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Original Research Paper

Preparation of Bi_2Te_3 thermoelectric powders by applying the recycled TeO_2 to wet chemical process

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ABSTRACT

Extraction of TeO_2 from the byproduct solution generated during the copper smelting process and application of the extracted TeO_2 to the preparation of Bi–Te alloy thermoelectric materials were performed via a wet chemical processes. In the wet chemical process, powder purifying steps were optimized by adjusting the pH of NaOH solvent to dissolve the initially extracted Te compounds and by washing the finally extracted powders. TeO_2 powders used in preparing the Bi–Te alloy thermoelectric materials could be successfully extracted from the byproduct solution by the optimized wet chemical process. Powders synthesized by applying the commercial and the extracted TeO_2 powders to the wet chemical process showed identical crystal structures of Bi_2Te_3 and a mean particle size of ~3 μm. Thus, it is believed that the recycled TeO_2 powders will be very useful in the preparation of Bi–Te alloy thermoelectric materials.

1. Introduction

Bi_2Te_3 is regarded as one of the best thermoelectric materials for thermoelectric applications at ambient temperatures [1–3]. Various methods for the preparation of Bi_2Te_3 have been developed, and the most widely used of these is the metallurgical melt process. To apply the metallurgical melt process to prepare Bi_2Te_3, pure elements should be melted at an elevated temperature, uniformly mixed for a prolonged period of time, and then cooled gradually to form Bi–Te alloys [1]. The chemical homogeneity of Bi_2Te_3 has a direct effect on its thermoelectric properties; therefore, it is crucial that the prepared Bi_2Te_3 should maintain a stable molar ratio of Bi–Te to ensure feasible thermoelectric properties. In the metallurgical melt process, it is difficult to prepare Bi–Te alloys with a relatively accurate molar ratio of 2:3 due to the different vapor pressures of Bi and Te at an elevated temperature. In addition, the metallurgical melt process requires a considerable investment in terms of both equipment and labor.

Chemical processes, such as coprecipitation, metal salt reduction, and solver thermal reaction processes, have been applied in the preparation of Bi_2Te_3 with relatively accurate molar ratios of Bi–Te, such as 2:3. Ritter [4] prepared Bi_2Te_3 powders through the hydrogen reduction of coprecipitated bismuth and telluride as oxides from an aqueous solution. Ritter and Maruthamuthu [5] introduced an alternative chemical process to prepare Bi_2Te_3 powders using organometallic precursors. Yu et al. [6] reported a solvothermal reaction of metal oxalate $Bi_2(C_2O_4)_3$ with Te in an organic solvent at a relatively low temperature that produced crystalline Bi_2Te_3. Chemical processes are highly promising means of obtaining Bi–Te alloy powders with a relatively accurate molar ratio. However, the metal precursors used with thermoelectric materials are very expensive. Therefore, the chemical process has no economic advantages over the metallurgical melt process. Thus, it is vital to secure inexpensive precursors for the preparation of high-performance thermoelectric materials via a chemical process.

The principal source of Te is anode sludges that are produced during the electrolytic refining of blister copper. The byproducts generated during the in Cu smelting process contain a large quantity of Te as well. In this study, therefore, the precursor for Te was initially secured by extracting the TeO_2 from the byproducts generated during the Cu smelting process. Subsequently, the recycled precursor was applied to the Bi_2Te_3 powder preparation.

2. Experimental

2.1. Extraction of Te precursor (TeO_2) from byproducts generated during the Cu smelting process

Byproducts generated during the Cu smelting process were used for the preparation of recycled Te precursor (TeO_2). LS-NIKKO Copper Inc., one of the largest Korean Cu smelting companies, supplied the byproduct. The byproduct was a NaOH solution with a

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Table 1
Concentrations of metal elements in the waste solution generated from copper smelting process.

Element	Concentration	
	(wt.%)	(mg/L; ppm)
Fe	–	0.96
Cu	ND	ND
As	–	150.3
Se	–	10.5
Te	17.4	–
Pb	ND	ND

large amount of tellurium and extremely small amounts of other elements, including Fe, Cu, As, Se, and Pb. The results of an ICP (inductively coupled plasma) analysis of the byproduct solution (Table 1) showed that the byproduct solution contained Te at ~17 wt.% with other elements at less than ~160 ppm. Fig. 1 shows the TeO_2 preparation process from the byproduct solution. In the removal of Fe, Cu, and Pb, NaSH was added to the byproduct solution. The reactions of Fe, Cu, and Pb with NaSH caused the productions of metallic sulfides of FeS, CuS, and PbS, and these metallic sulfides were removed by filtration. The extraction of TeO_2 from the byproduct solution after the removal of Fe, Cu, and Pb was performed simply by adjusting the byproduct solution pH to ~5.5. The extracted TeO_2 was dissolved in NaOH solutions of approximate pH 10–13 again. The process of the extraction and dissolution of the TeO_2 was repeated four times for the preparation of pure TeO_2. The finally extracted TeO_2 was subjected to a washing process, which was performed several times to rinse the Na_2SO_4 produced during the TeO_2 extraction process.

