that all of the primary branches within a given sheet are interconnected at Y-junctions. These junctions are the points where a subbranch was able to grow out into a full branch, as may be seen in the upper left section of Fig. 1. We found no case where the dendrites were interconnected between sheets, although such connection seems reasonable in the region where the dendrites originated.

Using back-reflection Laue techniques the dendrites were found to grow in the [110] direction in agreement with other work,[2,3] and the sheets were found to lie in the $(1\bar{1}0)$ plane. The orientation is illustrated in Fig. 2. This result was confirmed on samples grown at 70°C per cm and 51 μm per sec both with and without stirring and on a sample grown at 2.9°C per cm and 51 μm per sec without stirring. Lowering the temperature gradient at a constant rate caused the dendrite spacing to increase.[1] The characteristic morphology was maintained down to the lowest gradients studied. The secondary branches protruding out from the primary sheets were considerably longer at the low gradients and they displayed side branching. The sample grown at 2.9°C per cm and 51 μm per sec clearly showed these secondary branches growing normal to the primary sheets (*i.e.* in the (110) plane) in contrast to a study on Sn-Bi.[3] At the higher gradients stirring did not affect the dendrite morphology. However, the Laue patterns took on the appearance characteristic of cold-worked materials, which was impossible to remove in spite of extensive electropolishing. It appears that the fluid flow caused small crystallographic orientation differences among the various dendritic branches.

The tin dendrite morphology shown in Fig. 1 has been observed in metallographic studies by ourselves and others[4] in the Sn-Pb system and in the Sn-Bi[5] system. However, Ahearn and Flemings[3] have reported a slightly different morphology in Sn-Bi alloys. They also found that the primary dendrites grew in the [110] direction in sheets parallel to the $(1\bar{1}0)$ plane. However, the secondary branches growing out of the sheets were contained in the (112) planes which are 69 deg from the plane of the sheets rather than in the (110) planes at 90 deg from the sheets as found here. This difference in the morphology of the secondary branching is apparently real, and it must be due to differences in the growth conditions and/or the solute content between these studies.

An interesting conclusion may be deduced from the morphology of these dendrites. The tips of the subbranches on the primary stem never grow very far before they are terminated by encroachment of a subbranch from a neighboring stem. New subbranches must continually form by branching directly off of an old subbranch. This is true even though the primary stem is aligned in the heat flow direction. Consequently, there cannot be any steady-state primary dendrite tip configuration as has been observed in experiments on the growth of surface tin dendrites into the supercooled liquid[6] and as is assumed in theoretical treatments on dendrite growth.[7] We conclude that even though the experiments were performed under overall steady-state heat flow conditions the primary dendrite tip shape was not constant. The primary dendrites must have advanced with a pulsating tip configuration in a manner somewhat analogous to that directly observed in the succinonitrile-camphor system.[8]

The authors would like to acknowledge the assistance of Miss Denise Maze with both the X-ray and metallographic work. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Comission. Contribution No. 3129.

---

1. J. D. Verhoeven: *Met. Trans.*, 1971, vol. 2, p. 2673.
2. F. Weinberg and B. Chalmers. *Can. J Phys.*, 1952, vol. 30, p. 488.
3. P. J. Ahearn and M. C. Flemings. *Trans. TMS-AIME*, 1967, vol. 239, p. 1590.
4. F. R. Mollard and M. C. Flemings: *Trans. TMS-AIME*, 1967, vol. 239, p. 1967.
5. J. L. Dassel: *Dendritic Solidification in Unidirectionally Frozen Tin-Bismuth Alloys*, University Microfilms, Ann Arbor, Mich., 1969
6. M. E. Glicksman and R. J. Schaefer: *Acta Met.*, 1966, vol. 14, p. 1126.
7. R. Trivedi *Acta Met.*, 1970, vol. 18, p. 287.
8. L. R. Morris and W. C. Winegard: *J. Cryst. Growth*, 1967, vol. 1, p. 245.

Mass Spectrometric Study of the Thermodynamic Properties of the Ag-Sn System

TETSUO YAMAJI AND EIICHI KATO

A study of the thermodynamic properties of the Ag-Sn liquid alloys has been made with the combination of a Knudsen cell and a mass spectrometer.

The mass spectrometric apparatus, Knudsen cell assembly, experimental procedure, and temperature measurement techniques were essentially the same as have been previously described.[1] In this study, alumina Knudsen cells with a thin graphite liner and graphite Knudsen cells were used. The dimensions of the alumina cells were 19 mm OD by 19 mm high with 15 mm ID and a lid thickness of 1 mm. The orifice diameter was 0.7 mm giving the ratio of surface area to orifice area of 450:1. The dimensions of the graphite cells were 18 mm OD by 17 mm high with a 12 mm ID and a lid thickness of 3 mm. The orifice diameter was 0.8 mm and the ratio of surface area to orifice area was 225:1. The alloys were prepared *in situ* by melting together a total amount of 7 to 10 g of the component metals. The purity of the metals was 99.999 pct.

