Effect of the matrix material and electroplating process on the microstructure and properties of isolation switch contacts

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Abstract

In the KI system, Ag plating, hard-Ag plating and graphene-Ag plating were prepared on the surface of the copper and Cu–Cr alloy matrix materials by the electrodeposition method. The purpose of this paper is to define the copper-based material and related plating process suitable for the contacts of the isolating switch, obtaining excellent comprehensive properties and revealing the strengthening mechanism and wear mechanism of contact materials. Copper alloy was obtained by smelting in a high-frequency vacuum induction furnace, and then cold rolled. Effects of different plating processes and matrix materials on the microstructure, bonding degree between the plating and matrix, microhardness, contact resistance and wear resistance of copper-based contact materials were studied. The results showed that the matrix and the plating are well bonded. Both the Cu–Cr alloy matrix and the hard-Ag plating were rich in a large number of nano twins, dislocations and precipitates, which can strengthen the matrix and the plating. Moreover, they are beneficial to obtaining contact materials with high strength, high toughness and high conductivity. The contact resistance of the 3 kinds of plating changed little. The contact resistance of the Ag plating was the smallest, which was the largest of the hard-Ag plating, increased by 19.5%. The hard-Ag plating has the highest hardness and best wear resistance. Under the same test conditions, the combination of the hard-Ag plating and the Cu–Cr alloy matrix enables the copper-based contact material to obtain good cooperation of hardness, wear resistance and conductivity, and the comprehensive performance is the best.

1. Introduction

Electrical contact materials are widely used in many fields, such as relays and switches. They play a role in conducting current between fixed parts and moving parts. Therefore, it expects that contact materials have excellent cooperation of oxidation resistance, arc ablation resistance, conductivity, thermal conductivity, hardness and wear resistance [1]. In recent years, a large number of studies have shown that copper-based materials are widely used in contact materials due to their high conductivity and thermal conductivity, low friction coefficient, and good corrosion resistance, fatigue resistance and workability [2–5]. Moreover, the excellent weldability of copper-based materials can ensure the excellent bonding strength between the substrate and the plating after electroplating, while avoiding separation [2]. However, copper is easily oxidized and has poor wear resistance. The oxide layer and wear debris on the copper will increase the contact resistance of electrical contacts, and the copper is too soft and ductile, reducing its service life [1, 3, 4]. To improve the
oxidation resistance. The corrosion resistance of Ag in contact applications, due to the high oxidation resistance of Ag in contact applications, it is generally necessary to perform Ag plating on the surface of the copper matrix or add trace alloying elements and rare earth elements to the copper matrix. Corresponding heat treatment and deformation treatment are carried out to improve its properties [1, 4, 6, 7]. However, the high price of Ag is the main obstacle to its application, and the opening and closing actions during use and environmental corrosion will cause the Ag plating to peel off and copper leakage. On the one hand, the number of primary batteries will increase, and the protective effect on the substrate is lost, which accelerates the occurrence of electrochemical corrosion. On the other hand, the increase in contact resistance directly causes heating problems [3]. Therefore, we should look for cheap Cu–Cr alloys with better performance and corresponding plating materials to reduce the addition of precious Ag and improve plating performance [8].

Isolation switches are one of the most widely used equipment and critical components in the power transmission and transformation equipment of the power system. They are responsible for the functions of the isolation, transfer, connection, and disconnection. Their working status directly affects the safety and stability of the power system, and the personal safety of staff. Isolation switches need to bear the coupling effect of the electricity, heat, force and environment during use. And it has been subjected to the friction during frequent opening/closing operations and the corrosion by atmospheric pollutants in a long time, such as the salt fog, rain, sand, dirt, SO2, Cl , NH3, H2S, NO3, etc. These can easily cause the corrosion, wear, tear and contact deformation of the copper substrate and the Ag plating, increasing the contact resistance of the switching circuit and causing heating defects. Besides, the related corrosion products will also accumulate between the conductive contact surfaces, causing abrasive wear on the conductive contact surfaces, resulting in a furrow phenomenon and a reduction of the conductive contact area, which is one of the important factors that cause heating problems and aggravate the increase in contact resistance. In addition, the matrix will be exposed to the environment, causing the failure of the switch, which may lead to serious safety problems and shorten the service life of the isolation switch. Therefore, copper alloy materials require a good combination of corrosion resistance, wear resistance and mechanical properties [9, 11–14]. Lv et al [10] found that the corrosion behaviour of Cu in a 5% NaCl neutral salt spray environment is related to the magnitude of the current. The samples with external current have a faster corrosion rate than the samples without current. The reason may be that the corrosion process of electrical contacts is affected by current, and Cl is highly permeable and destructive. The combined action of Cl and current accelerates the corrosion of Cu [9]. Song et al [11] studied the air corrosion-corrosion (CE-C) behaviour of various copper alloys of marine propellers in a 3.5% NaCl solution containing sulfides. In the presence of sulfide, a thin film composed of copper oxide and sulfide is formed on the copper alloy, which has a loose structure, inadequate protection and severe corrosion. And the higher the sulfide concentration, the faster the corrosion rate of copper and its alloys, which reduces the CE-C resistance. Therefore, high hardness, high conductivity, high corrosion resistance and high wear resistance are the main requirements for improving the life of copper alloy isolation switch contacts. The development of new copper alloy materials and plating is becoming the essential means to alleviate or even solve these problems.

