Removal of Arsenic from Crude Tin by Vacuum Distillation

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1. Introduction

Arsenic is a highly toxic element. It exists not only in natural environment, but also in mining, smelting and coal-fired power plants and other industrial processes. Arsenic exists in various minerals, the most common of which are cassiterite and galena. Approximately 140 million people worldwide drink groundwater containing unsafe levels of arsenic13. In China, arsenic pollution has attracted attention. Mining and metallurgy activities are one of the core reasons of arsenic pollution22. Populations are at risk of exposure to excessive levels of arsenic in tin production areas and larger areas where arsenic is transported by water, soils, dust, food and so on3–9.

With the development and utilization of tin resources, the composition of tin ores has become more complicated, resulting in a large number of complicated compositions of tin-based alloy in the smelting process. In China and elsewhere, many tin ores contain arsenic. As a result, tin-based alloy contains impurities from the tin making process10. Arsenic is widely present in the process of ore-dressing, tailings recovery and smelting, which is poisonous and harmful. Current technologies which can treat tin ore or crude tin have not achieved satisfactory economic and environmental effects. In particular, the existing processes have poor effects on arsenic removal from raw materials. This paper adopted vacuum distillation to deal with crude tin. In the experimental research, tin was left as a residue after the distillation, and arsenic was volatilized into the gas phase as a volatile. The impurities in crude tin were effectively removed at 1473 K for 35 min and material weight of 80 g under 5 Pa. Under this condition, 98.67 mass% of tin in the residue can be recovered, and 84 mass% of arsenic in crude tin was removed by vacuum distillation. Arsenic can be removed effectively from crude tin by using vacuum distillation.

As a result of their toxicity22–25, arsenic compounds are used in industry and society. They can be used in wood preservatives, electronic components, coating, glass, alloys, and ceramics26. Some arsenic compounds can be used as medicines, most commonly in the treatment of cancer. Hence, it is of great interest to develop and implement both an environmentally friendly and technically feasible process to recycle the arsenic from crude tin.

Vacuum method is a new technology in the field of metallurgy, which shows many advantages such as high metal recovery rate, less consumption of resources and energy, no waste water or waste gas production, simple process and simple operation17–20. According to the characteristics of arsenic and the difference in the saturation vapor pressure of each substance in crude tin, the vacuum reduction method is investigated in this paper. During the vacuum treatment, it can not only guarantee the content of tin in the residue and the direct yield of tin but can also remove arsenic, i.e., arsenic in crude tin is evaporated at once to metals. Through vacuum distillation, 84% of arsenic is achieved in the open circuit, and arsenic is collected in the arsenic collector, which greatly reduces environmental risk.

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2. Experimental Methods

2.1 Experimental materials

The experimental material is provided by a tin smelter in China. Table 1 gives the main chemical composition of metals in the crude tin in the small experimental research. As shown in Table 1, there was 0.21 mass% arsenic and 0.25 mass% arsenic in the sample. The content of As, Fe and Cu are very small in crude tin. Even if they interact with themselves, the effect will be small. So, it will not influence for arsenic evaporation.

2.2 Apparatus

The experimental research was carried out on a homemade apparatus shown in Fig. 1. The vacuum furnace mainly consisted of a vacuum system, heating system and temperature control system.

2.3 Procedures

A graphite crucible was loaded with a certain amount of material, the furnace lid was covered and the vacuum valve was tightened. The cooling water valve was opened in order to ensure circulation of water, and then the vacuum pump was started. When the pressure was less than 20 Pa, the temperature was raised, and the heating rate was controlled. When the temperature increased to the set temperature, the power output was adjusted to control the temperature in the setting range. After the heat preservation stage, the power was disconnected to control the temperature in the setting range. After the heat preservation stage, the power was disconnected, the vacuum pump was kept on, and cooling water continued to run. When the furnace temperature dropped to room temperature, the vacuum furnace was opened and the volatiles were removed. The residues, weight, and sample were analyzed. The direct yield of tin (W) was calculated by the following formula:

\[ W = \frac{m_1 \times w_1}{m_2 \times w_2} \times 100\% \quad (1) \]

where \( m_1 \) is the mass of the product, \( m_2 \) is the mass of the raw materials, \( w_1 \) is the tin content in the products, \( w_2 \) is the tin content in the raw materials.

2.4 Theoretical analysis

2.4.1 Pure material boiling point

The boiling point of tin in crude tin is 2995 K. The boiling point of arsenic in crude tin is 876 K. It can be preliminarily judged that arsenic volatile has priority over tin in crude tin and is enriched in the gas phase. Tin remains in the residue to achieve the separation of arsenic from crude tin.

