

Indium Recovery from Indium Tin Oxide, ITO, Thin Film Deposited on Glass Plate by Chlorination Treatment with Ammonium Chloride

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In the focus of selective recovery of indium from waste flat panel display, we have studied chlorination treatment where ammonium chloride, NH_4Cl , has been used as chlorination reagent. Glass plate on which ITO is deposited, denoted hereafter as ITO glass, has been employed as model sample. It was found that indium could be successfully recovered from ITO glass in the form of volatile indium chloride by heating the mixture of ITO and NH_4Cl at the temperature of 400°C under inert atmosphere. The influence of process parameters, such as treatment temperature, milling condition of ITO glass and composition of NH_4Cl , was investigated in order to achieve high process efficiency. [doi:10.2320/matertrans.M2011106]

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1. Introduction

Indium tin oxide, ITO, is a well known transparent electrical conductor which is commonly used in flat panel display. The steady increase of the production of flat panel display causes a stronger demand for raw indium. In the view of a possible supply shortfall in the future, the establishment of the recovery process from indium-containing waste is, therefore, of great importance. Various techniques have been investigated so far, mainly based on the hydrometallurgical processes.^{1,2)}

Indium chloride has relatively high vapour pressure (1.6×10^{-3} atm at 400°C), so that the application of chlorination process is attractive for the selective indium recovery. Takahashi *et al.*³⁾ studied the indium recovery from ITO panel display by chlorination with concentrated HCl solution and the consequent heat treatment for the evaporation of indium chloride. Park *et al.*⁴⁾ utilized thermal degradation of poly(vinyl chloride) at 250°C , in which gaseous decomposition products, mainly hydrogen chloride gas, were passed thorough powder of ITO containing glass which was heated at 350°C . They reported 60 percents of indium is chlorinated. Further development of highly effective recovery process with low treatment cost is required.

In our previous paper⁵⁾ we reported a simple process to recover indium from dental metal recycling sludge, an indium-containing waste. The process is based on a chlorination treatment in which ammonium chloride, NH_4Cl , is employed. Volatile indium chloride condensates at cold part of the reactor, and can be easily collected by water or acid. There are several advantages to utilize ammonium chloride: (1) The handling of the chemical is easy, so that the process does not require severe gas-tight reaction line in contrary with the processes using toxic Cl_2 or HCl gas. (2) In

comparison with other salt type chlorination reagents such as NaCl and KCl, the reaction temperature is much lower ($\sim 400^\circ\text{C}$). (3) Both the decomposition products of ammonium chloride, i.e. acidic HCl and alkaline NH_3 , are employed in metal recovery. The former is used for the chlorination of indium, while the latter, released as flue gas, can be collected in a water trap and used for the formation of indium hydroxide. A treatment of reaction products, indium chloride, with aqueous ammonia solution results in the formation of the hydroxide, which can be further utilised in conventional metal recovery processes.

The positive result stimulates us to employ this process for the recovery of indium from flat panel display. Deposited indium tin oxide has typical thickness of a few nanometers on glass display material. A possible pre-treatment in indium recovery is crushing of waste display. Because of low indium concentration in display, it is important to study the influence of milling treatment, whereby mechanochemical reaction can lead to the change in activity coefficient of the indium specie, thus the recovery efficiency. We have also studied the influence of the presence of carbon powder and the mixing pattern of the display and the chlorination reagent.

2. Experimental

Powder form of ammonium chloride (99.5%, Wako pure chemicals Co., Ltd.) is used as chlorination reagent without further purification. A soda glass plate (25 mm \times 75 mm \times 1 mm thickness), on a single side of which indium tin oxide is physically deposited, is supplied from Aldrich and used as a model ITO glass. The thickness of ITO is given by the manufacturer as 120–160 nm. The composition of the soda glass is given by the manufacturer, as summarized in Table 1. For the determination of the amount of indium and tin, the glass plate was ground with a mortar grinder (RM0, Retsch) for 180 min, and the powder is dissolved in hydrofluoric acid. The solution was analyzed with an inductively coupled plasma spectrometer. The average amount of indium and tin are 0.275 ± 0.007 mg and 0.090 ± 0.009 mg per 1 g of ITO glass, respectively. It should be noted that the molar ratio of

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Table 1 Composition of soda glass plate on which ITO is deposited.

