Thermodynamics of removing impurities from crude lead by vacuum distillation refining

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Abstract: A novel technique was developed to remove impurities from crude lead by vacuum distillation. The thermodynamics on vacuum distillation refining process of crude lead was studied by means of saturated vapor pressure of main components of crude lead, separation coefficients and vapor−liquid equilibrium composition of Pb−i (i stands for an impurity) system at different temperatures. The behaviors of impurities in the vacuum distillation refining process were investigated. The results show that the vacuum distillation should be taken to obtain lead from crude lead, in which Zn, As and partial Sb are volatilized at lower temperature of 923−1023 K. Lead is distilled from the residue containing Cu, Sn, Ag and Bi at higher temperature of 1323−1423 K, but the impurity Bi is also volatilized along with lead and cannot be separated from lead.
Key words: crude lead; vacuum distillation; refining; removal; thermodynamics

1 Introduction

Crude lead produced by the traditional pyrometallurgy processes usually needs to refine so that it can be used widely. The refining of crude lead has fire refining process and electrolytic process [1,2]. At present, the fire refining has been used in more lead smelters, accounting for about 70% of the production of refined lead in the world, only some smelters use electrolytic process in Canada, Peru, Japan and China [3−5]. The refining of crude lead is aimed to remove the impurities to obtain the refined lead (purity over 99%), and to recover copper, silver and bismuth and other precious metals in the crude lead. Cu, Sn, Ag, Zn, As, Sb and Bi are the common impurities of crude lead. Whether fire refining process or electrolytic process, all that could obtain naturally the requirements to the quality of pure lead. But there are some serious problems in conventional refining process of crude lead. The fire refining process has some disadvantages, such as procedure complex, low direct rate of lead, bad state of operation and evident environment pollution [6−9]. The electrolytic process has some disadvantages, such as long production period, large investment, high energy consumption and low economic profits [10,11]. Vacuum metallurgy has many advantages, such as short flow, low pollution and low energy consumption [12,13], and can eliminate the disadvantages of traditional refining processes. Vacuum distillation has been studied and successfully used in separation of various elements from binary alloys, crude nickel and crude indium [14−18]. The investigation on the refining of crude lead by vacuum distillation has not been reported. Herein, in this work, the thermodynamic performance of components of crude lead in the vacuum distillation process was investigated systemically in order to provide a simple, clean, efficient and referential way for the removal of Cu, Sn, Ag, Zn, As and Sb from crude lead.

2 Relationship between saturated vapor pressure of main components and temperature

The impurity components can be removed from

crude lead by vacuum distillation based on the different properties of components of crude lead when vaporizing and condensing. The difference in saturated vapor pressure of main components is the basic principle for vacuum distillation of crude metal at different temperatures. Relationship between saturated vapor pressure of main components and temperature is shown in Eq. (1), and the evaporation constants A, B, C and D for different components are shown in Table 1.

$$\lg p^* = AT^{-1} + B\lg T + CT + D \qquad (1)$$

where p^* is the saturated vapor pressure; T is the temperature.

Table 1 Evaporation constants A, B, C and D for different components [16]

Component	A	B	C	D	T/K
Pb	−10130	−0.985	−	13.280	600−2013
Cu	−17520	−1.210	−	15.330	1356−2840
Sn	−15500	−	−	10.355	505−2473
Ag	−14400	−0.850	−	13.825	1233−2468
Zn	−6620	−1.255	−	14.465	692−1773
As	−6160	−	−	11.945	873−1773
Sb	−6500	−	−	8.495	904−1860
Bi	−10400	−1.260	−	14.470	544−1837

According to Eq. (1) and Table 1, the saturated vapor pressure can be calculated as shown in Fig. 1.

Figure 1 shows that the saturated vapor pressure of As or Zn are much higher than that of Pb at 873−1073 K. At 823 K, As begins to sublimate, which indicates that As and Zn are easily to volatilize into vapor phase and can be removed from crude lead completely. The saturated vapor pressure of Sb is also high in comparison
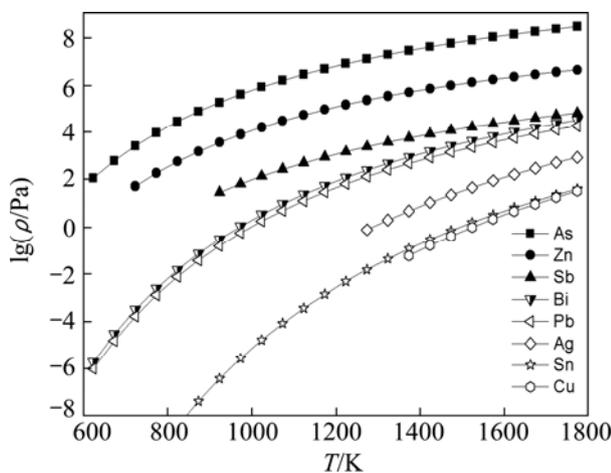

Fig. 1 lg p−T diagram of main components in crude lead with each element in pure state

with Pb, which can be partially removed at an appropriate temperature. The saturated vapor pressure of Cu, Sn or Ag is much lower than that of Pb at 1273−1523 K, which shows that Cu, Sn and Ag are difficult to volatilize into vapor phase and were concentrated in residual phase. It also can be seen that the saturated vapor pressure of Bi is close to that of Pb, which indicates that Bi cannot be separated from lead by vacuum distillation.

