Structure, Phase Composition and Mechanical Properties of “Nitride Coatings-Hard Alloy” System after Low-Energy High-CURRENT Electron Beams Influence

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Abstract – The influence of the energy density of the low-energy high-current electron beams treatment on structure, phase composition and micro-hardness of the “nitride coatings-hard alloy” systems has been studied.

1. Introduction

Ceramic coatings based on the nitride solid solutions like (Ti, Cr)N, (Ti, Al)N, (Ti, Zr)N are widely used for tool hardening. The formation of these coatings by arc vapour deposition is known to produce high compressive stresses (4–7 GPa) [1–3]. The further tools treatment by high power ion, electron, laser pulses and plasma flows is a promising approach to reduce compressive stresses, brittleness, defect density of ceramic coatings and, therefore, to improve wear resistance [4–7]. The materials modification by high power energy flows is realized by rapid heating of the surface layer above the melting point followed by its solidification with overcritical cooling rates ($10^3$–$10^5$ K/s) resulting in the formation of the layer with low mechanical stresses and fine-grained structure [4–7]. Modification effect is not limited by fused layer: microstructure, hardness and defect structure of steels and alloys are affected at the depth up to 10 µm [4, 5, 8]. Degree of structure-phase changes and modified layer depth are varied subject to power density of the flows.

In the paper the research’s results of the influence of a pulse irradiation by low-energy high-current electron beams (LEHCEB) on the structure and the phase composition, the microhardness and the friction coefficient [9, 10] of “(Ti, Cr) N coating-hard alloy T15K6” and “(Ti, Mo) N coating-hard alloy T15K6” systems’ near-surface layers are presented.

The choice of such coatings is conditioned by the fact, that (Me1Me2II) N coatings show advantages in certain application in comparison with MeN coatings. Besides (Ti, Cr)N and (Ti, Mo)N coatings are nowadays the most widely used for strengthening of the tools working in harsh environments.

2. Experimental procedures

The sintered hard alloy T15K6 (WC – 15 wt.% TiC – 6 wt.% Co) with the coatings (Ti, Cr)N and (Ti, Mo)N, deposited by condensation combined cathodic vacuum arc (CAVD) with bombardment by ions Ti, Cr, and Ti, Mo appropriately were used as the subject of the study. The researched samples in the form of the tetrahedral plates had the sizes 10×10×4 mm. The composition of the hard alloy after sintering included WC, (Ti, W)C and binder phase. Hardness of the alloy was 13 ± 2 GPa.

The condensation of the multielement nitride coatings on the samples of the hard alloy passed in two stages. In the beginning the samples’ surface was treated by titanium ions within one minute at negative potential of displacement 1 kV and the metal arc current of – 100 A. Then the deposition of the coatings was carried out for 10 minutes at nitrogen pressure in the chamber $10^{-1}$ Pa, the bias voltage of – 120 V and at simultaneous burning arches of two metal cathodes Ti and Cr, Ti and Mo with currents of burning for Ti and Cr – 100 A, and for Mo – 150 A.

Higher temperature of melting Mo has determined the application of the increased value of the arc current for its constant burning during the process of deposition. The corresponding coatings thickness was size of order 2 µm.

The treatment of the samples’ surfaces by electron beam was carried out by 5 pulses with duration of ~100 µs and the frequency of their following of 0.3 Hz. The scaleable parameter was the energy density by one pulse of the LEHCEB influence. The modes of the samples’ irradiation by LEHCEB are submitted in Table 1.

Table 1. The modes of the influence on the “nitride coating-hard alloy” systems by LEHCEB

<table>
<thead>
<tr>
<th>Pulse duration, µs</th>
<th>Number of pulses</th>
<th>Energy density by one pulse, J/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ti, Cr)N</td>
<td>– hard</td>
<td>– alloy</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>(Ti, Mo)N</td>
<td>– hard</td>
<td>– alloy</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
<td>70</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
<td>80</td>
</tr>
</tbody>
</table>
The phase composition and the parameters of the crystal structure of the modified layers after the LEHCEB influence were investigated by the X-ray diffraction analysis (XRD) in Bragg-Brentano geometry and CuKα-radiation using a DRON 4-13 diffractometer. The error of definition of the lattice parameters was approximately ± 0.0002 nm.

Cross section morphology as well as samples element composition was analyzed by means of scanning electron microscopy using a LEO1455VP device equipped with an energy-dispersive X-ray Röntec detector.

The microhardness of the samples was tested by means of a PMT-3 microhardmeter with a Vickers indenter under the load of 2.0 N.

3. Results and discussion

The XRD patterns of the coatings, formed by simultaneous condensation of Ti, Cr, and Ti, Mo plasma flows in nitrogen atmosphere, on the hard alloy T15K6 before the LEHCEB influence are presented in Fig. 1.

In the case of the combined condensation of Ti and Cr the (Ti, Cr)N coating is formed (Fig. 1, b). The solid solution (Ti, Cr)N has a cubic structure and texturing in the direction (200).

The multiphase (Ti, Mo)N coating is consist of the solid solution (Ti, Mo)N with a cubic structure and the texturing in the direction (200), MoN and Mo (Fig. 1, b).

The diffraction maxima from the carbides (Ti, W)C and WC, and also the peaks from the nitrides of the coatings’ metals are presented on the X-ray diffraction pattern of the “nitride coatings-hard alloy” systems (Fig. 1, a).

