The Structure and Properties of Multi-Component Nanocomposite Coatings System of Ti–C–Ni–Cr–Al–Si–Cu–N

S.V. Ovchinnikov, A.D. Korotaev*, Yu.P. Pinzhin, V.Yu. Moshkov, A.N. Tyumentsev, and D.V. Koshevoy*

Institute of Strength Physics and Material Science, 2/1, Akademichesky ave., Tomsk, 634021, Russia,
Phone: (3822) 53-15-69, E-mail: ovm@spti.tsu.ru
*Tomsk State University, 36, Lenina ave., Tomsk, 634050, Russia

Abstract – The distinctive features of structural and phase state as related to the mechanical properties of material were investigated using the methods of X-ray fluorescence, electron microscopy, X-ray diffraction analysis, measurement of microhardness and adhesion strength in scratch tests. The investigations were carried on for multi-component hard and superhard coatings of the system Ti–C–Ni–Cr–Al–Si–Cu–O–N subjected to deposition followed by annealing in vacuum. It is shown that with growing concentration of copper, the structure of coating would change from two-level columnar with submicron grain size to nanocrystalline one. The coating phase state was a heterogeneous mixture of B1 type structure and X-ray amorphous phase, which was unaffected by the deposition. Annealing was carried on at 800 °C for the test material; however, the structure and hardness of coatings remain practically the same despite precipitation of nanoparticles of solid Cu–Ni solution. Annealing was also carried on by steps at 800 and 900 °C to cause material hardness to decrease, which was due to the recovery of dislocation structure and to the occurrence of initial stages of recrystallization. Adhesion strength measurement was carried on using scratch-tests at loads up to 30 N. The friction factor obtained for a diamond indenter-coating pair has a low value (~ 0.15). No fracture or flaking of test coatings was observed, nor separation of the same from the substrates.

1. Introduction

Multicomponent composite synthesis is performed in non-equilibrium conditions, which provides for a wide variety of structural-phase and elastic-stress states. Therefore, the choice of multicomponent composites holds promise for creating very hard and superhard coatings having satisfactory fracture toughness. In choosing the elemental composition of such coatings, we were primarily guided by the basic requirement that formation of nanostructure state start concurrently with the emergence of islands of coating growth. For this reason, the elemental composition has to comprise several groups of elements. This would make possible concurrent nucleation of phases, which are insoluble or poorly soluble under precipitation conditions and have nearly the same formation enthalpies and nearly the same volume fractions, which provides for formation of nanostructure. It should be emphasized, however, that the formation of nanostructure and its high temperature stability are due not only to the nature of heterophase nanocrystalline state and conditions involved in the formation of such state but also to the enhanced stability of solid solution of multielement nanocrystals, which is attributed to a decrease in the Gibbs potential caused by mixing entropy [1, 2]. A coating has to combine high hardness and high fracture toughness; it is, therefore, essential that elements chosen to make up composition should form a very hard or superhard matrix basis containing inclusions of soft phases acting as solid lubricant. In our opinion, the above combination of characteristics could be obtained using alloyed phase compositions of the type nc-MeN/a-/Me (here nc-MeN corresponds to nanocrystalline nitride of transition metal; a-, to grain-boundary segregations of amorphous/X-ray amorphous phases and Me, to nanoparticles of soft metal insoluble in nitride).

Moreover, it might be of interest to estimate the effect on the solubility of the soft metal of grain structure dispersion, which is observed by alloying coatings based on transition metal nitrides, using silicon as alloying element [3, 4]. A change of solubility might involve qualitative changes in structure, mechanisms of deformation and fracture as well as in the properties and thermal stability of coatings. With the aim of experimental validation of the above, the distinctive features of structural-phase state as related to elastic-stress state were investigated for the Ti–C–Ni–Cr–Al–Si–Cu–O–N system coating, with nanocrystalline titanium nitride, TiN, being solid matrix basis for the same system. Alioying of the system coating was carried on using chromium, aluminum, carbon, copper and nickel as alloying elements with resultant formation of X-ray amorphous phases based on silicon, nitrogen, oxygen and carbon. The latter two elements insoluble in titanium nitride were used in different concentrations as soft phases.

1 The work was supported by Federal program 2009-1.1-207-024-037.
Coating Deposition

2. Experimental procedure

The deposition of coatings under study was carried on at the Tomsk State University by plasma-assisted magnetron sputtering on an installations “Sprut” and a PINK-type plasma source equipped with an incandescent cathode, with four magnetrons operating simultaneously. The cathodes used to sputter coatings were made from titanium VT1-0, copper M1-0 and Silumin (Al base; 10.2% Si; 0.27% Fe; 0.03% Zn; 0.02% Cu; 0.03% Mn, and 0.01% Mg; percent by weight). The composite Ti–C–Ni–Cr cathode had the following phase composition: 50% TiC; 40% Ni, and 10% Cr (percent by weight). Before sputtering, the substrate surface (Mo, stainless steel and hard alloy T15K6) was cleaned with argon plasma and heated to the temperature exceeding 500 °C, with two PINK-type plasma sources equipped with an incandescent cathode operating simultaneously (current 80 A). In the course of coating deposition the temperature dropped to ~300 °C.

