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Preparation of high-purity bismuth by sulphur deleadization in vacuum distillation^①

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Abstract: The feasibility of separation of impurities in refined bismuth and sulphur deleadization with vacuum distillation was studied theoretically. Experimental studies on sulphur deleadization were carried out under vacuum. The influences of amount of sulphur, distillation temperature, vacuum degree and distillation time on deleadization were investigated and an optimal technical condition was achieved. The content of lead in refined bismuth can be decreased from 30 $\mu\text{g/g}$ to 0.21 $\mu\text{g/g}$, which has reached the level of "5N" high-purity bismuth. Other impurities in refined bismuth can be also removed effectively under certain conditions.

Key words: vacuum distillation; sulphur deleadization; refined bismuth; high-purity bismuth

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1 INTRODUCTION

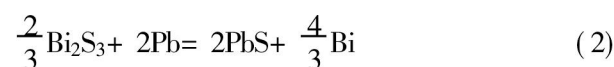
Poisonless and high-purity bismuth can be widely used for chemical compound semiconductor, high-purity alloy, electric refrigeration components, thermoelectricity transformation components and the refrigeration of the atomic nucleus reactor carrier in liquid state^[1]. The research and development of high-purity bismuth will have a bright future^[2]. Vacuum distillation and regional smelt are regarded as the most effective methods for metal separation and purification^[3, 4], which have been used for the preparation of many high-purity metals^[5-18], such as tellurium, dysprosium, gallium, scandium, terbium, niobium, indium, bismuth, selenium, zinc, lithium and so on. By far vacuum distillation is the most conventional way to purify industrial rich bismuth to 99.999% (5N)^[10-15]. But there still exist some problems in the conventional method due to the close saturation vapor pressure of bismuth and lead, i. e. the effect of deleadization is not very desirable and extra chloride deleadization is needed^[1]. To solve these problems, we are considering the addition of sulphur for deleadization in vacuum condition, that is, to remove lead by turning it into volatile lead sulphide. Thus we can effectively remove lead without prolonging the technological process for "5N" high-purity Bi. It aims at high rate of recovery, less pollution, less energy consuming and more economic benefit. According to Yunnan Scientific and Technological Intelli-

gence Research Institute, the preparation of high-purity Bi by addition of sulphur for deleadization is by far not reported.

2 THEORETICAL BASIS

2.1 Thermodynamics basis for sulphur deleadization of refined Bi in vacuum distillation

The chemical reactions related are^[19]:



According to Ref. [20], as for reaction (1), $\Delta G_{544}^\ominus = -1.35 \times 10^5 (\text{J/mol})$; to reaction (2), $\Delta G_{544}^\ominus = -1.55 \times 10^5 (\text{J/mol})$, therefore the above reactions are fairly complete from the left to the right in vacuum condition.

The fundamental condition to determine whether substance is separable in vacuum distillation is the differences of the vapor pressure in pure state. The relationship of vapor pressure and temperature between PbS and pure Bi is shown in Fig. 1. It shows when the temperature is higher than 900 K, the vapor pressure of PbS is greater than that of Bi, that is, at appropriate vacuum distillation temperature, PbS will volatilize prior to Bi. But the degree of separation is the key to the effect of deleadization.

In order to determine the possibility and the separa-

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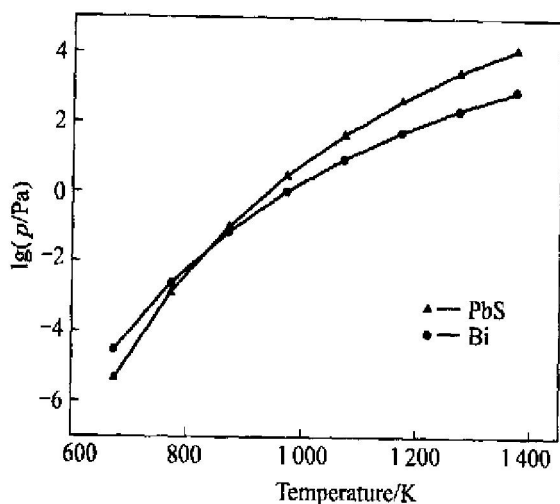