Electroplating, electroless plating, plasma spraying, and laser cladding are commonly used to produce Ag-plated copper. Ag plating got by electroless plating or electroplating is a beneficial method to improve the oxidation resistance of copper-based materials, increase their conductivity, reduce their contact resistance, and have a certain degree of air isolation and corrosion protection effects [3]. Wu et al pointed out that the oxidation resistance of the copper substrate can be improved by electroless Ag plating, and a uniform Ag plating can be obtained on the copper substrate [1]. But Chang et al pointed out that this method will reduce the conductivity of the sample and oxidize the sample during the contact operation, so the electroplating method is relatively good [1]. The current results show that, compared with the traditional Ag plating, due to the high chemical stability, high conductivity, high thermal conductivity and flexibility of graphene, the graphene-Ag plating has apparent advantages in corrosion resistance, contact resistance and mechanical properties [14–18]. Gülte et al [16] found that the conductivity and strength of graphene are higher than that of copper. Adding graphene to the copper matrix and making it evenly distributed can improve the thermal conductivity of the composite material. And the perfect bonding of the graphene and copper at the interface can significantly improve the mechanical properties (tensile strength, yield strength, ductility, etc) of composite materials [16]. Lv et al prepared Ag plating, graphite-Ag plating and graphene-Ag plating on the copper surface by the electrodeposition, and investigated their microstructure, wear resistance, corrosion resistance and contact resistance. The results show that the graphene-Ag plating has the lowest friction coefficient and the smallest wear width. The self-corrosion current density of the graphene-Ag plating in 3.5% NaCl solution is the smallest with 1.139 μA cm , and the addition of graphene has little effect on the contact resistance of the plating [14, 15]. Therefore, in order to further improve the mechanical properties and service performance of isolation switches, hard compounds or graphene can be added to Ag plating to form a hard-Ag plating or graphene-Ag plating, which has great potentiality for the application in isolation switches [1, 4, 14]. However, so far, few reports have systematically
investigated the Ag plating, hard-Ag plating and graphene-Ag plating of isolation switches, hindering the
development of isolation switches [14, 15].

Previous studies on electroplating coatings were mostly based on the preparation of cyanide solution
systems. Most commercial Ag plating is still carried out with cyanide formulations that are incredibly harmful to
the environment, so it must be gradually eliminated [15]. In this work, we used a Cu–Cr alloy substrate with
high-strength and high-conductivity. And we introduced graphene and hardened substances into the Ag plating,
forming Ag composite plating by non-cyanide electroplating. This novel electroplating process has advantages
of process and composition of Ag-Sb alloy plating with high conductivity and high wear resistance. And the Ag-
Sb/Cu interfacial reactions ensure good interface bonding, and the electroplating process is easy to operate.
Moreover, the plating performance on Cu matrix and Cu–Cr alloy matrix was systematically studied, which has
essential engineering practical significance [14, 17]. Therefore, this research aims to obtain the best production
process and excellent performance of isolation switches by investigating the conductivity and wear resistance of
the non-cyanide electroplating Ag plating, hard-Ag plating and graphene-Ag plating, and reveal the wear
mechanism, simplify the production process, reduce production costs, and protect the environment. It expects
to provide a reference for the material and process design of the isolation switch contacts, and offer a theoretical
basis for its engineering application.

