

Calorimetric Measurement on Bi- Sn System

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Abstract

In this era of lead-free soldering alloys with low melting point suitable for use in soldering joints are very important. Use of lead as a solder is considered dangerous for the environment due to the huge number of PCB and electronic devices, pipe joints etc. needed to be recycled from dumps.

The European Community, the US and Japan as well as the electronic industries have launched initiatives to look for lead-free solders having physic-chemical and technological properties comparable to or better than the Sn-Pb alloys in use. Even in India Government regulations are becoming stricter, and handlings of waste materials are becoming more regulated. The history of government regulation suggests that targeted materials often become the subject of a ban within a certain timeframe; lead in paint, lead in plumbing, and lead in gasoline have all been eliminated.

A rigorous literature survey has been done on In-Sn-Bi, In-Sn, In-Bi, Bi-Sn systems. Thermodynamics studies on the concerned binaries system have been done vary extensively both by Calorimetric and E.M.F. measurements. But very limited thermodynamic data on Bi- Sn system are available in the literature. E.M.F. measurements on system have been done by many investigators. No literature is available based on drop calorimetric technique. So the thermodynamic investigation by drop calorimetric technique is taken up

The metallic samples were prepared from Bi in the mass range from 0.75gm. Samples of Sn were dropped into the bath of pure Bi by using an automatic dropping device. System required 40min time interval after every sample of dropped. Calorimetric measurements were done at temperature 730K and 830K. The Integral and partial enthalpy of mixing were calculated at both temperatures.

Keywords

Drop Calorimetric Device, Calisto Software, Synthetic Sapphire

I. Introduction

Development of new lead-free solder requires a data base. The database will help us to avoid complicated and time consuming experiments. Information on thermodynamic properties such as mixing enthalpies is indispensable for the accurate thermodynamic optimization of phase diagrams, for the development of a lead-free solder database, and for the prediction of physical and chemical properties, such as surface tension and viscosity.

It is not possible so far to substitute lead by any single metal in the conventional lead-tin solder. So the attempt has been made to substitute lead by more than one metal. The systems are called multicomponent metallic solution. Like In- Sn- Bi, In-Sn-Zn, and In-Sn-Bi-Zn

A. Disadvantages of Lead in Lead-tin Solder

1. Thermal Stress of Components

Higher temperatures dramatically reduce the firmness of the solder joint during thermal cycling, due to greater plastic deformation of the solder and recrystallization and grain growth inside the

solder. At such high temperatures, the mechanical properties of the conventional alloys Sn62/Pb36/Ag2 (melting point 179°C) and Sn63/Pb37 (melting point 183°C) deteriorate.

II. Health Hazards

In the manufacturing environment, the only risk is caused by breathing in floating, dried powder particles, or through the occurrence of gross mistakes in safety measures. A greater danger lies in the contamination of groundwater and soil by electronic scrap (disposal of electronic circuit and solder dross). Several proposals have been made to ban the use of lead in electronics.

B. Experimental Setup & Procedure

1. All experimental measurements were performed by using the calorimetric drop method. Calorimetric measurements were carried out by using the MHTC96 high temperature drop calorimeter from Setaram, France.
2. It is a calorimeter with a thermopile of 20 thermocouples and a graphite tube resistance furnace operating up to 1723K. Control and data evaluation were performed using the software provided by the manufacturer. To prevent oxidation of the samples all measurements were taken in a atmosphere of flowing argon.
3. All measurements were carried out in an alumina crucible.
4. A motorized dropping device is placed on the top of the calorimeter. 23 samples can be installed at a time into it. It also consists of a vacuum pump.
5. An alumina tube connects the furnace to the dropping device. Sample is dropped from dropping device to the alumina crucible (placed in the furnace) by this tube.
6. Control and data evaluation were performed using the software provided by the manufacturer

