Electrotransport in the Sn-Bi Molten Alloys*

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By employing the modified capillary-reservoir technique capable of measuring an electrotransport mobility, the differential mobilities in Sn-Bi molten alloys were determined over the entire composition range at three temperatures in the range of 400 to 600°C, in an attempt to correlate with the TIE study exploring ionic species. The significant modifications were the uses of both a salt cover on the molten alloy and a glass cover on the cell.

As a consequence, the differential mobilities in experiments with the salt cover differed markedly from them without it, and minimums of both such mobility difference and the mobility value, occurred at or near the composition of $X_{Bi}=0.60$ associated with an inflection point on the liquidus.

The mobilities thus determined and then the effective valences calculated theoretically were discussed in comparison with the reference values.

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I. Introduction

In order to explore ionic species existing in the molten alloys the TIE technique has been employed⁽¹⁾. The present study was undertaken in an attempt to explain the electrotransport data in the molten alloys from such standpoints. In addition, it should be noted that the mobility is an important parameter in evaluating the usefulness of the electrotransport for purification or solute control upon solidification.

The mobilities of components in the molten alloys can be determined in two ways; i.e. one is by a steady-state method^{(2)~(5)} in which direct current is passed through the capillary until a stationary state is established and the other is an unsteady-state method^{(6)~(10)} which uses the initial linear portion of the resistivity vs time curve before a concentration gradient forms at the capillary mouth, while the data reported in

the present paper depend on the latter.

In reviewing the literature it is apparent that quantitative data for the mobilities of components in the molten alloys have been restricted mostly to the dilute solutions^{(11)~(21)} except some alloy systems.

Since the Sn-Bi system approximates an ideal solution⁽²²⁾, the analysis proposed by Verhoeven et al.⁽⁶⁾ becomes possible to establish a quantitative electrotransport data for the system under consideration and therefore the present study was carried out in order to determine the mobilities over the entire composition range.

The technique used to determine the mobility was a capillary-reservoir technique similar to that of Verhoeven et al. but modified to yield more precise data by means of employing both a salt cover to protect the alloy and a glass cell cover to introduce fresh alloy into the capillary.

The experiments were also carried out under a protective gas atmosphere only, for comparison with those performed with the salt cover.

II. Experimental Apparatus

Figure 1 illustrates a capillary cell and an experimental apparatus used in the present study, in which the capillary was made of Pyrex glass with 0.3 mm tungsten electrode sealed into one end. The silica crucible (22 mm I.D., 90 mm long) was placed into a Pyrex glass container (48 mm I.D., 360 mm long) with a brass cap. The

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- 1 Tungsten wires for current electrodes
- 2 Tungsten wires for voltage probes
- 3 Gas inlet or to vacuum pump
- 4 Gas outlet
- 5 Thermocouple
- 6 Wilson seal
- 7 Brass cap
- 8 Pyrex glass container
- 9 Electrotransport cell
- 10 Molten salt cover
- 11 Sn-Bi molten alloy
- 12 Silica crucibles
- 13 Refractory stand
- 14 Tungsten wires
- 15 Capillary
- 16 Glass cell cover
- 17 Cover bottom of thin wall

Fig. 1 Electrotransport apparatus.

crucible contained a Sn-Bi molten alloy with or without the salt cover. After the cell was lowered into the crucible as shown in Fig. 1(a), DC current was passed through the capillary. The brass cap had five holes, one of which could be sealed with Wilson seal so that its vertical movement became possible. Four tungsten wires were sealed in one end of the cell in which two wires sealed in the capillary were paired with two wires in the other tube of the cell respectively, and the current was passed through one of the wires while the other wire was connected to a potentiometer. Internal

diameters of the capillaries ranged 0.95 to 1.15 mm. It is necessary to know them quite accurately. To fill fresh molten alloy into the capillary as described below, the end of the cell was covered with the glass cover, whose bottom was expanded to a thin wall as shown in Fig. 1(b).