Fig. 1 $\lg p - T$ curves of PbS and Bi in pure state

tion degree of the two components in vacuum distillation, the separation coefficient β is introduced and according to Ref. [20]:

$$\beta = \frac{\gamma_A p_A^*}{\gamma_B p_B^*} \quad (3)$$

where γ_A and γ_B were the activity coefficients of component A and B, respectively; p_A^* and p_B^* are the saturation vapor pressures of A and B in pure state. As to rich Bi 99.999% with very few impurities, it can be regarded as the thin solution with the solvent Bi, hence the activity coefficient is close to 1, that is $\gamma(\text{Bi}) = 1$. By far the document about the activity coefficient of PbS is not reported, supposing $\gamma(\text{Pb}) = 1$, then $\beta = p_A/p_B$. Thus the separation coefficient (β) can be worked out as in Table 1.

Table 1 Saturated vapor pressure and separation coefficients of pure Bi and Bi_2S_3

Temperature/ K	Saturated vapor pressure/Pa		$p_{\text{PbS}}^*/p_{\text{Bi}}^*$	β
	Bi	PbS		
973	1.05	2.93	2.79	2.79
1 023	3.28	12.48	3.80	3.80
1 073	9.20	46.10	5.01	5.01
1 123	23.48	150.67	6.42	6.42
1 173	55.15	442.62	8.03	8.03

According to Table 1, the separation coefficient of pure Bi and PbS increased from 2.79 to 8.03 while the temperature increases from 973 to 1 173 K. The higher the temperature, the larger the β , which shows the possibility to separate Bi and PbS in vacuum distillation and it will be more favorable to separate with higher temperature.

According to the above analysis, theoretically it is feasible to purify Bi by the addition of sulphur for deleadization, and PbS can coacervate in the vapor prior to Bi. Besides, from reaction (1), impurity Bi_2S_3 will be produced together with PbS. The relationship of the saturated vapor pressure between Bi_2S_3 and the temperature is shown in Table 2. From Tables 1 and 2, the saturated vapor pressure of Bi_2S_3 is much greater than that of Bi at the same temperature, therefore, Bi_2S_3 will volatilize first. While the temperature is high enough to melt Bi_2S_3 , it can be decomposed into liquid Bi and gaseous sulphur and it's beneficial to increase the rate of Bi recovery in vacuum.

Table 2 Relationship between saturated vapor pressure of Bi_2S_3 and temperature^[1]

Temperature/K	973	1 073	1 173
$p_{\text{Bi}_2\text{S}_3}/\text{Pa}$	38.40	105.86	389.84

2.2 Thermodynamics basis for removal of other impurities in refined Bi in vacuum distillation

Fig. 2 shows the saturated vapor pressure of impurities and bismuth in refined bismuth at different temperatures. The separation coefficients of impurities and bismuth in refined bismuth are shown in Table 3. From Fig. 2 and Table 3, other impurities in refined bismuth can be separated with bismuth in vacuum distillation.

Table 3 Separation coefficients of impurities and bismuth in refined bismuth^[20]

System	T/K	p_i^0/p_{Bi}^0	γ_i^0	$\beta_{i-\text{Bi}}^0$
Bi-Cd	773	7.45×10^5	1.000	7.45×10^5
Bi-Cu	1 200	1.78×10^{-5}	2.236	3.98×10^{-5}
Bi-Ag	1 000	3.8×10^{-4}	3.519	1.34×10^{-3}
Bi-Au	973	4.47×10^{-9}	0.750	3.35×10^{-9}
Bi-Hg	594	5.43×10^{10}	1.410	7.66×10^{10}
Bi-Zn	873	2.16×10^4	2.822	6.10×10^4
Bi-Pb	700	0.95	0.467	0.444
Bi-Sb	1 200	14.12	1.293	18.25
Bi-Sn	600	7.59×10^{-10}	1.158	8.79×10^{-10}

3 EXPERIMENTAL

3.1 Materials and equipments

The material No. 1 refined Bi is provided by Zhuzhou Smeltery. The components are determined with ICP-MASS by Jiangxi Analysis Testing Center. Table 4 lists the amount of impurities in No. 1 refined Bi.