2. Materials and methods

2.1. Materials

In order to obtain isolating switch contact materials with higher wear resistance and conductivity to meet the
requirements of product application conditions, we designed a total of 6 sets of experiments. Copper and Cu–Cr
alloy were selected as the matrix materials, and the electroplating was Ag plating, hard-Ag plating and graphene-
Ag plating. According to the difference between the matrix material and the electroplating, they were marked as
A1, A2, A3, B1, B2, and B3, as shown in table 1. The composition of Cu–Cr alloy is 1.0 wt.% Cr, 0.06 wt.% Zr,
and the balance is Cu. The main components of the Ag plating bath are AgNO₃ solution and KSCN solution. The
main components of the hard-Ag plating bath are 20–30 g l⁻¹ L-antimony potassium tartrate, 0–20 g l⁻¹ K₂CO₃
solution, AgNO₃ solution, KSCN solution, and KCN solution. And that of the graphene-Ag plating bath are
30–40 g l⁻¹ AgNO₃ solution, 200–400 g l⁻¹ KI solution, 10–20 g l⁻¹ graphene solution, and 3–6 g l⁻¹ graphene
dispersant. The hard-Ag plating enhanced with L-antimony potassium tartrate can improve the oxidation
resistance of the plating and reduce production costs, and obtain high hardness and high thermal
conductivity [19].

Samples with the dimension of (15 × 15 × 5) mm were cut from rolled copper plates and rolled Cu–Cr
alloy plates by wire electric discharge machines for subsequent experiments. Before electroplating, the samples
were polished and pickled. The sample was electroplated at room temperature for 1.5–2 h, the current density
was 0.2–0.5 A dm⁻², and the magnetic stirring bath speed was 600–800 r min⁻¹. The thickness of the plating
can be controlled by the electroplating time, and the surface of the resulting plating is smooth without apparent
defects.

2.2. Methods

The surface of the sample was etched with FeCl₃ solution (1.4 g FeCl₃, 48 ml CH₃CH₂OH, 2 ml HCL) for 10 s,
and then the microstructure was observed by scanning electron microscopy (JSM-IT100). The TEM sample was
ground to a foil with a thickness of fewer than 60 μm, perforated to a disc shape with a diameter of 3 mm. Then
electrolytic double spray was performed until perforation occurred, and finally, ion thinning was performed.
The prepared samples were observed by TEM, high-resolution TEM (HRTEM) and the corresponding energy
spectrum (EDS) analysis on the JEM 2100 TEM equipped with GATAN 832 CCD and Oxford INCA
spectrometer. The acceleration voltage was 200 KV [18].

| Sample | Matrix | Plating     |
|--------|--------|-------------|
| A1     | Cu     | Ag          |
| A2     | Cu     | Hard-Ag     |
| A3     | Cu     | Graphene-Ag |
| B1     | Cu–Cr  | Ag          |
| B2     | Cu–Cr  | Hard-Ag     |
| B3     | Cu–Cr  | Graphene-Ag |
The hardness test on all samples was carried out by HV-1000A digital microhardness tester (100 gf load, the residence time of 10 s). The maximum and minimum were removed, and the average of the remaining 5 points was taken as the final hardness [20–22].

The friction coefficient and the wear volume loss of samples were measured by UMT-2 multifunctional friction and wear tester. The applied load was 10 N, the friction pair was made of GCr15 steel ball (ø6.3 mm) with a hardness of 700 HV0.1, the grinding path was 5 mm, and the speed was 5 mm s−1. The test time for each sample was 120 min, and each sample was tested 3 times. The sample was ultrasonically cleaned with acetone before testing. Then the wear volume loss (ΔV) of the sample before and after abrasion was measured with a three-dimensional profilometer by equation (1). The equation (1) is as follows:

\[
\Delta V = L \times \left( \frac{\pi R^2}{180} \sin^{-1}\left(\frac{W}{2R}\right) - \frac{W}{2} \sqrt{R^2 - \left(\frac{W}{2}\right)^2}\right)
\]

Where L is the perimeter of the wear mark (mm), R is the radius of the grinding ball (mm), W is the width of the wear mark (mm).

The average value of the ΔV of 3 specimens of each kind of sample was taken as the final ΔV to ensure the accuracy. SEM and three-dimensional profilometer were used to observe the wear surface morphology of the sample to understand the wear mechanism. The wear debris was analyzed by EDS [20–22].