The furnace employed for the measurements was a nichrome-wire winding vertical furnace and the temperature of the cell was measured by a calibrated alumel-chromel thermocouple. The furnace temperature was controlled within $\pm 1^\circ\text{C}$ by using an automatic temperature controller and also its distribution was $\pm 1^\circ\text{C}$ in the range of 10 cm in the middle part of the furnace. DC current was supplied through an automatic voltage regulator and then a rectifier from the power source AC 100 V. Purified argon gas or an Ar-5% H_2 gas mixture was introduced in the cell apparatus at a flow rate of 300 to 500 cc/mn. The vacuum system was a combination of an oil rotary with an oil diffusion pump.

III. Experimental Procedure

Metals of 99.95% Sn and 99.9% Bi, and chlorides KCl and LiCl of the high-purity commercial grade were used.

In order to carry out the electrotransport runs the following procedure was used. In the experiments with the salt cover, about 6 g of a chloride mixture of KCl and LiCl (corresponding to the thickness of 10 mm) was put in the silica crucible and melted using the burner. After the molten salt was dehydrated by adding a small amount of NH_4Cl , about 120 g of tin and bismuth, accurately weighed out, was put into the crucible and melted, and then agitated thoroughly with a glass rod. The crucible was placed in the Pyrex glass container immediately without allowing them to solidify and the container was inserted into the electric furnace heated to about 30°C above a desired run temperature. Then, after the cell was evacuated and the furnace temperature was regulated to the desired run temperature, the cell was held for 30 min to 1 hr prior to a run.

On the other hand, in the experiments under a protective argon atmosphere without the salt cover, initially weighed amounts of tin and bismuth were melted in the silica crucible under

the argon atmosphere and agitated thoroughly with the glass rod. The alloys were then cast into a 10 mm I.D. silica tube. The Sn-Bi alloy so prepared was put into a 22 mm I.D. silica crucible and its crucible was placed in the Pyrex glass container which was inserted in the furnace subsequently. The alloy was melted down in a stream of Ar-5% H₂ gas mixture and agitated by vertical motion of the Pyrex rod with an expansion at one end. The cell was evacuated and then held for 30 min to 1 hr.

To make a run, the cell was lowered into the reservoir, the cell cover was broken by pressing it against the bottom of the silica crucible and the capillary was filled with the fresh alloy by pressurizing with the argon gas of 1 atm. Two of the four tungsten wires sealed in the cell were connected with a DC power supply and the others with the potentiometer. DC current was passed down one tube and up the other. The change in the average concentration produced by the current within the cell was determined by calculating the resistivity change from the voltage change between the inside and outside electrodes.

The resistivities of pure molten tin were measured without the salt cover. Voltage drops at the capillary were measured at 10°C intervals with decreasing temperature in the range from the melting temperature to 600°C. Data was, however, checked by comparing them with the experiments made with increasing temperature.

The measurements consist of the readings for the voltage drop across the cell, the current flowing through the cell and the run temperature. The current must be maintained constant because it changes as the temperature decreases. From measurements on the variation in voltage drop across the cell with time the mean capillary resistivity was determined as a function of time. For several minutes after the current flowed, the current control was not stable and therefore it was sometimes regulated. Within about 5 min, the current was stabilized, so first voltage reading was made and then the readings were repeated every 10 min over the run-time of 120 to 180 min. Since during the measurements, the current changed slightly with the change of resistivity, it accordingly was regulated on all such occasions.

The measurement temperatures were 400, 500

and 600°C, and the composition range was X_{Bi} is 0.05 to 0.90. With different porarity such as the capillary containing a cathode or anode, each measurement was carried out. After each run it was necessary to etch the tungsten wires in the capillary in a 20% KOH aqueous solution to remove the oxide from the tungsten surface.

