PREFACE

Thermodynamic investigations of binary and multicomponent metallic systems are carried out with various objectives in view. In the first place, the processes used for the extraction and refining of metals in the field of chemical metallurgy and alloy development in physical metallurgy involve multicomponent metallic solutions. For the thermodynamic analysis of these processes it is necessary to know the thermodynamic properties of the solution with high accuracy.

Hence, the correct experimental technique is required to choose for the particular multicomponent solution along with the theoretical models. Second, the phase diagrams are very important for the materials engineers as far as the choice of materials for the particular application is concerned. It is necessary to determine the position of solidus and liquidus curve in the phase diagram with very good accuracy which is to be done by the careful thermodynamic analysis of the relevant system.

The thermodynamic analysis of the phase diagram requires reliable data with high degree of accuracy. Third, only electrical properties or magnetic properties or X – ray investigation cannot provide all the information about the constitution of the metallic system. Thus authentic thermodynamic data along with above investigations are essential to obtain the deeper insight into the constitution of the multicomponent metallic systems. The Bi-In-Sn is one of the multicomponent liquid alloys formed with low melting metals. These alloys are always characterized by the small positive enthalpy of formation with no intermetallic compound. The accurate thermodynamic properties of this system are very essential to understand the various metallurgical processes in which multicomponent solutions take part. Though the related binaries of this ternary system are very extensively studied, but a systematic thermodynamic investigation of this ternary system is not available in the literature. Therefore, the thermodynamic study of Bi-In-Sn system was undertaken.

Lead – tin alloys system are the most commonly used among many available solder alloys in electronic circuit and packaging, because of physical, chemical and mechanical properties, manufacturability and reliability. Due to the toxic nature of lead, its use is restricted in many applications. Several researches are currently carried out to develop lead free solder alloys. The most prominent lead free solder alloys are likely to be tin based multicomponent alloys. Bi-In-Sn system is considered to be one of the potential lead free solder materials among the available lead free solder alloys. Determination of phase diagram and thermodynamic properties of this system are a first step towards the design of the new solder alloys. Since, no thermodynamic properties are available in the literature, the thermodynamic investigations of the In-Sn-Bi were undertaken.

The Thesis has been divided into six chapters.

In Chapter - 1 Significance of various thermodynamic quantities and their role in understanding the behaviour of the metallic solutions and relation to the other physical properties have been highlighted. Thermodynamic properties of the metallic solution have also been discussed in brief. As entire discussion on behaviour of solutions is based on activity of components, a section has been devoted to various techniques of activity measurement in multicomponent metallic solutions. The special features, advantages and limitations of each technique have been highlighted. The techniques of vapour pressure and electrochemical measurements have been reviewed in detail where as the chemical equilibrium has been discussed in brief. Vapour pressure techniques including static, dynamic and effusion methods have been critically surveyed with reference to vapourisation studies of various metallic systems in various pressure ranges. Electrochemical techniques employing aqueous and organic, molten salts and solid electrolytes have been reviewed. The classification of calorimeters and different techniques of measurement of enthalpy have been discussed in details. Different measurement techniques as applied to metallic solutions and their relative merits and demerits have stated at the end of this chapter, followed by the scope of the present investigations.

In Chapter – 2 The Experimental procedure and technique have been described in this chapter. Basically two types of experimental techniques have been used in this study i.e EMF and Drop calorimeter measurements (MHTC-96 Line evo). Activity of indium in In-Sn-Bi system has been measured by EMF. In these techniques the thermodynamic properties are obtained by measuring the open circuit emf of a suitable electrochemical cell. The experimental technique and procedures have been outlined.

Purity, source and physical state of metals and salts used for the investigations have been presented in a tabular form. The electrochemical technique using molten salt electrolyte galvanic cell has been described in detail. The galvanic cell assembly was designed and fabricated out of indigenous materials. The details of cell assembly for activity measurements have been described. The methods of calculations of various thermodynamic properties by this technique have been discussed briefly.

