Research Progress of AgMeO Electrical Contact Materials

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Abstrct: Due to its excellent properties, silver metal oxide (AgMeO) has been widely applying as one of the electrical contact materials in the electrical industry. The preparation methods of AgMeO electrical contact materials and the advantages and shortages of these methods were reviewed. The influencing factors to material performance and research progress of four kinds of AgMeO electrical contact materials were introduced. Finally, development trends of AgMeO electrical contact materials were also proposed.
Key words: metal materials; silver metal oxide; electrical contact materials; preparation method; research development
CIF number: TG146.3^{+}2 **Document Code:** A **Article ID:** 1004-0676(2014)S1-0100-08

AgMeO 电触头材料的研究进展

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摘 要：由于优异的性能，AgMeO 作为一种电接触材料在电器工业中被广泛应用。综述了 AgMeO 电接触材料的制备方法及各方法的优缺点；介绍了电触头材料性能的影响因素和四类电触头材料的研究新进展；并对 AgMeO 电接触材料的发展趋势进行了展望。
关键词：金属材料；银金属氧化物；电接触材料；制备方法；研究进展

Electrical contact material is one of the important functional materials which was used as a current controller such as turned on or off and carry current in the circuit. Their performance directly affects the life and safety of the equipment. Therefore, they occupy an extremely important position in the electrical industry[1-3]. Compared with other contact materials, AgMeO electrical contact material can avoid the occurrence of fusion welding and corrosion because of the presence of metal oxides (MeO), when the electrical contact materials occurs fusion welding, the MeO will gather at the solid-liquid interface and to embrittle the contact point, Ultimately reduce the risk of fusion welding[4-5]. So the AgMeO material is now widely used in electrical instruments.

The AgMeO electrical contact material was developed in the 1920s. The earliest development and application of the AgMeO were silver cadmium oxide (AgCdO). It has been called the universal contact material due to the excellent performance in service[6-7]. But AgCdO contains a kind of toxic metal Cd, it can cause harm to the human body and

Received: 2014-07-29
Foundation item: the National Natural Science Foundation of China (No: 51361016) and School Foundation of Kunming University of Science and Technology.
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environment. As the need for development of electronic device miniaturization and the performance requirements becomes higher and higher, the work to seek alternatives to AgCdO material becomes one of the interesting points of research in the past thirty years. So far, people have developed many electrical contact materials to replace AgCdO, and $AgSnO_2$, AgZnO, AgCuO, Ag-REO(Silver rare earth oxides) were more widely used[8-13].

1 Preparation method of AgMeO

There are many ways to prepare AgMeO electrical contact material. Each preparation method has its advantages and disadvantages, and the material performance is also different.

1.1 Alloy internal oxidation method

The alloy internal oxidation method was first put forward in the 1950s by Schreiner[14]. The classic process is as follows: in the first, Ag-Me alloy is prepared according to the proportion of silver and Me, then through rolling, stamping and other crafts, finally, AgMeO is made by the internal oxidation processing. This method was not ideal in the preparation of electrical contact materials at first, cadmium oxide particles were very unevenly distributed in the silver matrix. After the development of Harrbye et al[15-17], the alloy internal oxidation method has now become a mature method of manufacturing electrical contact materials.

Alloy internal oxidation method has many advantages, such as: simple process, low cost, small electrical contact wear, long service life, convenient mass production; But the alloy internal oxidation is easy to produce poor oxides zone, MeO distribution is not uniform, causing poor properties of anti-fusion welding and abrasion.

1.2 Powder metallurgy method

Powder metallurgy is a traditional preparation method. This method is firstly mixing Ag powders and Me powders. Then get the contact material through pressing, sintering, and extrusion. Since 1954[18], China has begun to utilize this method for preparation of electrical contact materials. Powder metallurgy is a kind of highly efficient, low consumption, energy saving technology. However, the biggest drawback of this method is that the materials have low density, thick oxide particles and aggregation-prone, these shortcomings lead to poor electrical properties of silver metal oxide materials[19].

The researchers also combined internal oxidation with this method, the MeO was prepared through the atomizing manner powder oxidation after silver-Me alloy was made, finally, in accordance with the powder metallurgy method to prepare the AgMeO contact material. Therefore, this method is also known as the pre oxidation method[20].

1.3 In-situ reactive synthesis method

In-situ reactive synthesis is a new method developed for preparation of contact material. The basic principle of this method is using Ag_2O and Me as raw material, through mechanical mixing. After the suppression of sintering, using different elements or chemical substances react under certain conditions, causing production of MeO particles in the Ag matrix, and finally making the AgMeO contact material[21].

