Rare Metal Materials and Engineering
Volume , Issue ,
Available online at **www.rmme.ac.cn**

Science Press

Cite this article as:

ARTICLE

DOI: 10.12442/j.issn.1002-185X.20240439.

Preparation of 7N high-purity indium by vacuum distillation-zone refining combination

Tian Qinghua[1], Hu Zhixiang[1,2], He Zhiqiang[1], Guo Xueyi[1], Zhu Liu[2], Xu Zhipeng[1,*]

[1]. School of Metallurgy and Environment, Central South University, Changsha 410083, China. [2]. Vital Materials Co., Limited, Qingyuan 511500, China.

Abstract: High-purity indium finds extensive application in the aerospace, electronics, medical, energy, and national defense sectors. Its purity and impurity content significantly influence these applications. In this study, ultrahigh-purity indium was prepared by combining zone refining with vacuum distillation. The average removal efficiency of impurity Sb can approach 95%, while the removal efficiency of impurities Sn and Bi could reach over 95% and the removal efficiency of Si, Fe, Ni, and Pb could reach over 85%. Ultimately, the amount of Sn and Sb impurities was reduced to 2.0 ppb and 4.1 ppb, respectively, and the majority of impurities, including Fe, Ni, Pb, and Bi, were reduced to levels below the instrumental detection limit. The overall impurity removal efficiency was 90.9%, and the indium purity was 7N9.

Key words: Indium; High-purity; Vacuum distillation; Zone refining

1 Introduction

Indium has excellent properties such as good ductility, plasticity, corrosion resistance, and good light permeability and electrical conductivity, and is widely used in the fields of astronautics, electronics industry, medical, defense, and energy[1-4]. High-purity indium is widely used in the production of indium tin oxide (ITO) targets[5,6], CuInGaSe, $CuInSe_2$ thin-film solar cells[7], as well as other semiconductor compounds such as InSb, InAs[8] and InP[9]. In recent years, there has been a dramatic increase in the demand for high-purity indium not only for high-end technologies, but also for the purity itself, as even ppm-level impurities can affect the electron transfer behavior of electronic devices[10]. With the rapid development of microelectronics, semiconductors, and other cutting-edge technologies, efficient purification methods are receiving more attention than ever before[11,12].

The purification of indium using vacuum distillation technique has received wide attention from researchers[13-15]. By using vacuum distillation, Lei et al[16] obtained indium with a purity of 99.99% by controlling the distillation temperature and condensation temperature. Zhu et al[17] purified raw indium from 2N(99 wt.%) grade to 4N5(99.995 wt.%) grade by using vacuum distillation to firstly remove low-boiling point impurities such as cadmium, zinc, and lead, and then removing high-boiling point impurities such as copper and iron through second-stage vacuum distillation. Zhang et al[18] obtained refined indium with a purity of 4N by vacuum distillation graded condensation, with a recovery of more than 90.57%. Researchers generally use vacuum distillation to prepare indium with a purity of 5N and below, and less attention has been paid to the preparation of ultrahigh-purity indium by vacuum distillation. It was difficult to purify indium to 6N and above by vacuum distillation alone, so the technique of zone refining for the preparation of ultrahigh-purity indium has received wide attention.

The solute removal and optimization of processing parameters during zone refining have been explored by many researchers[19-23]. Wu et al[24] purified 5N indium to 6N grade by zone refining, but during the experiment several zone refining passes were carried out for better removal of impurity elements with equilibrium distribution coefficients close to 1, and the production efficiency was drastically reduced. Prasad et al investigated the effect of varying the number of zone refining

Received date:
Foundation item: the National Key Research and Development Program of China (2023YFC2907904); National Natural Science Foundation of China (52374364).
Corresponding author: Xu Zhipeng, Ph.D., Professor, School of Metallurgy and Environment, Central South University, Changsha 410083, China, Tel: 18175150670, E-mail: zhipeng.xu@csu.edu.cn

passes, zone width, and melting zone travel speed on the impurity removal efficiency in the process of refining tellurium (Te) and found that a moving speed of 30 mm/h could significantly separate impurities[25,26]. The zone refining technique can be applied to the preparation process of ultra-high purity metals, but the purification efficiency is low. In this study, a combination of vacuum distillation and zone refining was used to prepare ultrahigh-purity indium. Firstly, vacuum distillation was used to remove the impurities in indium initially, and then zone refining technology was used to further remove the trace impurities in depth to realize the preparation of ultra-high-purity indium. In addition, it was found that the content of impurity antimony was still high after the vacuum distillation-zone refining of indium. Therefore, hydrogenation technology was applied to further remove the impurity antimony to realize the preparation of 7N ultrahigh-purity indium.

2 Results and Discussion

2.1 Theory

(1) Vacuum distillation

Vacuum distillation technology has the advantages of non-pollution, high efficiency and high recovery rate, and is widely used in the separation and purification of alloys as well as the refining and purification process of crude metals[27,28]. By controlling the distillation temperature, condensation temperature, distillation time, vacuum conditions, etc., the impurity elements are selectively volatilised in the vacuum distillation process, and the volatiles are condensed at different locations, which makes the impurities and the main metal effectively separated. Thus, the purpose of purifying the main metal is achieved. The basic principle of vacuum distillation was to utilize the difference in vapor pressure of different metals for purification. In the purification of indium using vacuum distillation, indium was more volatile during the distillation process because of its higher vapor pressure. Segmented condensation collection was used to obtain high purity indium, while low volatile impurities were left in the distillation residue and high volatile impurities were condensed at the upper end of the collection. The vapor pressure of indium, P (Pa), was related to the temperature, T, by the following equation[29,30]:

$$\lg P = AT^{-1} + B\lg T + CT + D \quad (1)$$

Where P denotes the vapor pressure of the pure metal; T denotes the temperature, and A, B, C, and D denote constants.

