Structure and properties of multilayer plasma Ti-Cu coatings

In the article we used the cathodes Ti and Cu. The coatings were deposited on the steel samples by the ion-plasma method on the HNB-6.6I1 vacuum unit while simultaneously spraying the above cathodes. Multilayer coatings were created as follows: Ti was applied within 2 minutes, then Ti + Cu were applied within 2 minutes. Totally, 100 layers were applied in an atmosphere of argon and nitrogen. The Ti-Cu-N coatings synthesized by us possessed hardness with an average value of up to 32 GPa, an elastic modulus of 400–550 GPa, a degree of elastic recovery of 0.69, and a plasticity index of about 0.15, which in terms of parameters is one of the best examples among the well-known hardening coatings. The results of the tribological studies showed that the Ti-Cu-N coating deposited on the optimum mode of vacuum-arc evaporation of a composite Ti-Cu cathode with plasma assisting on a solid substrate has a low friction coefficient, the average value of which is $\mu = 0.31$. The results of X-ray fluorescence analysis confirm the presence of copper in the test coating. Therefore, it can be assumed that copper, without forming its own crystalline phase and not being in the crystal lattice of other phases, is located on the crystallite boundaries in the amorphous state. The time it takes for the copper atoms to form a closed shell around the growing TiN crystallite determines the growth time of the crystallite and, accordingly, its size. The results of studies of structural-phase, tribological and physicomechanical characteristics at high temperatures confirmed that multi-layer Ti-Cu-N nitride coatings can be used as wear-resistant to protect products made of hard metal in the temperature range of 25–700 °C. At temperatures above 700 °C, the structure and properties of the protective layer undergo changes, the coating degrades and does not perform protective functions.

Keywords: multilayer coatings, hardness, plasticity, friction, wear resistance.

Introduction

According to the magazine International Manufacturing Technology (Canada), the capacity of the global market for services for applying high-strength wear-resistant coatings is $1.2$ billion, with an annual growth of 10–15 %, the capacity of the world market for equipment for applying such coatings is $3.9$ billion, with an annual growth of 11 %. In the segment of equipment for applying protective — decorative coatings on consumer goods, the size of the world market is $100–200$ million. In the field of strengthening coatings, the size of the world market is $2–3$ billion a year.

World leaders in the field of PVD coatings — HAUZER TECHNO COATING (Holland) and INFICON (association of companies BALZERS, LEYBOLD, PFIFTER and US INFICON). The cost of the equipment of such companies is $1.2–1.45$ million (German installation of the SS800 is $1.2$ million, Japanese UBMS-707 by KOBE STEEL Co. is $1.45$ million, and the Dutch HTC-1000 is $1.2$ million.), and corrosion-resistant coatings are formed by creating an undercoat by electroplating before applying the PVD
coating. The current share of these companies in the EC countries is 38%. According to research by TRYKOR Inc. (USA), for a significant growth in the market for electro-plating substitutes, it is necessary to reduce the cost of PVD equipment by 2 times. The price of equipment for applying PVD protective — decorative coatings of the company «Elan-Praktik» (Russia) — $0.6 million.

The cost of our software-controlled vacuum unit containing the original plasma generator for cleaning and nitriding parts; original magnetron sputtering system with copper targets; and two arc evaporators with titanium cathodes do not exceed $0.14 million.

Along with the low cost of our installation, we can get cheap coatings due to simultaneous spraying of different cathodes and their multilayer alternation. This is the subject of this work.

**Overview of Ti+Cu coatings**

The use of the Cu element as an additive in TiN was considered in [1–8]. When used as an additive for Cu, Ag, Ni, etc. in the systems TiN, ZrN, CrN, AlN, etc., the following trend is observed (Fig. 1). An increase in the concentration of the dopant leads first to an increase in the hardness of the coating to a certain maximum (Fig. 1, b), after which an increase in the content of the additional element leads to a gradual decrease in hardness (Fig. 1, a).

![Figure 1. Dependence of PM — N hardness of films on the content of Cu and Ag dopants [9]. Figures 1–4 correspond to the data of [1–4]](image-url)

The vacuum-arc plasma assisted coating deposition method used in [9] is based on the use of a non-independent arc discharge with a combined hot and hollow cathode (a source of gaseous plasma «PINK») and an independent arc discharge with a CP (electric arc evaporator with integral cold cathode), the first stage was carried out in a gas-discharge inert gas plasma generated by the PINK plasma source, with a negative potential (up to 1 kV) applied to metal substrates [10, 11].

To identify the effect of plasma assisting on the structure, phase and elemental composition, as well as the physic mechanical characteristics of the coatings, thin (3–5 μm) nitride-titanium coatings are formed on substrates made of VK-8 alloy, molybdenum grade MP and stainless steel 12X18H10T in different vacuum modes arc deposition with plasma assisted [9]. The ratio of the ion current densities of the gas and metal components \(j_{\text{ion}}/j_{\text{d}}\) to the substrate was changed by spraying nitride coatings by changing the arc current of the original plasma source PINK from 0 to 1.6 at constant pressure of the working gas. A multilayer Ti/TiN coating with a layer thickness of 250 nm was also obtained [12–14]. A typical image of this coating is shown in Figure 2.
The results of X-ray diffraction analysis indicate that the Ti–Cu–N coating consists mainly of crystallites of titanium nitride. The presence of titanium with a hexagonal lattice type is due to the presence in the coating volume of a micro-droplet fraction characteristic of the vacuum-arc deposition method.