3 Possibility of impurities removal

The reason of refining of crude metal or separation of alloys by vacuum distillation is the composition difference between distilled vapor phase and liquid phase. As for crude lead, considering the effect of impurity composition and its component activities on separation efficiency, a concept β, i.e., separation coefficient, was introduced from theoretical derivation for Pb−i system, that is [16]

$$\beta_i = \frac{\gamma_i}{\gamma_{Pb}} \frac{p_i^*}{p_{Pb}^*} \qquad (2)$$

where γ_i and γ_{Pb} are activity coefficients of i and Pb components in crude lead, respectively.

Crude lead contains more than 92 % of Pb and other impurities including Cu, Sn, Ag, Zn, As, Sb and Bi. The composition i is less than 2 %. In the dilute solution, the impurity component i is considered the solute, and the activity coefficient of Pb is supposed as 1.

When $\beta_i > 1$ or $\beta_i < 1$, the separation of impurity component i from crude lead can be achieved. And the larger or smaller the value of β_i is, the better the removal efficiency will be. But when $\beta_i = 1$ or close to 1, it could not happen. Therefore, the separation coefficient of impurity component i, i.e. β_i, can be used to estimate whether the impurity component i can be separated by vacuum distillation for crude lead. When $\beta_i > 1$, impurity component i is concentrated in vapor phase, and Pb component is concentrated in liquid phase; when $\beta_i < 1$, impurity component i is concentrated in liquid phase, and Pb component is concentrated in vapor phase.

According to Eqs. (1) and (2), the separation coefficient of impurity component i can be calculated in the temperature range of 723−1773 K, as shown in Fig. 2.

Figure 2 shows that β_{Zn} and β_{Sb} are much more than 1 at 873−1073 K, which indicates that Zn and Sb are preferentially volatilized into vapor phase and Pb remains in residue. B_{Cu}, β_{Sn} and β_{Ag} are much less than 1 at 1273−1523 K, especially for β_{Cu} reaching 10^{-4}, which means that Cu, Sn and Ag are concentrated in residual

phase and Pb is volatilized into vapor phase. These conclude that Cu, Sn, Ag, Zn and Sb are excellently removed from crude lead. It also can be seen from Fig. 2 that β_{Bi} approaches 1 and it further confirms that Bi cannot be separated from lead by vacuum distillation. Due to the fact that the activity coefficient of As is not available, the thermodynamics could not be discussed regrettably.
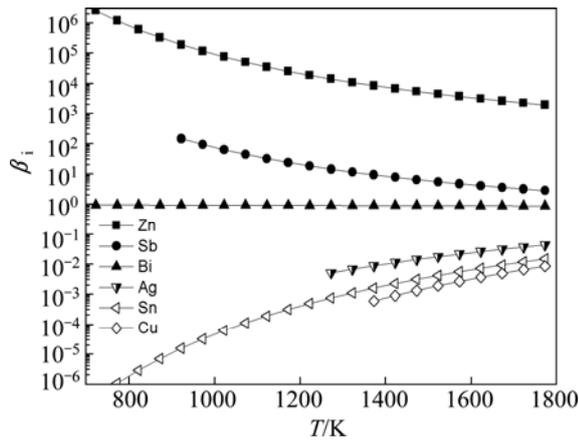

Fig. 2 Separation coefficient β_i of impurity component i in crude lead

4 Vapor−liquid equilibrium composition of Pb−i system

Equilibrium composition is significant to estimate the separation effect, conditions of operation and the products composition quantitatively. The purity of distilled lead can also be predicted by the vapor−liquid equilibrium composition. The content of impurity component i in vapor phase is expressed as[16]

$$C_{i(g)} = \left[1 + \frac{C_{Pb(l)}}{C_{i(l)}} \frac{\gamma_{Pb}}{\gamma_i} \frac{p_{Pb}^*}{p_i^*} \right]^{-1} \quad (3)$$

where $C_{i(g)}$ and $C_{i(l)}$ are the contents of component i in vapor and liquid phase, respectively; $C_{Pb(l)}$ is the content of component Pb in liquid phase.