The horizontal distillation furnace was used in the experiment, and the principle of sub-condensation of impurities in the distillation process was shown in Figure 1. Firstly, the saturated vapour pressures of the impurities in indium were calculated and analysed. The saturated vapour pressure of pure elements in indium raw material decreases in the order of P>S>Cd>Zn>Mg>Sb>Bi>Pb>In>Ag>Sn>Cu>Fe>Ni>Si.

When the system pressure is 10^{-2} Pa and the distillation temperature is 1000-1100°C, impurities such as P, S, Zn, Mg and Sb evaporate into the gas phase due to the high saturation vapour pressure, and impurities such as Sn, Cu, Fe, Ni and Si remain in the liquid phase. Therefore, it is appropriate to set the distillation temperature to 1000-1100°C during the experiment. Furthermore, since the impurities Sb, Bi, Pb, Sn, etc. in indium were close to the saturation vapour pressure of indium, it was difficult to remove these impurities in the process of indium vacuum distillation and purification. In order to effectively separate the impurities Sb, Bi, Pb, Sn from the main metal indium, two temperature control sections were used in the experimental process. The temperature of the condensation section was controlled to be 800-900°C, so that the volatiles could be fully condensed in the condensation section to improve the removal efficiency of the impurities. The schematic diagram was shown in Figure 1. The temperature in the distillation furnace gradually decreases from left to right, the first temperature is the distillation temperature, and the second temperature is the condensation temperature.

There were two drawbacks in the purification of indium metal by vacuum distillation, one was that it was difficult to remove the impurity elements such as Si, Fe and Sb, which were similar to the vapor pressure of indium, and the other was that the recovery rate would be drastically reduced if we want to obtain indium with higher purity. It could be seen that it is difficult to obtain higher purity indium by vacuum distillation alone. Compared to vacuum distillation, zone refining is a deep purification technique that could effectively produce ultra-high purity indium with a purity of 7N and above.

(2) Zone refining

In the early 1950s, W.G. Pfann first proposed the zone refining purification method[31,32]. Zone refining was to take advantage of the difference in solubility of impurities in the liquid and solid phases of the host metal to purify the metal. The purification of the host metal was achieved by localised melting of metal rods by heating, while controlling the directional movement of the melting zone to precipitate impurities and change their distribution[33]. Zone refining was basically the same principle as the polarization method and directional solidification[32,34-36]. The ratio of the concentration of impurities in the solid phase (C_s) to the concentration in the liquid phase (C_l) was defined as the equilibrium distribution coefficient k0 ($k_0 = C_s/C_l$). There were many factors affecting the purification effect of zone refining, such as the equilibrium distribution coefficient k_0, the travel speed of the melting zone, and the number of zone refining passes. Researchers have proposed the effective distribution coefficient (k_{eff}), and the relationship between k_{eff} and k_0 can be expressed as follows[37]:

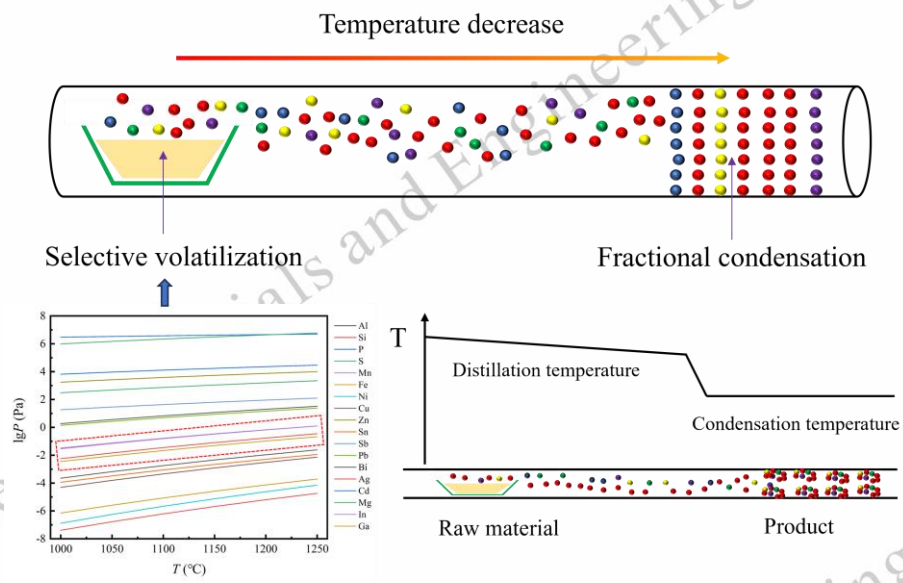

Fig.1 Schematic diagram of vacuum distillation

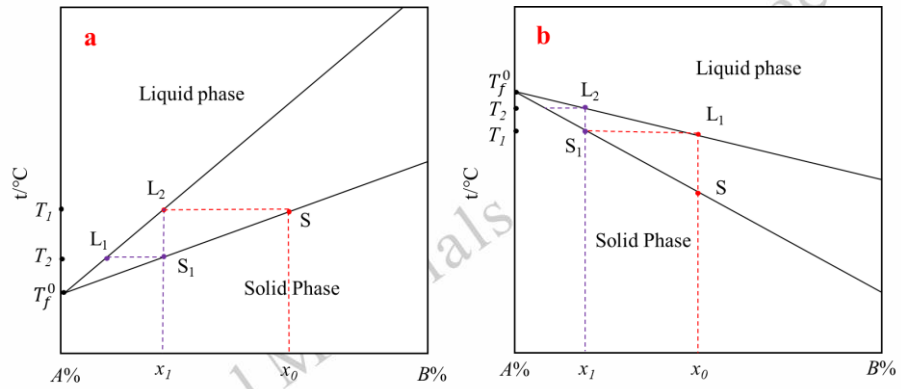

Fig.2 Ideal binary distribution graph[40]: (a) k_{eff} >1; (b) k_{eff} <1

$$k_{eff} = \frac{k_0}{k_0 + (1-k_0)\exp(-v\delta / D)} \quad (2)$$

where D is the impurity diffusion coefficient in the melt, δ is the thickness of the diffusion layer adjacent to the solidification interface, and v is the travelling speed in the molten zone.

