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A simple route for synthesis of SnO_2 from copper alloy dross

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Abstract Separation/recovery of valuable metals such as zinc, nickel or tin from copper alloy dross has recently attracted from the viewpoints of environmental protection and resource recycling. In this study, preliminary investigation on separation of tin (Sn) from copper alloy dross using selective dissolution method was performed. The tin in the copper alloy dross did not dissolve in an aqueous nitric acid solution which could allow the concentration/separation of tin from the copper alloy dross. Precipitation of tin as H_2SnO_3 (meta stannic acid)occurred in the solution and transformed to tin dioxide (SnO_2) after drying process. The dried sample was heat-treated at low temperature and its crystal structure, surface morphology and chemical composition were investigated.

Key words Selective recovery, SnO_2, Copper alloy dross

1. Introduction

Copper alloy dross resulting from pyrometallurgical copper processes is important by-products to be controlled in structure and chemical composition. Due to the significant volumes of dross compared with those of the target meal, it is mandatory to use the dross as a product. After matte smelting and standard dross cleaning in submerged arc furnaces, the alloy dross still contains copper and other valuable metals like nickel, cobalt or tin [1]. In addition, future regulations may restrict the heavy metal contents in ores to be decreased in the available deposits, much below the upper value of discarded dross. Therefore, sustainable dross management is necessary from the economical and environmental point of view. Moreover, the processing of secondary materials for the recovery of valuable metals in an environmentally acceptable manner with low energy, capital and operating costs has been given due attention in the metal extraction/recovery [2, 3]. In order to recover copper, nickel or tin as value added product from the dross generated in a copper alloy smelter, a process comprised of concentration and separation steps has to be developed.

Tin dioxide (SnO_2) is an important semiconducting material which has been widely used in an extensive range of applications such as catalysts, gas sensors, heat mirrors, varistors, transparent electrodes for solar cells and opto-electronic devices [4, 5]. Tin dioxide-based gas sensors are very important n-type semiconductor sensors which can be utilized to detect various inflammable and harmful gases such as hydrogen (H_2) and carbon dioxide (CO_2) [6]. Tin dioxide has been synthesized by various synthesis methods such as direct strike precipitation, two-step solid state synthesis, microemulsion, gel combustion technique and hydrothermal synthesis [7, 8]. In this study, preliminary study on concentration and separation of tin from copper alloy dross by a selective dissolution method using nitric acid was performed. The separated tin base precipitate was heat-treated to crystalline SnO_2 and its phase characteristics, surface morphology and chemical composition were investigated.

2. Experimental

The copper alloy dross used in this study was served from Seowon Co., Ltd. The chemical composition was analyzed by XRF (X-ray Fluorescence, mass %): 65.51 % Cu, 8.64 % Sn, 19.37 % Zn, and other metals (Pb, Ni, etc). The nitric acid was analytical grade without further purification. Dissolution experiment was carried out in 2 L beaker and concentration of nitric acid was fixed at 4 M. To minimize the effect of the exothermic reaction of nitrous oxide fumes and hydrogen evolution, 10 g of the copper alloy dross was added to 500 mL aqueous nitric acid solution. Magnetic stirring was controlled at 200 rpm for uniform dissolving and tem-

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perature of the solution was maintained at 85°C for 3 hrs.

After 3 hrs of dissolving time, the solution was centrifuged at 4,000 rpm for 5 min in order to separate precipitate. The centrifuged precipitate was dried at 120°C for 10 hrs. The phase analysis and thermal property of the precipitate was performed by XRD (X-ray diffraction) and TG-DT (Thermogravimetric-Differential thermal) analysis. The precipitate was calcined at 700°C based on the TG-DT result and the heat-treated sample was investigated using XRD and field emission scanning electron microscopy (FE-SEM) for crystalline phase and surface morphology. The chemical composition of the heat-treated sample was examined using x-ray fluorescence (XRF) analysis.

3. Results and Discussion

In general, the choice of a dissolving agent depends on various factors [9], which includes the chemical and physical characteristics of the material to be dissolved, selectivity, cost of the reagent and its ability to be regenerated. The performance of the dissolving agent for the precipitate of tin in the copper alloy dross was investigated using aqueous nitric acid solution. Nitric acid is a strong oxidizing reagent which is able to corrode most of the metals in the copper alloy dross. Its selectivity, in terms of dissolution properties for copper, lead, nickel, zinc and tin of the dross has considerable advantages over hydrochloric or sulfuric acid, which may present problems due to the formation of undesirable precipitates. In addition, the low cost of HNO_3 and the possibility of its easy regeneration and re-use is attractive.

