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PROPERTIES OF TI/CU MULTILAYER COATINGS

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In this work, we used the cathodes Ti and Cu. Coatings were deposited on steel samples by the ion-plasma method on a vacuum unit while simultaneously spraying the above cathodes. Multilayer 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. The optical microstructure was examined on a metallographic microscope Epiquant. The study of the microhardness of the coatings was carried out on a microhardness meter HVS-1000 A. The results of measuring the microhardness of TiN+(Ti+Cu)N in nitrogen show an increase in the hardness of the coating from the standard for titanium nitride TiN values H = 20 to H = 30 GPa. Electron microscopic studies have shown that TiN+(Ti+Cu)N coatings usually have a columnar structure with filamentous grains 2–5 nm in diameter, elongated in the direction of growth.

When titanium nitride TiN slides over ordinary carbon steel and at room temperature, the coefficient of friction is 0.9, and the coefficient of friction of the TiN+(Ti+Cu)N multilayer coating decreases by a factor of 3 and does not exceed 0.3. An increase in the hardness of the TiN+(Ti+Cu)N coating and a decrease in the friction coefficient by a factor of 3 together leads to a significant increase in wear resistance. This is especially important for cutting tools.If you add up all the advantages of the obtained coatings, including resistance to high-temperature oxidation and their relatively low cost, then you can expect that TiN + (Ti + Cu) N multilayer coatings will find wide application in the metalworking industry, engineering, energy and some other areas.

Keywords: coating, microstructure, microhardness, friction.

Introduction

According to the journal 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 per year. World leaders in the field of PVD coatings - HAUZER TECHNO COATING (Holland) and INFICON (association of companies BALZERS, LEYBOLD, PFIFFER 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 electroplating substitutes, it is necessary to reduce the cost of PVD equipment by 2 times. The price of equipment for applying PVD 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. 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 TiN, ZrN, CrN, AlN, etc. systems, the following trend is observed (Figure 1). An increase in the concentration of the alloying additive leads first to an increase in the hardness of the coating to a certain maximum (Figure 1, b), after which an increase in the content of the additional element leads to a gradual decrease in hardness (Figure 1, a).

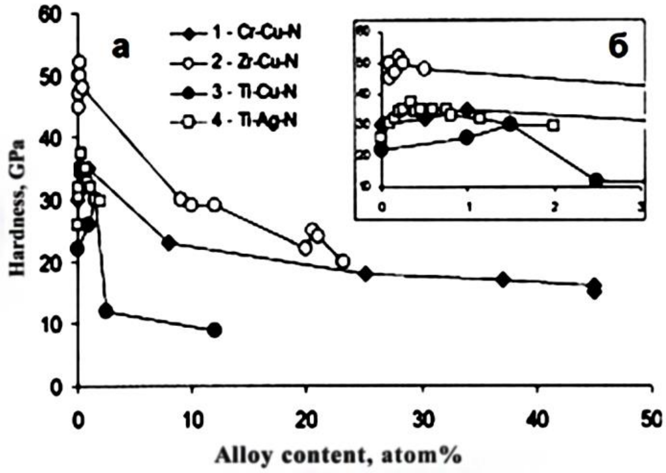

Fig.1 Dependence of the hardness of PM – N films on the content of Cu and Ag dopants [9]. Numbers 1–4 correspond to the data of [1–4].

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 reveal the effect of plasma assisting on the structure, phase and elemental composition, as well as the physicomechanical characteristics of the coatings, thin (3-5 μm) nitride-titanium coatings are formed on substrates made of VK-8 alloy, molybdenum grade MCh and 12X18H10T stainless steel arc deposition with plasma assisted [9]. The ratio of the ion current densities of the gas and metal components (jp / jd) 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 Fig. 2.

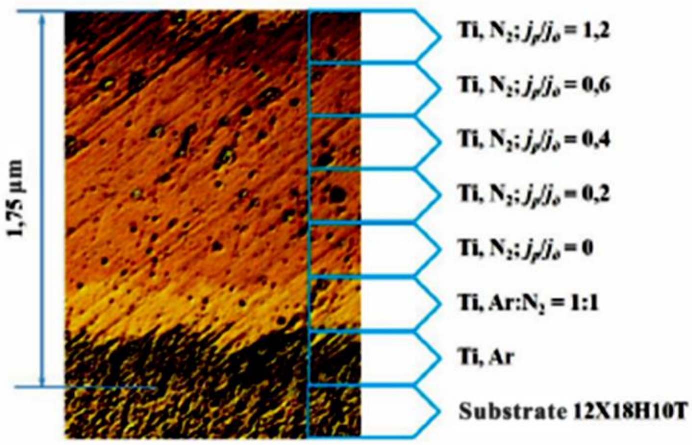

Fig. 2. A typical image of a transverse section of a multilayer Ti/TiN coating deposited on a steel substrate by a vacuum-arc plasma assisted method (optical metallography) [9].