	SiO ₂	Na ₂ O	CaO	MgO	Al ₂ O ₃	B ₂ O ₃
Composition/mass%	72.6	15.2	4.6	3.6	1.7	0.8

In and Sn is ca. 3.2, lower than that of the representative commercial ITO, i.e. ~ 9.8 .

The mixture of ITO glass and NH₄Cl is prepared either by mixing of milled glass and the ammonium chloride and by spreading the NH₄Cl powder onto an ITO-deposited side of the glass plate. In the former case, the ITO glass is ground with the mortar grinder for a given time, and the powder is mixed with ammonium chloride in a mortar for 5 min. In some cases, carbon powder (99.99%, Kojundo chem. Co., Ltd.) is mixed. The mixture is pelletized with the load of ca. 2.5×10^8 Pa into a disc of 12 mm in diameter. For the latter type of sample, the NH₄Cl-spread glass plate is used for chlorination reaction without milling.

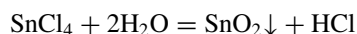
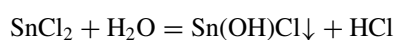
The chlorination treatment was carried out under helium atmosphere (Flow rate = 300 mL/min) in the similar way as that of the previous study.⁵⁾ A quartz reactor of 46 mm i.d. and 740 mm length was equipped in a horizontal electric furnace. After the temperature of high temperature zone of the furnace was stabilised, sample mixture put on a mullite reaction boat was introduced quickly from the cold part to the reaction zone inside the reactor. Typical reaction temperature was 400°C and the reaction time was 30 min, if not specified.

After a reaction run the condensation of yellowish material was observed at the cold part of the quartz reaction tube. This material is hereafter denoted as reaction products. The reaction product was carefully leached by pure water. The solution was then filtered with mixed cellulose filter paper with the average pore size of 0.1 μ m. The amount of metal ions in the filtrate was analyzed by ICP spectrometer. The recovery ratio is defined as $100 \times (\text{the amount of In in reaction products})/(\text{the amount of initial indium in the sample})$.

3. Results and Discussion

3.1 Influence of temperature on the indium recovery ratio

Figure 1 shows the recovery ratio of indium as a function of reaction temperature for pellet samples. The milling time was 60 min, and the concentration of NH₄Cl in the sample is 20 mass%. Obviously, recovery ratio of indium increases with temperature, while that of tin is almost constant. Low recovery ratio of the latter can be understood by the fact that tin is removed by filtration prior to ICP measurement. White precipitate is observed in the leaching procedure, which results presumably from hydrolysis of chlorides of tin as follows:



In the present cases, we are not aware of the detailed valency of the tin chlorides, because chemical analysis has not been possible due to the low concentration of tin in the reaction product. However, both divalent and tetravalent chlorides precipitate immediately during the treatment with water.

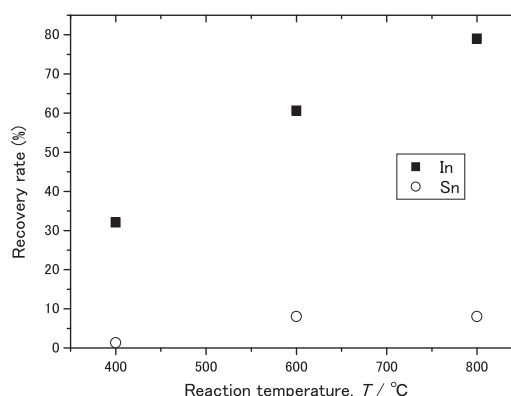


Fig. 1 Recovery ratio of indium and tin as a function of reaction temperature. The milling time of ITO glass is 60 min, and the reaction time is 30 min.

