Research on the preparation method, microstructure and performance of hard silver plated/Cu-Cr0.6-Zr0.02 alloy contact

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Abstract
This paper developed a new type of disconnect switch contact with high-conductivity, oxidation resistance and wear resistance. Contact material and preparation were researched. The Cu–Cr–Zr alloy was prepared by vacuum induction melting, then the plate was obtained after rolling and aging strengthening. Contact sample was formed by die stamping, at last, a wear-resistant coating/Cu–Cr–Zr alloy switch contact was manufactured, after the silver antimony alloy hard coating was electroplated on the surface. In order to further study the Cu–Cr–Zr alloy and hard silver coating of the contact, microstructure analysis and performance testing are carried out. A large number of nano-sized pure Cr phases were found to exist in the Cu–Cr–Zr alloy matrix, and the material conductivity was 76.3% IACS. Compared with T2 copper, its mechanical properties and oxidation resistance were significantly improved, which helped to delay the corrosion progress of the substrate after the coating disappeared. The hard silver coating contains 1% of the alloy element Sb. Compared with the silver coating, its wear resistance was increased by 135.30%. Cu–Cr–Zr alloy and hard silver plating technology are effective for improving strength, corrosion resistance and wear resistance of contact.

1. Introduction

The contact of the high-voltage isolating switch is one of the important conductor materials in the substation. The contact is composed of two parts: a moving contact and a static contact. Pure copper has excellent electrical conductivity, thermal conductivity and ductility, so it has become the main material for making switch contacts. However, pure copper has low strength and poor corrosion resistance, so the adverse effects on the electrical conductivity mainly include the following: due to the extremely poor conductivity of copper oxide, the contact resistance between the moving and static contacts will become very large after oxidation; and due to the low strength, pure copper is more susceptible to deformation, which will reduce the contact pressure and increase the contact resistance. Excessive contact resistance will cause an unacceptable temperature rise when a large current passes [1–3]. Compared with copper oxide, the oxide film of silver is more conductive and easier to be broken and decomposed. Therefore, in order to isolate the copper matrix and atmosphere, the contact is usually silver plated on the surface of pure copper, so as to avoid the problem of excessive temperature rise caused by contact surface oxidation [4, 5]. Due to the poor wear resistance of the silver-plated layer, the bare copper matrix will quickly oxidize after the coating disappeared, then cause the problem of heat generation of the isolation switch. The serious heating problem of the isolating switch is mainly caused by the excessive contact resistance.
between the moving and static contact parts. Factors such as friction, corrosion, and fouling will cause excessive contact resistance. The failure of the contact will cause problems such as safety accidents, large-scale power outages and high-cost maintenance, which seriously endanger the safe and stable operation of the power grid system [6–9]. Researchers have carried out certain studies on high-strength anti-oxidation contacts and wear-resistant electroplating layers. The addition of a certain amount of Cr, Ag, Sn, Zr or Al to copper in the literature has a significant effect, but it usually leads to a conductivity reduction below 75% IACS, so it cannot be applied to the contacts of high voltage lines. Literature and others have tried to coat the surface of the contact with a layer of graphene. Although the conductivity has been further improved, the improvement in oxidation resistance cannot be guaranteed due to the different detection methods, and the wear resistance has decreased. The literature and others use electroplating The hard silver method to replace the silver plating method to improve the wear resistance of copper products has certain reference value. In this paper, it has been determined through preliminary tests that the conductivity of copper alloys is sensitive to alloying elements Sn and Al. The addition of Ag has limited improvement in oxidation resistance and mechanical properties, but the conductivity and resistance of 0.6 wt.% Cr and 0.02 wt.% Zr are added. The comprehensive performance of oxidation and mechanical properties is very good; adding 1% of Sb to the silver plating layer can also significantly improve the wear resistance without significantly affecting the electrical conductivity. Therefore, in order to improve the service life of the contacts, this article adds 0.6 wt.% Cr and 0.02 wt.% Zr alloy elements to the copper matrix to improve its oxidation resistance and strength, and adds 1% alloy elements to the surface coating. Sb to improve its wear resistance. The addition of trace alloying elements Cr, Zr and Sb can retain the high conductivity of the contact. Based on the above, this paper has developed a new type of Ag–Sb hard silver plating wear-resistant layer composite Cu–Cr0.6–Zr0.02 alloy matrix with high conductivity, high strength, oxidation resistance and excellent comprehensive performance in wear resistance (below Referred to as hard silver plated/Cu–Cr–Zr alloy, in which Ag-Sb hard silver plating wear-resistant layer is referred to as hard silver plated, and Cu–Cr0.6–Zr0.02 alloy matrix is referred to as Cu–Cr–Zr alloy) contact, and research and The performance and microstructure of hard silver-plated/Cu–Cr–Zr contacts are analyzed, which provides a reference for the research on high conductivity, oxidation resistance and wear resistance of electrical contact products.