During the dissolving the copper alloy dross in aqueous nitric acid solution, copper reacts to form copper nitrate according to the reaction;

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO(\uparrow) \quad (1)$$

Lead is dissolved by nitric acid to form soluble lead nitrate by the following reaction;

$$Pb + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2(\uparrow) \quad (2)$$

Other important metals such as nickel and zinc also react with nitric acid. Nickel forms nickel(II) nitrate, and zinc is oxidized to zinc nitrate;

$$Ni + 4HNO_3 \rightarrow Ni(NO_3)_2 + 2H_2O + 2NO_2(\uparrow) \quad (3)$$

$$3Zn + 8HNO_3 \rightarrow 3Zn(NO_3)_2 + 4H_2O + 2NO(\uparrow) \quad (4)$$

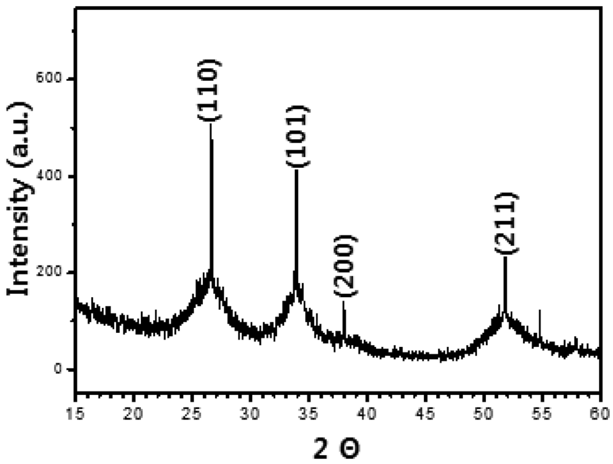
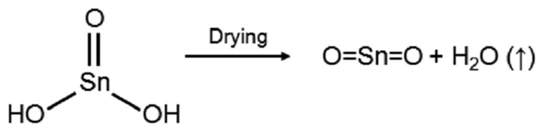


Fig. 1. XRD pattern of dried precipitate after centrifuge.

However, when tin is treated with nitric acid, a precipitate of hydrous stannic oxide (metastannic acid) is formed [10];

$$Sn + 4HNO_3 \rightarrow H_2SnO_3(\downarrow) + H_2O + 4NO_2(\uparrow) \quad (5)$$

Fig. 1 shows the XRD patterns of the precipitated sample after drying. Although the peaks are very broad, the XRD patterns confirm the presence of single phase SnO_2 (tetragonal system, JSPDS 41-1445) for all peaks. This indicates that tin was precipitated in a metastannic acid phase during dissolving in the aqueous nitric acid, and subsequently crystallized to tin dioxide (SnO_2) phase. During the subsequent drying process, H_2SnO_3 decomposed to produce H_2O and SnO_2. The synthetic route for tin dioxide can be expressed as follows based on the XRD result;



(6)

TG-DT analysis was performed to determine thermal behavior of the precipitated phase and hence to choose an optimum calcination temperature as shown in Fig. 2. Total weight loss is occurs in two stages as shown in TG curve. First, weight loss is observed lower than 250°C due to physically-adsorbed water. Secondly, chemically adsorbed water is removed from the sample from 250 to 600°C and this resulted in the endothermic peaks in DT curve. The results of TG-DT study indicates that when the precipitated sample is heated at temperatures to 600°C, all the reactions in the sample are complete. That is, further heating above 600°C of the precipitated sample does not cause any thermal and/or

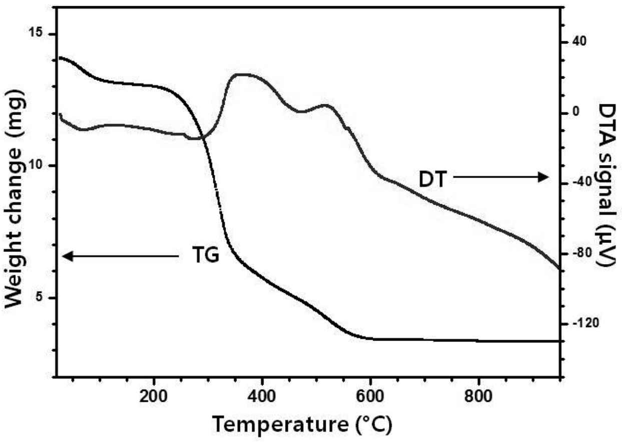


Fig. 2. TG-DTA curve for the dried precipitate.

