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Recoveries of Metallic Indium and Tin from ITO by Means of Pyrometallurgy[1]

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Abstract. With respect to a new pyrometallurgical process for the recoveries of metallic indium and tin from ITO (Indium Tin Oxide) scrap, laboratory scale experiments have been conducted to verify the proposed process for practical purpose. The process consists of two stages of reaction. At the first stage, ITO is reduced to In-Sn alloy with CO at a low temperature. At the second stage, indium in the In-Sn alloy preferentially vaporizes at a high temperature due to the difference between the vapor pressure of indium and that of tin. In the first stage of the process, 70 vol% CO, 1023 K and 90 min are desirable for reducing atmosphere, reduction temperature and reduction time, respectively, for the reduction of ITO with CO to In-Sn alloy. As for the second stage, the temperature more than 1373 K is required for rapid preferential vaporization of indium under vacuum.

Keywords. ITO (indium tin oxide), rare metal, recovery, recycling, pyrometallurgy, reduction, vaporization.

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1 Introduction

ITO (Indium Tin Oxide) is used for electrodes such as liquid crystal displays and organic electro-luminescence displays, since it has conducting and transparent properties. Indium consumption of approximately 90% is for the target material of the transparent electrodes and then the demand has increased in recent years in Japan [1]. In order to supply raw materials to industries, indium has been mainly provided by import, since the resource of indium is poor in Japan. However, there are many problems such as an overseas uneven distribution of the resource, economic strategy, uneasy political situation, and so on [1]. Securing of raw materials, in which amount and price are both stable, is strongly desired from the viewpoint of state stockpiling. Therefore, the stable supply of rare metal like indium and/or establishment of recycling technologies are then highly required [2].

Indium has been recovered and recycled previously from in-process scrap in ITO manufacturing, but has been done very few from end products. In the past few years, a hydrometallurgical method has been developed, where liquid crystal panels are chemically treated and recovered as indium hydroxide [3]. More recently, a reduction of indium oxide to metallic indium with lithium nitride was achieved through mechanochemical route from a basic research [4]. However, they have problems such as extensive use of acid-alkaline agents, a large amount of leaching residue, low rate of recovery, use of dangerous and expensive chemicals, and so on. Therefore, most appropriate material recycling process from artificial rare metal resource like ITO scrap, which is considered to be an urban mine, with economic and environmentally friendly is desired ardently [2].

The phase relations and equilibrium oxygen partial pressures in the In-Sn-O ternary system, which are of fundamental importance for discussing the recoveries of indium and tin from an ITO scrap, have been investigated and then a new pyrometallurgical process has been proposed in the previous work [2]. The process consists of two stages of reaction. At the first stage, ITO is reduced to In-Sn alloy with CO at a low temperature. At the second stage, indium in the In-Sn alloy preferentially vaporizes at a high temperature due to the difference between the vapor pressure of indium and that of tin [2]. The objective of the present work is to verify the proposed process on a laboratory scale for practical purpose.

2 Principle of Pyrometallurgical Process for Recoveries of Metallic Indium and Tin from ITO Scrap

Figure 1 shows the concept of the principle of pyrometallurgical process for the recoveries of metallic indium and tin from ITO scrap [2]. As mentioned above, the process consists of two stages of reaction for ITO scrap as a starting material.

At the first stage, ITO, that is, indium tin oxide is reduced to In-Sn alloy by CO at a low temperature. At the second

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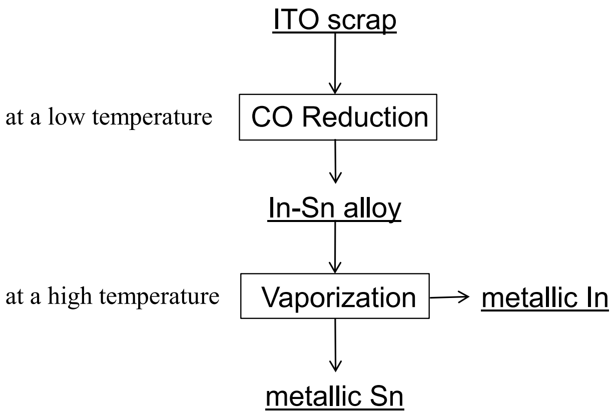


Figure 1. Concept of the principle of pyrometallurgical process for the recoveries of metallic indium and tin from ITO scrap.

