Facile synthesis of silver-tin oxide electrical contact materials by in-situ decomposition of a uniform mixture precursor

Z J Lin¹, X D Sun¹,⁴, S HLiu¹,², M Xie², J L Chen³ and J G Li³

¹ Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110819, China
² State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Kunming Institute of Precious Metals, Kunming 650106, China
³ Advanced Materials Processing Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0044, Japan

E-mail: xdsun@mail.neu.edu.cn

Abstract. A uniform mixture precursor containing Ag₂O and Ag₂SnO₃ was synthesized via a facile ion exchange reaction method. The influence of pH value on composition and precipitation rate of the precursor was investigated systematically. The Ag-SnO₂ composite powder was obtained by decomposition of the precursor at 600°C, and uniform mixing of elements was inherited from the precursor and fresh and intimate Ag-SnO₂ interfaces were created. The Ag-SnO₂ electrical contact material was prepared using this composite powder by hot-pressing method. It was found that nano-sized SnO₂ particles (about 20.6 nm) are homogeneously dispersed in the Ag-matrix. The as-prepared Ag-SnO₂ electrical contact material shows excellent performances, such as high hardness (154 MPa), high density (9.90 g/cm³) and good electrical conductivity (72.24 %IACS).

1. Introduction

As eco-friendly electrical contact materials, Ag-SnO₂ composite materials have been widely concerned [1-3]. It is believed that the Ag-SnO₂ samples reinforced by nano-sized SnO₂ would have great anti-arc performances due to the fast moving of arc-foot and easy decomposition of SnO₂ [4, 5]. However, traditional PM method reaches its limit for homogeneously mixing nano-sized SnO₂ and Ag powders [6]. It is urgently need to obtain an effective and convenient method for preparation of Ag-SnO₂ electrical contact materials reinforced by nano-sized SnO₂.

In 1997, Linke [7] reported the formation of Ag₂SnO₃ crystals by the solid state reaction method. The modulated structure of Ag₂SnO₃ was then investigated by Takeo [8]. Feng et al. [9, 10] calculated the thermodynamic, mechanical and electronic properties of Ag₂SnO₃, revealing its positive effect on Ag-SnO₂ electrical contact materials. An ion exchange method was used to synthesize nano-sized Ag₂SnO₃ by Yin et al. [11]. The as-prepared Ag₂SnO₃ shows excellent photocatalytic performance. The Ag-SnO₂ heterogeneous nanomaterial [12] was then in situ produced by thermal decomposition of...
Ag$_2$SnO$_3$. The heterogeneous nanomaterial has a unique advantage of good photocatalytic properties, because Ag and SnO$_2$ nanoparticles contact tightly with each other. In this work, the ion exchange method was used to synthesize a mixture precursor containing Ag$_2$O and Ag$_2$SnO$_3$. We investigated systematically the effect of pH value on phase composition and precipitation rate. The thermal behaviors of the as-prepared precursor were then studied. The Ag-SnO$_2$ composite powder was then in-situ produced from the precursor by direct thermal decomposition. Finally, the Ag-SnO$_2$ electrical contact material with good mechanical and electrical properties was made by hot pressing.

2. Experiment procedure
The starting materials including silver nitrate (AgNO$_3$), sodium stannate (Na$_2$SnO$_3$), sodium hydroxide (NaOH, analytical reagent), and nitric acid (HNO$_3$) were all analytical reagent and purchased from Sinopharm Chemical Reagent Co., and used as received without further purification.

0.816 mol silver nitrate and 0.080 mol sodium stannate were added into de-ionized (DI) water to make 1000 mL solutions, respectively. The two solutions were then mixed and magnetically stirred at room temperature. Sodium hydroxide and nitrate acid solution was used to adjust pH values. After 60 min aging, the precursor was collected via centrifugation, washed several times with DI water, and dried at 100°C for 24 h in air. The obtained precursors were calcined in a muffle furnace at 600°C. The Ag-SnO$_2$ composite powders were thus obtained and then used to prepared the electrical contact materials ($\Phi$12×10 mm) by hot-pressed at 700°C with a pressure of 60 MPa.

