Anti-Arc Erosion Properties of Ag-La₂Sn₂O₇/SnO₂ Contacts

Zhang Lingjie^{1,2}, Shen Tao², Shen Qianhong^{1,2}, Zhang Ji², Chen Lawson^{2,3}, Fan Xianping^{1,2}, Yang Hui^{1,2}

¹ Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China; ² Zhejiang-California International Nanosystems Institute, Zhejiang University, Hangzhou 310058, China; ³ Wenzhou Hongfeng Electrical Alloys Co. Ltd, Wenzhou 325603, China

Abstract: La₂Sn₂O₇/SnO₂ composite powder was synthesized by chemical co-precipitation, and Ag-La₂Sn₂O₇/SnO₂ electrical contact material was prepared by a powder metallurgy method. Anti-arc erosion properties, mass loss and Vickers hardness of the Ag-La₂Sn₂O₇/SnO₂ composite were investigated, and its anti-arc erosion mechanism was discussed. Results show that the welding force of Ag-La₂Sn₂O₇/SnO₂ composite is much better than that of Ag-SnO₂, because the new phase La₂Sn₂O₇ can increase the viscosity of melt pool and improve wettability between silver and tin oxide to some extent. Meanwhile, flatter arcing area and “beads-like” particles embedded scatteredly in the surface could decentralize arc energy via “pinning effect”, which decreases temperature rise and weakens the damage of surface structure, and better anti-welding property is obtained. Ag-La₂Sn₂O₇/SnO₂ composite could be a leading candidate material for electrical contacts in the future.

Key words: electrical contact material; silver; La₂Sn₂O₇/SnO₂; arc erosion; welding force

Silver-metal oxide (Ag-MeO) electrical contacts with outstanding electrical and endurance qualities play an important role in high reliability components of distribution switches, circuit breakers and contactors, among which, silver-cadmium oxide (Ag-CdO) has excellent comprehensive properties, such as anti-welding, and anti-erosion^[1-3]. However, hazardous Cd vapor occurs upon using and the Restriction of Hazardous Substances (RoHS) directive carried out by European Union made Ag-CdO replaced gradually. Silver tin oxide (Ag-SnO₂) contacts have been an potential candidate due to their higher thermal stability, anti-arc erosion^[2] and environmental friendly characteristic.

Ever since Ag-SnO₂ contacts were developed about forty years ago to replace undesirable silver cadmium oxide contacts, considerable work has been done on improving its performances and industrial applications^[4]. In Europe today almost all of the new generations of contactors operating in a current range >60 A are equipped with Ag-SnO₂. In the United

States and China, the replacement of Ag-CdO by Ag-SnO₂ has not proceeded completely due to different environmental regulations, lower costs for Ag-CdO, the technical improvement of Ag-SnO₂ in service^[5,6]. Recently, the researches on the surface arc erosion behavior and the failure mechanisms of Ag-SnO₂ contacts have been reported^[7-9]. Lungu et al. developed a new Ag-SnO₂-WO₃ (90:9.5:0.5) electrical contacts with a good behavior at $I_n = 200$ A and in AC3 working regime as a result of its ultrafine and uniformly dispersed microstructure^[10]. Wang et al.^[11] showed nano-composite La-doped Ag-SnO₂ contents with homogeneous dispersion structure can effectively decrease temperature rise of contact area, disperse the arc eroding energy and then improve the erosion resistant capacity of the arc. Zhu et al.^[12] concluded that La₂O₃ and Bi₂O₃ can effectively enhance anti-erosion and anti-welding. These infer that adding of rare earth elements and/or their compounds^[13] and tin oxide surface modification^[14,15] would be an effective method to

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Corresponding author: Yang Hui, Master, Professor, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China, Tel: 0086-571-88206798, E-mail: yanghui@zju.edu.cn

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optimize arc erosion behavior of silver tin oxide. Related studies have also shown that pyrochlore-type $\text{La}_2\text{Sn}_2\text{O}_7$ ($\text{A}_2\text{B}_2\text{O}_7$) has high melting point ($> 2000\text{ }^\circ\text{C}$), excellent thermal stability and catalytic activity at high temperature, and exhibits high oxygen ion conductivity by inducing disorder in oxygen sublattices^[16,17]. Extensive studies on $\text{La}_2\text{Sn}_2\text{O}_7$ mainly focus on its catalytic activity, but little work has been done on its electrical properties for electrical contact materials.

