Removal of Less Volatile Impurities from Crude Indium by Vacuum Distillation

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Abstract: The less volatile impurities has been eliminated by high temperature vacuum distillation of crude indium. The experiment was carried out in a self-designed vacuum distillation furnace. The temperature of distillation experiment was carried out at 1273~1373K and samples of condensate were collected at time intervals of 2, 3, 4 and 5 hour.The content of Ni, Cu, Fe in the crude indium have a little changed with the distillation time extension or the distillation temperature ascension. Both distillation temperature and holding time are principal factors that affected the removal of Sn from In by vacuum distillation. Compared with distillation time, temperature on the removal of less volatile impurities effects is more significant, So the distillation temperature was more important than distillation time. The best conditions of removal of less volatile impurities from crude indium under dynamic vacuum of 1~5Pa were as follows: 1348K and 2h. Under this condition, the content of impurities could be reduce to the standard of 5N such as Sn、Cu、Fe、Ni in the crude indium that have high boiling point. The ELEMENT-GD have been used in testing the element contents of the samples.

Introduction

Indium is applied to the lot of industrial products. As a strategic electronic material, high purity indium was used in electrical industries due to the excellent mechanical, physical and chemical performance. And it is extensively used in semiconductors, the manufacture of liquid crystal displays, infrared photodetectors and low-temperature solders [1]. By creating deep energy levels, the residual impurities even in 1ess than ppm level concentration play a major role in the electronic properties. So these industrial products demand high purity indium metal. There are several methods can prepare high purity indium such as electro-refining[2], vacuum distillation[3], low halide, the thin layer fused wall and zone refining[4], etc. In early research, the preparation of high purity indium metal by two-step vacuum distillation method has been studied[5-9].There are two factors such as distillation temperature and distillation time affecting the average content of impurity elements in the crude indium in the two-step vacuum distillation process. Two-step process are low temperature distillation and high temperature distillation. The low temperature distillation is the step one and the high temperature distillation is the step two. In the low temperature distillation step high vapour pressure impurities were carried out at a comparatively lower temperature under a dynamic vacuum, such as Zn, Cd, Tl, Pb. In this stage, Zn, Cd, Tl, Pb were collected on the condenser and less volatile impurities were left over in the bottom of the crucible. In the second step less volatile impurities were removed at a comparatively higher temperature under a dynamic vacuum. In this stage, Sn, Fe, Cu, Ni were left over in the bottom of the crucible and the indium was collected on the condenser. It found that the purification of the crude indium was very good by two vacuum distillation purification, except low boiling point impurities. Why is this so hard? The pollution in the process of distillation equipment was probably the main reason through the analysis of the experiment. Therefore the prophase vacuum distillation process will be changed: high temperature distillation will take place in the first phase and then to low temperature distillation. In this paper removal of less volatile impurities from the crude indium in the first phase was studied. The ELEMENT-GD produced by Thermo Scientific Company is one of the most advanced analysis equipment for detection the high-purity metals. It have been used in testing the element contents of the samples with its accuracy up to 10^{-9}(ppb).

Experimental

The distillation was carried out in a self-designed vacuum furnace system which consists of an resistance heated vacuum furnace, rotary-vane pump and temperature controlling system. The temperature controlling system is made up of thermocouple, temperature instrument and electrical source controller. The resistance heated vacuum furnace is made up of heating element, crucible, electrode and condenser. The schematic details of resistance heated vacuum furnace are shown in Fig.1. In order to change of condensation strength the condenser can be moved up and down. The content of indium as raw material is listed in Table 1（Indium content is 99.7%）.

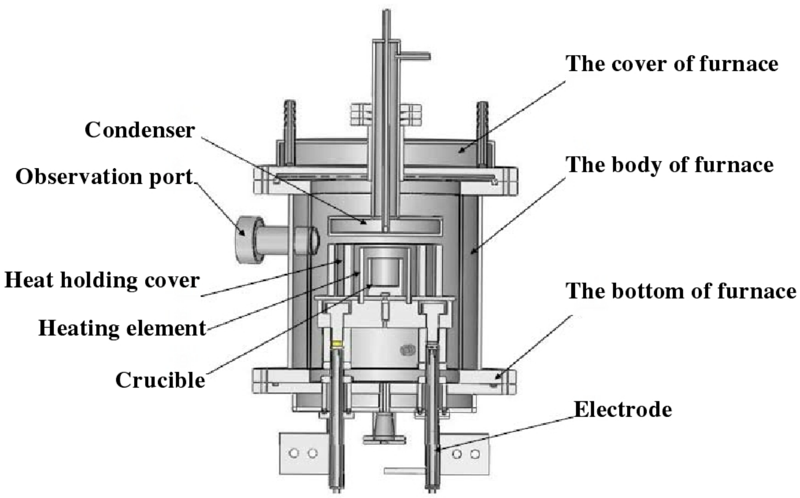

Fig.1 The resistance heated vacuum furnace

Table 1 The content of indium (all values in ppm)

