

Synthesis of nanocrystalline SnO₂ by a selective dissolution of copper alloy dross

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In this report, preliminary study on concentration and 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 H₂SnO₃ (metastannic acid) occurred in the solution and transformed to nanocrystalline tin dioxide (SnO₂) after drying process. The dried sample was heat-treated at low temperature and its phase characteristics, surface morphology and chemical composition were investigated.

Key words: Nanocrystalline SnO₂, Selective dissolution, Copper alloy dross.

Introduction

Tin oxide is a well-known functional material used for gas sensors and transparent electrodes [1-3]. The physical state of polycrystalline tin oxide, e.g., the grain size and morphology, is decisively important, particularly for gas sensors. Xu et al., for example, have reported that the gas sensitivity to reducing gases of sintered-block-type sensors using tin oxide depends on the crystallite size of the tin oxide [4]. The sensitivity begin to increase sharply as the crystallite size decreases below a critical value (6 nm), which is equal to twice the thickness of the Schottky barriers penetrating into the tin oxide grains. Tin oxide grains contained in gas sensors should be smaller than 20 nm and stable from thermal growth during the sensing operation at elevated temperature from 300 to 600 °C. These requirements have been met for sensor devices of the sintered-block or thick-film types, which are conventionally fabricated from a fine powder of tin oxide.

Since the beginning of the industrial era, dross or slags the glassy materials left over when metals are pyrometallurgically extracted from ores, have been considered waste. One such material is copper dross which is produced during matte smelting and converting steps of pyrometallurgical production of copper. Utilization of copper dross for application such as Portland cement replacement in concrete, and /or a

cement raw material has the dual benefit of eliminating the costs of disposal, and lowering the cost of the concrete. Therefore its use was explored by several investigations and they have utilized the dross in diversified ways like recovery of metal values [5].

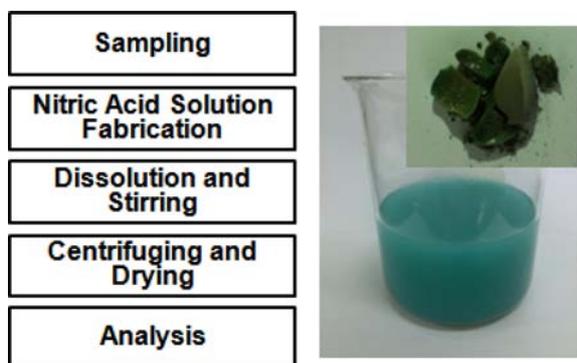
Copper alloy dross resulting from pyrometallurgical copper processes is important by-products to be controlled in structure and chemical composition. Due to the significant volumes of dross compared with those of the target meal, it is mandatory to use the dross as a product. After matte smelting and standard dross cleaning in submerged arc furnaces, the alloy dross still contains copper and other valuable metals like nickel, cobalt or tin [6]. 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 economic 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 [7, 8]. In order to recover copper, nickel or tin as value added product from the dross generated in a copper alloy smelter, a process comprising of concentration and separation steps has to be developed. In this study, preliminary study on concentration and separation of tin from copper alloy dross by selective dissolution method using nitric acid was performed. The separated tin base precipitate was heat-treated to nanocrystalline SnO₂ at low-temperature, and its phase characteristics, surface morphology and chemical composition were investigated.

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Table 1. Chemical composition of the copper alloy dross by XRF.

Chemical composition (mass %)					
Cu	Zn	Sn	Pb	Fe	Si
66.70	16.34	9.54	3.08	0.34	0.17

**Fig. 1.** Experimental procedure, the copper alloy dross solution and centrifuged precipitate (inset) are represented.

Experimental Procedure

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 %): 66.7% Cu, 9.54% Sn, 16.34% Zn, and other metals (Pb, Ni, etc) as shown in Table 1. 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 to 4 mol%. 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 temperature of the solution was maintained at 85 °C for 3 h.

