[Article ID] 1003- 6326(2001)06- 0937- 05

Vacuum distillation refining of crude lithium (Ⅰ) ①

——Thermodynamics on separating impurities from lithium

CHEN Wei-liang(陈为亮)[1], YANG Bin(杨 斌)[2], CHAI Li-yuan(柴立元)[1],
MIN Xiao-bo(闵小波)[1], DAI Yong-nian(戴永年)[2], YU Xia(于 霞)[1], ZHANG Chuan-fu(张传福)[1]
(1. Department of Metallurgical Science & Engineering, Central South University,
Changsha 410083, P. R. China;
2. Research Institute of Vacuum Metallurgy & Material, Kunming University of Science and Technology,
Kunming 650093, P. R. China)

[Abstract] Thermodynamics on vacuum refining process of the crude lithium has been studied by using separation coefficients of impurities in the crude lithium and vapor-liquid equilibrium composition diagrams of Li-i binary alloy (i stands for an impurity) at different temperatures. Behaviors of impurities in the vacuum distillation process have been examined. The results show that fractional vacuum distillation should be taken to obtain metal lithium with high purity more than 99.99% Li, in which metal K, Na and partial Mg are volatilized at lower temperature of 673~ 873 K. Lithium is distilled from the residual liquid containing other impurities, such as Ca, Mg, Al, Si, Fe and Ni at higher temperature of 873~ 1073 K and the chamber pressure is less than the critical pressure of lithium.

[Key words] lithium; refining; vacuum distillation; thermodynamics

[CLC number] TF 114.33 **[Document code]** A

1 INTRODUCTION

Lithium is widely used in the fields of aerospace, atomic energy, metallurgy, chemical engineering, electronics, glass and ceramics, battery, air-condition and refrigerant, lubricant, medicine, etc[1~ 3]. The crude lithium, produced by electrolytic or metallic thermoreduction methods, however, contains some impurities including Na, K, Mg, Ca, Al, Fe, Si, Ni and so on, which affect the physiochemical properties of lithium product.

Therefore, it is of importance that the lithium is refined by mechanical purification[4~ 6], chemical purification[6~ 8] and vacuum distillation[5, 9~ 15], which is selected to meet the necessity of final purity of the product. Studies on vacuum refining of the crude lithium were carried out, however were limited to the technological aspects. A fundamental study is absent in literatures, resulting in the vacuum refining technology of the crude lithium to progress slowly. It is necessary to study the thermodynamics and kinetics in vacuum refining process of the crude lithium. A series of papers are aimed at systemically discussing the thermodynamics and kinetics on crude lithium vacuum distillation to provide a theoretical base for pure lithium production.

2 BEHAVIORS OF IMPURITIES IN VACUUM DISTILLATION REFINING PROCESS

Based on the different properties of elements contained when vaporizing and condensing, crude metal can be separated from impurities by vacuum distillation refining. The difference in vapor pressure of each metal at different temperature is the basic principle of crude metal vacuum distillation. The relationships between vapor pressure (p^*, Pa) of pure metals in the crude lithium and temperature (T, K) are listed as[16]

$$\lg p^*_{Li} = -8415\,T^{-1} - \lg T + 13.465 \quad (453.6\sim 1615\,K) \tag{1}$$

$$\lg p^*_{Na} = -5780\,T^{-1} - 1.18\lg T + 13.625 \quad (298\sim 1156\,K) \tag{2}$$

$$\lg p^*_{K} = -4470\,T^{-1} - 1.37\lg T + 13.705 \quad (350\sim 1050\,K) \tag{3}$$

$$\lg p^*_{Mg} = -7780\,T^{-1} - 0.855\lg T + 13.535 \quad (298\sim 923\,K) \tag{4}$$

$$\lg p^*_{Mg} = -7550\,T^{-1} - 1.41\lg T + 14.915 \quad (923\sim 1363\,K) \tag{5}$$

$$\lg p^*_{Ca} = -9350\,T^{-1} - 1.39\lg T + 14.945 \quad (298\sim 1115\,K) \tag{6}$$

$$\lg p^*_{Ca} = -8920\,T^{-1} - 1.39\lg T + 14.575 \quad (1115\sim 1767\,K) \tag{7}$$