The results of X-ray analysis show that the Ti – Cu – N coating consists mainly of titanium nitride crystallites. 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 (CSR) 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 (0.42298 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 0.42614 nm. In this case, the lattice deformation Δd/d decreases by 4 times (from $7.7\ 10^{-3}$ to $1.9\ 10^{-3}$), which may indicate the relaxation of residual stresses [9].

1. 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 a HNB-6.6I1 vacuum unit while simultaneously spraying the above cathodes. Multilayer 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 an Epiquant metallographic microscope and, on a nanoscale, on an NT-206 atomic force microscope. The study of the microhardness of the coatings was carried out on the microhardness meter HVS-1000A.

2. 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.

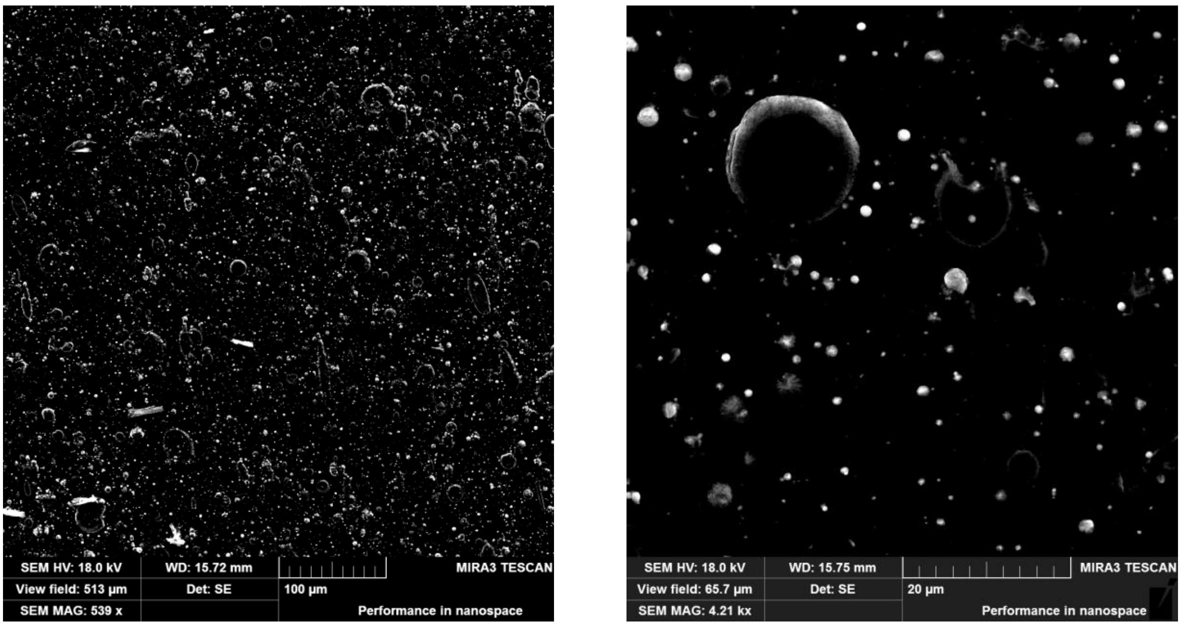

Fig. 3. SEM images of Ti/Ti+Cu at 2 magnifications

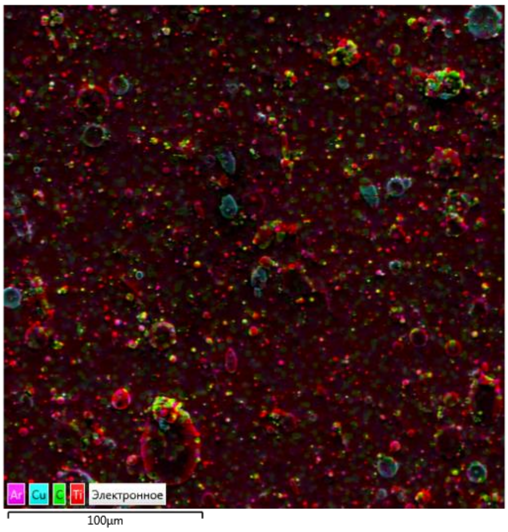

Fig.4. Multilayer EMF map

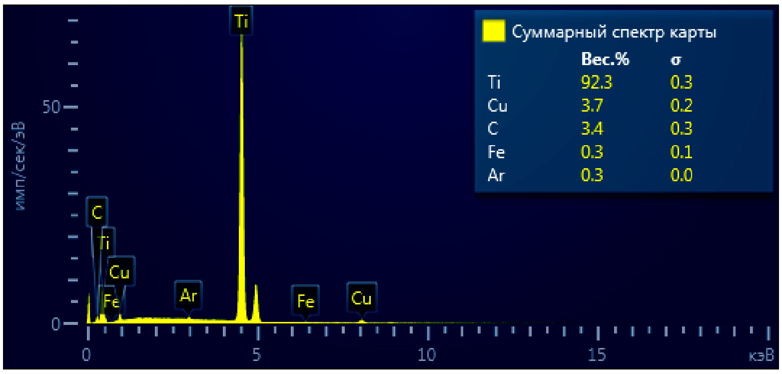

Fig.5. XPS spectrum of Ti / Ti + Cu coating

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.

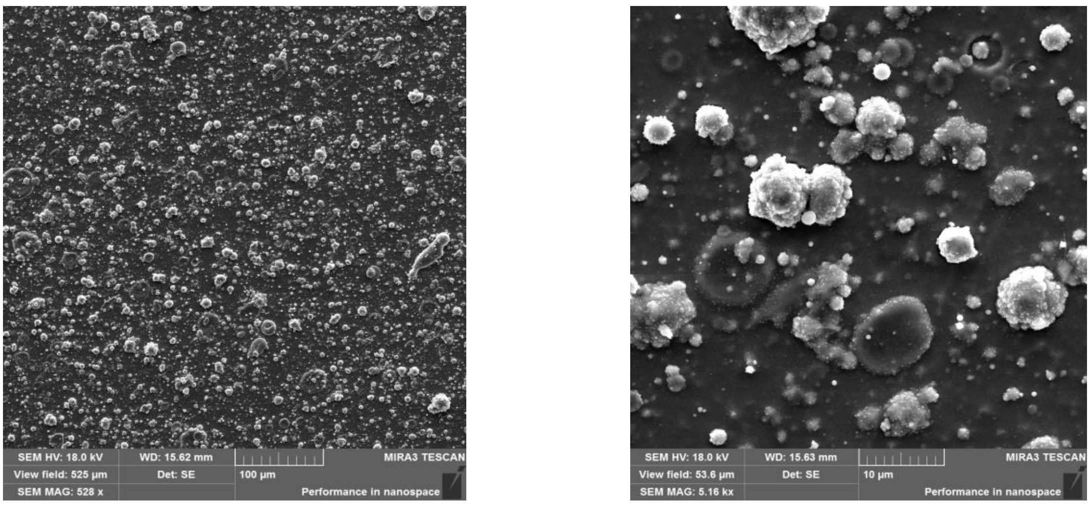

Fig.6. SEM images of TiN/(Ti+Cu) at 2 magnifications

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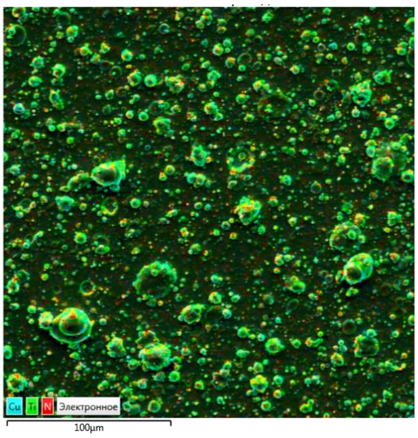

Fig.7. Multilayer EMF map

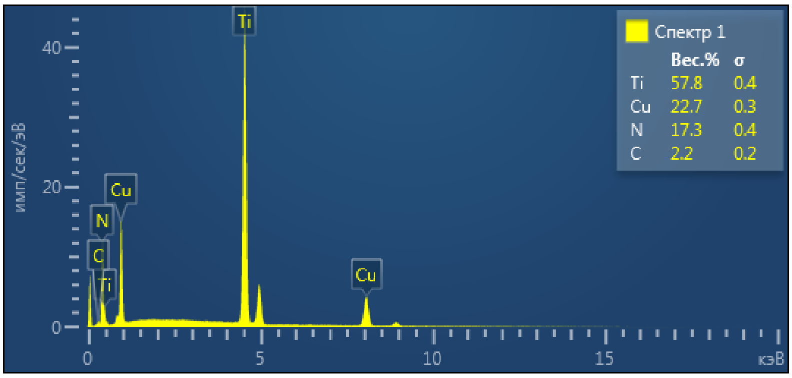

Fig.8. XPS spectrum of TiN/(Ti+Cu)N coating

The results of measuring the microhardness of Ti+(Ti+Cu) in argon and TiN+(Ti+Cu)N in nitrogen are presented in Table 1, and the optical images in Figures 9 and 10.