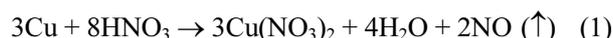
After 3 h of dissolving time, the solution was centrifuged at 4,000 rpm for 10 min in order to separate precipitate as shown in Fig. 1. The centrifuged precipitate was pulverized and dried at 100 °C for 24 h. The phase analysis and surface morphology of the dried sample was performed by XRD, FE-SEM, EDX and TEM.

Results and Discussion

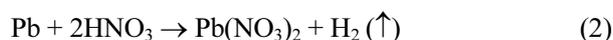
In general, the choice of a dissolving agent depends on various factors [9], which include the chemical and physical character of the material to be dissolved, selectivity, cost of the reagent and its ability to be regenerated. The performance of the dissolving agent for the precipitate of tin in the 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, hydrobromic and sulfuric acid, which may present problems due to the formation of undesirable precipitates. In addition, the low cost of HNO₃ and the possibility of its easy regeneration and re-use is attractive.

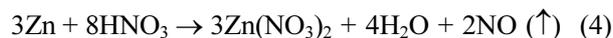
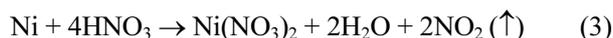
During the dissolving the copper alloy dross in aqueous nitric acid solution, copper reacts to form copper nitrate according to the reaction:



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



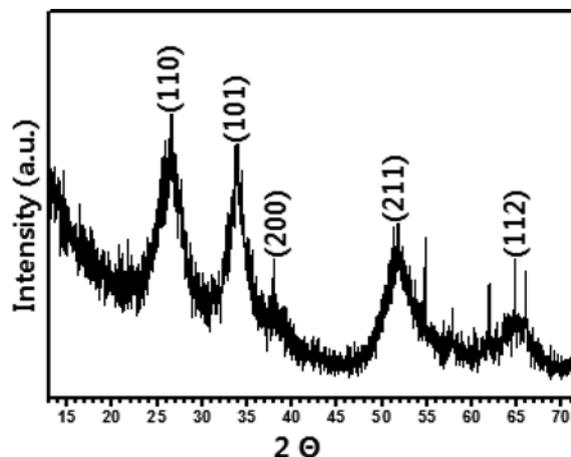
Other important metals such as nickel and zinc also react with nitric acid. Nickel forms nickel (II) nitrate, and zinc is oxidized to zinc nitrate:



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



Fig. 2 shows the XRD pattern of the precipitated sample after washing and drying. Although the peaks are very broad, the XRD patterns confirm the presence of single phase SnO₂ in rutile structure (tetragonal system, JSPDS 41-1445) for all peaks. This indicates that tin was precipitated in a metastannic acid phase

**Fig. 2.** XRD pattern of the dried precipitate after centrifuge process.

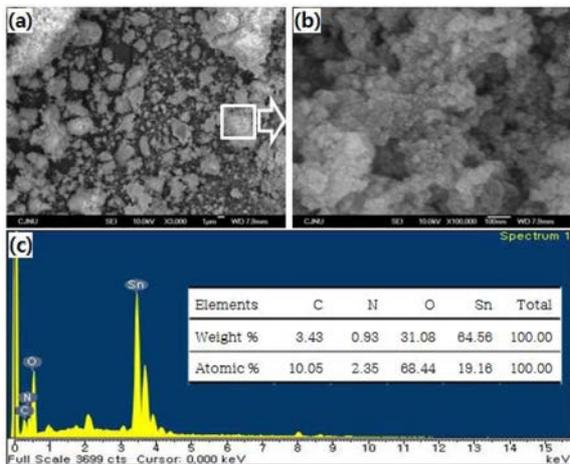


Fig. 3. FE-SEM pictures (a, b) and EDX spectrum of the dried SnO₂ sample (c).

Table 2. Chemical composition of the dried SnO₂ sample measured by XRF.