The starting materials are the metals reagent grade as powder. In (purity > 99.9%; $1\mu\text{m} < \text{Ø} < 2\mu\text{m}$), Bi (purity > 99.95%; $\text{Ø} < 25\mu\text{m}$) and Sn (purity > 99.9985%; $\text{Ø} < 20\mu\text{m}$). The Stoichiometric mixtures, in the appropriate molar ratio were carefully homogenized inside a glove box under purified argon gas in an agate mortar and compacted into 6mm diameter pellets. The pellets were cut into pieces and transferred from the glove box to the calorimeter using a special Ar-tight container in order to prevent any oxidation with air atmosphere. The Ar gas pressure and time in Analysis chamber is 1.5 bar & 15 min. while for furnace it is 1.5bar & 2min 30 sec.

The starting samples were placed alternatively in the container with reference α -alumina used for calibration The enthalpy variations of α -alumina between room and experimental temperatures are well established by Sabbah et al. [1]



Fig. 1: Drop Calorimeter Device

- Starting up the instrument
 - First switch on power to the instrument, the switch is located back of the instrument, Check the inlet gas pressure (about 3 to 3.5 bar) & also turn on the tap for cooling water.
- Starting up Calisto
 - Switch on the PC & wait for 5mins then start the Data Acquisition icon on the desktop.
- Programming an experiment
 - Go to the program experiments window & select a Standard zone as given

Table 1: Model of Programmed Software

#	Initial T (°C)	Final T (°C)	S.T. (K/min)	Time (s)	Values	C Flow	A Flow
1	50	50	0	5	500	0	0
2	50	1200	0	1000	1000	0	0
3	1200	1200	0	1000	1000	0	0
4	1200	1600	0	400	400	0	0
5	1600	50	0	1000	1000	0	0
6	50	50	0	3600	3600	0	0

- Sample Loading
 - Press the Black button on the in the front left side of instrument to move up the lift. Load the sample to alumina crucible and again press the button to move down the lift. Take the samples to be dropped and load into the motorized dropping device. Set the time interval 40 minutes between sample drop and α -Al₂O₃ drop respectively.
- Starting the experiment
 - After everything is ready we started the experiment under window tab.
 - After finishing the experiment the file can be opened in Calisto processing software & go for integrations and calculations

III. Method of Calculation

A. Determination of Heat Capacity

If there is not a transition or reaction occurring within the sample on the temperature range, the following heat relation is obtained

$$(H_{Sample,T_C} - H_{Sample,T_D}) = \int_{T_D}^{T_C} C_p dT$$

Determination of enthalpy of transition: For the temperature range under investigation, the sample can undergo a structure change (melting, crystallization, phase transition ...). The measured heat will contain the heat capacity contribution before and after the transformation and the corresponding heat of transition

$$(H_{Sample,T_C} - H_{Sample,T_D}) = \int_{T_D}^{T_{Tr}} C_p dT + \Delta H_{Tr} + \int_{T_{Tr}}^{T_m} C_p dT + \Delta H_{Tf} + \int_{T_m}^{T_C} C_p dT$$

- T_D = Dropping (Room) Temperature
- T_{Tr} = Transformation Temperature
- ΔH_{Tr} = Enthalpy change during transformation
- T_m = Melting Point
- ΔH_{Tf} = Enthalpy change during melting
- T_C = Temperature of the Calorimeter at which experiment is carried out.
- C_p was calculated using the following relation taken from the Metallurgical Thermo chemistry book [2].
- C_p = a+bT, Where a and b are the constants and T is temperature in Kelvin. Values of a and b are taken from the book. All the experiments were carried out at calorimeter temperature of 730K and drop temperature was 293K.
- Alpha alumina (α -Al₂O₃) was used for the calibration of the calorimeter for each experiment. Alpha alumina does not react with the molten alloy of In-Bi-Sn due to its high melting point. Molecular weight of the α -Al₂O₃ = 101.9613. ΔH Reaction for α -Al₂O₃ is zero. The molar enthalpy difference for α -Al₂O₃ Standard Reference Material 720 was taken from Standard Reference Material 720 Synthetic Sapphire certificate issued by National Bureau of Standards Certificate, Washington.

