Multi-phase ion-plasma Cu-Ti coatings deposited on copper and copper beryllium alloy

A V Kolubaev1, O V Sizova1, Yu A Denisova1,2, A A Leonov2, N V Teryukalova1 and O S Novitskaya1

1 Institute of Strength Physics and Materials Science, Siberian Branch of the Russian Academy of Sciences, 2/4, pr. Akademicheskii, Tomsk, 634055, Russia
2 Institute of High Current Electronics Siberian Branch of the Russian Academy of Sciences, 2/3, pr. Akademicheskii, Tomsk, 634055, Russia

E-mail: kav@ispms.ru

Abstract. The paper presents outcomes of vacuum-arc plasma-assisted deposition of titanium, titanium nitride and copper on copper (C11000) and the hardened copper beryllium alloy (C17200) at a temperature of 320–330°C. The study has revealed that multi-phase coatings form when varying discharge currents generated by arc evaporators and supply sequences of producer gas (argon) and nitrogen. An X-ray phase analysis has demonstrated these coatings to consist of copper, titanium and CuTi, CuTi2 and TiN compounds. Another important outcome to emerge from the study is that ion-plasma processing results in ageing of copper beryllium alloy and furthers the formation of CuBe particles. The microhardness of Cu-Ti coatings is as high as 400–540 HV0.05 provided that the elements are vacuum-arc deposited at a temperature of 320–330°C. The microhardness of a nitrogenized Cu-TiN surface layer is measured to be 760 HV0.05. The thickness of deposited coatings is within several micrometers, so the measured hardness hardly complies with the real characteristic of coatings because the indenter breaks a thin hard layer. In addition, vacuum-arc sputtering of titanium and copper cause metal drops on the surface, as a consequence, the hardness of coatings is below referential values.

1. Introduction

To date, ion-plasma coatings based on titanium, chromium, other materials and their compounds have been widely applied [1]. State-of-the-art deposition technologies of ion-plasma coatings are intended to provide high operation properties of tools and components of modern equipment. The mainstream processes in ion-plasma processing include plasma-magnetron sputtering [2] and vacuum-plasma sputtering by electric arc evaporators of metals [3]. The combination of functional properties in hard coatings makes machine parts more resistant to corrosion, erosion, abrasive and contact wear.

In general, coatings are produced on ferrous metals and alloys in industry. Non-ferrous metal are less sensitive to above mentioned factors. Nevertheless, a great number of items produced of copper and its alloys and used in electrical and chemical engineering for manufacturing radiators, pipelines, heat exchangers, etc. with high electrical and thermal conductivity also require corrosion, erosion and wear protection. In addition, copper alloys are characterized with relatively low hardness and fail to resist to adhesion and abrasive wear.

An application field of copper alloys in extreme operation conditions can be broadened by means of surface modification methods. An example is diffusion saturation of copper surface with titanium [4]. A binary copper-titanium phase diagram demonstrates that several intermetallic Ti–Cu phases can be produced in this system and significantly improve surface properties of copper alloys. This approach seems to be rather promising, especially for the enhancement of copper alloys surfaces, e.g. to make sliding electric contacts more wear resistant. The main point of methods to deposit coatings for protection of electric contacts from wear and corrosion is not to raise the electric resistance of a contact. For this purpose a component with high conductivity and filler with high electrical erosion resistance are introduced into the coating composition. For instance, electrical explosion sputtering of the CdO-Ag system on a copper surface [5] results in a multi-phase coating, components of which include submicro-crystalline copper and nano-dimensional inclusions of copper oxides, cadmium and Cd-Cu compounds.
The surface hardening process of future is suggested to be ion-plasma deposition of hard coatings, e.g. those based on nitrides of different elements [6, 7]. As a result of this processing hard layers form on the alloy surface and enhance significantly operation properties of products. However, there are some limitations in the application of hard coatings deposited on relatively soft substrates and intended to be used in extreme mechanical loading. A copper substrate tends to deformations and causes cracking and lamination of hard coatings. To minimize such negative effects hardness of a plastic copper substrate should be increased, what is a greater challenge in comparison to iron-based or hard alloys. Pre-hardening of a substrate surface is a method to make hard coatings more compatible with a plastic metal. It is a diffusion product of alloying elements into the substrate metal surface [8]. A number of hardening elements for copper and its alloys is limited [9], therefore composite layers [10] and multi-layered coatings where layers of copper alternate with those of its compounds [11] are produced to enhance hardness and tribotechnical properties of coatings via reducing residual stresses and increasing coating-substrate adhesion.

