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Preparation of 6N high-purity indium by method of physical-chemical purification and electrorefining

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The increasing demands for indium in recent years require high purity indium as raw materials. Physical-chemical purification and electrorefining have been performed to obtain 6N high purity indium. Indium is smelted by using NaOH, NaCl and $NaNO_3$ for 20 min at 400°C, the removing rate of Sn, Zn, Al reaches 40, 60 and 37% respectively. The removing rate of Cd is 90–95% and that of Tl reaches 40–60% when indium is smelted for 10 min by 20% glycerin solution of KI and I_2 at 180°C. When indium metal is vacuum refined in two stages: 800–900°C for 2 h and 950–1050°C for 2 h, the major impurity elements, Pb, Zn, and Bi, are effectively removed. When indium is electrolytic refined in $In_2(SO_4)_3$-H_2SO_4 system, in which indium content is 60–80 g/L, pH 2.0–3.0, current density 50–80 A/m^2, the content of impurities can be dropped and the product of indium reaches 99.9999%.

1. Introduction

Indium is a high versatile minor metal with a unique combination of properties. Physically, indium exhibits high ductility, low electrical resistivity and high thermal conductivity. Optically, thin films of doped indium oxides are transparent in the visible spectrum, reflecting in the infrared, and electrically conductive. This unusual set of properties makes indium indispensable to a broad range of industries, including flat panel display, fiber optics and a broad range electronics. Indium is used in the ITO thin-film, III-V semiconductor, fluorescent materials and metallorganic compound etc. The demands for indium, which need high purity indium as raw materials, have increased in recent years [1]. The methods of purifying indium include ionic exchange, vacuum distillation, region smelting, low halide and electrorefining [2–13]. Electrorefining, with short process flow, simple and convenient operation and little investment, is a usual purification method, which has been reported [14–16]. It is difficult to prepare high purity indium only by electrolysis unless several combinations of purification methods are applied. In this paper 6N high purity indium is prepared by using chemical purification, vacuum refining and electrorefining. From these experimental results, optimum condition of preparing high purity indium has been obtained.

2. Principle of experiment

2.1. Removal of Sn, Zn and Al by smelting of indium

Electrorefining can't remove all impurities, which, however, can be dropped by the method of chemical purification. Before electrorefining, rude indium is smelted by NaOH, $NaNO_3$ and NaCl, NaOH is used for preventing indium from oxidation and improving absorbility of impurities of metal. The contents of Sn, Zn, Al will drop when added $NaNO_3$ and NaCl to smelt.

$$Sn + 2NaOH = Na_2SnO_2 + H_2$$

$$5Sn + 6NaOH + 4NaNO_3 = 5Na_2SnO_3 + 2N_2 + 3H_2O$$

$$5Zn + 8NaOH + 2NaNO_3 = 5Na_2ZnO_2 + N_2 + 4H_2O$$

$$4Zn + 7NaOH + NaNO_3 = 4Na_2ZnO_2 + NH_3 + 2H_2O$$

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$$10Al + 4NaOH + 6NaNO_3 = 10NaAlO_2 + 3N_2 + 2H_2O$$

2.2. Removal of Cd and Tl

The standard potentials of Tl (−0.336 V) and Cd (−0.342 V) are similar to that of indium. Therefore, it is difficult to remove Tl and Cd only by electrorefining. In glycerin solution of KI, the chemical potential of cadmium and that of indium are so different that cadmium can be separated well, Tl also can react with I_2. Therefore, the contents of of Cd and Tl will drop at the same time.

$$KI + I_2 + Cd = K_2CdI_4$$

$$2Tl + I_2 = 2TlI$$

2.3. Vacuum distillation

Indium has low melting point and high boiling point, therefore, it is possible to remove the impurities with high vapor pressure by distilling indium at relatively low temperature under vacuum. And the separation factors of indium and other elements can be consulted in previous reference [17].

According to the reference, the separation factors of In, Zn and Cd are 10^5-10^9, which indicates Zn and Cd can be separated from indium easily; The separation factor of In and Tl is 406–4560, and that of In and Bi is 35.1–90.6, and that of In and Pb is 79.6–240, therefore, Tl, Pb and Bi can be separated by controlling the conditions of vacuum refining.

2.4. Electrorefining of indium

In electrorefining, rude indium is used as anode, high purity indium as cathode, and $In_2(SO_4)_3$- H_2SO_4 solution as electrolyte. According to electrochemical theory, indium dissolves on anode:

$$In - 3e \rightarrow In^{3+} \quad \Phi^0 = -0.33\,V$$

Standard potentials of metals such as Fe, Al, Zn and Ga are lower than that of indium. Therefore, those metals will dissolve in advance, and stay in electrolyte; Metals like Ag, Cu, standard potentials of which are higher than that of indium, will not dissolve and drop into the bottom of the bath, settle in the mud of the anode.

