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ARTICLE

Influence of SnO_2 Content on $AgCuOSnO_2$ Electrical Contact Performance

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Abstract: $AgCuOSnO_2$ electrical contact materials with different SnO_2 contents were prepared by reaction synthesis. FQR-7501 eddy current conductivity meter was used to measure the conductivity of the polished $AgCuOSnO_2$. The erosion morphology of the surface of the $AgCuOSnO_2$ electrical contact was observed by scanning electron microscope (SEM). The JF04C DC digital resistance tester was used to carry out 10 000 dot tests. The results show that the contact resistance of $AgCuO(10)SnO_2(5)$ and $AgCuO(10)SnO_2(8)$ electric contact materials is lower than 1.3 mΩ at U = 12 V and I = 15 A, and the fluctuation is the smallest; when I = 10 A, the welding force of $AgCuO(10)SnO_2$ (x) (x = 2, 5, 8, %, mass fraction) is less than 8 cN, and the welding force of $AgCuO(10)SnO_2(5)$ electric contact is small and stable when the current increases; when the arc erosion of $AgCuOSnO_2$ electric contact materials occurs, the material transfer way is from anode to cathode. With the increasing of SnO_2 content, the loss in the process of material transfer is restrained and reduced. There are a few pores and microcracks on the surface of the transferred electrical contact, and the surface morphology is relatively flat.

Key words: $AgCuOSnO_2$ electrical contact materials; electrical contact performance; arc erosion morphology

The electrical contact materials have been developed for more than one hundred years, and have experienced three different stages of pure metal, alloy and materials[1]. In the field of low-voltage and low-current, Ag-based composite materials are the mainstream used currently, among which AgCdO has been widely used due to its low contact resistance, anti-welding, arc erosion resistance, excellent processing performance and solderability[2]. The European Union has issued a series of bans on heavy metal elements with the "Waste Electrical and Electronic Equipment" Directive (WEEE) and the Directive on the Prohibition of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS)[3]. Since then, $AgSnO_2$ has been extensively studied as the most potential alternative material. It is found that $AgSnO_2$ has a different arc erosion resistance mechanism from AgCdO and its mass transfer performance is low[4]. Japanese workers M. J. Stumbock, A. SHIBATA, obtained In_2O_3 doped $AgSnO_2$ electrical contact materials by means of alloys, but due to different concentration gradients, an "oxide-depleted zone" were formed[5-7]. Li et al[8] compared the effect of SnO_2 particles and TiB_2 particles on the material transfer of Ag based contact materials. The results show that when TiB_2 content is 4 wt%, the material transfer amount is the smallest. The wettability of $AgSnO_2$ electrical contact materials due to metallic silver and SnO_2 poor, SnO_2 hardness and other characteristics, $AgSnO_2$ electrical contact materials have the characteristics of poor ductility and plasticity, high resistivity, difficult to process[9-11]. Zhou[12,13] found that AgCuO electrical contact materials have better ductility and plastic resistivity than

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$AgSnO_2$ electrical contact materials, but their arc erosion resistance is poor. Therefore, SnO_2 was added as a reinforcing phase to AgCuO electrical contact materials in order to obtain the performance superior to that of AgCuO and $AgSnO_2$.

1 Experiment

Experimental raw materials included: AgCu alloy powder, AgSn alloy powder, silver oxide alloy powder and Ag powder (particle size 40~50 μm; purity ≥ 99.99%). The amount needed to prepare different components of AgCuO(10)SnO_2(x), (x = 2, 5, 8) green ingot is shown in Table 1.

$AgCuOSnO_2$ electrical contact materials were prepared by reaction synthesis method. The AgSn powder, silver oxide alloy powder AgCu powder and Ag powder were put into QM-1SP2 planetary mill for ball milling. The ball material ratio was 10:1, the rotating speed was 1000 r/min, and the time was 5 h.