IV. Experimental Results

1. The cell constant of capillaries

If A and L denote the mean capillary cross-sectional area and the capillary length, respectively, the cell constant K is expressed as

$$K = A/L. \quad (1)$$

If ρ (Ω cm) and R (Ω) denote the resistivity of alloy and the resistance of total alloy in the capillary, respectively, the following equation can be established:

$$\rho = (A/L)R = KR. \quad (2)$$

The cell constant was determined by calibration with pure mercury at room temperature. The resistivity of mercury has been reported to be $94.07 \times 10^{-6} \Omega \text{ cm}^{(23)}$ at 20°C. Since R is calculated by dividing the voltage drop V across the capillary by the current I , the K value can be obtained by virtue of eq. (2). The internal diameter can be obtained by using the cross-sectional area A calculated from the length L . For the twelve cells employed in the present study, the internal diameters of the capillaries were 0.95 to 1.15 mm, the capillary lengths were 35.3 to 39.9 mm, and K values were 1.94 to 2.87.

2. The resistivities of pure molten tin and the Sn-Bi molten alloys, and their temperature dependences

Their resistivities were determined in the same type of capillary cells as used to measure the mobilities.

At a desired temperature, the capillary was filled with pure molten tin, the current was passed through the capillary and then the voltage drop across the capillary was measured at each temperature. The resistivity of the metal in the capillary was calculated from the voltage drop across it and is shown in Fig. 2 as a function of temperature. It is evident from Fig. 2 that the

Fig. 2 Variation in resistivity with temperature for pure tin.

resistivity changes abruptly at its melting point while the resistivity is found to increase linearly with temperature. The measured resistivities agree very well with the extrapolated values to $X_{Bi}=0$ for the molten alloys in Fig. 3 and their agreement with values of Takeuchi et al.⁽²⁴⁾ appears satisfactory. The resistivities for pure molten tin can be expressed by

$$\rho = 40.64 + 0.0268 T (^{\circ}\text{C}) \quad (\mu\Omega \text{ cm}) \quad (3)$$

By extrapolating the resistivity vs time curve into zero time as shown in Fig. 4, the value of the resistivity at the capillary mouth was obtained. Figure 3 shows the resistivities at three temperatures for the Sn-Bi molten alloys. It is evident from the figure that the linearity of the results is good. Thus, one obtains

$$400^{\circ}\text{C}: \rho = 51.53 + 83.59 X_{Bi} \quad (\mu\Omega \text{ cm}), \quad (4)$$

$$500^{\circ}\text{C}: \rho = 54.20 + 84.87 X_{Bi} \quad (\mu\Omega \text{ cm}), \quad (5)$$

$$600^{\circ}\text{C}: \rho = 55.72 + 88.68 X_{Bi} \quad (\mu\Omega \text{ cm}). \quad (6)$$

It should be noted that this capillary-reservoir technique can apply only to alloys with a linear ρ vs composition relationship.

3. Mobilities in the Sn-Bi molten alloys

Since the Sn-Bi system is nearly ideal and in addition its resistivity is found to be linear with mole fraction, the applicability of the equation proposed by Verhoeven⁽⁶⁾ would be expected.

If the functional relationship between alloy resistivity and composition is linear, ρ can be

Fig. 3 Resistivities of Sn-Bi molten alloys.

○ with salt cover
● without salt cover

related to the composition of the molten alloy in the capillary according to the relationship

$$\rho = \beta X_1 + \rho_0 \quad (7)$$

where β is a constant, and ρ , ρ_0 and X_1 denote the resistivities of alloy and pure solvent metal, and the mole fraction of the solute 1, respectively.

It can be also shown that the mean resistivity, $\bar{\rho}$, is the same linear function of the mean mole fraction, $\bar{X}_1$, over the tube length, and therefore

$$\bar{\rho} = \beta \bar{X}_1 + \rho_0. \quad (8)$$

When the current is passed through the capillary, if a flow of the solute is due solely to the electrotransport, a total mass flow across the capillary mouth may be written as

$$J_1 = N_1 U_1 E \quad (9)$$

where J_1 , N_1 , U_1 and E are the solute flux, the mole concentration and the electric mobility of solute, and the electric field intensity, respectively.