The increase of the indium recovery could be due either to increase of vapour pressure of indium chloride or to higher degree of chlorination at higher temperature. As for the first point, reaction residue in a mullite boat does not contain indium chloride even at lowest temperature (see section 3.3), so that all the chlorinated indium vaporises and condensates at the cold part of the reactor within the reaction time, i.e. 30 min. It should be also noted that the ammonium chloride decomposes and/or evaporates rapidly when a sample is brought to the hot zone of the reactor above 400°C. Therefore, the degree of chlorination reaction controls the indium recovery rate. With respect to this point we have considered thermodynamics of the chlorination reaction of the ITO glass. Figure 2 shows potential stability diagrams of the In-Cl-O and Sn-Cl-O systems at 400, 600 and 800°C, which are constructed with help of a software package FactSage Ver. 6.1 (Thermfact and GTT-Technologies). We have also evaluated the oxygen and chlorine partial pressure for sample mixture with composition of 20 mass% of NH₄Cl under inert atmosphere, assuming that indium, tin and the constituents of soda glass exist independently as solid oxides, namely In₂O₃ and SnO₂, and SiO₂ etc. All the activity of the oxides was, thus, taken as unity. The result of the calculated partial pressure is displayed as circle in the figure. It is clearly seen that the partial pressures move towards the chloride stable region with increasing temperature. Therefore, thermochemically favoured chlorination reaction at higher temperature leads to the higher recovery ratio of indium. Further detailed thermochemical study can predict the chlorination behaviour of indium in ITO, though this involves various complex issues such as evaluation of activities of all species. Moreover, the chlorination proceeds presumably through hydrogen chloride, a decomposition product of NH₄Cl. Thus, the influence of the specie should be considered for the detailed thermochemical analysis.

The present result suggests that higher temperature is favourable for the chlorination. However, we explored the improvement of indium recovery at low temperature. Thus, in the following sections we present experimental results at 400°C, discussing the influence of process factors including the milling treatment in order to achieve higher indium recovery.