The mixed $AgCuoOSnO_2$ alloy powder was put into a ϕ=27 mm cold press grinding tool; the forming pressure of the hydraulic press was 20 MPa, and the holding time was 2 min. The slow heating method was carried out in a box resistance furnace for a long time, and the sintering process was as follows: room temperature 100 °C (holding for 1 h) → 200 °C (holding for 1 h) → 400 °C (holding for 2 h) → 600 °C (holding for 2 h) → 750 °C (1 h) → 800 °C (holding for 36 h). In order to improve the densification degree of the green ingot, the process of repressing and refiring was selected. The ingot was heated to 810 °C, kept warm for 1 h, the mold was heated to 350 °C, the repressing pressure was 50 MPa and the holding time was 5 h.

A 315 kN oil press was used to extrude the sample to obtain the bar with a diameter of 6 mm. After several passes of drawing, the wire material $AgCuOSnO_2$ with diameters of 5.2, 3.8, 3.4, 2.5 and 2.0 mm was obtained. Finally, the rivet contact was formed by YFC-16 composite contact rivet mechanism.

X-ray diffraction analyzer was used to analyze the phase of the sample. Scanning electron microscope (SEM, model: PHILIPSXL30ESEM-TMP) was used to observe and analyze the morphology of the contact material after electrical erosion. The contact material was tested by JF04C contact material tester, whose load characteristics are purely resistive. The parameters and the test circuit setting are shown in Table 2 and Fig.1, respectively.

Table 1 Amount of raw materials to prepare $AgCuOSnO_2$ ingot (g)

No.	Material composition	Ag	$AgSn_{15}$	$AgSn_{40}$	$AgCu_{20}$	Ag_2O
1#	AgCuO(10)SnO_2(2)	28.777	21.007	-	79.608	70.608
2#	AgCuO(10)SnO_2(5)	0.749	52.467	-	-	89.175
3#	AgCuO(10)SnO_2(8)	3.336	-	31.508	-	107.544

Table 2 Electrical contact test parameters of $AgCuOSnO_2$ electrical contact materials

Parameter	Value
Voltage/V	12, 18
Current/A	10, 15, 20, 25
Times	10000
Interval	500
Contact pressure/cN	80
Time interval/ms	450
Test method	Open and close test
Contact distance/mm	1

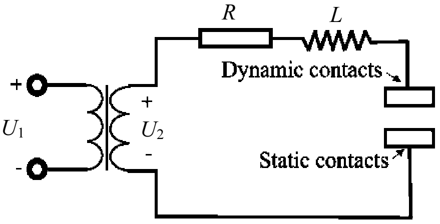

Fig.1 Test circuit of JF04C contact material testing machine

2 Results and Discussion

2.1 Phase analysis

XRD pattern of $AgCuOSnO_2$ electrical contact materials synthesized is shown in Fig. 2. It can be seen that $AgCuOSnO_2$ electrical contact materials contain three phases of Ag, CuO and SnO_2. It is indicated that both Sn and Cu in the raw material are oxidized after sintering to form CuO and SnO_2, and no other phase is formed.

2.2 Contact resistance

Fig.3 show the relationship between contact resistance and test times at different currents and SnO_2 contents. As shown in Fig. 3a~3d, the voltage and current are constant, the contact resistance gradually decreases with the increase of the number of tests. When the number of tests is close to 10 000 times, the contact resistance fluctuates near the lowest point of the contact resistance, showing a steady state. As shown in Fig.3b, when the voltage U=12 V and the