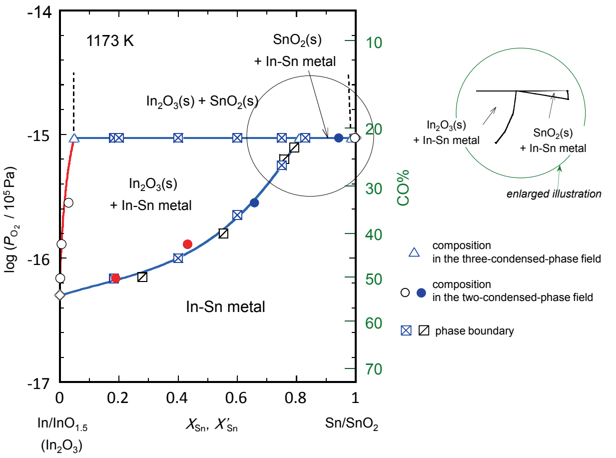


Figure 2. Relation between the partial pressure of oxygen and the composition of condensed phase at 1173 K, where $X_{Sn} = N_{Sn}/(N_{In} + N_{Sn})$ and $X'_{Sn} = N'_{Sn}/(N'_{In} + N'_{Sn})$ denote the molar ratio in alloy and oxide phase, respectively.

stage, the temperature is higher and indium in the In-Sn alloy preferentially vaporizes due to the difference between the vapor pressure of indium and that of tin. Indium vapor formed is cooled and recovered as metallic indium.

The principle is based on the reducing and vaporization characteristics in In-Sn-O system mentioned below. The relation between the partial pressure of oxygen and the composition of condensed phase in the In-Sn-O system at 1173 K is presented in Figure 2 [2]. In the figure $X_{Sn} = N_{Sn}/(N_{In} + N_{Sn})$ and $X'_{Sn} = N'_{Sn}/(N'_{In} + N'_{Sn})$ denote the molar ratio in In-Sn alloy and In-Sn-O oxide phase, respectively. N_i and N_i' are the mole fraction in the In-Sn-O ternary system in alloy and oxide phase, respectively.

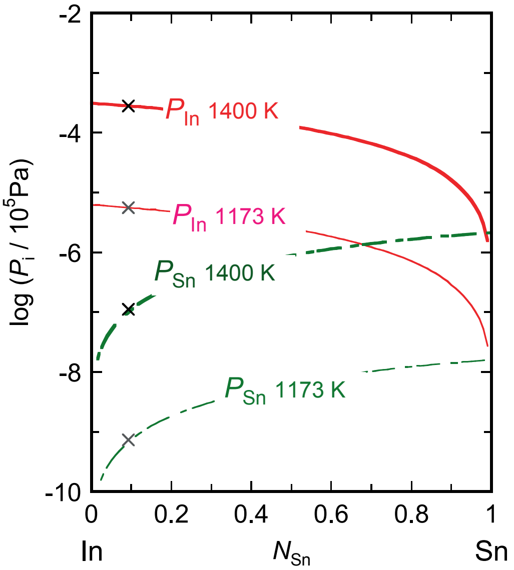


Figure 3. Vapor pressures of indium and tin in In-Sn alloy.

The basic reactions at the first stage of the process are expressed by Equations (1) and (2).

$$1/3In_2O_3(s) + CO(g, 10^5\ Pa) = 2/3In(l) + CO_2(g, 10^5\ Pa), \quad (1)$$

$$1/2SnO_2(s) + CO(g, 10^5\ Pa) = 1/2Sn(l) + CO_2(g, 10^5\ Pa). \quad (2)$$

The ITO composition is indicated to be 90 mass% In_2O_3, 10 mass% SnO_2 in the literature [5]. The composition taken in the In-Sn binary system is $N_{Sn} = 0.093$ [2], which corresponds to $X_{Sn} = 0.093$. Thus, it is found that ITO is easily reduced to In-Sn alloy under a reducing atmosphere of more than 60 vol% CO at 1173 K from the right-hand scale of the vertical axis in Figure 2.