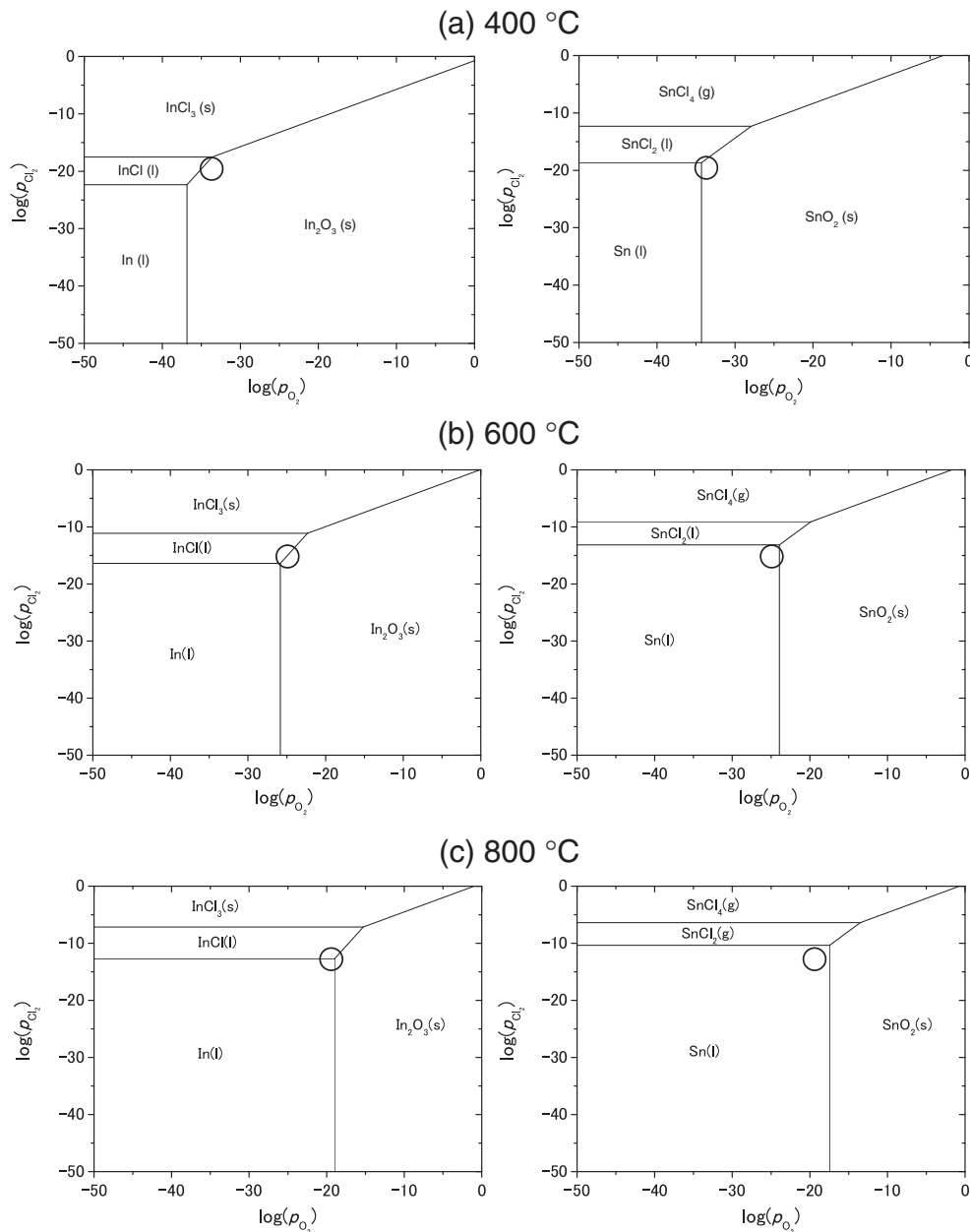


Fig. 2 Potential stability diagram of the In-Cl-O and Sn-Cl-O systems at 400, 600 and 800°C. A circle inside the figure is the partial pressure of oxygen and chlorine in the present experimental condition calculated with FactSage software on the assumption where starting materials contain indium tin and all the metal species as pure solid oxides with the activity of unity.

3.2 Influence of the addition of carbon powder on the indium recovery

As shown in Fig. 2, a chlorination treatment at high temperature has advantage to enhance the process efficiency, for which higher energy consumption should be in compensation. In the view of the establishment of process with low energy consumption, we examined to improve the indium recovery ratio at low temperature, i.e. 400°C, by addition of carbon powder. Figure 3 shows influence of the composition of carbon on the recovery ratio of indium. The milling time of ITO glass was 60 min, and the composition of ammonium chloride to ITO glass was 20 mass%. A small amount of carbon increases drastically the indium recovery ratio: 68% of recovery is achieved by the carbon addition of 0.5 mass%. The addition of carbon can lead to the decrease of the local

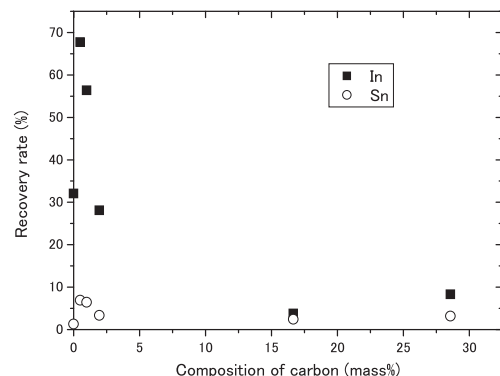


Fig. 3 Influence of the addition of carbon powder on the recovery ratio of indium and tin for the chlorination treatment of ITO glass milled for 60 min.