$$(H_{Sample,T_C} - H_{Sample,T_D}) = 45533 \text{ J/mole}$$

Enthalpy Calculation

The measured enthalpy (integrated heat flow at constant pressure) is given by

$$\Delta H_{Signal} = n_i (H_{Sample,T_C} - H_{Sample,T_D}) + \Delta H_{Reaction}$$

Partial enthalpy can be directly calculated

$$\Delta \bar{H}_i = \frac{\Delta H_{Reaction}}{n_i}$$

The integral enthalpy of mixing was calculated by summarizing the respective reaction enthalpies and division by the total molar amount of substance

$$\Delta H_{mix} = \frac{\sum \Delta H_{Reaction}}{(n_{Crucible} + \sum n_i)}$$

Calibration constant was calculated using area under the peak of dropped α -Al₂O₃ samples

$$\Delta H_{Signal} = n_i (H_{Sample,T_C} - H_{Sample,T_D})$$

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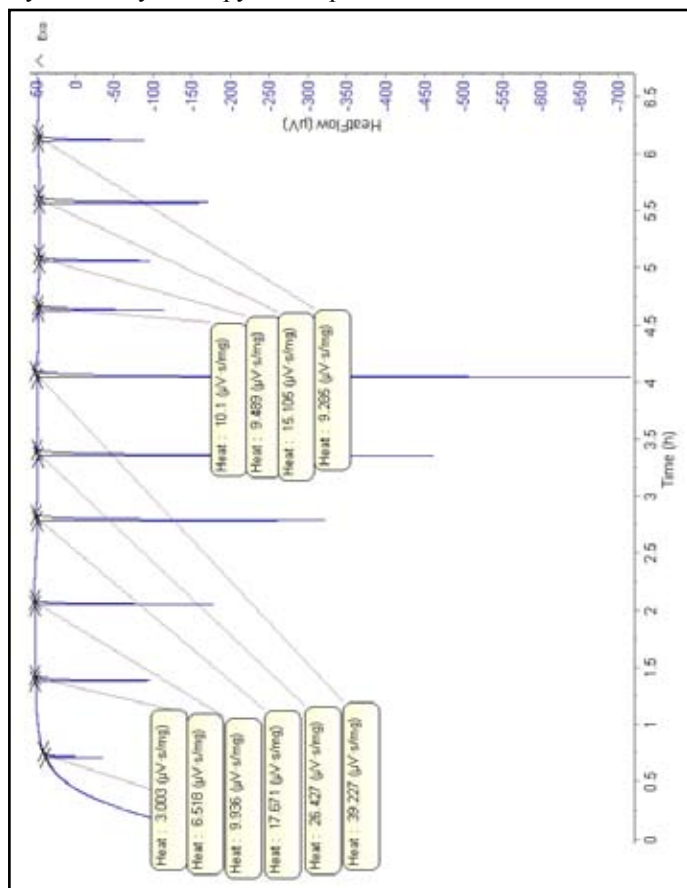
$$K = \frac{A}{\Delta H_{Signal}}$$

Where n_i is the number of moles of dropped α -Al₂O₃ samples. A is area under the peak in microvolt-second (μ v-s). ΔH_{Signal} is the heat absorbed in joule by n_i number of moles of α -Al₂O₃.

IV. Results & Discussion

Molten Bi held at temperature 730K according to pre-set time range in program and Sn is dropped in the crucible at a regular interval of 40 mins with the help of motorizing dropping device. In Graph-(1- 6) peaks shows the Heat involve due to Sn drop.

