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Short communication

Recovery of indium from In_2O_3 and liquid crystal display powder via a chloride volatilization process using polyvinyl chloride

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ABSTRACT

Indium (In) was recovered from indium oxide (In_2O_3) and liquid crystal display (LCD) powder via a chloride volatilization process using polyvinyl chloride (PVC) as the chlorination agent. The recovery of In from In_2O_3 increased with an increasing molar Cl/In ratio in N_2 and air atmospheres. The degree of In recovery at a Cl/In molar ratio of 11 and a temperature of 350 °C was 98.7% and 96.6%, for N_2 and air, respectively. The In recovery also increased notably with increasing temperature in N_2 atmosphere. In both atmospheres, the In recovery increased with an increasing degradation temperature of PVC. However, the In recovery from LCD powder was lower than that from In_2O_3. For LCD powder, the degree of In recovery at a Cl/In molar ratio of 11 and a temperature of 350 °C was 66.7% and 54.1%, for N_2 and air, respectively.

1. Introduction

Indium (In), a rare element present only in a few natural minerals, is obtained mainly from zinc minerals whose In content varies from 10 to 20 ppm. Due to its rising demands and difficulties in exploitation, a shortage of In and rising prices are expected for the future [1–3]. The rising demand is mainly due to the use of indium tin oxide (ITO) for transparent electrodes. About 84% of the worldwide indium consumption is used for the production of liquid crystal displays (LCDs). In 2004, the consumption of In used for ITO was about 470 t in Japan. An estimated 220 t of In were released as waste. In has been recovered from sputtering (42%), etching (11%), assembling (4.1%), and recycling (36%), but it has not yet recovered from used LCDs (6.4%) [4].

Developing a new process for an effective end of life utilization in both metal and plastic waste is necessary. We propose a combined recycling process composed of the thermal treatment of PVC and the simultaneous separation of the metal-containing waste. In this study, we investigated the applicability of a recovery process for In from LCDs using hydrochloric acid released during the degradation of PVC as a chlorination agent to produce volatile $InCl_3$. Generally, metal chlorides are known to be easily formed since they are thermodynamically favored. Volatile metal chlorides can be separated from nonvolatile oxides and chlorides and are obtained after condensation. However, besides In, other metals form volatile chlorides with different vapor pressures, making it possible to separate them by choosing an adequate condensation temperature. Thermal halogenation was mainly investigated for the recovery of valuable metals from waste materials or ores [5–10].

Furthermore, waste PVC is a problematic material due to its chlorine (Cl) content. The thermal degradation and stabilization of PVC has been investigated for about half a century [11–13]. Recently, the degradation behavior of PVC using coupled thermogravimetry–mass spectrometry (TG–MS) was examined by our research group to improve the dehydrochlorination process during feedstock recycling of plastic waste [14]. The dehydrochlorination of PVC at 650 °C in helium (He) is divided into three degradation stages, two dehydrochlorination steps, and a polyene-aromatic network breakdown. In addition, the effect of temperature on the dehydrochlorination of PVC in N_2 atmosphere during isothermal degradation has also been examined [15]. The degree of dehydrochlorination of PVC is nearly 100% at temperatures above 260 °C, and PVC is almost completely dehydrochlorinated at moderate temperatures.

This study has investigated the recovery of In from In_2O_3 by chloride volatilization process. PVC was examined as the chlorination agent for the effective use of waste PVC. The effects of temperature and the molar Cl/In ratio on the recovery of In from In_2O_3 were

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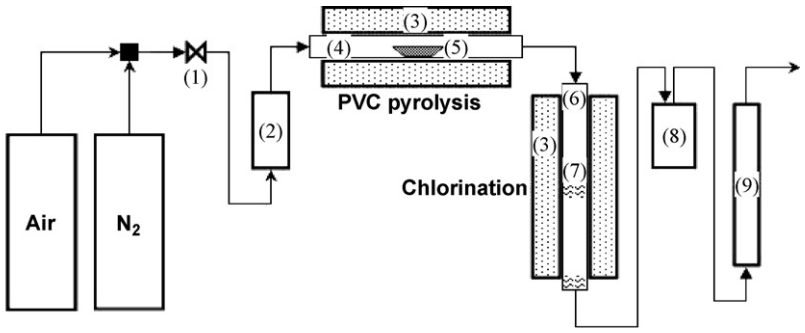

(1) On/off valve (2) Flowmeter (3) Electric furnace (4) Pyrex column (5) Crucible
(6) Quartz column (7) Quartz wool (8) 1 M NaOH solution (9) Active carbon trap

Fig. 1. Schematic diagram of the experimental apparatus.