2. Experimental procedure

The purpose of this paper is to improve the thermal problem of the disconnect switch. On the basis of ensuring higher conductivity, the mechanical properties and oxidation resistance of the copper matrix need to be improved, and the wear resistance of the surface coating needs to be improved. Based on the above design, a certain type of 40.5 kV, 1250A high-voltage isolating switch contact was used as the research object. The preparation method, microstructure and performance of a new type of high voltage isolating switch contact were studied. The Cu–Cr–Zr alloy was prepared by vacuum induction melting, then the plate was obtained after rolling and aging strengthening. Contact sample was formed by die stamping. At last, a hard silver plated/Cu–Cr–Zr, switch contact was manufactured, after the silver antimony alloy hard coating was electroplated on the surface.

In order to further study the Cu–Cr–Zr alloy and hard silver coating of the contact, microstructure analysis and performance testing were carried out. In this paper, the electroplated contacts were used for wire cutting sampling, and the test specimens were prepared. The JSM-IT100 scanning electron microscope (hereinafter referred to as SEM) and JEM 2100 transmission electron microscope (hereinafter referred to as TEM) equipped with energy dispersive spectrometer (hereinafter referred to as EDS) were used to analyze the microstructure of the Cu–Cr–Zr alloy and the hard silver coating layer. HV-1000 digital microhardness tester, contact resistance tester, universal tensile tester and salt spray tester were used to test the performance of Cu–Cr–Zr, copper material and hard silver coating. Performance test items include electrical conductivity, contact resistance, oxidation and corrosion resistance and mechanical properties. UMT-2 multifunctional friction and wear tester were used to test the wear resistance of hard silver-plated samples and silver-plated samples. The salt spray test conditions were: atomization temperature 55 °C, mass fraction 5% NaCl solution, and the corrosion resistance was characterized by the time when a certain amount of rust appears on the surface of the sample. Wear resistance test conditions were: applied load was 10 N, friction pair was GCr15 steel ball with hardness of 700 HV0.1 (diameter:φ6.3 mm), the grinding length was 5 mm, the speed was 5 mm s⁻¹, after the steel ball and the sample were repeatedly ground, calculate the wear volume (that was the wear volume of 5 mm length: optional scratches at 5 sections, take the sample plane as the reference, calculate the section area in mm², take the average and multiply by 5 mm), and the wear resistance was characterized by the inverse of the wear volume. The mechanical performance test conditions: the sample size for testing tensile strength and yield strength was 5 mm × 10 mm × 100 mm, of which the gauge length was 40 mm.
Among them, the test standards for electrical conductivity, corrosion resistance, mechanical properties and wear resistance of Cu–Cr–Zr alloys were ASTM B63-2007(R2018), ASTM B117, ASTM B598-86 and ISO8251-87).

3. Melting and cold rolling processing of Cu–Cr–Zr alloy

3.1. Composition design
Alloying can improve the conductivity, hardness and oxidation resistance of copper materials, which is the main direction of copper-based contact materials research [1, 3–5]. After adding Cr element to Cu, part of the Cr element is dissolved in the matrix, and the others are precipitated as the second phase. These two forms of Cr element can significantly improve the oxidation resistance and mechanical properties of copper alloys [10–13]. The addition of Zr element to the copper–chromium alloy can promote the precipitation and ordering process of the precipitated phase. The stable CuCrZr phase and Cu5Zr phase are formed in the copper–chromium–zirconium alloy, which has little effect on the electrical conductivity of the copper matrix, and has a positive effect on the mechanical properties, high-temperature creep resistance and fatigue resistance. Copper–chromium–zirconium alloy can improve fusion welding resistance and arc erosion resistance as an electrical contact material [14–16]. However, with the addition of Zr element, the electrical conductivity of copper alloys is significantly reduced. Moreover, Zr and Cr form the second phase of Cr3Zr, which reduces the content of Cr in the matrix, thereby reducing the oxidation resistance of the alloy. Excessive addition of Zr is detrimental to the performance of the contact.

In this paper, a small amount of Cr and very trace amount of Zr were added to Cu to obtain a copper–chromium–zirconium alloy with good electrical conductivity, hardness and wear resistance. Combining the results of previous tests, Cu–Cr–Zr alloy was used as the base material of the high-voltage isolating switch contacts, and the composition design is shown in table 1.