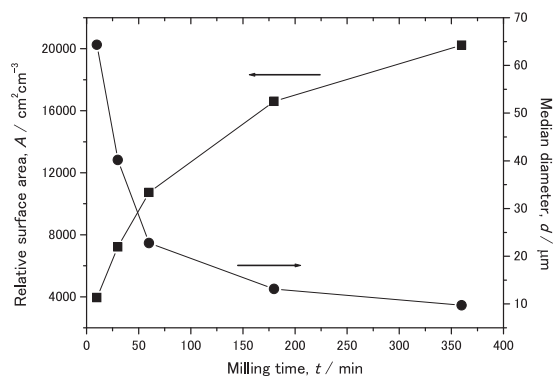


Fig. 4 Change in relative surface area and median diameter of ITO glass particles during the milling treatment.

oxygen partial pressure, which is favourable for the chlorination of indium (see Fig. 2). Further increase of carbon content decreases, however, the efficiency of the indium recovery. A small portion of carbon can reduce the local partial pressure of oxygen, and thus increases that of chlorine. On the other hand, further increase in the composition of carbon results in the increase in the inter-particle distance between ITO and ammonium chloride. More studies, such as experiments with different carbon particle size, are required to clarify the influence of the addition of the carbon particles.

3.3 Mechanochemical effect in the milling treatment of ITO glass

A milling treatment of glass can cause mechanochemical reactions, one of which being the inclusion of indium into glass matrix. We have examined the influence of milling time on the recovery ratio of indium. Figure 4 shows the change in relative surface area and median diameter of the ITO sample as a function of milling time. The average diameter changes from 65 μm at first five minutes to 10 μm after 2 h. It should be noted that the diameter of ammonium chloride is 0.5–1 mm as confirmed by a SEM observation.

The change in indium recovery as a function of milling time is plotted in Fig. 5. It is clearly seen that the recovery ratio decreases with increasing milling time: maximum recovery ratio being ca. 50% in the examined conditions. On the other hand, the recovery ratio of tin is low, which is explained by the observation as mentioned above. The present result of indium recovery suggests the inclusion of indium into the glass matrix. In order to confirm the point, we have examined the mass balance of indium. For this purpose the reaction residue was first leached with pure water, then with aqua regia, and finally with hydrofluoric acid. First leachant may contain indium chloride that did not vaporise. Second one may be owing to indium oxide that is not chlorinated, while the last to indium that is included in glass matrix. The results including the amount of reaction product are displayed in Fig. 6. In all the cases satisfactory mass balance is observed. The amount of indium leached both with aqua regia and with HF acid increases with the increase of milling time. The profile of indium leached with aqua regia can be understood by the following reason. The increase in milling time leads to the increase in the apparent area of glass surface on which ITO is not deposited, that means that the

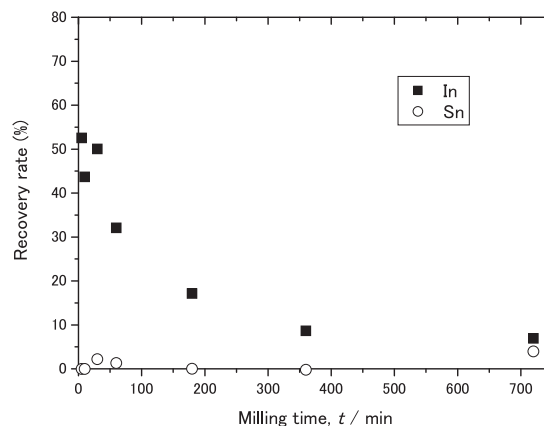


Fig. 5 Effect of milling treatment on the recovery rate of indium and tin. The composition of ammonium chloride is 20 mass%.

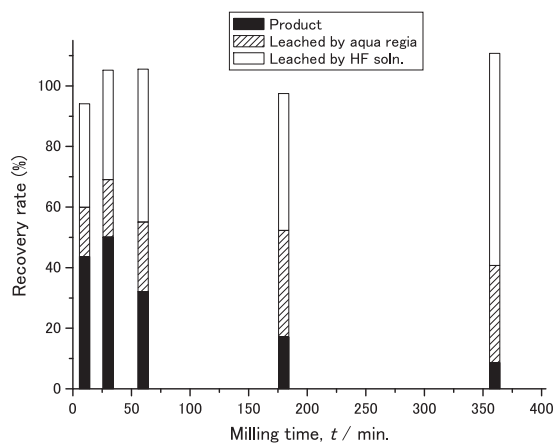


Fig. 6 Relationship between mass balance of indium and milling time of ITO glass plate. The composition of ammonium chloride is 20 mass%, and the reaction temperature is 400°C.

contact area between ITO and ammonium chloride decreases. This is in conjunction with the increase of the contribution of non-reacted indium oxide with increasing milling time. The profile of indium leached with HF clearly indicates the increase of the embedding of indium into glass. Therefore, the activity of indium is decreased.