3. Results and discussion

3.1. Microstructure evolution and strengthening mechanism

The metallographic structure and SEM of the copper and Cu–Cr alloy matrix materials are shown in figures 1 and 2, respectively. It can be seen that the matrix structure is dominated by uniformly distributed slender grains, containing only a few small equiaxed grains and irregular grains. The internal segregation of the grains is small, and the surface of the grains has few protuberances, but the segregation between grains is serious. Combined with EDS analysis, it can be found that there are a large number of bright white copper compound precipitated particles in the Cu–Cr alloy microstructure in figure 2. In addition, it can be seen from figure 1 that the crystal grains are elongated along the deformation direction and extend in multiple directions, changing from multiple deformations to flat or elongated shapes. It can be concluded that the structural deformation is not uniform.

Figure 3 shows the TEM and HRTEM of the microstructure around the interface between the Cu–Cr alloy and Ag plating. It can be seen from figure 3(a) that the Ag plating is tightly bonded with the Cu–Cr alloy matrix, the interface is well bonded. There are a large number of parallel-distributed deformed nano twins and a small number of dislocations in the Ag plating microstructure. It is known that nano twins are beneficial to improving strength, toughness, and conductivity, and dislocations can play a role of dislocation strengthening. Therefore, nano twins and a small number of dislocations can strengthen the matrix and the plating. Moreover, they are beneficial to obtaining contact materials with high strength, high toughness and high conductivity. The good combination of the Ag plating and the matrix at the interface can significantly improve the strength, stress relaxation resistance, softening resistance and bending formability of the matrix [23, 24]. From the HRTEM of the Ag plating in figures 3(b) and (c), it can find that the Ag plating microstructure contains a small number of precipitated phases and slip systems. This is mainly because the precipitates in the microstructure play a pinning
role in the rolling deformation process, which hinders the slip of dislocations, causing the dislocations piling up around the precipitates. Besides, the fine precipitates and dislocations in Ag plating can play a role in solid solution strengthening, dispersion strengthening and dislocation strengthening, and improve the strength and wear resistance of the alloy [17, 25].

The surface scanning results and EDS analysis of figure 3(d) are shown in figures 4 and 5, respectively. From figure 4, we can find that the distribution of elements in both the plating and the matrix is relatively uniform. The Ag element mainly exists in the plating and diffuses into the matrix in a small amount, which indicates the degree of bonding tightness of the plating and the matrix to a certain extent. The diffusion phenomenon of Cu element is inapparent and it mainly distributes in the matrix, which shows that its diffusion ability is weaker. Combining with figures 4 and 5, it can find that there is a few of strengthening elements Cr and Si near the interface, which provides favourable support for the sample to obtain high strength.

Figure 6 shows the TEM and HRTEM of the microstructure around the interface between the Cu–Cr alloy matrix and the hard-Ag plating. Figures 7 and 8(a) are the surface scanning results of figures 6(e), and 8(b)–(d) are the spot scanning results of figures 6(b)–(d), respectively. From figure 6(a), it can be found that the bonding interface between the substrate and the plating is clear, and the microstructure similarity of the plating and the substrate is higher. Both the matrix and the plating contain a large number of dislocations, which can be strengthened by dislocations, and the dislocations at the bonding interface help to reduce the mismatch strain.
Figure 4. Surface scanning results of the area around the interface between the matrix and the Ag plating.

