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The Structure and Properties of Single-Layer and Gradient-Layered Coatings of the Ti–Al–Si–Cr–Mo–S–N System

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Abstract. Using the method of microprobe analysis and transmission electron microscopy, the influence of obtaining conditions upon particular elemental composition and growth structure coatings of Ti–Al–Si–Mo–S–N system was studied. The possibility of formation and characteristics of the structural and elastic-stress state single-layer coatings with nanoscale columnar or equiaxed grains and gradient-layered, combining two types of selected structure, was defined. On the basis of hardness, tribological properties and coating hardness, a conclusion was made about the relative prospects of its use as wear-resistant coatings with a nanocrystalline structure.

INTRODUCTION

For the synthesis of wear-resistant coatings an important task is to reduce the frictional force in contact while maintaining a high load-bearing capacity, fracture toughness and durability of coatings in a wide range of temperature and force influence. In our opinion the Ti–Al–Si–Cr–Mo–S–N system is a promising element system meeting all the necessary requirements owing firstly, to the ability to control the strength of a coating by the adjustment of degree of dispersion structure and of solid-solution strengthening; secondly, by reducing the load and contact stress relaxation (increase of fracture toughness) in the precipitation of soft phase particles of molybdenum disulphide. Research results of the hardness and tribological characteristics of Ti–Si–Mo–S–N systems show promise for their use due to the growth of wear resistance and hardness with a decrease in the friction coefficient [1]. Implementation of these features is determined by conditions of deposition and a corresponding structural state, which can vary in the range from nano-sized up submicrocrystalline grain structure because of the presence of silicon. Such changes, like changing the content of molybdenum disulfide, will optimize the ratio of hardness values and friction coefficient for increasing wear resistance. Therefore, the identification of characteristics and mechanisms of structure formation of such coatings using direct methods for its study is a topical problem in material science. In this regard, the structure and properties of these coatings obtained within different conditions of synthesis were studied.

EXPERIMENTAL PROCEDURE

Coatings were prepared by reactive magnetron sputtering targets Ti (alloy BT1-0 (Ti—99.24–99.7%, Fe—to 0.25%, C—to 0.07%, Si—to 0.1%, N—to 0.04%, O—to 0.2%, H—to 0.01%, wt %), sputtering power 1.8 kW), Al–Cr–Si–Mo–S (obtained by hot pressing of powder mixtures of individual elements and disulfide MoS2) in argon and nitrogen medium assisted by two sources of gas (nitrogen) plasma on the substrate of steel 316L, hard alloy T15K6 (79% WC, 15% TiC, 6% Co, wt %) with planetary rotation. The coating deposition was performed at a pulsed bias potential ranging from –100 to –50 V and a substrate temperature of about 150°C. For the synthesis of gradient coatings during the growth capacity changed Al–Cr–Si–Mo–S sputtering target in the range 0.25–0.55 kWh with a corresponding increase in flow rate of the reactive gas. The coating hardness was measured by a Table Indentation System (TTX NHT^2), the strength characteristics of coatings were determined by a scratching Rockwell indenter

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radius of 200 μm, tribological characteristics were checked at room temperature of the friction pair of these coatings with a ball made of alloy WCo. Research of the growth structure, deformation and fracture characteristics of coatings was conducted by scanning and transmission electron microscopy using a dark-field technique of electron microscopic analysis of the bending-torsion of the crystal lattice [2], the elemental composition analysis was carried out by microprobe analysis.