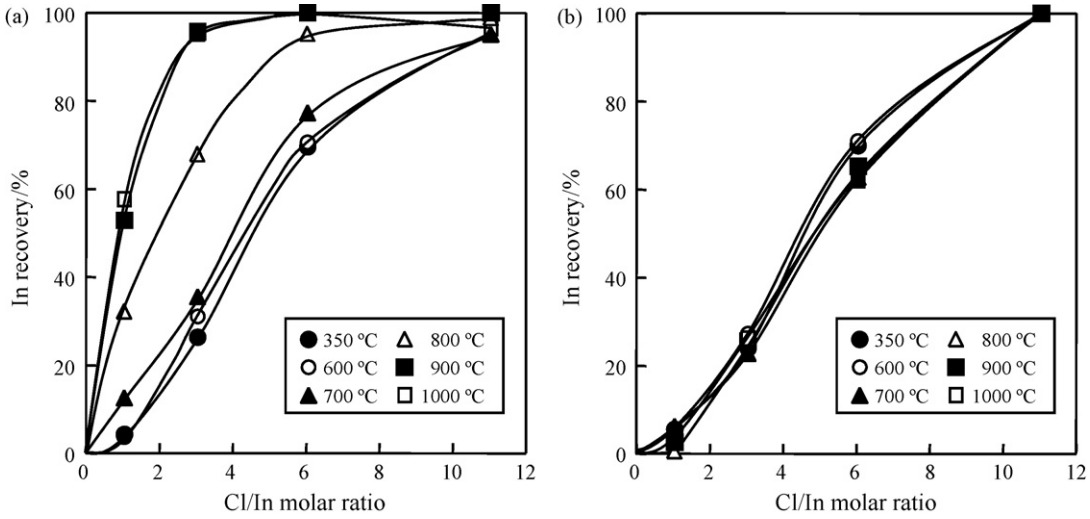

Fig. 2. Effects of the temperature and the molar Cl/In ratio on the In recovery from In_2O_3 under (a) N_2 and (b) air atmosphere. Degradation temperature of PVC: 250 °C.

investigated. The recovery of In from LCD powder was examined based on the results obtained.

2. Experimental procedures

The In_2O_3 (Kanto Chemical, Tokyo, Japan) used in this study was of high purity (>99.9 wt%). The chemical composition of the LCD powder is shown in Table 1. Aluminum oxide (Al_2O_3) and In_2O_3 were the main components of the LCD powder. The PVC (M_n = 62,000 Da) used was purchased from Kanto Chemical. For the analysis of the products, concentrated nitric acid (HNO_3; 60–61%; Kanto Chemical) was used.

A schematic diagram of the experimental apparatus used is shown in Fig. 1. The main apparatus consisted of two electric furnaces (ARF-40K; Asahi Rikagaku, Tokyo, Japan) with temperature controllers (AMF-S; Asahi Rikagaku). The PVC degradation reactor consisted of a pyrex column (I.D. 26 mm × O.D. 30 mm × L 38 cm) heated by one of the electric furnaces. PVC was placed in an alumina boat in the middle of the degradation reactor. A quartz column (I.D. 16 mm × O.D. 20 mm × L 44 cm) containing quartz wool on a perforated plate was used as chlorination reactor. The In_2O_3 and LCD powder were placed upon the quartz wool to maintain a good contact between the oxide and the gas. The cold end of the reactor was closed with quartz wool acting as a filter to prevent the condensing metal chloride from leaving the reactor.

The thermal degradation of PVC was performed between 250 and 350 °C. The resulting HCl was driven out at a flow of 50 ml min^{-1} by N_2 and air, separately, and pipelined for 1 h through 0.1 g In_2O_3, and 0.5 g LCD powder. The molar Cl/In ratio was varied between 1 and 11 at temperatures between 350 and 1000 °C.

The products were collected from the inside wall of the quartz column and from the quartz wool at the end of the quartz column. The products were dissolved in HNO_3, and the In content was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; SPS7800; Seiko Instruments Inc., Tokyo, Japan). The products were identified by X-ray diffraction (XRD) using the K_α line of Cu.

3. Results and discussion

The chlorination of In_2O_3 results in the production of $InCl_3$, as shown in Eq. (1):

$$In_2O_3 + 6HCl \rightarrow 2InCl_3 + 3H_2O \quad (1)$$

Since the Gibbs energy (ΔG) for the reaction (1), calculated from thermodynamic databases [16,17], is negative at any temperature in the investigated temperature range (ΔG: −8.0 kJ mol^{-1} at 600 °C, −3.8 kJ mol^{-1} at 1000 °C), the reaction should proceed in the expected way.

Fig. 2 shows the effects of the temperature and Cl/In molar ratio on the In recovery from In_2O_3 under the flow of (a) N_2 and (b) air. In both cases, the degree of In recovery increased with increasing Cl/In molar ratio regardless of temperature. The degree of In recovery at a Cl/In molar ratio of 11 and a temperature of 350 °C was 98.7% and