 1 h in a vacuum furnace VNT 8/22–GR Nabertherm GmbH.

The phase and structural analysis was made using the X-ray diffractometry in the Cu$K\alpha$ radiation on a DRON-4 plant.

The hardness of coatings was measured by the Vickers method at the indentation load of 50 g using a DM-8 hardness tester. The elemental compositions of coatings were studied by analyzing spectra of the characteristic X-ray radiation that was generated by the electron beam in a scanning electron microscope FEI Nova NanoSEM 450. The spectra were taken using the PEGAS system energy dispersive X-ray spectrometer of the EDAX Company installed in the microscope.

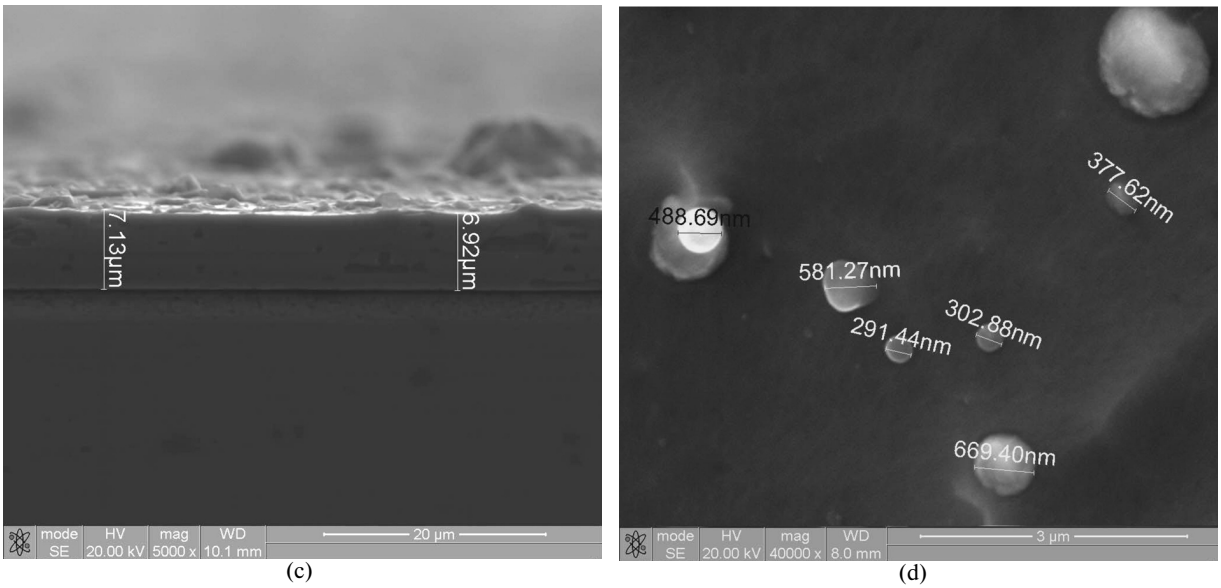
3. RESULTS AND DISCUSSION

The analysis of the lateral section morphologies and the appearance of the surfaces of coatings produced at different p_N and U_{pp} showed that at the increasing of the displacement potential the mean thickness of the forming coating decreases due to the action of the secondary sputtering [21] and a drop phase on the surface is of a lower mean size. In the greatest degree this refers to coatings produced at the lowest working pressure $p_N = 6.0 \times 10^{-4}$ Torr (Fig. 1), at which because of a lower density of a gaseous medium and, accordingly, long



(a) (b)

Fig. 1. Cross-sections and appearance of the surfaces of coatings produced at $U_{pp} = -100$ V, $p_N = 6.0 \times 10^{-4}$ Torr (a, b) and $U_{pp} = -200$ V, $p_N = 6.0 \times 10^{-4}$ Torr (c, d).

