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Non-thermal reduction of indium oxide and indium tin oxide by mechanochemical method

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ABSTRACT

A non-thermal process for reducing indium(III) oxide (In_2O_3) and/or indium tin oxide (ITO) into indium-metal by milling with lithium nitride (Li_3N) under (NH_3) or nitrogen (N_2) gas environment is proposed in this paper. Milling operation causes mechanochemical reaction in the systems of In_2O_3/ITO and Li_3N , to form In and LiOH. The latter is soluble in water, so that the milled sample was subjected to washing with water, enabling us to recover indium-metal. According to the characterization of the milled products by X-ray diffraction (XRD), the reduction of In_2O_3/ITO can be achieved in a short period of time. Analytical data by inductively coupled plasma (ICP) from dissolution of the pellets in acidic solution clearly shows that indium-metal concentration is over 95% and the yield of In from the starting oxide sample is more than 97%, depending on the milling condition. The reaction mechanism between In_2O_3/Li_3N and NH_3/N_2 is also discussed in the paper, and this could be applied to recover indium-metal from electric device wastes containing ITO.

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1. Introduction

Indium (In), a rare metal, is generally found in low concentrations in sulphide ores, and most commonly associated with zinc-bearing materials and less in copper and lead from which indium is obtained in by-products such as residues, flue dusts, and slags. It has many important applications; mainly as thin films of indium tin oxide (ITO) for liquid crystal displays (LCDs). It also finds application as constituent of fusible alloys with precious and base metals, lowering their melting points, in electrical components and semiconductors in the form of indium phosphide (InP), among others [1-4]. Demand for indium in Japan reached 888 t in 2006, of which about half of the material was recovered from scrap and a large amount could be recovered from weld metal alloys, scraped ITO and indium phosphide in LCDs [1]. Recovery of indium from sulfate or chloride leach liquors by hydrometallurgical processing routes followed by solvent extraction, cementation etc. is widely reported in literature [5–9]. However, there has still been a strong demand to recover indium (metal) from a waste material containing In. Recently, Zhang et al. have reported on application of mechanochemical phenomena to recover useful materials from wastes [10-13]. Similarly, Kano et al. have reported mechanochemical reaction between gallium (Ga) and/or gallium oxide (Ga_2O_3) and Li_3N under NH_3 , preparing GaN as a main product. This reaction seems to be non-thermal reduction of oxide through mechanochemical reaction with an aid of reducing agents. The reducing agents are Li_3N and NH_3 in this case, and they play a significant role in the reduction of the oxides. Kano et al. have extended their reduction process to In_2O_3 to form In-metal [14–16].

The main purpose of this paper is to provide information on a non-thermal process for recovering In–metal through mechanochemical reduction of In_2O_3/ITO by its milling with Li_3N under non-oxidation state of NH_3 and/or N_2 gas environments. The milled sample was subjected to washing with water to recover In–metal as pellets. The purity of the recovered In–metal is over 95%.

2. Experimental

In₂O₃ and Li₃N used as starting materials were supplied by Wako Pure Chemical Industries, Ltd., Japan and ITO sample was supplied by Aldrich.

A planetary ball mill (P-7, Fritcsh, Germany), having a pair of ZrO₂ mill pots, charged with 24 × 10 mm diameter ZrO₂ balls each was used for the milling of In₂O₃ and Li₃N, and was conducted under either NH₃ or N₂ gas atmospheres, respectively to induce mechanochemical reaction between the starting materials. The diameter and length of the mill pots are the same values as 40 mm and inner pot volume of ca. 45 cm³. 2.76 g sample mixture of In₂O₃ (2.0 g) and Li₃N (0.76 g) (1:3 (mol/mol) ratio) was carefully mixed inside a glove box under argon gas environment, and charged into the mill pot and the pot was set in a container made of stainless steel (overpot). The inner air in the mill pot was degassed with a vacuum pump, and NH₃ and/or N₂ gases were charged at 0.8 MPa, respectively. Both charged mill pots were set on mill device and rotated at 300 rpm for different times ranging from 30 to 180 min.