RESULTS

Study of the elemental composition of coatings shows that concentrations of the elements can vary in these ranges: Ti—25–35%, N—30–45%, Al—10–12%, Si and Cr—3–4.5%, Mo and S (total)—1.5–5%, depending on the deposition conditions. The ratio of alloying elements (Cr, Si, Mo, S) in the concentration of coatings does not correspond to the same value target, so that the coating relative proportion of Mo and S atoms is approximately 1.5–2 times lower than that in the target. Furthermore, the change in potential substrate bias from –100 to –50 V leads to an increase in the concentration of atoms of molybdenum disulfide by ~25% of the silicon atoms—10%, with an almost constant content in Al and Cr coating. These facts indicate the fact of secondary sputtering atoms Mo, S, Si from the surface of a growing coating. It is established that these conditions of synthesis define the formation of single-phase of doped titanium nitride coatings with different structures: homogeneous single-layer with columnar grains of a few tens of nanometers, or nanocrystalline with a crystal size of 5–7 nm; gradient-layered coatings that combine both types of the given structural states (Fig. 1). It was found at the initial stages of formation of columnar monolayer coatings changing in the mechanism of their growth, expressed as the transition from nanocrystalline, near the substrate, a state with equiaxed grains to nanocolomnar structure (Fig. 1a). It results not only in the size of the characteristic dark-field images of crystals in the respective layers coating (shown in Fig. 1a), but also in diffraction patterns (insets in Fig. 1a) of the structure showing growth intensity and reduction in the number and width of reflections during the transition to columnar coatings. It is obvious that these data illustrate the competitive growth of columnar grains of different crystallographic orientations [3].

Due to electron-microscopic dark-field studies of moving extinction contours values of bending-torsion of the crystal lattice and the level of the elastic-stress state in separate nanocrystals of a single-layer coating were defined. Figure 1b and 1c illustrate a fragment of such a study showing the conditions when tilted foil $\Delta\varphi \sim 0.5°$ contour extinction corresponding to the current reflection of $\langle 220 \rangle$ is moved at a distance of $r \sim 1$ nm. Such movements are connected with a quasi-continuous elastic bending of the crystal lattice, the measure (component χ_{21} tensor bending-torsion) can be determined from the ratio [2]:

$$\chi_{21} = \Delta\varphi \sin\beta / r, \qquad (1)$$

where $\beta \sim 90°$ is the angle between the foil tilt axis projection and the direction of current reflection. Substituting in (1) the numerical values gives $\chi_{21} \sim 500°\ \mu m^{-1}$. The elastic bending of the crystal lattice is connected with elastic stresses (σ), the amount of which is determined by the expression [2]:

$$\sigma = E\, \chi_{21}\, d_{cr}, \qquad (2)$$

where E is the Young's modulus, d_{cr}—a crystal size and equals to ~E/20–E/25. It was found out that for combined structure coatings the increase in the concentration of insoluble alloying elements leads to a change in the structure of the coarse nanocolomnar (grain diameter 50 nm) by finely columnar (diameter 15–20 nm) to the nanocrystalline state with equiaxed grains to 10 nm (Fig. 1d). At the same time, the inhomogeneity of a size diameter of columnar grains and the distance from the surface of the substrate on which the structure changes into nanocrystalline state were marked at cross sections in the longitudinal direction at distances of a few hundred nm established in the upper layers of the columnar structure. Study of bending-torsion of the crystal lattice in these coatings shows an increase in its value in the columnar structure with increasing thickness to the order of 110°–120° μm^{-1}, whereas in the nanocrystalline layer of the highest values of bending lattice are comparable with the values given above for a single-layer nanocrystalline coating.

Hardness measurement by nanoindentation at print depths is not more than 10% of the thickness of coatings (Fig. 2a) and shows a significant effect of the structural state on its value: single-layer coatings with a columnar structure have the highest hardness (~21.5 GPa), a single-layer nanocrystalline coating have the lower (~11.0 GPa), while coatings with a combined structure are characterized by a medium value of ~16.5 GPa. A similar proportion is suitable for the values of Young's modulus, which decrease at an average of ~325 GPa to 200 GPa, upon the transition from columnar to nanocrystalline single-layer coatings. However, scratch test results of coatings indicate that the loading scheme change shows a greater strength in a resource nanocrystalline coating on a hard alloy.

