2) **Oscillation phenomenon in inhibitor range** In the case of the inhibitor concentration above 0.03%, the protective effect was satisfactory, however, the corrosion potential did not settle at a constant value and showed a oscillatory behavior.

3) **Relation between the polarization characteristics and the inhibitor concentration** The

polarization curve of aluminum immersed into the viscoplastic substance is shown in Fig. 6. In the case of 0.01% addition, the inhibition of the cathodic reaction was greater than that of the anodic reaction and the corrosion potential was shifted toward less noble as compared with that of the case of no addition, and the corrosion current was smaller than that of the case of no addition (so as to avoid the complication of the figure, the curve of 0.01% addition was omitted).

In the case of 0.02% addition, the inhibition of the anodic reaction was greater than that of the cathodic reaction and the corrosion potential began to shift toward more noble and the corrosion current was more diminished.

In the case of above 0.03% addition which was in the inhibitive range, the remarkable inhibition was observed both in anodic and cathodic reactions and the corrosion potential was shifted to ward more noble side and the corrosion current was extremely small.

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Fig. 6 Influence of the addition of inhibitor on the polarization characteristics

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

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In this study the zinc vapor pressure on Zn-Sn-Al ternary alloy solution at 720°C was determined by the carrier gas technique. The apparatus were the same as those reported in the previous papers¹⁻³. The zinc vapor pressure of the alloy solution at eleven different compositions was determined as shown in Fig. 1. From these vapor pressure values, the activities of zinc were calculated. These are given by the numerical values in Fig. 1. Based on these activities, the iso-activity curves were obtained as shown in Fig. 2.

This ternary solution was found to have positive deviations from Raoult's law at all compositions.

The excess free energy of this solution was calculated by equation (1), because the data on the Al-Sn system was not available.

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

In order to calculate the integral values in the brackets, $\bar{F}_{Zn}^{xs} / (1 - N_{Zn})^2$ was plotted as a function of N_{Zn} as shown in Fig. 3. By the graphical integration of Fig. 3, the excess free energy was obtained at twelve different compositions as shown in Fig. 4. Based on these numerical values, the iso-excess free energy curves were represented in Fig. 5.

It is seen that the excess free energy shows a maximum at $N_{Zn}=0.55$, and $N_{Al}=0.45$ and it decreases gradually with changing its composition. From the iso-excess free energy curves, $\bar{F}_i^{xs}$ of each component

Fig. 1 Activity of zinc at 720°C in the Zn-Sn-Al melt

Fig. 2 Isoactivity lines of zinc in the Zn-Sn-Al melt at 720°C

Fig. 3 Free energy function of zinc at 720°C in the Zn-Sn-Al melt

Fig. 4 Excess free energy in the Zn-Sn-Al melt at 720°C (cal/mol)

Fig. 5 Excess free energy of the surface of the Zn-Sn-Al melt at 720°C in every 100 cal/mol steps

Fig. 6 Curves of excess partial molar free energy of solution in the Zn-Sn-Al melt at 720°C

Fig. 7 Isoactivity lines of aluminum and tin in the Zn-Sn-Al melt at 720°C

Fig. 8 Excess free energy and heat of mixing in the Sn-Al melt at 720°C

for the binary and pseudo-binary lines of the ternary system were obtained as shown in Fig. 6. Furthermore, the activities of aluminum and tin were calculated and the results were shown in Fig. 7 as iso-activity curves. It is seen that the activity has positive deviations from Raoult's law.

The Al-Sn binary alloy solution of which activity has not been determined experimentally will be considered below. From the results of the Zn-Sn-Al ternary alloy solution, the properties of Al-Sn binary alloy solution can be deduced according to the equation³⁾.

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

In this method the calculated value has considerable error due to several graphical integrations and the result is not so accurate as described in the earlier paper³⁾. The data of heat of mixing on Al-Sn system can be seen in Kubaschewski's table⁴⁾ and the excess free energy can be calculated from Hansen's equilibrium diagram⁵⁾. Fig. 8 represents these three different results. If Al-Sn solution is regarded as a regular solutions, the results should agree with each other. However, the disagreement among these three results should be concluded to arise from the deviation from regular solution rather than from experimental error.

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