Figure 5. EDS of the surface scanning area.
Combining with figures 6(a), (e) and 8(a), it can be found that the main elements around the bonding interface are Ag and Cu. The bonding interface contains more Si and S elements. The white clusters at the bonding interface are AgS. Si plays a key role in the refinement and uniform distribution of the precipitated phase, which can strengthen the interface and the plating, and increase the hardness and oxidation resistance temperature of the sample [5]. Figure 6(b) shows that there are many parallel dislocations, nano precipitated particles and deformation twins in the matrix, which play a significant role in strengthening the matrix. Quantity of twins and dislocations are found in figure 6(c). The dispersed particles of the precipitated phase pin the dislocations, and a small number of dislocations entangle with each other, which play a strengthening role. Combined the diffraction spots in figure 6(c) and the EDS analysis in figure 8(c), it can be found that the two black irregular particles in figure 6(c) are Ag-rich nanoparticles (Ag-containing compounds), showing a bcc crystal structure. These soft particles are randomly distributed in the plating structure. They have good deformability, which can coordinate the deformation of the structure, making the dislocations accumulate and entangle together. And they may lead to the formation of potential deformation bands and twins, which can effectively strengthen the plating. In addition, the plastic deformation of metal is controlled by both slip and twins. When dislocations are fixed by precipitated phases and grain boundaries, dislocation entanglement and dislocation density increase, leading to slip barriers, and twins will play an important role. The formation of twins changes the orientation of the crystals. It transfers the unfavourable slip system of some atoms to positions favourable to slip, which stimulates the further slip and crystal deformation [26]. Combining figures 6(c) and (d), it can be found that the twin thicknesses are all small, which is conducive to increasing the dislocation storage capacity [5]. Moreover,
the existence of nano twin is beneficial to obtain high strength, high toughness and high conductivity. Combined figures 6(d) and 8(d), it can be found that the twin in the hard-Ag plating has a solid solution of Si element, which can strengthen the twin. The diffraction pattern in the figure corresponds to point 4 of the twin. From the HRTEM of the plating (figure 6(f)) and the substrate (figure 6(g)), it can find that dislocation walls and dislocation clusters are widespread [27].

Figure 9 shows the TEM and HRTEM of the microstructure around the interface between the Cu–Cr alloy matrix and the graphene-Ag plating. Figures 10 and 11(a) are the surface scanning results of figures 9(a), and 11(b)–(e) are the spot scanning results of figures 9(b) and (c), respectively. It can be seen from figures 9(a) and (c) that the substrate and the plating are well bonded. Combining the EDS results of figures 11(b), (c), and (e), it can be found that the bright white areas in figures 9(a) and (c) are the plating areas and show a clear lamellar structure. Figure 9(d) is the HRTEM of the plating at point d in figure 9(a). It can be seen from figure 9(c) that there are obvious precipitated phase particles in the plating and the matrix, and the matrix contains a lot of delicate precipitated phases and dislocations, and the dislocations entangle with each other. They effectively improve the strength of the plating and the matrix through precipitation strengthening and dislocation strengthening. Moreover, these precipitated phases effectively hinder the dislocation slippage, and the precipitated phases located at the grain boundary and sub-grain boundary can effectively limit the movement of the grain boundary and pin sub-grain boundary, making the Cu–Cr alloy difficult to recrystallize during the hot processing and improving its thermal stability, so that the alloy has higher strength at high temperatures [28].

Figure 7. Surface scanning results of the area around the interface between the matrix and the hard-Ag plating.
addition, these delicate precipitated phases can play the role of precipitation strengthening and Orowan strengthening, which significantly contributes to the improvement of the yield strength of the alloy [18, 24]. Combining figures 9(b) and 11(d), it can find that the white precipitates in the matrix are Cr particles, and the surrounding structure plays an excellent supporting role on them. Its formation is due to the poor mutual solubility of Cr and Cu during the solidification of the alloy [2, 6]. The interaction between the nano Cr precipitates formed in the Cu–Cr alloy and the surrounding dislocations can effectively prevent the movement of grain boundaries and dislocations, which not only improves the strength of the alloy, but also helps to
enhance the conductivity of the alloy [5, 6, 18, 25, 27, 29, 30]. Moreover, it is found that bcc Cr exhibits an N-W orientation relationship (OR) in the Cu matrix, it can avoid oxidation and reduce crack nucleation, which is beneficial to improving the mechanical properties of the alloy. However, when the Cr is oxidized to form a chromium compound, it will become hard and brittle, reducing the comprehensive properties of Cu–Cr alloy [6].

Through the above analysis, it can find that the strengthening effect of Cu–Cr alloy is mostly provided by nano twins, dislocations and nano-scale Cr second phase, and it promotes the improvement of its conductivity. The strengthening mechanism is mainly nano twin strengthening, solid solution strengthening, precipitation strengthening and Orowan strengthening [19, 31].