Table 1 The distribution coefficient of impurities in the indium[38]

Element	k_0	Element	k_0
Al	<1	Ni	0.01-0.06
Si	<0.1	Cu	0.06-0.08
Cd	0.67-0.72	Zn	0.36-0.43
S	<0.1	Sn	0.73-0.8
Mn	<0.5	Tl	≈1
Fe	<0.1	Pb	1-1.07
Mg	1.33-1.77	Ag	0.06-0.09

The distribution coefficients of the main impurities in indium were shown in Table 1, from which it can be analyzed that the distribution coefficients of the impurities Tl, Pb, Mg, Sn and Cd in indium are close to 1, so it is more difficult to be removed in the zone refining process.

Compared with other methods, zone refining had the advantages of high purification limit, no pollution to the environment during the experimental process and simple operation[39]. In the zone refining process, the distribution of impurities in the ideal state was shown in Figure 2, when the k_{eff} > 1 of impurities, the solubility of impurities in the solid phase was greater than that in the liquid phase, and the impurities were enriched toward the solid phase region, as shown in Figure 2(a). The upper part of the figure was the liquid phase region, the middle part was the liquid-solid equilibrium region, and the lower part was the solid phase region. Conversely, when k_{eff} < 1 of the impurity, the solubility of the impurity in the solid phase was less than that in the liquid phase, and the impurity was enriched toward the liquid phase region, as shown in Figure 2(b).

In this experiment, the four melting zones were used for the zone refining of indium, and the schematic diagram was shown in Figure 3. The use of multiple melting zones for zone

refining can effectively improve the purification efficiency and shorten the experimental period. After multiple passes of zone refining, the impurities were enriched at the first and last ends of the metal rods, and the impurity-enriched areas at the two ends were removed, and the middle part was the high-purity product. For example, most of the impurities such as Al, Si, Fe, Cu, Ni, Sn, etc. migrate to the tail end of the indium rods, and impurities such as Pb, Mg, etc. migrate to the front end of the indium rods.

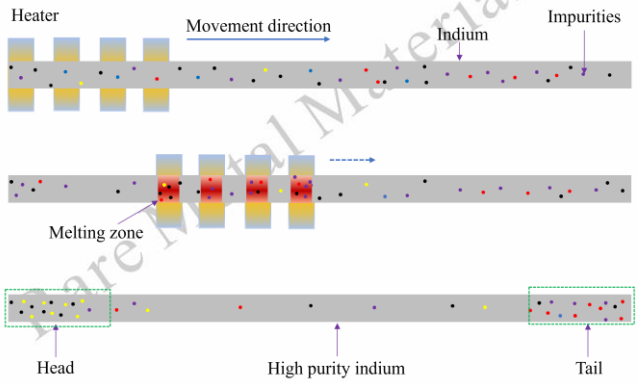

Fig.3 Schematic diagram of zone refining

After zone refining, the content of most impurities such as Si, Fe, and Sb in indium metal can be reduced. After that, the purified indium was loaded into a graphite boat for hydrogenation and ingot casting to obtain 7N ultrahigh-purity indium products (see Figure 10).

2.2 Materials and procedure

The raw material used in the experimental process was obtained from Vital Materials Co., Limited. with a purity of 6N (99.9999 wt.%). The raw materials were firstly tested by GDMS and the content of each impurity was shown in Table 2. The material used for each group of experiments was 4.0 kg, and the boat material was quartz, and the length of quartz was 500 mm. The equipment was produced by Gaomi Putte Electronic Equipment Co., Ltd. There was no fixed model number as the equipment was all customised.

Table 2 Impurity content of raw materials

Element	μg/kg	Element	μg/kg
Al	<2	Ni	4.9
Si	11	Cu	<0.5
P	0.5	Zn	0.5
S	1.2	Sn	55
Mn	<0.5	Sb	56
Fe	5.6	Pb	8.2
Bi	42	Total	184.9

First, 4.0 kg of raw material was loaded into a quartz boat, which was then loaded into a vacuum distillation furnace. The experiments were carried out at a distillation temperature of 1073°C, a vacuum of 1.0×10^{-4} and a distillation time of 40 h. The experiment's distillation products were obtained at the conclusion.

Subsequently, the refined distillation products were reloaded into a sanitized quartz boat and placed within the zone refining furnace. Zone refining was conducted under the following experimental conditions: five passes of zone refining, a zone movement rate of 30 mm/h, and a nitrogen flow rate of 2 L/min. Nitrogen ventilation was implemented in order to keep indium from oxidizing while the zone refining process was underway. The zone refining temperature was 250-350°C. Four melting zones were used for purification in the experimental process, and the length of the melting zones was controlled to be 6-8 cm.

The zone refining process resulted in a high-purity product that was hydrogenated in the end. The hydrogenation temperature of 615°C, the hydrogenation period of one hour, and the hydrogen flow rate of 2 L/min were the experimental parameters. The trials were repeated five times under the identical conditions as described above, and the outcomes are displayed below.

The hydrogenation process was used to further reduce the volatile impurities in indium metal, while the hydrogen atmosphere protects against oxidation of indium during the preparation of indium standard samples. The dimensions of the indium standard sample are 300 mm in length and 40 mm in width.

2.3 Sample Detection

The purified sample was taken out of the equipment and transferred to a clean bench for sampling. After vacuum distillation the sample was fused and cast, the sample was cut with a high purity titanium tool. After removing the head and tail of the sample after zone refining, the sample was sampled in the part near the head and tail. Samples after hydrogenation were homogeneous and could be sampled directly. Solid samples were analysed and tested directly by GDMS (glow discharge mass spectrometry), and the same batch of samples was tested by the same equipment to ensure the stability of the test. The GDMS analysis technology has the advantages of low risk of contamination in the testing process, strong anti-interference ability and low detection limit, which enables the analysis of trace elements. The detection limit for most of the impurities, such as Si, Fe, Ni, Cu, Zn, etc., is <0.5 ppb, and the detection limit of Al, Pb, Bi, Sn and other impurities is less than 1.0 ppb. However, the purity of the current products does not include the interstitial impurities, such as C, N, O, H and others.