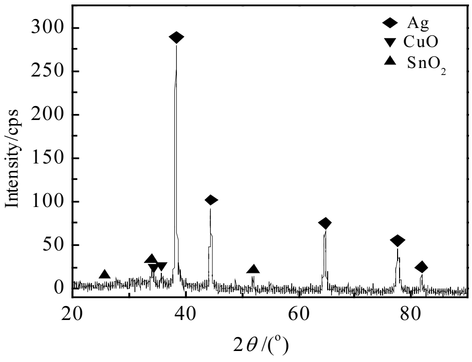

Fig.2 XRD pattern of AgCuO(10)SnO_2(2) electrical contact material

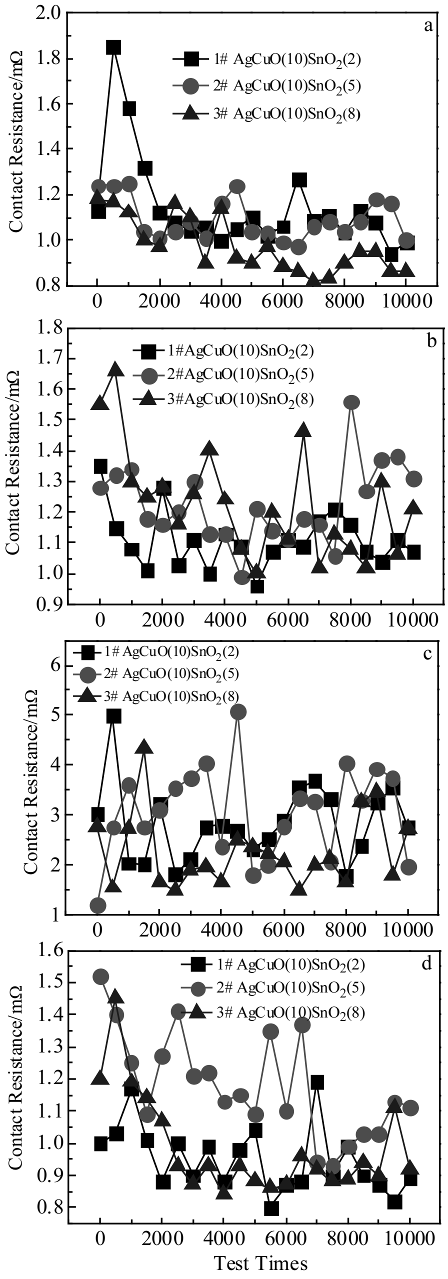

Fig.3 Relationship between contact resistance and test time of AgCuOSnO$_2$ electrical contacts with different SnO$_2$ contents at voltage of 12 V and different currents: (a) 10 A, (b) 15 A, (c) 20 A, and (d) 25 A

current *I*=15 A, the contact resistance fluctuates between 0.8 and 1.3 mΩ. The resistance value is the smallest and the fluctuation range is narrow. As shown in Fig.3c, when the current is *I*=20 A, the contact resistance value is up to 5.2 mΩ, and the fluctuation range is the widest. As the SnO$_2$ content increases, the effect of SnO$_2$ on the contact resistance is bidirectional. When the SnO$_2$ content is 5%, the contact resistance value reaches the highest peak, and when the SnO$_2$ content is 8%, the contact resistance value is minimized. In the multicomponent alloy system, because of the molecular sieve effect[14], the macromolecular substance (CuO) has a larger diameter and a larger gap between molecules. Small molecular substances (SnO$_2$) are affected by concentration gradients. Small molecules (SnO$_2$) are not only adsorbed around the macromolecular (CuO) clusters, but some small molecular (SnO$_2$) particles will enter the micropores inside the large (CuO) clusters. This combination makes the resistance of the AgCuOSnO$_2$ contact material at a lower level. Compared with 30 mΩ of AgSnO$_2$, the contact resistance of AgCuOSnO$_2$ is much lower, which indicates that the addition of SnO$_2$ can effectively improve the electrical contact characteristics of AgCuOSnO$_2$ material without affecting the contact resistance. The research shows[15] that the shrinkage resistance depends on the conductivity of the material itself and the effective contact area when the contact is in sliding contact. The conductivity of AgCuOSnO$_2$ decreases gradually as the content of SnO$_2$ increases. As the current increases, the arc erodes the contact surface. The ability is gradually improved, and the effective contact area is improved during the sliding process. As shown in Fig.3a~3d, the side effect of SnO$_2$ on the contact resistance of AgCuOSnO$_2$ reaches the peak at *I*=20 A. With the further increase of current, the contact resistance of AgCuOSnO$_2$ decreases significantly when the current is *I* = 25 A.

The sum of membrane resistance and shrinkage resistance is collectively referred to as contact resistance of contact surface. The membrane resistance and shrinkage resistance together determine the magnitude of the contact resistance of material. The membrane resistance value depends on the stability of the internal composition of the material. The oxides CuO and SnO$_2$ in the silver matrix Which possess stable existence, are not easy to decompose and thus a new oxide film will not form to affect the membrance resistance. The membrance resistance does not cause the cross-sectional area of the true conductive material to shrink due to the increase in the number of contacts of the electrical contacts, resulting in an increase in circuit resistance. The value of the shrinkage resistance depends on the conductivity of the contact material itself and the effective contact area of the contact head. The contact surface after sliding of the electric contact is not an ideal plane[11] and there are many protrusions and grooves of different sizes. During the sliding contact, the convex portions of the two sides come into contact or one convex portion comes into contact with the other plane. Under the action of the arc, the protruding portions form a molten pool which is in contact with each other. After the separation of the sliding, the molten pool solidifies and the convex portion changes so that the contact position and the effective contact area of the seconds sliding contact change, and the behaviors cause the fluctuation of the value of contact resistance.