3.2. Preparation of Cu–Cr–Zr alloy ingot
When smelting copper–chromium–zirconium alloys, elements such as zirconium and chromium have serious burning problems. In this paper, a vacuum intermediate frequency induction melting furnace was used for smelting, and the copper–chromium–zirconium alloy ingot was obtained after being poured into a graphite mold. The raw materials include electrolytic copper, copper–chromium alloy, copper–zirconium alloy and so on. Taking into account the burning loss of the alloy, the adding ratio of the copper–chromium alloy and the copper–zirconium alloy raw materials were appropriately increased, and the mixed alloy ingredients were put into the smelting furnace. After vacuuming, alloys were heated to 1400 °C molten metal. After holding for 2 h, the components in the molten metal were melted uniformly, and then poured into the prefabricated graphite mold. Before pouring, the mold in the vacuum furnace was operated to bake and preheat above the molten metal. After the alloy had solidified, a Cu–Cr–Zr alloy ingot with uniform composition was obtained. The riser and the surface part with quality defects are cut off from the cooled ingot to obtain a qualified ingot. Figure 1 is a vacuum intermediate frequency induction melting furnace.

| Table 1. Composition design of Cu–Cr–Zr. |
|----------------------------------------|
| Elements | Cu | Cr | Zr | Others (E.g Fe, Pb or Sb) |
| Content (wt.%) | Balance | 0.6 | 0.02 | <0.05 |

3.3. Cold rolling processing of Cu–Cr–Zr
The Cu–Cr–Zr alloy ingot was placed in a heat treatment furnace, and after 960 °C × 1 h solution heat treatment and water quenching process, the scale was removed [17]. The copper alloy was placed on a cold rolling mill and rolled into a 5 mm thick plate through multiple passes. When the Cu–Cr–Zr alloy ingot was processed into a 5 mm thick plate, the deformation should be ensured to be no less than 80%.

Put the Cu–Cr–Zr alloy sheet into an argon-protected tube-type resistance furnace. After 450 °C×2 h artificial aging and air cooling, the stamping blank was obtained. Figure 2 is a gas protection tube type resistance furnace.
4. Stamping forming and electroplating processing of contacts

4.1. Stamping forming of contacts
For a large number of contact samples, products with contour features and hole structures were processed by stamping dies; for small batches of trial samples, they were processed by cutting and drilling. Moving contacts and static contacts need to be plug-in connection, so the consistency of the shape is very high. And the contact surface of the static contact is a boss structure. The above two points determine that the best bending forming method of the contact is to use a mold for pressure processing. Taking into account the small number of samples needed in this article, and the easy forming of copper alloys and the low structural rebound, this article determined the processing flow of the small batch of contacts, as shown in figure 3. After the 5mm thick Cu–Cr–Zr alloy sheet was laser cut and drilled, movable contacts were stamped and formed by a mold at one time, and static contacts were stamped and formed by a press-bending and bead-pressing compound mold at one time. figure 4 is the physical drawing of the stamping die.

4.2. Hard silver plating processing of contacts
In the application process of the high-voltage isolating switch, the problem of the conductive circuit overheating has not been solved, which seriously affects the performance of the high-voltage isolating switch. At present, silver plating is used to improve the heating problem caused by surface oxidation and corrosion. The early use effect is good. Due to the poor wear resistance of the silver-plated layer, the contact will be worn off after a period of use and the copper matrix will leak out. At this time, the contact needs to be replaced to avoid heat generation caused by the oxidation of the copper matrix.
In order to obtain an isolating switch contact coating with excellent electrical conductivity and abrasion resistance, to meet the requirements of product application conditions, hard silver plating on the surface of the Cu–Cr–Zr alloy contact was processed in this paper. The thickness of the hard silver plating layer was about 30 μm, and the main composition includes 1% alloying element Sb and other Ag. The main components of the hard silver plating solution were: 50 g l\(^{-1}\) silver nitrate, 1 g l\(^{-1}\) potassium antimony tartrate, 50 g l\(^{-1}\) potassium sodium tartrate, 80 g l\(^{-1}\) Potassium cyanide. After electroplating, a high-hardness and wear-resistant silver-antimony alloy plating layer is formed on the surface of the copper-chromium-zirconium alloy. Figure 5 shows the hard silver coating/Cu–Cr–Zr alloy contact.
5. Microstructure and performance

5.1. Microstructure of Cu–Cr–Zr alloy

The high-strength and high-conductivity Cu–Cr alloy is a typical aging precipitation-strengthened copper alloy. By adding a small amount of Zr and Fe alloy elements and aging treatment, it can obtain excellent comprehensive performance and become an ideal material for the key parts of UHV switches. Figure 6 shows the SEM picture of the Cu–Cr–Zr alloy and the EDS results at three positions. It can be seen that the mass fraction of Cr in the microstructure is 0.92%–1.62%, the mass fraction of Zr in some areas is 0.18%, and Zr is not found in more areas. Through SEM observation, the Cr and Zr elements are unevenly distributed, and no precipitated phases of Cr and Zr were observed. This paper analyzes that in some areas, Cr and Zr are precipitated in the matrix with smaller nano-scale size, so the content of Cr and Zr in the corresponding area is relatively high.