Indium deposits on cathode:

$$In^{3+} + 3e \rightarrow In \quad \Phi^0 = -0.33\,V$$

Metals such as Fe, Al and Zn will not deposit on the cathode and stay in electrolytic solution because of their lower standard potentials and concentration.

3. Methods of experiment

Indium (99.9%) is put into a nickel pot, and then some solid of NaOH is added to cover indium, with a little $NaNO_3$ and NaCl being added, after then indium is smelted. The smelted indium is washed by deioned water and dried before it is measured. The process can remove the impurities, such as Sn, Al and Zn.

Glycerin and solid KI are dropped into the beaker and they are heated and agitated to promote dissolving. Some indium is added and heated to smelt, then iodine is added in order to keep solution brown and agitated to the degree that the surface of metal has brown material. Indium is taken out and dried, part of Cd and Tl can be removed.

About 10 g of indium metal is put in a quartz boat (volume 11 cm^3). The surface area of molten metal exposed to the vapor phase in the boat is 10 cm^2, determined from the dimension of the quartz boat. This boat is then placed in a quartz tube, the one end of which is sealed. This quartz tube is loaded in a horizontal electric tube furnace and evacuated using a set of rotary and diffusion pumps. The vacuum pressure in the quartz tube is measured by Penning vacuum gauge. Once the desired temperature is reached, the temperature is maintained for certain time. The mass change of indium metal is measured by inductively coupled plasma-atomic emissive spectrum (ICP-AES) after vacuum refining.

Pre-purified indium is dissolved in low concentration solution of H_2SO_4, and some sulfocarbamide and gelatin solution are added, then pH is adjusted to 2–3. Electrolyte is dropped into electrolytic bath and with agitation. Electrolysis is done in different conditions and electrolyzed product is dried by vacuum dry box, 2K-82B type. The acidity of solution is measured by pH meter and the content of impurity of is measured by ICP-AES.

4. Results and discussion

4.1. Effect of $NaNO_3$ on removal of Sn, Zn and Al

Indium is smelted by NaOH at 400°C, then a little $NaNO_3$ and NaCl is added, and the contents of impurities are analyzed. The results are shown in Fig. 1.

Fig. 1 indicates that, with smelting, the content of Sn, Al and Zn are dropped and the effect of smelting is better when adding both $NaNO_3$ and NaCl than only adding NaOH. Because $NaNO_3$ is a strong oxidant, Sn, Al and Zn are easy to be oxidized into salt. Elastic-viscious degree of alkali fusion mud will be eliminated by adding chlorinated soda into melting indium and

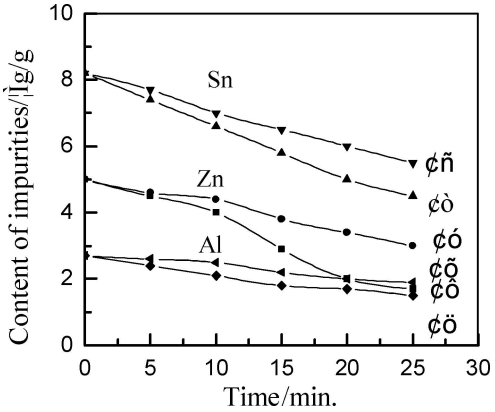

Figure 1 Content of impurities vs. time I, III, V–only NaOH was added; I, III, V–NaOH, $NaNO_3$ and NaCl were added; II, IV, VI–only NaOH was added.

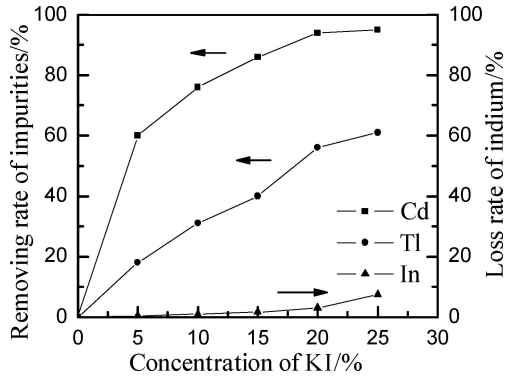

Figure 2 The effect of content of KI on the results of smelting indium.

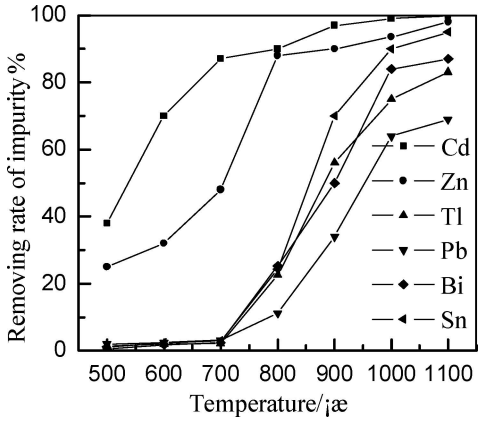

Figure 3 The effect of refining temperature on the removing of impurities.