2.3 Welding force

Fig.4a~4d show the test results of the welding force at a voltage U = 12 V and different currents I = 10, 15, 20 and 25 A. When the voltage U=12 V and current I=10 A, the anti-welding performance of the three samples' values are basically maintained between 0~10 cN, the welding force value of the 3# sample is the smallest, and those of the 1# sample and the 2# sample are almost the same. When the current is increased to 15, 20, 25 A, the range of the welding force fluctuation becomes wider, and the value of the welding force increases. When the SnO_2 content is 2% and 8%, the welding force increases with the increase of current, and the fusion welding force of $AgCuOSnO_2$(2%) is slightly lower than that of $AgCuOSnO_2$(8%); when the content of SnO_2 is 5%, the welding force fluctuates with the increase of current. When the current I=20 A, the welding force value is the smallest. Fig. 4e~4h show the test results of the welding force when the voltage U=18 V, current I=10, 15, 20 and 25 A. When the current I=10 A, the welding force of the three samples fluctuates between 0~10 cN, the welding force of the 1# sample is the smallest, and the welding force of the 2# sample and the 3# sample is basically the same. When the current increases, the value of the welding force increases. When the content of SnO_2 is 2%, the fusion force of $AgCuOSnO_2$ (2%) reaches the peak when the current is I=15 A; when the content of SnO_2 is 5% or 8%, the fusion welding force of $AgCuOSnO_2$ has different degrees with the increase of current. The $AgCuOSnO_2$ (8%) has the largest increase in weldability.

In the theory of electrical contact[16] the welding force of the electrical contact mainly depends on the temperature of the contact, the real contact area, and the tensile strength. The welding force is an important parameter for distinguishing the electrical contact material. As shown in Fig. 3a, the contact resistance value is small. During the slow heating process, under the same test conditions, the effective area of the molten pool is small, and the welding surface of the material is small, resulting in less welding force; the