In the present work, $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ composite powder was produced by a low-cost chemical co-precipitation process, and $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ contacts were fabricated by a powder metallurgy method. The anti-arc erosion properties, the surface morphology and the microstructure were investigated, and anti-arc erosion mechanism was discussed.

1 Experiment

In the present study, silver powder was commercially available and $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ composite powder was prepared by a simple chemical co-precipitation method. Tin (IV) tetrachloride pentahydrate (SCR, A. R., 99%) and lanthanum nitrate hexahydrate (Aladdin, A. R., 99%) were used as the starting materials for $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ content, while ammonium bicarbonate (NH_4HCO_3 , A. R.) and ammonium hydroxide ($\text{NH}_3\text{H}_2\text{O}$, A. R.) were used as precipitants. The silver powder with a mean particle size of $1\text{ }\mu\text{m}$ (99.9%) was produced by Wenzhou Hongfeng Electrical Alloy Co. Ltd. (Wenzhou, China). Two groups of powder mixtures, $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and Ag-SnO_2 , were designed.

Before mixing, the $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ composite powder and SnO_2 powder were first dispersed by ultrasonication for 30 min. Then the dispersed $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ composite powder (12 wt%) together with silver powder (88 wt%) were ball-milled for 4 h in an agate container using agate balls and ethyl alcohol as the grinding medium. Subsequently the slurry was dried and then passed through a $74\text{ }\mu\text{m}$ sieve. The sieved powders were added into a stainless steel die ($\Phi 10\text{ mm}$) and uniaxially pressed at a pressure of 1000 MPa for 15 s and specimens with a size of $10\text{ mm} \times 4.5\text{ mm}$ (diameter $\times$ length) were obtained by sintering at $880\text{ }^\circ\text{C}$ for 6 h. Ag-SnO_2 composite was also prepared under the same conditions for comparison. The sintered specimens were finished by machining before testing. All samples were smoothly polished using a diamond paste and ultrasonically cleaned. A minimum of five specimens were tested for each experimental condition.

The anti-arc erosion property was tested in a contactor on $2.5\text{ mm} \times 4.2\text{ mm}$ (diameter $\times$ length) cylinders, and the contacts were aligned vertically with the movable contact above the static contact. The test parameters are shown in Table 1. The microstructure was characterized by field emission scanning electron microscopy (FESEM, SIRON, Holland). X-ray diffraction (XRD, PANalytical B. V., Empyrean 200895) analysis was performed to determine the crystalline phases in the specimens using Cu K α radiation. The scanning rate was

Table 1 Technical parameters of electrical contact materials

Technical item	Parameter
Load type	Resistive load
Specimens of contact materials	Ag-SnO_2 ; $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$
Electrodes size of specimens/mm	2.5 (diameter) $\times$ 4.2 (length)
Test voltage/V	380
Test current (AC)/A	17
Contact pressure/cN	25
Breaking speed/ m s^{-1}	1×10^{-3}
Making speed m s^{-1}	1×10^{-3}
Break-make duration/s	1 (break 0.5 and make 0.5)
Number of operations	20000
Contact gap/mm	1

Not: name of equipment: electrical life testing arrangement; manufacturer: Kunming Institute of Precious Metals; test requirements: GB14048.4-2010, JB/T7435-2006

$2^\circ/\text{min}$ and the scanning angles ranged from 10° to 80° with a sampling width of 0.02. Microhardness was measured by Vickers' indentation on polished sections with a load of 4.9 N and a dwell time of 15 s. Composition distribution was evaluated by energy dispersive spectrometer (EDS).

2 Results and Discussion

2.1 Phase composition and morphology of $\text{La}_2\text{Sn}_2\text{O}_7$ composite powder

The phase composition of $\text{La}_2\text{Sn}_2\text{O}_7$ composite powder is shown in Fig.1. It can be seen that the composite powder consists of $\text{La}_2\text{Sn}_2\text{O}_7$ and SnO_2 , which is short for $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ in the following section. The morphologies of $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and SnO_2 powders are shown in Fig.2a and 2b, respectively.

