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The Vapor Pressure of Binary Liquid Metals*

(Mercury-Bismuth-Lead System)

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Experiments have been made to verify the effectiveness of a boiling separation in a boiling separator which will be used in a two-component MHD generator cycle. The vapor pressure vs. temperature relations are obtained at various mole fractions of mercury. The activity coefficient of mercury in the liquid metal is found to approach unity as the temperature increases and the liquid metal can be regarded as an ideal solution. It is also found that, when the liquid metal with a mercury mole fraction of 15 per cent is boiled at 600°C, the concentration of bismuth and lead in the vapor is 10^{-5} mole per cent and that the two-components can be almost completely separated by boiling.

1. Introduction

In a liquid-metal MHD generator cycle, a liquid metal has to be efficiently accelerated by thermal energy. It is well known that the efficiency of a two-component liquid-metal MHD generator cycle is higher than that of a one-component cycle⁽¹⁾. In the former cycle, however, the separation of the components is necessary before or after the generator. The losses in this separator deteriorate the overall cycle efficiency. To avoid these difficulties, a cycle with a boiling separator has been suggested⁽²⁾. In this cycle, one component of the working fluid vaporizes in a boiler and can be separated from the other component which remains in the liquid state. The efficiency of the cycle with a boiling separator is affected by the concentration in the vapor of the component which should remain in the liquid state. The concentration of each component in the vapor and in the liquid can be calculated from the vapor-liquid equilibrium of a two-component liquid metal used in an MHD cycle. Only a few reports, however, have been published on the vapor-liquid equilibrium of two-component liquid metals.

Eastman et al.⁽³⁾ and Hildebrand et al.⁽⁴⁾ ob-

tained relations between vapor pressure and mercury concentration in binary liquid metals composed of mercury and other metals at a constant temperature around 300°C. Both authors showed that the activity coefficient was larger than unity and that the binary liquid metal could not be regarded as an ideal solution. But, because these measurements have been made at rather low temperatures, it is not clear whether these results can be applied to a liquid metal MHD cycle or not, where the temperature is much higher than 300°C. Furthermore, the vapor-liquid equilibrium of a binary liquid metal was not shown clearly in the above reports.

Then, in this report, measurements are made on the relation of vapor pressure vs. temperature as a function of the mercury concentration in binary liquid metals. The activity coefficient of binary-liquid metals is obtained as a function of the temperature and the effectiveness of boiling separation is discussed.

Most of the working fluids suggested for liquid metal MHD cycles are alkali metals which are not easy to handle. In this study, therefore, a ternary alloy composed of mercury (Hg), bismuth (Bi) and lead (Pb) is used. This ternary alloy can simulate binary liquid metals used in MHD cycles. Because the boiling points of bismuth and lead are nearly equal and much higher than that of mercury, this alloy can be regarded as a binary liquid metal in our experimental range, which is composed of mercury and bismuth-lead alloy. Mercury simulates a working fluid for liquid loop. Mercury, bismuth

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and lead can be perfectly soluble at any ratio.

2. Experimental method and apparatus

The vapor pressure of the liquid metal was measured by a method of balancing the vapor pressure with the pressure of an inert gas as shown in Fig. 1. The test section has two containers, one of which is a heated section and the other is a measuring section, and they are connected with each other through a pipe. The heated section is placed in the center of a vertical electric furnace. To make the temperature of the heated section spatially uniform, the electric heater of the furnace is divided into three groups vertically and the power input of each heater is controlled separately. The temperature of the heated section is measured by chromel-alumel thermocouples set in the wall. When the temperature of the heated section is raised, the liquid level in the heated section is pressed down by the vapor pressure and the liquid level in the measuring section becomes higher. Then argon is introduced into the measuring section to depress the liquid level down to the prescribed level. The liquid level is measured by contact-type level gauges. The pressure of argon, which is equal to the vapor pressure, is measured by a mercury U-tube and a Bourdon-tube manometer.

The concentration of the component in the tested liquid metal is shown in Table 1. In these liquid metals, the mole ratio of bismuth to lead is kept constant (55:45).

The experiments were carried out in the following procedure. A sample put into the storage tank was melt at 200°C in argon atmosphere to

prevent the oxidization, and the whole container was heated to a temperature which was a little higher than the melting point of the liquid metal. After the whole container was evacuated enough, the liquid metal was introduced into the test section through a filter from the storage tank. Then, the valve was shut tightly to prevent the liquid metal from falling down during the experiments, and the heated section was heated up and the argon gas was introduced into the measuring section. The temperature of the heated section was varied from 200 to 650°C. The temperature measurement system had been calibrated using the melting points of tin (321.9°C), lead (327.4°C), zinc (419.5°C) and aluminum (660.2°C). The temperature difference between the upper and the lower part of the heated section was within 3°C. This difference caused an error under 7% in the measurement of the saturation vapor pressure. The error in the measurement of the liquid level was 2 mm. This corresponds to an error in the vapor pressure of 0.0004 kg/cm², and this is very small compared with the minimum value of the vapor pressure in the present experimental range.