Prior to the recording of any data, the temperature of the Knudsen cell was raised to about 1250°C and held for 15 to 20 min. The ion currents of silver and tin were then measured and the temperature was lowered to a new value. The measurements were taken at successively lower temperatures. This procedure was repeated until constant ion currents at the same temperature were obtained. For silver-rich alloys, a long time was required to obtain constant ion currents. The loss in weight was between 4 and 20 mg for many alloys. In the case of silver-rich alloys, however, weight losses of up to 170 mg were observed owing to the long time needed for homogenizing.

TETSUO YAMAJI, formerly Graduate Student, Department of Metallurgical Engineering, Waseda University, Tokyo, Japan, is now with OKI Electric Industry Co. Ltd., Tokyo. EIICHI KATO is Professor, Department of Metallurgical Engineering, Waseda University.

Manuscript submitted August 16, 1971.

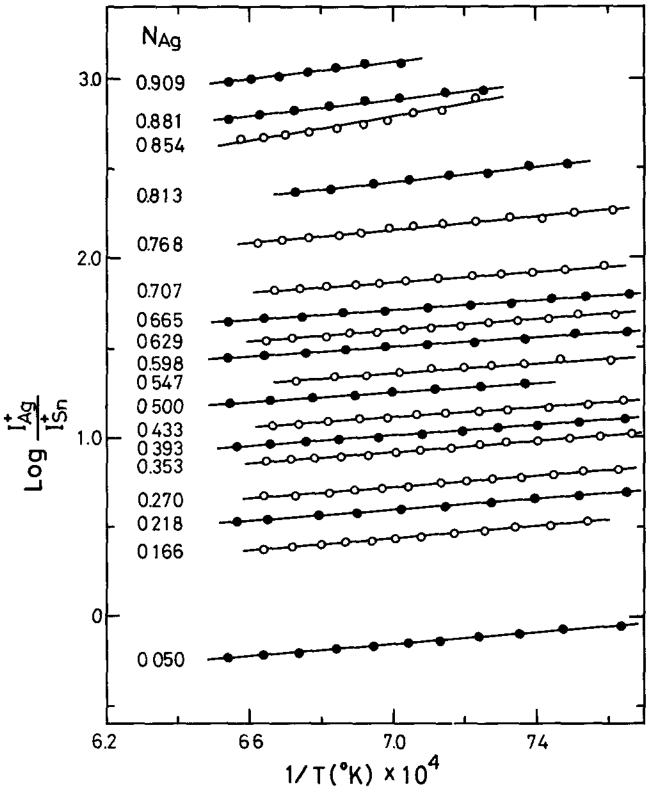

Fig. 1—Experimental values of the ion current ratio for the Ag-Sn alloys. The open circles represent the work with an alumina cell; closed circles, graphite cell.

Table I. Thermodynamic Quantities for the Ag-Sn System at 1150°C

Atom Fraction of Silver	a_{Ag}	γ_{Ag}	a_{Sn}	γ_{Sn}	$\Delta\bar{H}_{Ag}$	$\Delta\bar{H}_{Sn}$
0.00	0.000	0.494	1.000	1.000	300	0
0.10	0.051	0.505	0.899	0.999	-70	20
	(±0.000)	(±0.003)	(±0.000)	(±0.000)	(±70)	(±1)
0.20	0.104	0.518	0.794	0.993	-410	80
0.30	0.162	0.539	0.686	0.980	-710	180
0.40	0.226	0.566	0.574	0.956	-960	320
0.50	0.301	0.601	0.455	0.909	-1180	500
	(±0.002)	(±0.004)	(±0.001)	(±0.001)	(±60)	(±20)
0.60	0.395	0.658	0.325	0.813	-1290	610
0.70	0.519	0.741	0.196	0.652	-990	-20
0.80	0.690	0.862	0.082	0.410	-440	-1630
0.90	0.868	0.964	0.022	0.217	-110	-3520
	(±0.002)	(±0.002)	(±0.003)	(±0.003)	(±10)	(±190)
1.00	1.000	1.000	0.000	0.106	0	-5630

The experimental values of the ion current ratio are presented in Fig. 1. The activity coefficients and the partial molar heats of mixing were calculated by Gibbs-Duhem integration, as proposed by Belton and Fruehan.[2] The thermodynamic values were calculated from the data obtained by using the graphite cells, because the graphite cells gave better temperature-dependent results than the alumina cells coated with graphite. The precise answer to this difference could not be obtained, and a possible explanation would be that the coated graphite could not completely prevent the surface diffusion in the cell. The calculated values for γ_{Ag}, γ_{Sn}, $\Delta\bar{H}_{Ag}$, and $\Delta\bar{H}_{Sn}$ are tabulated in Table I. The uncertainties shown in the table have been calculated by integrating the several possible lines through the points in the Gibbs-Duhem integration plots. The calculated activities are plotted in Fig. 2 with previous values.