To sum up, ion-plasma alloying makes it possible to vary broadly surface properties of different alloys, e.g. copper-based ones and allows their application in the deposition of wear and corrosion resistant coatings on machine elements manufactured of copper alloys and operated in extreme loading conditions. The most promising products in this respect are multi-phase and multi-component functional coatings on the base of metal nitrides, oxides and carbides which form a complex “substrate-modified surface layer” with smoothly varying physical and mechanical properties responsible for high operation characteristics.

2. Materials and Methods of Research
In the research 8.0 mm high cylindrical samples of copper and beryllium alloy (C17200) were used which were fabricated from a hot-rolled rod with a diameter of 5 mm, water-quenched at a temperature above 800°C and quenched with the subsequent ageing at a temperature of 315°C within 2 hours. Samples of copper (11000) represented 15×15×5 mm plates.

The vacuum-arc plasma-assisted deposition of coatings was carried out using a unit “KVADRO”, a part of unique electro-physical facilities at the Institute of High Current Electronics, Siberian Branch of the Russian Academy of Sciences. To generate a metal plasma flow we used two electric arc evaporators with cylindrical titanium (Grade 2) and copper (C1100) cathodes 80 mm in diameter, as well as a gaseous plasma source with a heated and hollow cathode “PINK”. The gaseous plasma source was used for pre-cleaning of product surfaces from leftover dielectric, e.g. oxide films, with the help of ion etching, heating the substrate, as well as additional ionization of gas and assisting in the process of coating deposition. To obtain a necessary element composition of the Ti-Cu coating we selected a balance between discharge currents of electric arc evaporators. Samples were placed in the center of the chamber on the holder at a level of output apertures of plasma sources.

Prior experimenting, the pressure of 10⁻⁶ Pa was generated in the 650×650×650 mm vacuum chamber then argon was supplied through the plasma generator “PINK”, and the pressure of 0.3 Pa was generated. When starting a gaseous discharge with a current of about 40A and setting the shift voltage of (600) V substrates on the holder were heated up to a temperature of 320-330°C. As the surface of samples was cleaned via ion bombardment and chemically activated, charges were started in the electric arc evaporators, and a coating was sputtered. When depositing nitrides we used nitrogen, whereas we applied argon for sputtering compounds of pure metals. Coatings were produced according to three modes presented in Table 1. The samples were rotated on the holder in the center of the chamber at a speed which furthered smooth deposition of several nanometer thin titanium and copper layers, their remixing and mutual diffusion.

| Mode | Current of evaporator 1 (Ti) | Current of evaporator 2 (Cu) | Current of gaseous plasma source | Shift voltage when sputtering | Process temperature | Operation gas | Period of deposition |
|------|-----------------------------|-----------------------------|---------------------------------|-----------------------------|---------------------|---------------|---------------------|
| №1   | 90                          | 90                          | ≈ 40                            | 100                         | 320-330             | Ar            | 120                 |
| №2   | (30-90)*                    | 90                          | ≈ 30                            | 100                         | 320-330             | Ar            | 240                 |
| №3   | (30-90)*                    | 90                          | ≈ 50                            | 100                         | 320-330             | Ar (10% Ar+90% N2)** | 240                 |

* a start current value 30 A increased by 5 A every 20 min to get a value of 90 A.
** 40 min sputtering of TiCu first in the Ar atmosphere and then in the 10% Ar + 90% N2 gas mixture at the initial pressure of 0.1 Pa, increased by 0.02 Pa every 20 min to get a value of 0.3 Pa.