The size of coherent scattering regions for Ti–Cu–N coatings before and after annealing, determined from the width of x-ray lines, increases from 16 to 20 nm, and to 25 nm, for the initial sample with a Ti–Cu–N coating, and after annealing at temperatures of 600 and 1100 °C. The lattice parameter for the initial Ti–Cu–N coating is slightly lower (0.423 nm) than the standard value for TiN (0.425 nm). After annealing at a temperature of 600 °C, the lattice parameter remains almost unchanged; after annealing at 1100 °C, its value increased to 0.426 nm. In this case, the lattice deformation Δd/d decreases by a factor of 4 (from 7.7 $10^{-3}$ to 1.9 $10^{-3}$), which may indicate the relaxation of residual stresses [9].

**Experimental technique**

In this work, we used the cathodes Ti and Cu. The coatings were deposited on the steel samples by the ion-plasma method on the NNV-6.6I1 vacuum unit while simultaneously spraying the above cathodes. Multi-layer coatings were created as follows: Ti was applied for 2 minutes, then Ti + Cu for 2 minutes. A total of 100 layers were applied in an atmosphere of argon and nitrogen.

An electron microscopic study was carried out on a MIRA 3 scanning electron microscope of the TESCAN company. The studies were carried out at an accelerating voltage of 20 kV and a working distance of about 15 mm. For each sample 4 shots were taken from 4 surface points at different magnifications: 245 times, 1060 times, 4500 times and 14600 times. Energy dispersive analysis was also performed at 4 points on the surface of each sample.

The optical microstructure was studied on the Epicuant metallographic microscope, and at the nanoscale — on the NT-206 atomic force microscope. The study of the microhardness of the coatings was carried out on the microhardness meter HVS-1000A. Tribological studies were carried out on the installation described in [15].

**Experimental results**

Figure 3 shows the SEM image of the Ti / Ti + Cu multilayer coating, Figure 4 shows the multilayer EMF map, and Figure 5 shows the XPS spectrum.
Figure 3. SEM images of Ti/Ti+Cu at 2 magnifications

Figure 4. Multilayer EMF map

Figure 5. XPS spectrum of Ti/Ti+Cu coating
Figure 6 shows the SEM image of the TiN/(Ti+Cu) N multilayer coating, Figure 7 shows the multilayer EMF map, and Figure 8 shows the XPS spectrum.

Figure 6. SEM images of TiN/(Ti+Cu) at 2 magnifications

Figure 7. Multilayer EMF map
The results of measuring the microhardness of $\text{Ti}^{+}(\text{Ti} + \text{Cu})$ in argon and $\text{TiN}^{+}(\text{Ti} + \text{Cu})\text{N}$ in nitrogen are presented in Table 1, and the optical images in Figures 9 and 10.

**Table 1**

<table>
<thead>
<tr>
<th>Coating</th>
<th>HV0.1</th>
<th>HV0.025</th>
<th>HV0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ti}^{+}(\text{Ti} + \text{Cu})$</td>
<td>499.4</td>
<td>539.9</td>
<td>559.8</td>
</tr>
<tr>
<td>$\text{TiN}^{+}(\text{Ti} + \text{Cu})\text{N}$</td>
<td>2288.2</td>
<td>2828.5</td>
<td>3227.3</td>
</tr>
</tbody>
</table>

The average value $\mu = 2781$ HV in nitrogen is almost 5 times greater than in argon $\mu = 533$ HV.

Figure 8. XPS spectrum of $\text{TiN}^{+}(\text{Ti} + \text{Cu})\text{N}$ coating

Figure 9. Pictures of $\text{Ti}^{+}$ coating ($\text{Ti} + \text{Cu}$) in argon

Figure 10. Pictures of $\text{TiN}^{+}(\text{Ti} + \text{Cu})\text{N}$ coating in nitrogen
The results of measuring the friction coefficient of Ti + (Ti + Cu) in argon and TiN + (Ti + Cu) N in nitrogen are presented in Table 2.

