Activity of Zinc in Fused Ternary Alloy (Zn-Al-Mg System)

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The authors already reported the vapor pressure of Zn measured with several molten binary alloys^{1),2)}. In this paper the vapor pressure of zinc in Zn-Al-Mg ternary alloy melt at 720°C is reported, and a few the thermodynamic properties of this melt are treated. Experimental method and apparatus were the same as those reported in the previous papers^{1),2)}.

The vapor pressure of zinc was determined at twelve different compositions of the molten alloy as shown in Fig. 1, the numerical values in which show the activity of zinc.

Fig. 1 Activity of Zinc in Zn-Al-Mg ternary alloy melt at 720°C

Fig. 2 Isoactivity lines of Zinc in Zn-Al-Mg melt at 720°C

Based on these experimental results, the *iso*-activity curves are obtained and shown in Fig. 2. The excess free energy, F^{xs} , of this metallic melt can be obtained by means of the equations both derived by Darken³⁾.

$$F^{xs} = (1 - N_{Zn}) \left[\int_1^{N_{Zn}} \frac{\bar{F}_{Zn}^{xs}}{(1 - N_{Zn})^2} dN_{Zn} \right]_{N_{Al}/N_{Mg}} + N_{Al} [\bar{F}_{Al}^{xs}]_{N_{Zn}=1} + N_{Mg} [\bar{F}_{Mg}^{xs}]_{N_{Zn}=1} \quad (1)$$

$$F^{xs} = (1 - N_{Zn}) \left[\int_0^{N_{Zn}} \frac{\bar{F}_{Zn}^{xs}}{(1 - N_{Zn})^2} dN_{Zn} + F_{binary\ Al-Mg}^{xs} \right]_{N_{Al}/N_{Mg}} \quad (2)$$

The activities of Zn-Al and Zn-Mg systems were reported by the present authors, while the activity of Al-Mg system was reported by Schneider. From above results, F^{xs} at any compositions can be calculated with equation (1) or alternatively by means of Equation (2).

The *iso*-excess free energy curves are obtained by calculation with Equation (2) which is more reliable than Equation (1).

From the results shown in Fig. 3, the $\bar{F}_i^{xs}$ at various compositions of the binary and pseudo-binary lines in the ternary system are obtained (Fig. 4). These values are determined by the slope-intercept method or by means of the Gibbs-Duhem equation.

Also the activities of Al and Mg are calculated with ease and shown in Fig. 5.

Using the results for Zn-Al and Zn-Mg binary systems, F^{xs} is calculated with Equation (1), and the F_{Al-Mg}^{xs} may be evaluated by the help of the following Equation (3).

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Fig. 3 Excess molal free energy (F^{xs}) for Zn-Al-Mg at 720°C in 100 calorie steps

Fig. 4 Excess partial molal free energy ($\bar{F}_i^{xs}$) for Zn-Al-Mg melt at 720°C

Fig. 5 Isoactivity lines of aluminum and magnesium in Zn-Al-Mg melt at 720°C

$$F_{\text{Al-Mg}}^{xs} = - \left[\int_0^1 \frac{\bar{F}_{\text{Zn}}^{xs}}{(1-N_{\text{Zn}})^2} dN_{\text{Zn}} \right]_{N_{\text{Al}}/N_{\text{Mg}}} + N_{\text{Al}} [\bar{F}_{\text{Al}}^{xs}]_{N_{\text{Zn}}=1} + N_{\text{Mg}} [\bar{F}_{\text{Mg}}^{xs}]_{N_{\text{Zn}}=1} \quad (3)$$

The value calculated by the above equation does not agree with the results obtained by Schneider. This discrepancy may be caused by the error in graphic integration and also by the difficulty in accurately evaluating the $\bar{F}_{\text{Zn}}^{xs}/(1-N_{\text{Zn}})^2$ for such a highly concentrated Zn-solution. Finally, the F^{xs} was calculated, referring to an equation recently derived by Ptak⁵⁾.

In an earlier paper²⁾ the present authors have shown the following relations with respect to Zn-Al and Zn-Mg binary alloy melts.

$$\begin{aligned} \text{Zn-Al system} & \begin{cases} \log r_{\text{Zn}} = (480/T - 0.1195)(1 - N_{\text{Zn}})^{1.3} \\ \log r_{\text{Al}} = (480/T - 0.1195) \left[(1 - N_{\text{Zn}})^{1.3} - \frac{1.3}{0.3} (1 - N_{\text{Zn}})^{0.3} + \frac{1}{0.3} \right] \end{cases} \\ \text{Zn-Mg system} & \begin{cases} \log r_{\text{Zn}} = (-1019/T + 0.666)(1 - N_{\text{Zn}})^{1.55} \\ \log r_{\text{Mg}} = (-1019/T + 0.666) \left[(1 - N_{\text{Zn}})^{1.55} - \frac{1.55}{0.55} (1 - N_{\text{Zn}})^{0.55} + \frac{1}{0.55} \right] \end{cases} \end{aligned}$$

From Schneider's results, the next equation is obtained with respect to Al-Mg system.

$$\begin{aligned} \text{Al-Mg system } \log r_{\text{Mg}} &= (-2280/T + 1.708)(1 - N_{\text{Mg}})^{3.9} \\ \log r_{\text{Al}} &= (-2280/T + 1.708) \left[(1 - N_{\text{Mg}})^{3.9} - \frac{3.9}{2.9} (1 - N_{\text{Mg}})^{2.9} + \frac{1}{2.9} \right] \end{aligned}$$

From the above six equations, the following equation can be derived.

$$\begin{aligned} F^{xs} &= (7320 + 1.825 T) N_{\text{Al}} \{1 - (1 - N_{\text{Zn}})^{0.3}\} + (-8460 + 5.54 T) N_{\text{Mg}} \{1 - (1 - N_{\text{Zn}})^{0.55}\} \\ &\quad + (-3600 + 2.70 T) N_{\text{Al}} \{1 - (1 - N_{\text{Mg}})^{2.9}\} \end{aligned}$$

The *iso*-excess free energy curves are plotted on the basis of the values calculated from the above relations (Fig. 6).

Fig. 6 Calculated excess molal free energy (F^{xs}) for Zn-Al-Mg melt at 720°C in 100-calorie steps

These values agree fairly well with the experimental results in Fig. 3. The following equations for the heat of mixing and excess entropy, respectively, were also derived.

These calculated values are graphically shown in Fig. 7 and Fig. 8.

$$\begin{aligned} \Delta H &= 7320 N_{\text{Al}} \{1 - (1 - N_{\text{Zn}})^{0.3}\} - 8460 N_{\text{Mg}} \{1 - (1 - N_{\text{Zn}})^{0.55}\} \\ &\quad - 3600 N_{\text{Al}} \{1 - (1 - N_{\text{Mg}})^{2.9}\} \\ S^{xs} &= 1.825 N_{\text{Al}} \{1 - (1 - N_{\text{Zn}})^{0.3}\} - 5.54 N_{\text{Mg}} \{1 - (1 - N_{\text{Zn}})^{0.55}\} \\ &\quad - 2.70 N_{\text{Al}} \{1 - (1 - N_{\text{Mg}})^{2.9}\} \end{aligned}$$

Fig. 7 Calculated heat of mixing (ΔH) for Zn-Al-Mg melt at 720°C in 200 calorie steps

Fig. 8 Calculated excess molal entropy (S^{xs}) for Zn-Al-Mg melt at 720°C in 0.2 calorie steps

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