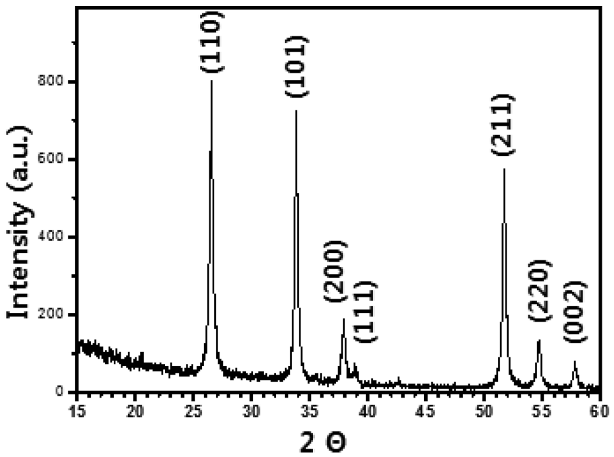


Fig. 3. XRD result of the SnO_2 after heat-treatment at 700°C for 1 h.

weight changes. These TG-TD results are also in agreement with the previous studies using conventional synthetic routes [11]. Based on the TG-DT analysis, the precipitate was calcined at 700°C for 1 h, and the XRD pattern for the heat-treated sample is shown in Fig. 3.

Table 1
The chemical composition of the heat-treated SnO_2 sample measured by XRF

Chemical composition (mass %)									
Cu	Pb	Fe	Sn	Al	Ni	Zn	Sb	Si	Mn
3.32	0.21	0.37	91.50	-	-	2.35	-	-	0.02

The heat-treated sample exhibit single SnO_2 phase with high crystallinity compared to the precipitate before heat-treatment.

Table 1 shows the chemical composition of the heat-treated SnO_2 sample measured by XRF analysis. As shown in Table 1, the heat-treated SnO_2 sample was composed of 91.50 % Sn, 3.32 % Cu, 2.35 % Zn, 0.21 % Pb, 0.37% Fe and 0.02 % Mn, which indicates the selective dissolution method can be a simple and efficient separation method for tin metal from copper alloy dross.

Fig. 4(a) shows TEM and electronic diffraction pattern (EDP) of the heat-treated SnO_2 particles. The EDP of SnO_2 particles showed clear ring patterns, corresponding to the highly crystallized phase. TEM morphology in Fig. 4(a) showed that the sizes of the SnO_2 particles are under 10 nm with primarily spherical shape. Fig. 4(b) shows FE-SEM of the heat-treated SnO_2 particles which are composed of conglomerates of nanosized crystals with spherical and homogeneous morphology corresponding to the TEM results.

4. Summary

The recovery/separation of tin (Sn) from copper alloy dross has been successfully achieved using a selective dissolution method in aqueous nitric acid. The tin in the copper alloy dross didn't dissolve in the aqueous nitric acid solution which could allow the concentration/sepa-

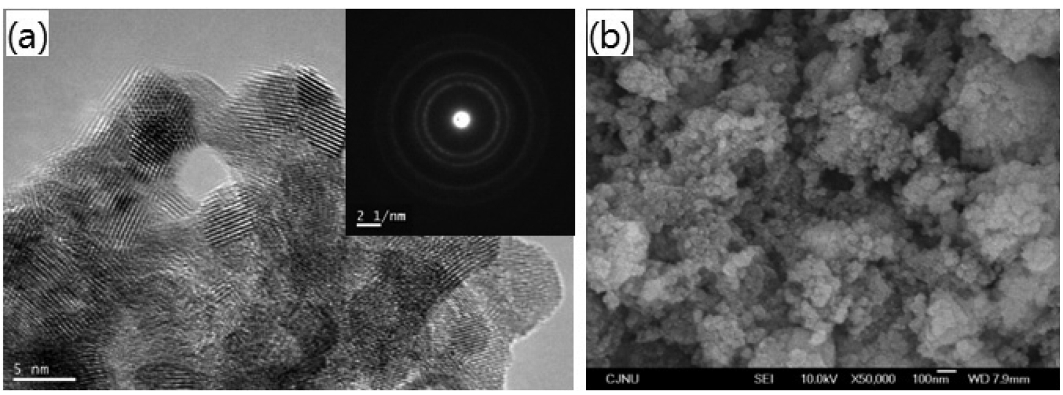


Fig. 4. Microscopic observation of the heat-treated SnO_2 sample; (a) TEM with EDP (inset) and (b) FE-SEM picture.

ration of the tin from the copper alloy dross. The solid phase H_2SnO_3 was precipitated in the solution and transformed to tin dioxide (SnO_2) after drying process. Highly crystallized SnO_2 powder was obtained by a low-temperature heat-treatment, which indicates the selective dissolution method can be a simple and efficient separation for valuable metal resource from copper alloy dross.

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