By same way enthalpy all the peaks can be obtained



Graph-1: Peak areas with enthalpy values

Molar mixing Enthalpies and Partial Enthalpies with composition (Table 2 & 3)

X _{sn}	ΔH _{MIX} (Joule/mole)
0.1	40.27759
0.2	151.754
0.3	292.1128
0.4	469.3475
0.5	570.039
0.6	605.922
0.7389	569.9107
0.8093	450.1246
0.832	392.1039
0.8498	339.8457
0.8642	286.1929
0.8861	229.9907
0.8946	165.0691
0.9019	85.15358

Calibration constant was calculated using area under the peak of dropped α-Al₂O₃ samples

Table 2: Partial Enthalpies With Composition

X _{sn}	Partial Enthalpy (J/mole)
0.1	1352.665878
0.2	606.035198
0.3	515.5397029
0.4	945.0941891
0.5	883.0229295
0.6	667.9512507
0.7389	535.4989169
0.7796	106.1237565
0.8642	-30.5927125
0.8946	-104.2914341
0.9019	-370.2476901

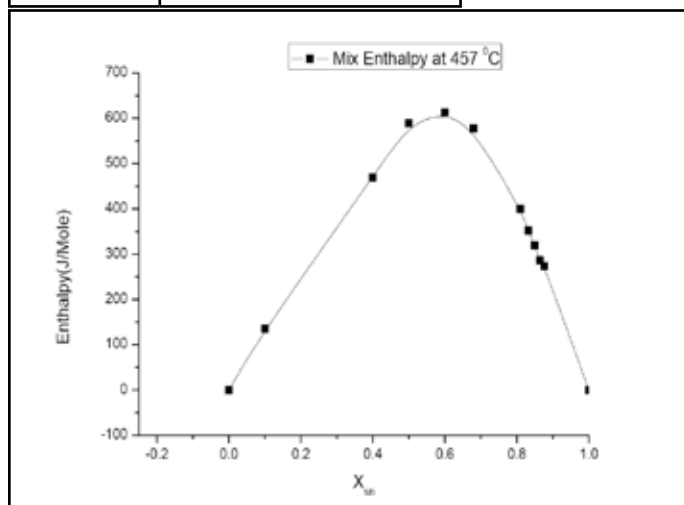


Fig. 3: Variation of Mixing Enthalpies with X_{sn}

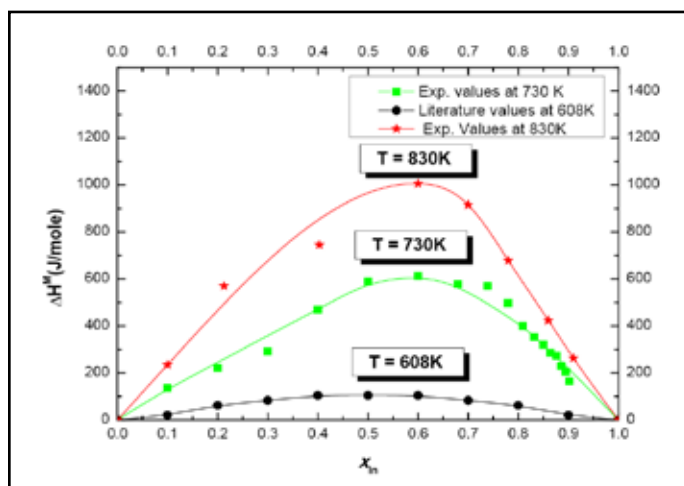


Fig. 4: Comparisons of Mixing Enthalpies With Literature Data

we find that first the value of Enthalpy is increasing with composition of Sn and at X_{sn} = 0.59, the value of Enthalpy is Maximum for all the temperatures. This is an agreement with the literature. That means at this point reaction is more Endothermic in nature and after this composition Enthalpy goes on decreasing as shown in Fig. R.Hultgrenet[3] have got the maximum value of enthalpy at X_{sn} = 0.6 is ΔH_{mix} = 146.37 J/mol at 608K. we have obtained the maximum values of enthalpy at X_{sn} = 0.6 is ΔH_{mix} = 1005.9061 J/mol at 830K, and is ΔH_{mix} = 612.33 J/mol at 730 K.

it has been observed that enthalpy of mixing in the system Bi- Sn is more endothermic in nature with the temperature.