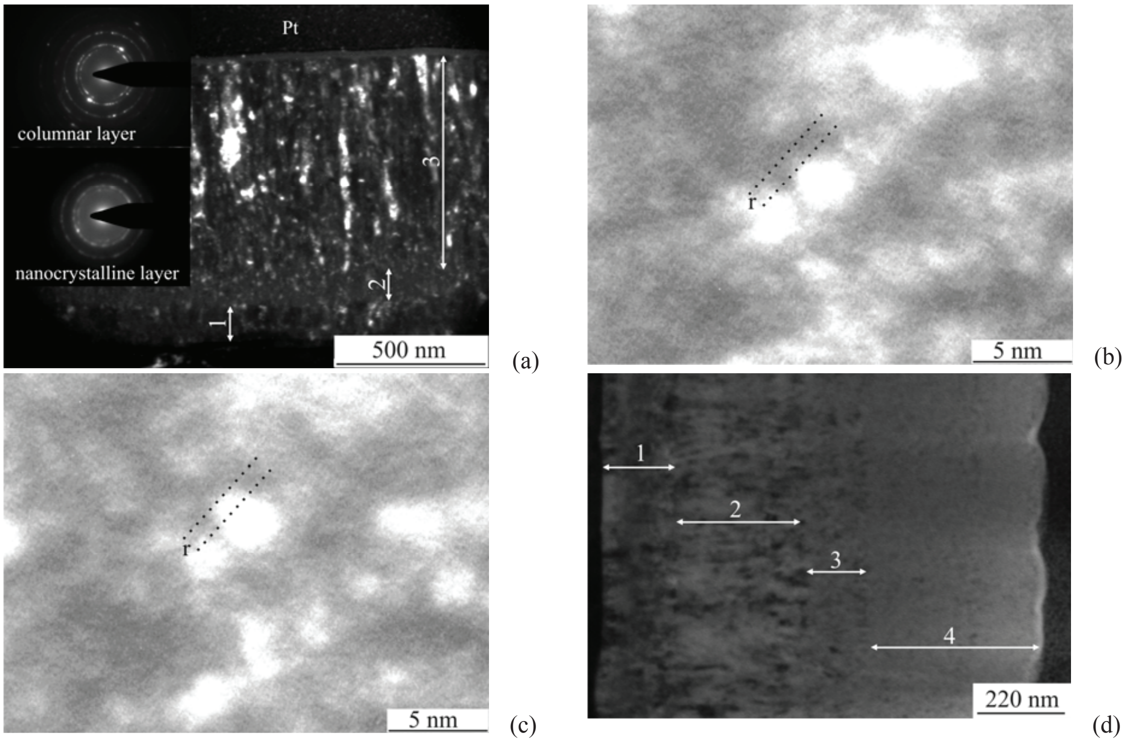
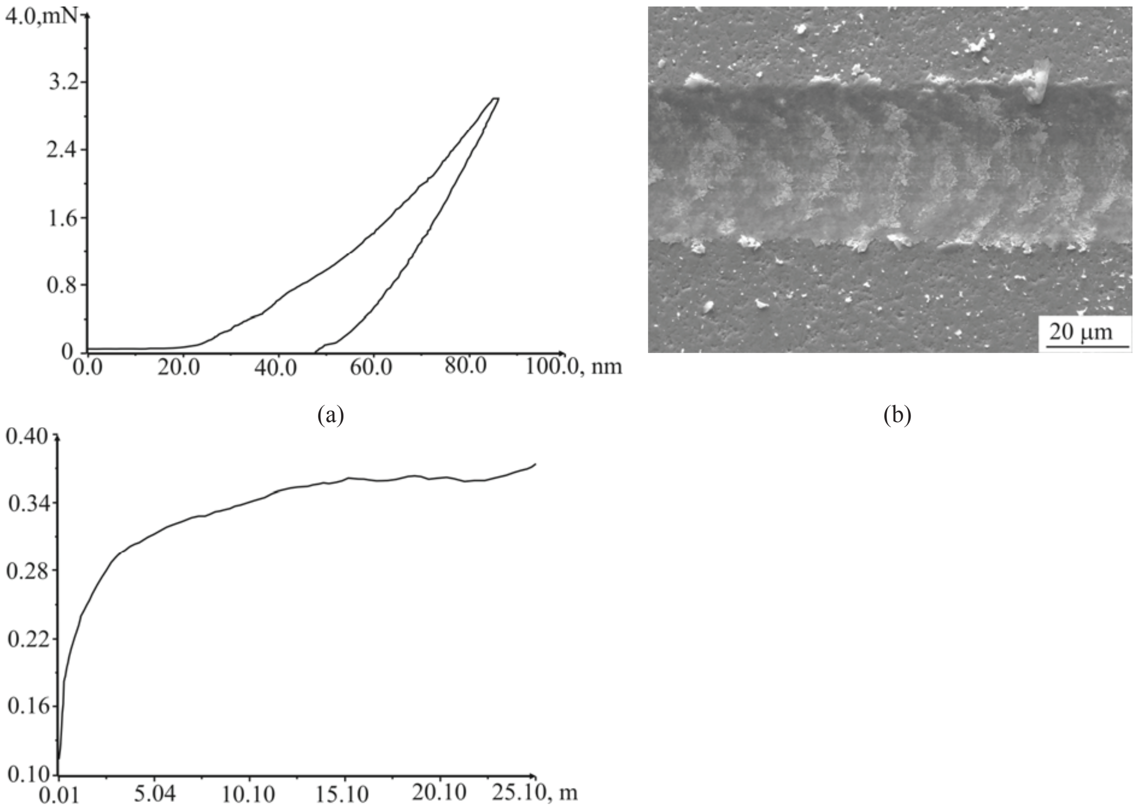


