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A novel route to prepare and characterize Sn–Bi nanoparticles

Hongjie Chen, Zhiwei Li, Zhishen Wu, Zhijun Zhang*

Key Laboratory of Special Functional Materials, Henan University, Kaifeng 475001, China

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Abstract

A sonochemical method of synthesis for Sn–Bi nanoalloy directly from bulk Sn–Bi alloy is introduced in this paper. The nanoparticles were found to be monodispersed and the size distribution was influenced by the ultrasonic power. The formation and composition of the as-prepared Sn–Bi nanoparticles were revealed by X-ray diffraction (XRD), differential thermal analysis (DTA) and thermogravimetry (TG), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). It was found that the Sn–Bi eutectic alloy nanoparticles consisted of the tetragonal phase of tin and the rhombohedral phase of bismuth. In addition, we also found the powder had excellent antiwear properties through tribological test results.

Keywords: X-ray diffraction; Differential thermal analysis; Thermogravimetry; Transmission electron microscopy

1. Introduction

When two or more kinds of metals are melted together, the melting point, rigidity, conductivity and extensibility will change considerably, so that nanoalloy materials can exhibit many novel properties, including electronic, catalytic, magnetic and corrosion-resistant properties [1,2]. In fact, nano-sized solids often exhibit many properties distinct from those of the bulk, in part because nano-clusters have electronic structures that have a high density of states, but not yet continuous bands [3,4]. In recent years, many methods have been developed to prepare nanoalloy materials including ball milling (BM) [5,6], reduction [7–11], crystallization of non-crystalline state [12,13], pulsed electrodeposition [14] and laser vaporization controlled condensation (LVCC) [15]. In addition, the sonochemical method has become a new route for preparing metal or alloy nanoparticles. In liquids irradiated with high intensity ultrasound, acoustic cavitation leads to a collapse of bubbles producing intense local heating (5000 °C), high pressures (1000 atm), at a very short lifetime (heating and cooling rates above 10^{10} K/s). The transient, localized hot spots can generate high-energy chemical reactions [16,17]. Suslick and co-workers [18,19], and Kurikka et al. [20,21] have made a complete and deep study in this field. Many nano-sized metal and alloy particles prepared by sonochemical method have been reported in the last few years [22–25]. All the metal or alloy nanoparticles produced by this method used volatile organometallic compounds (usually metal carbonyls) as precursors, which made the process difficult for the following reasons: the as-prepared nanoparticles can easily agglomerate, the preparation processes needs to be performed under inert gas, the precursors have a strong toxicity.

To our knowledge, no fusible binary or multicomponent nanoalloy system prepared by ultrasonic radiating bulk alloy directly in the liquid has been reported so far in the literature. Here we will discuss, the sonochemical synthesis and characterization of Sn–Bi alloy nanoparticles. The possible growing mechanism of the Sn–Bi nanoparticles includes three processes: melting, dispersion and homogenization. In this paper, we provide detailed characterizations including X-ray diffraction (XRD), thermogravimetry–differential thermal analysis (TG–DTA), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) to study the shape, composition and structure of Sn–Bi nanoalloy. We also studied the antiwear properties of the Sn–Bi nanoparticles.

* Corresponding author.
E-mail address: chjhenan@yahoo.com.cn (H. Chen).

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2. Experimental

Tin (99.9% pure) and bismuth (99.5% pure) granules were from Tianjing Nankai Chemical Co. and Tianjing Dongda Chemical Co., respectively. Paraffin oil and Chloroform were both of AR grade from Luoyang Chemical Co. and Laiyang Chemical Co., respectively.

Twenty grams Sn and 30 g Bi were melted together in a vessel to obtain the bulk Sn–Bi alloy and the Sn–Bi alloyed nanoparticles were prepared by sonochemical method. In a typical synthesis, 0.5 g bulk Sn–Bi alloy was added to 30 ml paraffin oil in a horniness test tube and the system was ultrasonic irradiated at 1000 W cm^{-2}, under ambient pressure and room temperature, with a high intensity ultrasonic probe (Sonics and Materials, Model KS-1500, 1.8 cm Ti horn, 20 kHz, 1500 W cm^{-2}). Two hours later, the liquor was centrifuged after cooled to room temperature and washed for at least three times with chloroform, at last, dried to get some gray-black powder.

