RECOVERY OF INDIUM FROM In_2O_3 AND LIQUID CRYSTAL DISPLAY POWDER USING DEHYDROCHLORINATION OF POLY (VINYL CHLORIDE)

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Abstract: Indium (In) was found to be recovered from In_2O_3 and LCD powder using poly (vinyl chloride) (PVC) as chlorination agent by chloride volatilization process. For In_2O_3, the degree of In recovery increased with increasing the molar ratio of Cl in PVC to In in In_2O_3 (Cl/In molar ratio) under the flow of N_2 and air. Particularly, the degree of In recovery increased notably with increasing temperature under the flow of N_2. The degree of In recovery from Liquid Crystal Display powder was lower than that from In_2O_3.

1. Introduction

Generally, the content of In in the ore is 10~20 ppm, and it exists more in the zinc deposits (New Brunswick, 280ppm). Due to the small content of In in the ore and the by-product of primary metals (mainly Zn), In is hard to correspond to the rapid demand variation [1-3]. In is used to fabricate ITO (Indium Tin Oxide) for transparent electrodes. Particularly, about 84 % of In in worldwide is used to produce ITO due to the recent development of LCD (Liquid Crystal Display) industry. The increase of In demand causes its rapid price increase [4]. Waste In is mainly generated in the LCD panel process. In Japan in 2004, 470 t-In is used in ITO for transparent electrodes, out of which 220 t-In is dissipated or potentially dissipated [5]. The dissipated In, which comes from sputtering (42.7 %), etching (10.5 %), assembling (4.1 %), recycling (36.3 %), is currently recovered and reused for the LCD panel process. However, the potential dissipated In (6.4 %), *i.e.*, In in the LCD panel, is not recycled but wasted. It is hereafter necessary to recover In from the waste LCD panel in order to correspond to the increase of In demand. In this paper, the application of chloride volatilization process for the recovery of In from the waste LCD panel has been examined. The chloride volatilization process generates metal chloride through the reaction between metal oxides and chlorination agent. The metal chloride is recovered in a gas phase, resulting in the separation from the reactant. The metal chloride gases have different condensation temperature, so it is possible to gain the selective recovery of target metal chlorides through the control of cooling temperature. The research for chlorination has been preceded mainly for the recycling of the valuable metals in the waste resources or in the ore [6]. Furthermore, PVC is examined as the chlorination agent for the effective use of waste PVC, because the thermal degradation of PVC generates HCl [7,8]. This study has investigated the recovery of In from In_2O_3 by chloride volatilization process. The effects of temperature and Cl/In molar ratio on the recovery of In from In_2O_3 have been examined. Based on the obtained results, the recovery of In from LCD powder was examined.

2. Experimental procedures

The purity of In_2O_3 used in this study was 99.9 %. The LCD powder is composed of 75.6 wt% Al_2O_3, 12.0 wt% In_2O_3, 4.5 wt% Fe_2O_3, 1.6 wt% SnO_2, and so on. The thermal degradation of PVC was performed at 250 ºC. Under the flow of N_2 and air at 50 ml/min, 0.1 g In_2O_3 or 0.5 g LCD powder was reacted with HCl from the PVC with the Cl/In molar ratio of 1-11 at 350-1000 ºC for 1 h. The products were identified by X-ray diffraction (XRD) analysis using Cu Kα radiation. After the dissolution of the products in HNO_3, In in the sample solutions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (SPS7800, Seiko Instruments Inc.).

3. Results and discussion

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

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

Since the Gibbs energy (ΔG) for the reaction (1), calculated from thermodynamic databases [9,10], is negative at any temperature in the investigated temperature range (ΔG: $-8.0\ \mathrm{kJ\ mol^{-1}}$ at 600 °C, $-3.8\ \mathrm{kJ\ mol^{-1}}$ at 1000 °C), the reaction should proceed in the expected way.

