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.

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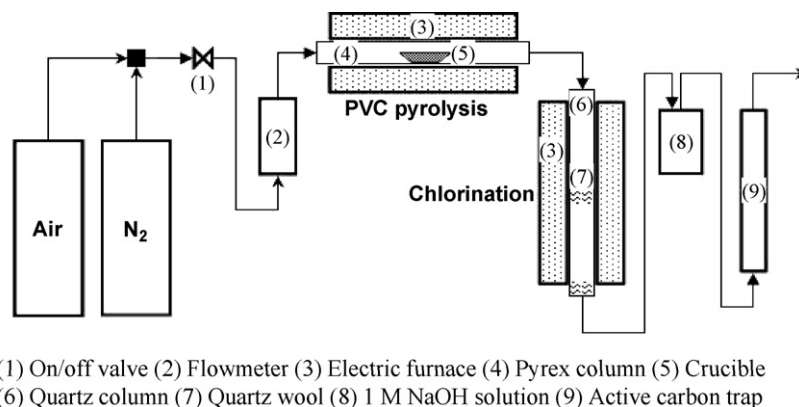
(1) On/off valve (2) Flowmeter (3) Electric furnace (4) Pyrex column (5) Crucible
(6) Quartz column (7) Quartz wool (8) 1 M NaOH solution (9) Active carbon trap

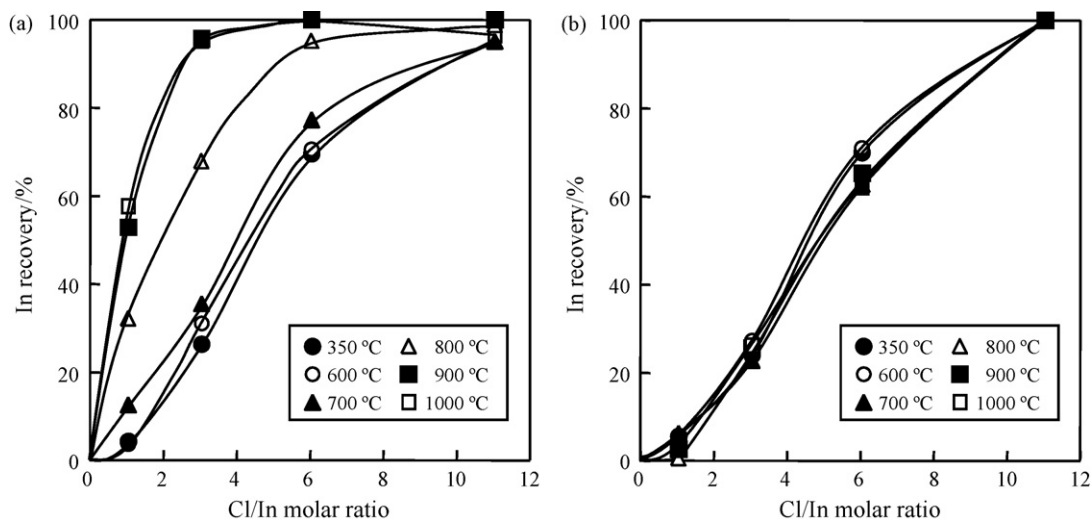**Fig. 1.** Schematic diagram of the experimental apparatus.

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):

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

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

Table 1
Chemical composition of the LCD powder.

Al_2O_3	In_2O_3	Fe_2O_3	SnO_2	TiO_2	Cr_2O_3	SiO_2	NiO	CuO	Other
75.6 wt%	12.0 wt%	4.5 wt%	1.6 wt%	0.8 wt%	1.0 wt%	0.8 wt%	0.4 wt%	0.2 wt%	3.1 wt%
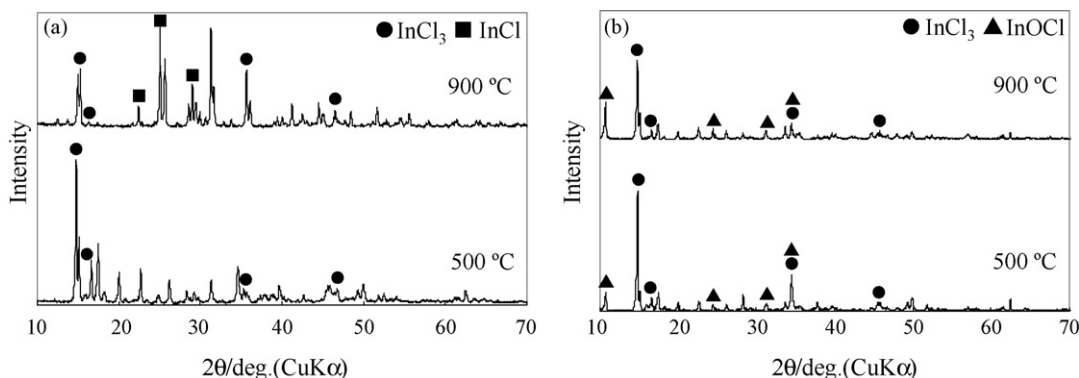
Fig. 3. XRD patterns of the products obtained after the chlorination of In_2O_3 in (a) N_2 and (b) air atmosphere. Degradation temperature of PVC: 250 °C.

Table 2
Effect of degradation temperature of PVC on the recovery of indium from In_2O_3.

	Temperature (°C)		
	250	300	350
N_2	69.6%	72.5%	81.1%
Air	70.0%	74.8%	85.4%

Chlorination temperature: 350 °C. Cl/In molar ratio: 6.

Table 3
In recovery from LCD powder via chlorination.