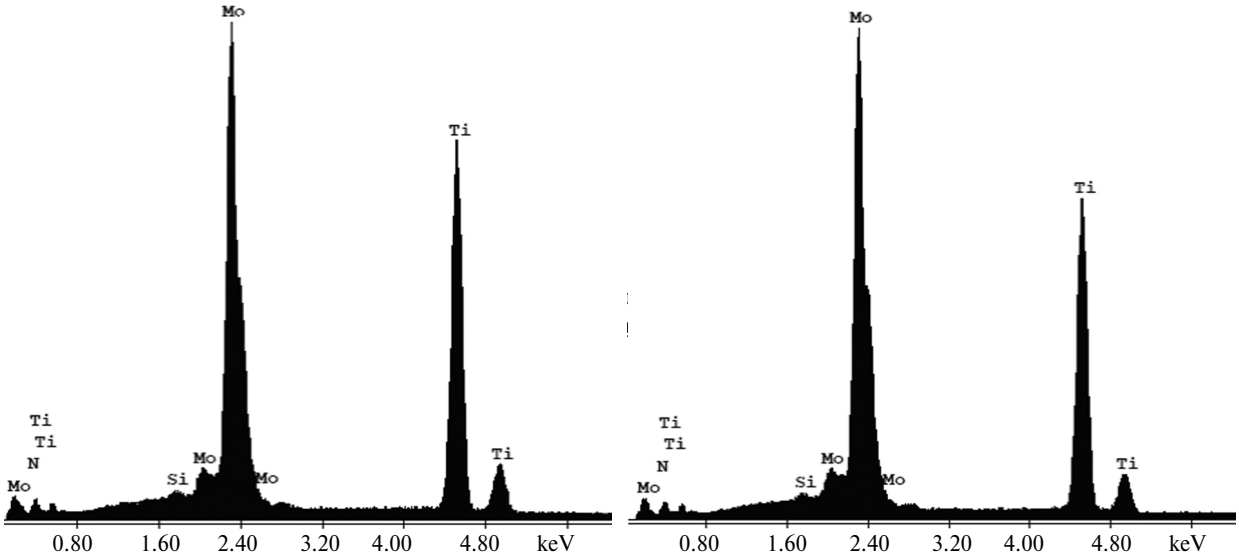


(c) (d)

Fig. 1. (Contd.)

length of the particles free path, the mean loss of the energy of particles vaporized from a cathode at their movement from the vaporizing cathode to the substrate is the lowest [22].

The analysis of the elemental composition showed that after a high-temperature annealing the relative contents of the coating metal components did not practically change. A comparison of the spectra and elemental compositions defined from them (Fig. 2) indicates that in the course of annealing a redistribution of the light elements takes place. In this case some increase of the silicon atoms relative content as compared with the nitrogen atoms content in the coating is caused by the higher binding energy (and accordingly, by the heat of formation) in the Ti–Si system compared with the Ti–N.



Element	at %
N	14.71
Si	1.24
Mo	34.32
Ti	49.73
	100

(a)

Element	at %
N	14.32
Si	1.34
Mo	34.92
Ti	49.52
	100

(b)

Fig. 2. Energy dispersive spectra and elemental composition of coatings produced at $U_{pp} = -100$ V, $p_N = 1.0 \times 10^{-3}$ Torr before (a) and after (b) the high-temperature annealing.

The tendency to a relative decrease of the Si content (Fig. 3a) and to the increase of the ratio of Mo and Ti atoms C_{Mo}/C_{Ti} (Fig. 3b) with increasing p_N remains in the annealed coatings virtually as well as it was before the annealing but with somewhat greater decrease of the Si concentration (by 0.2–0.4 at %).