3.4 Selective recovery of indium by controlling the deposition temperature

As mentioned above, indium and tin can be separated by leaching of the reaction products with pure water and the consequent filtration. This is a simple process to separate indium from the mixture of chlorides of indium and tin. On the other hand, the hydrolysis reaction and precipitation kinetics are strongly influenced by treatment conditions including the pH value of the leaching solution and the reaction temperature. Thus, a possible scale-up of the process can lead to a contamination of tin in the reaction products.

In order to explore the possibility of the selective recovery of indium at the chlorination reaction stage, the influence of condensation temperature on the amount of the reaction product was examined. For this purpose we have collected the reaction products with aqueous HCl solution at different

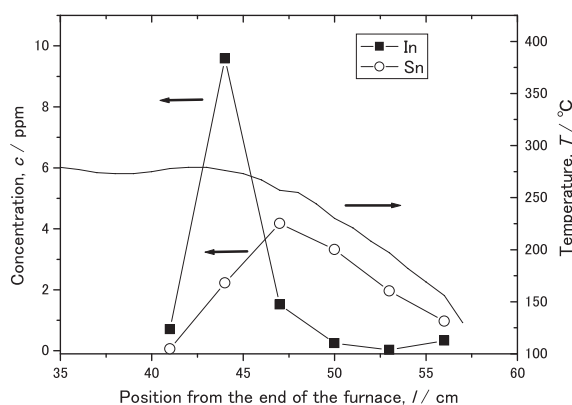


Fig. 7 Recovery ratio and the corresponding average temperature at condensation point. The composition of ammonium chloride is 20 mass%.

positions along the reaction tube. The leaching with the HCl solution can avoid the hydrolysis of tin chlorides.⁵⁾ The average temperature of each position was measured prior to chlorination reaction. Figure 7 shows the recovery ratio of indium and tin and the corresponding temperature along the reaction tube. The chlorination reaction was carried out at 400°C for the composition of 20 mass% of NH_4Cl (milling time of ITO glass = 60 min.). The separation of indium and tin inside the reaction tube is obvious in the figure. Indium chloride is mainly collected at 270°C, while the tin chloride is collected at lower temperature (~250°C). The tendency of the separation is similar to the result of the chlorination treatment of dental metal recycling sludge by ammonium chloride.⁵⁾ From the result, selective collection of indium is possible by the control of the deposition temperature.

3.5 Chlorination treatment of ITO glass without milling

As discussed in 3.3, the milling treatment of ITO glass reduces considerably the recovery ratio of indium. The result of Fig. 5 suggests that higher indium recovery is anticipated for un-milled glass. In this section we report some result of the chlorination treatment for ITO glass plate on which powder of ammonium chloride is pasted. A difficulty arose with respect to the homogeneous contact between ITO and NH_4Cl . Among the examined methods the best result was obtained for sample prepared in the following way. A given amount of NH_4Cl was put homogeneously on the ITO glass plate, a few droplets of distilled water were then put on it, which was then air-dried. At the low NH_4Cl composition, saturated aqueous ammonium chloride solution was sprayed onto the ITO glass surface, which was then air-dried. In both cases the composition of the ammonium chloride was determined by the weight difference of the ITO glass. Figure 8 shows the indium recovery ratio for ITO glass without milling treatment that is plotted against the composition of ammonium chloride. Also shown in the figure is the result for pellet samples where ITO glass is milled for 60 min. It is clearly seen that significantly high recovery ratio is observed for un-milled ITO glass. The ratio reaches over 80 percent at NH_4Cl composition of 26 mass%, while the highest indium recovery of pellet sample (milled glass) is ~30%. Two factors are involved for the increase in recovery ratio by chlorination of un-milled ITO glass: (1) The contact