3.2. Mechanical properties and conductivity
The microhardness of the copper and Cu–Cr alloy substrates used in this experiment are 75.4 HV_{0.1} and 158.5 HV_{0.1}, respectively. The improvement of Cu–Cr alloy performance is mainly attributed to the addition of trace Cr and Zr elements. Trace Cr and Zr can improve the uniformity of the alloy single-phase structure, form the precipitated phase and refine the grain size of copper, enhance the strength and hardness of the alloy. And the precipitated dispersed phase can weaken the hindrance of the solute element to the movement of electrons to a certain extent, reduce the scattering of free electrons and improve the conductivity of the alloy. Which is conducive to obtaining an excellent combination of high strength and high conductivity, and is extremely

![Figure 10. Surface scanning results of the area around the interface between the matrix and the graphene-Ag plating.](image-url)
important for improving the performance of the contact switch [6, 27, 28, 32]. Moreover, when a small amount of Cr and Zr are incorporated into copper, it will cause the lattice distortion of copper, increase the yield stress, and produce solid solution strengthening, precipitation strengthening, and dislocation strengthening [6, 18, 19, 33]. Besides, the addition of a small amount of Cr can improve the corrosion resistance and oxidation resistance of the matrix. The addition of trace Zr reduces the stacking fault energy and promotes the formation of deformation twins, and helps to refine the microstructure of the Cu–Cr alloy, improves the grain boundary strength, conductivity and softening resistance of the alloy at high temperature, but the corrosion resistance of the matrix tends to decrease [6, 28–30, 33, 34]. Besides, the increased dislocation density of Cu–Cr alloy during cold rolling deformation causes an increase in yield stress and helps to form precipitates, which makes the alloy obtain excellent mechanical properties and conductivity [5, 18].

The microhardness and contact resistance of each plating are shown in figures 12 and 13, respectively. It can be seen that the hardness and contact resistance of hard-Ag plating are the highest, and that of Ag plating are the lowest. Compared with the Ag plating, the hardness of the hard-Ag plating and the graphene-Ag plating is increased by 47.4% and 27%, respectively. The contact resistance of the three kinds of plating changes little. The changes in these properties are related to the plating structure. Combining with figures 3, 6 and 9, it can be found that there are more precipitated phases in the hard-Ag plating, and more fine strengthening phases with the dispersed distribution. The dislocation density is higher, and the dislocations are entangled. Hence the hardness of the plating increases. However, the high dislocation density and solid solution strengthening phase in the microstructure hinder the movement of electrons to a certain extent, which makes the conductivity of the plating worse and the contact resistance increase [6, 27, 28, 35]. It can be seen from figure 9 that the dislocation density in the graphene-Ag plating is small, so its hardness improvement is small, and the change of its contact resistance is related to the hindering effect of graphene on electron scattering and the lamellar structure of graphene. As a result, its contact resistance is less than that of hard-Ag plating [16]. In addition, the clean and tightly bonded interface between the substrate and the graphene increases the thermal conductivity of the
plating, so the graphene-Ag plating may be beneficial to improving the ability of the isolation switch to resist the damage of high voltage or high current to the matrix material [14–16].

3.3. Wear resistance
When these platings are applied to the matrix of isolating switches, they should exhibit excellent friction reduction and wear resistance [14, 15]. For this reason, the wear volume loss (ΔV) and friction coefficient changes of samples with different substrates and platings were studied, as shown in figure 14. The wear resistance of the sample is evaluated by combining the ΔV and the friction coefficient. From figure 14(a), it can find that the changing trend of ΔV of different plating samples has nothing to do with the type of the substrate. The ΔV of the Ag plating sample is the largest, and that of the hard-Ag plating sample is the smallest. When the substrate is copper, the ΔV of the sample is larger, and the plating properties have a greater influence on the ΔV of the sample. Compared with the Ag plating sample, the ΔV of the graphene-Ag plating sample is reduced by 50.8%, the ΔV of the hard-Ag plating sample is reduced by 65.5%, and the wear resistance of the hard-Ag plating sample is increased by 140%. When the substrate is Cu–Cr alloy, the ΔV of the sample is greatly reduced, and the influence of the plating properties on the ΔV of the sample is reduced. Compared with the Ag plating sample, the ΔV of the graphene-Ag plating sample is reduced by 16.3%, the ΔV of the hard-Ag plating sample is reduced by 57.5%, and the wear resistance of the hard-Ag plating sample is improved by 135%.