In this paper, the microstructure of the area with higher Cr content was further observed by transmission electron microscope (TEM). Figure 7 shows the TEM image and EDS analysis result of the matrix in Cu–Cr–Zr. It can be seen that Cr atoms are solid-dissolved in the Cu matrix, and the mass fraction of Cr is about 0.4%. The diffraction spot analysis of the matrix can find the second-order rotationally symmetric twin diffraction spots. Combined with the diffraction spot calibration results, the matrix exhibits the characteristics of...
of face-centered cubic Cu twin crystal lattice. The formation of twin Cu can reduce the grain boundary energy, and block the large-angle grain boundary. These can interrupt the corrosion process along the grain boundary and therefore help to improve the corrosion resistance of the material.

Figure 8 shows the Cr-rich region TEM image and the second phase analysis result of Cu–Cr–Zr. The atomic percentage of Cr in the second phase is as high as 93.96%, which can be considered as a pure Cr phase. The precipitated pure Cr second phase is pinned in the copper matrix in the form of nano-scale equiaxed grains. After diffraction spot calibration, the pure Cr phase has a bcc structure. The pure Cr phase of the bcc structure exhibits an N–W orientation relationship (OR) in the Cu matrix, which can prevent the alloy from oxidation and reduce crack nucleation. The latter helps to improve the mechanical properties of the alloy. During the cooling process after the alloy is poured, Cr has a higher melting point and crystallizes first. Because the amount of Cr added in the alloy prepared in this article is very low, the superheat of the liquid alloy can meet the requirements of uniform nucleation. Therefore, some of the Cr elements are dissolved in the copper matrix as a solute, which has a strengthening effect, and other Cr elements are precipitated in the form of fine second equiaxed grains. The second phase can play a role of dispersion strengthening. More Cr element in the form of the second phase is beneficial to the oxidation and corrosion resistance of the metal.

5.2. Performance of Cu–Cr–Zr alloy

Conductivity, contact resistance and corrosion resistance were tested on T2 copper and Cu–Cr–Zr alloy. The results are shown in Table 2. Compared with T2 copper, the corrosion resistance of Cu–Cr–Zr alloy is significantly improved, the conductivity is reduced to 76.3% IACS, and the contact resistance is basically unchanged. The reason is that Cr and Zr elements exist in the form of solid solution or second phase precipitation, which reduces the electrical conductivity of the material. At the same time, the precipitated pure Cr phase can form a Cr$_2$O$_3$ oxide layer on the surface to inhibit further oxidation of the alloy. After corrosion of the sample for 24 h through the salt spray test, the contact resistance of the copper sample doubled, while the contact resistance of the Cu–Cr–Zr alloy sample increased slightly. This comparison shows the advantage of Cu–Cr–Zr alloy in resisting the increase in contact resistance caused by corrosion factors. This is because the Cu–Cr–Zr alloy has higher oxidation resistance, inhibits the formation of oxides and slows down the change of contact resistance, which corresponds to the salt spray test results.

| Material            | Conductivity (%IACS) | Contact resistance (μΩ) | Contact resistance after 24 h of corrosion (μΩ) | Salt spray test (time for large areas of patina, Unit: hour) |
|---------------------|----------------------|-------------------------|-----------------------------------------------|-------------------------------------------------------------|
| T2 copper           | 100.6                | 13.1                    | 27.8                                          | 48                                                          |
| Cu–Cr–Zr alloy      | 76.3                 | 13.3                    | 16.4                                          | 72                                                          |

| Material            | Hardness (HV) | Yield Strength (MPa) | Tensile strength (MPa) |
|---------------------|--------------|----------------------|------------------------|
| T2 copper           | 75.36        | 291.33               | 313                    |
| Cu–Cr–Zr alloy      | 171.17       | 383.5                | 431.5                  |
Table 3 shows the mechanical properties of T2 copper and Cu–Cr–Zr, including hardness, tensile strength and yield strength. It can be seen that, compared with T2 copper, the hardness of Cu–Cr–Zr can be increased by 127.14%, the yield strength is increased by 31.64%, and the tensile strength is increased by 37.86%. Using the material composition and technology designed in this article, the added Cr and Zr alloy elements are partially solid-dissolved in the copper matrix, and the others are precipitated in the form of the second phase. The second phase is dispersed in the form of particles. The crystal lattice change caused by the solid solution and the second phase particles precipitated will hinder the dislocation and improve the mechanical properties of the alloy.

