SYNOPSIS

The aim of the present reseach work is to understand the thermodynamics and microstructural evolution of the alloys which are subjected to different processing routes The systems chosen for this investigation are those exhibiting phase separation due to stable and metastable miscibility gaps A thermodynamic analysis is carried out with a special emphasis on phase separating systems It deals with a model to interpret the thermodynamic properties This is followed by a kinetic study to investigate the morphology of the phases in Zn Bi and Zn Pb monotectic alloys The experiments are conducted through the directional solidification processing route where the external parameters can be controlled independently Finally, the submerged immiscible system such as Fe Cu system is processed through non equilibrium routes such as rapid solidification and mechanical alloying route

I Thermodynamics

In order to study the thermodynamic properties, a function is deduced based on Maclaurin infinite series This model uses the excess integral properties of binary systems The series is expressed in the neighbourhood of each of the pure components with appropriate boundary conditions The final expression is a four parameter function which is correlated with the infinite dilution constants and the first order interaction parameters It is found that the present model has an excellent capability of predicting the thermodynamic properties for binary systems

II Controlled cooling experiments on monotectic Zn-Bi and Zn-Pb alloys

The solidification behavior of monotectic system is studied using Zn Bi and Zn Pb alloys by directional solidification processing A vertical Bridgeman type of furnace with traction device is designed and installed for this purpose The results suggest that the morphological features are predominantly dependent on the solidification conditions and the interfacial energies of the phases Under certain growth conditions a regular morphology with aligned rod of second phase (L_2) in the Zn matrix along the growth direction can be observed The morphology differs from grain to grain This clearly establishes the effect of surface energy anisotropy on the morphology The quantitative estimation on the aligned rod morphology is carried out and compared with the existing models for coupled growth Our results cannot be explained by the existing models The change over from a regular rods to random droplets morphology is observed which is governed by the temperature gradient and growth velocity This is related to the stability of the growing interface The stability of the co operative growth is modelled in order to support the present observation

It is observed that the arrayed droplets form behind the solidification front because of the break down of the rods due to Rayleigh perturbation The dendrites within the droplets indicate that the break down has taken place during the time when the phase is still in the liquid state An attempt is made to interpret the nature of the break down quantitavely with the help of a model for Rayleigh perturbation This model deals with the criterion of transition from the stable to unstable rod morphology as a function of growth velocity

III Non-equilibrium processing of Fe-Cu system

The positive heat of mixing of a binary system causes phase separation in both liquid and solid phases In Fe Cu system the flat liquidus line indicates that the system is prone to have liquid immiscibility Thus, the

undercooled liquid separates into two immiscible liquids when it undergoes rapid solidification processing This is evident from the transmission electron microscopy observations of the results on the twin rolled Fe Cu alloys The compositions of 18 and 25 at%Cu alloy show nanodipersoids of fcc within bcc matrix The reverse is true for higher concentration

When the powder mixures of Fe and Cu are mechanically alloyed by high energy ball milling, they form a solid solution through out the range of compositions The alloys containing up to 20 at% Cu show only the existence of bcc phase, whereas only the fcc phase is detected in the alloys of composition beyond 34 at% Cu Dual phases exist in 25at%Cu alloy The grain sizes and lattice strains are calculated from the peak broadening of X ray diffraction pattern while precision lattice parameters are calculated by extrapolating Nelson Riley function The results are complemented with magnetic property measurements to gain an insight into the evolution of the structural and microstructural changes with the progress of mechanical alloying The results suggest that during the mechanical alloying the high input energy is responsible for the attainment of nanometric grain at the early stage of the milling along with the high strain This creates a high diffusivity path and assists solutionization A simple model calculation shows that there can be a driving force to form solid solution beyond a critical size of the particles At this size the effect of entropy contribution on the total free energy becomes prominent and the powder mixture can form solid solution