When the substrate is Cu–Cr alloy, the wear resistance of each plating sample is higher. The reason is that the copper substrate is relatively soft and has a poor supporting effect on the plating, making the plating material unable to effectively resist the damage caused by the wear, so the wear resistance of the sample is poor. Combining figures 14(a) and (b), it can be found that when the hard-Ag plating is plated on the Cu–Cr alloy substrate, the ΔV of the B2 sample is the smallest, the friction coefficient is the smallest and more stable, and the wear resistance is the best. It can be seen from figures 3, 6, 9 and 12 that the significant improvement of the wear resistance of the B2 sample has a great relationship with the microstructure and hardness of the substrate and the plating [6]. The size and distribution of the strengthening phase in the substrate and the dislocations density...
contribute greatly to wear resistance. The dislocation density in the hard-Ag plating is more extensive, and it contains more nano twins. The formation of parallel shear bands composed of high-density dislocations in the plating seriously hinders the slip of the dislocations, resulting in an increase in the strength of the plating [35].

The dispersed nano Cr particles in the Cu–Cr alloy matrix can be used as a support framework to effectively resist the damage to the alloy plating by the wear debris in the wear process and protect the metal matrix from being eradicated [21]. From figure 12, we can find that the hardness of the hard-Ag plating is higher, and the higher hardness of the Cu–Cr alloy matrix can provide adequate support for the plating. Therefore, the synergy effect between the enhanced metal matrix and the plating in the wear process can effectively improve the wear resistance of the B2 sample [21]. However, when the hardness of the substrate is low, the plating will not be effectively supported by the substrate in the wear process. It will easily peel off from the surface of the substrate, so the ΔV of the A1 sample is massive and the wear resistance is poor. In addition, when the plating is a graphene-Ag plating, the performance of the matrix has little effect on the wear resistance of the sample. Combining figures 12 and 14, it can be seen that the above changes in wear resistance are closely related to the hardness of the plating and the substrate. Hardness is the primary determinant of wear resistance, but high hardness is not the only decisive factor for improving the wear resistance of plating materials. The high-strength and flexible graphene in the graphene-Ag plating acts on a self-lubricating and friction reduction effect, which plays a key role in enhancing the wear resistance of the sample [1, 4].

In order to better explain the above wear phenomenon, figures 15 and 16 show the SEM and three-dimensional morphologies of the wear surfaces of samples, respectively. It can find from figure 15 that there are a large number of micro-cutting scratches, micro-grooves, wear debris and apparent delamination on the surface of the Ag plating sample, and the wear debris generated by the fracture of the plating will activate the three-body abrasive wear. Therefore, the main wear mechanisms of the alloy are abrasive wear and oxidation wear [36]. The wear of the A1 and B1 specimens surface (figures 15(a), (b)) are severe. Quantity of large-scale peeling pits and micro-grooves appear on the wear surface of the A1 sample, as well as a peeling layer formed by micro-cutting. The wear surface of the B1 sample contains a lot of wear debris, the size and the number of the microgrooves are small, and there are a few cracks at the delamination. In the wear process, the debris can be removed by the combined action of micro-cutting and micro-cracks. The wear surfaces of A2 and B2 samples are relatively clean, and there are many cracks on the wear surface of the A2 sample. The wear degree of the B2 sample is weaker, which is mainly caused by micro-cutting scratches in wear surface. There are serious micro-cutting scratches and delamination on the worn surface of the A3 sample, and the delamination is accompanied with cracks, which is easy to cause the removal of materials. The wear surface of the B3 sample is relatively clean, and the wear surface contains a lot of small-sized peeling pits. The reason for the above phenomenon is that the wear behaviour is not only related to the hardness of the alloy and plating, but also affected by the microstructure of the alloy and plating [6]. It can be seen from figure 12 that the hardness of the plating and the substrate of the A1 sample is low, and they cannot effectively resist the crushing damage of the wear debris and the cone, so that there are more micro-grooves and peeling pits on the surface, and the wear resistance is poor. The hardness of the plating and the matrix of the B2 sample is larger, and the content of nano twins, dislocations and precipitates in the structure is higher. Under their synergistic effect, the coordination of mechanical and tribological responses of the sample is improved, so its wear degree is the weakest [6]. Because the softer substrate cannot effectively support the
harder coating, a large number of cracks appear on the wear surface of the A2 sample, weakening the synergistic effect between the substrate and the plating. The contribution of deformation twins in the plating to the plastic deformation ability of the sample cannot be offset by the detrimental effect of stress concentration caused by dislocation entanglement [35].