The LEHCEB treatment at 10 J/cm² on the hard alloy T15K6 with the (Ti, Cr)N nitride coating results in the reduction of the intensity of the (Ti, Cr)N diffraction line at simultaneous appearance of the (Ti, W)C and WC maxima (Fig. 2, a).

The increase of the LEHCEB influence’s energy density to 30, 50 J/cm² results in the formation of the complex carbide Co3W9C4 (Fig. 2, a). The intensity of the diffraction reflexes from WC in the interval of...
small diffraction corners (2θ up to 30°) grows that testifies to the increasing of the tungsten carbides’ fraction in the near-surface layer. In addition there is decomposition and fusion the (Ti, Cr) N coating and the alloy’s carbides (Fig. 2, a).

As a result of its following crystallization the phases ε-TiN, CrN and the more enriched by metal compounds W₂N, Cr₂N are formed.

The feature of the LEHCEB influence on the “(Ti, Mo)N coating-hard alloy T15K6” system with the energy density from 60 up to 80 J/cm² will consist in the transformation WC in W₂C (more high-temperature modification of tungsten carbide), and also in the increasing of the fraction of tungsten in (Ti, W)C (Fig. 2, b).

It is revealed, that with the increasing of the energy density of the LEHCEB influence the (Ti, W)C lattice parameter decreases (Table 2).

Table 2. The (Ti, W)C lattice parameter after the LEHCEB treatment

<table>
<thead>
<tr>
<th>The energy density by one pulse, J/cm²</th>
<th>The (Ti, W)C solid solution lattice parameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>“(Ti, Cr)N” – hard alloy”</td>
<td></td>
</tr>
<tr>
<td>unirradiated</td>
<td>0.4326</td>
</tr>
<tr>
<td>10</td>
<td>0.4323</td>
</tr>
<tr>
<td>30</td>
<td>0.4318</td>
</tr>
<tr>
<td>50</td>
<td>0.4310</td>
</tr>
<tr>
<td>“(Ti, Mo)N” – hard alloy”</td>
<td></td>
</tr>
<tr>
<td>unirradiated</td>
<td>0.4324</td>
</tr>
<tr>
<td>60</td>
<td>0.4317</td>
</tr>
<tr>
<td>70</td>
<td>0.4310</td>
</tr>
<tr>
<td>80</td>
<td>0.4302</td>
</tr>
</tbody>
</table>

The atomic radius of tungsten (0.141 nm) is known to be less, than the titanium one (0.149 nm). Hence, the reduction of the value of the solid solution parameter testifies to the continuous increasing of the tungsten contents and the reduction of the carbon concentration in it.

The changes of the near-surface layers’ phase composition of the researched systems are caused by the pulse character of the LEHCEB irradiation where the role of a thermal influence is great. The temperature rising results in the redistribution of the systems’ components, the transport of element with smaller atomic radius occurring more intensively owing to their higher mobility. Lack of carbon in WC causes in the transformation WC → W₂C, in its turn transformation CrN → Cr₂N is occurred as a result of the nitrogen contents reduction in the initial nitride phases.

The appearance of the new diffraction lines on the XRD patterns of carbides WC and (Ti, W)C at the increasing of the energy density of the LEHCEB influence is caused by the (Ti, Cr)N and (Ti, Mo)N coatings partial decomposition (Fig. 3, a), alloying of the coatings’ components in the carbides of the hard alloy. At full fusion of the coatings’ and alloy’s surface layer the precipitation of the additional nitride and carbide phases occurs owing to convective mixing [11] and mutual diffusion of the systems’ components.

In the range of the energy density 10–30 J/cm² the hardness of the “(Ti, Cr)N – hard alloy” system decreases as a result of recrystallization and (Ti, Cr)N partial decomposition, the hardness increasing after the LEHCEB treatment at the energy density more than 30 J/cm² due to formation of a thin (at the average 1.5 μm) disperse (500 nm) melted layer (Fig. 3, b) and the transformation CrN → Cr₂N (the Cr₂N micro-hardness – 15.71 GPa, for comparison the CrN micro-hardness – 10.93 GPa [12]).

Thus, the microhardness of the hard alloy increases in 2.6 times as a result of the combined influence consisting of preliminary CAVD deposition coatings and subsequent influence on them by the LEHCEB.
In the case of the influence on the “(Ti, Mo)N – hard alloy” system it’s microhardness rises more than in 3 times as compared with the hard alloy’s initial one due to the transformations WC → W2C (the W2C microhardness – 29.4 GPa, for comparison the WC microhardness – 24 GPa [12]) and CrN → Cr2N and also the formation of a deep layer (more than 10 μm) enriched with W and characterized by a constant distribution of the other elements (Fig. 4).

4. Conclusions

It is established that the hard alloy’s treatment consisting of CAVD deposition nitride coatings and subsequent influence on them by LEHCEB allows to synthesize very hard supersaturated multielement solid solutions of nitrides and carbides due to melting, mixing and a high cooling rate.

It is revealed, that the dissolution of the initial phases at simultaneous formation of the second nitride and carbide phases, and also transformations WC → W2C (only for the “(Ti, Mo)N coating-hard alloy” system) and CrN → Cr2N occur as a result of convective mixing and mutual diffusion of the systems’ components at full fusion of the coatings’ and alloy’s surface layers after the influence by electron beam on the researched systems.

It is shown, that the microhardness of the hard alloy increases in 2.6 times after the LEHCEB influence on the “(Ti, Cr)N coating-hard alloy”. In the case of the (Ti, Mo)N coating deposition the hard alloy’s hardness is more than in 3 times as compared with the hard alloy’s initial one.

References