3 Results and discussion

3.1 Purity of indium

The contents of the main impurities in the samples and the purity of indium were shown in Table 3.

Table 3 Indium purity and impurity content (μg/kg)

Element	Raw material	Exp.1			Exp.2			Exp.3			Exp.4			Exp.5		
		①	②	③	①	②	③	①	②	③	①	②	③	①	②	③
Al	<2	＜2	< 2	< 5	＜2	< 5	< 2	＜2	< 5	< 1	＜2	< 5	< 2	＜2	< 2	< 2
Si	11	35	< 0.5	1.1	10	< 0.5	1.3	24	< 0.5	3.7	37	3	2.7	20	1.2	< 0.5
P	0.5	0.5	< 0.5	< 0.5	＜0.5	< 0.5	< 0.5	＜0.5	< 0.5	< 0.5	＜0.5	< 0.5	5.7	＜0.5	< 0.5	< 0.5
S	1.2	＜0.5	3.9	9.2	＜0.5	< 0.5	< 0.5	＜0.5	< 0.5	0.6	＜0.5	1.1	7.1	1.6	< 0.5	8.8
Mn	<0.5	＜0.5	< 0.5	< 0.5	＜0.5	< 0.5	< 0.5	＜0.5	< 0.5	< 0.5	＜0.5	0.5	0.5	＜0.5	< 0.5	< 0.5
Fe	5.6	1.5	0.9	< 0.5	5.2	< 0.5	< 0.5	3.6	< 0.5	1.2	8.5	0.6	1.1	2.2	1.8	0.7
Ni	4.9	＜0.5	< 0.5	1.7	3.5	< 0.5	< 0.5	1.1	< 0.5	1.1	5.7	< 0.5	1.8	＜0.5	< 0.5	< 0.5
Cu	<0.5	＜0.5	< 0.5	< 0.5	0.6	< 0.5	< 0.5	0.8	< 0.5	< 0.5	0.7	< 0.5	< 0.5	1.2	< 0.5	< 0.5
Zn	0.5	0.5	0.5	0.6	＜0.5	0.6	< 0.5	＜0.5	< 0.5	6.1	＜0.5	< 0.5	2.5	＜0.5	< 0.5	0.5
Sn	55	＜2	< 2	< 2	＜2	4.2	< 2	＜2	< 2	< 2	＜2	< 2	< 2	＜2	< 2	< 2
Sb	56	19	23	3.3	14	26	4.1	18	7.1	< 1	16	7.1	3.1	21	9.8	2.5
Pb	8.2	＜1	< 1	< 1	＜1	< 1	< 1	＜1	< 1	< 1	＜1	< 1	< 1	＜1	< 1	< 1
Bi	42	＜1	< 1	< 1	＜1	< 1	< 1	＜1	< 1	< 1	＜1	< 1	< 1	＜1	< 1	< 1
In	6N8	7N4	7N7	7N8	7N6	7N7	7N9	7N5	8N2	7N8	7N3	7N8	7N7	7N5	7N8	7N8

‘ <’ in the table indicates that it is below the detection limit of the instrument. ①: Vacuum distillation; ②: Zone refining; ③: Hydrogenation.

After vacuum distillation, the contents of impurities Sn, Pb and Bi were obviously reduced; the content of impurity Sb was reduced to a certain extent, but the content in the product was still high; the content of impurity Fe was not reduced significantly, while the content of impurity Si was increased, which was possibly contaminated by the quartz boat in the experimental process. It can be seen that during the purification of indium by vacuum distillation technology, the removal of impurities Sn, Pb and Bi was more effective, followed by impurity Sb, and the removal of impurities Fe and Si was less effective. After vacuum distillation, the purity of indium can be purified from 6N8 to about 7N5.

From the above analysis, it can be seen that after vacuum distillation, the content of impurities Si, Sb and Fe in the sample was still high. When the sample goes through zone refining, the content of impurities Fe and Si was effectively reduced, and the content of impurity Sb was further reduced. It can be seen that the zone refining technology can effectively remove the impurities Fe and Si that cannot be removed during vacuum distillation, and it also had a certain effect on the removal of impurity Sb.

After vacuum distillation and zone refining, most of the impurities have been effectively removed from the raw indium, and only the content of impurity Sb was still high. After hydrogenation, the contents were all below 5 ppb. The purity of the sample can reach 7N8.

Analysed from Table 3, in five groups of experiments, the experimental conditions were consistent, and the purities were as follows: after vacuum distillation, the purity of the products was 7N4-7N6; after purification by zone refining, the purity of the products in two groups of experiments was 7N7, and the purities of the products in the other three groups of experiments were 7N8, 7N8, and 8N2, respectively; and then, after purification by hydrogenation, the purity of the products in three groups of experiments was 7N8, and the purities of the products in the other two groups were 7N7 and 7N9, respectively. The purity of one of the samples after zone refining was 8N2, which might be a testing error according to the data analysis. The other test data were relatively stable. This indicated that the repeatability of the experiment and the repeatability of the test were high and the results of the experiment were scientific.

3.2 Efficiency of impurity removal in different processes

From the above analysis, it can be seen that the removal efficiency of impurities by different processes is not the same. In order to further analyze the effect of different processes on the removal of major impurities in indium, the following classification of major impurities in indium was analyzed.

