Materials Research. 2019; 22(3): e20180901
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2018-0901

Contrastive Research on Electrical Contact Performance for Contact Materials of Cu-$SnO_2$and Cu-ZnO_2 Alloys

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Received: December 14, 2018; Revised: February 17, 2019; Accepted: March 09, 2019

Herein, SnO_2- and ZnO_2-doped (1.5 wt.%) composite Cu powder was prepared by mechanical alloying (MA) respectively, and both the contact materials of oxide-doped Cu alloys were subsequently obtained by canned hot-pressing powder sintering with hot extrusion combined. Scanning electron microscopy (SEM), laser scanning confocal microscopy (LSCM) and self-designed electrical breakdown device were used for investigating the microstructure and properties including electric conductivity and hardness, especially for electrical contact performance of the Cu-SnO_2 alloy and in compared with the Cu-ZnO_2 alloy. The experimental results show that the hardness of Cu-SnO_2 and Cu-ZnO_2 contact materials are 103.5±1 HV and 192.7±1 HV, respectively, which meet the hardness standard of national standard electrical contact materials. Meanwhile, the relative conductivity *%IACS* are 7.24% and 6.20%, respectively, which are higher than the traditional Cu-based contact materials. This electrical life simulation test system was designed independently, and the results indicate that the switching times of Cu-SnO_2 contact materials are much more than that of Cu-ZnO_2. The addition of SnO_2 can effectively improve the arc extinguishing characteristics and the anti-welding performance of the contact materials is enhanced. In summary, SnO_2-doped Cu-based contact materials possess excellent comprehensive properties, which can provide reference for potential applications in contact materials.

Keywords: *Cu-based contact materials, SnO_2 and ZnO_2 doping, electrical contact performance, arc extinguishing characteristics, anti-welding performance.*

1. Introduction

Electrical contacts, also referred to as contacts or connectors, are responsible for the operation of switching on, conducting and breaking current. The performance of switching directly affects the operational reliability and the life of the switchgear[1-3]. With a rapid development of the modern industry, especially the electrical and electronic industry, switch electrical appliances are developing in the direction of high current, miniaturization, high voltage and long life, and the arc extinguishing performance and anti-erosion performance of the contact materials and contact systems are proposed higher requirements[4-6]. The ideal contact materials should have excellent electrical conductivity, thermal conductivity, anti-fusion welding, resistance to material transfer, arc erosion resistance and low and stable contact resistance[7].

Recently, with the widespread use of low voltage electrical contact elements, the amount of electrical contact materials has increased dramatically. General industrial application electrical contact materials are made of Ag-based composite materials with Ag content of 80-90%[8-10]. The Ag of the contact materials is difficult to recycle, and the production of which is relatively limited. Therefore, most of scientists in the world have been working on Ag-free contacts to achieve the purpose of saving Ag. From the use of pure precious metals to Ag-containing alloys and Ag-based composites, researchers have gradually evolved to replace expensive Ag with Cu. W-Cu alloys have been used in the field of electrical contacts due to their high electrical and thermal conductivity, high arc corrosion resistance and fusion resistance[11-14].

However, in compared with the Ag-based contacts, the existing Cu-based contacts have shortcomings such as short service life, insufficient connection performance, and poor arc-extinguishing performance. Generally, second phase is added to improve the arc extinguishing performance of the contact or improve the viscosity of the molten pool to reduce the melt splashing. In recent years, many researchers have modified the microstructure and electrical contact properties of Cu alloys by adding different elements (W, Ni, Ag, Ce, Y, Cr)[1,5,12,15,16] or oxides (CdO, SnO_2, CeO_2)[9,11,17]. Among these, the action of some oxides is more significant and effective to electrical contact properties than that of elements. Such as CdO, it can improve the anti-welding performance of contact materials. It plays the role of arc extinguishing, reduces the viscosity of contact surface melting pool, and is beneficial to counter spatter[17]. However, Cd is a toxic element, and the concept of "cadmium free" has been clearly proposed in some newly designed electric contact materials. By consulting a large amount of literature, we attempt Cu as the matrix metal to add SiC, SnO_2 or ZnO_2 powders, and used hot-pressing powder sintering and hot extrusion processes[18,19] to prepare