Fig.1 shows the effects of temperature and Cl/In molar ratio on 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 at any temperature. The degree of In recovery was 98.7 and 96.6 % with Cl/In molar ratio of 11 at 350 ºC, respectively. For (a) N_2, the degree of In recovery was almost similar at 350-700 ºC at any Cl/In molar ratio. However, the degree of In recovery increased with increasing temperature from 700 to 900 ºC at any Cl/In molar ratio, and the behavior of In recovery was almost similar at 900 and 1000 ºC. More than 95 % of In recovery was obtained with Cl/In molar ratio of 3 at 900 and 1000 ºC and with the molar ratio of 6 at 800 ºC, although it was obtained with the molar ratio of 11 at 350-700 ºC. The increase of temperature was found to result in the increase of degree of In recovery. In contrast, the behavior of In recovery was almost similar at any temperature under the flow of (b) air. Almost 100 % of In recovery was obtained with Cl/In molar ratio of 11 at any temperature. The difference of behavior of In recovery between N_2 and air is attributed to the difference of products obtained by the chlorination of In_2O_3. From the XRD patterns of products obtained by the chlorination of In_2O_3 under the flow of N_2, $InCl_3$ was observed to be produced at 500 ºC. This confirms that In recovery from In_2O_3 by the chlorination is due to the production of $InCl_3$. At 900 ºC, InCl was produced in addition to $InCl_3$. Therefore, the high degree of In recovery at high temperature with low Cl/In molar ratio is considered to be caused by the production of InCl. For air, in contrast, InOCl was produced in addition to $InCl_3$ at 500 and 900 ºC. The similar products at any temperature probably results in the similar degree of In recovery with any Cl/In molar ratio.

The In recovery from LCD powder by the chlorination for Cl/In molar ratio of 11 at 350 ºC was 66.7 % for N_2 and 54.1 % for air. In both atmospheres, the degree of In recovery from LCD powder was lower than that from In_2O_3. The LCD powder contains Al_2O_3, FeO, and SnO_2, in addition to In_2O_3, leading to the less chance to contact of In_2O_3 with HCl. Furthermore, HCl is probably consumed by the reaction with other metal oxides, resulting in the prevention of production of $InCl_3$.

4. Conclusions

In was found to be recovered from In_2O_3 and LCD powder using PVC as chlorination agent by chloride volatilization process. For In_2O_3, the degree of In recovery increased with increasing the Cl/In molar ratio under the flow of N_2 and air. Particularly, the degree of In recovery increased notably with increasing temperature under the flow of N_2. The difference of behavior of In recovery between N_2 and air is attributed to the difference of products obtained by the chlorination of In_2O_3, *i.e.*, the production of $InCl_3$ and InCl for N_2, and $InCl_3$ and InOCl for air. The degree of In recovery from LCD powder was lower than that from In_2O_3. The LCD powder contains Al_2O_3, FeO, and SnO_2, in addition to In_2O_3, leading to the less chance to contact of In_2O_3 with HCl. Furthermore, HCl is probably consumed by the reaction with other metal oxides, resulting in the prevention of production of $InCl_3$.

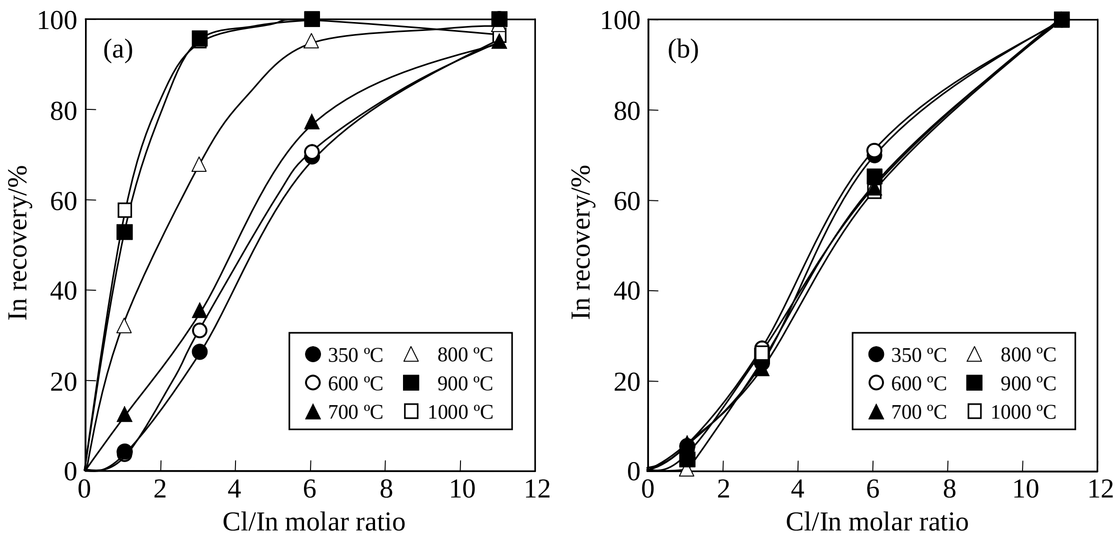

Fig.1 Effects of the temperature and the molar Cl/In ratio on the In recovery from In_2O_3 under(a)N_2 and (b) air atmosphere[1]

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