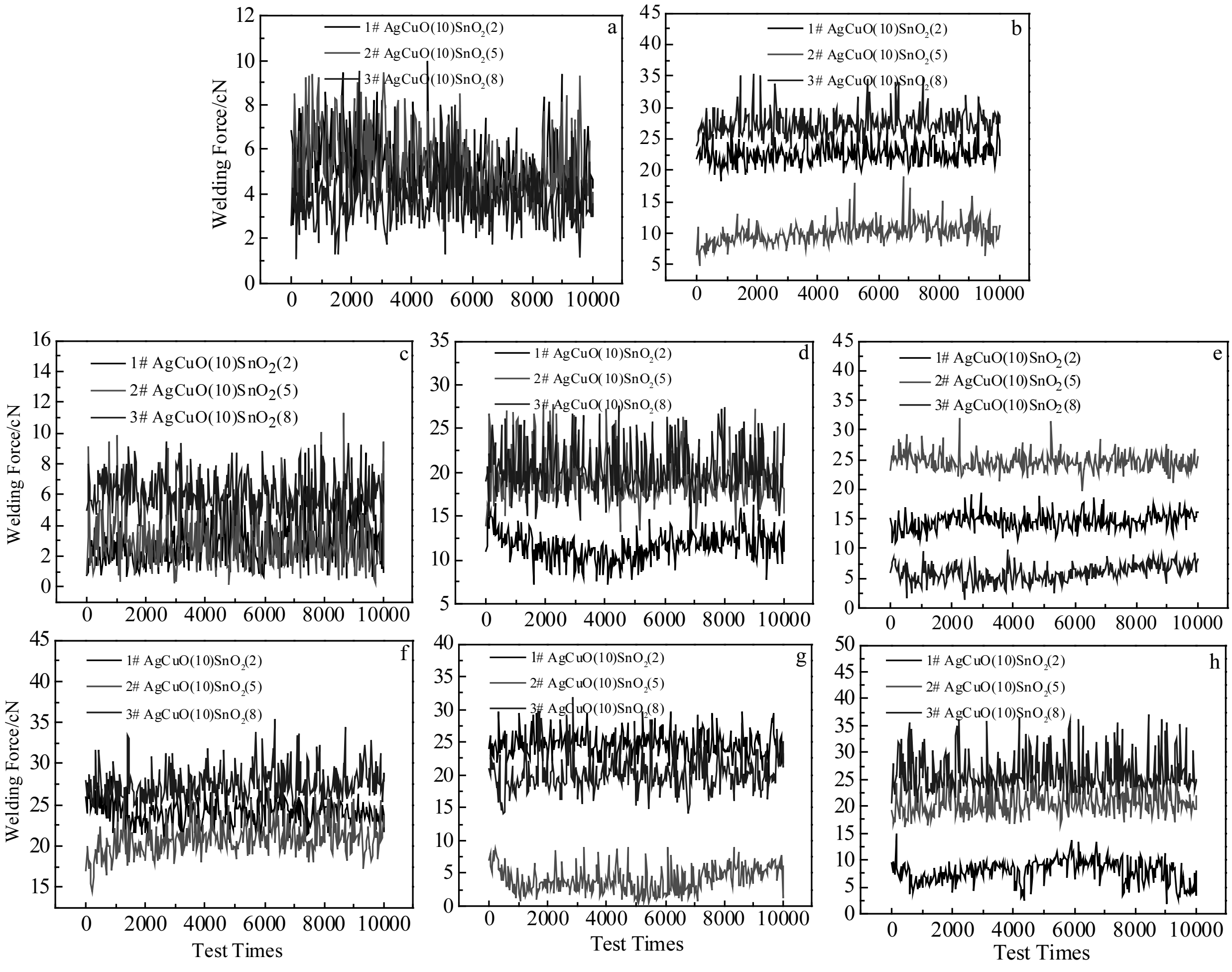

Fig.4 Relationship between welding force and test times of $AgCuOSnO_2$ electrical contacts: (a) 12 V, 10 A; (b) 12 V, 15 A; (c) 12 V, 20 A; (d) 12 V, 25 A; (e) 18 V, 10 A; (f) 18 V, 15 A; (g) 18 V, 20 A; (h) 18 V, 25 A

contact resistance of AgCuOSnO$_2$(8) is the smallest when U=12 V, I=15 A. During the sliding contact process, the electrical contact part heats up under the action of current, heat forms a molten pool, and is measured when the sliding is broken. The welding force value is the smallest, and the result is shown in Fig.4b. The influence of contact resistance on the welding force is single. The reference contact resistance can only qualitatively analyze the welding force. The influence factors of the welding force are complex and varied. The exact theory about the welding force remains to be studied.