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two types of products. The Cu-SnO_2 and Cu-ZnO_2 contact materials were designed to follow the principle of non-toxic and environmental protection. This paper mainly compares the physical properties and mechanical properties of the both novel contact materials, further to explore the electrical contact performance, and expect to achieve the requirements of electrical contacts in low-voltage electrical appliances.

2. Experiments

2.1 Material preparation

Electrolytic Cu powder with a purity of 99.95% and an average particle size of 45µm was used as the matrix metals. SiC particles with an average particle size of 5µm were selected as the reinforcing phase to improve the strength of the novel contact materials. With a purity of 99.99% and an average particle size of 0.1µm, SnO_2 and ZnO_2 are selected to be the metal oxide components in the contact materials. The mass ratio (wt.%) of the components is as follows: SiC is 1.5%, SnO_2 or ZnO_2 is 1.5%, and the balance is Cu. Therefore, the above two type contact alloys are denoted by Cu-SnO_2 and Cu-ZnO_2, respectively.

Currently, the preparation of the contact materials is mainly accomplished by hot-pressing powder sintering process. Powder sintering is an advanced technology for energy-saving, material-saving, high-efficiency, near-end molding and less pollution, which is an important method for preparing metal and metal oxide materials. This method mixes powder and suppresses sintering and the material is then extruded for further use in making contacts. The oxide-doped samples in this research were prepared by powder sintering, which process is shown in Figure 1.

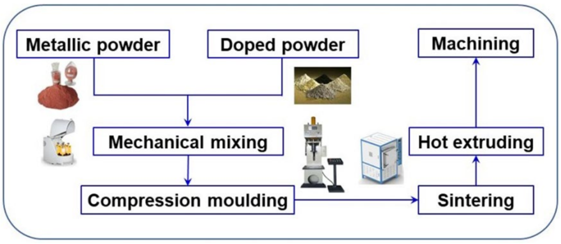

Figure 1. Flow chart of hot-pressing powder sintering process of Cu-based alloys[20,21]

2.2 Physical performance test

In this work, the electrical resistance is measured by digital micrometer (type: HZ2522). The measuring accuracy of the instrument is 0.1 µΩ, which can meet the resistance measurement requirements of Cu-based electrical contact materials with small resistance. The samples are processed into cylinder of Φ3×45 mm, the electrical resistance of the material is measured at room temperature (RT), and then the electrical resistivity ρ and relative conductivity $\%IACS$ of the materials are calculated according to formula (1) and formula (2), respectively[22].

$$\rho = R \times \frac{S}{L} \tag{1}$$

where R-the measured resistance (Ω); S-cross-sectional area (mm^2); L-sample length (mm).

$$\%IACS = \frac{1.724}{\rho} \times 100\% \tag{2}$$

As an important index of contact materials, hardness affects their electrical life. A lower hardness will lead to low resistance to surface deformation of the contact, which is not conducive to maintaining the contact surface state, and is prone to fusion welding, while a higher hardness is against the stability of contacting between dynamic and static contacts. The impact force is large, during its contact process, which is easy to cause the material loss of the contact surface. And hardness of the material was measured by microhardness tester (type: HV-1000). The load is 100 g (~0.98 N) and the loading time is 15 s. Before measuring, the upper and lower sides of the samples were polished to ensure that the two sides were parallel. Each sample was measured by 10 times of the hardness, and then calculated the average values.