After the milling operation, a small amount of the product was removed for characterization and the milled product was further washed in the same mill with

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Fig. 1. Schematic illustration of the experimental procedure used to effect mechanochemical reduction of In₂O₃/ITO.

water for 10 min to remove the by-product. A schematic flow of the operation to form In from the oxides is given in Fig. 1.

The milled samples were characterized by XRD analysis using Rigaku, RINT-2200/PC system with a CuK α irradiation source (λ = 1.5405 Å) at 40 kV and 20 mA in a continuous scan mode between 10° and 60° in 2 θ . 0.1 g of the solid pellets obtained after washing was dissolved in nitric acid for analysis by ICP (Optima 3300, PerkinElmer) to evaluate purity and recovery of indium.

3. Results and discussion

3.1. Milling under NH₃ and N₂ gas environments

Fig. 2 shows XRD patterns of the samples of In_2O_3 , and the mixture of In_2O_3 and Li_3N at (1:3) molar ratio each milled for 120 min under NH₃ and N₂ gas environments. The XRD patterns of the milled mixtures indicate that complete reduction of In_2O_3 to In-metal has been achieved under both gas environments, with no significant effect, except for the peak height. The height of the main peak for NH₃ is slightly higher than that for N₂, suggesting that NH₃ is rather effective reductant than N₂. All the same, peaks of the starting materials in both products are not seen in the patterns, indicating complete reduction of oxide is achieved within 120 min of milling under this condition.

Fig. 3 shows XRD patterns of In_2O_3 sample and other three kinds of mixture of In_2O_3 and Li_3N at different molar ratios of (1:1) to (1:3), each milled for 120 min under NH₃ gas atmosphere. It is seen that the sample of In_2O_3 without Li_3N (1:0) shows no peaks of In-metal in the pattern. As for the milled mixtures, significant peaks of In are seen in the patterns, and the peaks of In for the (1:3) mixture is more sharp than those for the (1:2) mixture. This means that the amount of Li_3N added to In_2O_3 is important and more amount of Li_3N is better for the reduction of In_2O_3 . In other words, excess Li_3N is appropriate to cause the reduction of In_2O_3 into In in the milling condition.



Fig. 2. X-ray diffraction patterns showing effects of NH₃ and N₂ gases during MC reduction of ln_2O_3 by milling in the presence of Li₃N. Mixing ratio of ln_2O_3/Li_3N was fixed at (1:3) moles and milling conducted for 120 min at 300 rpm.

Fig. 4 shows XRD patterns of a mixture of In_2O_3 and Li_3N at (1:3) molar ratio milled for different periods of time under NH₃ gas atmosphere. Peaks of In-metal clearly appear for the sample mixtures milled for 30 min and as milling is progressed, the In_2O_3 peaks completely disappear from the patterns. It is seen that intensity of In-metal peaks significantly increase in the patterns of the mixtures as milling progresses. However, further milling for more



Fig. 3. X-ray diffraction patterns showing effect of Li_3N addition from 0 to 3 mols $(In_2O_3/Li_3N = 1:0, 1:1, 1:2, 1:3)$ on MC reduction of In_2O_3 by milling in NH₃ gas for 120 min at 300 rpm.



Fig. 4. X-ray diffraction patterns of In_2O_3/Li_3N (1:3) mixture milled in NH_3 gas environment for different milling times at 300 rpm.

than 120 min does not make sense, and no significant change in the pattern for the samples milled for 120 and 180 min. Consequently, prolonged milling is preferable for the reduction of In_2O_3 , but too much milling is not effective at all.

3.2. Washing the milled sample to collect In-metal

Washing the mixtures of In_2O_3 and Li_3N prepared at (1:3) molar ratio, milled for different periods of time was performed to collect In-metal.

