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Comparison of indium purification between vacuum refining and electrowinning

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Vacuum refining and electrowinning experiments of indium metal with 99.97% purity have been performed to compare the behavior of impurity metals during refining. When indium metal was vacuum refined at 1000°C and 1.32×10^{-8} atm for one hour, the major impurity elements, Pb and Bi, were effectively removed while Al, Cu and Sn were not removed. During electrowinning, solution pH, temperature and NaCl concentration had negligible effects on the current efficiency of electrowinning from the chloride solutions in the experimental ranges. However, a high concentration of indium and NaCl was important in achieving high energy efficiency. By employing electrowinning, the impurity metals in the indium such as Bi, Pb, Al, Mg and Cd were removed while copper was not removed.

1. Introduction

High-purity indium is needed as a raw material for semiconductor applications. Vacuum refining, electrolwinning, zone refining and recrystallization have been employed to purify the indium metal [1–7]. It was reported that the electrolytic purification could remove tin, nickel and lead from the indium metal. By zone refining, Cd, Cu, Zn, Au, Ag and Ni can be eliminated. Vacuum refining could remove Cd, Se, Te, Zn, Pb and Tl. In these impurity elements, lead and tin present in the indium metal have a effect on the properties of the semiconductor made from indium [8].

Indium metal has low melting point and high boiling point. Therefore, it is possible to remove the impurity metals with high vapor pressure by distilling indium metal at relatively low temperature under vacuum. The impurity metals, which are not well removed by chemical method, are easily removed by vacuum refining at relatively low temperatures. Thus purification of metals by vacuum refining is widely practiced. Generally vacuum refining is employed after the electrolytic step to further reduce the level of volatile impurities in the indium metal.

In this study, the effects of temperature and time on the vacuum refining of indium metal have been investigated. From the experimental results, optimum condition to purify indium was obtained. In addition, purification of indium by electrowinning from chloride solutions have been performed. The effects of electrowinning conditions on the current efficiency and on the chemical compositions of electrodeposited indium were investigated. From these experimental results, optimum electrowinning condition was obtained.

2. Experimental

The chemical composition of indium crude metal (Aldrich Chemical Co., purity of 99.97%) used in the experiments is shown in Table I. Fig. 1 is a schematic diagram showing an experimental apparatus for vacuum refining. About 8.3 g of indium metal was put in a quartz boat (volume 11 cm^3). The surface area of molten metal exposed to the vapor phase in the boat was 10 cm^2, determined from the dimension of the quartz boat. This boat was then placed in a quartz tube, the one end of which was sealed. This quartz tube was loaded in a horizontal electric tube furnace and evacuated using a set of rotary and diffusion pumps. The vacuum pressure in the quartz tube was measured by Penning vacuum gauge. Once the desired temperature was reached, the temperature was maintained for certain time. The mass change of indium metal was measured by a mass balance (Mettler Model No. AE 160) after vacuum refining experiments.

The electrolyte solutions for electrowinning experiments were prepared by dissolving the indium metal in

TABLE I Chemical composition of indium crude metal (ppm)

