Study on the mechanical alloying process for preparing Ag/LSCO electrical contact material

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Abstract

The mechanical alloying process for preparing Ag/LSCO electrical contact materials were explored, and process parameters were optimized, such as reaction environment, process control agent types and dosage, high-energy ball milling time and the composition of Ag@LSCO intermediate composite particles. The results show that Ag/LSCO electrical contact sheet with compact structure were successfully achieved, when the reaction environment is air, 3wt% PEG6000 was employed as process control agent, the high energy ball milling time is 40h, and the Ag@LSCO intermediate composite particles were made of Ag and LSCO powders with mass ratio of 80:20. More importantly, the density, Vickers hardness and resistivity of Ag/LSCO electrical contact sheet all met or exceeded the requirements for practical application. Consequently, this study can provide a significant reference for industrial production of Ag/LSCO and other environmentally friendly silver-based electrical contact materials.

Keywords: Ag/LSCO; Ag@LSCO; mechanical alloying process; environmentally friendly; electrical contact material

Nomenclature

LSCO La0.5Sr0.5CoO3-δ
Ag@LSCO Ag-coated LSCO composite particles
Ag/LSCO(12) Ag/La0.5Sr0.5CoO3-δ, electrical contact material, in which LSCO content is 12wt%
MA Mechanical alloying
PCA Process control agent
BPR Ball-to-powder ratio

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1. Introduction

Environmentally friendly electrical contact materials are attracting more and more attention as the hazardous Ag/CdO material has being phased out in recent years[1-3]. Ag/La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (Ag/LSCO) is one of the latest environmentally friendly electrical contact material, in which Ag matrix is strengthened by evenly dispersing LSCO particles. In addition, the high electrical conductivity of LSCO is conducive to the Ag/LSCO materials to maintain low and stable contact resistance[4-5]. More importantly, LSCO can partially be decomposed at the temperature near the melting point of Ag while giving off O$_2$, which is similar to the thermal decomposition behavior of CdO, and this makes LSCO favorable for the high resistance to welding and arc erosion of Ag/LSCO material[6]. Therefore Ag/LSCO is one of the most promising environmentally friendly electrical contact materials.

The production method of silver/metal oxide(Ag/MeO) electrical contact material is mainly divided into two categories: powder metallurgy and internal oxidation method. Variety manufacturing methods around the world are all derived from the two methods[7-11]. In internal oxidation method, the metal indium must be added in the production process to improve the speed of internal oxidation[12-14]. However, the prices of indium continue to rise in recent years, and in order to control the cost, powder metallurgy method has become the most important industrialized production method of Ag/MeO electrical contact material. Mechanical alloying(MA) is a kind of powder metallurgy method. It shows the advantages of simple flow scheme, low cost and flexible composition control, and can also obtain compound with components almost atomically homogeneous[15-16]. However, few studies on the mechanical alloying process for preparing Ag/LSCO electrical contact materials have been reported by other authors so far as we know.

2. Experimental

2.1. Synthesis

Fig. 1 shows the procedure for preparation of Ag/LSCO electrical contact material by mechanical alloying. Ag and LSCO powders were employed as raw materials. With an average particle size of 6.43μm, Ag powder whose purity was 99.9%, was provided by the Wenzhou Hongfeng Electrical Alloy Co., Ltd. LSCO powder was prepared by modified sol-gel method and its particle size was approximately 50nm. The surface morphology of Ag and LSCO powders were shown in Figure 2(a) and (b) respectively. Firstly, Ag and LSCO powders were weighed according to various mass ratios and put into the milling tanks. Process control agent(PCA) was then added into the mixture and the reaction environments in milling tanks could be chosen as air or ethanol before high energy ball milling. The mechanical alloying process was carried out in the QM-WX4 horizontal planet ball mill with a speed of 300r/min, and the ball-to-powder ratio(BPR) was 10 to 1. After mechanical alloying for several hours, Ag-coated LSCO composite particles(Ag@LSCO) were obtained. The Ag@LSCO particles were sieved with a 200-mesh screen and then mixed with silver powder for 4 hours. With the balance of silver powder, mixed powders could be obtained, in which LSCO content is 12wt% (Ag/LSCO(12)). The mixed powders were then pressed into wafers of Φ18mm at 600MPa for 2 minutes. The wafers were heated to 600°C in air and held for 2 hours in order to exclude the PCA or other volatiles attached to raw material powders. Afterwards the wafers were continue to be heated to 880°C and held for 6 hours, followed by cooling to ambient temperature. Finally, the wafers were repressed at 800MPa for 2 minutes and resintered under the same sintering schedule to form Ag/LSCO(12) electrical contact material. As the Ag@LSCO particles prepared by mechanical alloying is the key step of the whole process, the parameters of the MA process, such as the reaction environment, PCA types and dosage, high energy ball milling time and the composition of Ag@LSCO composite particles, were investigated.
2.2. Characterization