Compared with the previous two methods, in situ synthesis method has the advantages of short process flow, no pollution in the production process, the prepared silver metal oxide contact material has the advantages of higher electrical life and some other advantages. However, the microstructure of the synthesized silver oxide electrical contact material is not uniform, this is also the reason that influence the application of the method[22].

1.4 Other methods

In addition to the above three kinds of preparation methods, deposition method and ultrasonic embedding method are also commonly used methods [4, 23-24].

Deposition method includes chemical deposition and spray deposition. The former is adding the precipitating agent to the metal salt solution, then get the material after the deposition, finally get the electrical contact material after pressing, sintering processes. Therefore, this process is very complex，difficult to control the quality of products, and needs to dispose of waste chemicals. The latter is using

molten material, then the liquid material onto the substrate to obtain the required materials by rapid cooling spray nozzle. The main problem of the method is hard to control the size of the MeO.

Ultrasonic embedding method is to disperse oxide particles by using ultrasonic, silver can be attached on the surface of MeO. Finally, after pressing, sintering, rolling, the AgMeO contact materials can be obtained. This method is better than that of powder metallurgy, but it will pollute the environment. In order to reduce the manufacturing cost, some new preparation technologies were introduced to prepare electrical contact material, such as Jin Hong and coworkers used the upward continuous casting technology to prepare AgMeO[25].

2 The factors influencing on the structure and properties

The preparation method, composition and content have important influence on the microstructure and properties of AgMeO electrical contact material. Zhou Xiaolong and his partners have studied the microstructure of three different electrical contact materials $AgSnO_2$, AgCuO and AgY_2O_3, which were prepared by in situ reaction synthesis. Research shows that the three electrical contact materials have different microscopic morphologies under the same conditions, They think that the main reason of the above mentioned results is attributed to different diffusion mechanisms which are caused by different element natures in the alloy system[26]. Wang song, et, al, studied the microstructure of $AgSnO_2$, which was prepared by internal oxidation and powder metallurgy method, the results show that the SnO_2 particles are smaller, and distributed uniformly in the matrix of silver without any of the significant reunion, inclusions and other defects by internal oxidation; but there are coarse particles, poor dispersion and easy to generate agglomerate phenomena by powder metallurgy method[27].

Effect of preparation method, composition and content on the properties of AgMeO electrical contact material were studied, as shown in Tab.1[28]. The data show that: the preparation methods have a greater impact.

Tab.1 Effect of preparation method, composition and content on the properties of AgMeO electrical contact material

表1 制备方法、组成成分及含量对AgMeO电接触材料性能的影响

AgMeO	MeO content / (%)	Density /(g/cm^3)	Elec. Resistivity/ (μΩ·cm)	Hardness HV/ (MPa)	Manu-facturing process
AgZnO	8±1	≥9.65	≤2.30	≥750	ASE: Atomizing - Sintering-Extrusion
	10±1	≥9.50	≤2.50	≥800	
AgCdO	10±1	≥10.00	≤2.20	≥640	
	12±1	≥9.90	≤2.30	≥690	
	15±1	≥9.75	≤2.5	≥740	
$AgSnO_2$	8±1	≥10.00	≤2.30	≥700	
	10±1	≥9.90	≤2.40	≥700	
	12±1	≥9.80	≤2.50	≥750	
AgZnO	8±1	≥9.70	≤3.40	≥690	I.O: Internal Oxidation
	10±1	≥9.55	≤3.50	≥740	
AgCdO	10±1	≥10.00	≤3.20	≥690	
	12±1	≥9.90	≤3.40	≥690	
	15±1	≥9.75	≤3.50	≥740	
	18±1	≥9.60	≤3.60	≥740	
$AgSnO_2$	6+In_2O_3(4)	≥9.80	≤3.30	≥720	
	8+In_2O_3(4)	≥9.75	≤3.40	≥760	
	9+In_2O_3(4)	≥9.75	≤3.50	≥780	
AgZnO	8±1	≥9.50	≤2.6	≥600	MCS: Mixing Compac-ting Sintering
	10±1	≥9.40	≤2.70	≥650	
$AgSnO_2$	10±1	≥9.80	≤2.10	≥650	
	12±1	≥9.78	≤2.20	≥650	
	15±1	≥9.50	≤2.50	≥650	

On the performance of AgMeO electrical contact material, the internal oxidation method has the best performance in the following three ways; also, the additive can greatly improve the performance of AgMeO material. Therefore there have importance sense of improving the performance of AgMeO material, to choose the best process condition and composition.

