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INVESTIGATION OF THE BINARY Pb-Sn SYSTEM BY DTA

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ABSTRACT

The phase diagram of the binary Pb-Sn system was determined by a modified DTA aparatus. The heat of mixing in liquid and solid state were also determined by quantitative DTA.

INTRODUCTION

Pb and Sn form a simple eutectic diagram with no intermediate phases. The solidus and liquidus lines and the eutectic temperature have already been (1-4) determined with sufficient accuracy. The method of DTA has also been used (5) to establish the phase diagrams of Bi-Sn and Pb-Sn systems with solvus lines included as well as the heat of mixing in liquid and solid state. However, it was felt that the accuracy of quantitative caloric measurements by the use of DTA might be significantly improved by certain modification of DTA apparatus. The theoretical background of the modified apparatus has been given elsewhere (6). The aim of this work was to improve the experimental technique and to test the applicability of the modified DTA apparatus for quantitative calorimetric measurement.

EXPERIMENTAL

For the difference from previous investigations(5) when pure aluminium was used for reference the temperature of cylindrical nickel block of 40 mm diameter and 120 mm height with a central bore of 8 mm diameter and 70 mm depth for test tube served as the reference. Samples of different composition over the whole concentration range (X_{Sn} = 0.1 .. 0.9) were prepared by melting the calculated amount of tin in quartz glass test-tube which served for sample holder. Thermocouple protection tube was placed in the center of molten tin. After the solidification a disc-like Pb sample with a central hole for thermocouple protection tube was pushed down the thermocouple protection tube in the immediate vicinity of the tin sample fused in the bottom of sample holder. The metals were not allowed to be in the contact in order to preclude the alloying which would otherwise occur during the heating up to the melting point of lead. The geometrical shape and total volume of the prepared samples were the same.The temperature difference between the block and the sample placed in its centre was measured by a Pt-Pt10Rh thermocouple. Both thermocouple junctions were protected by alumina tubes. The reference junction was inserted into 3 mm diameter hole bored at 18 mm radial distance from the block centre. A simple vertical electric furnace was used. Typical heating rates used were 8 - 10 K/min. The apparatus was calibrated by melting pure Pb, Zn, Cd,

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In, Bi and Sn. The well known heats of fusion and the peak areas obtained were used to determine the calibration constant of the apparatus. Each sample was melted twice. Freshly prepared sample composed of separated tin and lead was heated up to produce the melting of Sn, Pb and the mixing of both in liquid state. Total peak area obtained corresponds to the consumed heat, i.e.

$Q_1 = C A_1$

$C A_1 = n [X_{Sn}L_{Sn} + (1 - X_{Sn})L_{Pb} + \Delta H_{liq.}]$ After the solidification the sample was melted once more. The peak area obtained during this second melting coresponds to the previously consumed heat diminished by the heat of formation of solid solution, i.e. $Q_2 = C A_2$

$C A_2 = n [X_{Sn}L_{Sn} + (1 - X_{Sn})L_{Pb} + \Delta H_{liq.} - \Delta H_{sol.}]$

where:

Q_1 - the heat consumed in the first melting (J)
Q_2 - the heat consumed in the second melting (J)
C - calibration constant (J/K s)
n - number of moles
X - mole fraction
A_1 - peak area obtained in the first melting (K s)
A_2 - peak area obtained in the second melting (K s)
L - heat of fusion (J/mole)
$\Delta H_{liq.}$ - heat of formation of liquid solution (J/mole)
$\Delta H_{sol.}$ - heat of mixing in solid state (J/mole)

RESULTS

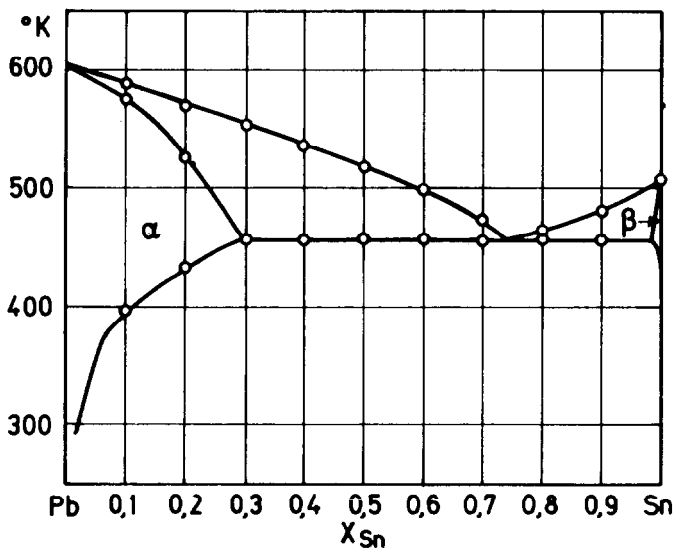

Fig. 1 Phase diagram of Pb - Sn system

Fig. 1 shows the phase diagram of system Pb - Sn. It can be seen that the results obtained by the use of modified DTA aparatus agree fairly well with reference data (7). The results of calorimetric measurements of the heats of formation of liquid and solid solution are presented in Table 1 wherein reference data (7) are also given for comparison purposes.

Table 1 Heat of liquid and solid solution in J/mole (cal/mole)

	Modif. DTA results		Reference (7)	
X_{Sn}	$\Delta H_{liq.}$	$\Delta H_{sol.}$	$\Delta H_{liq.}$	$\Delta H_{sol.}$
0.1	550 (131)	700 (167)	(130)	-
0.2	900 (215)	1400 (334)	(220)	-
0.3	1150 (275)	2000 (477)	(280)	-
0.4	1300 (310)	1900 (453	(320)	-
0.5	1350 (322)	1700 (406)	(330)	-
0.6	1250 (299)	1400 (334)	(310)	-
0.7	1150 (275)	1100 (263)	(280)	-
0.8	850 (203)	850 (203)	(210)	-
0.9	500 (119)	550 (131)	(120)	-

CONCLUSIONS

The modified DTA aparatus can be successfully employed not only for the construction of binary phase diagram but also for calorimetric measurements. A further improvement in experimental technique can probably increase the accuracy of DTA calorimetric measurement which is estimated as better than 8 %.

REFERENCES

1 Raynor, G. V. Annotated Equil. Diagram Series, Institue of Metals, London, 1947.
2 Metals Handbook, 1948.
3 Kawakami, M., Sci. Reports Tohoku Imperial University *
4 Elliot, J. F. and J. Chipman, Journal of the American Chemical Society, 73 (1951).
5 Dobovišek, B. and N. Smajić, Mining and Metall. Quarterly, (1962) p.353-360.
6 Smajić, N.,Thermal Analysis, vol. 1, Proc. 4th ICTA,Budapest, 1974, Akademiai Kiado, Budapest, 1975, p. 271-280.
7 Hultgreen, R. et al., Selected Values of Thermodynamic Propertites of Metals and Alloys, John Wiley & Sons, New York, 1963, p. 900.