**Table 2**

<table>
<thead>
<tr>
<th>Coating</th>
<th>( \mu_1 )</th>
<th>( \mu_2 )</th>
<th>( \mu_{cp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated substrate</td>
<td>0.154</td>
<td>0.148</td>
<td>0.151</td>
</tr>
<tr>
<td>Ti+(Ti+Cu)</td>
<td>0.247</td>
<td>0.220</td>
<td>0.234</td>
</tr>
<tr>
<td>TiN+(Ti+Cu)N</td>
<td>0.306</td>
<td>0.310</td>
<td>0.308</td>
</tr>
</tbody>
</table>

**Discussion of the results of the experiment**

By varying the discharge current of the PINK plasma source and the substrate potential, it is possible to regulate the plasma concentration, the ion current density on the substrate, the energy of ions entering the substrate, which allows the surface layers of the material of the required thickness to be etched and to obtain the necessary characteristics of its surface (hardness, roughness), at the stage of cleaning, heating and activation before coating. The obtained data on the rate of etching of stainless steel in argon plasma of a non-self-sustained arc discharge, depending on plasma parameters, can also be used to optimize the process of etching substrates as an independent finishing process of ion-plasma treatment.

In this case, a non-porous coating is formed (without the introduction of gas atoms), and the continuous bombardment of a growing coating with low-energy ions of the working gas allows removing adsorbed residual gas from the surface and crushing the crystallite size of the growing coating.

The hardness of the TiN coating is 23 GPa, which is lower than the hardness of the Ti — Cu — N multilayer coating (Table 1). The degree of elastic recovery of Ti-Cu-N coatings is higher than that of TiN coatings \( \approx 2 \) times.

For resistance to abrasive and adhesive wear of the coating, they must have a high hardness and a high value of elastic recovery, which is especially important in terms of impact, abrasive and erosion effects. Such a value as \( H/E \), characterizing the stability of the material to elastic deformation of fracture and called the plasticity index, can be used to assess the wear resistance of coatings. The plasticity index \( H/E \) for superhard coatings should be \( \approx 0.1 \) and more. For this, a coating with high hardness \( H \) must have a relatively low modulus of elasticity \( E \).

The Ti-Cu-N coatings synthesized by us possessed hardness with an average value of up to 32 GPa, an elastic modulus of 400–550 GPa, a degree of elastic recovery of 0.69, and a plasticity index of about 0.15, which in terms of parameters is one of the best examples among the well-known hardening coatings.

The results of tribological studies (Table 2) showed that the Ti-Cu-N coating deposited in the optimum vacuum-arc evaporation mode of a composite Ti — Cu cathode with plasma assisting on a solid substrate has a low friction coefficient, the average value of which is \( \mu = 0.31 \).

The results of X-ray fluorescence analysis, shown in Figure 8, confirm the presence of copper in the coating under study. Therefore, it can be assumed that copper, without forming its own crystalline phase and not being in the crystal lattice of other phases, is located on the crystallite boundaries in the amorphous state. The time it takes for the copper atoms to form a closed shell around the growing TiN crystallite determines the growth time of the crystallite and, accordingly, its size.

The results of studies of structural-phase, tribological and physicomехanical characteristics at high temperatures confirmed that multi-layer Ti-Cu-N nitride coatings can be used as wear-resistant to protect products made of hard metal in the temperature range of 25–700 °C. At temperatures above 700 °C, the structure and properties of the protective layer undergo changes, the coating degrades and does not perform protective functions.

Multicomponent superhard (\( \geq 30 \) GPa) coatings (1–5 µm) with a nanocrystalline structure based on titanium nitride, such as Ti-Cu-N, can be used to protect parts, tools and other products from premature wear. Deposition of such coatings increases the performance properties of products: wear resistance, service life, etc.

Thus, the application of wear-resistant Ti-Cu-N coating, both monolayer and as part of a two-layer or multi-layer one, guarantees a fold increase in the wear resistance of parts and products from high-speed steels, hard alloys and composites. The results obtained confirm that the Ti-Cu-N coatings can be used to increase the performance characteristics of parts and products in mechanical engineering, metalworking and tool industry, etc.
**Conclusion**

It was shown that the addition of a copper element with a concentration of up to 12 at % to a titanium-based coating allows to obtain a vacuum-arc plasma-assisted method using multilayer nitride coatings of Ti-Cu-N composition with a nanocrystalline structure, where the TiN crystallites with an average size \( \approx 20 \text{ nm} \) are surrounded by an amorphous copper layer with a thickness of 2–3 monolayers, while the copper concentration in the coating is 12 at %, and the coatings have a hardness (up to 35 GPa), a low friction coefficient (0.3), high adhesion to the metal substrate (\( > 30 \text{ N} \)), increased degree of elastic recovery \( (<50 \%) \), high wear resistance \( (<2600 \mu m^2/N \text{ m}) \), good thermal stability (up to 1100 °C), increased resistance to oxidation (up to 800 °C).

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**References**


Плазменные покрытия Ti-Cu копировались в универсальной установке HNB-6.6I1 при одновременном распылении указанных выше катодов. Создавались многослойные покрытия, используя слои из меди, меди титана и меди-кобальта. Все покрытия наносились на сталь 32 ГПа, модуль упругости 400–550 ГПа, среднее арифметического расстояния 0,69 и индексом пластичности около 0,15. Температура плазменной стадии варьировалась в диапазоне 25–500 °C.

Ключевые слова: многослойные покрытия, твердость, пластичность, трение, износостойкость.

References