Substituting the γ_i, γ_{Pb}, p_i^* and p_{Pb}^* into Eq. (3), the relationship diagram of $C_{i(g)}$−$C_{i(l)}$ can be developed as shown in Fig. 3 and Fig. 4 at the required temperatures, that is the vapor−liquid equilibrium composition for Pb−i system. It shows the change of equilibrium composition of vapor and liquid at different temperatures.

It can be seen from Fig. 3 that the impurities of Zn and Sb can be easily removed from lead by vacuum distillation at 873−1073 K from the view of thermodynamics, while Bi can hardly be removed from crude lead. For the sake of achieving better removal of Zn and Sb from lead and ensuring less loss of lead, vacuum distillation should be proceeded in an
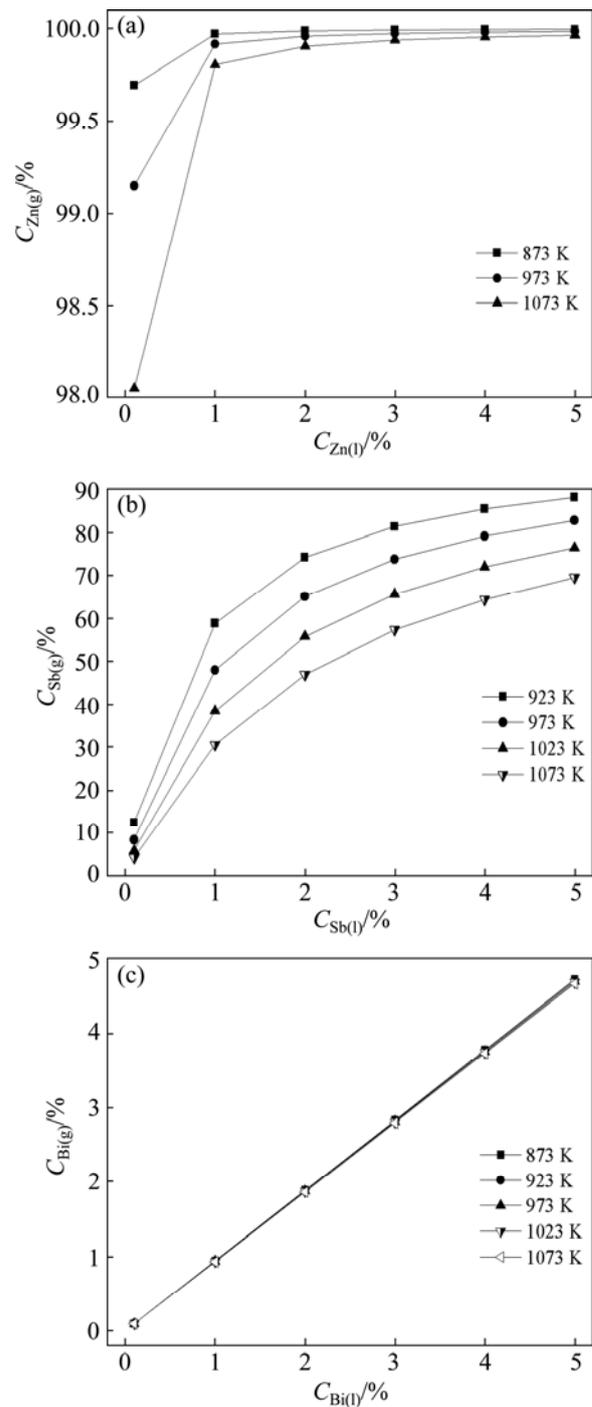

Fig. 3 Vapor−liquid equilibrium composition of Pb−Zn system (a), Pb−Sb system (b) and Pb−Bi system (c) at 873−1073 K