A large number of investigations were carried out at the end of the nineteenth century on the aqueous electrolytes and till the middle of the current century by molten salt electrolyte. The experimental cell assembly, schematically was made of BOROSIL glass. For heating of the electrochemical cells a Kanthal (A-I grade) wound silica tube furnace of 55 cm height and 60 mm I. D. was used. This furnace had constant temperature zone (within ± 0.5 K) of at least 15 cm long. The temperature of the furnace was controlled by PID based Digital Temperature Controller (Servotronics, India; Model: 192) with an accuracy of better than ± 0.5 K.

The procedure and techniques for the measurements of enthalpy of mixing by MHTC-96 Line evo drop calorimeter has been discussed. The calibration of the calorimeter is discussed in this chapter. The methods for the calculation of mixing from the peak is discussed with suitable equations. Thermodynamic properties of Bi-In-Sn system have been discussed in

In Chapter – 3 Activity of Indium in liquid Bi-In-Sn alloys has been measured by electrochemical technique based on molten salt electrolyte galvanic cell in the temperature range 723-855 K along the three sections of $(Sn_{0.33}Bi_{0.67})_{1-x}$, $(Sn_{0.50}Bi_{0.50})_{1-x}$ and In_x $(Sn_{0.67}Bi_{0.33})_{1-x}$ In_x. From the emf values measured at different temperatures presented, activity of Indium in Bi-In-Sn liquid alloys was calculated and the calculated corresponding values of the activity coefficient of Indium (γ_{In}) calculated at different temperature. The excess molar free energy, enthalpy and entropy were computed by the Darken's treatment of the ternary solutions using published data of the relevant binary solutions and ternary system investigated. The excess molar free energy surface of the ternary confirms substantially to what one would expect from the knowledge of the corresponding curves of the component binary systems. The excess molar free energy surfaces have the maxima in the Bi-In side. It is observed that the negative values of excess free energy is predominant inside the ternary triangle i.e for most of the compositions. It could be inferred that there is strong interactions among the indium, tin and bismuth atoms in the solutions.

In chapter 4 the calorimetric measurement of boundry binary system were carried out.

Chapter – 4. Boundry binary Bi-Sn , Bi-In and In-Sn system has been measured in this chapter. It has done at similar temperature 767-855 K with the variation of dropping elements Sn, In and In in Bi-Sn, Bi-In and In-Sn system respectively. Calibration of the calorimeter was done by dropping four pieces of α-Al_2O_3 at the drop temperatures. The measured enthalpies of mixing are plotted against dropping element and found endothermic in nature for all the compositions in the case of Bi-Sn while exothermic nature have been observed for Bi-In and In-Sn system. The binary interaction parameters are determined for all the three boundry binary system using R-K-Polynomials. These interaction parameters are used for the calculation of the ternery interaction parameters in chapter 4. In the last Drop calorimetric measurement of Bi-In-Sn system have been discussed in **Chapter – 5**. The measured enthalpy of mixing of Bi-In-Sn system is a prime step parameter to evaluate phase diagram of this system is required in the development of its alloys. In this a fully automated high temperature drop solution calorimeter has been used to determine the integral enthalpy of mixing of Bi-In-Sn system at 767, 813 and 855 K using drop technique. The measurements were carried out for three different cross sections of $(Sn_{0.33}Bi_{0.67})_{1-x}$ In_x, $(Sn_{0.50}Bi_{0.50})_{1-x}$ In_x and $(Sn_{0.67}Bi_{0.33})_{1-x}$ In_x. The indium was dropped to the Bi-Sn alloys over the entire composition of indium. Partial enthalpies of mixing for the indium were calculated from the integration of the heat flow curve by the CALISTO software. Subsequently, integral enthalpies of mixing were calculated from the partial enthalpies of mixing. Enthalpies of mixing are found to be almost temperature independent in Bi-In-Sn system. Iso-enthalpy curves for the molar enthalpy of mixing were plotted at 813 K. The experimental data were treated with a least square fit using the Redlich – Kister – Muggianu polynomial to determine the ternary interaction parameter.

The overall conclusions of this work have been presented in **Chapter- 6** followed by scope for the future work.