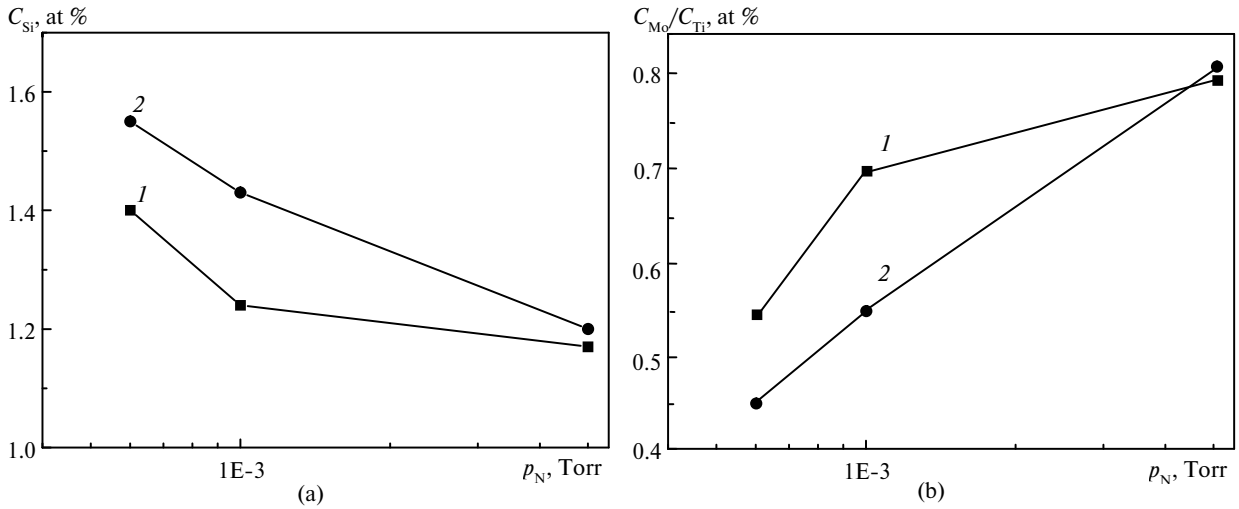


Fig. 3. Dependences of the change of the silicon atoms content (a) and ratio of Mo and Ti atoms concentration (b) in coatings on the nitrogen pressure: $U_{pp} = -100$ (*1*), -200 (*2*) V.

One may assume that the reason for the relative increase of the Mo content in coatings with increasing pressure, p_N, is a decrease in the evaporation rate of the (Ti + 6 wt % Si) cathode due to its "contamination" and nitrides formation on the surface [23]. In comparison with the Mo cathode this "contamination" affects a cathode with strong nitride generating components Ti + 6 wt % Si, which results in a change of the relative density of a flow of depositing particles into the side of the increase of Mo component.

The variations in the coating elemental composition are observed in the phase composition and structural state as well. This follows from the results of X-ray phase and structural analysis.

Figure 4 presents sections of diffraction spectra of coatings produced at pressures 6.0×10^{-4} and 1.0×10^{-3} Torr. It is seen that after the deposition two-phase structures form in the layers based on Mo (a-Mo (PDF card 42-1120) and γ-Mo_2N (PDF card 25-1366)) and layers based on Ti (α-Ti (PDF card 44-1294), TiN (PDF card 38-1420)).

With the pressure increase the relative concentration of the metal component (Mo, Ti) decreases, as evidenced by the relative decrease of the intensities of reflexes from crystallites of these phases on diffraction