The static contact is deformed after long-term use, which will cause insufficient pressing force and increase contact resistance. When the Cu–Cr–Zr alloy is used as the contact matrix material, the increase of its strength and hardness will help delay the deformation process of the static contact. This effect can ensure the contact pressure and control the contact resistance, thereby delaying the heating problem and increasing the service life of the isolation switch. In addition, the improvement of the contact strength also helps to reduce the weight of the moving and static contacts, thereby reducing the amount of metal materials and reducing manufacturing costs. The higher hardness of the contact can enhance the supporting effect of the contact base material, thereby increasing the service life of the surface coating.

5.3. Microstructure and performance of the coating

Figure 9 shows the SEM image of the hard silver-plated sample and the EDS analysis result of the plating layer. It can be seen that the combination of the coating layer and the Cu–Cr–Zr alloy matrix is very good, and the coating layer is mainly Ag and contains about 1% of the alloy element Sb. Silver antimony alloy is a copper alloy surface electroplating layer with excellent wear resistance. The Sb element in the Ag-Sb coating prepared in this paper is evenly distributed.

Table 4 shows the test results of the contact resistance, coating microhardness and wear volume of silver-plated contacts and hard silver-plated contacts. Compared with silver-plated contacts, the contact resistance of hard silver-plated contacts is increased by 18%, the hardness of the coating layer is increased by 47.45%, and the wear resistance of hard silver-plated contacts is increased by 135.30%. Adding 1% of the alloying element Sb to the silver plating layer will reduce the conductivity of the sample to a certain extent, but it can significantly improve the hardness and wear resistance of the plating layer. It is an ideal process for obtaining wear-resistant plating contacts.

Table 5 shows the test results of the contact resistance and wear volume of Cu–Cr–Zr alloy and T2 copper. The results show that compared with T2 copper, Cu–Cr–Zr alloy can significantly reduce the contact resistance after corrosion after 24 h and 48 h NaCl salt spray test. This is because Cu–Cr–Zr alloy has excellent corrosion...
Table 5. Test results of contact resistance and wear volume of Cu–Cr–Zr alloy and T2 copper.

| Material       | Contact resistance in initial state (μΩ) | Contact resistance after corrosion for 24 h (μΩ) | Contact resistance after corrosion for 48 h (μΩ) | Wear volume (mm³) |
|----------------|-----------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------|
| Cu–Cr–Zr alloy | 13.3                                    | 16.4                                          | 18.2                                          | 0.013           |
| T2 copper      | 13.1                                    | 27.8                                          | 41.5                                          | 0.068           |

resistance, so can reduce the copper oxide content of the contact surface. Compared with T2 copper, the wear resistance of Cu–Cr–Zr alloy is increased by 423.08%. This is due to the crystal lattice change caused by the solid solution of Cr and Zr in the Cu matrix and the effect of the second phase particles on the dislocations, which makes the hardness and strength of the alloy are improved, and the wear resistance is significantly improved.

6. Conclusion

(1) After adding 1 wt.% Sb to the silver plating layer on the surface of the copper alloy contact, the hardness of the plating layer is increased by 47.45%, and the wear resistance is increased by 135.30%, but the contact resistance is only increased by 4 μΩ. On the one hand, the overall performance is better.

(2) 0.6 wt.% Cr and 0.02 wt.% Zr are added to Cu. After solution treatment and aging treatment, the alloying elements exist in the form of solid solution and nano-scale second phase particles, which play the role of solid solution strengthening and precipitation strengthening. Compared with T2 copper, the hardness of Cu–Cr–Zr alloy is increased by 127.14%, and the yield strength and tensile strength are both increased by more than 30%, which has significant mechanical properties. The wear resistance is increased by 423.08%, but the contact resistance is only increased by 0.2 μΩ. Therefore, the overall performance is better in terms of mechanical properties, wear resistance and conductivity.

(3) The time for Cu–Cr–Zr alloy to appear large-area patina in the salt spray test is 72 h, which is significantly longer than the 48 h of T2 copper, so it has better corrosion resistance, so it can significantly reduce the contact resistance after corrosion, which helps to alleviate the contact heat problem caused by the oxidation and corrosion of the copper matrix.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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