2.4.2 Saturated vapor pressure of pure substances

The principle of vacuum distillation is using different vapor pressures of components to separate elements at different temperatures. Under the condition of the same temperature, the more saturated the vapor pressure in a certain group, the more volatile it is.

The relation of saturated vapor pressure and temperature of a pure substance can be expressed as:

\[ \lg p = AT^{-1} + B \lg T + CT + D(Pa) \quad (2) \]

A, B, C, and D in the formula represent evaporation constants. As can be seen in Table 2, formula 1 can be used to calculate and draw the relationship between saturated vapor pressure and temperature. As the Fig. 2 showed:

From Fig. 2, with the increase of melt temperature, the vapor pressure of each group increased exponentially. Judging by the saturated vapor pressure, we can see that arsenic volatile has priority over tin, so arsenic and tin can be separated.

Based on the above principle, due to the low dew point temperature of arsenic, we segmented the control condenser temperature in the process of vacuum distillation and condensation, causing arsenic to transform from gas into a solid

<table>
<thead>
<tr>
<th>element</th>
<th>Sn</th>
<th>Pb</th>
<th>Sb</th>
<th>Bi</th>
<th>As</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material A/mass%</td>
<td>93.42</td>
<td>5.31</td>
<td>0.50</td>
<td>0.27</td>
<td>0.21</td>
<td>0.025</td>
<td>0.094</td>
</tr>
<tr>
<td>Raw material B/mass%</td>
<td>92.22</td>
<td>5.21</td>
<td>0.71</td>
<td>0.36</td>
<td>0.25</td>
<td>0.55</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Fig. 1 Internal structure schematic diagram of vacuum furnace.

1 furnace lid 2 furnace body 3 furnace bottom 4 electrode 5 condensation plate 6 observation door 7 heat holding cover 8 heating unit 9 crucible.

Fig. 2 The relationship between saturated vapor pressure and temperature.
and to achieve its condensation.

3. Results and Discussion

The factors influencing the evaporation percent of arsenic in crude tin of the small experimental research were studied under different experimental conditions including distillation temperature, material thickness and soaking time. The industrial experiment research was studied in terms of product weight, percent recovery and volatilization rate.

3.1 Effect of distillation temperature

The effect of distillation temperature on the impurity content in the residue was investigated in the range from 1173 to 1573 K using a gradient of 100 K, at residual gas pressure of 5 Pa, soaking time of 15 min and raw material weight of 80 g. The relationship between distillation temperature and tin content in the residue and the direct yield of tin is shown in Fig. 3(a) and 3(b). The relationship between distillation temperature and arsenic content in the residue is shown in Fig. 4.

As shown in Fig. 3(a) and 3(b), the content of tin in the residue increases with the increase of temperature, and the direct yield of tin reduces. When the temperature is 1473 K, the contents of tin in the residue are 98.49 mass%(A) and 97.98 mass%(B) (A indicates material A and B indicates material B in this paper). With the increase of temperature, the content of tin in the residue increases slowly. When the temperature is 1173 K, the direct yields of tin are 99.41%(A) and 99.99%(B). When the temperature rises to 1473 K, the direct yields of tin are 97.92%(A) and 98.29%(B), this is because the amount of volatile impurities decreases in the residue. With further increase of temperature, the direct yield of tin falls sharply, and when the temperature is 1573 K, the direct yields of tin are 93.82%(A) and 95.02%(B). This is because when the temperature is higher than 1473 K, the volatile tin can no longer be ignored under vacuum conditions, leading to the content of tin decreasing in the residue. As shown in Fig. 4, when the temperature is 1573 K, the content of arsenic(A) is down to 0.021 mass% from 0.2 mass%, and the content of arsenic(B) is down to 0.025 mass% from 0.26 mass%. It can be seen from Fig. 4 that the high temperature is conducive to the removal of arsenic, the higher the temperature, the better the removal, and the high content of arsenic in crude tin has better removal effect. With the increase of temperature, the content of arsenic decreases gradually, and the decrease rate gradually slows down. Although the effect of high temperature on arsenic removal is obvious, taking into account the large amount of volatile tin under this temperature and that the effect of impurity removal is no longer obvious, 1473 K is the best temperature, which can ensure the removal of the effect of arsenic, the content of tin in the residue and the direct yield of tin.

3.2 Effect of material weight

The experiments were conducted with material weight ranging from 60 g to 140 g. Respectively taking 60 g, 80 g, 100 g, 120 g, and 140 g of material, the temperature was maintained at 1473 K with a soaking time of 15 min, corresponding to residual gas pressure of 5 Pa. The following experimental results are obtained. The relationship between material weight and tin content in the residue and the direct yield of tin is shown in Fig. 5(a) and 5(b). The relationship between arsenic content in the residue and material weight is shown in Fig. 6.