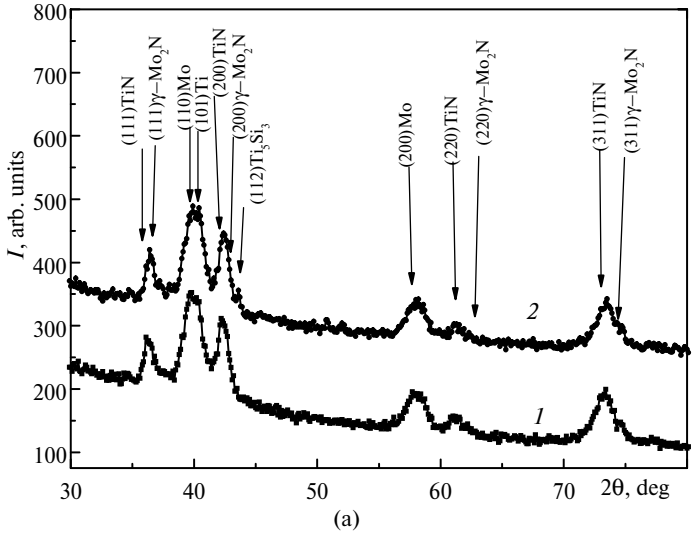
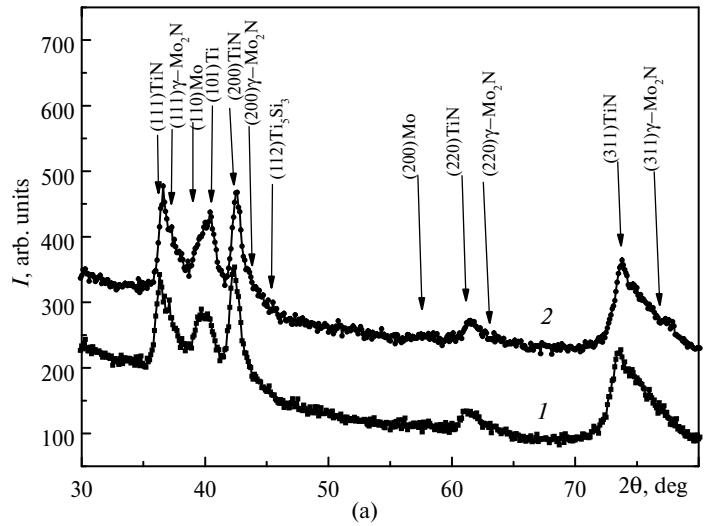


Fig. 4. Sections of the diffraction spectra of coatings produced at $p_N = 6.0 \times 10^{-4}$ (a) and 1.0×10^{-3} (b) Torr before (*1*) and after (*2*) annealing; $U_{pp} = -100$ V.



(a)

Fig. 4. (Contd.)

spectra up to their total absence in the coatings spectra taken at the highest pressure of (5.0×10^{-3}) Torr. In this case the redistribution of the intensities of reflexes indicating a change of the axis of the crystallites preferential growth from the lowest [100] to the highest [311] pressure takes place. The latter is characteristic of the γ-Mo_2N phase [18], and its arrival in this case may indicate the determinative effect on the texture formation of the Mo_2N layers.

The diffraction spectra of coatings after their annealing (Figs. 4a, 4b, spectra *2*) indicate that besides the keeping the initial phases, the annealing gives rise to the formation of a new phase Ti_5Si_3 (PDF card 29–1362). The formation of this phase becomes possible owing to the relatively low (to 20 at %) nitrogen content of the coatings, which is caused with a sufficiently great mobility of Ti and Si atoms in the Ti_5Si_3 phase in the course of annealing.

The investigation of the hardness, which is a universal express-method to study mechanical properties of coatings showed that the annealing, which stimulates the formation of silicide phases in coatings results in hardening by 1–7 units compared with the initial state. The highest absolute values of hardness after the annealing are attained in coatings produced at the relatively low (–100 V) negative potential of displacement and at $p_N = 5.0 \times 10^{-3}$ and 1.0×10^{-3} Torr are 40.3 and 45.2 GPa, respectively.

3. CONCLUSIONS

At the formation of multilayer coatings with thin layers (about 7 nm) a high mobility of light nitrogen atoms in the course of the deposition leads to their directional diffusion to the regions with the strong nitride-forming elements to form a nitride/metal composition.

The application of the compound cathode of Ti and Si allows the formation of the structural state that tends to the ordering with the formation of the titanium nitride phases and Ti_5Si_3 silicide phase.

The formation of the two-phase state from the nitride and silicide phases results in the increase of hardness up to the value exceeding 45 GPa.

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