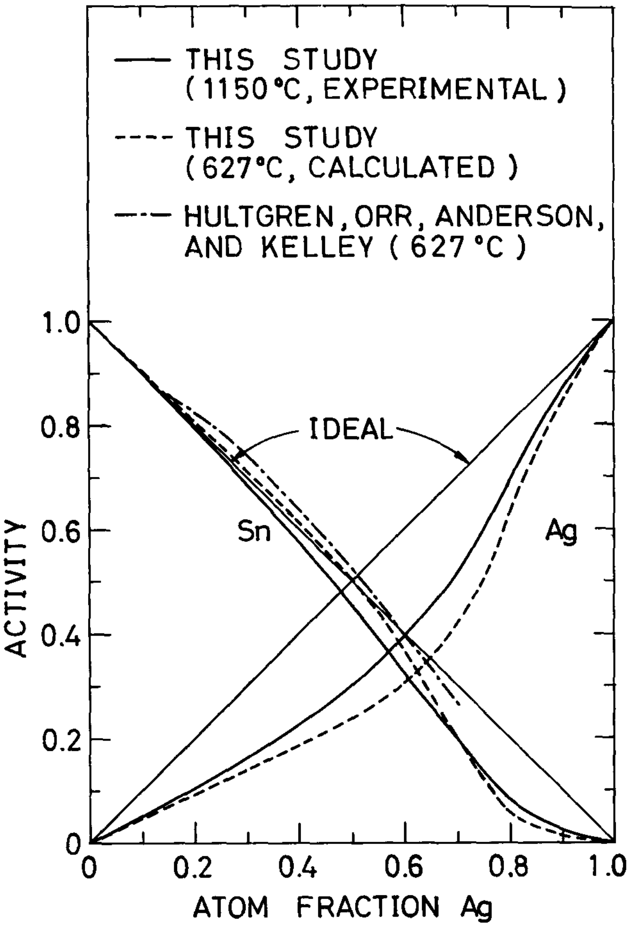

Fig. 2—Activities in the Ag-Sn system.

The electromotive force measurements of this system have been made by Yanko, Drake, and Hovorka[3] between 333° and 413°C in the range $0.86 \leqq N_{Sn} \leqq 0.994$, and also by Frantik and McDonald[4] at 627°C in the range $0.3 \leqq N_{Sn} \leqq 0.9$. Hultgren, Orr, Anderson, and Kelley[5] estimated the activity of tin in these alloys by using the data obtained from these measurements.

The a_{Sn} values obtained in this study indicate a Raoultian behavior at high concentration of tin. The a_{Sn} at 627°C was calculated from the relation

$$\frac{d\,\Delta\bar{G}_{Sn}/T}{dT} = -\frac{\Delta\bar{H}_{Sn}}{T^2}$$

and the values of $\Delta\bar{H}_{Sn}$ given by the authors (assuming $\Delta\bar{H}_{Sn}$ to be temperature-independent). The results are also shown in Fig. 2 and are very similar to those given by Hultgren *et al.*

The relation between log γ and the atom fraction of components at 1150°C can be partially represented by the quadratic approximation given by Darken:[6]

$$\log \gamma_{Ag} = -0.0586(1 - N_{Ag})^2 - 0.249 \quad (0 \leqq N_{Ag} \leqq 0.20)$$

$$\log \gamma_{Sn} = -1.627(1 - N_{Sn})^2 + 0.653 \quad (0 \leqq N_{Sn} \leqq 0.20)$$

---

[1] S. Nakamura, T. Yamaji, and E. Kato. *Met. Trans.*, 1970, vol. 1, pp. 2645-46.

[2] G. R. Belton and R. J. Fruehan: *J Phys Chem.*, 1967, vol. 71, pp. 1403-09.

[3] J. A. Yanko, A. E. Drake, and F. Hovorka: *Trans. Electrochem. Soc.*, 1946, vol. 89, pp. 357-72.

4 R. O. Frantik and H. J. McDonald: *Trans. Electrochem. Soc.*, 1945, vol. 88, pp. 253-62.
5. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley: *Selected Values of Thermodynamic Properties of Metals and Alloys*, pp. 388-92, John Wiley and Sons, New York, 1963.
6. L. S. Darken: *Trans. TMS-AIME*, 1967, vol. 239, pp 80-89.