① **[Foundation item]** Project (99E005G) supported by the Natural Science Foundation of Yunnan Province
[Received date] 2001- 04- 30; **[Accepted date]** 2001- 06- 20

$$\lg p^*_{Al} = -16380T^{-1} - \lg T + 14.445 \quad (934 \sim 2523\,K) \qquad (8)$$

$$\lg p^*_{Si} = -23550T^{-1} - 0.565\lg T + 14.475 \quad (298 \sim 1687\,K) \qquad (9)$$

$$\lg p^*_{Fe} = -21080T^{-1} - 2.14\lg T + 19.015 \quad (298 \sim 1808\,K) \qquad (10)$$

$$\lg p^*_{Ni} = -22500T^{-1} - 0.96\lg T + 15.725 \quad (298 \sim 1728\,K) \qquad (11)$$

The activity coefficients of the compositions in Li-i alloy (i stands for an impurity contained in the crude lithium) are γ_{Li} and γ_i, respectively. The separation coefficient β_i can be used to determine whether two elements separate from each other by vacuum distillation[17]:

$$\beta_i = \frac{\gamma_i}{\gamma_{Li}} \cdot \frac{p^*_i}{p^*_{Li}} \qquad (12)$$

1) When $\beta_i = 1$, the compositions of Li and i in vapor and liquid phase are the same, Li can't be separated from i.

2) When $\beta_i < 1$ or $\beta_i > 1$, impurity i can be separated from lithium by vacuum distillation. Impurity i is concentrated in liquid phase at $\beta_i < 1$, and in vapor phase at $\beta_i > 1$.

The purity of distillated lithium can be predicted by the vapor-liquid equilibrium composition diagram. For the binary alloy of Li-i, their contents in vapor and liquid are represented by $w_g(Li)$, $w_g(i)$, $w_l(Li)$, $w_l(i)$, respectively. The content of i in vapor is expressed as[17]:

$$w_g(i) = [1 + (w_l(Li)/w_l(i)) \cdot (r_{Li}/r_i) \cdot (p^*_{Li}/p^*_i)]^{-1} \times 100\% \qquad (13)$$

A relationship between $w_g(i)$ and $w_l(i)$ can be figured at a specific temperature.

In general, the crude lithium contains Li more than 99% and other impurities including Na, K, Mg, Ca, Al, Si, Fe and Ni. An impurity i is less than 1% in purity, it is assumed that the impurity i can be considered as the solute in dilute solution. The activity coefficient of Li is supposed as $\gamma_{Li} = 1$ and those of impurities as $\gamma_i = 1$ except γ_{Mg} is considered as 0.054 in Li-Mg system at 1000 K[17]. The mass percentages of every impurity element i in liquid lithium are selected for the calculation as 0.001%, 0.005%, 0.01%, 0.05%, 0.1%, 0.5% and 1.0%, respectively.

2.1 Behaviors of Na and K

According to Eqns. (1) ~ (3), (12) and (13), the separation coefficients of Na and K were calculated in the temperature range of 573 ~ 1073 K as presented in Table 1. The vapor-liquid equilibrium composition diagrams of Li-Na and Li-K binary alloys are also shown in Figs. 1, 2.

It can be seen from Table 1 that β_{Na} and β_K are much more beyond 1 ($10^6 \sim 10^2$). It can be concluded that Na and K are concentrated into vapor phase and can be separated from Li completely in thermodynamics. Figs. 1, 2 illustrate that the proper temperature is in the range of 673 ~ 873 K to ensure less evaporating loss of lithium, in which lithium with less than 0.001% Na or K can be obtained by vacuum distillation.