Table 1 - Microhardness Ti+(Ti+Cu) in argon and TiN+(Ti+Cu)N in nitrogen

coating	HV0.1	HV0.025	HV0.01
Ti+(Ti+Cu)	499,4	539,9	559,8
TiN+(Ti+Cu)N	2288,2	2828,5	-

The mean value μ = 2558 HV in nitrogen is almost 5 times greater than in argon μ = 533 HV.

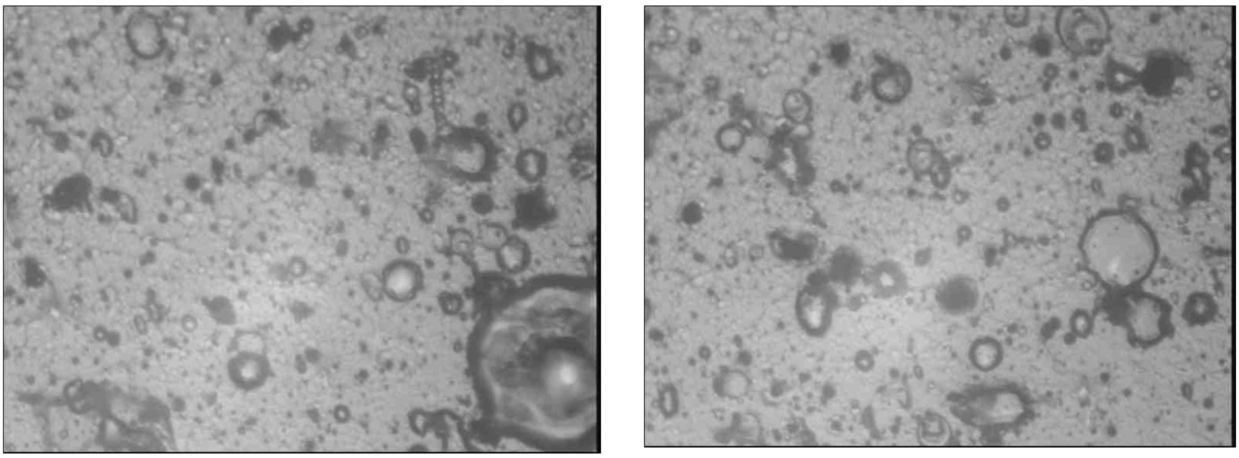

Fig.9. Pictures of the coating Ti+(Ti+Cu) in argon

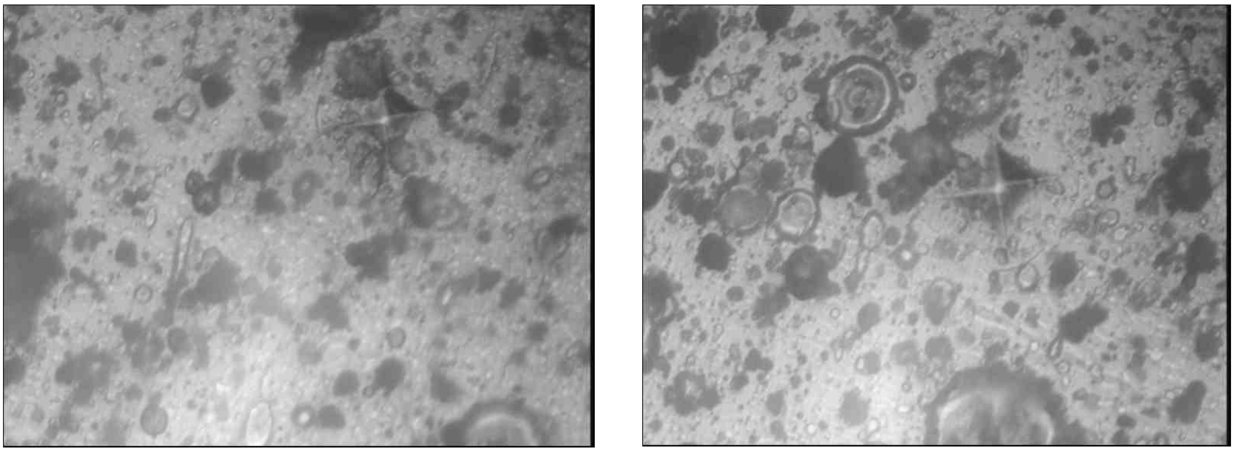

Fig.10. Pictures of TiN+(Ti+Cu)N coating in nitrogen

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 - Coefficient of friction of Ti+(Ti+Cu) coatings in argon and TiN+(Ti+Cu)N in nitrogen