At the second stage, the basic reaction of the process is expressed by Equation (3).

$$In(l) = In(g, 10^5\ Pa). \quad (3)$$

The vapor pressures of indium and tin are presented as a function of the composition of In-Sn alloy in Figure 3 [2]. In the figure the solid and dashed-dotted lines correspond to the vapor pressures of indium and those of tin, respectively. The point × denotes the In-Sn alloy composition $N_{Sn} = 0.093$, where ITO composition [5] is taken in the In-Sn binary system to discuss the case that ITO is reduced to In-Sn alloy with CO. The most important observation is that the vapor pressure of indium is three orders of magnitude larger than that of tin in In-Sn alloy at the ITO composition × at both the temperature. This indicates that the separation of indium and tin from In-Sn alloy by vaporization is basically possible. The In-Sn alloy can be obtained by reduction of ITO with CO. However, at the lower temperature 1173 K the vapor pressures of both the components in In-Sn alloy are less than 1 Pa at the ITO composition ×, suggesting that both the components cannot vaporize at a low temperature like 1173 K. At the higher temperature 1400 K, however, the vapor pressure of indium in In-Sn alloy is more than 10 Pa at the ITO composition ×. Thus, indium will vaporize preferentially from In-Sn alloy at the high temperature 1400 K. The recoveries of metallic indium and tin from ITO scrap by the two-stage pyrometallurgical process mentioned above are thermodynamically understood.

3 Experimental

3.1 Reduction of ITO with CO

The samples used in the reduction experiment were analytical reagent grade In_2O_3 (99.9mass% purity), SnO_2 (99.8 mass% purity) and ITO (Indium Tin Oxide, 99.99 mass% purity). The ITO composition was determined to be 93.3 mass% In_2O_3, 6.7 mass% SnO_2 by inductively coupled plasma (ICP) spectrometry. The phase of ITO was identified to be the $In_2O_3+SnO_2$ two-condensed-phase combination by X-ray diffraction technique (XRD) as shown in Figure 4. The mean particle diameter was 11.2 μm.

Figure 5 shows the schematic diagram of the experimental setup for reduction. The powder sample was put in an alumina crucible of 18 mm inner diameter (i.d.), 22 mm outer diameter, 30 mm length. The crucible was suspended from the electronic balance into a quartz reaction tube with 33 mm i.d. by a piece of 0.5 mm Φ stainless steel wire to measure the sample mass change. The temperatures examined were 973, 1023 and 1073 K. While the sample was being heated to the experimental temperature, the reaction tube was purged with argon gas. When the temperature of the sample had reached the desired temperature, the inert argon gas was switched to CO-CO_2 gas mixture with the same flow rate as that of argon, and then the measurement of the mass change was commenced. After some definite time the CO-CO_2 gas mixture was switched to argon, the sample was cooled to room temperature and then weighed. The vapor pressures of pure metallic indium and tin are 7×10^{-2} Pa [6] and 1×10^{-4} Pa [7] at 1073 K, respectively. The mass change was thus considered the oxygen mass loss in the sample as the result of reduction with CO-CO_2 gas mixture. The reduction ratio was then calculated from the mass loss. The composition of CO-CO_2 gas mixture was adjusted by regulating the gas ratio of CO/CO_2 and then set to be 70 vol% CO. The flow rate of gas mixture was 5×10^{-6} m^3 (STP) · s^{-1}. The mass of In_2O_3, SnO_2 and ITO used for each experimental run were 0 to 1.00 g, 0.814 g and 0.985 g, respectively, which corresponded to the same amount of reducible oxygen in each sample so as to compare the reduction rate. All the experiments were carried out more than twice for each experimental condition in order to confirm the reproducibility of the experimental data.

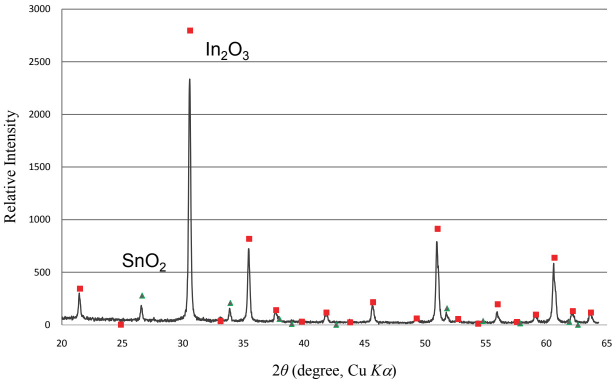


Figure 4. X-ray Diffraction pattern of ITO.