The deposition of TiN substrate 50 nm thick was carried on for about 5 min; then Ti–C–Ni–Cr–Al–Si–Cu–O–N system coatings were formed on the substrate surface. By the sputtering of Ti, Ti–C–Ni–Cr, Al–Si, and Cu targets, the power was 5.0, 3.8, 2.5, and 0.15–0.4 kW, respectively. The volume fractions of argon and nitrogen in the gas mixture were in the ratio 1:3; the gases had purity grade 99.98% and 99.999%, respectively; the pressure of the gas mixture was 4.6⋅10⁻³ Torr. The PINK-type plasma source created current of 30 A; the bias potential on the substrate was ~50 V.

Thorough investigations were performed for synthetic coatings subjected to deposition and vacuum annealing treatment at ~10⁻⁵ Torr. The coatings subjected to deposition treatment had thickness ~1.5 μm. The elemental composition of coatings was determined by X-ray fluorescence analysis. The structural and phase state of coatings was examined by the method of X-ray structural analysis in conjunction with electron microscopic technique, using a XRD-6000 Shimadzu diffractometer and CM-12 and CM-30 microscopes. Microhardness measurements were performed on a special attachment to the optical microscope Neophot 21, using loads 0.2 N. Scratch tests were carried on to determine adhesion strength, using a Micro Scratch Tester (CSM) unit and a diamond pyramid indenter having radius 200 μm; the loads used were ≤ 30 N.

3. Results and discussion

The elemental composition of coatings is presented in the Table. As is seen from the results, in the case of No. 1 coating, the total content of metallic elements (Al + Cr + Ti) is close within measurement error to that of nonmetallic ones (C, N, O), while in the case of No. 2 coating, the former group of elements is about 3.5 at. % less than the latter group. The above difference suggests that in the case of No. 2 coating, the surface of growing crystals having B1 structure becomes enriched in impurities. At the same time, it is assumed that low concentrations of aluminum and silicon occurring would determine formation in the coatings of metastable uni- or heterophase mixture of isomorphic solid solutions of the type (Ti, Cr, Al)(Si, C, N, O). This might be due to crystal growth having low activation energy (\( T_{\text{dep}} \approx 300 \, ^\circ \text{C}; \, U_c \approx -50 \, \text{V} \)). Apparently, the effect of grain-boundary segregation of silicon on crystal growth is rather limited although such segregation is expected to occur in crystals having size of about 10 nm [5]. In view of the above, it is expected that (i) a difference in the concentrations of copper and nickel that are insoluble in titanium nitride would affect the structural state of coating material; (ii) amorphous/X-ray amorphous phases would form in the main phase since it comprises numerous insoluble and poorly soluble elements; (iii) subsequent thermal treatments would result in the formation of phases on the base of poorly soluble elements. Indeed, the results obtained by electron microscopy technique show that the coatings under study have uniphase FCC structure (see Figs. 1, a and 2) having lattice parameter ~0.419 nm. The X-ray diffraction examination provided evidence for “traces” of FCC phase having lattice parameter ~0.426 nm.

<table>
<thead>
<tr>
<th>Coating No.</th>
<th>Composition of coatings, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti Al Si Ni Cr Cu C O N</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>29.5 9.8 1.6 7.7 3.9 3.6 4.1 1.2 36.8</td>
</tr>
<tr>
<td>2</td>
<td>26.8 9.0 1.5 7.3 3.7 8.5 4.9 0.8 37.5</td>
</tr>
</tbody>
</table>

The latter might be either solid Ti(C, N) solution or titanium carbide, TiC, which isomorphic with respect to TiN and is under-stoichiometric with respect to carbon.

At the same time, high background intensity is observed in the low-diffraction angles region (< 20°) (Fig. 2), which is indicative of a high volume fraction of X-ray amorphous phase (several tens of percent). Using the methods of dark-field analysis of lattice bending-twisting, the structure of coatings having different compositions was investigated. It was found that No. 1 coating having low concentrations of copper and nickel (~11.4 at.%) has columnar weakly textured structure (Fig. 1, b). The structure is characterized by submicron grain size (\( d \leq 0.3 \mu m \)); the grains are fragmented by the small-angle boundaries (reorientation angles ≤ 5°) to give subgrains having size of several tens of nanometers, with dislocations occurring in some of the subgrains. The bending-twisting tensor components were determined by measuring...
averaged misorientations (with regard to continuous and discrete ones); the values obtained are 40–50 deg/μm, which corresponds to the excess density of dislocations of the same sign of about $3 \times 10^{11}$ cm$^{-2}$.

The total concentration of Cu and Ni in No. 2 coating increases up to about 16 at. %, which brings about formation of disperse structure characterized by random orientation of crystals corresponding to coherently scattering regions having size of 20–30 nm.