The morphologies of samples were investigated by thermal field emission scanning electron microscope (FSEM, SIRION-100, FEI Co., Netherlands). The chemical composition ratio of the Ag@LSCO composite particles were determined by X-ray energy dispersive spectroscopy (EDS, GENESIS4000, EDAX Co., USA) attached to FSEM. The microstructures of Ag/LSCO(12) electrical contact materials were observed using inverted optical metallurgical microscope (OM, GX40, JVC Co., Japan). The density of Ag/LSCO(12) samples was tested using the Archimedes method. Vickers hardness was determined by the HBRVU-187.5 hardness tester. The resistivity was characterized by the D60K digital metal conductivity measuring instruments.

3. Results and discussion

3.1. Optimization of reaction environments

Table 1 shows different reaction environments and other process parameters of Ag@LSCO samples prepared by mechanical alloying. There are two groups of samples prepared in air and ethanol respectively, and other process parameters are the same. PEG6000 is employed as PCA and the dosage is 1g for each 100g mixed powders. The obtained samples are denoted as Ag@LSCO(air) and Ag@LSCO(ethanol). The morphologies of the two samples are shown in Fig. 3(a) and 3(b), and element analyses are shown in Fig. 3(c) and 3(d), respectively.

It can be seen from Fig. 3(a) and 3(b) that the raw materials began to form Ag@LSCO composite particles after mechanical alloying for 10 hours both in air and ethanol. Under the effect of high-energy ball milling, Ag particles are extended and LSCO particles are embedded in Ag matrix, the two kinds of raw materials are kneaded into Ag@LSCO composite particles. However, there are still some scattered Ag and LSCO particles as the milling time is too short or PCA is not optimized and so on. Ag@LSCO(ethanol) samples have smaller particle size but higher agglomeration degree than Ag@LSCO(air) samples. This is because ethanol plays an important role in dispersing the powder and curbing the newly formed Ag@LSCO composite particles from aggregation in the mechanical alloying process, but later in the process of drying, severe aggregation occurs among the Ag@LSCO(ethanol) particles, which is disadvantageous in the subsequent processes. Fig. 3(c) and 3(d) show that Al peak appears in the EDS patterns of Ag@LSCO(air) samples, which is because the information of the aluminum foil substrate between scattered Ag@LSCO(air) particles is detected. The particle size of Ag@LSCO(ethanol) aggregates covering the substrate is much bigger, so there is no Al peak in the EDS patterns of Ag@LSCO(ethanol) samples. Relatively speaking, the silver content in Ag@LSCO(air) samples is more in line with the ratio of raw materials than that in Ag@LSCO(air) samples, according to the EDS element analyses after normalization. That is to say the mechanical alloying reaction is likely to be carried out more completely in air. In addition, the mechanical alloying process is more simple and there is no need to use anhydrous ethanol in air. Above all, the air is more favorable in the preparation of Ag@LSCO composite particles. So the samples are prepared in air in all the following experiments.

