THE SEPARATION CRITERION OF IMPURITIES IN CRUDE METALS BY VACUUM DISTILLATION①

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ABSTRACT Separation criteria of impurities by vacuum distillation in crude metals were analysed. The separation coefficient, which was deduced from the gas-liquid equilibrium theory, was proved to be the perfect one.

Key words: separation criterion impurities crude metals vacuum distillation

The refinement of crude nonferrous metals by vacuum distillation has a lot of advantages[1]. The main impurities in some crude metals are shown in Table 1.

Whether can the impurity be separated from crude metals by vacuum distillation and to what extent? The separation criteria should be conducted by using gas-liquid equilibrium theory.

1 BOILIING POINT AND VAPOR PRESSURE OF PURE METAL

The possibility of separation of impurities in crude metals or alloys can be determined by comparing their boiling points or their vapor pressure. The boiling points of some metals are shown in Table 2. In general, low boiling point components are easier to be evaporated than high boiling point components; therefore, we can determine that Pb-Zn, Zn-Cd, Pb-Sn alloys can be separated and that crude zinc containing lead and cadmium, crude tin containing lead can be refined by vacuum distillation.

Because the difference of the active force between alloying elements is ignored, this criterion is unsuitable to judge the separation of Pb-Sb, Pb-Bi, Zn-As and Sn-As-Pb alloys.

Table 1 The main impurities in crude nonferrous metals

Crude metal	Main impurities							
lead	As	Sb	Bi	Sn	Ag			
zinc	Pb	Cd	Sn	Fe	Cu	Sb		
copper	As	Sb	Bi	Zn	Pb	Fe	Ag	Au
tin	Pb	Fe	As	In				
nickel	Fe	Co	S					
aluminium	Si	Fe	P					

Table 2 Boiling points of some metals

Element	Hg	As	Cd	Zn	Bi	Sb
boiling point/K	630	876	1 038	1 180	1 837	1 948
Element	Pb	In	Ag	Sn	Fe	
boiling point/K	2 013	2 346	2 473	2 896	3 343	

2 ACTUAL VAPOR PRESSURE

The actual vapor pressure of each element in solution is:

$$P_i = \gamma_i N_i P_i^0 \quad (1)$$

where $N \in [0, 1]$ and γ varies widely, for example,

In Pb-Zn system(723 K)[2]:

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$N_{Pb} = 1$, $\gamma^0_{Zn} = 7.94$

$N_{Zn} = 1$, $\gamma^0_{Pb} = 34.6$

In Cu-Zn system(773 K)[2]:

$N_{Cu} = 1$, $\gamma^0_{Zn} = 0.014$

$N_{Zn} = 1$, $\gamma^0_{Cu} = 0.018$

Evidently, P_i is a more rational criterion than P_i^0 in judging the possibility of separation by distillation.

3 DISTRIBUTION FACTOR

The distribution factor K[3, 4] is the ratio between the concentration of a component in a solution to that in the vapor.

$$K_A = \frac{N_{A,g}}{N_{A,l}} \qquad (2)$$

$$K_B = \frac{N_{B,g}}{N_{B,l}} \qquad (3)$$

The more the value of K_A or K_B differs from unity, the more complete is the separation.

4 RELATIVE VOLATILITY COEFFICIENT

The relative volatility coefficient[6] α is a direct index for determining the separation tendency in the distillation or rectification of liquid substance. For binary mixture:

$$\alpha_{AB} = \frac{\dfrac{N_{A,g}}{N_{A,l}}}{\dfrac{N_{B,g}}{N_{B,l}}} = \frac{\dfrac{N_{A,g}}{N_{B,g}}}{\dfrac{N_{A,l}}{N_{B,l}}} = \frac{K_A}{K_B} \qquad (4)$$

Generally speaking, α_{AB} depends on evaporation temperature and pressure. It determines the concentration degree of low boiling substance in vapor phase. If α_{AB} is equal to unity, no preferential separation is possible. As the concentration of the two components in the vapor will tend to be the same as that in the liquid phase, substances that can be readily separated should exhibit large or small values of α_{AB}.