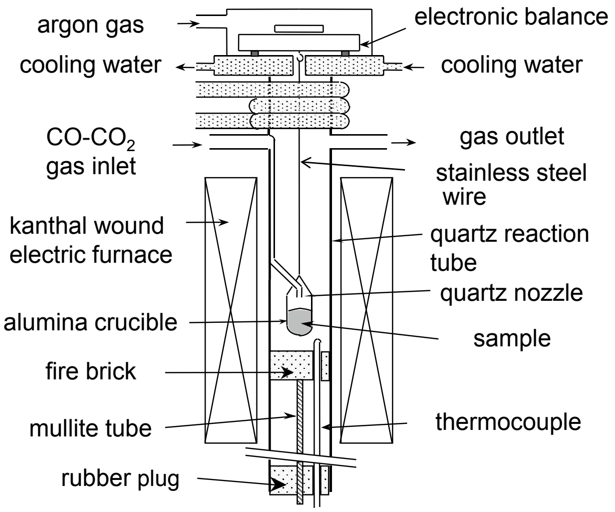


Figure 5. Schematic diagram of the experimental setup for reduction.

3.2 Vaporization of In-Sn alloy Under Vacuum

The sample used in the vaporization experiment was In-Sn alloy preliminarily reduced with 70 vol% CO-CO_2 gas mixture from ITO. Figure 6 shows main part of the experimental setup for vaporization. The alumina crucible with alloy sample was suspended from the Cahn's electrobalance into a quartz reaction tube of 36 mm inner diameter by a piece of 0.5 mm Φ stainless steel wire to measure the mass change. The temperatures examined were 1273, 1323, 1373, 1393 and 1413 K. While the sample was being heated to the experimental temperature, the reaction tube was filled with argon gas. When the temperature of the sample had reached the desired temperature, the reaction tube was evacuated to about 1 Pa (1×10^{-5} atm) by using a rotary pump and the measurement of the mass change was commenced. After

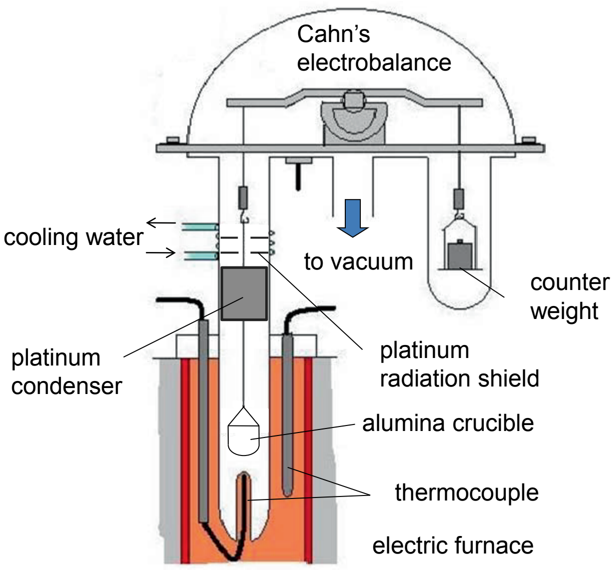


Figure 6. Main part of the experimental setup for vaporization.

the vaporization experiment, the sample was cooled to room temperature and then weighed. In order to know the ratio of indium to tin in the vaporized substance, a cylindrical platinum foil condenser was placed under a platinum radiation shield in the reaction tube as seen in Figure 6. Indium and tin contents in the condensed substance were determined by ICP spectrometry.

4 Results and Discussion

4.1 Reduction of ITO with CO

Figure 7 shows the relation between the reduction ratio and time for In_2O_3 and SnO_2. As mentioned above, 1.00 g and 0.814 g was weighed for each reduction experiment, respectively, so as to compare the reduction rate of each oxide with the same amount of reducible oxygen. In the figure the solid and dashed lines correspond to In_2O_3 and SnO_2, respectively. The reduction rate increases with increasing the temperature for both the oxide. In the temperature range of 1023 to 1073 K, the reduction rate of SnO_2 is a little faster than that of In_2O_3, while at 973 K the reduction rate of In_2O_3 is slightly faster than that of SnO_2. This is possibly due to the difference of temperature dependence of the reduction rate for each oxide. Meanwhile the reduction ratio of In_2O_3 exceeds unity at the end of the reduction at higher temperature than 1023 K. This suggested that the evaporable suboxide In_2O formed by the following reaction [8].

$$In_2O_3(s) = In_2O(g, 10^5\ Pa) + O_2(g, 10^5\ Pa). \qquad (4)$$

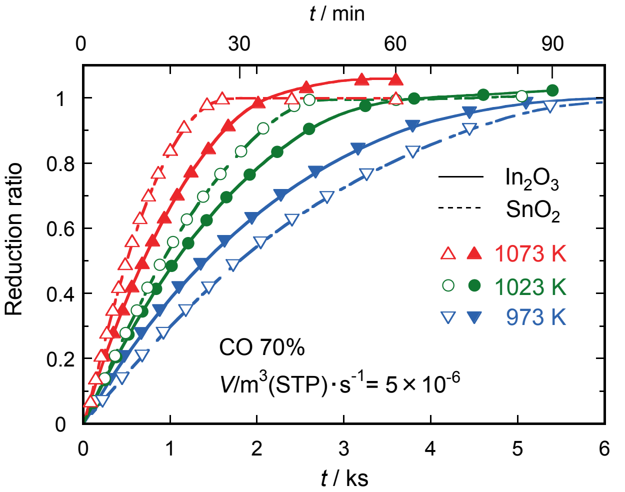


Figure 7. Relation between the reduction ratio and time for In_2O_3 and SnO_2.