The sulphur used is sublimated with the content of 99.5%. The experiment is carried out with

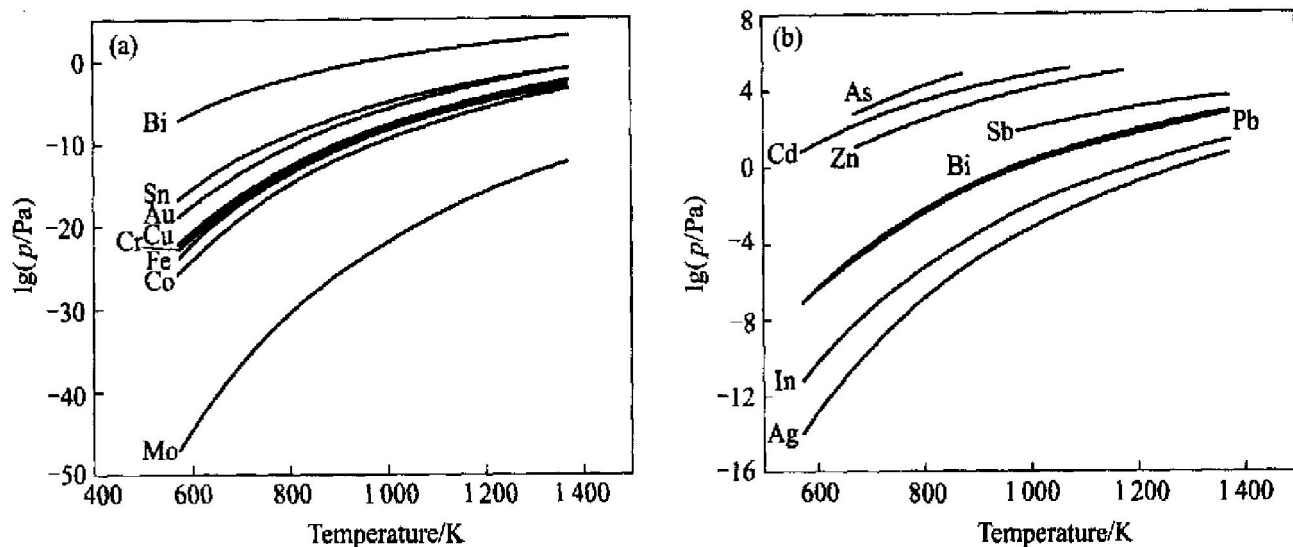


Fig. 2 Saturated vapor pressure of impurities and bismuth in refined bismuth

Table 4 Chemical composition of refined bismuth (mass fraction, %)

Element	Pb	Sb	As	Mn	Sn	In	Cd	Mo
Content	0.003 0	0.000 1	0.000 05	0.000 1	0.000 05	0.000 05	0.000 05	0.000 4
Element	Zn	Co	Hg	Cr	Fe	Ag	Au	Bi
Content	0.000 8	0.000 1	0.000 05	0.003 6	0.000 2	0.000 05	0.000 01	99.990 79

equipment made up of vacuum space, heater, system of controlling and taking temperature, the system of acquiring vacuum and measuring. Vacuum gauge is Mr-styled with measuring range from 0.1 to 150 Pa. When the pressure is greater than 150 Pa, U-shaped manometer is used. The temperature is taken with platinum-platinum-rhodium thermocouple and controlled with controllable silicon temperature controller.

3.2 Operating process

The refined Bi is ground to size of less than 45 μm , and put into graphite crucible with sulphur in certain proportion, then heated with vacuum stove. The inner pressure will keep more or less the same by inputting nitrogen. When the temperature is high enough, make it vacuum and distillate for a while, then cut off the power, refrigerate. The condensate and residue are taken out and weighed. Make sure the amount of lead in the residue meets the requirement of high-purity Bi. Further distillation is carried out at another temperature and then the residue is analyzed.

4 RESULTS AND DISCUSSION

4.1 Influence of content of sulphur on effect of deleadization of refined Bi

Fig. 3 shows the effect of deleadization when the sulphur amount ranges from 0.01 ~ 0.05 g with the temperature of 800 K, pressure of 5 Pa and distillation time of 20 min. It shows that the amount to lead decreases with the

addition of sulphur and the volatilization rate increases. While the content of lead in the residue and the volatilization rate of Bi will remain the same with 0.02 ~ 0.05 g/g sulphur. Thus the content of sulphur should be best at 0.02 g/g.