2.2 Anti-arc erosion properties and microstructure of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ composite

2.2.1 Anti-arc erosion properties

A pair of contacts of the circuit are composed of a movable and a static contacts. One commonly fixed contact is called static contact, and the other is movable contact. The anti-arc erosion properties of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and Ag-SnO_2 when

Fig.1 XRD patterns of $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and SnO_2 powder

Fig.2 SEM morphologies of $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ (a) and SnO_2 (b) powder

the contacts break are shown in Fig.3. The average arcing time of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and Ag-SnO_2 is about 15 ms, but the arcing time of the latter increases sharply around the 5000th operations. Accordingly, the regulation of arcing energy and bouncing times of both specimens are similar to that of arcing time for Ag-SnO_2 . The welding force of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ are smaller and more stable than that of Ag-SnO_2 , while contact resistance of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ is triangular distribution. The highest value is observed at about the 10000th operation. These results indicate that $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ shows better welding force compared to Ag-SnO_2 .

Mass loss of both contacts after 20 000 operations is shown in Table 2. The mass losses of the movable and static contacts of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ are higher than those of Ag-SnO_2 . The hardness of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ is lower than that of Ag-SnO_2 . In general, there should be larger contact area for the former, which is beneficial to reducing contact resistance. However, the changed surface morphology and the lower hardness of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ lead to unsteady contact resistance during the electrical testing process, and especially the higher contact resistance appears around the 10 000th operations (Fig.3d).

2.2.2 Microstructure of arced areas

Surface morphologies of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and Ag-SnO_2 contacts after arc erosion at low magnification ($35\times$) are shown in Fig.4. Part of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ is transferred to the edge of the contact, and irregular shape is formed, which is due to the lower hardness $\text{HV}_{0.5}$ of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ (808 MPa) compared with Ag-SnO_2 (1014 MPa). This may cause a higher mass loss, which is consistent with the result in Table 2. From Fig.4, it can also be observed that the surface of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ contact is flatter than that of Ag-SnO_2 , and this corresponds

Fig.3 Anti-arc erosion properties of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ (a~e) and Ag-SnO_2 (f~j) when the contacts break

Table 2 Mass loss of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and Ag-SnO_2 after 20 000 operations and their hardness

Material	Mass loss/mg		Hardness, $\text{HV}_{0.5}/\text{MPa}$
	Movable	Static	
$\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$	0.0022	0.0072	808
Ag-SnO_2	0.0009	0.0010	1014

with the effect of welding force. When welding occurs, the welding force will change the surface of the contact from a smooth one to an irregular one (see Fig.4b₁). Therefore, when the movable contact and the static contact impact each other time by time, the contact surface status changes and then makes

Fig.4 Morphologies of Ag-La₂Sn₂O₇/SnO₂ (a₁, a₂, a₃) and Ag-SnO₂ (b₁, b₂, b₃) static contact

the welding force fluctuating. From Fig.4a₂, 4a₃, 4b₂ and 4b₃), the surface morphology of Ag-SnO₂ is more complicated than that of Ag-La₂Sn₂O₇/SnO₂. The distribution of components is different in the raised and depressed areas, which leads to the differences of arcing energy and arcing time. This may be the reason for the sharp increase of arcing energy, arcing time and bouncing times of Ag-SnO₂ around the 5000th operation.

2.2.3 Discussion of anti-arc erosion mechanism

Surface morphologies and the corresponding content of each element after electrical life-testing are shown in Fig.5. The erosion mode inferred for Ag-La₂Sn₂O₇/SnO₂ is different from that of Ag-SnO₂.

From SEM and EDS analysis of Ag-La₂Sn₂O₇/SnO₂ (Fig.5a and 5b), some line-traces and small silver particles similar to “beads of sweat” appear on the surface of the movable contact, and scattered leaf-like particles attached at static contact are composed of silver and tin elements. Under arcing, silver and lanthanum stannate particles haven’t separated and no distinct enrichment area appears. While for Ag-SnO₂, obvious arc crater exists and enriched silver area (area 3) is observed (Fig.5c and 5d), which may be due to the poor wettability between silver matrix and tin oxide. These phenomena indicate that the pyrochlore-type La₂Sn₂O₇ can increase the viscosity of melt pool to some extent, and improve the binding force and the wettability between silver matrix and tin oxide, which lower surface damage with smooth arced area and better welding resistance. This could be detected by the relative stability of bouncing times and lower welding force as shown in Fig.3.