It can be seen from figures 16 and 17 that each sample exhibits different wear profile characteristics, and has prominent ploughing characteristics of abrasive wear. The appearance of these phenomena is related to the hardness of the sample and the removal of materials [21]. The wear resistance of the material can be improved by manufacturing high strength and high hardness copper alloy, and the removal and delamination of the material on the contact surface can be inhibited [6]. The A2 and B2 samples have a higher resistance to wear due to their higher hardness. Their wear surfaces are relatively flat, the jagged peaks and valleys are shallow and regular, and
the depth of grooves and cutting scratches on the wear surface of the B2 sample is small. Because of the low hardness, the worn surface of the A1 sample is rough, and there are many discontinuous peaks and valleys on the wear surface, the depth and width of cutting scratches and grooves fluctuate greatly, which shows the removal of large pieces of material. There are many discontinuous peaks and valleys on the wear surface of the B1 sample, and the depth is smaller and the width is larger of the peaks and valleys. Therefore, the smaller the groove depth of the wear surface of the sample, and the smaller the fluctuations in the depth and width of the peaks and valleys, the harder the material on the wear surface is to be removed and the better the wear resistance of the sample.\[21\].

In addition, when the plating is worn through, the microstructure and hardness of the matrix material play a key role in its ability to resist wear. From figures 16(a), (b), (e) and (f), it can be seen that the copper exhibits plastic deformation during wear, while the Cu–Cr alloy shows signs of brittle fracture. The reason is that, on the one hand, the Cr phase in the Cu–Cr alloy helps to improve the wear resistance of the matrix, on the other hand, it can act as abrasive particles.\[7\].

Figure 18 shows the SEM morphology of the wear cross-sections of samples with different substrates and plating. The EDS analysis of the plating cross-section finds that the Ag plating is mostly composed of Ag, the hard-Ag plating is mainly composed of Ag and Sb, and the graphene-Ag plating is primarily composed of Ag and Sb.
Figure 17. Comparison of the wear profile height with different matrix materials and platings.

Figure 18. The SEM of the worn subsurface morphology of samples with different matrix materials and platings: (a), (c), (e) copper matrix; (b), (d), (f) Cu–Cr alloy matrix; (a), (b) Ag plating; (c), (d) hard-Ag plating; (e), (f) graphene-Ag plating.
C. When the substrate is Cu–Cr alloy, the surface of the plating is relatively flat and dense, the plating and the substrate are well bonded. The bonding surface of the graphene–Ag plating is relatively good, the interface between the substrate and the plating is clear, and the matrix and plating are tightly bonded at the interface without apparent defects. The thicknesses of A1, B1 and A3 plating are all relatively thin, which indicates that their wear is more serious. There are obvious cracks, holes and peeling phenomena in the wear section of the plating of A1, B1, A3 and B3 samples, which will be helpful for the further removal of the plating in the wear process. The wear cross-section of A2 and B2 samples plating contains relatively few defects, exhibiting evident cutting traces [20]. The comprehensive comparative analysis shows that A2 and B2 samples have better wear resistance.

4. Conclusion

In this paper, effects of different plating processes and matrix materials on the hardness, wear resistance and conductivity of copper-based contact materials were systematically investigated, and the strengthening mechanism of the plating and matrix materials was revealed. The following main conclusions can be drawn.

1. The interface between the substrate and the plating is well bonded. Both the Cu–Cr alloy substrate and the hard-Ag plating contain a lot of nano twins, dislocations and precipitated phases, which play an excellent role in strengthening the substrate and the plating. The main strengthening mechanisms of the hard-Ag plating and Cu–Cr alloy matrix are solid solution strengthening, dislocation strengthening, precipitation strengthening and nano twin strengthening.

2. The contact resistance of the three kinds of plating is almost the same. The Ag plating has the smallest contact resistance, and that of the hard-Ag plating is the largest.

3. The hardness of the hard-Ag plating is the highest, reaching 129.9 HV0.1. The cooperation of the Cu–Cr alloy matrix and the hard-Ag plating gives the contact material the highest wear resistance. The wear morphology of the plating is dominated by straight furrows, and the wear mechanism is mainly abrasive wear.

4. The combination of the hard-Ag plating and Cu–Cr alloy matrix achieves good cooperation of hardness, wear resistance and conductivity, and obtains excellent comprehensive properties. It has a high engineering application value and is determined as the best combination for this research.

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