3 Research status of AgMeO electrical contact material

3.1 $AgSnO_2$

$AgSnO_2$ electrical contact materials attracted people's attention in the mid 1970s, the Japanese scholar reported for the alloy prepared by internal oxidation of $AgSnO_2$ contact materials at the Seventh International Conference on electrical contacts[29] . Since then, the researches on the $AgSnO_2$ material increased significantly, positively advances have been achieved in the various $AgSnO_2$ components, process, material physical properties etc. In 1980s, the German company Degussa announced that the company developed a new $AgSnO_2$ contact materials by powder sintering advanced for ten years. so that the $AgSnO_2$ material research can come into a new step , and replaced the AgCdO electrical contact materials in some switch electric appliances[30].

Although $AgSnO_2$ electrical contact materials is considered as the most promising alternative to AgCdO electrical contact materials , but it was found that $AgSnO_2$ material when used as electric contact material has the following fatal problems: Firstly because of the high hardness of SnO_2, $AgSnO_2$ electrical contact material has relatively low plasticity, difficult to machining , and the yield is low; Secondly, under the action of the arc-work , SnO_2 enrichment at the contact surface to make the contact resistance increasing and large temperature rising; and under the conditions of AC3, the electrical life of $AgSnO_2$ electrical contact materials is low.

In the use of $AgSnO_2$ electrical contact material, people haven't entirely understanded the $AgSnO_2$ arc corrosion performance, it greatly limits the application of $AgSnO_2$ electrical contact material. Therefore, aiming at solving the problems of $AgSnO_2$ in the use of materials, people try to improve the properties from the components, preparation, surface modification, nano and other aspects[31-36]. As Kharin found in the study of short arc of silver based contact materials, that adding Ta can improve the arc erosion resistance of $AgSnO_2$ materials[31]. Lungu studied the effects of grain-refining and microstructure homogenization on properties of $AgSnO_2$ material, the results show that $AgSnO_2$ sintered electrical contacts SnO_2 with ultrafine and uniformly dispersed in Ag substrate can greatly improve the performance of resistance to erosion, hardness, and other aspects of $AgSnO_2$ electrical contact material[32]. Zhang[33] studied the additives, dispersing agent and chemical plating technique of surface modification effect on the microstructure and properties of $AgSnO_2$ electrical contact material. The results show that surface modification can improve the wettability of Ag and SnO_2, and reduce the surface energy, hinder the agglomeration of SnO_2 particles, so as to solve the problem of processing difficulty and high contact resistance in $AgSnO_2$ electrical contact materials.

Liu Linjing[37] used the First Principles Method to analyze the path SnO_2 during the process of forming $AgSnO_2$ by in-situ reactive synthesis, the synthesis path is shown in Fig.1. Yu et al[38] used molecular dynamics simulation and experiment to study the microscopic mechanism for the arc quenching of the molten pool behavior of $AgSnO_2$ electrical contact material, results show that: the material movement and existing state within the molten pool are the key factors for electrical erosion resistance; Arc quenching can be realized by increasing the oxygen composition in $AgSnO_2$ electrical contact material, and the oxygen occurs resolution reaction and phase change.

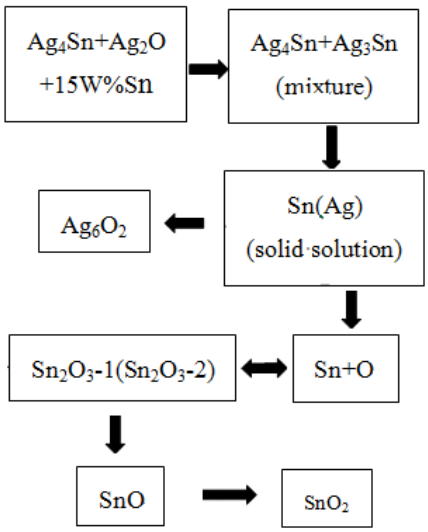

Fig.1 The formation process of SnO_2 in $AgSnO_2$ by in-situ reaction synthesis

图 1 原位反应合成法制备 $AgSnO_2$ 过程中 SnO_2 形成路径

3.2 AgCuO

Silver copper oxide (AgCuO) is a type of environmental friendly electrical contact materials, has higher resistant fusion-weld, the performance in DC contactor is better than $AgSnO_2$ and AgNi electrical contact materials[28]. The copper oxide has high stability, and exists good interfacial compatibility, and it has other good characteristics, so that the AgCuO electrical contact material attracts attention. As early as in the former Soviet Union period AgCuO electrical contact material was applied to medium and heavy load and low voltage power distribution equipment, such as magnetic switch, relay and controller[39], AgCuO electrical contact obtained good effect. This shows that the silver copper oxide is a kind of a wide range of applications of silver base electrical contact compound material.