As seen from Fig. 5(a) and 5(b), along with an increase in the material weight, the content of tin in the residue is gradually decreased. Although there are fluctuations in the process, the overall trend declines, which is due to the evaporation of the impurities at the evaporation surface. The diffusion distance of the impurities in the liquid phase in-
creases, which makes the evaporation of the impurities difficult, eventually leading to the decrease of the content of tin in the residue. The direct yield of tin increases obviously as the material weight increases. When the material weight reaches more than 100 g, there are fluctuations in Fig. 5(a). When the material weight is 100 g, the direct yield of tin is 97.69% (A), and when the material weight is raised to 120 g, the direct yield of tin is 97.58% (A), which may be due to test error. From Fig. 5(b), along with the increase of material weight, the yield of tin increases. When the material weight is 120 g, the yield of tin is 99.16%. With continued increase of the material weight, the numerical value slightly decreases, showing that when the material weight reaches a certain value, the yield of tin is stabilized. As seen from Fig. 6, with the increase of material weight, the content of arsenic in the residue increases slightly. The contents of arsenic remain between 0.08 mass%–0.09 mass% (A) and 0.04 mass%–0.05 mass%, and there is a rising trend. To remove arsenic and to ensure the yield of tin and the content of tin, the final selection of the material weight is 80 g for the best condition.

3.3 Effect of soaking time

The objective of the experiments in this series is to observe the influence of soaking time on the percent of arsenic in crude tin. The effect of soaking time was investigated in the range from 15 to 55 min, respectively taking soaking times of 15 min, 25 min, 35 min, 45 min, and 55 min when the temperature is 1473 K, material weight is 80 g and residual gas pressure is 5 Pa. The relationship between soaking time and tin content in the residue and the direct yield of tin is shown in Fig. 7(a) and 7(b). The relationship between volatile impurities content in the residue and soaking time is shown in Fig. 8.

As shown in Fig. 7(a) and 7(b), the content of tin in the residue increases gradually as the soaking time is increased. When the soaking time reaches 35 min, the tin contents are 98.67 mass% (A) and 98.48 mass% (B). When the soaking time reaches 55 min, the tin contents are 98.69 mass% (A) and 98.85 mass% (B), which are still less than 99 mass%. This is because of the copper and iron in the raw material that cannot be removed by vacuum treatment, so the tin content in the residue reaches the limit. With the continued increase of soaking time, the tin content cannot be increased. The direct yield of the tin decreases with the prolonging of soaking time. When the soaking time is 35 min, the direct yields of tin are 97.60% (A) and 97.80% (B), and when the soaking time is 55 min, the direct yields of tin are 96.77% (A) and 96.27% (B). The direct yield of tin obviously decreases, which is due to the volatilization of tin to reduce its direct yield. As shown in Fig. 8, for raw material A, the removal of arsenic has reached the limit, and the content of arsenic is approximately 0.04 mass%. When the soaking time is 35 min, the content of arsenic is 0.038 mass%. Such a removal rate of arsenic is high in the main-process stream. For raw material B, the arsenic content is 0.066 mass% at the beginning. After the experiment, approximately 0.04 mass% can be obtained. When the soaking time is 35 min, the arsenic content is the lowest which is 0.038 mass%. With the continued increase of the holding time, there is little effect on the removal of arsenic, and prolonging the soaking time will result in more energy consumption, which is a disadvantage. Based on the above analysis, soaking time of 35 min is the best option.

Through the small experiment, under the conditions of distillation temperature of 1473 K, material weight of 80 g and soaking time of 35 min, 98.67 mass% of tin in the residue and direct yield of tin of 97.60% can be obtained, and the arsenic content decreases from 0.25 mass% to 0.04 mass%. 84 mass% of arsenic in crude tin is removed by
vacuum distillation.

4. Conclusion

According to the pure material boiling point and saturated vapor pressure of pure substances, arsenic volatile goes into the gas phase in the vacuum distillation process, and tin is enriched in the liquid phase. It can be concluded that arsenic and tin can be separated by vacuum distillation. The vacuum distillation purification experiment showed that 1473 K distillation temperature, 80 g material weight and 35 min soaking time were the best optimum separation conditions, in which 98.67 mass% of tin in the residue can be obtained, and 84 mass% of arsenic in crude tin was removed by vacuum distillation.

The experimental results showed that vacuum distillation is an advanced technology of clean metallurgy. Arsenic can be removed effectively by the processing of crude tin.

Acknowledgments

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