2.3 Electrical contact test and surface analysis

The electrical life simulation test system of contact materials (GB/T 14598.5-93)[23] was used to investigate the arc extinguishing performance and anti-welding performance of the contact materials, observe the status of surface burnout, and analyze the effect of different material composition on arc erosion through the electrical life test. The circuit diagram of the analog test system is shown in Figure 2.

One of the static contacts in the analogue relay was replaced by the prepared sample for testing, and the distance between the static and dynamic contacts is 2 mm. What's more, the test voltage is 220 V, the current is 2 A, the time interval is 0.5 s, and the test conditions are atmospheric environment at room temperature.

The microscopic morphology of the samples after arc-burning was observed by optical microscopy (OM, type: Axiouert 40), scanning electron microscopy (SEM, type: FEI Quanta 650 FEG) and laser scanning confocal microscopy (LSCM, type: Zeiss LSM-700).

X-ray photoelectron spectroscopy (XPS) was used to analyze the component of the material surface after arc erosion. The instrument model was PHI5700 X-ray photoelectron spectroscopy analyzer. The target power is 250 W and voltage is 12.5 kV.

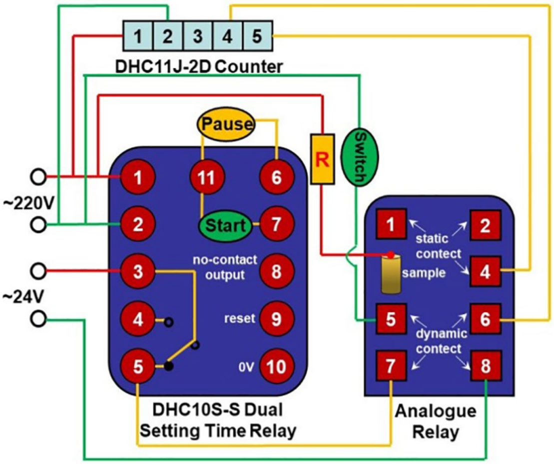

Figure 2. Circuit diagram of the electrical life simulation test system of the contact materials.

3. Results and Discussion

3.1 Physical properties and microstructure analysis

The resistivity ρ, relative conductivity %*IACS* and hardness of Cu-SnO_2 and Cu-ZnO_2 contact materials are listed in Table 1. Comparative analysis shows that the relative conductivity of Cu-SnO_2 and Cu-ZnO_2 contact materials are 7.24% and 6.20%, respectively, which means that the conductivity of Cu-SnO_2 is relatively better. The hardness of these two contact materials are 103.5±1 HV and 192.7±1 HV, respectively, which are in line with national standards and can be practically applied.

Figure 3 shows the OM metallographic morphology of Cu-SnO_2 and Cu-ZnO_2 as prepared. We can know that the grain distribution of the two contact materials is uniform. It can be seen from the metallographic structure before the electrical contact test that the grain size of the Cu-ZnO_2 contact materials is uniform and fine, while the grain size of the Cu-SnO_2 contact materials is coarse and as a reaction of hardness, which of Cu-ZnO_2 contact materials is higher, as listed in Table 1.

3.2 Electrical Contact Properties

Figure 4 shows the SEM surface morphology of the Cu-based contact materials after arc erosion. It can be found that the material erosion is serious at the center of the arc action, and the morphology is the trace left on the surface after repeated arc discharge, which is the superposition effect of arc action. There are a lot of micro-protrusions and pores, as shown in Figure 4 b). And there also exist a large number of splatters and some micro-cracks in the burnt zone, as shown in Figure 4 d).

The splatters were formed as the substance in a fused spot rapidly flows and splashes under the action of arc. When the arc is burning, the root of the arc has a large diameter with its energy rising sharply. Then the contact material melts, and the melting spots formed on the surface of the material. The molten metal in the spot splashes under the action of the arc formed splashes, and some of the spatters are sprayed out of the contact gap area, causing material loss. After the arc had been extinguished, the molten layer on the surface of the metal material was rapidly cooled to form a fast-cooling structure for its good thermal conductivity, which includes two forms. One is the small droplets, which are mainly the rapid cold form of the splash, and the other is the quenching structure, as shown in Figure 4 d), which is the mainly tissue formed by spreading the surface of the material outward.

