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PREPARATION OF NANOCRYSTALLINE ANTIMONY POWDERS BY USING γ-RAY RADIATION METHOD

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ABSTRACT

Pure nanocrystalline antimony powders have been prepared by using γ-ray radiation method in ambient pressure and room temperature. Transmission electron micrographs and X-ray powder diffraction patterns show that the smallest average particle size is 8 nm and the particle size distribution of this sample is from 5 to 25 nm

KEYWORDS: A. metals, A. nanostructures, B. chemical synthesis, C. electron microscopy, C. X-ray diffraction

INTRODUCTION

There has been considerable interest in preparing and studying nanocrystalline metal materials because of the size effect of their structure, physical and chemical properties and potential applications [1]. Nanosized metal powders are expected to display better properties than antimony powders of course grain in, for example, catalyst [2] and recording materials [3,4]. Gas-evaporation method was applied to produce ultrafine antimony powders, but it requires vacuum and as low as liquid nitrogen temperature [5]. Nanocrystalline antimony powders might be synthesized by homogeneous reduction with alkalides or electrides in aprotic solvents at –50 °C, where the experimental conditions were very strict and the procedure was complicated [6]. Oxide-coated nanocrystalline antimony particles were prepared by irradidating solid metal azides with electron beam in electron microscope, the disadvantages of which were that the product was not pure and the procedure was not suitable to produce in large scale [7]. In this paper, we report the preparation of nanocrystalline antimony powders by irradiating aqueous solutions of antimonous chloride with γ-ray under ambient pressure in room temperature. The basic principle of this method is as follows:

$$H_2O \xrightarrow{\text{radiate}} H_2O_2, OH, HO_2, H, H_3O^+, H_2, e^-_{aq}$$

where e^-_{aq} can effectively reduce metal ions (M^{m+}),

$$e^-_{aq} + M^{m+} \rightarrow M^{(m-1)+}$$

$$e^-_{aq} + M^{+} \rightarrow M$$

then metal atoms novelly produced aggregate in aqueous solution, and form nanocrystalline particles.

EXPERIMENTAL

Solutions were prepared by adding analytical grade antimonous chloride $SbCl_3$ in distilled water, dropping sodium hydroxide to prevent Sb^{3+} from hydrolysis. Polyvinyl alcohol (PVA) or sodium dodecyl sulfate (SDS) was chosen as a surfactant and isopropanol as a scavenger for hydroxyl radicals. All solutions were bubbled with nitrogen for 1 hour to remove oxygen, then irradiated in a field of a 70,000 Ci ^{60}Co γ-ray source. Antimony sediment was separated from irradiated system by directly precipitating for several hours. The precipitate was washed with degassed distilled water and alcohol and dried in a vacuum drier at 60 °C. The antimony powders are grey black.

X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of 0.05° S^{-1} with a Japan Rigaku D_{max} γ_A X-ray diffractometer, using monochromatic high-intensity Cu K_α radiation (=1.5418 Å). TEM images were taken with a Hitachi model H-800 transmission electron microscope (TEM), operating at 200 KV accelerating voltage. The particle sizes of powders were measured from microphotographs and calculated from XRD patterns according to Scherrer formula $L = K\lambda/(\beta\cos\theta)$, where L is average particle size.

RESULTS AND DISCUSSION

Typical XRD pattern of pure antimony powders of sample 2 (in Table 1) is given in Figure 1 (a). Only the samples dried in vaccum are pure antimony powders. The XRD pattern of sample 2 dried in air at 60 °C, given in Figure 1 (b), shows that the sample contains some impurity of Sb_2O_3 (indicated by solid circles). This case has proven that reactive metal antimony in nanosize is not stable in air above 60 °C. The average particle size calculated from Figure 1 (a) is 20 nm.

The microphotographs in Figure 2 show the quasi-sphere shape of the antimony particles for samples 2 and 9 (Table 1). The average particle sizes are consistent with those caculated from XRD. The distribution range of particle sizes is 5-25 nm for sample 2 and 5-30 nm for sample 9, respectively. The TEM images also show that the particle size of sample 2 is greater than that of sample 9.

Our experimental conditions have an influence on particle size and yield of antimony powders. The correlations between the experimental conditions and average particle sizes are listed in Table 1. Table 1 reveals that the concentration of Sb^{3+}, the concentration of the

TABLE 1
The Correlations Between the Experimental Conditions and the Experimental Results

Sample No.	Sb^{3+} ion (M)	Surfactant	Radiation dose	Average particle size (nm)	Yield rate (%)
1	0.005	0.1% PVA	5.14×10^4 Gy	15	
2	0.01	0.1% PVA	..	20	45
3	0.01	0.1% PVA	..	24	
4	0.02	0.1% PVA	..	26	
5	0.03	0.1% PVA	..	29	
6	0.01	0.01% PVA	..	42	
7	0.01	0.05% PVA	..	33	
8	0.01	0.2% PVA	..	8	
9	0.01	0.01% MSDS	..	24	
10	0.01	0.04% MSDS	..	8	
11	0.01	0.1% PVA	6.24×10^4 Gy	42	62
12	0.01	0.1% PVA	8.82×10^4 Gy	56	70

surfactant, and the radiation dose have an influence on particle size. An increase of Sb^{3+} concentration results in a slight increase in the average particle size. As the Sb^{3+} concentration changes from 0.005 to 0.03 M, the average particle size correspondingly changes from 15 to 29 nm.