LCD powder		In_2O_3	
N_2	Air	N_2	Air
66.7%	54.1%	98.7%	96.6%

Chlorination temperature: 350 °C. Cl/In molar ratio: 11. Degradation temperature of PVC: 250 °C.

96.6%, for N_2 and air, respectively. In N_2 atmosphere, the In recovery showed no major differences between 350 and 700 °C, but increased with increasing temperature from 700 to 900 °C. A further rise in the temperature showed little effect on the recovery of In. More than 95% of the In was obtained at a molar Cl/In ratio of 3 at 900 and 1000 °C or with a molar ratio of 6 at 800 °C, while this In recovery rate was only obtained at a molar Cl/In ratio of 11 at 350–700 °C.
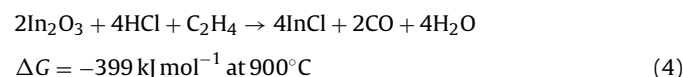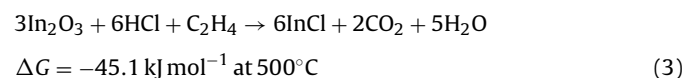
In contrast, the recovery of In was almost identical at any temperature under the flow of air. Almost 100% of the In was recovered at a molar Cl/In ratio of 11 at any temperature. The In recovery was comparable to that in N_2 atmosphere at low temperatures.

The difference in the In recovery between N_2 and air was attributable to the change in the product distribution after the chlorination of In_2O_3. Fig. 3 shows the XRD patterns of the products obtained via the chlorination of In_2O_3 in N_2 and air atmospheres, respectively. In the N_2 atmosphere, $InCl_3$ was obtained as the main product at 500 °C, while both $InCl_3$ and InCl were produced at 900 °C. This explained the high recovery rate for low molar Cl/In ratios at high temperatures.

$$InCl_3 \rightarrow InCl + Cl_2 \quad \Delta G = 156 \text{ kJ mol}^{-1} \text{ at } 900\,^\circ\text{C} \quad (2)$$
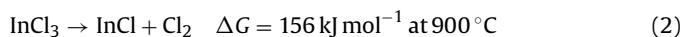
Since ΔG is positive for the reaction, the formation of InCl seems doubtful and is unlikely to occur in a pure HCl atmosphere. However, the degradation of PVC provided more compounds than HCl.

Hydrocarbons were also present in the gas flow.

$$3In_2O_3 + 6HCl + C_2H_4 \rightarrow 6InCl + 2CO_2 + 5H_2O$$

$$\Delta G = -45.1 \text{ kJ mol}^{-1} \text{ at } 500\,^\circ\text{C} \quad (3)$$

$$2In_2O_3 + 4HCl + C_2H_4 \rightarrow 4InCl + 2CO + 4H_2O$$

$$\Delta G = -399 \text{ kJ mol}^{-1} \text{ at } 900\,^\circ\text{C} \quad (4)$$

As shown in reactions (3) and (4), ΔG is estimated to decrease significantly in the presence of PVC degradation products (e.g., ethylene).

In contrast, besides $InCl_3$, InOCl was also produced in the air atmosphere (Fig. 3b) and was observed at both 500 and 900 °C. Two reasons may explain the lower recovery in air atmosphere. First, InOCl was obtained by the oxidation of InCl since the oxidation of $InCl_3$ is not thermodynamically favored. Second, the degradation products of PVC are oxidized in air and unable to support the formation of InCl, thus resulting in a lower In recovery.

Table 2 shows the effect of the degradation temperature of PVC on the In recovery. In both atmospheres, the In recovery increased with increasing degradation temperature of PVC. The increased the degradation temperature probably resulted in a larger amount of HCl being generated from the PVC, leading to a higher yield of $InCl_3$. However, it should be aware that the actual waste PVC will contain additives like Cd, Sn, Pb and $CaCO_3$ which can lead to loss of HCl. This may result in a low yield of $InCl_3$.

Table 3 presents the In recovery from LCD powder via the same chlorination process used for the experiments with pure In_2O_3. In both atmospheres, the In recovery from the LCD powder was lower than that from In_2O_3. In addition to In_2O_3, the LCD powder also contained Al_2O_3, FeO, and SnO_2, leading to reduced contact between In_2O_3 and HCl. Furthermore, HCl was probably also consumed by reaction with other metal oxides, resulting in less $InCl_3$ being produced.

4. Conclusions

In was recovered from In_2O_3 and LCD powder via a chloride volatilization process using PVC as a chlorination agent. For In_2O_3, the degree of the In recovery increased with an increasing molar Cl/In ratio in N_2 and air atmospheres. The In recovery increased notably with increasing temperature in the N_2 atmosphere. The

difference in the behavior of the In recovery between N_2 and air was attributable to the change in the product distribution after the chlorination of In_2O_3, i.e., the production of $InCl_3$ and $InCl$ in the N_2 atmosphere and that of $InCl_3$ and $InOCl$ in the air atmosphere. In both atmospheres, the In recovery increased with an increasing degradation temperature of PVC. The raised degradation tempera- ture probably led to an increasing amount of HCl being generated from the PVC, yielding more $InCl_3$. The In recovery from the LCD powder was lower than that from In_2O_3. The LCD powder contained Al_2O_3, Fe_2O_3, and SnO_2 in addition to In_2O_3, leading to a reduced contact between In_2O_3 and HCl. Furthermore, HCl was probably consumed by the reaction with other metal oxides, resulting in a reduced production of $InCl_3$. The recovery of In metal from $InCl_3$, etc. obtained by the chlorination of In_2O_3 and LCD powder is currently under consideration.

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