3. Results and discussions

3.1 The relation of vapor pressure vs. temperature—Latent heat of vaporization

The vapor pressure of the liquid metal at various mole fractions of mercury was obtained as a function of temperature. The results are plotted in Fig. 2. The Hg mole fraction is represented as a parameter x_1 . The vapor pressure of pure mercury which has been measured by Sugawara et al.⁽⁵⁾ is also shown in this figure for comparison.

The experimental results show that the vapor pressure of the liquid metal depends on the Hg mole fraction. As the Hg mole fraction decreases, the vapor pressure becomes smaller and the slope of the vapor pressure vs. temperature curve becomes also smaller. And the saturation temperature is found to become higher with the decrease of the Hg mole fraction at a given pressure. From these results, various thermodynamic properties of

Table 1 Composition of liquid metal alloys (mole %)

Component No.	Mercury Hg	Bismuth Bi	Lead Pb
I	5	52.7	42.3
II	15	47.2	37.8
III	40	33.3	26.7
IV	70	16.6	13.4

Fig. 1 Experimental apparatus for vapor pressure measurements

the binary liquid metal can be calculated.

The latent heat of vaporization of the binary liquid metal can be calculated from the following equation, which is derived from the Clapeyron-

Fig. 2 Vapor pressure of Hg-Bi-Pb alloy

Fig. 3 Dühring line of Hg-Bi-Pb alloy

Fig. 4 Latent heat of vaporization of Hg-Bi-Pb alloy

Clausius equation assuming that the gas constant R of the binary liquid metal is nearly equal to that of the one-component liquid metal.

$$\frac{r}{r_1} = \left(\frac{T}{T_1} \right)^2 \frac{dT}{dT_1} \quad (1)$$

where r is the latent heat, T is temperature and suffix 1 denotes the value of one-component liquid metal. To calculate the latent heat, it is convenient to use the Dühring line which shows the relation between the saturation temperature of a solution and that of a pure liquid at constant pressure. The value of dT_1/dT in Eq. (1) corresponds to the slope of the Dühring line. The Dühring line of the binary liquid metal used in our experiments is shown in Fig. 3. The latent heat of vaporization r , which is calculated from Eq. (1) using Fig. 3, is plotted as a function of the Hg mole fraction in Fig. 4. The figure shows that the latent heat of vaporization of the binary liquid metal gradually decreases with the decrease of the Hg mole fraction. Figure 4 also shows that the experimental values are little smaller than the calculated ones with the assumption that the binary liquid metal is an ideal solution. But the difference between them is smaller than 10% except for the case of the Hg mole fraction below 0.05. Therefore, the binary liquid metal can be regarded as an ideal solution within the error of 10%.

3.2 The relation of vapor pressure vs. mole fraction of mercury activity coefficient

The vapor pressure of the binary liquid metal depends on the Hg mole fraction, as is shown in Fig. 2. In order to make this dependence clearer, the values of p/p_1^0 are plotted in Fig. 5, where p and p_1^0 are the vapor pressures of the binary liquid metal and the pure mercury, respectively at the

Fig. 5 Ratio of vapor pressure of Hg-Bi-Pb to Hg

same temperature. The experimental results show that, when the Hg mole fraction is 0.05, the vapor pressure of the binary liquid metal is less than one tenth of the vapor pressure of pure mercury. The results also show that the vapor pressure of the binary liquid metal approaches, as the temperature increases, to the vapor pressure calculated by assuming it as an ideal solution. To show the difference of the measured value from the calculated one and its dependence on the temperature, p/p_1^0 is also plotted as a function of the mole fraction of Hg in Fig. 6. In this figure, the values calculated using Raoult's law, the data of Hg-Bi measured by Eastman et al.⁽³⁾ and the data of Hg-Pb obtained by Hildebrand et al.⁽⁴⁾ are also shown for comparison. Figure 6 indicates that, although the vapor pressure of the binary liquid metal deviates from that of an ideal solution, the deviation becomes smaller with the increase of temperature. The activity coefficient is often used to represent the degree of this deviation. The vapor pressure is usually expressed as follows;

$$p = \gamma_1 x_1 p_1^0 \quad (2)$$

where γ_1 denotes the activity coefficient of mercury.