2.4 Arc erosion morphology

The researchers define the phenomenon that the thermal effect of the electrode surface arc causes the contact material to evaporate, liquid splashing and solid state falling off as arc erosion. The SEM morphology of anode and cathode of AgCuO(10)SnO$_2$(5) contact material after electric erosion is shown in Fig. 5. Bridge transfer and arc erosion are the two main causes of material transfer[12,13]. Under the action of electric arc, the temperature of the contact surface transition zone of electric contact rises rapidly, and the contact point softens, melts and vaporizes at one time. In the melting process, the metal liquid flows under the action of internal and external mechanical forces in the molten pool, and the splashing behavior will occur if the speed is too fast; boiling and vaporization will occur in the process of vaporization, which is the process of vaporization in the molten pool, as well as boiling. It will cause splashing in the molten pool. It can be seen from Fig. 5a that the cathode surface of the electric contact forms a convex peak, and the anode electric contact surface in Fig. 5b forms a concave peak, indicating that during the electric contact process, some materials are transferred from the anode to the cathode, that is, the anode quality decreases and the cathode quality increases. The local erosion morphology of the cathode and anode arc of AgCuO(10)SnO$_2$(5) under the test voltage of 12 V and current of 15 A is shown in Fig. 5c and 5d. The part circled in the white circle in Fig. 5c is the terraced molten metal like surface formed after the solidification of the cathode melting pool of the electric contact. The reason for this result is that the number of contacts keeps increasing. Under the multiple actions of the arc, the heat generated by the arc is concentrated in the convex part of the electric contact. In this way, the convex part is heated rapidly and melted to form a molten pool. The molten pool boils under the action of electric arc and flows in the form of wave under the action of external force. When the arc erosion ends and the heat source leaves, the molten metal in the molten pool solidifies in an instant before spreading, forming a micro uneven surface morphology. As shown in Fig. 5d, there are a few air holes and cracks on the anode surface of electric contact. Due to the erosion of electric arc, a liquid molten pool is formed on the surface of electric contact, and the solubility of liquid metal to gas is much higher than that of solid state to gas. When the contact is disconnected, the liquid metal cools instantly, and some air cannot escape, forming pores inside or on the surface of electric contact; there is a crack in Fig.5d. There are differences in the coefficient of thermal expansion between silver, CuO and SnO$_2$. Under the action of arc erosion, the material heats up rapidly, and each phase deforms with the increase of temperature in different degrees. After the electric contact is disconnected, the Ag matrix, CuO and SnO$_2$ contract in different degrees. Under the repeated erosion of arc, the Ag matrix is under the repeated action of compressive stress and tensile stress. A crack is formed between the oxides.

In Fig. 5a, and 5b, the surface morphology of the molten pool has little fluctuation, and the number of cracks and holes is very small, indicating that the prepared AgCuOSnO$_2$ electrical contact material has excellent performance. First, the wettability of the AgCuO electric contact material is excellent. When the SnO$_2$ is not more than CuO, the wettability of the material is damaged little. The added SnO$_2$ increases the resistance to fusion welding and thermal stability of the material, which can reduce the splashing of

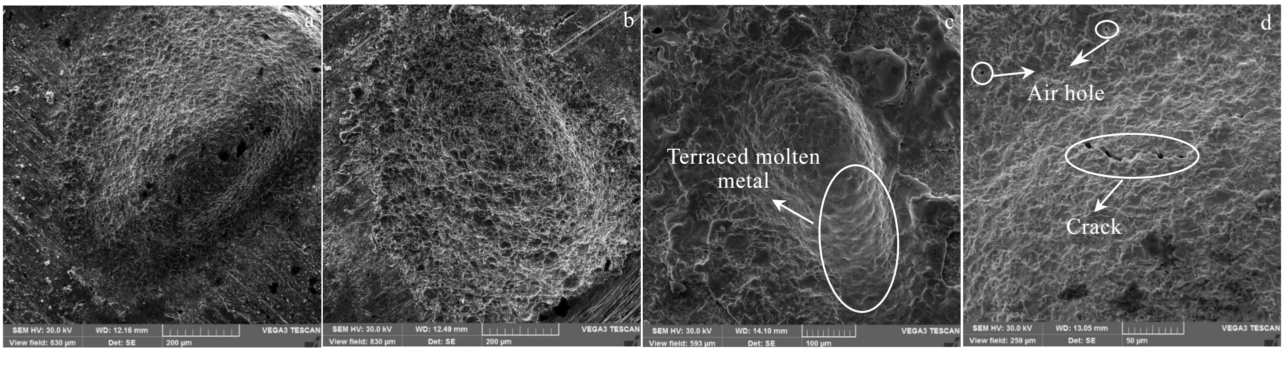

Fig.5 SEM images of cathode and anode of AgCuO(10)SnO$_2$(5) under 12 V: (a) cathode contact, (b) anode contact, (c) melting zone, and (d) crack area

the molten liquid to a certain extent. Second, the AgCuOSnO$_2$ has good thermal conductivity. After the contact is disconnected, the temperature of the surface of the electric contact drops rapidly, and the molten pool part can solidify at the same time, The silver matrix has good conductivity, which can reduce the Joule heat and the splashing of solution to a certain extent[15].