Table 1 Variation of β_{Na} and β_K with temperature in binary alloys of Li-Na and Li-K

T/K	β_{Na}	β_K
573	1.829×10^4	1.271×10^6
673	3.684×10^3	1.136×10^5
773	1.119×10^3	1.883×10^4
873	4.456×10^2	4.685×10^3
973	2.139×10^2	1.545×10^3
1073	1.176×10^2	–

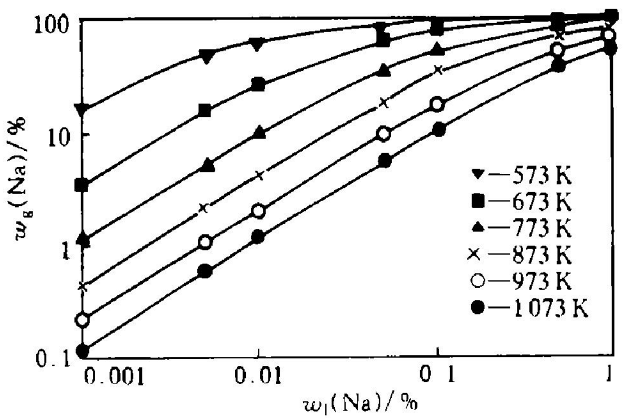

Fig. 1 Vapor-liquid equilibrium composition diagram of Li-Na alloy

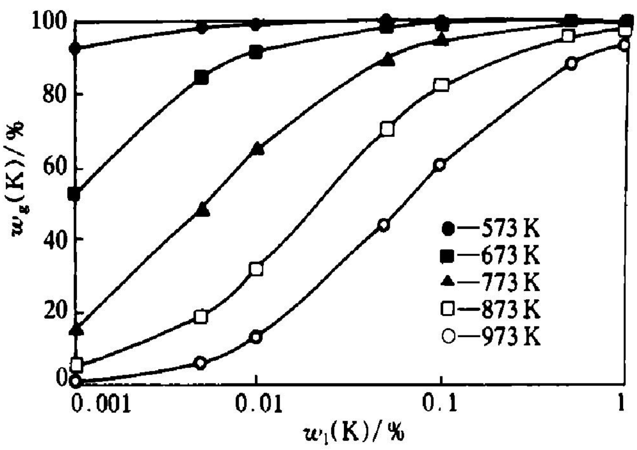

Fig. 2 Vapor-liquid equilibrium composition diagram of Li-K alloy

2.2 Behavior of Mg

According to Eqns. (1), (4), (5), (12) and

(13), the separation coefficient of Mg was evaluated in the temperature range of 573~ 1 273 K, as listed in Table 2. The vapor-liquid equilibrium composition diagram of Li-Mg binary alloy was illustrated in Fig. 3.

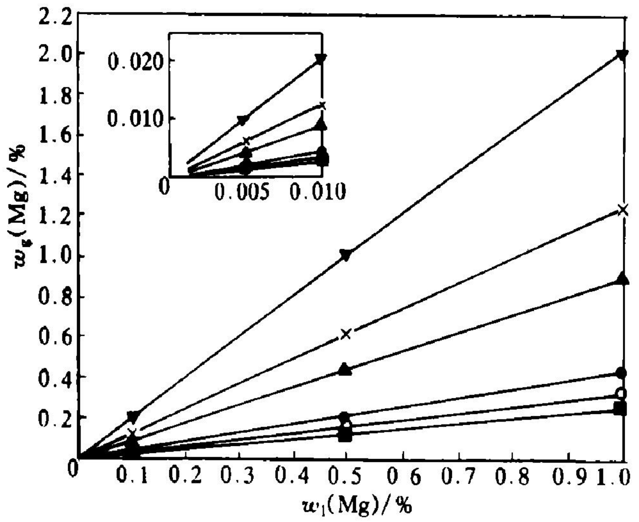

Fig. 3 Vapor-liquid equilibrium composition diagram of Li-Mg alloy
▼ —573 K; × —773 K; ▲ —873 K;
● —973 K; ○ —1 123 K; ■ —1 273 K

It is shown from Table 2 that β_{Mg} is small (2.044~ 0.27) and reduces with increasing temperature in the range of 573~ 1 273 K. Metal Mg is enriched in vapor phase below the temperature of 800 K and in liquid phase over 800 K. Fig. 3 shows that Mg is difficult to separate from Li in thermodynamics since β_{Mg} is close to 1. However, β_{Mg} decreases with the increase of temperature, resulting in difficult removal of Mg from the crude lithium effectively by only one vacuum distillation operation. Therefore, it is necessary to employ fractional vacuum distillation for obtaining lithium with less than 0.01% Mg from the crude lithium.