The electric mobility of the solute in a dilute solution thus is given as

$$U_1 = L^2 K \bar{\rho} / I \rho_m X_m \beta$$

$$= L^2 K \dot{\rho} / I \rho_m (\rho_m - \rho_0) \quad (10)$$

where subscript m refers to conditions at the capillary mouth, and I and $\dot{\rho}$ denote the current through the capillary and the change in resistivity with time, respectively. It should be noted that this expression is useful as long as the experiment is restricted to the dilute solution.

For the molten alloys over the entire composition range, if the differential mobility, U_{12} or U_{21} , is defined as the difference of individual electric mobilities,

$$\begin{aligned} U_{12} &= U_1 - U_2, \\ U_{21} &= U_2 - U_1, \end{aligned} \quad (11)$$

the differential mobility⁽⁶⁾ becomes

$$\begin{aligned} U_{12} &= -U_{21} = (dV/dt)/(X_1 X_2 \rho)_m \beta (I/A)^2 \\ &= L^2 K \dot{\rho} / (X_1 X_2 \rho)_m \beta I \end{aligned} \quad (12)$$

where V is the voltage drop across the capillary.

$\dot{\rho} = \Delta\rho/\Delta t$ can be determined from the slop in the resistivity vs time relationship and also ρ_0 , ρ_m and β can be determined once the resistivity vs composition relationships are established.

Figure 4 is a plot of typical results for the variation of resistivity with time during the initial linear portion before a concentration gradient is formed at the capillary mouth.

Experimental results performed with the salt cover are depicted in Figs. 5 to 7[†], the polarity change indicating the apparent effect on the measured mobilities. On the other hand, the experimental results without the salt cover are given in Figs. 8 to 10[†], showing no detectable effect of the polarity change.

There appears naturally a tendency that the mobility obtained from eq. (10) is closer to the value from eq. (12) as the solution becomes more dilute.

V. Discussion

Table 1[†] indicates that the current density ranged from 150 to 500 A/cm² has an insignificant effect upon the differential mobility in the system under consideration.

Good agreement shown in Fig. 2 lends confidence to accuracy of the reported values.

For comparison^{(25)~(27)}, variations of the resistivity with the mole fraction are shown in

Fig. 4 Typical resistivity vs time relationships.

Fig. 11, from which it appears that the results of the present study agree fairly well with those of Verhoeven et al., Matsuyama and Tomlinson et al. though there is some disagreement.

Figure 12 shows a comparison of the average

Table 1 Effect of current density on differential mobility.

$T(^{\circ}\text{C})$	X_{Bi}	I (A/cm ²)	$\frac{U_{\text{Bi-Sn}}}{\times 10^3}$ (cm ² /V-sec)	Polarity of electrode	Existence of salt cover
400	0.30	236	1.13	+	C
400	0.30	498	1.06	+	C
500	0.05	219	1.67	+	C
500	0.05	221	1.56	+	C
500	0.05	499	1.61	+	C
500	0.20	279	1.20	+	C
500	0.20	346	1.25	+	C
500	0.30	161	1.08	—	G
500	0.30	313	1.13	—	G
500	0.70	236	0.571	—	C
500	0.70	400	0.556	—	C
500	0.80	236	0.952	+	C
500	0.80	236	1.01	+	C
500	0.80	395	0.989	+	C

+ Capillary contains anode
 — Capillary contains cathode
 C With salt cover
 G Without salt cover

[†] For the facility of comparison, the differential mobilities are now expressed as $U_{\text{Bi-Sn}}$ on the assumption of eq. (12) without distinction of the polarity change. Thus, the reason why the difference of the mobilities result with the polarity change, will be then discussed in detail in the next section.