By observing the surface morphology of the electrical contact materials after arc erosion, it can be also found that a large number of pores are formed on the surface of the material. These pores are mainly of two types: the first type is the pores generated on the surface of the contact materials under the action of the arc, which are formed during the solidification process and are the main form of the material pores. In the process of separating the contacts, the molten metallic Cu will absorb a large amount of gas. After the arc is extinguished, the matrix Cu will rapidly cool, the solubility of the absorbed gas will drop sharply, and the gas will be quickly discharged. Besides, there may be some volatile phases in the matrix and thus forming pores on the rapidly cooled surface. The second type of pores is generated by the combination of arc and cyclic stress, at the time when the second phase particles are peeled off, and the number of these pores is relatively small. In addition, there may be a small amount of pores left in the material due to the fact that it has not reached full density during the preparation process.

Figure 5 exhibits an illustration of the LSCM surface morphology and three-dimensional (3D) morphology of Cu-SnO_2 and Cu-ZnO_2 contact materials after arc erosion. The surface morphology of the electrical contact can mainly reflect the electric erosion phenomenon and melting phenomenon after surface arc-burning, and the degree of melting is more intuitive. The 3D morphology of the electrical contact materials after burning can more clearly reflect the degree of arc erosion. According to the extent of burnout, the erosion can be divided into three areas: the arc-ablation area, the arc-affected area and the arc-inactive area. The arc-ablation area is obvious, while the arc-affected area is not. As shown in Figure 5 a) and 5 c), the arc-inactive area has a bright metallic luster while the arc-ablation area is dark. The area of electrical erosion and the area of melting are part of the arc-ablation. And the area of electric erosion increases with the increase of switching times. The melting

Table 1. Physical properties parameters of both type Cu-based contact materials.

Alloy type	ρ	***%IACS***	Hardness
Cu-SnO_2	23.8 Ω•m	7.24%	103.5±1 HV
Cu-ZnO_2	27.8 Ω•m	6.20%	192.7±1 HV

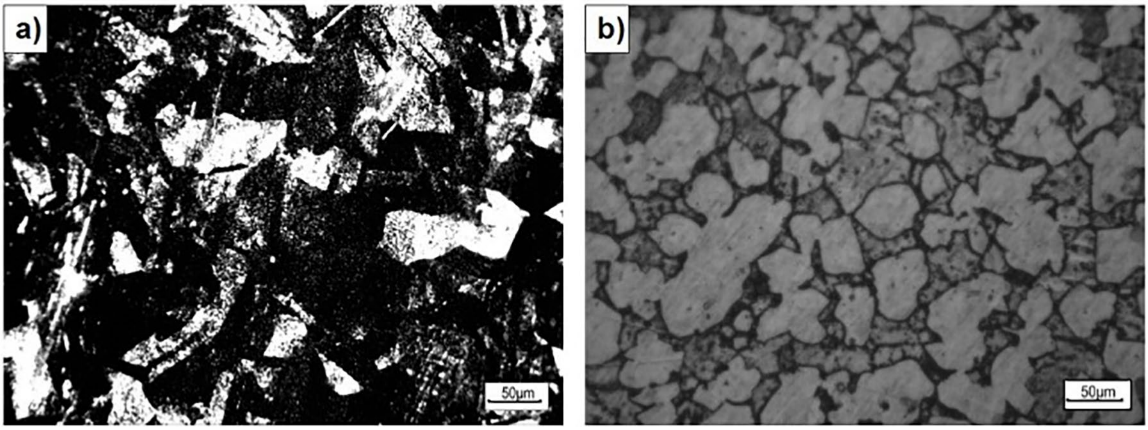

Figure 3. OM metallographic structure of a) Cu-SnO_2 alloy and b) Cu-ZnO_2 alloy.