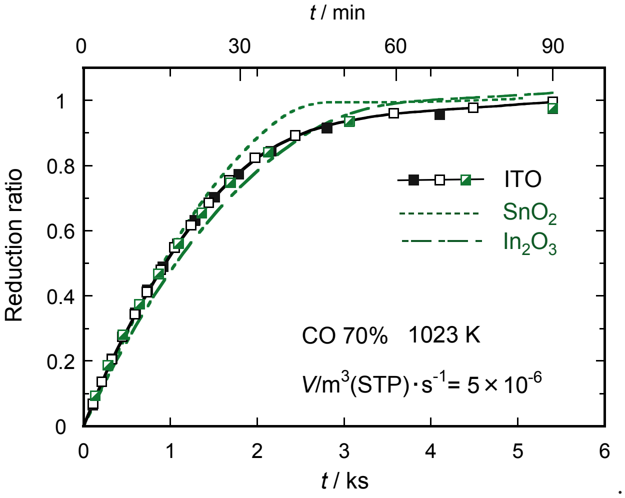


Figure 8. Relation between the reduction ratio and time for ITO.

Then the mass change observed was considered as the total of the reduced oxygen and the evaporation of suboxide In_2O. The evaporation of In_2O results in indium loss during the first stage. Therefore, a lower temperature is favorable for the reduction of ITO in terms of suppression of evaporable suboxide In_2O. Then the reduction experiment for ITO was conducted at 1023 K as mentioned next.

The relation between the reduction ratio and time for ITO at 1023 K is shown in Figure 8, together with the results of SnO_2 and In_2O_3. In the figure the symbols denote three experimental results, which are for confirmation of the reproducibility of the experimental data. It is found that the ITO behaves in almost the same reduction rate as SnO_2 and In_2O_3. Furthermore, the reduction ratio of ITO did not exceed unity, indicating that the evaporation of In_2O was negligibly small. Then, the reduction condition was deter-

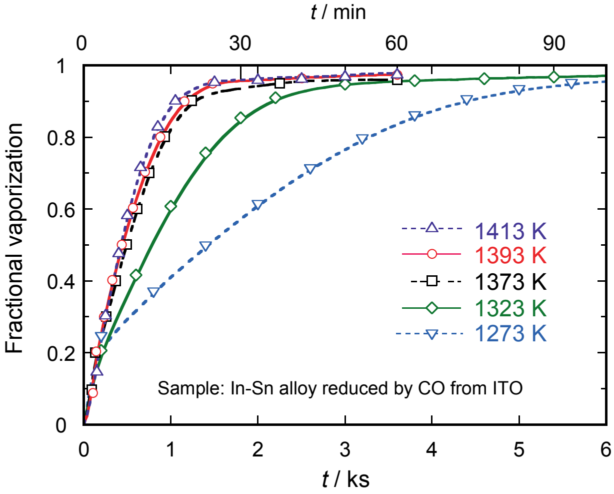


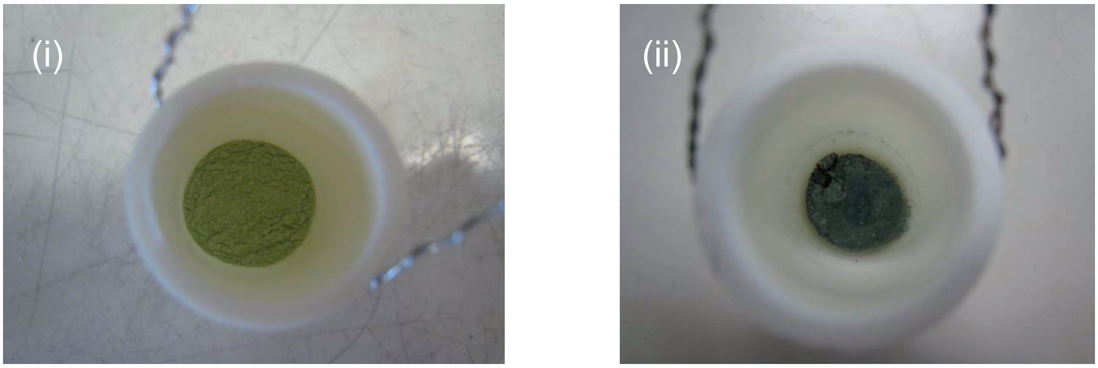
Figure 9. Relation between the fractional vaporization and time in the temperature range of 1273 to 1413 K for In-Sn alloy reduced at 1023 K from ITO.