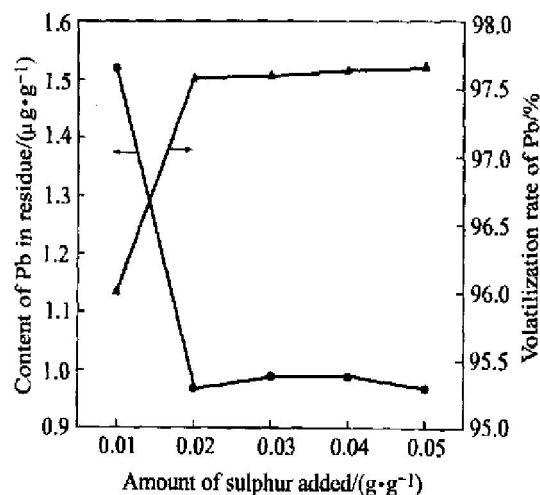


Fig. 3 Relationship between content of Pb in residue and volatilization rate of Pb and amount of sulphur added

4.2 Influence of distillation temperature on effect of deleadization of refined Bi

Fig. 4 represents the fact of deleadization at different temperatures with the pressure of 5 Pa, sulphur content of 0.05 g/g, distillation time of 20 min. It shows that the volatilization ratio of lead increases and the amount in Bi

decreases when the temperature increases, which is up to the theoretical analysis. While it increases to 1 123 K or so, the content of sulphur added with the increasing temperature, so is the volatilization of PbS and Bi. When it reaches a certain temperature, the volatilization of Bi will also increase, a small portion of lead in the residue has not turned into PbS, so the content of lead in residue will increase at another high temperature. The experiment indicates the appropriate temperature should be 1 073 K or so.

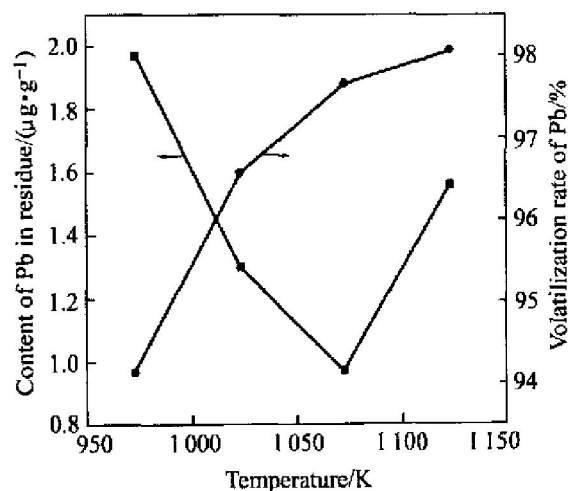


Fig. 4 Relationship between content of Pb in residue and volatilization rate of Pb and distillation temperature

4.3 Influence of vacuum degree on effect of deleadization of refined Bi

Fig. 5 shows the effect of deleadization with distillation temperature of 1 073 K, sulphur content of 0.05 g/g, distillation time of 20 min while the pressure is at 5 Pa, 10 Pa, 16 Pa, 20 Pa, 30 Pa respectively.

According to Fig. 5, the vacuum degree will

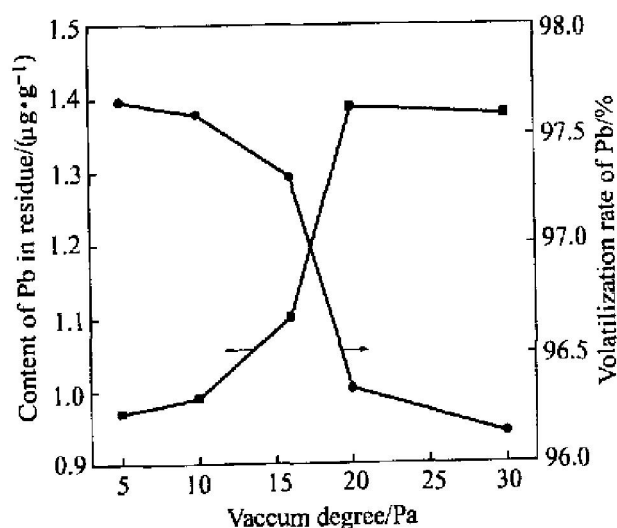


Fig. 5 Relationship of content of Pb in residue and volatilization rate of Pb to vacuum degree