Table 1. Deposition parameters of coatings
The phase composition, morphology and microstructure of coatings were explored using the methods of optical and scanning electron microscopy with a laser confocal microscope LEXT OLS4000 in optical and laser modes, a scanning electron microscope Philips SEM 515 tooled with an energy-dispersive X-ray microanalyzer “Genesis” in the Collective Resource Center of National research Tomsk State University and with a scanning electron microscope “LEO EVO 50” in the Core Facilities Center of Institute of Strength Physics and Materials Science, Siberian Branch Russian Academy of Sciences “NANOTECH”. The structure of coatings was analyzed with an X-ray diffractometer DRON–3.0 in the CuKα radiation. To determine the phase composition software PowderCell was used.

3. Results and Discussion

The metallographic research of coated copper samples revealed an insignificant thickness difference of samples fabricated in different modes. The coatings were deposited as a solid uniform in thickness layer with a distinct coating-substrate boundary line. Figure 1 (a) demonstrates as an example a coating produced in the first mode. A microanalysis (Fig. 1, b) detected copper and titanium in the surface layer and suggested it was a result of the subsequent deposition of several nanometer thick titanium and copper layers when rotating samples in the chamber, their remixing and mutual diffusion. Owing to this method of Ti and Cu sputtering on a copper sample the surface hardness was higher (400 HV0.02) than that of pure copper (75 HV0.02). A coating produced according to the second mode is similar in appearance to that produced in the first mode. There is also copper and titanium in the coating but its hardness is significantly higher – 540 HV0.02. The reason might be a thinner copper layer on the coating surface (Fig. 2) in comparison to that sputtered in the first mode. These differences depend on uncontrolled deviations when coating.

![Figure 1](image1.png)

**Figure 1.** The Cu-Ti coating on copper – product of the first mode (a), the pattern of elements in the coating (b).

![Figure 2](image2.png)

**Figure 2.** The pattern of elements in the coating – product of the second mode.

The effect of nitrogen plasma on the structure, phase composition and hardness of Cu-Ti coatings was revealed via sputtering thin nitride layers on copper and copper beryllium substrate in conditions of plasma-assisted vacuum-arc deposition (mode 3). When plasma nitriding with switched on Cu and Ti electric arc evaporators we used a gaseous plasma source “PINK”. An X-ray phase analysis disclosed a multi-phase layer (Figure 3) consisting of Cu, CuTi3, and TiN (Figure 4) – a product of the nitride deposition on a copper substrate. According to the X-ray spectral analysis the coating thickness was below 6 µm. The micro-hardness of the azotized coating was as high as 760 HV0.02. Importantly, it was concluded [12] a soft copper substrate might influence measured micro-hardness.
Unlike copper, strength and antifriction characteristics of copper beryllium alloys, as well as their corrosion resistance are quite good. The specified operation qualities of the alloy are possible due to thermal treatment – quenching and ageing – resulting in the two-phase alloy comprising α-solid solution with a low beryllium percentage and sporadic decomposition zones – ultra-dispersive γ′-phase particles (CuBe). Ageing in the range of 300-400°C makes the alloy harder and stronger. Ion-plasma coatings deposited at a temperature of 315°C on the quenched alloy (C17200) brings about both its ageing and a hard layer on its surface.

Figure 5 presents a cross section of a beryllium bronze sample coated with copper and titanium according to mode 1 and its element composition. The thickness of a composite coating was measured to be 5÷7 μm; a layerwise microanalysis detected almost the same patterns of Ti and Cu in the coating section. It is a result of the sequential deposition of copper and titanium in the process of rotating samples in the chamber, their remixing and mutual diffusion. An element microanalysis of the coated alloy under consideration showed there is titanium in the substrate material since titanium diffuses into it when depositing a coating layer. CuBe particles forming in the bronze ageing were also found in the substrate material. Their maximal size was 300 nm.