Table 1. Different reaction environments of the mechanical alloying process for preparing Ag@LSCO samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>The mass ratio of components</th>
<th>Milling time (h)</th>
<th>Reaction environment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
<td>LSCO</td>
<td>PEG6000</td>
</tr>
<tr>
<td>Ag@LSCO(air)</td>
<td>40</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>Ag@LSCO(ethanol)</td>
<td>40</td>
<td>60</td>
<td>1</td>
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</tbody>
</table>
3.2. Optimization of PCA

Process control agent in the process of mechanical alloying can inhibit intergranular welding or agglomerate, as it can be adsorbed on powder surface and reduce surface gibbs free energy. An appropriate amount of PCA can shorten milling time and make the obtained particles finer, but excess PCA will affect atomic diffusion and contaminate samples. Generally speaking, the proportion of the amount of the PCA and the total amount of the raw material powders is from 1:100 to 5:100. In addition to the physical properties of raw material, the PCA types and dosage have significant influence on the size, shape, purity and yield of the final composite particles\cite{17}. Actually, the target compound yield is often used to evaluate the efficiency of PCA. If the target compound yield is high, the PCA added will be evaluated as valid, and vice versa.

There are six groups of samples, in which stearic acid and PEG6000 are employed as PCA, and the proportion of PCA dosage and the total mass of raw material powders were selected as 1%, 3% and 5%, respectively. Other process parameters are the same. The obtained Ag@LSCO composite particles are denoted as 1~6# samples sequentially, as shown in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>The mass ratio of components</th>
<th>Milling time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
<td>LSCO</td>
<td>Stearic acid</td>
</tr>
<tr>
<td>1#</td>
<td>40</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>2#</td>
<td>40</td>
<td>60</td>
<td>3</td>
</tr>
<tr>
<td>3#</td>
<td>40</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>4#</td>
<td>40</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>5#</td>
<td>40</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>6#</td>
<td>40</td>
<td>60</td>
<td>0</td>
</tr>
</tbody>
</table>

As can be seen from Table 2, the yield of 1~3# samples is generally lower than that of 4~6# samples. It illustrates that PEG6000 is more effective than stearic acid as process control agent used in the mechanical alloying process for preparing Ag@LSCO samples. Further more, the yield of Ag@LSCO composite particles successively increases with the increase of dosage of PEG6000 from 1% to 3% to 5%. The yield of Ag@LSCO has already reached 98.8% when the PEG6000 dosage is 3%, which is only 0.1% less than the yield of Ag@LSCO while the PEG6000 dosage is 5%. Considering the contamination brought by excess PCA, the appropriate amount of PEG6000 should better be 3%. In all the following experiments, 3% PEG6000 is employed as PCA.
3.3. Optimization of milling time

Milling time is one of the most important parameters in the process of mechanical alloying. Suryanarayana C. et al. pointed out that the appropriate milling time is precisely the time needed in MA process. The contamination degree increases when the milling time exceeds the time needed[18]. Table 3 shows the different milling time and other process parameters of Ag@LSCO samples prepared by mechanical alloying. There are three groups of samples of which the milling time is 10h, 20h and 40h respectively, and other process parameters are the same. The obtained samples are denoted as Ag@LSCO(10h), Ag@LSCO(20h), and Ag@LSCO(40h). The morphologies of the samples are shown in Fig. 4(a), 4(b) and 4(c), and the element analyses of the samples are shown in Fig. 4(d), 4(e) and 4(f), respectively.

As can be seen from the Fig. 4, with the milling time increasing from 10h to 20h to 40h, the particle size of Ag@LSCO composite particles becomes smaller and more homogeneous, and the scattered Ag and LSCO particles become less and less, and the morphologies of the samples are gradually close to the Ag@LSCO ideal model which is like a smooth sphere pitted by chicken pox, and the silver content in samples is more and more in line with the ratio of raw materials according to the EDS element analyses after normalization. The Ag@LSCO(40h) samples just accord with anticipate. In order to control the contamination degree which increases with the milling time and control costs as well, the appropriate milling time is considered as 40h, and the Ag@LSCO composite particles are prepared by mechanical alloying for 40h in all the following experiments.