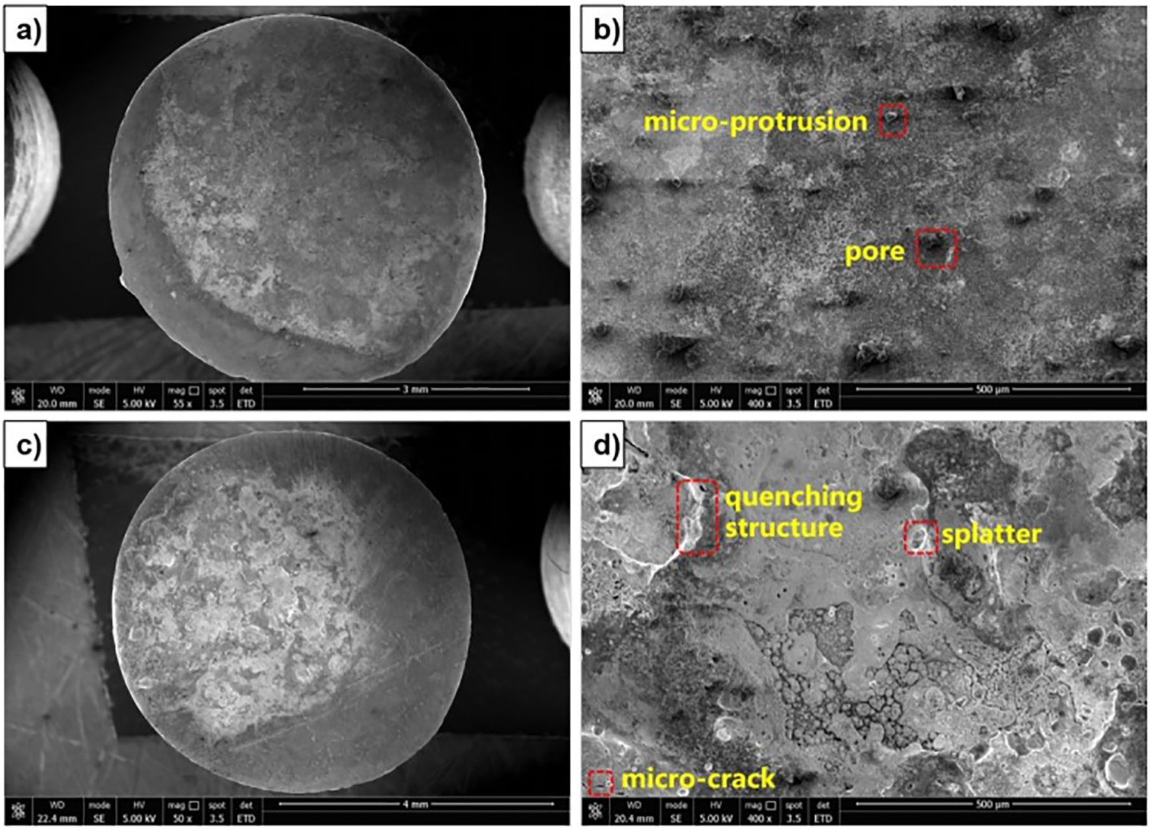

Figure 4. SEM macroscopic surface morphology a) and microscopic morphology b) of Cu-SnO_2 after 10,000 times switching; SEM macroscopic surface morphology c) and microscopic morphology d) of Cu-ZnO_2 after 3,000 times switching.

areas indicated by Figure 5 c) shows obvious melting phenomenon and the electric erosion and electrofusion of the contact materials are expanded from the contact center to the edge. The 3D morphology analysis of the surface after arc erosion shows that the Cu-SnO_2 contact materials forms a height difference of 1.0 mm between the most severely burnt area and unburned area after 10,000-time switching (as shown in Figure 5 b)). After the 3,000 times switching of the Cu-ZnO_2 contact materials, the most severely burned area and the unburned area formed a height difference of 1.3 mm, as shown in Figure 5 d). It can be concluded that the anti-welding performance of Cu-SnO_2 contact materials is relatively better than that of Cu-ZnO_2 contact materials.