The experimental values are compared with the literature and found some scatter due to difference in experimental constraints.

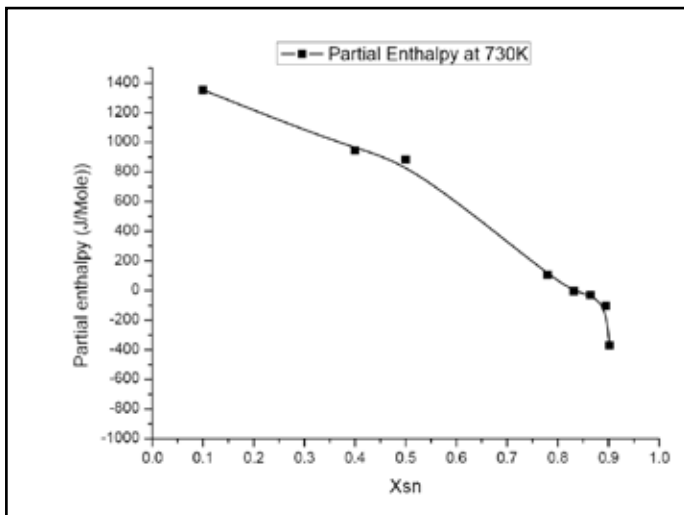


Fig. 5: Partial Enthalpy vs. Composition

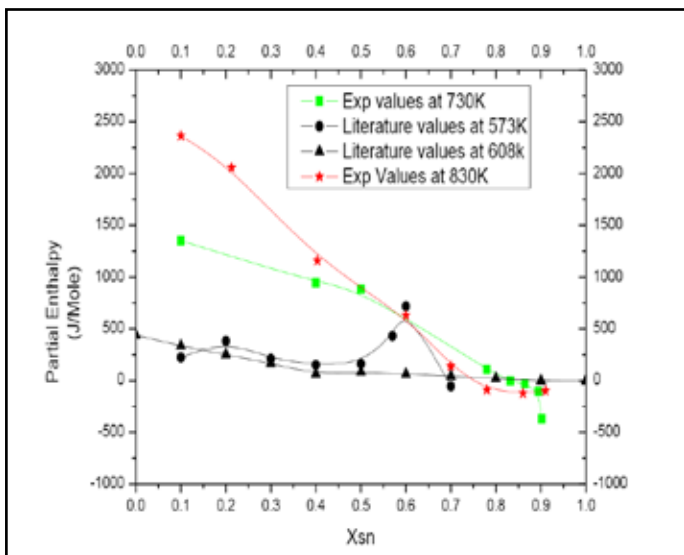


Fig. 6: Comparison of Partial Enthalpies with Literature data with

It is observed that partial enthalpy of mixing decreases with temperature. The experimental values show some scatter from the literature[3,4]. The reason for the scatter may be due to different techniques used for the experimental measurement in the Bi-Sn system. The second reason may be the experiments are carried out at different temperatures. For example the Partial enthalpies values obtained from the literature are calculated values from EMF measurement but our values are obtained directly from the enthalpy measurement by calorimeter at 730K and 830 K.

V. Conclusion

The Enthalpy change of Bi- Sn system is measured at temperature 730K and 830K by Drop calorimetric technique and following conclusions are made

The Integral enthalpy of mixing in Bi- Sn system at 730K and 830K is endothermic in nature throughout the composition and its maximum value at X_{sn} = 0.6, is 605.922 J/mol and 1005.9061 respectively

The partial molar enthalpy of Sn is endothermic in nature and decreases with the composition of tin for most of the composition except Sn rich composition.

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