The dark-field analysis of variations in crystal lattice orientation was performed for some nanocrystals. It was found that the largest crystals have block structure, which is characterized by quasi-continuous misorientations of blocks having size of 10–15 nm ($\leq 1.5$°), with the diffraction contrast persisting in some of these blocks in the interval of several degrees (see, for example, the diffraction contrast denoted by 1 in Fig. 1, c). On the base of the above the quasi-continuous bending-twisting tensor components were determined from the well-known relations [6]; the values obtained are $\chi_{21} \sim (120–150)/\mu$m and $\chi_{31} \sim 100/\mu$m. By estimating the stress, however, one has to take into account the nature of structural defects which determine the stress field. Assume that nanocrystals having sizes of 10–20 nm contain no defects [7] and the elastic bending of the lattice in the same is due to partial disclinations occurring in the lattice boundary [8]. Then in the context of disclination model of lattice boundary, the stress field dependence of lattice boundary having variable misorientation vector can be written in cylindrical coordinates [9], i.e.

$$\sigma_{\phi\phi}(r) = \frac{E \times r \times \partial \theta}{2 \times \pi \times \partial r}.$$ (1)

Substitution of $\frac{\partial \theta}{\partial r} \sim 100$ deg/μm and $r \sim 0.01$ μm into the latter expression yields $\sigma_{\phi\phi} \sim E/400$. It is thus concluded that Nos. 1 and 2 coatings have high hardness, i.e. ~ 47 and 38 GPa, respectively, which is due to the hetero-phase state and high-defect structure of coating material. The scratch-tests were conducted using the Rockwell diamond pyramid indenter having radius of 200 μm at loads up to 30 N; the scratches were examined by the method of scanning electron microscopy. The results obtained suggest that the coating continuity and adhesion to the substrate remains intact; besides, the friction factor obtained for the indenter-coating pair is $\leq 0.18$ (Fig. 3).

Nos. 1 and 2 coatings were vacuum-annealed for 1 h at $10^{-5}$ Torr at 800 °C. A two-stage vacuum-annealing was also performed for the same coatings for 1 h at 800 °C and for 1 h at 900 °C. The thermal stability of as-treated coatings was investigated. It was found that in the case of No. 1 coating, the structure and hardness were unaffected by the annealing treatment at 800 °C, while in the case of as-treated No. 2 coating, ~10% decrease in hardness had occurred. In the latter case, the defect material microstructure was examined using electron microscopy technique and was found to remain unchanged. It was found, however, that the phase composition of No. 2 coating had changed due to the formation of solid Cu–Ni solution.
Coating Deposition

nanoparticles. The microdiffraction pattern was found to contain reflections of the latter phase similar to that of <200> type. The above suggests that composite coatings on the base of transition metal nitrides would preserve high hardness at annealing temperatures exceeding 700 °C – even if they contain insoluble metals in concentrations of > 10 at.%. In this respect, they are thought to be superior to well-known coatings of the MeN/Me type [10], which might be attributed to the stability of material structure due to solid-solution hardening and to the X-ray amorphous phase retaining its thermal stability at temperatures ≤ 800 °C.

The above structural and phase transformations and a decrease in material hardness are found to cause no fracture or separation of the coating from the substrate during scratch-tests; however, the friction factor has a low value; the acoustic emission level also grows less. The as-annealed coatings evidently preserve carrying capacity intact – possibly due to the formation of soft nanophases, i.e. solid Cu–Ni solution, HCP AlN, etc., which cause the fracture toughness of the composite coating to increase, and to the low friction factor observed for the indenter-coating pair.

4. Conclusion

The most significant results of our experimental investigations are as follows.

1. Hard and superhard multi-component coatings (H ≤ 47 GPa) have been obtained on the base of TiN, alloyed Ni, Cr, Al, Si and Cu, which contain high concentrations (~ 10–15 at. %) of the soft metals Cu and Ni insoluble in TiN and a significant volume fraction (a few tens of percent) of X-ray amorphous phase.

2. It is found that with the concentration of copper increasing from ~3.5 to 8.5 at. %, the coating structure changes from columnal (grain size of less than a micron) to disperse nanocrystalline structure (size of crystals in the range of 10–30 nm), which is characterized by a high level of lattice bending-twisting (up to 100–150 deg/μm).

3. It is shown that vacuum annealing treatment of investigated coatings carried on at 800 °C causes practically no change in the structure and properties of material, even if precipitation of solid Cu–Ni solution nanoparticles occurs in as-treated coatings having high concentration of copper. The annealing treatment carried on at 900 °C, on the contrary, brings about precipitation of nanoparticles of solid Cu–Ni solution and possibly of HCP AlN, β-Si₃N₄, and β-Ti₂N. This suggests that the processes of structure recovery and recrystallization are evolving in as-treated coating. A concurrent decrease would occur in material hardness (26–30 GPa).

4. Scratch tests performed for investigated coatings have shown that no fracture or separation of coating from the substrate occurs at loads ≤ 30 N; besides, the friction factor obtained for the diamond indenter-coating pair has low value.

References