FIGURE 1. Dark-field (a–c) and bright-field (d) images of a coating structure: (a) a single layer with a columnar structure: *1*—a nitrided layer α-Ti, *2*—a nanocrystalline transition layer, *3*—a layer with a columnar structure; (b, c) a nanocrystalline structure of single-layer coating and extinction contour displacement (*r*) at an inclination foil 0.5°; (d) a structure of a gradient-layered coating: *1*—a nitrided layer α-Ti, *2*—a coarsely dispersed columnar structure, *3*—a finely dispersed columnar structure, *4*—a nanocrystalline structure

Critical loads of its fracture is ~52 N and delamination from the substrate is ~72 N, which is 2.5–3 times higher than for a single-layer coating with a columnar structure. As for hardness, the coatings with combined structures have medium values of indicated loads within ~25 and ~35 N, respectively, but the highest value (120 N) of the load bearing capacity characterizing the coating. It was found that with high loads near the substrate coating, the fracture is inhomogeneous with alternating areas with or without coating (Fig. 2b). However, measurement and evaluation of tribological characteristics with low loads (less than 2 N) show the best properties of a nanocrystalline single-layer coating on hard alloy, the friction coefficient of which (Fig. 2c) reaches about 0.37 when changing along the track coefficient wear rate is in the range of $5.5\times10^{-16} \div 2\times10^{-15}$ $m^3/N\times m$. The friction coefficients of two other types of coatings are higher up to 10–20% of the given above when fold increase in the rate of wear. At the same time, the coating with a combined structure has a better wear resistance (wear rate coefficient is about 3.5×10^{-16} $m^3/N\times m$) on the mild steel substrate.

CONCLUSION

This research has shown that coatings with one type of structural state—single-layer with columnar grains or nanocrystalline and gradient-layered coatings with a combined structure can be obtained upon changing the conditions of deposition of Ti–Al–Si–Cr–Mo–S–N system. The effects of selective sputtering of alloying elements, the competitive growth of columnar crystals, the values of the bending-torsion of the crystal lattice and its changing for coatings with different structures were established. It has been shown that a columnar structure has the greatest hardness, whereas the higher strength and tribological characteristics belong to a single-layer nanocrystalline coating.



(c)

FIGURE 2. A nanoindentation curve of single-layer columnar coating (a), an image of secondary electron mode of a gradient-layered coating fracture in a scratch track zone at a load of approximately 100 N (b) and the measure change of the friction coefficient upon tribological tests of a single layer nanocrystalline coating (c)

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