Al	Mg	Cu	Cd	Sn	Pb	Bi
2	0.1	1.7	0.5	5	30	61

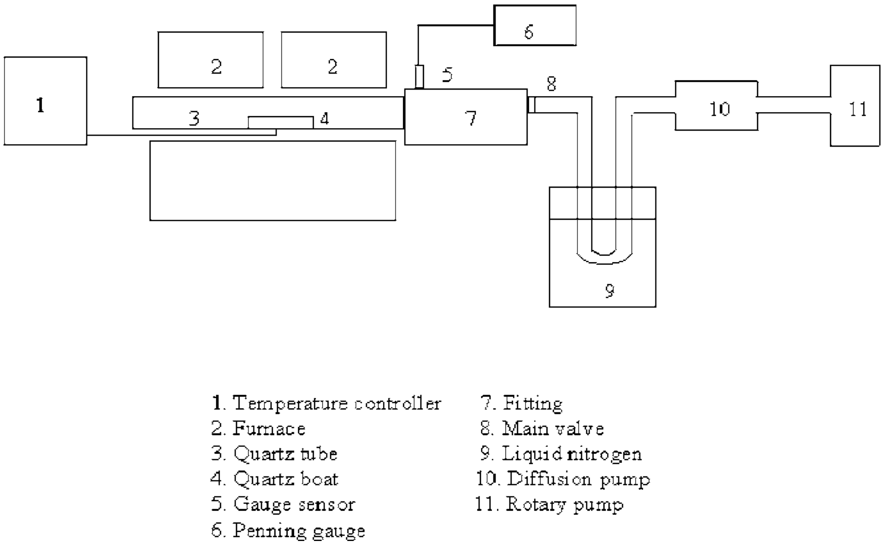

Figure 1 Schematic diagram of experimental apparatus.

the hydrochloric acid solutions. Solution pH was controlled by adding HCl and NaOH. The cathode, with a surface area of 3 × 10 cm^2, was stainless steel and the anode was graphite. Saturated calomel electrode was used as a reference electrode. The cathode and anodes were polished with alumina papers of different grades and then washed with distilled water several times. The distance between electrodes was maintained at 5.5 cm.

The electrowinning experiments were performed using a constant temperature water bath. Electricity of 250 Coulomb was supplied by Potentio/Galvanostat (Hokuto Denko Co. Ltd., Model HA-320). At the end of electrowinning experiments, the cathodes were washed with distilled water and dried to measure the weight of electrodeposited indium.

After dissolving indium metals, which were obtained from the vacuum refining and electrowinning experiments, in hydrochloric acid solutions, the concentrations of impurity metals were measured by A.A. (Perkin-Elmer, Model No. 3030B) and I.C.P. (Thermo Jarren Ash, Model No. Polyscan 61E). The detection limits of impurity metals are represented in Table II.

3. Results

3.1. Vacuum refining

The boiling point of indium at 1 atm is 2062°C and the heat of vaporization of indium is 231.8 kJ/mol [9]. The boiling point of indium at 1.32×10^{-8} atm was calculated by inserting these physical values into Clausius-Clapeyron equation and the estimated value was 653°C. Therefore, indium metal was refined at temperatures ranging from 650 to 1050°C at a vacuum pressure of 1.32×10^{-8} atm. The effect of refining temperature on the recovery of indium metal is shown in Fig. 2. The recovery percentage of indium metal did not significantly decrease up to 850°C, under which it maintains more than 97%. At temperatures above 850°C, however, the recovery percentage decreased at higher rates, the rate of which was accelerated with increasing temperatures. As the temperature was over 1000°C, the recovery percentage decreased at even faster rates and lowered to the level of 50% at 1050°C.

The effect of reaction time on the vaporization rate of indium at 1.32×10^{-8} atm was investigated at various reaction temperatures. The variation of mass change (ΔW) of indium with reaction time at various temperatures is shown in Fig. 3. Fig. 3 represents that the mass change of indium increases linearly with increasing exposure time. As the temperature increased from 950 to 1050°C, the rate of mass change increased more than three times.

TABLE II Detection limit of various elements (ppm)