X-ray diffraction measurements were performed on an X'Pert Philips diffractometer equipped with Ni-filtered Cu Kα radiation and operating at 40 kV and 40 mA. Differential thermal analysis and thermogravimetry (using an Exstar 6000 thermal system) were conducted on the powder in the 20–600 °C temperature range, with a heating rate of 10 °C/min and in dynamic air. Transmission electron microscopy, high-resolution TEM images were obtained using a JEOL-2010Ex microscope (Japan) (at an acceleration voltage of 200 kV) with the sample deposited on a carbon-coated copper grid. The preparation of a sample for TEM involved deposition of a drop of colloidal solution onto a carbon-coated copper grid. The antiwear properties were tested with a four-ball machine, under the conditions of an angular velocity of 1450 rpm, 30 min for each and ambient temperature. A ball of 12.7 mm in diameter, with a hardness of HRc 64–66, was used. The base fluid was analytical pure paraffin oil with boiling point above 300 °C. At the end of each test, the mean wear scar diameter on the three lower balls was measured using a digital-reading optical microscope with an accuracy of 0.01 mm.

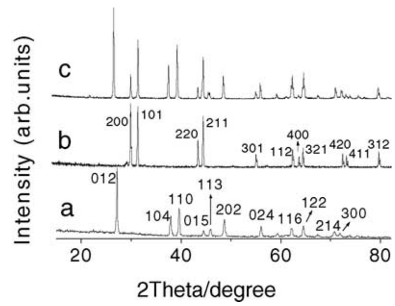

Fig. 1. Powder X-ray diffraction pattern for Sn–Bi eutectic alloy nanoparticles.

3. Results and discussion

The XRD patterns shown in Fig. 1 are obtained from (a) bismuth, (b) tin and (c) the as-produced Sn–Bi nanoparticles, respectively. It is clear that the prominent peaks occurring in the XRD pattern of the Sn–Bi nanoalloy contain all the peaks shown in the XRD patterns attributed to the metals bismuth and tin. In addition, no other peaks that might be attributed to metal oxides were found in pattern (c), which indicated that no oxidation reactions took place in the process. To find out the composition of the powder, we studied the DTA curve of the sample as shown in Fig. 2. It is apparent that only one sharp and narrow endothermic peak was found at 140.8 °C in the curve. It reveals that the powder consists of Sn–Bi eutectic alloy nanoparticles and not simply of a mixture of tin and bismuth nanoparticles. The XRD pattern of the Sn–Bi eutectic alloy nanoparticles is completely the same as that of the bulk alloy, which indicates that the crystal shape of Sn–Bi alloy has not changed in the process of ultrasonic irradiation. The peaks at scattering angles (2θ) of 30.64, 32.02, 43.88, 44.91, 55.34, 62.53 and 79.51, are assigned to scattering from the 200, 101, 220, 211, 301, 112 and 312 tetragonal tin lattice planes, respectively.

In addition, the peaks at scattering angles (2θ) of 27.33, 38.27, 39.86, 48.93, 56.03 and 64.68, are assigned to scattering from the 012, 104, 110, 202, 024 and 122 rhombohedral bismuth lattice planes, respectively. From the discussion above, it can be concluded that the Sn–Bi nanoparticles are the eutectic alloy, which consists of the tetragonal phase of tin and the rhombohedral phase of bismuth.

Fig. 2 displays the thermal stability of Sn–Bi nanoparticles, which was studied by DTA/TG. It is apparent that the sample shows an endothermic region and an exothermic region on the DTA curve. The endothermic peak at 140.8 °C is attributed to the melting point of the Sn–Bi eutectic alloy nanoparticles in the sample. The exothermic peak at 290 °C and the corresponding large mass increase, evidenced by the TG curve, are mainly due to the oxidation of Sn–Bi nanoalloy in the sample above 280 °C, while below 250 °C, no mass increase was found, which indicates that the nanoalloy was steady in a wide temperature range. In addition, the decomposition of organic residuals will result in a little decrease in the sample weight, which is much very smaller than the

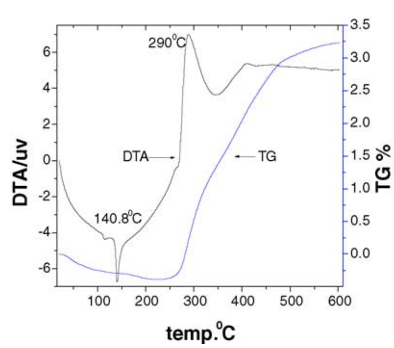

Fig. 2. DTA/TG curves of Sn–Bi nanoparticles.