Unlike the coating produced in the first mode the second one displays a gradient pattern of elements in the section; this is caused by the conditions of sputtering titanium. In the substrate material, similarly to the first case, there is titanium which might form a solid titanium solution in copper. The thickness of this surface layer is up to 8 μm (Figure 6). The coatings produced according to the first and second modes had the hardness of 530-540 HV₀.₀₂ like that of a coating deposited on copper. These coatings are assumed to have the same phase composition because of relatively equal hardness values. It is worth saying the hardness of the aged substrate when sputtering the coatings was 350 HV₀.₀₂.
An X-ray phase analysis of the coatings demonstrated elements to be deposited form a multi-phase structure on the copper beryllium alloy surface: its components are copper, titanium and CuTi and CuTi$_2$ compounds (Figure 7). Since it is not thick, X-rays penetrate the substrate material; therefore a copper reflex can be formed either by substrate reflexes or pure copper of the coating.

![Figure 6. The Cu-Ti coating on C17200 deposited in the second mode.](image)

**Figure 6.** The Cu-Ti coating on C17200 deposited in the second mode.

![Figure 7. The X-ray diffraction pattern of the Cu-Ti coating on C17200. 1 – a coating in the first mode, 2 – a coating in the second mode.](image)

**Figure 7.** The X-ray diffraction pattern of the Cu-Ti coating on C17200. 1 – a coating in the first mode, 2 – a coating in the second mode.

4. Conclusion

The results presented demonstrate copper and titanium coatings deposited on copper and copper beryllium alloy consist mostly of copper, titanium and compounds on the Cu-Ti base. Intermetallic Ti – Cu compounds on the surface of copper and beryllium bronze formed using the vacuum-arc plasma-assisted method have a significant increasing effect on hardness up to 530-540 HV$_{0.02}$, irrespectively to a deposition mode. Owing to the Cu-TiN coating formed on copper and the C17200 alloy the hardness is 760 HV$_{0.05}$, therefore it can be used in sliding friction units.

Acknowledgment

The deposition of coatings on copper (C11000) was studied within the Program of State Order. The research on the structure and properties of C17200 alloy was granted by Russian Foundation for Basic Research (project # 20-58-00048 Bel_a).

References

[1] Zhang X, Tian X-B, Zhao Z-W, Gao J-B, Zhou Y-W, Gao P. and Lv Z 2019 Surface & Coatings Technology 364 135
[2] Wei R, Vajo JJ, Matossian JN and Gardos MN 2002 Surface & Coatings Technology 158–159 465
[3] Akhmadeev YH, Denisov VV, Koval NN, Kovalsky SS, Lopatin IV, Schanin PM and Yakovlev VV 2017 Plasma Phys. Rep. 43(1) 67
[4] Cherenda NN, Basalai AV, Uglov VV, Laskovnev AP, Astashynski VM and Kuzmitski AM 2019 Vacuum 167 452
[5] Romanov DA, Moskovskii SV, Gromov VE, Ivanov YF, Semin AP and Filyakov AD 2019 Fundamental’nye problemy sovremennoi materialovedeniya 16(1) 62
[6] Audisio SC and Leidheiser H, Jr. 1972 J. Electrochem. Soc. 119 408
[7] Carrasco C, Segers L, Benavente B and Vergara V 2004 J. of Materials Processing Technology 145(3) 371
[8] Li Y, Ye Q, Zhu Y, Zhang L, He Y, Zhang S and Xiu J 2019 Surface & Coatings Technology. 362 27
[9] Britchi M, Branzei M and Gheorghe D 2002 International Journal of Materials and Product Technology 17(8) 659
[10] Yan MF, Zhu YD, Zhang CS, Zhang YX, Wang YX and Yang L 2015 Materials and Design 84 10
[11] Kim GS, Lee SY, Hahn JH, Lee BY, Han JG, Lee JH and Lee SY 2003 Surface & Coatings Technology 171(1–3) 83
[12] Iost A, Guillemot G, Rudermann Y and Bigerelle M 2012 Thin Solid Films 524 229