Purification of indium by vacuum distillation and its analysis

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Abstract: High purity (99.999% or 5N, mass fraction) indium (In) was obtained through vacuum distillation using a 2N (99%) In as input material under a dynamic vacuum of 5 Pa. The glow discharge mass spectrometry (GDMS) was applied for the analysis of input material and the distilled indium. The results indicate that high-volatile impurities namely Cd, Zn, Tl and Pb can be removed from the indium matrix at the low fraction stage of 1 223 K for 120 min; Low-volatile impurities such as Fe, Ni, Cu, Sn can be reduced at the high fraction stage of 1 323 K for 120 min. The separation coefficient $\beta_i$ and activity coefficient $\gamma_i$ of impurities are calculated according to the experiments to fill the inadequate data of the thermodynamics.

Key words: vacuum distillation; indium; separation; refining

1 Introduction

Indium is a metallic element in the IIIA column of the periodic table and is incorporated into III–V compound semiconductor materials, such as indium arsenide (InAs) and indium phosphide (InP) [1]. It has emerged as an important strategic metal that is extensively used in electrical industries for its excellent chemical, physical and mechanical performances [2]. Indium and its compounds have numerous industrial applications, and it is extensively used in the manufacture of liquid crystal displays, semiconductors, low-temperature solders and infrared photo-detectors [3–4]. The major uses are derived from indium metal, its alloys and indium-tin oxide (ITO) [5]. More than one-half of the world’s indium consumption is for indium-tin oxide (ITO) coatings. ITO, which is a sintered alloy containing a large portion of indium oxide and a small portion of tin oxide, is an optically transparent conductor and is used in making thin-film transistor liquid crystal displays (TFT-LCDs) for television screens, portable computer screens, cell phone displays and video monitors [6–10].

The demand for the preparation of ultra high purity (UHP) In has been primarily promoted by the recent developments in semiconductor industry. The residual impurities even in less than $10^{-6}$ level concentration in semiconductor materials play a major role in the electronic properties by creating deep energy levels [11–12]. The preparation of UHP metals requires first to get a basic knowledge of the identity and the concentrations of impurities present in the starting material, which is normally a commercial grade material. Subsequently, schemes for purification by multistage processes need to be worked out, such as hydro-chemical processing, electrolysis, ion-exchange, solvent extraction, vacuum refining, zone refining and electron migration, [13–16]. Both vacuum distillation and zone refining processes have distinct purification roles. Vacuum distillation is more viable than the time consuming zone refining, because a higher purification yield is reached in less time [17–18].

In this work, indigenous indium was used as input material and vacuum distillation process was firstly alone employed to prepare 5N indium. This is a new process and a new technology that has the advantages of shorter flow-sheet, pollution-free and lower energy consumption.

2 Theoretical basis

The difference in vapor pressure of each metal at
different temperatures was the basic principle of crude metal vacuum distillation [19]. The relationships between vapor pressure ($p/\text{Pa}$) of pure metals in the crude indium and temperature ($T/\text{K}$) are listed as

$$\lg p_{\text{Cd}} = -5.819T^{-1} - 1.257\lg T + 14.412 \quad (594-1050\text{K}) \quad (1)$$

$$\lg p_{\text{Zn}} = -6.620T^{-1} - 1.255\lg T + 14.485 \quad (692-1800\text{K}) \quad (2)$$

$$\lg p_{\text{Tl}} = -9.307T^{-1} - 0.892\lg T + 13.225 \quad (700-1080\text{K}) \quad (3)$$

$$\lg p_{\text{In}} = -12.580T^{-1} - 0.45\lg T + 11.915 \quad (429-2346\text{K}) \quad (5)$$

$$\lg p_{\text{Sn}} = -15.500T^{-1} + 10.355 \quad (504-2876\text{K}) \quad (6)$$

$$\lg p_{\text{Cu}} = -17.520T^{-1} - 1.21\lg T + 15.335 \quad (1357-2836\text{K}) \quad (7)$$

$$\lg p_{\text{Fe}} = -19.710T^{-1} - 1.27\lg T + 15.395 \quad (1811-3135\text{K}) \quad (8)$$

$$\lg p_{\text{Ni}} = -22.400T^{-1} - 2.01\lg T + 19.075 \quad (1728-3187\text{K}) \quad (9)$$

The saturated vapor pressure of indium and other impurities under different temperatures were calculated. And they are shown in Fig. 1. It was indicated that the saturated vapor pressure of Pb, Cd, Zn and Tl was higher than that of indium. These impurities with low boiling point could volatilize prior to indium during distillation. On the contrary, the saturated vapor pressure of Sn, Fe, Cu and Ni was lower than that of indium. The impurities with high boiling point would remain in residual and indium would volatilize. So, a two-step distillation method was adopted to obtain the high purity indium.

Fig. 1 $\lg p-T$ plot of indium and impurities

3 Experimental

The vacuum distillation system consisted of an evaporator, that was made up of an isostatic fine grain high-density graphite crucible in the cylindrical shape of dimensions $50 \text{ mm} \times 40 \text{ mm} \times 80 \text{ mm}$ (outer diameter$<\text{inner diameter}<\text{height}).$ The condenser was made up of stainless steel comprising of water cooled tubes to collect the distillate. The diagram of vacuum furnace along with crucible, condenser and pit retort is shown in Fig. 2. The crude indium to be distilled was kept in the graphite crucible and placed in the retort that was closed with condenser. The furnace was evacuated for about 3 h at 673 K to remove any moisture. A dynamic vacuum level of approximate 5 Pa was maintained in the vacuum furnace containing graphite crucible and collector using appropriate combination of rotary and diffusion pumps. As the temperature inside the chamber surpassed the boiling point, the material started evaporating and condensed at the bottom of cooled collector placed on top leaving high melting point. The experiment was conducted in two steps. In the first phase, called as low fraction stage, the distillation experiment was carried out at a comparatively lower temperature 1223 K to remove high-volatile impurities. As the temperature in the chamber ceased to room temperature, the condenser was cleaned off. Then the balance indium material in the graphite crucible was used in the second phase, called as high fraction stage. Distillation temperature about 1323 K was maintained for second phase and indium was condensed with variable time factors. The experimental flow sheet is shown in Fig. 3. The material left in the bottom of the crucible after high fraction experiment was called the “Residue”. Samples

Fig. 2 Experimental equipments: 1– Cover of furnace; 2– Body of furnace; 3– Bottom of furnace; 4– Electrode; 5– Condenser; 6– Observation port; 7– Heat holding cover; 8– Heating element; 9– Crucible