Al	Bi	Cd	Cu	Mg	Pb	Sn	Zn
0.05	0.1	0.05	0.01	0.01	0.5	0.1	0.1

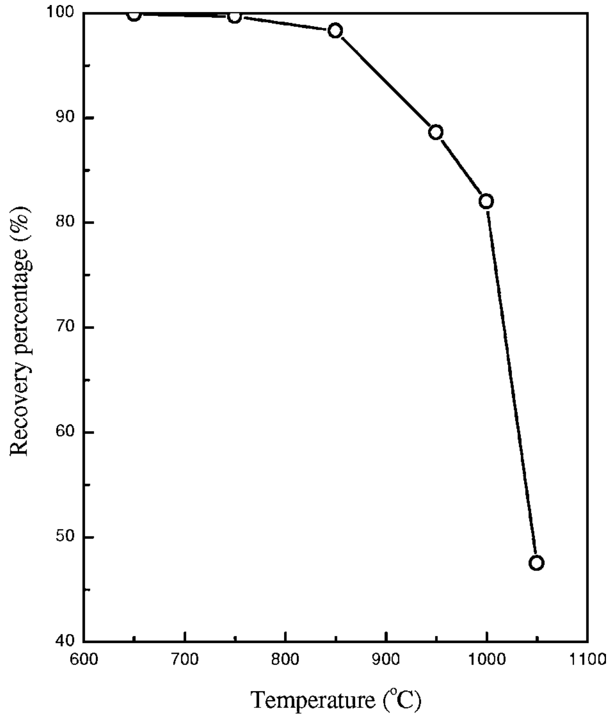

Figure 2 Effect of temperature on the recovery percentage of indium ($P = 1.32 \times 10^{-8}$ atm, Time = 2h).

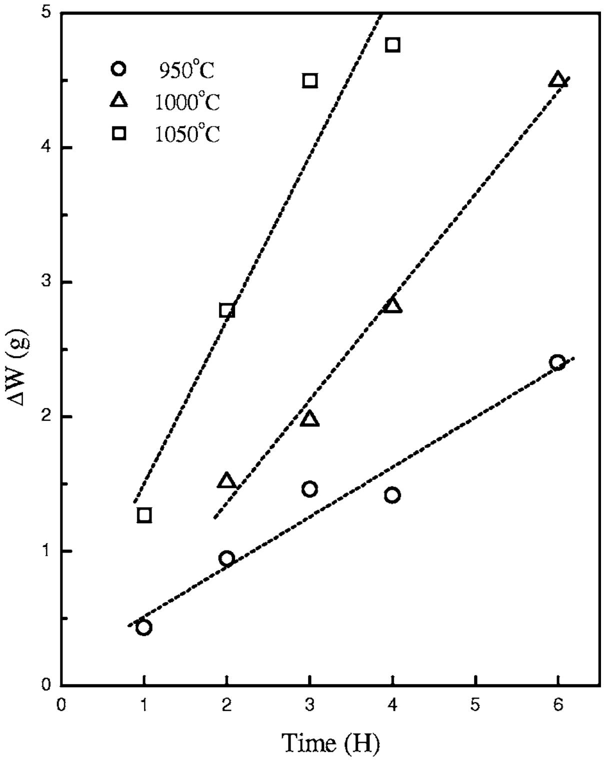

Figure 3 Effect of temperature and time on the mass change of indium. ($P = 1.32 \times 10^{-8}$ atm).

The maximum rate of vaporization at reduced pressure is given by Langmuir equation, which is represented by Equation 1. This Langmuir equation is applied to the vaporization at low pressure when no energy of activation is required [10].

$$\text{Rate}_{\text{max}} = 44.3\frac{P_{\text{i}}}{\sqrt{M_{\text{i}}T}}\left(\frac{\text{mole}}{\text{cm}^2 \times \text{s}}\right) \quad (1)$$

In the above equation, P_{i} represents the vapor pressure (atm) and M_{i} the molecular weight of the vaporizing species (g/mol) and T the reaction temperature (K).

The maximum rate of vaporization of indium was obtained by inserting the necessary physical values of indium into Equation 1. Multiplying the maximum rate of vaporization with the surface area of molten metal (10 cm^2) gives the maximum rate of mass change of indium. The experimental values of the rate of mass change for indium were obtained from the slopes of mass change vs. reaction time plot in Fig. 3. The experimental mass change rates were compared with those calculated by Equation 1 in Table III. Table III shows that the mass change rates obtained experimentally were much smaller than those calculated by Equation 1.