Element	Sn	Fe	Cu	Ni	Cd	Zn	Tl	Pb	S	As	Al	Ag	Mg	Si
Content	66.627	0.067	6.548	0.243	40.253	0.155	2848.042	49.350	3.973	0.949	0.007	0.009	0.002	0.741

Note：The elements are according to the standard of high indium in worldwide in the table, such as China, USA, Japan, England and Russia.

The difference in vapor pressure of each metal at different temperatures was the basic principle of crude metal vacuum distillation [10]. The relationships between vapor pressure(P/Pa) of pure metals in the crude indium and temperature (T/K) are listed as

$$\lg p_{Cd} = -5819T^{-1} - 1.257\lg T + 14.412 \qquad (594\sim1050K) \qquad (1)$$

$$\lg p_{Zn} = -6620T^{-1} - 1.255gT + 14.465 \qquad (692\sim1180K) \qquad (2)$$

$$\lg p_{Tl} = -9300T^{-1} - 0.892gT + 13.225 \qquad (700\sim1800K) \qquad (3)$$

$$\lg p_{Pb}=-10130T^{-1}-0.985\lg T+13.285 \qquad (600\sim2023K) \qquad (4)$$
$$\lg p_{In}=-12580T^{-1}-0.45\lg T+11.915 \qquad (429\sim2346K) \qquad (5)$$
$$\lg p_{Sn}=-15500T^{-1}+10.355 \qquad (504\sim2876K) \qquad (6)$$
$$\lg p_{Cu}=-17520T^{-1}-1.21\lg T+15.335 \qquad (1357\sim2836K) \qquad (7)$$
$$\lg p_{Fe}=-19710T^{-1}-1.27\lg T+15.395 \qquad (1811\sim3135K) \qquad (8)$$
$$\lg p_{Ni}=-22400T^{-1}-2.01\lg T+19.075 \qquad (1728\sim3187K) \qquad (9)$$

The saturated vapor pressure of indium and other impurities under different temperatures were calculated. So they are shown in Table 2. From Table 2, it could be seen that Sn, Cu, Fe, Ni can be removed from the crude indium by high temperature vacuum distillation. They can be left over in the bottom of the crucible and the indium can evaporate into the gas phase. The distillation temperature should be 1273~1573K under dynamic vacuum of 1~5Pa. Because the amount of impurity elements in the gas phase will increase along with distillation temperatures rising at the same time. The study have used lower temperature and the prolonged distillation time in order better to remove the less volatile impurities. The vacuum distillation experiment was carried out at 1273~1373K：1273K，1298K,1323K,1348K,1373K. Samples of condensate were collected at time intervals of 2, 3, 4 and 5h, in case of high fraction experiment after the melt has attained the respective distillation temperature.

Table 2 Saturation Vapor Pressure of Indium and the Impurity Elements（Pa）

T/K	In	Tl	Cd	Zn	Pb	Sn	Fe	Cu	Ni
773	1.8×10^{-6}	3.6×10^{-2}	1.7×10^{3}	1.7×10^{2}	1.9×10^{-3}	2.0×10^{-10}	——	——	——
873	3.1×10^{-5}	3.1×10^{-1}	5.4×10^{3}	6.7×10^{2}	1.5×10^{-2}	5.0×10^{-9}	——	——	——
973	4.3×10^{-3}	9.9×10^{0}	4.7×10^{4}	8.1×10^{3}	8.4×10^{-1}	2.6×10^{-6}	——	——	——
1073	6.7×10^{-2}	7.1×10^{1}	——	3.1×10^{4}	7.2×10^{0}	8.1×10^{-5}	——	——	——
1173	6.4×10^{-1}	3.6×10^{2}	——	2.3×10^{5}	4.2×10^{1}	1.4×10^{-3}	——	——	——
1273	4.3×10^{0}	1.4×10^{3}	——	——	1.8×10^{2}	1.5×10^{-2}	——	——	——
1373	2.2×10^{1}	4.5×10^{3}	——	——	6.5×10^{2}	1.1×10^{-1}	——	6.1×10^{-2}	——
1473	8.8×10^{1}	1.2×10^{4}	——	——	1.9×10^{3}	6.8×10^{-1}	——	4.1×10^{-1}	——
1573	2.9×10^{2}	2.8×10^{4}	——	——	4.9×10^{3}	$\mathbf{3.1\times10^{0}}$	——	$\mathbf{2.1\times10^{0}}$	——
1673	8.8×10^{2}	6.1×10^{4}	——	——	1.1×10^{4}	1.2×10^{1}	——	9.2×10^{0}	——
1773	2.3×10^{3}	1.2×10^{5}	——	——	2.4×10^{4}	4.1×10^{1}	——	3.3×10^{1}	8.1×10^{-1}
1873	5.3×10^{3}	2.2×10^{5}	——	——	4.5×10^{4}	1.2×10^{2}	$\mathbf{5.2\times10^{0}}$	1.0×10^{2}	$\mathbf{3.4\times10^{0}}$
1973	1.1×10^{4}	3.7×10^{5}	——	——	8.0×10^{4}	3.1×10^{2}	1.6×10^{1}	2.9×10^{2}	1.2×10^{1}
2073	2.3×10^{4}	——	——	——	——	7.5×10^{2}	4.7×10^{1}	7.3×10^{2}	3.9×10^{1}