From the above analysis of the surface morphology, it can be found that the substances on the surface of the materials have a flow along the surface. There are scattered micro-protrusions and multi-holes on the surface, and some metallic droplets form splashes, indicating that under the

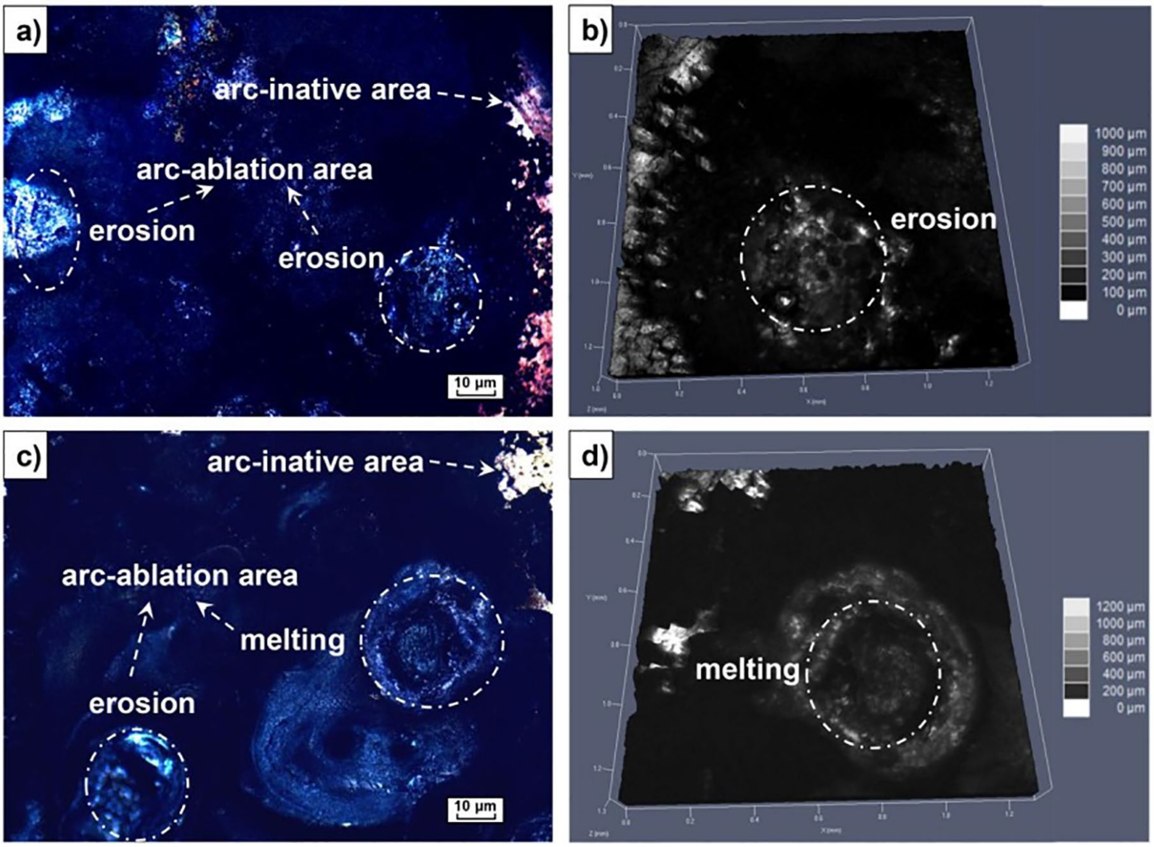

Figure 5. LCSM surface morphology a) and LCSM 3D morphology b) of Cu-SnO_2 contact materials after arc erosion; LCSM surface morphology c) and LCSM 3D morphology d) of Cu-ZnO_2 contact materials.

combined action of the heat and force of the arc, the substance on the surface of the contact materials is transferred, which includes both matrix and the second phase additive therein.