The vapor pressures of bismuth and lead are ignored in Eq. (2), because their vapor pressures are much smaller than that of mercury. The activity coefficient γ_1 , which is calculated from the data in Fig. 6 using Eq. (2), is shown in Fig. 7 as a function of Hg mole fraction. This figure shows that the activity coefficient γ_1 becomes smaller with the increase of Hg mole fraction and of the temperature. Hence, in order to obtain a relation of activity coefficient vs. temperature, the activity coefficient is represented as a function of temperature in Fig. 8. Figure 8 shows that $\log \gamma_1$ is proportional to $1/T$ for various mole fractions of mercury. From the above experimental results,

Fig. 6 Vapor pressure vs. mole fraction of Hg

the activity coefficient γ_1 in the binary liquid metal is found to be expressed as follows;

$$\log \gamma_1 = \frac{141/T}{\left(1 + 0.283 \frac{x_1}{1-x_1}\right)^2} \quad (3)$$

The calculated values by Eq. (3) at 400°C ($T = 673^\circ\text{K}$) are shown in Fig. 7 by a solid line. Equation (3) shows that the activity coefficient becomes smaller and approaches unity with the increase of temperature. This means that the binary liquid metal can be seen as an ideal solution since the liquid metal MHD generator cycle is usually operated at high temperatures above 800°C.

3.3 The relation of the saturation temperature vs. the Hg mole fraction—The vapor-liquid equilibrium

The vapor-liquid equilibrium is shown by the saturated liquid line and the saturated vapor line. The former line gives the relation of the saturation temperature (or the boiling point) vs. the mole

Fig. 7 Activity coefficient vs. mole fraction of Hg

Fig. 8 Activity coefficient vs. temperature

fraction of a component at constant pressure, while the latter line gives the relation of the condensation temperature of the vapor vs. the mole fraction of a component. The saturated liquid line of the tested liquid metal can be made up of the data in Fig. 2. Saturation temperatures of various mole fractions of mercury at various pressures are plotted in Fig. 9. The solid lines are saturated liquid ones of the binary liquid metal used in this experiment. Although the boiling point of bismuth-lead is very high (1670°C), the boiling point of the binary liquid metal suddenly decreases when a small amount of mercury is added. It falls to 370°C at the Hg mole fraction of 0.05 and becomes nearly equal to the boiling point of mercury (357°C). The boiling point of the binary liquid metal gradually decreases as the Hg mole fraction increases above 0.05. When a binary liquid metal of composition A under the pressure of 1 kg/cm² is heated up to the temperature of point B, the liquid metal begins to boil. When the liquid metal is heated up further to the temperature of point C, the composition of the liquid metal in the liquid state changes from point B to D, and the vapor of composition E is generated. Due to the fact that the saturated liquid line is nearly horizontal, the distance between point C and D is large and the mole fraction of bismuth-lead in the liquid becomes much larger with boiling. The composition in the vapor

can be calculated from the activity coefficient. The activity coefficient of bismuth-lead γ_2 can be calculated from that of mercury γ_1 , which has already been shown in Fig. 7, using the Gibbs-Duhem equation⁽⁶⁾;

$$\ln \gamma_2 = - \int_0^{x_1} \frac{x_1}{1-x_1} d(\ln \gamma_1) \dots\dots\dots (4)$$

The Hg mole fraction y_1 and that of bismuth-lead y_2 in the vapor can be calculated from the activity coefficients γ_1 and γ_2 as follows;

$$y_1 = \frac{\gamma_1 x_1 p_1^0}{p} \dots\dots\dots (5)$$

$$y_2 = \frac{\gamma_2 x_2 p_2^0}{p} \dots\dots\dots (6)$$

where suffixes 1 and 2 denote mercury and bismuth-lead respectively. When the liquid metal with Hg mole fraction of 0.15 is heated up to 600°C, γ_2 is about 1.1, $y_1 \approx 1.0$ and $y_2 \approx 10^{-5}$. For the temperature range from 350 to 650°C, almost the same concentration is occurs in the vapor. Then the saturated vapor line in Fig. 9 is very close to the vertical axis ($x_1=1.0$) when the temperature is not near the boiling point of Pb-Bi. These results show that the vapor is composed of almost pure mercury and that two components in the binary liquid metal can be separated almost completely. Such an equilibrium line as shown in Fig. 9 is obtained because the boiling points of each component in the binary liquid metal differ very much.

4. Conclusions

From the results presented in this paper, the following conclusions can be drawn;

(1) The latent heat of vaporization of the binary liquid metal can be calculated within an error of about 10 %, by assuming it as an ideal solution.

(2) The activity coefficient of the binary liquid metal is obtained as a function of the temperature and the concentration of mercury in the liquid metal. It approaches unity as the temperature and the concentration of mercury increase.

(3) When the boiling points of two components in a binary liquid metal differ much, the components can be separated almost completely by boiling.

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Errata (Vol. 15, No. 81, March, 1972)

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A. ISHIBASHI et al.	397	left	10 from the bottom	were	wear
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