The effects of citric acid on the synthesis and performance of silver–tin oxide electrical contact materials

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ABSTRACT

A sol–gel auto-combustion method was developed to synthesize the Ag–SnO$_2$ composite powders, which were then used as the starting material to prepare Ag–SnO$_2$ electrical contact materials by hot pressing. It was found that citric acid strongly influences the thermal behaviors, phase evolution, morphology and composition distribution of the Ag–SnO$_2$ composite powders. During the synthesis of Ag–SnO$_2$ composite powders, citric acid can facilitate the formation of sol solution, lower the energy required for the decomposition of dry gel, and reduce the agglomeration of particles. Besides, a comparatively high molar ratio of citric acid to metal ions prevents effectively the occurrence of composition segregation in the Ag–SnO$_2$ electrical contact materials. Therefore, the prepared Ag–SnO$_2$ electrical contact materials have good performances in density, hardness and electric conductivity.

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1. Introduction

As an eco-friendly electrical contact material, Ag–SnO$_2$ has been the focus of attention over the past two decades and exhibits excellent behaviors in hardness, arc erosion and anti-welding properties [1–6]. Usually, Ag–SnO$_2$ electrical contact materials are produced via internal oxidation (IO) [7–11] and powder metallurgy (PM) [12–20]. Due to the high cost in high pressure equipment, application of the IO method is limited. Furthermore, radial composition segregation usually exists in the IO process. The PM method has a vast potential due to its advantages of controllable composition, simple equipment and less erosion [21]. As is known, nano-scale SnO$_2$ particles can increase the mechanical properties of Ag–SnO$_2$ electrical contact materials and decrease erosion rate to some extend [22,23]. However, it was found that fine SnO$_2$ particles tend to aggregate in the Ag–SnO$_2$ composites in the conventional PM method, even though the overall conductivity of sample would be raised, but on the other side it is detrimental to mechanical properties [6,24]. For industrial applications, the SnO$_2$ clusters can be dispersed via severe plastic deformation [25], but this measure prolongs production time and raises energy consumption. An electroless plating method was once developed by Wolmer et al., [22,26] through which the as-prepared fine SnO$_2$ particles (around 100 nm) were distributed into the Ag-matrix, and mechanical and anti-erosion properties of the Ag–SnO$_2$ electrical contact materials were thus improved. Yet, Ag–SnO$_2$ electrical contact materials with evenly distributed nano-size SnO$_2$ particles (below 50 nm) have rarely been reported. There is an urgent need for convenient methods to improve the dispersion of SnO$_2$ in the Ag matrix to achieve high performance of the contact materials.

Recently, the sol–gel auto-combustion method has been widely used to synthesize alloys and composite materials because of its advantages of simple equipment, low process temperature, short time consumption and mixing of composition at molecular level. The kind of fuel is a rather important parameter, and in the previous researches different fuels such as urea [27], citric acid [28–32], glycine [33,34], EDTA [34] and ethylene glycol [35] were studied. Considering the strong chelating capacity with silver [36–38] and tin [39] ion, citric acid was chosen as the complexant in the present Ag–Sn system. The steric-hindrance effect of citric acid was also taken into account for obtaining uniform particles.

In this work, Ag–SnO$_2$ electrical contact materials were made by hot pressing, using Ag–SnO$_2$ composite powders synthesized by the sol–gel auto-combustion method. We systematically investigated the influence of citric acid on thermal behaviors, phase evolution, morphology and composition distribution of the Ag–SnO$_2$ composite powders, as well as the corresponding performance of the Ag–SnO$_2$ electrical contact materials.

2. Experiment details

2.1. Reagents

The starting materials including silver nitrate (AgNO$_3$, analytical reagent), tin (Sn, 99.999% in purity), citric acid anhydride (C$_6$H$_8$O$_7$·H$_2$O, analytical reagent), and nitric acid (HNO$_3$, analytical reagent) were purchased from Sino-platinum metals and Sinopharm Chemical Reagent Co., and used as received without further purification. Tin (II) nitrate solution was obtained by dissolving the tin granules with 3 mol L^{-1} HNO$_3$ in an ice water bath.

2.2. Synthesis of the Ag–SnO$_2$ composite powders and contact materials

The mass radio of Ag to SnO$_2$ is 88:12 in the final electrical contact materials. The synthesis condition of dry gel precursors of the Ag–SnO$_2$ composite powders with or without citric acid was as follows.

Without citric acid: In a typical synthesis, silver nitrate and tin (II) nitrate were mixed and magnetically stirred at 55 °C in DI water until the dark red colloids disappeared, and milk white colloids appeared instead. The red and white colloids were separately collected via centrifugation, washed several times with DI water, rinsed with ethanol, and dried at 80 °C for 24 h in air. The milk white colloids were then heated up to 100 °C to condense the solution into cellular dry gels under mild stirring.

With citric acid: In a typical synthesis, silver nitrate and tin (II) nitrate were mixed with citric acid solution, and then the mixture were stirred at 55 °C until a colorless transparent colloid solution was obtained. The colloid solution was finally heated to 100 °C to condense into cellular dry gels under mild stirring.

The obtained dry gels were calcined in a muffle furnace. Brown gases (mixture of NO$_x$ and CO$_y$) released during the calcination process. The Ag–SnO$_2$ composite powders were thus obtained and then hot-pressed to fabricate the electrical contact materials (Φ20 × 5 mm) in a graphite die at 700 °C with a pressure of 60 MPa under the protection of argon.