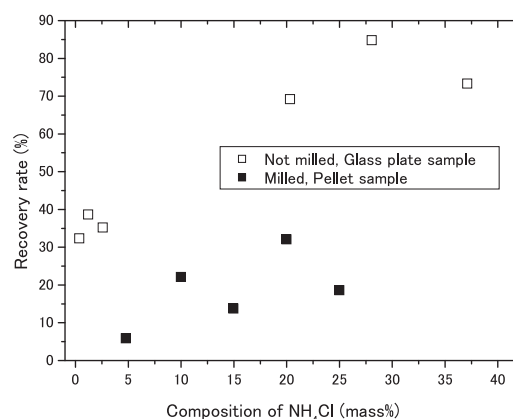


Fig. 8 Comparison of indium recovery between milled and un-milled ITO glass plate plotted as a function of composition of ammonium chloride.

Table 2 Comparison of indium recovery ratio for chlorination treatment of ITO glass- NH_4Cl system (the composition of ammonium chloride = 20 mass%) under different atmosphere. The reaction temperature was 400°C, and the reaction time was 30 min.

	Helium	Nitrogen	Air
Recovery ratio%	61	61	62

between ITO and ammonium chloride is increased, (2) The mechanochemical effect resulting from milling is avoided.

The amount of indium on ITO glass plate, i.e. ca. 0.3 mg In/g ITO glass, requires stoichiometrically less than a milligram of NH_4Cl per 1 g of ITO glass, i.e. $\sim 10^{-2}$ mass% of NH_4Cl . The present result indicates that excess amount of ammonium chloride is needed to achieve the sufficient recovery ratio. The chlorination is strongly influenced by gas flow pattern of HCl resulting from the decomposition of NH_4Cl . Thus, excess amount of ammonium chloride is required for the chlorination of indium. Moreover, the increase in the concentration of NH_4Cl results in the increase in the partial pressure of chlorine, which enhances the chlorination of indium.

A preliminary work showed that the indium recovery was independent on the reaction atmosphere, as shown in Table 2 for the recovery ratio of indium at NH_4Cl composition of 20 mass%. The result indicates that the atmosphere at the local interface between ITO and ammonium chloride, which is not influenced by the bulk gas phase, is essential for the chlorination reaction.

In summary, a chlorination treatment without milling is very attractive for recover of indium from ITO flat panel display, because the energy-consumable milling process is omitted. The present result also suggests the establishment of a continuous process of deposition of NH_4Cl , chlorination reaction, and the recovery of indium.

4. Summary

In the present paper we have addressed the chlorination treatment of ITO glass plate utilizing ammonium chloride. The milling of ITO glass results in the decrease of indium

recovery due to the mechanochemical effect and to the decrease of the contact between ITO and ammonium chloride. The addition of small amount of carbon powder increases considerably the recovery ratio. A significant improvement in the recovery ratio is achieved by the chlorination of un-milled glass plate. In this case, the oxygen partial pressure does not affect obviously the recovery ratio of indium. This is a great advantage with respect to the application of the process, because the inert atmosphere is not required for the chlorination reaction, thus reducing the cost of the process. Further improvement in the contact between ITO and chlorination reagent is one of the future projects in order to develop a continuous treatment process. And further studies, including the experiments at higher temperatures and the application of the present method to different kinds of ITO films, should be also carried out.

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REFERENCES

- 1) A. P. Paiva: *Sep. Sci. Technol.* **36** (2001) 1395–1419.
- 2) T. Honma and T. Muratani: *Sharp Technical J.* **92** (2005) 17–22 (In Japanese).
- 3) K. Takahashi, A. Sasaki, G. Dodbiba, J. Sadaki, N. Sato and T. Fujita: *Metall. Mater. Trans. A* **40** (2009) 891–900.
- 4) K.-S. Park, W. Sato, G. Grause, T. Kameda and T. Yoshioka: *Thermochimica Acta* **493** (2009) 105–108.
- 5) O. Terakado, T. Saeki, R. Irizato and M. Hirasawa: *Mater. Trans.* **51** (2010) 1136–1140.