Chemical composition (mass %)					
Cu	Zn	Sn	Pb	Fe	Si
1.56	0.85	95.64	0.21	–	–

during dissolving in the aqueous nitric acid, and subsequently crystallized to tin dioxide (SnO₂) phase. During the subsequent drying process, H₂SnO₃ decomposed to produce H₂O and SnO₂. The evaporation of H₂O can create nanopores in the SnO₂ particles [11] and synthetic route for tin dioxide can be expressed as follows based on the reaction (5). The crystallite sizes of the dried SnO₂ sample was calculated by means of XRD line broadening measurement according to Scherrer's equation [12]. The calculated crystallite size was 6.5 nm.

Figure 3 shows the FE-SEM micrographs at different magnifications and EDX spectrum of the dried SnO₂ sample. Fig. 3(a) and (b) represent aggregates of very fine nanoparticles that cannot be virtually distinguished or measured whose sizes are less than 10 nm with primarily spherical morphology. The micrograph shows a homogeneous distribution of the nanoparticles, which appear to have particle size less than 10 nm, and particle size distributions are uniform. The chemical composition analyzed by EDX was almost tin and oxygen, which indicates the selective dissolution may be an efficient method for recovery of Sn from copper alloy dross.

Table 2 shows the chemical composition of the dried SnO₂ sample analyzed by XRF. As shown in Table 2, the dried SnO₂ sample was composed of 95.64% Sn, 1.56% Cu, 0.85% Zn and 0.21% Pb, which is consistent with the EDX result.

Figure 4 shows TEM micrograph with different magnification and electronic diffraction pattern (EDP) of

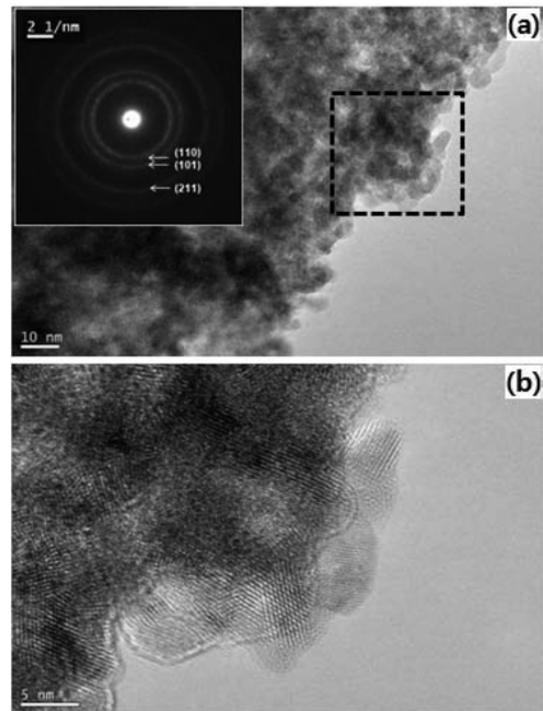


Fig. 4. TEM micrographs with different magnification and EDP patterns (inset).

the dried SnO₂ precipitate. The EDP of SnO₂ particles showed clear ring patterns, corresponding to crystallized phase of the XRD result. The TEM micrograph shows a uniform and homogeneous distribution of the nanoparticles, which appear to have particle size less than 10 nm, which is consistent with XRD and FESEM results. TEM morphology in Fig. 4(a) and (b) showed that the sizes of the SnO₂ particles are distributed from 5 to 10 nm and though some larger nanoparticles can be seen, they are likely to be aggregates of the still smaller particles as shown in (b). Therefore, the XRD, FE-SEM, TEM results indicate that the selective dissolution method can be a good choice for the selective recovery of tin and synthesis of tin oxide (SnO₂) from copper alloy dross.

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 separation of the tin from the copper alloy dross. The solid phase H₂SnO₃ was precipitated in the solution and transformed to highly crystallized tin dioxide (SnO₂) after drying process, which indicates the selective dissolution method can be a simple and efficient separation for valuable metal resource from copper alloy dross.

Acknowledgments

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