2.5 Materials transfer

The transfer characteristic of electrical contact material is one of the key indexes to measure the service life of electrical contact. In the process of closing and breaking the electric contact, the molten metal pool will splash and vaporize, which will damage the electric contact. Fig.6 shows the relationships between test current and transfer mass of AgCuOSnO$_2$ electrical contacts. After 10000 on-off tests, the influence of environmental factors on the experiment can be ignored. When the test voltage is 12 V and the current is 10 A, the loss of the electrical contact material is low after 10000 times of on-off experiments. The loss of 1# samples is 0, the loss of 2# samples is -0.0001 g, the loss of 3# samples is -0.0002 g. When the current is 15 A, the fluctuation range of the total consumption is small, and the maximum loss of 2# samples is - 0.0003 g. When the current is 20 and 25 A, the transfer amount and total consumption of the material increase obviously. When the current is 25 A, the mass loss of the anode is -0.0011 g, and the total consumption of three samples are -0.009 g. In general, with the increase of test current, the total consumption of AgCuOSnO$_2$ electrical contact material increases. With the content of SnO$_2$ increasing, the total consumption of AgCuOSnO$_2$ is not only inhibited, but also the transfer and total consumption of material is reduced. AgCuO(10)SnO$_2$(8) has good resistance to fusion welding.

Each on-off behavior of contact will affect the transfer of contact material. Metal evaporation and bridge transfer are two ways of material transfer. In the process of on-off contact, the metal on the electrode surface is heated and vaporized rapidly by arc discharge, and the vapor metal is ionized. Metal cations bombard the cathode under the action of electric field, which changes the surface morphology of the cathode; electrons bombard the anode under the action of electric field of the anode, which has a certain impact on the anode morphology. As shown in Fig.5a and 5b, a small concave convex part is generated on the contact surface, which is a way for the anode material to be transferred to the cathode material. In the process of arc erosion, according to Thomson, Peltier and Kohler effect, the number of contact points and contact pressure between contacts decrease, the current density of contact point increases sharply, high temperature occurs at the bridge, and the bridge will break at the highest temperature. As the cathode temperature is slightly lower than the anode temperature, the highest temperature of the bridge deviates from the center of the bridge and is close to the anode. During the fracture process, some anode materials are transferred to the cathode along with the bridge fracture, and the schematic diagram is shown in Fig.7.

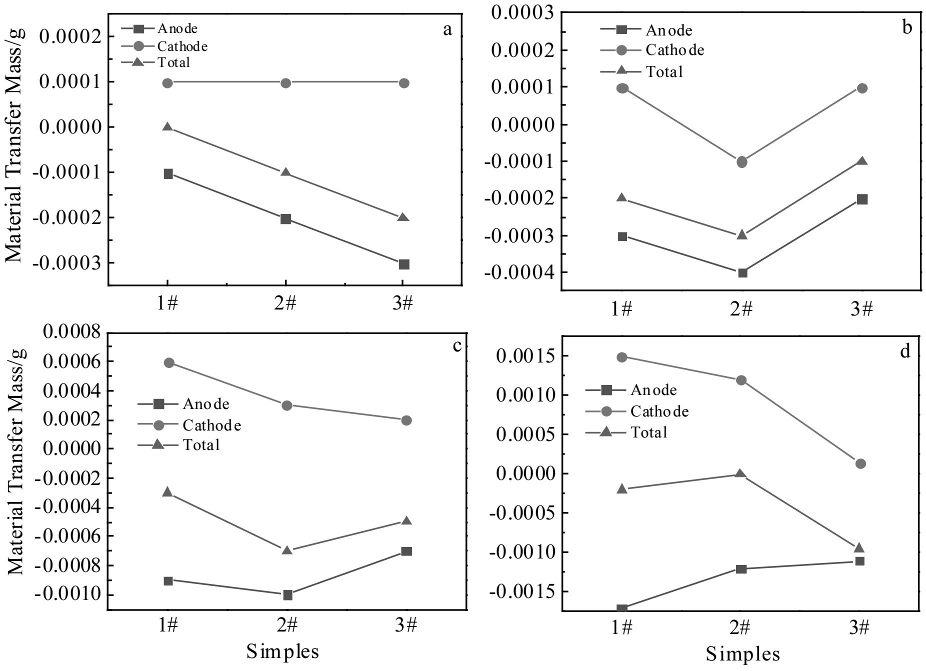

Fig.6 Relationship between current and transfer mass of AgCuOSnO$_2$ electrical contacts: (a) 12 V, 10 A; (b) 12 V, 15 A; (c) 12 V, 20 A; (d) 12 V, 25 A