Fig. 5 Differential mobilities in Sn-Bi molten alloys at 400°C. (With salt cover)

Fig. 6 Differential mobilities in Sn-Bi molten alloys at 500°C. (With salt cover)

Fig. 7 Differential mobilities in Sn-Bi molten alloys at 600°C. (With salt cover)

Fig. 8 Differential mobilities in Sn-Bi molten alloys at 400°C. (Without salt cover)

Fig. 9 Differential mobilities in Sn-Bi molten alloys at 500°C. (Without salt cover)

Fig. 10 Differential mobilities in Sn-Bi molten alloys at 600°C. (Without salt cover)

values of Figs. 5 to 7 with the salt cover and Figs. 8 to 10 without it with the reference values obtained by Verhoeven et al.⁽⁶⁾ and those converted from the effective valences by Belashchenko⁽⁴⁾. At three temperatures the mobilities by the present study curved concave upwards and minimums clearly occurred at or near the composition $X_{Bi}=0.60$. However, with respect to the shape of the mobility curve, the present result resembled that of Belashchenko.

The agreement among the data has not been good, but such an extent in the difference cannot necessarily be said to be large considering the uncertainty of the data due to the experimental difficulty.

However, the use of the glass cell cover has the

advantage that the fresh alloy can be filled in the capillary. Some oxygen contamination occurs from the argon gas regardless of the care taken in purifying the gas and the contamination of the molten alloy is assumed to be the prime source of the lack of precision in all the measurements. Consequently, one of the reasons for such a difference would be attributed to the use of the glass cell cover and therefore the reference values are less reliable.

The back diffusion in the capillary will not give erroneous values of the mobility as long as the experiment is terminated before an appreciable concentration gradient is established at the capillary mouth.

It seems very important that in the

Fig. 11 Comparison of the present results on the resistivity of the Sn-Bi system with literature values.

Fig. 12 Comparison of present results with literature values for differential mobility.

experiments with the salt cover there is a significant difference in the measured mobility with the change in polarity as shown in Figs. 5 to 7.

Now, special attention is given to a comparison of data obtained with the phase diagram⁽²²⁾ of the considered system. Figure 13[†] is presented for the purpose of comparing them.

Fig. 13 Differential mobilities related with the phase diagram of the Sn-Bi System.

It is of interest to note that the mobilities determined from runs in a cathod-containing capillary approach very closely the reversed polarity runs at $X_{Bi} = 0.60$ which corresponds to an inflection point in the liquidus. The inflection point is somewhat indistinguishable because of its small curvature, but it seems certain that there exists the inflection at $X_{Bi} = 0.60$.

Since Belashchenko et al.⁽²⁸⁾ have determined effective valences Z_{Sb}^0 in the In-Sb system from the measurements over a wide composition range, these values were converted to the mobilities by virtue of eq. (13) which will be described later. Figure 14 shows these values thus obtained, and the compound tendency is found to hinder transport notably in the molten alloys, since the minimum of the mobility curve occurs at the composition of the intermetallic compound InSb⁽²⁹⁾.

Although it has been described already⁽³⁰⁾ that the solution behavior is strongly influenced by such factors as the compound and the inflection point of the liquidus, the same is true for the mobility curve in the present study. It is thus believed that the cluster or anti-compound corresponding to the inflection composition $X_{Bi} = 0.60$ correctly minimized the mobility and made the mobility difference smallest.

A number of theoretical treatments have recently appeared in the literature, but it can be

Fig. 14 Differential mobilities related with the phase diagram of the In-Sb system.

shown that under certain assumptions these theories have reduced to an expression for the effective valence.

Therefore, the effective valence will now be calculated from a theoretical equation⁽⁶⁾ though the theoretical developments are not yet complete. The effective valence Z_i^0 can be expressed through Darken's relation as follows:

$$Z_1^0 = X_2 U_{12} k T d \ln a_1 / e \bar{D} d \ln N_1 \quad (13)$$

where subscripts 1 and 2 denote the components 1 and 2, and k , T , e , $\bar{D}$, a_1 and N_1 are Boltzmann's constant, the absolute temperature, the electronic charge, the interdiffusion coefficient defined as $\bar{D} = X_1 D_2 + X_2 D_1$, and the activity and the molar concentration of component 1, respectively.