2.3. Characterization techniques

Density of the Ag–SnO$_2$ contact materials was measured by Archimedes method. Hardness was determined using a Vickers hardness tester. An FQR 7051 vortex conductivity apparatus was used to investigate the electric conductivity of the Ag–SnO$_2$ contact materials. DTA/TG analysis of the precursor was made under flowing oxygen with a heating rate of 10 °C/min (Model SETSYS Evolution-16; SETARAM, Lyons, France). DSC measurement was carried out under nitrogen atmosphere at a heating rate of 10 °C/min (DSC 404 F3 Pegasus; NETZSCH, Sleb, Germany). FT-IR spec-troscopy was performed by the standard KBr method (Spectrum RXI; Per-kin–Elmer, Shelton, CT). XRD analysis was conducted under 40 kV/40 mA using nickel-filtered Cu Kα radiation (Model PW 3040/60; PANALYTICAL B.V, Almelo, the Netherlands). Particle morphologies were observed via FE-SEM with an acceleration voltage of 10 kV (Model JSM-7001F; JEOL, Tokyo, Japan). Microstructures of the Ag–SnO$_2$ electrical contact materials were examined by SEM (JSM-6510A; JEOL, Tokyo, Japan).

3. Results and discussion

3.1. Ag–SnO$_2$ composite powders prepared in the absence of citric acid

Fig. 1 shows XRD patterns and appearances of the red and milk white colloids obtained in the absence of citric acid. Dark red colloids appeared immediately when silver nitrate and tin (II) nitrate were mixed. XRD analysis indicates that the dark red colloid is a mixture of silver and tin hydroxide, as shown in Fig. 1a. It seems that an oxidation–reduction reaction occurred first in the process according to Eq. (1), and the hydrolysis reaction occurred subsequently via Eq. (2). The colloids turned milk white after 4 h mild stirring at 55 °C, corresponding to the dissolution of silver element, as shown in Fig. 1b. With the raising of temperature, the equilibrium of the redox reaction in Eq. (3) moves to the right, resulting in the disappearance of silver in the reaction solution. Tin hydroxide remained, as shown in Fig. 1b. The early precipitation of tin hydroxide tends to lead to the phase separation in the final electrical contact materials.
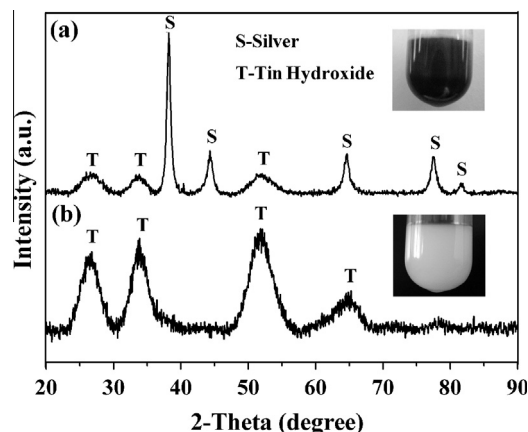
$$Sn^{2+} + Ag^+ \rightarrow Sn^{4+} + Ag \downarrow \tag{1}$$

$$Sn^{4+} + H_2O \rightarrow Sn(OH)_4 \downarrow + H^+ \tag{2}$$

Fig. 1. XRD spectra of the two kinds of colloid appeared in the sol–gel process without adding citric acid. (a) The dark red colloids obtained when tin (II) nitrate and silver nitrate mixed immediately, (b) the milk white colloids obtained after the colloids being heated at 55 °C for 4 h. The insets show the images of the corresponding colloids, respectively.

$$Ag + H^+ + NO_3^- \rightarrow Ag^+ + NO \uparrow + H_2O \tag{3}$$
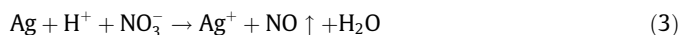
Thermal behaviors of the gel precursors have been investigated via DTA/TG, and the results are shown in Fig. 2. A three-step weight loss process was observed from the TG curve. The first step shows a slight weight loss in the region 100–220 °C, which is characterized by two endothermic peaks. The endothermal peak located at about 181 °C on the DTA curve indicates the decomposition of tin (IV) hydroxide. The other endothermic peak at 210 °C may be due to the melting of silver nitrate. A noticeable endothermic peak on DTA curve between 250 °C and 300 °C corresponds to the loss of water in SnO$_2$·xH$_2$O, with a slight weigh loss of 0.5%. The third step on the TG curve shows a weight loss of about 31%, which is accompanied by an intense endothermic peak at 400 °C on the DTA curve, indicating the decomposition of silver nitrate to form silver metal. The phase evolution is verified by XRD analysis, as shown in Fig. 3. Diffraction intensity of the tin oxide increases with increasing temperature owing to the gradually enhanced crystallization of the tin oxide.

Fig. 4 shows SEM image of the Ag–SnO$_2$ composite powders calcined at 400 °C in air. It can be seen that the composite powders after calcination were severely agglomerated, which may be attributed to the melting of silver nitrate.

3.2. Ag–SnO$_2$ composite powders prepared in the presence of citric acid

The inset in Fig. 5 shows the appearance of transparent sol solution obtained when citric acid was introduced into the reaction
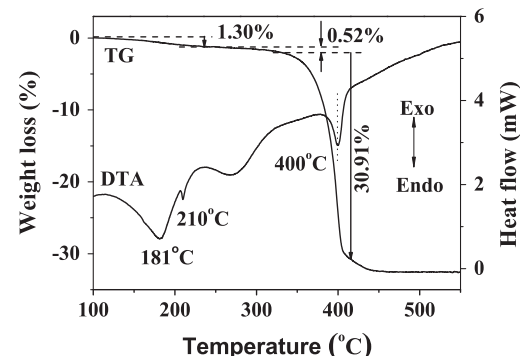

Fig. 2. DTA/TG test of the obtained gel precursors, synthesized without adding citric acid, at the heating rate of 10 °C/min in oxygen.