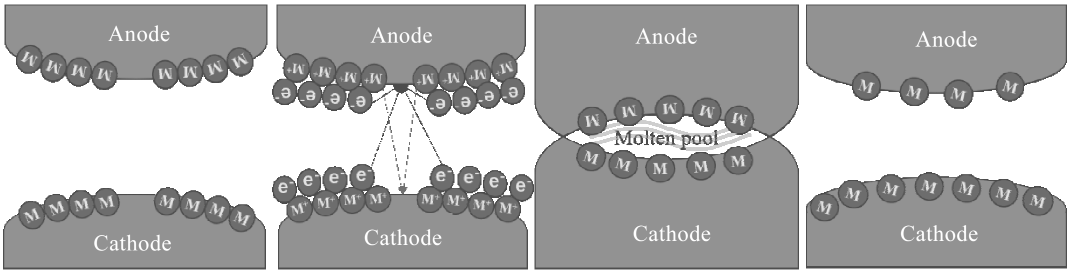

Fig.7 Flow chart of material transfer process under the action of arc erosion

3 Conclusions

1) The contact resistance of AgCuOSnO$_2$ electrical contact material is small, except for the voltage U = 12 V, I = 20 A, The contact resistance of AgCuOSnO$_2$ is all lower than 1.9 mΩ, and the contact resistance of AgCuO(10)SnO$_2$(5) is the smallest and the most stable. When the voltage and current remain unchanged, the contact resistance of the samples decreases slowly with the increase of test times and finally tends to be stable; when the current is different, the contact resistance of the sample decreases. When the voltage U = 12 V, I = 15 A it is the most stable.

2) When U = 12 V, I = 10 A, the welding force fluctuates between 3~8 cN. When the current increases from 15 A to 25 A, the welding force first increases and then decreases. The range of the change of the AgCuOSnO$_2$ electric contact material with the times is small, and the influence of the voltage on the welding force of the AgCuOSnO$_2$ electric contact material is relatively small. The direction of material transfer is the anode transfer, which means the mass of anode decreases and the mass of cathode increases. With the increase of test current, the transfer and total consumption of anode electric contact material increase. When the test current is 10, 15, 20 or 25 A, the minimum consumption of electric contact material is 0 g or very close to 0 g, which shows that the addition of SnO$_2$ is helpful to improve the transfer characteristics of AgCuOSnO$_2$ electric contact material and reduce the material loss in the erosion process.

3) The concave peak on the surface of the positive electromechanical contact are erosion pits, and the materials from original concave peak are transferred to the surface of the cathode electrical contact to form bulges, and the terraced molten metal is formed on the surface. The transfer mode of the AgCuOSnO$_2$ material is fusion bridge. The surface morphology of the electrical contact is relatively flat, with a small number of pores and cracks. The addition of SnO$_2$ makes the surface morphology flatter.

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SnO_2含量对$AgCuOSnO_2$电接触性能的影响

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摘　要：采用反应合成法制备了不同SnO_2含量的$AgCuOSnO_2$电接触材料。采用FQR-7501型涡流电导率仪测量抛光$AgCuOSnO_2$的电导率。用扫描电镜（SEM）观察和研究了$AgCuOSnO_2$电接触表面的侵蚀形貌。JF04C直流数字电阻测试仪用于进行10 000点测试。结果表明，$AgCuO(10)SnO_2(5)$和$AgCuO(10)SnO_2(8)$电触头材料在U=12 V和I=15 A时的接触电阻小于1.3 mΩ，波动最小；当I=10 A时，$AgCuO(10)SnO_2(x)(x=2, 5, 8)$的熔焊力小于8 cN，$AgCuO(10)SnO_2(5)$电触头的熔焊力较小，当电流增大时熔焊力较为稳定；当$AgCuOSnO_2$电触头材料发生电弧侵蚀时，材料从阳极向阴极转移。随着SnO_2含量的增加，材料传输过程中的损耗得到抑制和降低。所转移的电触头表面有少量的气孔和微裂纹，表面形貌较为平坦。

关键词：$AgCuOSnO_2$电接触材料；电接触性能；电弧侵蚀形貌

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