After the contact materials are burnt by the arc, the surface is covered with a layer which is different from the matrix structure. It is believed that this film layer is mainly composed of cooled metallic droplets, oxidation products of the contact materials components, and fine particles in the atmosphere. In order to further understand the composition of the film structure, an analysis was carried out by using X-ray photoelectron spectroscopy analyzer. Considering that SiC does not change greatly under the action of the arc in this test, only the added phases of SnO_2 and ZnO_2 are considered. The second phase of the electrical contact materials has two main functions: on the one hand, the second phase consumes energy in its own decomposition form to quickly extinguish the arc to reduce the arc energy of the contact materials, thereby reducing the evaporation of the matrix material[24]. For instance, the addition of CdO can effectively accelerate the extinguishing of the electrical arc; on the other hand, the second phase increases the viscosity of the molten metal and reduces the amount of sputtering. For example, properly adding SnO_2 to increase the viscosity of molten Ag-based material.

Figure 6 shows the surface XPS spectrum of the Cu-SnO_2 and Cu-ZnO_2 contact materials after electrical contact test. From the narrow spectrum analysis, the binding energy of Sn is about 497.2 eV, which indicates that Sn is mostly in the form of SnO_2. There is no elemental Sn or other valence Sn in the material. The binding energy of Zn is around 1021.8eV, also indicating that Zn is mostly in the form of ZnO_2.

In summarizing, it is obviously shown that the role of SnO_2 in the Cu-based contact materials is similar to that in the Ag-based contact materials, which mainly increases the viscosity of the base material, thereby reducing the splash of the matrix material and improving the resistance to arc burning by enhancing the anti-welding properties of the contact materials. Although ZnO_2 doping can also increase the viscosity of the Cu matrix, the effect is not that well. Two types of novel contact materials possess an excellent electrical conductivity, but the Cu-SnO_2 alloy is better to be applied in practice. On the other hand, although Ag-plated or Ag-based contact materials have advantages in electrical properties compared with Cu-based contact materials[17], Ag-plated contact materials inevitably cause pollution in