PVA and SDS were used as surfactants in this experiment. The higher the PVA concentration is in the solutions, the smaller the average particle size obtained. As the PVA concentration increases from 0.01% to 0.2%, the average particle size decreases from 42 nm to <10 nm. The effectof SDS is the same as that of PVA. It is better for PVA to produce even particle size.

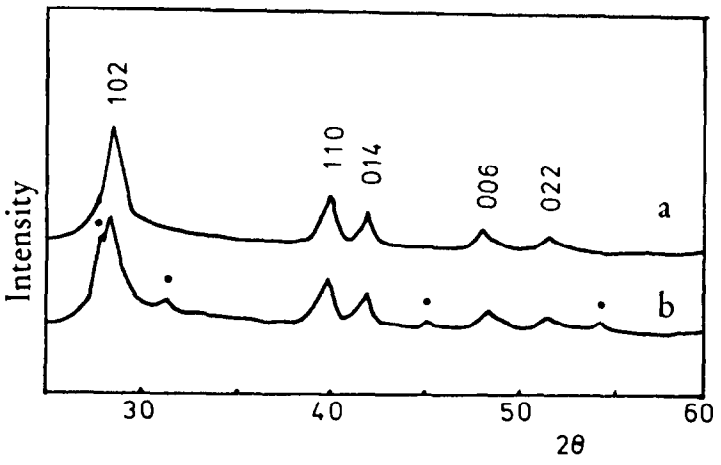

FIG 1
XRD patterns of antimony powders of sample 2 (Table 1): (a) dried in vacuum and (b) dried in air at 60 °C. Solid circles indicate impurity of Sb_2O_3.

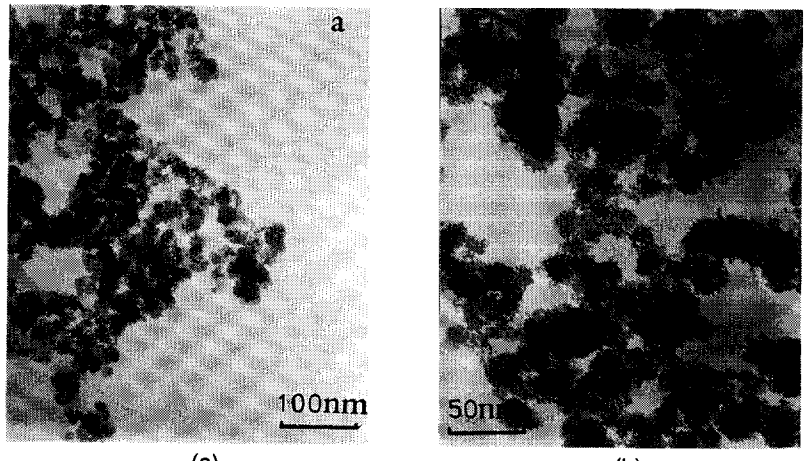

FIG. 2
Microphotographs of antimony powders of (a) sample 2 and (b) sample 9.

Increase of radiation dose can increase yield. As the radiation dose 4 4 changes from 5.14 $\times 10^4$ Gy to 8.82 $\times 10^4$ Gy, the yield changes from 45% to 70%. But the yield decreases when Sb^{3+} concentration increases if the radiation dose is the same, because the more Sb^{3+} ions in solution cannot be reduced by hydrated electrons (e^-_{aq}). Since too high of a radiation dose apparently causes the increase in particle size of molybdenum powders (such as sample 11), the radiation dose should be controlled in the range of 5.0×10^4 Gy to 6.5×10^4 Gy.

CONCLUSION

Pure and narrowly distributed nanocrystalline antimony powders have been prepared under ambient pressure and in room temperature under the following experimental conditions: 0.005-0.03 M Sb^{3+} ion concentration, 0.01-0.2% PVA concentration, radiation dose of 5.0×10^4 Gy-6.5×10^4 Gy, and dried in vaccum. The optimum condition of preparation is 0.01 M Sb^{3+}, 0.2% PVA or 0.04 M SDS and 2 M isopropanol in solution; the solution is radiated with 5.14×10^4 Gy. Under this condition, the average particle size of antimony powders is 8 nm and the distribution of particle size is from 5 to 25 nm.

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