Table 2 Variation of β_{Mg} with temperature in binary alloy of Li-Mg

T/K	β_{Mg}	T/K	β_{Mg}
573	2.044	973	0.437
723	1.245	1 123	0.334
873	0.904	1 273	0.270

2.3 Behavior of Ca

The separation coefficient of Ca was calculated in the temperature range of 673~ 1 273 K according to Eqns. (1), (6), (7), (12) and (13), and the results are listed in Table 3. The vapor-liquid equilibrium composition diagram of Li-Ca binary alloy is shown in Fig. 4.

It is drawn from Table 3 that β_{Ca} is smaller (0.097~ 0.318). It can be concluded that Ca is mainly remained in liquid phase during the distillation process. It can be seen from Fig. 4 that Ca is difficult to separate from Li effectively in thermodynamics by only one vacuum distillation operation. In order to achieve better separation of Ca from Li and ensure a higher evaporation rate of Ca and less loss of lithium, fractional vacuum distillation should be carried out in an appropriate temperature range of 873~ 1 073 K. The process should be carried out below the critical pressure of lithium in order to have a high distilling rate of lithium.

Table 3 Variation of β_{Ca} with temperature in binary alloy of Li-Ca

T/K	β	T/K	β
673	0.097	1 073	0.267
823	0.161	1 173	0.304
973	0.226	1 273	0.318

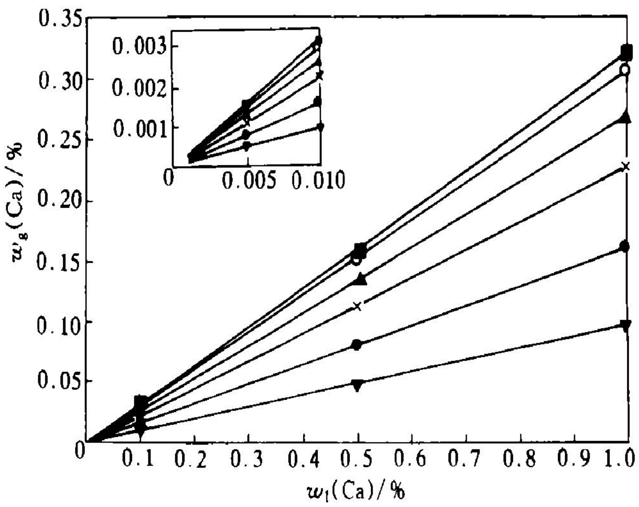

Fig. 4 Vapor-liquid equilibrium composition diagram of Li-Ca alloy
▼ —673 K; ● —823 K; × —973 K;
▲ —1 073 K; ○ —1 173 K; ■ —1 273 K

2.4 Behaviors of Al, Si, Fe and Ni

The vapor pressure values of pure substances Al, Si, Fe and Ni calculated from Eqns. (8) ~ (11) are very low, 10^{-6} ~ 10^{-2} Pa at 1 273 K. Therefore, their behaviors will be the same when the crude lithium are distillated in vacuum. According to Eqns. (1) and (8) ~ (13), the separation coefficients of Al, Si, Fe and Ni were calculated in the temperature range of 973~ 1 273 K, as listed in Table 4. Their vapor-liquid equilibrium composition diagrams are depicted in Figs. 5~ 8.

With respect to impurities Al, Si, Fe and Ni, it can be seen from Table 4 that their separation coefficient values are much smaller (10^{-14}~ 10^{-6}). They can be easily separated from lithium in thermodyna-

Table 4 Variation of β_{Al}, β_{Si}, β_{Fe} and β_{Ni} with temperature in binary alloys of Li-Al, Li-Si, Li-Fe and Li-Ni

T/K	$\beta_{Al}/10^{-7}$	$\beta_{Si}/10^{-13}$	$\beta_{Fe}/10^{-10}$	$\beta_{Ni}/10^{-12}$
973	0.622	0.569	0.134	0.801
1073	3.60	16.7	1.96	18
1173	15.5	277	17.9	237
1273	52.9	2960	115	2090