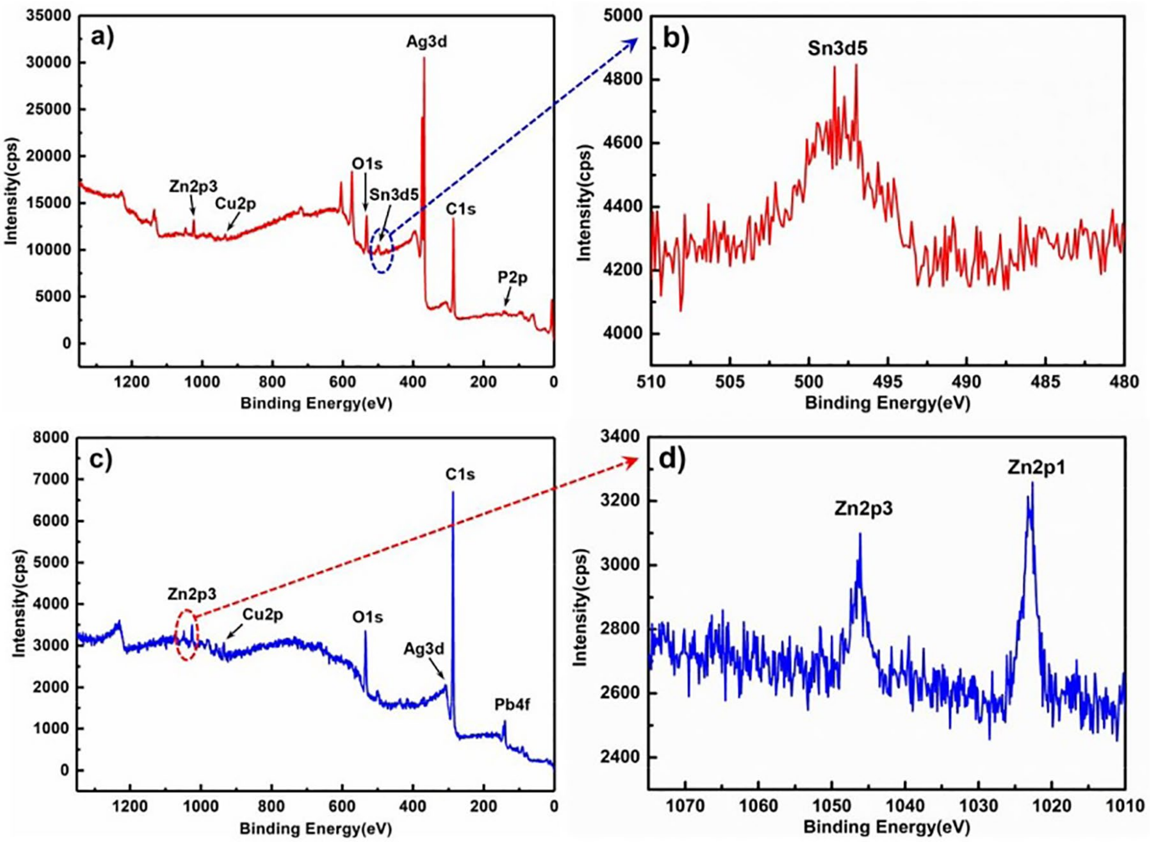

Figure 6. Surface XPS wide scan full spectrum a) and narrow spectrum b) of Cu-SnO_2 alloy after 10,000 times switching, and surface XPS wide scan full spectrum c) and narrow spectrum d) of Cu-ZnO_2 alloy after 3,000 times switching.

its manufacturing process and the cost of Ag-based contact materials is higher. These novel SnO_2 and ZnO_2 doped contact materials meet the basic needs of use, while taking environmental protection and cost into consideration.

4. Conclusion

In summarizing, from the above results and analysis, we can draw the following conclusions:

1. Cu-based contact materials were successfully prepared by hot-pressing powder sintering and hot extrusion processes. The hardness of Cu-SnO_2 contact materials is 103.5 HV and the hardness of Cu-ZnO_2 contact materials is 192.7 HV. The relative conductivities %*IACS* of Cu-SnO_2 and Cu-ZnO_2 are 7.24% and 6.20%, indicating that the conductivity of Cu-SnO_2 is relatively better.
2. Cu-SnO_2 contact materials only show arc erosion after 10,000-time switching while Cu-ZnO_2 contact materials exhibit arc erosion and electrofusion after 3,000 times of switching, which means that the anti-welding performance of Cu-SnO_2 contacts is better than that of Cu-ZnO_2 contact materials.
3. The SnO_2 and ZnO_2 doped in Cu-based contact materials are not decomposed judged by XPS analysis. The improvement of the anti-weld properties of the Cu-ZnO_2 contact materials is due to the improvement of the viscosity of the contact materials, thereby improving the arc extinguishing characteristics of the contact materials. And the Cu-SnO_2 alloy is more suitable in preparing contact materials.

5. Acknowledgement

This work was financially supported by National Natural Science Foundation of China (NSFC) under grant nos. 51561026 and 51871124, Ministry of Education Fok Ying-tung Foundation for Young Teachers (no. 161043), Program for Young Talents of Science and Technology in Universities of Inner Mongolia Autonomous Region (no. NJYT-17-B07), and the Scientific Research Foundation of Inner Mongolia University of Technology (no. ZD201405).

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