TABLE III Comparison of mass change rates of indium obtained from vacuum refining experiments and those calculated by Langmuir equation

Temperature (°C)	P_{In} (atm)	Rate (g/h)	Rate$_{\text{max}}$ (g/h)	Rate/Rate$_{\text{max}}$
950	1.93×10^{-5}	0.37	9.42	0.04
1000	4.72×10^{-5}	0.76	22.6	0.03
1050	1.08×10^{-4}	1.22	50.8	0.02

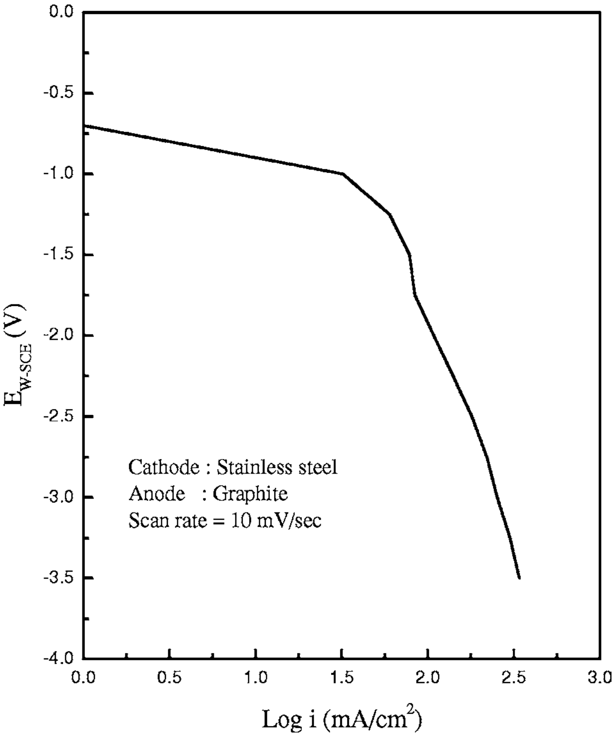

Figure 4 Polarization curve for the electrowinning of indium from hydrochloric acid solution.

The ratio of experimental mass change rate to the maximum rate of mass change was very low, which was approximately 0.03 as shown in Table III. The difference between the experimental values and the calculated rates may be related to the formation of oxide layers on the surface of molten metal during experiments.

3.2. Electrowinning

The polarization curve for the electrowinning of indium from hydrochloric solution on a stainless steel cathode is shown in Fig. 4. This polarization curve was obtained under potentiostatic conditions in the range between −0.5 to −3.5 V/SCE and the scan rate was 10 mV/sec. Fig. 4 shows that appreciable electrowinning rate of indium was achieved when more than −1.5 V/SCE was applied to the cathode. For higher overvoltage to the cathodic reaction than −1.5 V, the overvoltage increased linearly with the logarithm of current density.

Fig. 5 shows the variation of cell voltage and current efficiency with the current density. It is seen in Fig. 5 that cell voltage increases linearly with the current density in the experimental range. However, current density had a negligible effect on the current efficiency of the electrowinning reaction. In the electrowining of indium metal from hydrochloric solutions, the cell voltage is composed of the following electrode reactions [11].

$$\text{Cathode: } \text{In}^{3+} + 3\text{e} = \text{In}, E^\circ = -0.34 \text{ V} \quad (2)$$

$$2\text{H}^+ + 2\text{e} = \text{H}_{2(\text{g})}, E^\circ = 0.0 \text{ V} \quad (3)$$

$$\text{Anode: } 2\text{Cl}^- = \text{Cl}_{2(\text{g})} + 2\text{e}, E^\circ = -1.36 \text{ V} \quad (4)$$

$$\text{H}_2\text{O}_{(\text{l})} = 0.5\text{O}_{2(\text{g})} + 2\text{H}^+ + 2\text{e},$$
$$E^\circ = -1.23\ V \quad (5)$$