2.2. Preparation of Bi_2Te_3 by applying the extracted (TeO_2) to a wet chemical process

Fig. 2 shows the preparation process of Bi_2Te_3 powders by applying the prepared TeO_2 to a wet chemical process. Aqueous solutions of 0.1 M bismuth chloride ($BiCl_3$; Sigma–Aldrich, St. Louis, MO) and 0.1 M tellurium oxide, as prepared in this study, were prepared by dissolving the precursors in HCl. NaOH (9 N) solution was also prepared by dissolving NaOH (Kanto chemical, Tokyo, Japan) in distilled water. Bismuth chloride (20 mL) solution was mixed with 30 mL of tellurium oxide solution by continuous magnetic stirring in a flask. The NaOH solution was added to the mixture until the pH was ~7, and the final mixture was refluxed at ~100 °C for ~30 min. The precipitants were then separated by centrifugation, washed in distilled water, and dried in an oven at 60 °C for ~24 h.

2.3. Characterization

Crystal structure analyses of the prepared powders were performed using an X-ray diffractometer (XRD; D/Max 2200, Rigaku, Tokyo, Japan) with CuKa radiation. The morphologies of the prepared powders were examined by field emission scanning electron microscopy (FE-SEM; S4200, Hitachi, Tokyo, Japan).

3. Results and discussion

During the purification of the extracted TeO_2 powders, the pH of the NaOH solvent has a significant effect on the purity of the TeO_2.

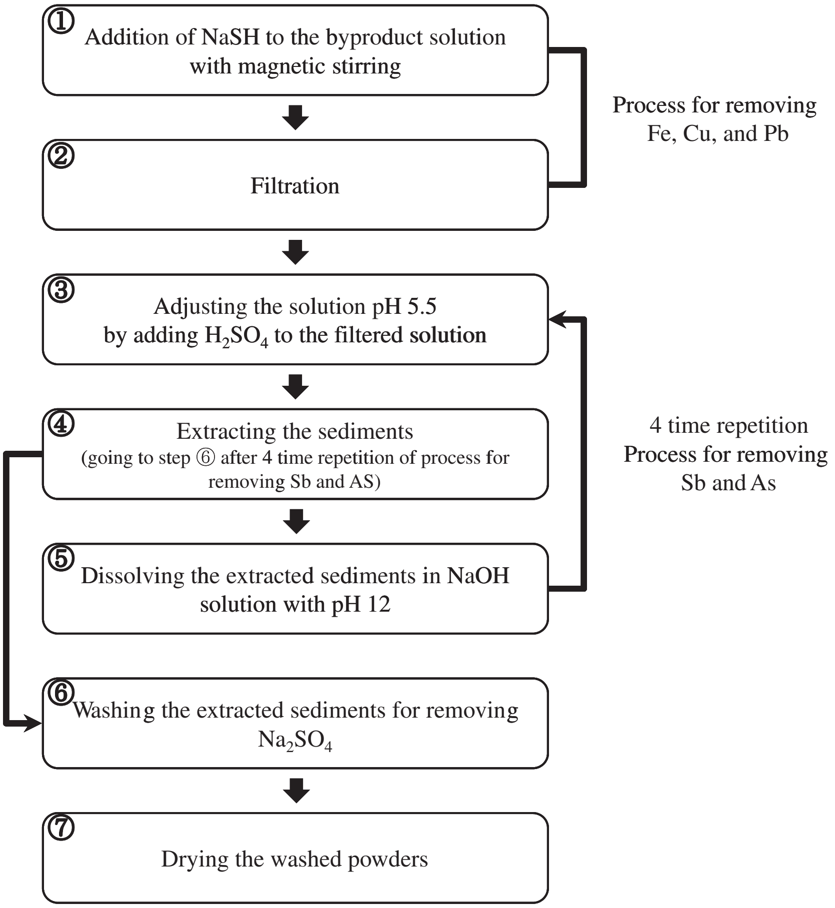

Fig. 1. Experimental flow chart for extraction of TeO_2 powders in waste solution generated from copper smelting process.