Inverse Segregation in Unidirectionally Solidified Al-Cu Alloys

K. P. EDWARDS AND J. A. SPITTLE

It has previously been reported,[1] from examination of unidirectionally solidified ingots, that inverse segregation is time-dependent. This is indisputable, since, for any alloy exhibiting such segregation, solidification occurs over a temperature range. A solid + liquid region therefore exists in the ingot which, in the early stages of freezing, permits solute-rich liquid (assuming that the equilibrium partition coefficient for the solute has a value less than unity) to flow towards the chill surface. Inverse segregation is therefore time-dependent, developing as solidification progresses. However, the particular dependence on time discussed[1] was considered to be associated with a transition from a columnar to an equiaxed grain structure which occurred at a certain distance from the chill face. It appeared, from observations on ingots that underwent such a transition, that inverse segregation in the region of the chill face was not established prior to the transition. The origin of the inverse segregation was therefore directly attributed to the nucleation and growth of solid in the bulk liquid. It was assumed that this resulted in solute enrichment of the liquid, ahead of the macroscopic solidification front, which then infiltrated the already-formed shell adjacent to the chill surface. The technique used[1] for examining this apparent dependence of inverse segregation on structure transition was to cast, under identical conditions, samples having the same composition and of equal size into a mold designed to produce unidirectional solidification. Ingots of various heights were obtained by decanting the liquid from the solid after different lengths of time following the onset of freezing. These were analyzed by X-ray fluorescence to show the solute distribution as a function of the distance from the chill face.

During the solidification of an ingot, the bulk liquid concentration could only approach that of the interdendritic liquid in the already formed solid + liquid shell, if the growth of solid ahead of the macroscopic solid-liquid interface was associated with massive undercooling of the bulk liquid. In conventional ingots, the composition of the bulk liquid cannot rise to a value greater than that of the interdendritic liquid since the bulk liquid temperature is unable to fall below that of the macroscopic solid-liquid interface. This places some doubt on the above explanation of the origin of inverse segregation in ingots undergoing a structure transition. It has been observed, in unidirectionally solidifying ingots,[2] that thermal supercooling can develop in the liquid ahead of the macroscopic interface because of some heat loss from the mold walls. However, it is unlikely that growth of solid in the liquid at this small undercooling would have any significant influence on the bulk liquid concentration. The object of the present investigation was to redetermine whether in fact inverse segregation is related to the growth of solid in the bulk liquid.

Ingots of Al-Cu of different height were obtained, by unidirectional solidification, under conditions that resulted only in columnar growth. This was achieved using a laboratory scale 25 K.W. electroslag remelting unit. Initially an alloy of nominal composition Al-4.5 wt pct Cu was cast and then rolled into an electrode 1.3 cm in diam. The procedure then adopted for the production of each ingot was as follows. The slag, a mixture of KCl and LiCl of eutectic composition, was first melted *in situ* in the mold. The latter consisted of a cylinder of fused silica 3.8 cm in diam mounted on a water-cooled copper base plate. The electrode was then located in the slag, with the operating voltage selected, and the slag temperature allowed to come to equilibrium without melting of the electrode taking place. Melting of the electrode was then initiated by lowering it at a fixed rate into the slag. When the desired metal height in the mold was reached, the power was switched off leaving the remaining liquid pool, on top of the already-formed ingot, to completely solidify. In this way several ingots of different height were produced under almost steady-state conditions, from the same electrode. The sustained positive temperature gradient in the melt ahead of the macroscopic solid-liquid metal interface ensured columnar growth over the complete ingot length in all cases. A typical columnar structure is illustrated in Fig. 1. The ingots were analyzed, using X-ray fluorescence, to give the copper concentration as a function of the distance from the chill face. Analyses were carried out on a rectangular cross-sectional area 1.5 by 2.0 cm and the results obtained are shown in Fig. 2.

It is clear from Fig. 2 that even in the shortest ingot inverse segregation has occurred. This ingot is comparable in height to that previously examined[1] in which no inverse segregation was detected. The segregation observed cannot have arisen because of growth of solid in the bulk liquid since all the ingots were completely columnar. The origin of the inverse segregation must therefore be the transport of the solute-rich interdendritic liquid. Clearly, in the earlier investigation,[1] interdendritic liquid, in addition to the bulk liquid, must have been decanted. The effect of this will be most marked in those ingots where solidification has proceeded only a short distance from the chill. The interdendritic liquid channels, especially in alloys having a wide freezing range, will then extend back close to and may even reach the chill face. If this liquid is decanted an almost uniform solid composition will be determined over the ingot height.

K. P. EDWARDS and J. A. SPITTLE are Postgraduate Research Student and Lecturer, respectively, Department of Metallurgy, University College, Cardiff, Wales, United Kingdom.

Manuscript submitted September 20, 1971.