Moreover, dispersing beads-like particles are observed on the surface of Ag-La₂Sn₂O₇/SnO₂ contact. They are probably depleted particles or droplets that re-condensed back to contact surface and some are stretched into leaf-like particles by continuous arcs striking. The beads embedded scatteredly in the surface can be called “pinning effect”. When arcing, arc column

Fig.5 Surface morphologies and EDS analysis of Ag-La₂Sn₂O₇/SnO₂ (a-movable contact, b-static contact) and Ag-SnO₂ (c-movable contact, d-static contact) after electrical life-testing

would be split out and arc energy is decentralized on the arced areas by the “pinning effect”, which thus decrease the temperature rise, and weaken the damage of surface structure. According to the analysis of the surface morphologies and EDS (Fig.4 and Fig.5), $\text{La}_2\text{Sn}_2\text{O}_7$ could improve the micro-structure of arced area, uneasy to form arc crater and other uneven surface. However, higher mass loss of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ appears which is mainly ascribed to the lower hardness mentioned above and the higher splashing speed of droplets than recondensing speed under the effects of arc and mechanical forces. It can be inferred that the droplets splashing could be the erosion mode of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ after 20000 operations. For Ag-SnO_2 , however, the uneven surface with some large crater corresponds to its unstable electrical-life curve and less mass loss (shown in Table 1). It can be inferred that the erosion of Ag-SnO_2 is due to very low concentration of tin element, i.e. tin oxide or tin metal in uncombined form could stem from the sublimation of tin oxide under high temperature arcing, which loses the function of improving the strength of silver matrix and viscosity of melt pool under arcing^[11,18].

3 Conclusions

1) $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ powder can be synthesized by chemical co-precipitation and $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ contact materials can be prepared by a powder metallurgy method.

2) The arced area and “beads-like” particles embedded scatteredly in the surface of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ could decentralize arc energy by “pinning effect”, which decreases temperature rise and weakened the damage of surface structure. And better anti-welding property of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ contacts is obtained.

3) The lower hardness of $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ and mechanical and arc forces could be the main reason for its higher mass

loss.

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Ag- $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ 电接触材料的抗电弧侵蚀特性研究

张玲洁^{1,2}, 沈涛², 申乾宏^{1,2}, 张继¹, 陈乐生^{2,3}, 樊先平^{1,2}, 杨辉^{1,2}

(1. 浙江大学 材料科学与工程学院, 浙江 杭州 310027)

(2. 浙江大学 浙江加州国际纳米技术研究院, 浙江 杭州 310058)

(3. 温州宏丰电工合金股份有限公司, 浙江 温州 325603)

摘要: 采用化学共沉淀法合成了 $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ 复合粉体, 并通过粉末冶金法制备了 $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ 电接触材料; 研究了复合材料的抗电弧侵蚀性能, 并对抗电弧侵蚀机理进行了探讨。结果表明: 与 Ag-SnO_2 相比, $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ 电接触材料经电弧作用后表面形貌较为平整, 表现出较低的熔焊力。这可能是由于在电弧作用下 $\text{La}_2\text{Sn}_2\text{O}_7$ 的存在有助于提高熔池的粘滞性, 同时 $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ 触点表面分布的“小汗珠”状颗粒能够起到分散电弧能量的作用, 从而可以降低侵蚀区域的温升、减弱表面结构的破坏程度, 获得较好的抗熔焊性能。 $\text{Ag-La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$ 有望作为一种环保型电接触材料得到广泛应用。

关键词: 电接触材料; 银; $\text{La}_2\text{Sn}_2\text{O}_7/\text{SnO}_2$; 电弧侵蚀; 熔焊力

作者简介: 张玲洁, 女, 1985 年生, 博士, 助理研究员, 浙江大学材料科学与工程学院, 浙江 杭州 310027, 电话: 0571-88206798,

E-mail: zhanglingjie@zju.edu.cn