*Note：Black part indicated that the vacuum distillation carried out under dynamic vacuum of 1~5Pa.

Results and Discussion

Calculated the metal evaporation rate

The influence of temperature and time on the metal evaporation rate was shown in Fig.2. The metal evaporation rate is equal to (weight of the raw material minus weight of the residue) divide by weight of the raw material ╳100%. Because the content of indium is greater than 99.7% in the crude indium, it believe that the rate of evaporation metal is equal to the rate of evaporation indium in the distillation process. From Fig.2, it could be seen that distillation time and distillation temperature are the factors influencing indium volatile. The evaporation rate of indium increased along with the distillation temperature ascension or the distillation time extension. At the same distillation time, for example, 3 hour, the evaporation rate of indium was 50.37% when the distillation temperature has been raised to 1273K. And the evaporation rate of indium was 99.75%

when the distillation temperature has been rised to 1348K. At the same distillation temperature, for example1323K, the evaporation rate of indium have been raised from 81.35% to 99.98% with the distillation time extended from 2 h to 4 h.

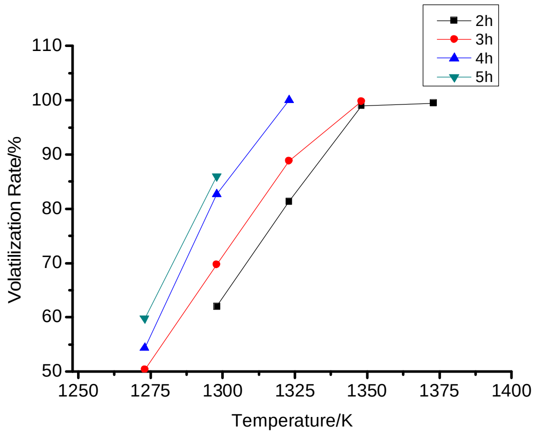

Fig.2. Influence of temperature and time on the metal evaporation rate

*Note：The temperature of the data points from left to right are 1273K,1298K,1323K,1348Kand1373K under dynamic vacuum of 1~5Pa

Behavior of Less Volatile Impurities from Crude Indium

Distillation at 1273~1373K and a residual gas pressure of 5Pa, the residue form the distillation—about 1% of the starting material—contained the less volatile elements, such as Cu, Fe, Sn, Ni. The influence of temperature and time on the content of less volatile impurities(Sn, Cu, Ni) in the condensate were shown in Fig.3.to Fig.5. From Fig.3, it could be seen that the content of Ni in the crude indium has a little changed with the distillation temperature ascension or the distillation time extension. The content of Ni was less than 0.003. Since the saturated vapor pressure of Ni was 10000 times lower than indium in 1273~1373K. So，there would be little of Ni volatilized along with indium. Cu and Fe are identical with Ni because the saturated vapor pressure of those was 100 times lower than indium in 1273~1373K. It could be seen in Fig.4 that there are a little increased of the content of Cu in the condensate along with the distillation temperature ascension or the distillation time extension.