appropriate temperature range of 923−1023 K. Figure 4 shows that Cu, Sn and Ag are easy to remove completely from lead in thermodynamics by vacuum distillation only one time at 1273−1473 K, in which Cu, Sn and Ag are concentrated in the distilled residual liquid while lead is concentrated in vapor phase, but Bi cannot be removed at a higher temperature. In order to attain a high distilling rate of lead and remove Cu, Sn and Ag completely, vacuum distillation should be performed in the proper temperature range of 1323−1423 K.
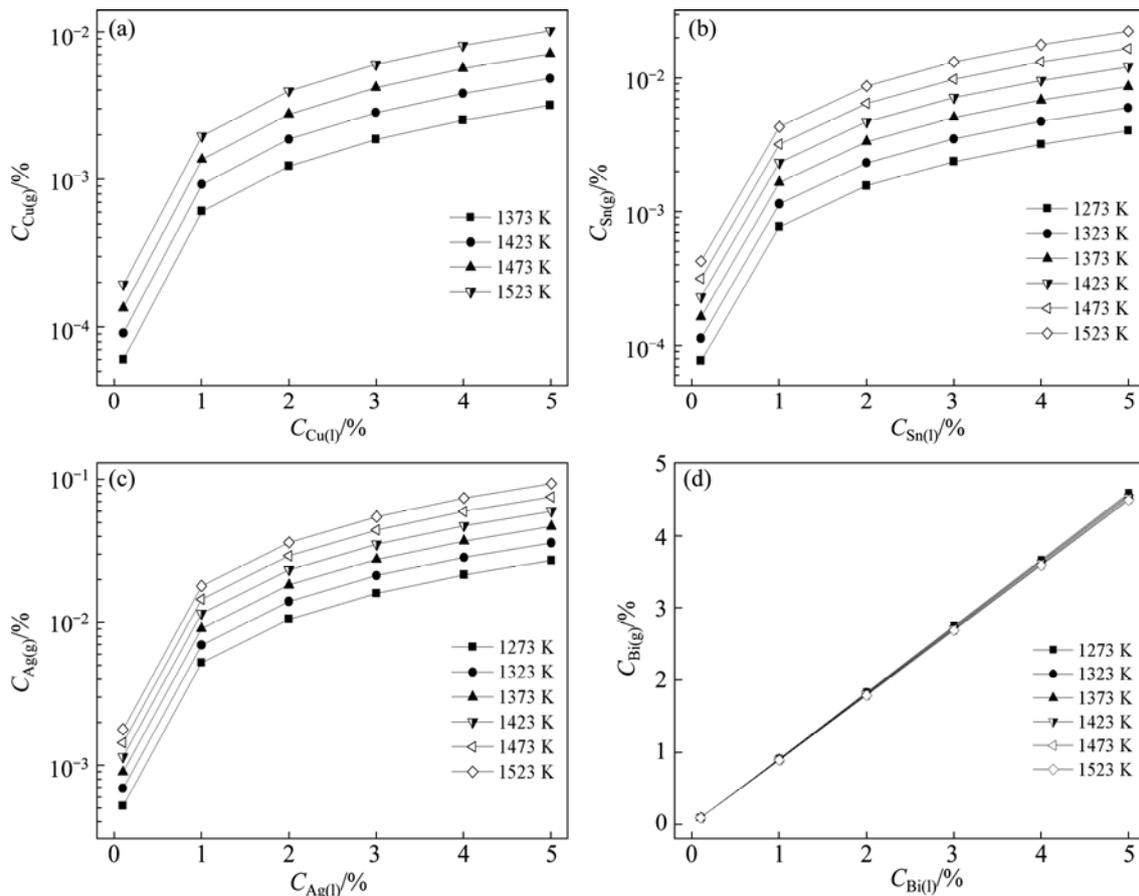
Fig. 4 Vapor−liquid equilibrium composition of Pb−Cu system (a), Pb−Sn system (b), Pb−Ag system (c) and Pb−Bi system (d) at 1273−1523 K

5 Conclusions

1) The impurities of Cu, Sn, Ag, Zn, As and Sb in the crude lead can be easily removed by vacuum distillation in thermodynamics, but Bi cannot be removed.

2) The vacuum distillation should be taken to obtain lead from crude lead. Zn, As and Sb are removed at lower temperature of 923−1023 K. Lead is distilled from the residual liquid containing Cu, Sn, Ag and Bi at higher temperature of 1323−1423 K, and Cu, Sn and Ag are concentrated and remain in the residual liquid.

3) The sufficient thermodynamic calculations are helpful to choose the conditions of operation and acquire reliable results in vacuum distillation refining process for crude lead.

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粗铅真空蒸馏精炼杂质脱除的热力学

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摘　要：采用纯物质饱和蒸气压、分离系数和 Pb−i 系气−液相平衡成分图从热力学上分析粗铅真空蒸馏精炼脱除杂质的可行性。探讨粗铅中常见的杂质铜、锡、银、锌、砷、锑、铋在真空蒸馏精炼过程中的行为规律。结果表明：粗铅低温(923~1023 K)真空蒸馏时，锌和砷挥发进入气相而被除去，大部分锑挥发进入气相而实现与铅的分离，而铋则随铅残留于液相中无法除去。粗铅高温(1323~1423 K)真空蒸馏时，铅挥发进入气相冷凝，铜、锡、银不挥发而富集于残留物中被除去，铅挥发的同时铋也随着铅一起挥发进入气相无法除去。此理论为真空蒸馏脱除粗铅中的杂质提供新的思路，并能有效富集贵金属银等，对粗铅采用真空蒸馏精炼除杂具有一定的指导意义和实用价值。

关键词：粗铅；真空蒸馏；精炼；脱除；热力学

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