If the system approximates an ideal solution,

$$Z_1^0 = X_2 U_{12} k T / e \bar{D}. \quad (14)$$

The intrinsic diffusion coefficients for the Sn-Bi molten alloys have been obtained by Niwa et al.⁽³¹⁾,

$$D_{\text{Sn in Bi}} = 5.2 \times 10^{-4} \exp(-3200/RT), \quad (15)$$

$$D_{\text{Bi in Sn}} = 1.3 \times 10^{-3} \exp(-5000/RT). \quad (16)$$

The Z_{Sn}^0 values calculated from eq. (14) are

Fig. 15 Effective valences of tin in Sn-Bi molten alloys.

shown in Fig. 15 together with the reference values for the comparison. The Z_{Bi}^0 values are of the same order of magnitude as that for Z_{Sn}^0 .

The notable difference of the mobilities resulted with the polarity change will be discussed next in consideration of the results investigated by the TIE method while the data is insufficient for an exact analysis.

It is significant that the marked mobility difference by the polarity change would have to be attributed entirely to the use of the salt cover and particular attention is directed to the role of the alloy surface for the ionic conductivity. Consequently, the TIE data⁽¹⁾ described already will considerably aid in understanding the observed abnormal phenomena for the electrotransport.

The TIE study has led to the conclusion that negative ions of bismuth and tin, and positive ions of tin can coexist in the Sn-Bi molten alloys though limited to only the composition $X_{\text{Bi}} = 0.5$. Since the Sn-Bi system is eutectic, two ionic species of like sign can be expected to coexist as described already, but positive ions seems also possible to exist because under a sufficiently high pressure, a new phase appears which is believed to be the intermetallic compound SnBi. Subsequently, when such ionic species coexist and the capillary contains an anode, the negative ions of bismuth and tin enter the capillary and the

positive ions of tin leave it. The change in resistivity may be caused by relative mobility differences among different ionic species of bismuth and tin.

The TIE study has suggested that ions exist mainly on the surface of the molten alloys, but the present study may lend support to this problem. That is, an important role of the alloy surface is suggested by the fact that the use of the salt cover has a significant effect upon the mobilities.

The reason why the polarity change yields notable mobility difference will be considered now.

The differential mobilities measured in the cathode-containing capillary are smaller than in the reversed polarity in which the mobilities may be affected by the conducting mechanism that the positive ions of tin on the alloy surface become difficult to migrate because they are fixed in the molten salt. There appears a tendency that the mobility difference by the polarity change becomes smaller as the temperature decreases. This is probably due to the temperature dependence of the positive ions of tin as discussed in a previous paper⁽¹⁾.

Yamamura et al.⁽³²⁾ have reported that when the current was passed through lithium bromide-potassium bromide molten salt, a salt mixture of a significant composition, i.e. eutectic composition in this case, was produced in the anode compartment. This study seems to be very useful in formulating an empirical basis for discussion of the problems encountered. Since the resistivity of the molten salt is large compared with that of the molten alloy, the current passing through the salt would be expected to be negligible. By making use of the argument advanced by Yamamura et al., the data lead to the prediction that the positive ions of tin cannot decrease but increase because of the tendency to become a constant composition such as the aforementioned eutectic since the positive ions existing on the interface between the molten salt and alloy are very few. This suggests that when the capillary contains a cathode the positive ions of tin would be fixed at this interface.

Of course, discussions of the electrotransport will remain empirical by the limited TIE studies until more quantitative data become available.

This view is further supported by a study of the solid electrolyte⁽³³⁾ in which the surface conductivity of the ions is remarkable.

In the view of these facts, ionic conductance through the alloy surface must be of particular importance though the alloy body cannot be ignored.

VI. Summary

By a modified capillary-reservoir technique the mobilities in the Sn-Bi molten alloys were determined successfully in the temperature range of 400 to 600°C.

It was noted that the mobilities in experiments with the salt cover remarkably differed from those without it.

The minimums of the mobility and the its difference occurred at the composition of $X_{Bi} = 0.60$ associated with the inflection point on the liquidus. The present study seems to be significant in drawing attention to the role of the alloy surface in the solution behavior.

Effective valences of tin were calculated and the values were a little different from the reference values.

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