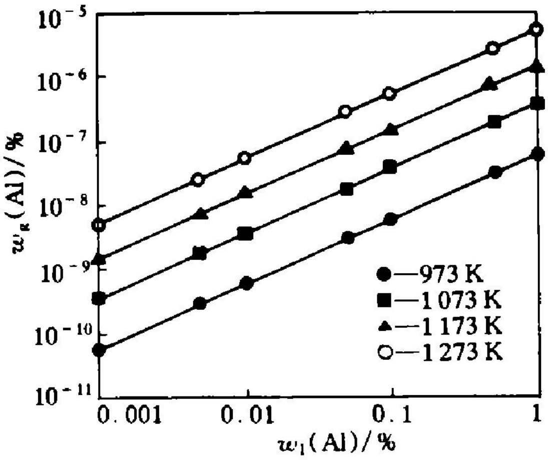

Fig. 5 Vapor-liquid equilibrium composition diagram of Li-Al alloy

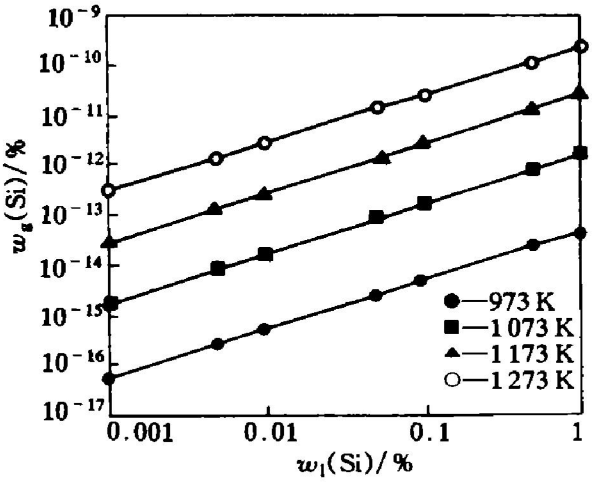

Fig. 6 Vapor-liquid equilibrium composition diagram of Li-Si alloy

mics by vacuum distillation in a temperature range of 973~ 1273K because they are concentrated in the distilled residual liquid completely while lithium is enriched in vapor. It can be derived from Figs. 5~ 8 that each of those four impurities can be reduced to the level below 6×10^{-8} (mass fraction) in distilled lithium. Considering the content of Ca contained in the crude lithium comprehensively, the suitable distillation temperature in this process should be in the range of 873 ~ 1073K to ensure Ca is mainly

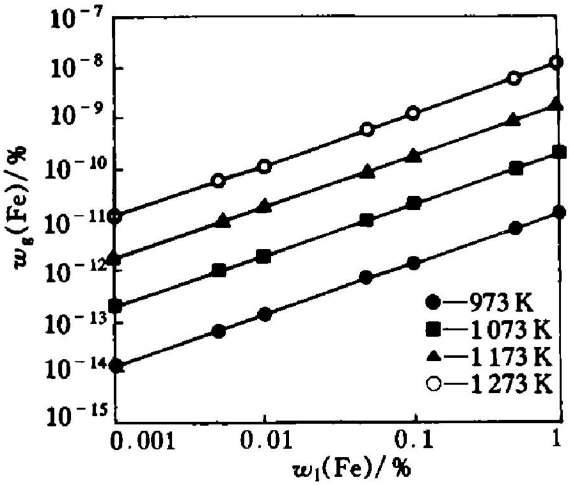

Fig. 7 Vapor-liquid equilibrium composition diagram of Li-Fe alloy

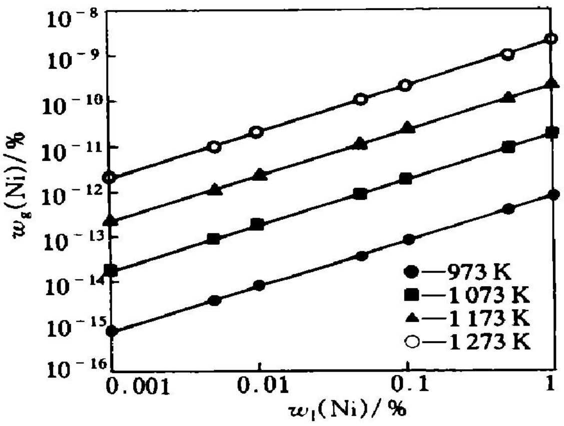

Fig. 8 Vapor-liquid equilibrium composition diagram of Li-Ni alloy

remained in residual liquid and the chamber pressure should be no more than the critical pressure of lithium.