coating	μ_1	μ_2	μ_{cp}
Uncoated substrate	0,154	0,148	0,151
Ti+(Ti+Cu)	0,247	0,220	0,234
TiN+(Ti+Cu)N	0,306	0,310	0,308

3. Discussion of the results of the experiment

From table 1 it follows that the average value μ = 2558 HV in nitrogen is almost 5 times greater than in argon μ = 533 HV. These values are obtained at optimal values of the arc current, the pressure of the reaction gas, the magnitude of the reference voltage and the temperature of the substrate. We have established:

- grinding the grain structure of the coating material with increasing substrate temperature is accompanied by an increase in hardness to some critical average size of nanograin. The decrease in hardness with a further decrease in the average grain size in the coating is due to slippage along grain boundaries (rotational effect). In this case, to further increase the hardness, it is necessary to slow down the process of sliding along grain boundaries. Such inhibition can be achieved due to the formation of an appropriate nanostructure with hardening of grain boundaries. The optimum temperature of the substrate or part is 400 - 450 ° C;
- in most cases, with an increase in the arc current of the evaporator, the microhardness decreases. This is due to the fact that with an increase in the arc current of the evaporator, the coating thickness increases quite quickly, and this leads, in turn, to an increase in the dislocation density in the coating being formed. The optimal value of the arc current I = 110 A;
- it was experimentally shown that the samples obtained at nitrogen pressure P = 0.081–0.81Pa have the most evenly distributed fine dense structure, the minimum content of the droplet phase, pores, influxes, delaminations and the highest microhardness values;
- variation of the reference voltage leads to a significant (more than two times) change in the microhardness of the coatings. Thus, the reference voltage is an important technological regime that determines the strength properties of coatings. It should be noted that the main reason for the reduction of microhardness is the microstructure of the coating, so in the absence of a reference

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voltage, the coating is characterized by equiaxial grain size, while at U = -210 V there is a columnar structure germinating from the substrate.

Conclusion

The results of measuring the microhardness of TiN+(Ti+Cu)N in nitrogen show an increase in the hardness of the coating from the standard for titanium nitride TiN values H = 20 to H = 30 GPa. Electron microscopic studies have shown that TiN+(Ti+Cu)N coatings usually have a columnar structure with filamentous grains 2–5 nm in diameter, elongated in the direction of growth.

An increase in the hardness of multilayer coatings with a layer thickness of about 100–150 nm is due to the fact that the generation of dislocations is retarded by the Frank – Read mechanism [15]. If the coating thickness does not exceed 100 - 300 nm, then the film, as a rule, has not a solid, but an “island” structure. A multilayer coating of layers whose thickness does not exceed 300 nm is a special kind of material, the so-called multilayer composite (nanocomposite) [16]. In fact, a multilayer composite combines high-strength, virtually defect-free layers and defects in the form of interfaces between the layers. The essence of the proposed technology for deposition of multilayer nanostructured vacuum ion-plasma coatings of the Ti-Cu-N system is that in a single operating cycle it is provided to combine arc discharges of cathodes made of titanium and copper burning in pairs with a non-self-sustained high-current discharge [9-11].

When titanium nitride TiN slides over ordinary carbon steel and at room temperature, the friction coefficient is 0.9. From table 2 it can be seen that the coefficient of friction of the TiN+(Ti+Cu)N multilayer coating decreases by a factor of 3 and does not exceed 0.3. An increase in the hardness of the TiN+(Ti+Cu)N coating and a decrease in the friction coefficient by a factor of 3 together leads to a significant increase in wear resistance. This is especially important for cutting tools [17].

If you add up all the advantages of the obtained coatings, including resistance to high-temperature oxidation and their relatively low cost, then you can expect that TiN+(Ti+Cu)N multilayer coatings will find wide application in the metalworking industry, engineering, energy and some other areas.

The obtained experimental data show the promise of the developed coatings in many branches of industrial production. In carrying out this work, the fundamental results obtained in the Laboratory of Plasma Emission Electronics (LETEE) of the Institute of Electrical Engineering, Siberian Branch of the Russian Academy of Sciences were taken into account.

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