5 MOLECULAR DISTILLATION COEFFICIENT

Making use of the Langmiur maximum evaporation rate[8, 9]:

$$\omega_i = 4.37 \times 10^{-4} P_i \sqrt{\frac{M_i}{T}} \qquad (5)$$

assuming metal vapor was ideal gas, and gas phase had the same molecular weight and molecular structure as the liquid phase for each element, Olette[7] got the following equation for binary system:

$$\frac{N_{A,g}}{N_{B,g}} = \frac{\gamma_A N_{A,l} P_A^0}{\gamma_B N_{B,l} P_B^0} \sqrt{\frac{M_A}{M_B}} \qquad (6)$$

which can be rearranged to yield:

$$\beta_A' = \frac{\dfrac{N_{A,g}}{N_{A,l}}}{\dfrac{N_{B,g}}{N_{B,l}}} = \frac{\gamma_A P_A^0}{\gamma_B P_B^0} \sqrt{\frac{M_A}{M_B}} \qquad (7)$$

When $\beta_A' > 1.0$, A is concentrated in vapor, B is concentrated in liquid;

When $\beta_A' < 1.0$, B is concentrated in vapor, A is concentrated in liquid;

When $\beta_A' = 1.0$, the compositions of vapor and liquid phase are the same, A and B can not separated from each other by distillation.

If β_A' is used to evaluate a dilute solution, i. e., crude B with minor impurities: $\gamma_B = 1$, γ_i^0 = constant, consequently we have the result:

$$\beta_i'^0 = \gamma_i^0 \frac{P_i^0}{P_B} \sqrt{\frac{M_i}{M_B}} \qquad (8)$$

β_A' not only depends on activity and vapor pressure, but also depends on molecular mass.

Harris[10] yielded a general expression for the polyatomic molecular separation coefficient:

$$\beta_{i,n}'^0 = n\gamma_i^0 N_i^{n-1} \frac{P_{i,n}^0}{P_A^0} \sqrt{\frac{M_A}{M_B}} \qquad (9)$$

It is clearly seen that for $n = 1$, the polyatomic separation coefficient reduces to that of Olette, and for $n \geqslant 2$, the separation coefficient depends on solute concentration.

The evaporation rate of elements in alloys or crude metals not only depends on pressure, but also on heat and mass transfer. Only when chamber pressure is perfect vacuum and condenser rate as well as heat and mass transfer are infinite can the evaporation rate reach its maximum. In industrial processes, the rate determining step is heat and mass transfer when chamber pressure is lower than a certain value. At this time, the chamber pressure needn't drop further, the distillation does not reach the molecular distillation, and the evaporation rate does not reach the maximum.

6 SEPARATION COEFFICIENT

The authors think that the separation criterion of impurities in crude metals should be a thermodynamic criterion. The separation coefficient conducted according to the gas-liquid equilibrium is the perfect one. Some separation coefficients of impurities in crude nonferrous metals are shown in Table 3.

Assuming metal vapor was ideal gas, and gas phase had the same molecular weight and molecular structure as the liquid phase for each element, Dai Yongnian[5] conducted the separation coefficient according to thermodynamic equilibrium theory, for A-B alloy:

$$\frac{N_{\mathrm{A,g}}}{N_{\mathrm{B,g}}} = \frac{\gamma_{\mathrm{A}} N_{\mathrm{A,l}} P_{\mathrm{A}}^{0}}{\gamma_{\mathrm{B}} N_{\mathrm{B,l}} P_{\mathrm{B}}^{0}} \tag{10}$$

which can be rearranged to yield:

$$\beta_{\mathrm{A}} = \frac{\dfrac{N_{\mathrm{A,g}}}{N_{\mathrm{A,l}}}}{\dfrac{N_{\mathrm{B,g}}}{N_{\mathrm{B,l}}}} = \frac{\gamma_{\mathrm{A}} P_{\mathrm{A}}^{0}}{\gamma_{\mathrm{B}} P_{\mathrm{B}}^{0}} \tag{11}$$