3 CONCLUSIONS

1) The impurities in the crude lithium, such as K, Na, Al, Si, Fe and Ni, can be easily eliminated by vacuum distillation in thermodynamics, while Ca and Mg are difficult to remove.

2) A fractional vacuum distillation should be taken to obtain lithium with high purity more than 99.99%Li. Metal K and Na are volatilized at lower temperature of 673~ 873K, in which a little amount of Mg can be removed. Lithium is evaporated into vapor, separating from other impurities Ca, Mg, Al, Si, Fe and Ni remained in the residual liquid at higher temperature of 873~ 1073K.

[REFERENCES]

[1] The Editorial Board of Handbook of Rare Metals. Hand-

book of Rare Metals (Part Ⅺ) [M], (in Chinese). Beijing: Metallurgical Industry Press, 1995. 25- 27.
[2] LIU Shi-you. Application of lithium in battery industry and its development trend [J]. Shanghai Nonferrous Metals, 1998, 19(2): 87- 90.
[3] YANG Bin, DAI Yong-nian, WANG Da-jian. The preparation and application of lithium metal [J]. Journal of Kunming University of Science and Technology, 1996, 21(6): 42- 45.
[4] Mebarek A H, Walter S, Diyani S. Preparation of high purity alkali metals by near melting point segregation [J]. Journal of Thermal Analysis, 1997, 49(3): 1283- 1288.
[5] Horsley G W. Filtration and vacuum distillation unit for the purification of alkali metals [J]. J Appl Chem, 1958, (8): 13- 18.
[6] Hoffman E E. Solubility of nitrogen and oxygen in lithium and methods of lithium pourification [A]. Symposium on Newer Metals [C]. San Francisco: ASTM-Spec Techn Publ, 1960, (272): 195- 206.
[7] Weed H C, Krikorian O H. Preparation of high-purity lithium by a gettering technique [J]. Journal of Nuclear Materials, 1974, 52(2): 142- 156.
[8] Ishikawajima-Harima Heavy Industries Co Ltd. Apparatus for Purification of Liquid Lithium [P]. JP5943834, 1984.
[9] Rogers R R, Viens G E. Effect of pressure on the refining of lithium by distillation [J]. J Electrochem Soc, 1951, 98(12): 483- 487.
[10] Paul H S. Purification of lithium metal by high-vacuum fraction distillation [J]. J Electrochem Soc, 1966, 113 (2): 201- 204.
[11] Roumieu R. Method and Apparatus for Purifying Lithium [P]. FR2581080, 1986.
[12] Ward A G, Broomfield G H. The purification of lithium by vacuum distillation [J]. J Appl Chem, 1963, 13 (8): 329- 334.
[13] Winkler O, Bakish R. Vacuum Metallurgy [M], (in Chinese). Shanghai: Shanghai Science & Technology Press, 1982. 115.
[14] LAN Hai-cang, ZHAO Wei, HU Chun-qian, et al. Preparation of high purity lithium in industry scale by vacuum distillation [J]. Chinese Journal of Rare Metals, (in Chinese), 1998, 22(4): 286- 289.
[15] CHEN Wei-liang. Study on Refining Lithium by Vacuum Distillation and Preliminary Study on Preparing Lithium from Li_2CO_3 by Vacuum Carbothermic Reduction [D]. Kunming: Kunming University of Science and Technology, 2000. 35- 42.
[16] Kubaschewski O, Alcock C B. Metallurgical Thermochemistry [M], (in Chinese). Beijing: Metallurgical Industry Press, 1985. 486- 513.
[17] DAI Yong-nian, ZHAO Zhong. Vacuum Metallurgy [M], (in Chinese). Beijing: Metallurgical Industry Press, 1988. 114- 115.

(Edited by LONG Huai-zhong)