3. Characterization techniques
Density of the Ag-SnO$_2$ contact materials was measured by the Archimedes principle. A Vickers hardness tester was used to measure the Hardness. The electric conductivity of samples was measured by an FQR 7051 vortex conductivity apparatus. DSC-TG analysis of the precursor was taken under flowing air with a heating rate of 10°C/min (QMS 403D; NETZSCH Slep, Germany). Phase identification was performed by XRD (Model PW 3040/60; PANALYTICAL B.V, Netherlands) operated at 40 KV per 40 mA, using nickel-filtered CuK$\alpha$ radiation. The contents of Ag and Sn in supernatant liquid were determined using ICP/AES (ProdigyXP; LEEMAN LABS, USA). FE-SEM was used to observed microstructures of the Ag-SnO$_2$ composite powders and electrical contact materials with an acceleration voltage of 15 kV (Ultra Plus, Carl Zeiss AG, German).

![Figure 1. XRD patterns of the precursors prepared at various pH values. Letters S, T, and O represent Sn(OH)$_4$, Ag$_2$SnO$_3$, and Ag$_2$O, respectively.](image1)

![Figure 2. The residual ratios of Ag and Sn elements in the supernatant liquid as a function of pH value.](image2)
4. Results and discussion

4.1. Preparation and characterization of the precursors

Figure 1 shows XRD patterns of the precursors synthesized at different pH values. It was found that the phase components of the precursors are highly dependent on pH value of the reaction solution. The Ag₂SnO₃ compound can only be obtained in a certain range of pH value (6~8). When the pH value is lower than 4, the Sn element exists mainly as Sn(OH)₄. While the pH value is increased to 12, Ag⁺ is captured by the extra OH⁻ to form Ag(OH), which will decompose into Ag₂O in a short time, as shown by equation (1).

\[ \text{Ag}_2\text{SnO}_3 + 2\text{OH}^- \rightarrow \text{Ag}_2\text{O} + \text{SnO}_2^{2-} + \text{H}_2\text{O} \]  

Figure 2 shows the residual ratios of Ag and Sn elements in the supernatant liquid at different pH values. The results show that both Ag and Sn rarely exist (over range of measurement) in the supernatant liquid when pH=8, indicating complete precipitation of the elements.

Figure 3. Morphology of the precursor synthesized by the in-situ reaction method (SEM) (a); the EDS maps for Ag (b) and Sn (c); EDS analysis for the three selected zones in (a): (d) zone 1, (e) zone 2 and (f) zone 3.
Figure 3 shows morphology and element distribution of the precursor synthesized at a pH value of 8. The concentration of Ag and Sn elements varies synchronously in the EDS maps. The EDS quantitative analyses were taken for three selected areas in figure 3(a). The molar ratio of Sn/Ag varies from 0.096 to 0.107, indicating that Ag and Sn elements are basically homogenously mixed in the precursor.

Figure 4. DTATG test of the Ag-Sn-O precursors at a heating rate of 10°C/ min in flowing air.

Figure 5. XRD patterns of the precursors calcined at various temperatures. Letters O, S, A and T represent Ag₂O, Ag₂SnO₃, Ag and SnO₂, respectively.

4.2. Preparation and characterization of the Ag-SnO₂ composites

The thermal decomposition behaviors were shown in figure 4. The TG curve can be described as a four-step weight loss, claimed by a series of endothermic processes, respectively. The first endothermic process below 200°C, with a weight loss of about 1.42%, is largely due to the evaporation of surface adsorbed water. The exothermic peak located at 171.2°C on the DSC curve is due to the crystallization of compounds. A sharp endothermic peak located at 354°C, accompanied by a main mass loss about 4.09%, can be attributed to the decomposition of Ag₂O. The last step weight loss starts at 400°C, with a series of fluctuate endothermic peaks in the DSC curves, which may be due to the decomposition of Ag₂SnO₃, as shown in equation (2).

\[
2\text{Ag}_2\text{SnO}_3 \rightarrow 4\text{Ag} + 2\text{SnO}_2 + \text{O}_2 \uparrow
\]  

(2)

XRD analysis also demonstrates the above results, as shown in figure 5. The existence of silver metal phase for the products calcined at 200°C may be attributed to the photodecomposition of silver compounds. The precursor was transformed into Ag-SnO₂ composite at 600°C. Crystallinity of the SnO₂ was further improved at 800°C.