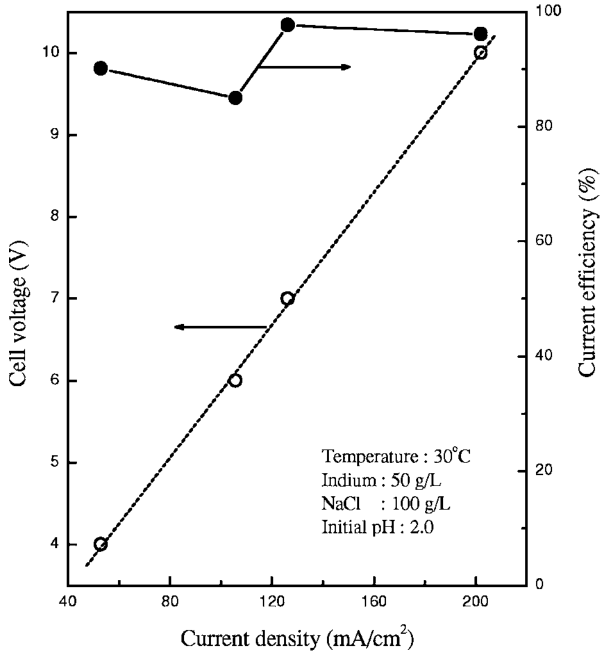

Figure 5 Variation of cell voltage and current efficiency with the current density.

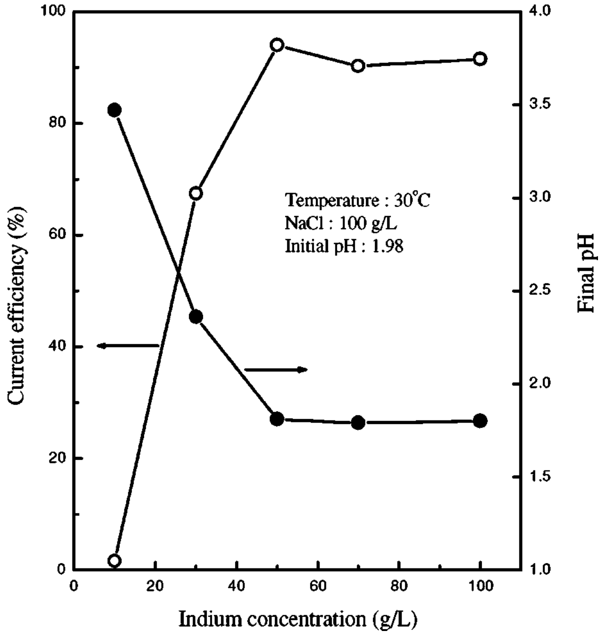

Figure 6 Effect of indium concentration on the current efficiency and final pH of solution.

From the above values of electrode potential, it is known that 1.7 V of the cell voltage is required for the electrowinning of indium. Fig. 5 indicates that more than 2 V of overvoltage is needed to initiate the electrowinning of indium from hydrochloric acid solution.

From preliminary experiments about the effects of reaction temperature and solution pH on the current efficiency of the electrowinning, it was found that these factors had negligible impacts on the current efficiency in the experimental conditions of temperatures between 30 and 60°C and of solution pH between 0.5 and 2.5. The main goal of electrowinning is to produce a dense deposit with high purity at the maximum current efficiency. Therefore, the reaction temperature, current density and solution pH were maintained at 30°C, 100 mA/cm^2 and 2.0, respectively in the following experiments. This condition is referred as the standard experimental condition of electrowinning hereafter.