At present, The research of AgCuO electrical contact materials also gets some achievements, such as Fuda company prepared AgCuO electrical contact material by using atomized - sintered extrusion process, and the resistivity of the electrical contact material is lower than $AgSnO_2$ electrical contact material[28]; AgCuO contact material instead of AgCdO electrical contact material than $AgSnO_2$ contact materials in electrical conductivity has great advantage.

A patent was proposed, the first step is surface treatment for silver and copper oxide powder, forming a contact interface fresh wave of particles, in order to increase the binding energy[40]. It is helpful to improve the bonding strength of materials and improve the performance of electrical contact. Zhou Xiaolong[41] studied the synthesis of in situ reaction synthesis of AgCuO electrical contact material, it was found that there are two cubic monoclinic crystal structure existing in CuO particles，one is cubic structure，the other is monoclinic structure. The study showed that the cubic structure CuO particles variables can be up to 300%. Cubic copper oxide deformation in the plastic deformation process, it can form fibrous CuO reinforcement, the reinforcement can significantly improve the performance of AgCuO electrical contact. Zhou[26] also used cumulative extrusion deformation technology to improve the performance of AgMeO reaction, b means of comparing with the $AgSnO_2$, AgY_2O_3, microstructure of AgCuO contact materials at different plastic deformation conditions, he found that cumulative extrusion deformation technology can significantly improve the microstructure of AgCuO contact material, this method can promote the metal oxide enhanced dispersed phase, so as to achieve the purpose of microstructure homogenization. He also pointed out[42]: AgMeO with microstructure homogenization can be obtained if we can get a small or nano-sized second phase particles in the process of large plastic deformation; the selection of large plastic deformation intensity should be determined by the AgMeO system and the characteristics of electrical contact materials.

3.3 AgZnO, Ag-REO

In addition to the above several AgMeO electrical contact materials, AgZnO, AgREO electrical contact materials have also been concerned. AgZnO electrical contact material is not widely used as AgCdO and $AgSnO_2$ electrical contact materials. AgZnO electrical contact material is the only alternative to $AgSnO_2$ electrical contact material in some areas[6]. In recent years, scholars have made certain progress in the study of AgREO. AgREO electrical contact material has the arc erosion resistance, welding resistance, excellent performance, low contact resistance, long life and other characteristics. AgREO could meet the electrical performance of high-power relay demanding. Study on silver rare earth oxides mainly includes $AgLa_2O_3$, AgY_2O_3, $AgCeO_2$ etc[43-45]. However, because of the rare earth is expensive, and the difficult to processing, these problems limit its development.

Silver conductive ceramic electric contact material is developed to improve the $AgSnO_2$ contact material defect model of silver metal oxide contact materials. Such as Wang Chengjian used conductive ceramic reinforced silver based electric contact materials to solve the problem of temperature rise of $AgSnO_2$ material. They mainly studied $AgLa_2NiO_4$ and $Ag/LaFe_{1-x}Ni_xO_3$ two composite electric contact materials, and achieved good results[46-47]. Guan Weiming[48] reported the electrical contact properties

of $AgLaNiO_3$ conductive ceramic contact material, results show that this kind of material has good electrical contact performance. However, the study of the silver conductive ceramic contact material has just started, some issues are not clear.

The research status of the silver metal oxide can be seen, over the past few decades, we improve the performance of the electric contact material simply by selecting the types of metal oxide, diameter of oxide particle, and the interface relations of oxide and silver substrate, etc., rather than radically to design and change the silver metal oxide. Therefore, by changing the silver metal oxide micro structure to improve the performance of Ag based electrical contact material is an important trend in the development of electrical contact materials.

4 Summary and outlook

AgMeO material has become an indispensable contact material in electrical and electronic industry, and shows a good application prospect. After a long time study, AgMeO contact materials in the preparation process, composition, surface modification and other aspects of the organization has made many improvements, and the performance has been greatly improved. However, the study on the structure and properties of AgMeO is not deep enough; it restricts the development of AgMeO materials.

With the expansion of precision micro electronic industry and the market demand, research and application of AgMeO contact material have more brilliant prospects. In order to develop a more environmentally friendly, more efficient, more economic model of AgMeO contact materials, researchers should make efforts in the following aspects. Firstly, people should carry out basic research, study the relationship between microstructure and electrical properties of AgMeO materials. Secondly, combine the computer simulation technology and experimental methods, to improve the efficiency of the experiment. Finally, we need to pay attention to the recovery of precious metal and AgMeO waste utilization.

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