mined as 70 vol% CO for reducing atmosphere, 1023 K for reduction temperature and 90 min for reduction time.

4.2 Vaporization of In-Sn alloy under Vacuum

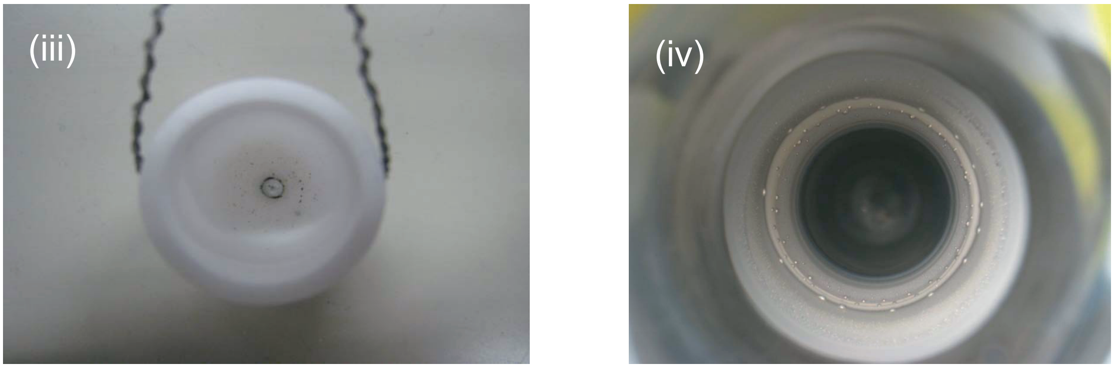
Figure 9 shows the relation between the fractional vaporization and time in the temperature range of 1273 to 1413 K for In-Sn alloy preliminarily reduced at 1023 K from ITO. The vertical axis is fractional vaporization based on the mass change of the sample. According to the chemical analysis by ICP spectrometry, tin in the condensed substance was less than 0.4 mass% in all the vaporization experiments. Thus, it was found that indium vaporized preferentially from In-Sn alloy under vacuum. The vaporization of indium proceeds faster at higher temperatures. At 1273 K indium vaporized after 90 min and 60 min at 1323 K, while at more than 1373 K indium rapidly vaporized in 30 min.

The observed photos are presented in Figure 10 for (i) ITO sample before reduction, (ii) In-Sn alloy reduced at 1023 K from ITO (after reduction), (iii) Sn metal (after vaporization), and (iv) In metal drops condensed inside the reaction tube wall. Therefore, as expected in the preceding principle section mentioned, the recoveries of metallic indium and tin from ITO was successfully verified.



(i) ITO sample before reduction

(ii) In-Sn alloy reduced at 1023 K from ITO (after reduction)



(iii) Sn metal (after vaporization)

(iv) In metal drops condensed inside the reaction tube wall

Figure 10. Observed photos for (i) ITO sample before reduction, (ii) In-Sn alloy reduced at 1023 K from ITO (after reduction), (iii) Sn metal (after vaporization), and (iv) In metal drops condensed inside the reaction tube wall.

5 Conclusions

In order to verify and demonstrate the new pyrometallurgical process for the recoveries of metallic indium and tin from ITO scrap which has been proposed in the previous work, laboratory scale experiments have been conducted for practical purpose. The process consists of two stages of reaction. At the first stage, ITO is reduced to In-Sn alloy with CO at a low temperature. At the second stage, indium in the In-Sn alloy preferentially vaporizes at a high temperature due to the difference between the vapor pressure of indium and that of tin. Indium vapor formed is cooled and recovered as metallic indium. In the first stage of the process for the reduction of ITO with CO, 70 vol% CO, 1023 K and 90 min are desirable for reducing atmosphere, reduction temperature and reduction time, respectively. In the second stage of the process for rapid preferential vaporization of indium, the temperature more than 1373 K is required under vacuum.

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