3.2.1 Vacuum distillation

After vacuum distillation, the average content and removal efficiency of the main impurities in indium were shown in Figure 4. The impurities Sn and Bi were reduced from 55 μg/kg and 42 μg/kg to 2 μg/kg and 1 μg/kg, and the removal efficiencies reached 96.36% and 97.62%, respectively. The removal efficiencies of impurities Pb and Ni were 87.80% and 53.88%, respectively, and the total removal efficiency was 70.81%. The impurity Si content in the product was higher than that of the raw material, probably due to the distillation product condensing on the quartz tube, which resulted in Si contamination. The impurity Si can be removed by zone refining.

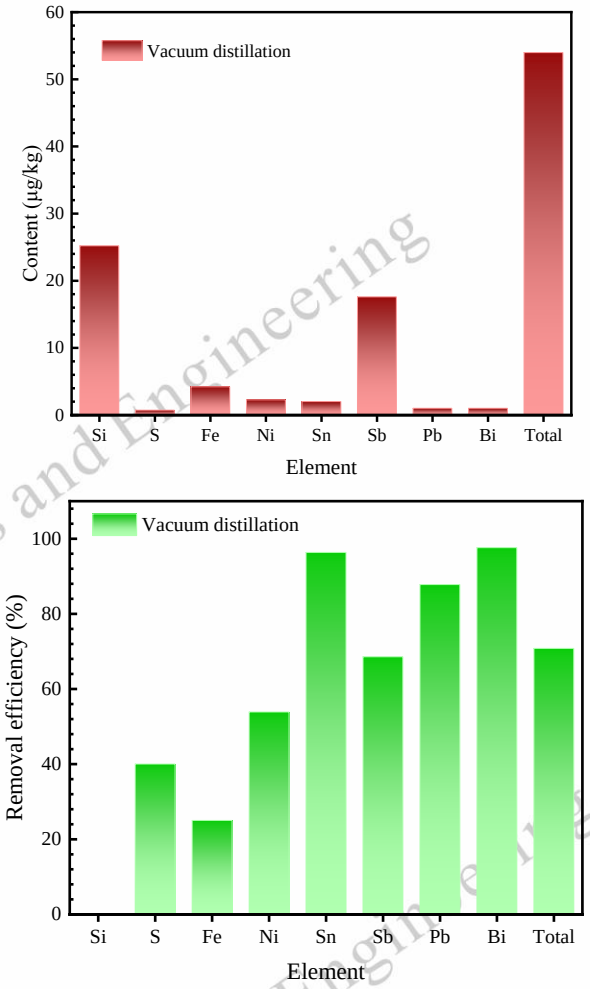

Fig.4 Impurity content and removal efficiency after vacuum distillation

As theoretically analyzed in section 2.1, the use of two-stage temperature control was advantageous for the removal of impurities Sn, Pb, Bi and so on. By controlling the condensation temperature and slowing down the change of temperature gradient in the condensation section, the difficult-to-remove impurities were fully separated in the condensation section, thus improving the removal efficiency of impurities.

The direct recovery ratio of indium distillation process was shown in Table 4, and the average direct recovery ratio of indium vacuum distillation was 82.7%.

Table 4 Direct recovery ratio for indium distillation process (kg)

Experiment	Raw material	Product	Distillation residue	Direct Recovery Ratio
Exp.1	4.0099	3.4771	0.4815	86.7%
Exp.2	4.0057	3.1193	0.7531	77.9%
Exp.3	3.9981	3.2585	0.5927	81.5%
Exp.4	4.0054	3.3491	0.4708	83.6%
Exp.5	3.9934	3.3491	0.1411	83.9%
Average	4.0025	3.31062	0.48784	82.7%

3.2.2 Zone refining

The average content and removal efficiency of major impurities in indium after zone refining using distillation products as raw materials were shown in Figure 5. After zone refining, the removal efficiencies of impurities Si, Fe, and Ni reached 95.48%, 79.52%, and 77.88%, respectively, with a total removal efficiency of 57.69%. The content of impurity Sb was further reduced, and the average content was reduced to 14.6 μg/kg.

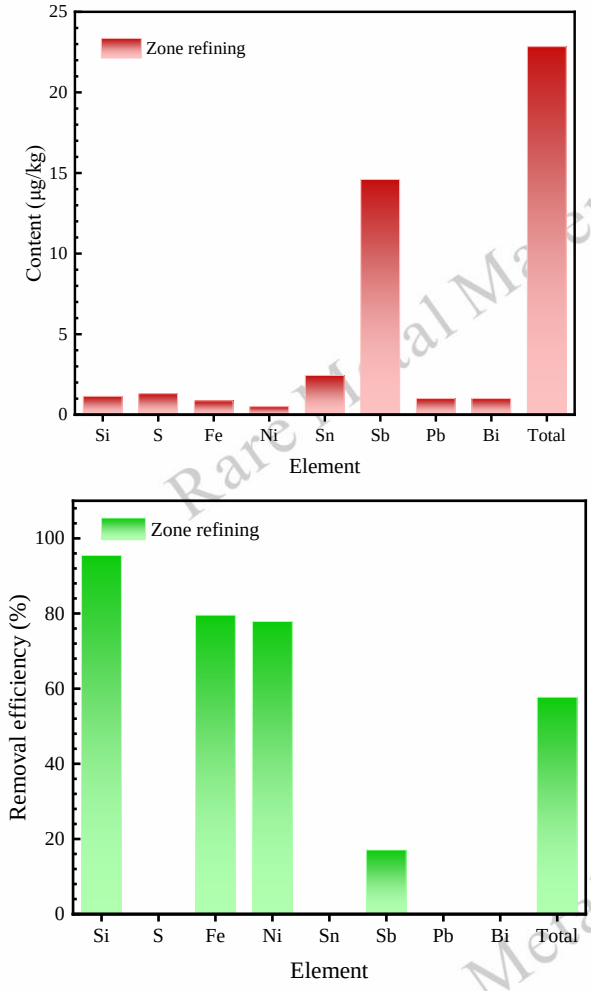

Fig.5 Impurity content and removal efficiency after zone refining

From the analysis in part 2.1, it can be seen that the distribution coefficients of impurities Sn, Pb, Bi, etc. are close to 1, so the zone refining process was ineffective in removing them. The distribution coefficients of impurities Si, Fe, Ni, etc. are much less than 1, so the removal efficiency was higher in the zone refining process.