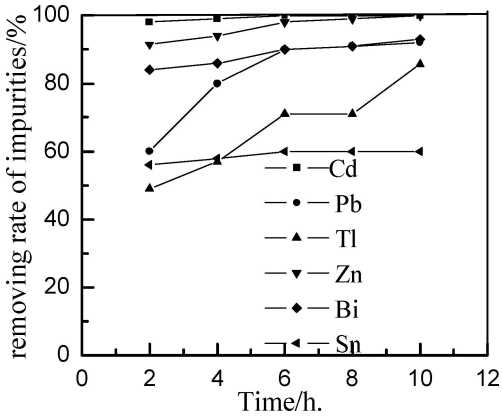

Figure 4 The effect of refining time on the removing of impurities.

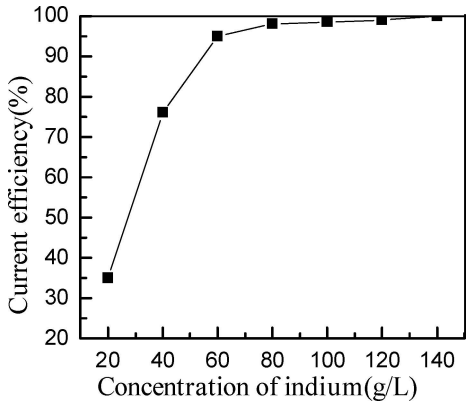

Figure 5 The effect of indium concentration on the current efficiency.

sodium hydroxide, which improves absorbility of impurity of metal. Therefore, the purpose of separation can be realized. According to experiment results, the best time of smelting is 20 min.and the removing rate of Sn, Zn and Al is about 40, 60 and 37% respectively.

4.2. Effect of the content of glycerin solution of KI and I_2 on removing Tl and Cd

Indium is smelted in the glycerin solution of KI and I_2 at 180°C and smelting time is controlled 10 min, the effect of content of KI on the results of smelting indium is shown in Fig. 2.

Fig. 2 shows: when the content of KI increases, the removing rates of Tl and Cd increase, however, the loss rate of indium keeps low and changes slowly. When the content of glycerin solution of KI exceeds 20%, the removing rates of Tl and Cd change little while the loss rate of indium increases. The reason is that when he contents of glycerin solution of KI and I_2 increase, the reaction of indium with iodine becomes easy and its loss rate increases. Therefore, the best content range of glycerin solution of KI is around 20%. The removing rate of Cd is 90–95%, and the removing rate of Tl is 40–60%, while the loss rate of indium is low 3.0%.

4.3. 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. The boiling point of indium at 1 Pa is calculated by inserting these physical values into Clausius Clapeyron equation and the estimated value is 915°C.Therefore, indium metal is refined at temperatures ranging from 500 to 1100°C at a vacuum pressure of 1 Pa. The effect of refining temperature on the removing of impurities in indium metal is shown in Fig. 3.

From Fig. 3, we can conclude that when temperature increases, the removing rates of impurities increase and the level of impurities decreases. It is also shown that when indium is refined for 2 h at lower temperature (800–900°C), the level of Cd and Zn in indium is very low; At higher temperature (950–1050°C), the level of impurities, such as Tl and Bi is low and a large part of Pb can be removed. Therefore, we can control the temperature in two stages: 800–900°C for 2 h and 950–1050°C for 2 h to remove impurities effectively (seen in Table I).

At 1000°C, the removing rates of impurities are investigated under the different time, the result is shown in Fig. 4.

TABLE I Removing rate of impurities in indium after 2 h vacuum refining (mass fraction, %)

Temperature	Fe	Cu	Sn	Ni	Pb	Sb	Tl	Bi	Mg	Zn	Cd	As
800°C	14.2	40.3	24.3	15.2	11.2	81.3	22.5	25.2	42.7	88.1	99.1	99.9
1000°C	14.8	70.5	40.1	18.7	63.9	97.2	75.1	90.1	60.5	93.5	99.9	99.9

TABLE II Level of impurity in indium in different content of In^{3+} at 25°C (mass fraction, 10^{-6})

	Content of In^{3+}/g· L^{-1}						
Impurity	20	40	60	80	100	120	140
Cu	0.30	0.30	0.04	0.05	0.30	0.40	0.42
Fe	0.80	0.40	0.20	0.10	0.20	0.30	0.50
Pb	0.40	0.20	0.10	0.25	0.35	0.42	0.41
Ag	0.10	0.10	–	–	–	0.10	0.10
Sn	0.70	0.70	0.30	0.40	0.50	0.50	0.60
Cd	0.10	0.05	–	–	–	–	0.05
Tl	0.30	0.30	0.10	–	0.10	0.20	0.30
Zn	0.20	–	–	–	0.10	0.20	0.20

