Activity of the Component Metals in Fused Binary Alloys (Zn-Al System and Zn-Mg System)

Zensaku KOZUKA, Jyoichiro MORIYAMA and Isao KUSHIMA*

In the previous paper¹⁾, the results on the thermodynamic study of Z-Cd and Zn-Sn binary solutions were treated. The equilibrium vapor pressures of Zn in Zn-Al and Zn-Mg alloy solutions at 670°, 720° and 770°C were determined by the carrier gas techniques according to the previous method. From these results of vapor pressure measurement, the thermodynamic quantities of these binary metallic solutions are discussed in this paper.

Experimental techniques and equipments were essentially similar to those described previously, but the method for the preparation of Zn-Mg alloys was somewhat different from the previous one. Zinc and magnesium were alloyed under a cover of special flux (KCl 20 %, MgCl 50 %, CaF₂ 15 %, MgO 15%) to prevent oxidation.

The procedure adopted for the chemical analysis of Zn and Mg in the condensed alloys was as follows: The sample was dissolved in hydrochloric acid, and the resulting solution was diluted moderately, to which excess ammonia solution and ammonium phosphat were added to precipitate Mg as Mg NH₄PO₄. After separation, Zn and Mg contents were determined by means of chelating titration using BT indicator.

Results obtained from the equilibrium vapor pressure measurement of the molten alloys are shown in Figs. 1 and 2. From these values, the activities of Zn can be calculated. The excess free energy, F^{xs} , heat of mixing, ΔH , excess entropy, S^{xs} , are obtained from the data with the following equations.

Fig. 1 Equilibrium vapor pressure of Zn in the Zn-Al alloy solution

Fig. 2 Equilibrium vapor pressure of Zn in the Zn-Mg alloy solution

$$\bar{F}_{Zn}^{xs} = RT \ln a_{Zn} - RT \ln N_{Zn} = RT \ln \gamma_{Zn}$$

$$\Delta \bar{H}_{Zn} = -RT^2 \frac{d \ln a_{Zn}}{dT}$$

$$\bar{S}_{Zn}^{xs} = -R \left(T \frac{d \ln a_{Zn}}{dT} + \ln a_{Zn} \right) + R \ln N_{Zn}$$

$$F^{xs}(\Delta H, S^{xs}) = N_{Al}(N_{Mg}) \int_0^x \bar{F}_{Zn}^{xs} (\Delta \bar{H}_{Zn}, \bar{S}_{Zn}^{xs}) dx$$

$$x = N_{Zn}/N_{Al} \text{ (or } N_{Mg})$$

These values are plotted as a function of composition in Figs. 3–10. The values of heat of mixing obtained in this study agree with those which were listed by Kubaschewski²⁾. From the above Figures, it will be seen that the values of excess free energy of Zn-Al binary solution are independent of temperature,

* Department of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto

The original written in Japanese can be seen in J. Electrochem. Soc. Japan 28, 523 (1960).

Fig. 3 Activity of Zn as a function of N_{Zn} for the Zn-Al system

Fig. 4 Activity of Zn as a function of N_{Zn} for the Zn-Mg system

Fig. 5 Excess free energy for the molten Zn-Al alloy

Fig. 6 Excess free energy for the molten Zn-Mg alloy

Fig. 7 Heat of mixing for the molten Zn-Al alloy

Fig. 8 Heat of mixing for the molten Zn-Mg alloy

Fig. 9 Excess entropy for the molten Zn-Al alloy at 720°C

Fig. 10 Excess entropy for the molten Zn-Mg alloy at 720°C

and the maximum value is about 530 cal/mol which appears near $N_{Zn}=0.6$, and that the value of heat of mixing also shows a maximum value 570 cal/mol at $N_{Zn}=0.45$ and that the value of excess entropy shows a maximum value 0.07 cal/degree mol. This value may be regarded almost equal to zero,

It will be seen also with the system Zn-Mg that the values of excess free energy show the next minimum values -530, -490, and -430 cal/mol respectively at each temperature at $N_{Zn}=0.55$, and the value of heat of mixing shows a minimum -1400 cal/mol near $N_{Zn}=0.6$, and the value of excess entropy shows a minimum -1.05 cal/mol at $N_{Zn}=0.5$.

From $S^{xs} \approx 0$ for Zn-Al system, this solution may be regarded as regular one. Other properties of this solution have the following regular characteristics; the value of excess free energy is independent of temperature and is nearly equal to the value of heat of mixing.

Hildebrand and Wood have shown that the relation :

$$RT \log \gamma_{Zn} / (1 - N_{Zn})^2 = \text{const.},$$

Fig. 11 $\log \gamma_{Zn}$ as a function of $(1 - N_{Zn})^2$ for the Zn-Al system

Fig. 12 $\log \gamma_{Zn}$ as a function of $(1 - N_{Zn})^2$ for the Zn-Mg system

is derivable from statistical mechanics for regular solution as far as some special properties are provided. Figs. 11 and 12 show the plots $\log \gamma_{Zn}$ against $(1 - N_{Zn})^2$ to discuss this relation. The above relation is not always sufficient for both binary systems. The curves of ΔH and F^{xs} as function of N_{Zn} are not parabolic and symmetrical with respect to the line $N_{Zn}=1/2$. These disagreements would be studied lately.

Using the procedure which recently reported by W. Ptak³⁾ for binary and ternary alloys, the following relations with respect to $\log \gamma$ and N_{Zn} are introduced :

$$\begin{aligned} \text{Zn-Al system} \quad & \log \gamma_{Zn} = (480/T - 0.1195) (1 - N_{Zn})^{1.3} \\ & \log \gamma_{Al} = (480/T - 0.1195) [(1 - N_{Zn})^{1.3} - 4.34(1 - N_{Zn})^{0.3} + 3.33] \\ \text{Zn-Mg system} \quad & \log \gamma_{Zn} = (-1019/T + 0.666) (1 - N_{Zn})^{1.55} \\ & \log \gamma_{Mg} = (-1019/T + 0.666) [(1 - N_{Zn})^{1.55} - 2.82(1 - N_{Zn})^{0.55} + 1.82] \end{aligned}$$

The calculated values from above relations are plotted as a function of mole fraction in Figs. 13 and

Fig. 13 Activity coefficients of components in the molten Zn-Al alloy

Fig. 14 Activity coefficients of components in the molten Zn-Mg alloy

14. A good agreement is obtained between the calculated values and our experimental results (X).

(Received Feb. 2, 1960)

Literature :

- 1) Z. Kozuka, et al. This Journal 28 E-167 (1960).
- 2) O. Kubaschewski, E.L.L. Evans, "Metallurgical Thermochemistry" p. 350 (1956), Pergamon Press, London.
- 3) W. Ptak, *Bergakademie*, (11-3) 168 (1959).