Thermodynamic Study on Fused Binary Alloys by Electromotive Force Measurement (Zn-Sb System)

Zensaku KOZUKA, Jyoichiro MORIYAMA, and Isao KUSHIMA*

Dept. of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto

In this paper, the result obtained for the thermodynamic properties of Zn-Sb binary solution by *e. m. f.* measurement is reported. In respect to this system, Seltz *et al.*¹⁾ presented that its solution has unusual thermodynamic property.

The cells of the following type were operated and the apparatus used was shown in Fig. 1.

Zn/LiCl-KCl (eutectic)+5%ZnCl₂/Zn-Sb

The sample container consisted of tubes of high alumina content and its walls had a small hole through which electrolyte could pass. After the bath was kept at a constant temperature for several hours in argon atmosphere, the equilibrium *e. m. f.* was measured at 550~650°C. The results obtained are shown in Fig. 2.

A: A-A' section B: Sample containing tube

- 1: Alumel-chromel thermocouple
- 2: Pure zinc
- 3~6: Alloy
- 7: Pipe for pouring argon gas
- a: Heating furnace
- b: Electrolyte (LiCl, KCl+ZnCl₂)
- c: Asbestos
- d: Water jacket
- e: High alumina block
- f: Asbestos plate
- g: Stainless steel plate
- h: Rubber stopper
- i: K-2 type potentiometer
- j: Turning switch
- k: Pyrometer
- l: Automatic temperature controller
- m: Tungsten wire
- n: Rubber stopper
- o: Terex glass pipe
- p: High alumina tube
- q: Pure zinc or alloy

Fig. 1 Experimental apparatus

Fig. 2 Electromotive force for Zn-Sb binary alloy solution

The activity of zinc was calculated according to equation (1) from these results, and the activity of antimony was also calculated according to the Gibbs-Duhem equation.

$$\log a_{Zn} = -2EF/4.574 T \quad (1)$$

The results calculated at 600°C are shown in Fig. 3. With use of the equations (2), (3) and (4), partial molal free energy, entropy and heat of mixing were calculated. And these integral values were determined according to equation (5).

$$\Delta \bar{F}_{Zn} = RT \ln a_{Zn} = 4.574 T \log a_{Zn} = -2 EF \quad (2)$$

$$\Delta \bar{S}_{Zn} = 2F (\partial E / \partial T) \quad (3)$$

$$\Delta \bar{H}_{Zn} = -2F [E - T(\partial E / \partial T)] = \Delta \bar{F}_{Zn} + T \Delta \bar{S}_{Zn} \quad (4)$$

$$\Delta F(\Delta H, \Delta S) = N_{Sb} \int_1^{N_{Zn}} \Delta \bar{F}_{Zn}(\Delta \bar{H}_{Zn}, \Delta \bar{S}_{Zn}) / (1 - N_{Zn})^2 dN_{Zn} \quad (5)$$

Figs. 4, 5 and 6 represent excess free energy, heat of mixing and excess entropy of the solution, to compare the property of the solution with that of ideal and regul solutions.

As shown in Fig. 3, it is observed that the activity of antimony has a negative deviation from Rault's law at all compositions, but that of zinc has a positive or negative deviation in accordance with the mole fraction of zinc being more or less than 0.64. The excess entropy has maximum values at two different

Fig. 3 Activities of Zinc and antimony in Zn-Sb binary alloy solution (600°C)

Fig. 4 Excess free energy for Zn-Sn binary alloy solution (600°C)

Eig. 5 Excess entropy for Zn-Sb binary alloy solution (600°C)

Fig. 6 Heat of mixing for Zn-Sb binary alloy solution (600°C)

Fig. 7 Function $\log \gamma_{Zn} / (1 - N_{Zn})^2$ for Zn-Sb binary alloy solution (600°C)

compositions as shown in Fig. 5.

Fig. 6. shows the heat of mixing. From these results the solution has a positive or negative heat of mixing in accordance with its zinc content.

Peculiarity of this solution can be shown most distinctly by means of function $\log \gamma_{Zn}/(1-N_{Zn})^2$ which consists of two straight lines with intersect at $N_{Zn}=0.45$ (Fig. 7).

It was concluded that Zn-Sb binary alloy solution has a considerable deviation from ideal and regular solutions and that a drastic change in the behavior of antimony atom occurs at $N_{Zn}=0.45$.

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Literature:

- 1) B. J. De Witt, H. Seltz, *J. Am. Chem. Soc.* **61**, 3170 (1939).

Thermodynamic Study of Fused Ternary Alloys by Electromotive Force Measurement (Zn-Cd-Sn System)

Zensaku KOZUKA, Jyoichiro MORIYAMA and Isao KUSHIMA

Dept. of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto

In respect to the Zn-Cd-Sn ternary alloy solution, Fiorani¹⁾ reported the experimental results and recently Ptak²⁾ has given a mathematical formula for calculation of the thermodynamic properties.

In this study the properties of Zn-Cd-Sn ternary alloy solution and of three binary alloy solutions composed of these elements at 450~600°C were determined by the electromotive force measurement. The experimental apparatus and technique were similar to those reported in the previous paper,³⁾ but in the case of Cd-Sn system pure Cd was used as a reference electrode and the electrolyte consisted of LiCl-KCl eutectic mixture containing 5% CdCl₂.

The experimental data are shown in Figs. 1~4 and Table 1. From these results the excess free energy, F^{xs} , excess entropy, S^{xs} and heat of mixing, ΔH , of these binary and ternary alloy solutions at 500°C were calculated by the same procedure as reported in the previous paper^{3),4)}.

①-⑦: The compositions of binary alloys were shown in Table 1.

Fig. 1 The relation between e. m. f. and temperature (Zn-Cd system)

①-⑦: The compositions of binary alloys were shown in Table 1.

Fig. 2 The relation between e. m. f. and temperature (Zn-Sn system)