TABLE III The optimum technical conditions of electrolytic refining

Process	Current density/A/m^2	Bath voltage (V)	Temperature (°C)	pH
Electrorefining	50–80	0.2–0.3	20–30	2.0–3.0
Process	Interelectrode distance/mm	Rate of residual electrode/%	Content of $In_2(SO_4)_3$-H_2SO_4	Content of NaCl
Electrorefining	70	30–35	60–80	60–80

TABLE IV Level of impurity in indium in electrolytic refining (mass fraction 10^{-6})

Component	Ag	Pb	Cu	Cd	Al	Fe	Zn	Sn	Tl	Mg	Si	S	Ni	As
Vacuum refining	0.2	0.5	0.5	0.1	1.0	1.0	0.3	1.0	0.4	0.5	0.4	0.4	0.5	0.05
Electrorefining	–	0.1	0.05	–	–	0.1	–	0.2	–	0.1	0.1	0.1	–	–
In-06 standard	–	0.1	0.1	0.05	–	0.1	–	0.3	–	0.1	0.1	0.1	–	–

As time increases, the removing rates increase. However, after 2 h of vacuum refining, the removing rates of impurities increase slowly. Among the impurity metals in the indium, it is difficult to remove Fe, Sn and Ni by vacuum refining because of low vapour pressure of these metals. However, nearly almost of Bi, Pb, Mg and Cd can be removed by vacuum refining at 1000°C within two hours because these metals have higher vapour pressures than indium. Therefore, the suitable time is 2 h. After vacuum refining, the level of impurities in indium decreases and the product of indium reaches the national standard of 99.999% high purity indium.

4.4. Effect of electrolytic refining

Impurities in indium can be removed by electrolytic refining by controlling the component of electrolyte and selecting suitable electrolytic conditions. The effect of indium concentration on the current efficiency is investigated by varying the indium concentration from 20–140 g/L under the conditions of 25°C, cell voltage 0.2–0.3 V (shown in Fig. 5).

Fig. 5 indicates that when the concentration of indium is about 60 g/L, the current efficiency is over 90%. However, when the concentration of indium is below 60 g/L, the current efficiency decreases with decreasing indium concentration. The dependence of current efficiency on the concentration of indium is related to the current density. As indium ions as well as hydrogen ions are reduced in cathode to maintain the current density, the current efficiency decreases with decreasing indium ion concentration. The concentration of indium has negligible effects on the quality of indium, Level of impurities in product of indium in different content of indium at 25°C is shown in Table II.

Table II indicates that the quality of indium will be worse when its concentration is high or low. When the content of indium is in excess low, the cathode potential will increase. Therefore, impurity will deposit in indium and product of indium will not be dense. On the other hand, when the content of indium is in excess high, the density and viscosity of electrolyte will increase. Therefore, the anode mud and other impurity grain in electrolyte will subside slowly, which leads to the content of impurity in the cathode high. As far energy efficiency and the quality of indium are concerned, the optimum concentration of indium is 60–80 g/L.

The electrolytic purification can remove tin, nickel and lead from the indium metal by controlling the component of electrolyte and selecting suitable electrolytic conditions. The reason is the standard potentials of metals, such as Sn, Ni and Pb, are lower than that of indium. Therefore, those metals will dissolve in advance and stay in electrolyte. The optimum technical conditions are shown in Table III. After electrolytic refining, the impurities can be removed effectively, and 6N high purity indium could be obtained (seen in Table IV).

5. Conclusions

High purity indium is needed as a raw material for applications because it is used in the ITO thin-film, III–V semiconductor, fluorescent materials and metallorganic compound etc. Impurity elements, such as lead and tin, have effects on the properties of the semiconductor made from indium. It is important to drop the level of impurities in indium by selecting and controlling

suitable conditions. From the physical-chemical purification and electrolytic refining indium, the following conclusions are obtained.

By adding $NaNO_3$ into fusion of NaOH and indium replacing traditional method in which only NaOH is used, the removing rate of Sn, Zn, Al reaches 40, 60 and 37% respectively when smelting time is about 20 min at 400°C. Both Cd and Tl can be removed by 20% glycerin solution of KI and I_2 at 180°C, and the removing rate of Cd and Tl is 90–95%, 40–60% respectively. When indium metal was vacuum refined at 800 and 1000°C for two hours respectively, the major impurity elements, such as Pb, Zn and Bi, have been effectively removed. When indium is electrorefined in $In_2(SO_4)_3$-H_2SO_4 system, in which indium content is 60–80 g/L, pH 2.0–3.0 and current density 50–80 A/m^2, the impurities can be removed and the refining indium reaches 99.9999%.

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