3.2.3 Hydrogenation

The average content and removal efficiency of major impurities in indium after hydrogenation casting using zone refining products as raw materials were shown in Figure 6. After hydrogenation ingot casting, the content of impurity Sb was further reduced to 2.8 μg/kg, and the total impurity content was 16.72 μg/kg, with a total impurity removal efficiency of 26.80%.

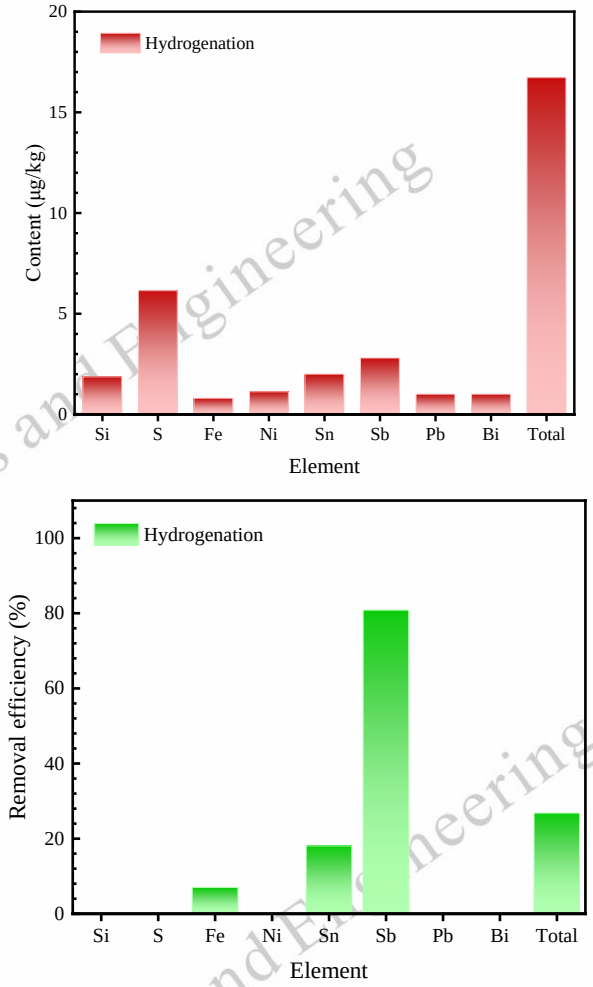

Fig.6 Impurity content and removal efficiency after hydrogenation

There were two main effects of hydrogenation: on the one hand, it prevented indium from being oxidized during the experiment, and at the same time, it removed oxides from the surface of indium. After hydrogenation, indium had a more metallic luster. On the other hand, after vacuum distillation and zone refining, the content of impurity Sb was still high. The impurity Sb was volatile, and it would be further volatilized during the hydrogenation process, thus improving the removal efficiency of the impurity Sb. It was shown that hydrogenation was beneficial in removing impurities from indium.

3.3 Removal efficiency of impurities

In order to further analyze the effectiveness of different processes in removing impurities from indium, the following analyses were performed. The removal efficiency of impurities Fe, Sb, Si, Ni was shown in Figure 7. From the analysis of the figure, it can be seen that Fe, Sb, Si, Ni and other elements can not be effectively removed only by vacuum distillation, and the removal efficiency of the impurities can be effectively improved after zone refining again, in which the impurities Fe, Si, Ni were more obviously enhanced. After hydrogenation operation again, the removal rate of impurity Sb can be further improved, and there was no beneficial effect on impurity Fe, Si, Ni, on the contrary, the removal efficiency will be reduced. Therefore, for indium raw materials with low impurity Sb content, only vacuum distillation and zone refining processes were required, and hydrogenation again will not have a beneficial effect on the purification of indium metal.

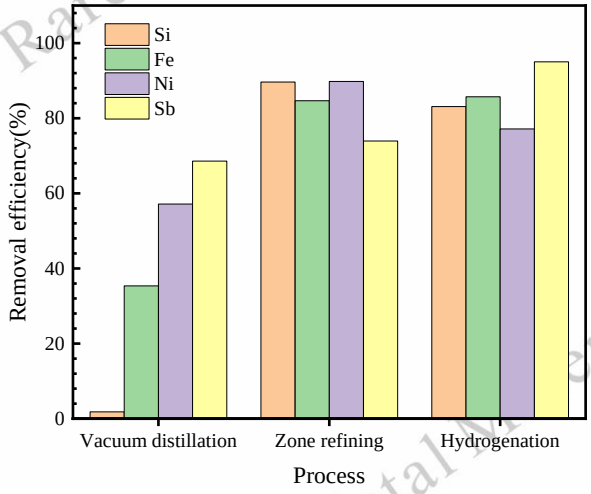

Fig.7 Removal efficiency of impurities Fe, Sb, Si, Ni

The removal efficiency of impurities Bi, Sn, and Pb was shown in Figure 8. From the analysis of the figure, it can be seen that vacuum distillation was more effective in removing impurities Bi, Sn, and Pb from indium, and the efficiency of impurity removal was not improved after the samples were again subjected to zone refining and hydrogenation operations. It suggests that if indium mainly contains impurities such as Bi, Sn, and Pb, and the content of other impurities was low, indium can achieve a high purity by vacuum distillation process alone. When calculating the removal efficiency of impurities, the impurity content below the detection limit was calculated as the detection limit.

The above analysis proves again that for most of the impurities can be effectively removed after vacuum distillation and zone refining process, but the content of impurity Sb was still high. For example, the removal efficiency of impurities Sn and Bi can reach more than 95%, the removal efficiency of impurities Si, Fe, Ni and Pb can reach more than 85%, while the removal efficiency of impurity Sb was only less than 75%, and the total removal efficiency of impurities was 87.6%. After the hydrogenation process, the impurity Sb can be further removed, and the total removal efficiency of impurities reaches 90.9%.