Fig. 5 shows photographs of In-metal pellets recovered from the sample mixtures milled for different periods of time. It is seen that In-metal can be recovered from the mixture milled for only 30 min, and it looks almost the same figures in all the milling periods of time.

The induced solid state reaction between In_2O_3 and Li_3N under NH_3 and N_2 gas atmospheres could be given by the following Eqs. (1) and (2):

$$In_2O_3 + Li_3N + NH_3 \rightarrow 2In + 3LiOH + N_2$$
(1)

$$In_2O_3 + 2Li_3N + N_2 \rightarrow 2In + 3Li_2O + 2N_2$$
(2)

In the preliminary experiment, milling the staring mixture $(In_2O_3 \text{ and } Li_3N)$ for 120 min in the absence of NH₃ and N₂ gases gave us the result of the formation of indium–metal in the product, although, peaks of In_2O_3 remained as a dominant component in the product. Thus, a partial reaction between In_2O_3 and Li_3N would be shown as below, when NH₃ and N₂ gases are not present;

$$In_2O_3 + 2Li_3N \rightarrow 2In + 3Li_2O + N_2$$
 (3)

Chemical constituents of the In–metal pellets recovered are shown in Table 1. The purity of indium in the pellets is around 95% in spite of the milling periods of time. As for the lithium as impurity in the pellet, it shows around 0.5% or less. Total percent is accounted as a sum of In purity (%) and Li impurity (%), and these values are ranged from 94.5% to 97.1% for all milling conditions. These data are slightly lower than those in In recovery calculated from the weight of the starting sample and In purity. This may be due to experimental loss detected and the main loss would be caused from the un-reacted In_2O_3 during the milling operation.



Fig. 5. Shows photographs of In-metal pellets obtained after milling In₂O₃/Li₃N (1:3) mixture in NH₃ gas atmosphere for different times between 30 and 180 min and washed in water for 10 min resulting in formation of pellets.

Table 1

Evaluation of purity and recovery for In-metal as a function of grinding time from data obtained by ICP analysis.

Grinding time (min)	In purity (%)	Li impurity (%)	Total (%)	In recovery (%)
30	95.73	0.41	96.14	98.12
60	96.76	0.37	97.13	97.25
120	94.21	0.39	94.61	97.11
180	94.25	0.29	94.54	97.39



Fig. 6. X-ray diffraction patterns of indium tin oxide (ITO) and Li_3N samples (1:3 = ITO/Li_3N) milled in NH₃ gas atmosphere for 120 min at 300 rpm.

Substituting In_2O_3 with indium tin oxide (ITO) and milling the sample with Li_3N under NH_3 gas atmosphere was made to confirm the reduction of ITO by similar mechanochemical reaction. We have found that the similar reaction has been taken place by the milling condition, and Fig. 6 is as evidence showing XRD patterns of the sample mixture milled for 120 min at 300 rpm under NH_3 gas atmosphere. It is seen that ITO is reduced to In–metal formed in the product, and no significant peaks of the starting samples in the pattern.

4. Conclusion

This work was done to find out the possibility that the mechanochemical reduction of In_2O_3 by milling with Li_3N under NH_3 and N_2 gas atmosphere can be achieved. Followings are the summary of this work:

- A non-thermal reduction of In₂O₃ to In–metal by mechanochemical route to induce solid state reaction conducted under NH₃ and N₂ gas environments in the presence of Li₃N was confirmed.
- 2. NH₃ is more effective than N_2 in terms of the reduction of In_2O_3
- 3. In the milling operation (planetary mill used in the experiment), prolonged milling is more effective than short milling times, but, much longer milling times for more than 120 min does not make sense. Moderate mill speed at 300 rpm is enough to cause the reduction.
- 4. Washing the milled sample enables us to collect high purity In-metal from the milled sample. The purity of In-metal collected is around 95% in all experimental condition.
- 5. This process can be extended to reduce ITO for In and is confirmed by its reductive reaction and experimental results.

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