Table 3. Different milling time of the mechanical alloying process for preparing Ag@LSCO samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>The mass ratio of components</th>
<th>Milling time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag@LSCO(10h)</td>
<td>40 60 3</td>
<td>10</td>
</tr>
<tr>
<td>Ag@LSCO(20h)</td>
<td>40 60 3</td>
<td>20</td>
</tr>
<tr>
<td>Ag@LSCO(40h)</td>
<td>40 60 3</td>
<td>40</td>
</tr>
</tbody>
</table>

![Fig. 4. SEM images of Ag@LSCO samples with different milling time: (a) 10h, (b) 20h, (c) 40h, the inserts are magnified SEM images, and patterns of EDS element analyses of the Ag@LSCO samples with different milling time: (d) 10h, (e) 20h, (f) 40h](image)

3.4. Optimization of the composition of Ag@LSCO intermediate composite particles

In this experiment, the optimization results of the mechanical alloying process are evaluated by the physical properties of the final Ag/LSCO(12) electrical contact materials, in which the mass percentage of LSCO is 12%. The Ag@LSCO intermediate composite particles' composition determines not only its own properties, but also the amount of Ag powder
used in the follow-up mixing step, and will have a significant impact on the performances of the final Ag/LSCO(12) sheet. There are three groups of Ag/LSCO(12) samples made of Ag@LSCO particles with different compositions, namely the mass ratio of Ag and LSCO is 40:60, 60:40 and 80:20 respectively, and other process parameters are the same. The obtained Ag/LSCO(12) sheets are denoted as 1–3# samples sequentially. The Metallograph of the 1–3# samples are shown in Fig. 5(a), 5(b) and 5(c) respectively, and the physical properties of the 1–3# samples are shown in Table 4.

As can be seen from Fig. 5, the white area represents Ag, the dispersed gray area represents LSCO and the disorderly distributed black dots represent tiny holes. There are quite a few holes in both 1# and 2# Ag/LSCO(12) samples, and the average pore size of 1# sample is slightly bigger than that of the 2# sample. The amount of holes in 3# sample decreases significantly and there is a much denser texture. According to Table 4, density, Vickers hardness and resistivity values of the 1# and 2# sample are almost alike, except the values of 2# sample are slightly higher. However, the density and Vickers hardness of 3# sample have been greatly improved, and the resistivity has been reduced significantly too, which is consistent with what the metallographic photos illustrate. Therefore, the optimal ratio (mass ratio) of Ag and LSCO is 80:20 for Ag@LSCO composite particles.

![Fig. 5. Metallograph of Ag/LSCO(12) electrical contact material made of Ag@LSCO intermediate composite particles with different compositions (mass ratio): (a) Ag : LSCO = 40 : 60, (b) Ag : LSCO = 60 : 40, (c) Ag : LSCO = 80 : 20.](image)

![Table 4. Physical properties of the Ag/LSCO(12) sheet made of Ag@LSCO particles with different compositions](table)

<table>
<thead>
<tr>
<th>Sample</th>
<th>The mass ratio of components in Ag@LSCO</th>
<th>The physical properties of Ag/LSCO(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
<td>LSCO</td>
</tr>
<tr>
<td>1#</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>2#</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>3#</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

4. Conclusions

The mechanical alloying process for preparing Ag/LSCO electrical contact materials were explored, and process parameters such as reaction environment, PCA types and dosage, high energy ball milling time and the composition of Ag@LSCO intermediate composite particles were optimized. Under the optimum technological condition that the reaction environment was air, PEG6000 was employed as PCA and its dosage was 3%, the milling time is 40h and the Ag@LSCO intermediate composite particles were made of Ag and LSCO powders with mass ratio of 80:20, the final obtained Ag/LSCO(12) electrical contact materials had the best comprehensive properties.

In practical applications, the performance of Ag/MeO(12) sheet generally claims for the density value greater than or equal to 9.5g/cm³, Vickers hardness value greater than or equal to 70 and the resistivity value less than or equal to 3.5μΩ•cm. The Ag/LSCO electrical contact sheet prepared under the optimum technological condition can meet or exceed all the physical requirements for practical application. Therefore, it has broad application prospects in the field of environmentally friendly silver-based electrical contact materials. And at the same time, the optimize technical parameters in this study can provide a reference for industrial production of Ag/LSCO and other electrical contact materials. However, the mechanical alloying process for preparing Ag/LSCO electrical contact materials is very complex. There are still a lot of factors, such as ball-to-powder ratio, fill factor, milling speed and so on, which are not embodied in this study. Consequently, the whole mechanical alloying process has yet to be further studied and improved.
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