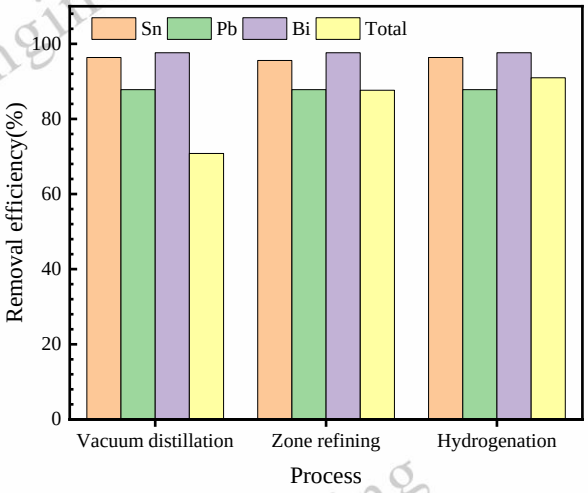

Fig.8 Removal efficiency of impurities Bi, Sn, Pb

The final removal of impurities after vacuum distillation - zone refining-hydrogenation of indium was shown in Figure 9.

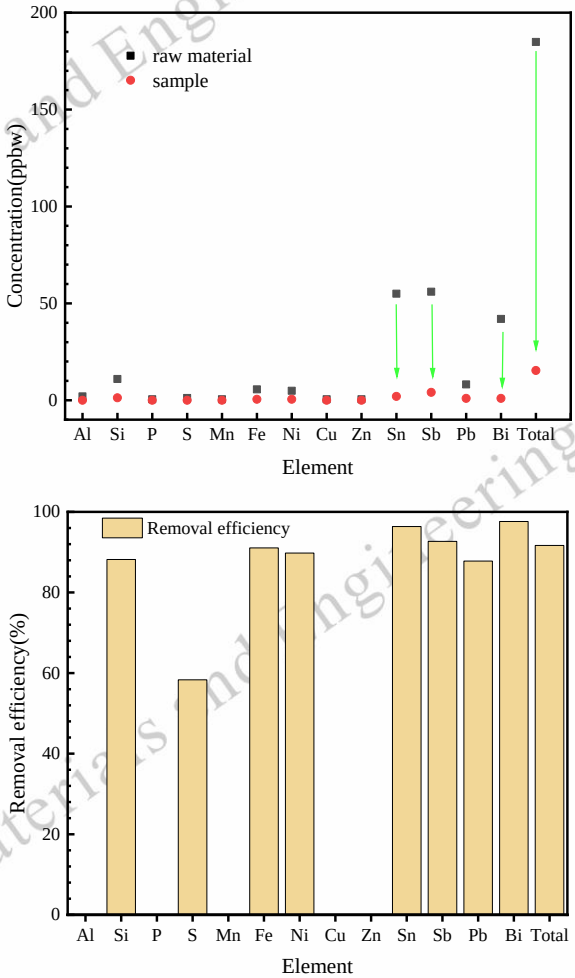

Fig.9 Removal state of impurities after vacuum distillation-zone refining-hydrogenation

After vacuum distillation-zone refining-hydrogenation of

indium, the contents of impurities Sn and Sb were reduced from 55 ppb and 56 ppb to 2.0 ppb and 4.1 ppb, with the removal efficiency reaching 96.4% and 92.7%, respectively; the contents of impurities Fe and Ni could be reduced to less than 0.5 ppb, with the removal efficiency reaching 90%; the contents of impurities Pb and Bi could be reduced to less than 1.0 ppb; and the total impurity removal efficiency reached 91.67%. In Figure 10, a standard 7N product was shown after hydrogenated ingot casting, which can be sold as a high-end raw material.

Comparison of the impurity content in the sample with the industry standard was shown in Table 5. It can be seen that the purity of the sample meets the 7N indium industry standard.

Fig.10 Indium products after hydrogenation

Table 5 Comparison of impurity content in samples with industry standards (μg/kg)

Element	Standards	Concentration	Element	Standards	Concentration
Ag	2.0	<1.0	Ca	/	<2.0
Cd	5.0	<5.0	Co	/	<0.5
Cu	5.0	<0.5	V	/	<0.5
Fe	5.0	<0.5	Cr	/	<0.5
Mg	5.0	<0.5	Ga	/	<5.0
Ni	5.0	<0.5	Mn	/	<0.5
Pb	10.0	<1.0	Na	/	<0.5
Zn	2.0	<0.5	Ti	/	<0.5
Al	/	<2.0	Tl	/	<2.0
Au	/	/	Total	100	<22.5

4 Conclusions

In this study, 7N ultrahigh-purity indium was successfully prepared using 6N high-purity indium as raw material after vacuum distillation - zone refining - hydrogenation process. After the vacuum distillation - zone refining - hydrogenation process, the contents of impurities Sn, Sb, and Si were reduced from 55 ppb, 56 ppb, and 11 ppb to 2.0 ppb, 4.1 ppb, and 1.1 ppb, respectively, and the impurities Fe, Pb, Bi, and Ni could be reduced below the instrumental detection limit, and the total impurity content was reduced from 184.9 ppb to 10.4 ppb. And the total removal efficiency of impurities reached 90.9%, the purity of indium metal reached 7N9.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Key Research and Development Program of China (Grant No. 2023YFC2907904), National Natural Science Foundation of China (Grant No. 52374364).

Conflicts of interest

The authors declare no conflicts of interest.