From Fig.5, it could be seen that the content of Sn in the condensate has increased obviously along with the distillation temperature ascension at the same distillation time. There were a large number of volatile of indium when the distillation temperature was more than the boiling point of indium, for example 1273K. The content of Sn was in the lowest 0.0443 ppm because of Sn was little evaporated in this condition. The Sn in the solution began to evaporate gradually and condense correspondingly on the condenser together with indium as distillation temperatures continue to rise.The content of Sn in volatiles increased to 1.165 ppm when the distillation temperature have been raised to 1373K. So the both distillation temperature and holding time are principal factors that affected the removal of Sn from the crude indium by vacuum distillation. Compared with distillation time, distillation temperature on the removal of impurity effects is more significant, So the distillation temperature was more important than distillation time.

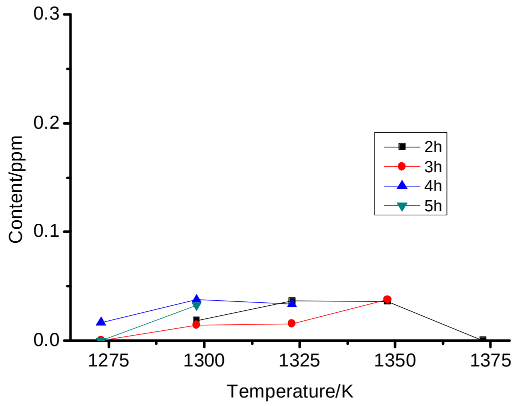

Fig.3. Influence of temperature and time on the content of Ni in the condensate

*Note：The temperature of the data points from left to right are 1273K,1298K,1323K,1348Kand1373K under dynamic vacuum of 1~5Pa

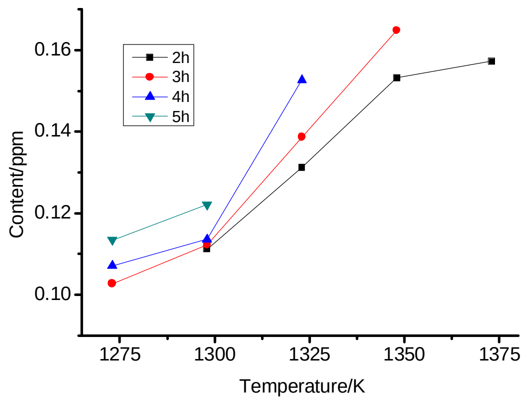

Fig.4. Influence of temperature and time on the content of Cu in the condensate

*Note：The temperature of the data points from left to right are 1273K,1298K,1323K,1348Kand1373K under dynamic vacuum of 1~5Pa

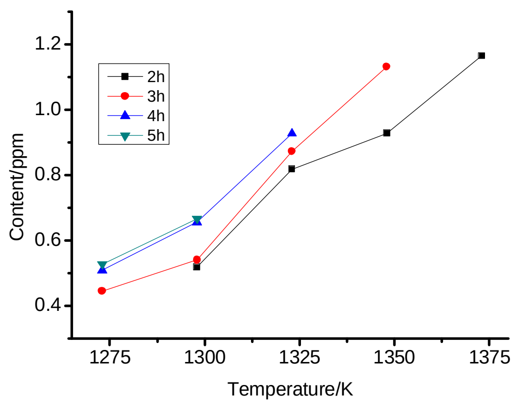

Fig.5. Influence of temperature and time on the content of Sn in the condensate

*Note：The temperature of the data points from left to right are 1273K,1298K,1323K,1348Kand1373K under dynamic vacuum of 1~5Pa

Considering the effect of impurity removal of impurities and the indium metal evaporation rate, the best conditions of removal of less volatile impurities from the crude indium were as follows: distillation temperature for 1348K, distillation time for 2h. The content of impurities which have high boiling point namely Sn, Cu, Fe, Ni in crude indium could be reduce to the standard of 5N: the content of Sn in the condensate is 0.9286ppm，the content of Cu in the condensate is 0.1532ppm, the content of Ni in the condensate is 0.357ppm.

Conclusions

The vacuum distillation has the low energy consumption, the non-chemical reagent pollution, the gas flows too easy to control and advantages to the environmental protection and other characteristics. The residues and the distillate material are easy to recycle processing by the vacuum distillation processing.

1）The content of Ni, Cu, Fe in the crude indium have a little changed with the distillation temperature ascension or the distillation time extension.

2) Both distillation temperature and holding time are principal factors that affected the removal of Sn from the crude indium by vacuum distillation. Compared with distillation time, distillation temperature on the removal of impurity effects is more significant, So the distillation temperature was more important than distillation time.

3) The best conditions of removal of less volatile impurities from crude indium under dynamic vacuum of 1~5Pa were as follows: distillation temperature for 1348K, distillation time for 2h.

Acknowledgments

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