The effect of the indium concentration on the current efficiency was investigated by varying the indium concentration from 10 to 100 g/L under standard experimental condition and the results are shown in Fig. 6. Fig. 6 indicates that when the concentration of indium is about 50 g/L, the current efficiency is over 90%. However, when the concentration of indium was below 30 g/L, the current efficiency decreased with decreasing indium concentration. The dependence of current efficiency on the concentration of indium is related to the current density. Since indium ions as well as hydrogen ions were reduced at cathode to maintain the current density, the current efficiency decreased with decreasing indium ion concentration. Fig. 6 also shows that the variation of the final pH of the solution with indium concentration. When the indium concentration was below 30 g/L, both the indium ions and hydrogen ions were reduced at cathode and solution pH was rapidly increased. Since indium ions are precipitated around pH 2.7 [12], the solution pH must be maintained below this pH value. Therefore, the optimum concentration of indium adequate for electrowinning was 50 g/L.

The effects of NaCl concentration on the cell voltage and the current efficiency were investigated by varying NaCl concentration from 1 to 100 g/L under standard experimental condition and the results are shown in Fig. 7. It is known from Fig. 7 that the cell voltage increases greatly with decreasing NaCl concentration. The dependence of cell voltage on the NaCl concentration verifies the fact that the major role of NaCl in the electrowinning of indium is to increase the conductivity of the electrolyte solution and thus to lower the

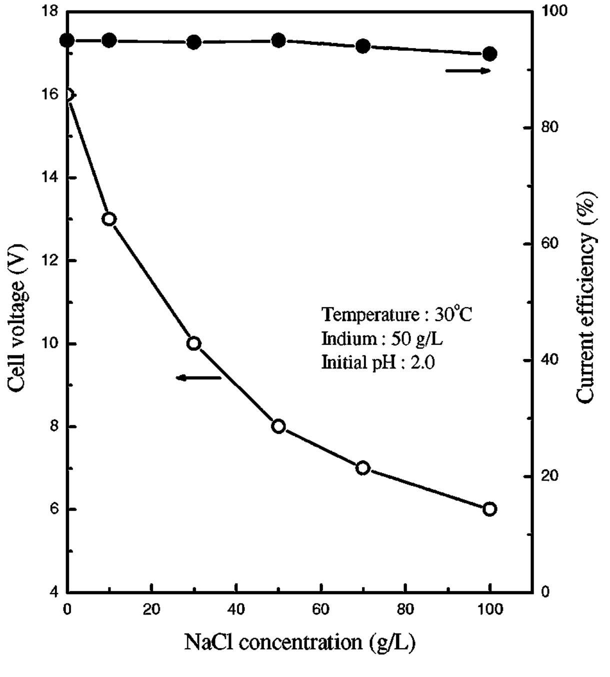

Figure 7 Effect of NaCl concentration on the cell voltage and current efficiency of electrowinning.

TABLE IV Chemical composition of indium metal obtained from various experimental conditions of vacuum refining (ppm)

Experimental conditions	Mg	Cu	Pb	Bi
Starting material	0.1	1.7	30	61
850°C, 2 h	<0.01	1.6	20	47
950°C, 2 h	<0.01	2.0	<0.5	10
1000°C, 1 h	<0.01	2.2	<0.5	<0.1
1000°C, 2 h	<0.01	2.0	<0.5	<0.1
1000°C, 3 h	<0.01	2.6	<0.5	<0.1
1000°C, 4 h	<0.01	2.6	<0.5	<0.1
1000°C, 6 h	<0.01	2.6	<0.5	<0.1

IR drop across the solution between electrodes. Fig. 7 also shows that the NaCl concentration has a negligible effect on the current efficiency in the experimental ranges. As far as energy efficiency is concerned, more than 50 g/L of NaCl is needed for the electrowinning of indium from chloride solution.