effect the results of deleadization more or less. The content of lead in residue increases and its volatilization ratio decreases by the addition of pressure when the temperature is at 1 073 K or so. But when the pressure is less than 16 Pa, its influence is rare. According to Refs. [20, 21], at the temperature of 1 073 K, the critical pressure is 10 Pa, thus the loss of Bi will be decreased without affecting the deleadization if the experiment is carried out with the pressure of 16 Pa.

4.4 Influence of distillation time on effect of deleadization

Distillation time is considered for further investigating the volatilization of sulphur. The experiment is carried out with the temperature of 1 073 K, sulphur content 0.05 g/g, vacuum degree of 5 Pa. The results are shown in Fig. 6 and Table 5. It shows the volatilization will speed up as distillation time lasts. While the speed of volatilization will keep unchanged when exceeding 15 min, which is critical. Table 5 shows that the distillation time has little effect on deleadization.

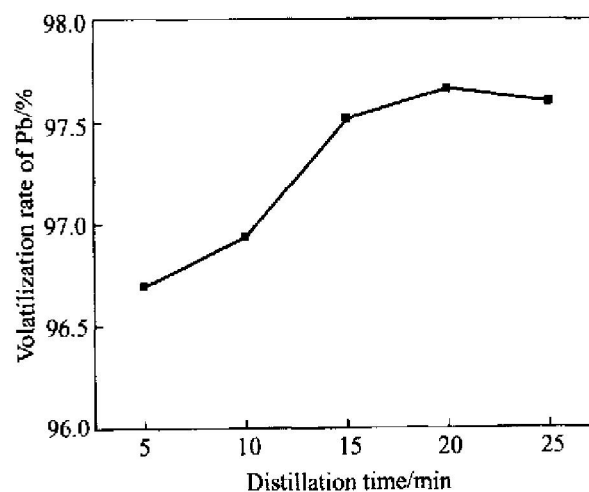


Fig. 6 Relationship between distillation time and volatilization rate of Pb

Table 5 Effect of distillation time on sulphur deleadization

Distillation time/min	5	10	15	20	25
Content of Pb in residue/($\mu\text{g}\cdot\text{g}^{-1}$)	1.19	1.17	0.99	0.97	1.22

4.5 Influence of way of adding sulphur on effect of deleadization

With the same content of sulphur (0.02 g/g), the influence on deleadization with a small amount of sulphur frequently is listed in Table 6. Decreasing the amount every time while increasing the time can improve the effect of deleadization.

4.6 Removal of other impurities in refined Bi

Table 6 Effect of distillation times on sulphur deleadization

Distillation times	1	2	3
Content of Pb in residue/ ($\mu\text{g}\cdot\text{g}^{-1}$)	1.19	0.52	0.21

From Table 7 we can see that the content of impurities (except for Fe) has attained the goal of “5N” refined Bi. The reasons why Fe is a little more than the others lie in the contact with Fe while grinding, sampling and refrigerating.

Table 7 Content of impurities and bismuth in refined Bi ($\mu\text{g}\cdot\text{g}^{-1}$)

Pb	Zn	Hg	Sb	Ag	As
0.40	0.98	0.024	0.0098	0.0098	0.0098
Co	Mn	Cd	Fe	Mo	Ni
0.024	0.074	0.0098	0.98	0.02	0.049
Sn	Cr	Au	In	Bi	
0.0098	0.0098	0.0098	0.0098	99.99976	

5 CONCLUSIONS

1) It is feasible to prepare high-purity Bi with sulphur deleadization in vacuum distillation. Compared with traditional chloride deleadization, sulphur dedeacidization is characterized by simple technological process, working condition and efficiency improvement.

2) With the temperature of 1 073 K, the addition of sulphur 0.02 g/g, the content of lead can be decreased from 30 to 0.21 $\mu\text{g/g}$ and the deleadization rate is 99.3%.

3) “5N” high-purity Bi can be obtained by sulphur deleadization in vacuum distillation in industry.

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