Reference

1 Wang X W, Wang W, Chen W, et al. Materials Characterization[J], 2021, 177: 111157.

2 Li L B, Li Q, Wang H, et al. Rare Metal Materials and Engineering[J], 2015, 44(6): 1374.

3 Kwon Y, Kim S. NPG Asia Materials[J], 2021, 13(1): 36.

4 Zhu Y, He Y, Jiang S, et al. Journal of Semiconductors[J], 2021, 42(03): 27.

5 Ma X B, Zhang W J, Wang D X, et al. Rare Metal Materials and Engineering[J], 2015, 44(12): 2937.

6 Fan Y, Liu Y, Niu L, et al. Separation and Purification Technology[J], 2021, 269: 118766.

7 Cojocaru-Mire´Din O, Choi P, Wuerz R, et al. Ultramicroscopy[J], 2011, 111: 552.

8 Wade T L, Vaidyanathan R, Happek U, et al. Journal of Electroanalytical Chemistry[J], 2001, 500: 322.

9 Ajayan J, Nirmal D, Ravichandran T, et al. Int. J. Electron. Commun. (AEÜ)[J], 2018, 94: 199.

10 Baek K, Jang K, Lee Y-J, et al. Thin Solid Films[J], 2013, 531: 349.

11 Zhang H, Wang S, Tian Y, et al. Nano Materials Science[J], 2021, 42: 304.

12 Yu Y, Song J, Bai F, et al. Int. Journal of Refractory Metals and Hard Materials[J], 2020, 2(2): 164.

13 Chen L, Wang Y, Kong L, et al. Journal of Materials Research and Technology[J], 2024, 28: 1382.

14 Zhang X W, Wang Z Q, Chen D H, et al. Rare Metal Materials and Engineering[J], 2016, 45(11): 2793.

15 Li Z, Chen Z, Ma W, et al. Vacuum[J], 2024, 221: 112884.

16 Lei H C, Deng Y, Liu D C, et al. Journal of Kunming University of Science and Technology (Natural Science)[J], 2019, 44(05): 8.

17 Zhu E W, Chen Y H. World Nonferrous Metals[J], 2018, 11: 168. (In Chinese)

18 Zhang D C, Deng Y, Yuan C C, et al. Chinese Journal Of Vacuum Science And Technology[J], 2017, 37(01): 94. (In Chinese)

19 Wang Y, Jin Q, Duan X, et al. Vacuum[J], 2023, 217: 112557.

20 Tian Q, He Z, Xu Z, et al. Metallurgical and Materials

Transactions B[J], 2024, 55(2): 772.
21 Yu L, Kang X, Chen L, et al. Materials[J], 2021, 14(8): 2064.
22 Roussopoulos G S, Rubini P A. Journal of Crystal Growth[J], 2004, 271(3-4): 333.
23 Huang J, Ren Q B, Hu Z Q, et al. Rare Metal Materials and Engineering[J], 2017, 46(12): 3633.
24 Wu M Z, Zhang C J. Mining & Metallurgy[J], 2016, 25(01): 59. (In Chinese)
25 Prasad D S, Munirathnam N R, Rao J V, et al. Materials Letters[J], 2006, 60(15): 1875.
26 Munirathnam N R, Prasad D S, Rao J V, et al. Indian Academy of Sciences[J], 2005, 28(4): 309.
27 Zha G, Yang C, Wang Y, et al. Separation and Purification Technology[J], 2019, 209: 863.
28 Cheng K, Yi J, Zha G, et al. Separation and Purification Technology[J], 2022, 278: 119531.
29 Dai Y N, Zhao Z. Vacuum Metallurgy [M]. Metallurgical Industry Press, Beijing:1988. (In Chinese)
30 Li D S, Dai Y N, Yang B, et al. Journal of Central South University[J], 2013, 20: 337.
31 Pfann W G. JOM[J], 1955, 7: 297.
32 Pfann W G. JOM[J], 1952, 4(7): 747.
33 Huan Z, Zhao J, Xu J, et al. Russian Journal of Non-Ferrous Metals[J], 2020, 61(1): 9.
34 Pfann W G. Metallurgical Reviews[J], 1957, 2(1): 29.
35 Lan C W. International Journal of Heat and Mass Transfer[J], 2000, 43: 1987.
36 Zhang X X, Friedrich S, Friedrich B. Metals[J], 2021, 11(2): 201.
37 Duan M P, Zhao J Y, Xu B Q, et al. Transactions of Nonferrous Metals Society of China[J], 2023, 33: 2843.
38 Deng Y, Li D S, Yang B, et al. Chinese Journal of Vacuum Science And Technology[J], 2014, 34(7): 754. (In Chinese)
39 Wan H, Xu B, Yang B, et al. Vacuum[J], 2020, 171: 108839.
40 Zhang X, Friedrich S, Friedrich B. Journal of Crystallization Process and Technology[J], 2018, 08(01): 33.

真空蒸馏-区域熔炼联合法制备 7N 高纯铟

田庆华[1]，胡智向[1,2]，何志强[1]，郭学益[1]，朱刘[2]，许志鹏[1]

(1. 中南大学冶金与环境学院，中国 长沙 410083)

(2. 先导稀材股份有限公司，中国 清远 511500)

摘　要：高纯铟广泛应用于航空航天、电子、医疗、能源和国防领域。铟的纯度和杂质含量对这些应用有着重要影响。本研究采用真空蒸馏和区域熔炼相结合的方法制备了高纯铟。实验结果表明，杂质 Sn 和 Bi 的去除率超过 95%，杂质 Sb 的平均去除率接近 95%，Si、Fe、Ni 和 Pb 的去除率超过 85%。最终，杂质 Sn 和 Sb 分别降低至 2.0 ppb 和 4.1 ppb，包括 Fe、Ni、Pb 和 Bi 等多数杂质均降低至仪器检测限以下。总体杂质去除率为 90.9%，铟纯度达到 7N9。

关键词：铟；高纯；真空蒸馏；区域精炼

通讯作者简介：许志鹏，博士，副教授，中南大学冶金与环境学院，中国 长沙 410083，电话：18175150670，E-mail: zhipeng.xu@csu.edu.cn