4. Discussion

The chemical compositions of indium obtained at various vacuum refining conditions are shown in Table IV. Table IV represents that the rate of refining is significantly influenced by the operating temperature and exposure time. The removal mass percentage of Bi and Pb remarkably increased with increasing temperatures. When the refining temperature was 850°C, Bi and Pb, which are the major solutes of the indium metal, were removed by only 23% and 33%, respectively during two hours. At 1000°C, however, most of them were removed from indium metal: 99% and 98%, respectively within an hour of exposure time. Among the impurity metals in the indium, it is difficult to remove Al, Sn and Cu by vacuum refining because of low vapor pressure of these metals. However, nearly almost of Bi, Pb, Mg and Cd were removed by vacuum refining at 1000°C within an hour because these metals have higher vapor pressures than indium. In those impurity elements that are detrimental to the properties of semiconductor made from indium (i.e., lead and tin), lead was removed to less than detection limit by vacuum refining at above 950°C. However, tin was not removed by vacuum refining in the experimental conditions employed in this study.

The variation of the concentrations of impurity elements present in indium metal with the electrowinning condition is shown in Table V. From Table V, it is known that the final pH of solution decreases with decreasing NaCl concentration. The decrease in the final pH of the solution is related to the anode reaction. With decreasing NaCl concentration, the evolution of oxygen gas and the production of hydrogen ion ($H_2O_{(l)} = 0.5O_{2(g)} + 2H^+ + 2e$) are occurred at the anode. Therefore, solution pH decreases with decreasing NaCl concentration due to the increase in the concentration of hydrogen ion.

TABLE V Chemical compositions of the electrodeposited indium metal at various electrowinning conditions

Experimental conditions	pH_I	pH_F	Cd	Cu	Al	Pb	Bi
Starting material			0.5	1.7	2	30	61
In 50 g/L + NaCl 100 g/L	1.98	1.67	<0.05	7.8	<0.05	<0.5	<0.1
In 50 g/L + NaCl 50 g/L	1.98	1.37	<0.05	5.7	<0.05	<0.5	<0.1
In 50 g/L + NaCl 1 g/L	1.98	1.18	<0.05	12	<0.05	<0.5	<0.1

Reaction time: 5.5 h.
pH_I: Initial pH.
pH_F: Final pH.

Table V also shows that except copper, the impurity elements in the indium were removed to less than 1ppm by electrowinning. Since the reduction potential of copper ion is higher than that of indium ion, most of the copper ions in the solution are reduced at cathode. Therefore, copper cannot be removed by electrowinning. The standard reduction potentials of bismuth and lead ion are 0.32 and −0.13 V, respectively [11]. Although the reduction potentials of bismuth and lead ion are higher than that of indium ion, these ions were not reduced at cathode in the experimental ranges. One explanation for this result is the kinetic aspects of the reduction reaction of bismuth and lead ion in the experimental conditions considered in this study. Further research on the reduction behavior of bismuth and lead ion on to stainless steel is required to explain the results obtained in this study.

Copper ions present in the electrolyte could be removed by the following cementation reaction with crude indium metal.

$$3Cu^{2+} + 2In = 3Cu + 2In^{3+} \tag{6}$$

Hence, addition of stoichiometric amount of crude indium metal into the electrolyte solution would result in the decrease of copper concentration in the electrolyte. After removing copper from electrolyte by the above cementation reaction, the subsequent electrowinning of indium would yield indium metal with exceeding 99.999% purity.

5. Conclusions

From the vacuum refining and electrowinning experiments of indium, the following conclusions were obtained.

1. The major impurity elements in the indium metal, Bi and Pb, were nearly removed by vacuum refining at 1000°C and 1.32×10^{-8} atm within one hour. However, Al, Sn and Cu were not removed by vacuum refining due to their lower vapor pressures.
2. The impurity elements in the indium such as Bi, Pb, Al, Mg and Cd were removed to less than 1ppm by electrowinning while copper was not removed.
3. The initial concentration of indium should be higher than 50 g/L to achieve current efficiency of 90% at the current density of 100 mA/cm^2.
4. By employing cementation reaction of copper ion with crude indium metal prior to electrowinning, it would be possible to obtain indium metal with more than 99.999% purity by electrowinning.

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