If β_{A} is used to evaluate a dilute solution, i. e., crude B with minor impurities: $N_{\mathrm{B,l}} = 1$, $N_{\mathrm{B,g}} = 1$, $\gamma_{\mathrm{B}} = 1$, $\gamma_i^0 =$constant, Eqn(11) can be re-writen as:

$$\beta_i^0 = \gamma_i^0 \frac{P_i^0}{P_{\mathrm{B}}^0} = \frac{N_{i,\mathrm{g}}}{N_{i,\mathrm{l}}} \tag{12}$$

Table 3 Some separation coefficients of impurities in crude nonferrous metals[5, 11]

Impurity	Crude metal					
	Aluminium	Cobalt	Copper	Lead	Zinc	Tin
Ag	3.7E-0		1.1E-2	1.1E-3	1.5E-10	1.2E-1
Al		7.5E-1	1.5E-2	6.1E-4	4.8E-10	
As		1.2E-6*	9.2E-1	6.5E-4*	1.0E-10*	
Au	3.7E-8		2.1E-3	8.6E-10	5.7E-19	
Bi	1.3E-5	3.7E-3*	2.5E-3	5.5E-1	3.1E-4	1.9E-4
Ca	1.3E-6*	5.5E-4*		1.2E-2*	7.0E-4	
Cd	8.3E-9	1.5E-6	1.1E-6	3.4E-5	7.6E-0	
Co			1.3E-1	4.1E-10*		
Cu	2.8E-3	8.7E-2		6.3E-6	1.5E-13	3.0E-2
Fe	1.6E-5	1.6E-0*	6.5E-1	5.6E-9*		
Li	3.0E-6					
Mg	3.4E-6	8.7E-5*	5.0E-4	6.7E-2	5.9E-3	
Mn	3.6E-2	1.3E-3*	1.8E-2*	1.9E-1		
Na	6.5E-10			4.2E-2	8.9E-3	
Ni		1.1E-0*	2.6E-2	2.4E-10*	5.3E-18	
Pb	4.0E-5	2.7E-3*	4.8E-3		1.4E-4	7.2E-4
Sb		5.6E-2*	1.6E-0	6.9E-3	2.2E-8	3.8E-4
Se			1.9E-0			
Si	1.9E-6					
Sn	8.6E-1		8.8E-2	9.0E-6	1.4E-11	
Te			5.4E-1			
Zn	3.1E-8	3.9E-6*	3.5E-5	1.0E-6		

Remarks: * — $\gamma = 1.0$

Rewriting Eqn(12) in logarithmic form:

$$\lg N_{i,\,g} = \lg\beta_i^0 + \lg N_{i,\,l} \qquad (13)$$

At specific temperature, γ_i^0, P_i^0, P_B^0 are constant, then β_i^0 is constant; $\lg N_{i,\,g}$ is linear with $\lg N_{i,\,l}$, and the slope is 45°. Therefore, there is no limitation to purify metals by vacuum distillation.

Converting mole fraction into mass percentage, the similar equations can be obtained.

For the polyatomic separation coefficient, Eqn(12) can be converted to:

$$\beta_{i,\,n}^0 = \frac{\gamma_{i,\,n}^0}{n}\frac{P_i^0}{P_B^0} \qquad (14)$$

7 CONCLUSION

The separation criteria of impurities by vacuum distillation in crude metals are analysed. The separation coefficent, which is conducted according to gas-liquid equilibrium theory, is the perfect one. i.e., for A-B alloy:

$$\beta_A = \frac{\dfrac{N_{A,\,g}}{N_{A,\,l}}}{\dfrac{N_{B,\,g}}{N_{B,\,l}}} = \frac{\gamma_A P_A^0}{\gamma_B P_B^0} \qquad (15)$$

For crude metal B:

$$\beta_i^0 = \gamma_i^0 \frac{P_i^0}{P_B^0} \qquad (16)$$

Symbols:

K	distillation factor;
M	molecular weight, g/mol;
N	molecular fraction;
P	pressure, Pa;
ω	maximum evaporation rate, kg/m^2•s;
α	relative volatility coefficient;
β	separation coefficient;
β'	molecular distillation coefficient;
γ	Raoultian activity coefficient;
T	temperature, K;

Subscripts:

i, A, B	each element;
g	gas phase;
l	liquid phase;
n	polyatom number;

Superscripts:

0	pure metal or crude metal.

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