The morphology and element distribution of the obtained Ag-SnO₂ composite powders calcined at 600°C are shown in figure 6. The concentration of silver and tin elements varies synchronously in the EDX maps. During the thermal decomposition, both silver and tin oxides are in-situ created from the precursor. Therefore, the Ag-SnO₂ composites inherit the uniform mixing from the precursor.

4.3. Preparation and characterization of the Ag-SnO₂ electrical contact materials

XRD pattern of the Ag-SnO₂ electrical contact material reveals that the sample is composed of metal Ag and SnO₂. No other phases exist, as shown in figure 7. The size of the SnO₂ particles is about 20.6 nm calculated by the Scherrer equation.

Microstructure of the Ag-SnO₂ electrical contact materials are shown in figure 8. Higher magnification observation indicates that the SnO₂ particles (black color) are distributed uniformly in the Ag-matrix. Lower magnification observation reveals that the uniform distribution exists in a large
Figure 6. SEM image of the Ag-SnO$_2$ composite powders calcined at 600°C (a), and the EDS maps for Ag (b) and Sn (c).

Figure 7. XRD pattern of the Ag-SnO$_2$ electrical contact materials prepared by hot-pressing. Letters S and T represent Ag and SnO$_2$, respectively.

area. In our previous work [13], nano-sized SnO$_2$ reinforced Ag-SnO$_2$ electrical contact materials were prepared by the sol-gel method. The physical and electrical properties of the Ag-SnO$_2$ electrical
Figure 8. Microstructure of the Ag-SnO$_2$ electrical contact materials prepared by hot-pressing (SEM), with (a) lower magnification and (b) higher magnification.
contact materials are compared in table 1. The relative density of both samples is higher than 99.5% (the theoretical density is about 9.92 g/cm$^3$), indicating the effective densification by the hot-pressing method. In contrast to the sample prepared by the sol-gel method, the sample prepared by the present ion exchange method shows a higher values of hardness, density and electrical conductively, which may be due to the uniform mixture and strong bonding between tin oxide and silver matrix. The contact resistance between the SnO$_2$ particles and Ag matrix is therefore significantly reduced in the sample prepared by the ion exchange method.

**Table 1.** Physical and electrical properties of the Ag-SnO$_2$ electrical contact materials.

| Sample          | Hardness (MPa) | Density (g/cm$^3$) | Electrical conductively (%IACS) |
|-----------------|----------------|-------------------|-------------------------------|
| In-situ method  | 154            | 9.90              | 72.24                         |
| Sol-gel method  | 123            | 9.87              | 68.97                         |

5. Conclusion

In this work, a mixture precursor containing Ag$_2$O and Ag$_2$SnO$_3$ was synthesized via an ion exchange method using sodium stannous and silver nitrate as the starting materials. A homogeneous precursor mixture of Ag$_2$O and Ag$_2$SnO$_3$ was obtained. The precursor was decomposed into a mixture of Ag and SnO$_2$ after being calcinated at 600°C. During the calcination process, the Ag and SnO$_2$ particles were in-situ created from the precursor and inherited the uniform mixing of different phases. The Ag-SnO$_2$ electrical contact material was fabricated by hot-pressing. The nano-sized (about 20.6 nm) SnO$_2$ particles are homogeneously dispersed in the Ag-matrix. Fresh and stable interfaces between the SnO$_2$ particles and the Ag-matrix may be formed by the in-situ reaction. The contact resistance between the SnO$_2$ particles and the Ag-matrix is therefore significantly reduced. As a consequence, the as-prepared Ag-SnO$_2$ electrical contact material shows good performance in hardness, density and electrical conductively.

Acknowledgments

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