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Ultrasonic velocities and elastic constants in tin-indium alloys

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Abstract. Ultrasonic velocities, elastic constants and internal friction are studied in Sn-In alloys in the concentration range of 0 to 30 wt% of In using composite oscillator technique. Anomalies observed in the vicinity of the phase transitions of these alloys at fourteen concentrations are interpreted in the light of the phase changes in the phase diagram.

Keywords. Ultrasonic velocities; Young's modulus; rigidity modulus; Poisson's ratio; bulk modulus; internal friction.

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1. Introduction

The study of ultrasonic velocities, elastic constants and internal friction in alloys has received considerable interest as these parameters are structure-dependent. Some alloys such as Sn-In form homogeneous phases (solid solutions) in certain concentration ranges, separated by a wide range of intermetallic phases; further these homogeneous phases possess different structures. Considerable interest has been shown by different investigators to study Sn-In system from various aspects. Osipenko (1970) has studied the thermal conductivity in Sn-In system at concentrations of 0, 19·5, 52, 74·4 and 100 wt% of In and has reported a eutectic point at 52 wt% of In, where the thermal conductivity was minimum.

The various properties of Sn-In system have been extensively studied; *e.g.* thermo-EMF by Yatsenko and Golovin (1974), the In-Sn phase diagram and superconductivity in In_3Sn by Bartram *et al* (1978) superconductivity of Sn-In alloys—magnetization and electrical resistance by Aomine and Shibuya (1968). The structure studies of liquid and solid alloys in indium-tin, indium-bismuth and bismuth-thallium are due to Predel and Sandig (1970) who carried out electrical conductivity investigations in molten alloys of In-Sn system. They have observed anomalies in conductivity coefficients at 46 at % and 90 at % of Sn at which intermetallic phases exist in the solid state. Thermoelectric EMF was measured for In-Sn alloys at 100°C by Zelyavskii and Khar'kov (1972). They found that the Seebeck coefficient E declined monotonically from $+0{\cdot}9$ at 100% In to $-1{\cdot}6$ at 0% In concentration. They interpreted the results theoretically on the basis of Ziman's model.

Ultrasonic investigations on the phase diagrams of alloys are very few. Mention may be made of the work by Subrahmanyam (1972) on Sn-Ag, Cu-Sn, Cu-Sb and Sn-Sb alloys and Varkey and Padmini (1978) on Pb-Bi system. Recently ultrasonic velocity in the In-Bi system has been studied by Patil and Padmini (1980). All these workers have reported anomalies in ultrasonic velocities and elastic constants near phase transitions.

Though considerable work has been done to study other properties of In-Sn system, hardly any investigation on ultrasonic velocity and elastic properties of indium-tin appears to have been carried out. The present investigation attempts to study the effect of phase changes on ultrasonic properties in Sn rich In alloys in the concentration range 0 to 30 wt% of In.

2. Experimental details

Metals of five-*n* grade (99·999%) purity, procured from Nuclear Fuel Complex, India were used to prepare the Sn-In polycrystalline alloy specimens. The method of preparation of the samples and testing of isotropy were reported earlier (Gopinathan and Padmini 1974). The surfaces of the alloy specimens were observed using a Vicker's projection microscope after etching ($CH_3COOH : H_2O :: 1 : 1 + 1$ drop of H_2O_2 (30 vol)). Metallographic examinations were made on the alloys after polishing. The actual impurity content of the samples was estimated from density measurements by the Archmedean method, to an accuracy of 10^{-4} g cm^{-3}. Ultrasonic velocities, internal friction and density of the three specimens from the same sample showed the same values which confirmed the isotropic and homogeneous nature of the alloys. All the samples were annealed in vacuum at 100°C for 48 hr for homogenisation. Ultrasonic velocity was measured at room temperature (34·5°C) using a composite oscillator technique originally developed by Balamuth (1934). The RF output of 1 V from a Radart (type 925) signal generator was amplified to 100 V and applied to the quartz transducer. The output voltage across the resistance which is connected in series with the crystal, was applied to a Simpson (727-I) vacuum tube voltmeter. As the frequency of the signal generator is varied, the amplitude of the current which flows through the quartz varies critically with frequency (Seigel and Quimby 1936; Zacharias 1933), in the neighbourhood of certain resonance frequencies at which the amplitude passes through a maximum. If f_1 denotes one of these frequencies, then at a frequency f' slightly less than f_1, the voltage passes through a maximum and at a frequency f'' slightly greater than f_1, it passes through a minimum. If V' and V'' denote respectively the maximum and minimum values of voltage amplitude, then f_1 the resonance frequency of the transducer is given by

$$f_1 = f' + V'' \frac{(f'' - f')}{V' + V''}.$$

The transducer was cemented to the specimen by a suitable bond (Salol) and the resonance frequency of the composite system was determined (f_0). Assuming all the frequencies to be nearly equal ($\pm 10\%$), the resonance frequency of the specimen (f_r) can be obtained by the equation due to Birch (1950)

$$f_r = f_0 + (f_0 - f_1)\frac{m_1}{m_2},$$

m_1 and m_2 are the masses of the transducer and specimen respectively. The frequency was measured using an Aplab (type 1102) digital frequency counter to an accuracy of 1 in 10^6. The length of the specimen was determined using a comparator with an accuracy of 0·001 cm. An X-cut quartz rectangular bar crystal of fundamental frequency 187 kHz was used for longitudinal waves and a Y-cut cylindrical quartz crystal of fundamental

frequency 120 kHz is used for shear waves. In all the above measurements the transducer was excited at the fundamental and the specimen at the third harmonic. The velocity measurements were accurate to 0·1 %, while the modulus values were accurate to 0·2 %.

The internal friction was measured using the same technique (Markx 1951) with the X-cut quartz crystal. The amplitudes of vibration were noted for different frequencies including the resonance frequency and the resonance curve was drawn. From this curve the frequency f_{max} corresponding to maximum amplitude, and the frequencies f_1 and f_2 on either side of resonance corresponding to half the maximum amplitude were noted. The internal friction was estimated from the formula (Postnikov *et al* 1967). The accuracy of internal friction was about 6–8 %.

$$Q^{-1} = \Delta f / f_{max} \sqrt{3}, \text{ where } \Delta f = f_2 - f_1.$$

3. Results and discussion

Ultrasonic velocities were measured in Sn alloys having concentrations of 0, 3, 6, 9, 10·5, 12, 15, 18, 19·5, 21, 24, 25·5, 27 and 30 wt % of In (table 1). From the values obtained V_L, V_S and the densities, various elastic constants were estimated using the following relations:

$$E = \rho V_L^2 \qquad K = (3E - 4n)/3,$$

$$n = \rho V_S^2 \qquad \sigma = (3K - 2n)/6K + 2n,$$

where E is the Young's modulus, n the rigidity modulus, σ the Poisson's ratio, K the bulk modulus and ρ the density of the alloy. The values reported are the average ones from the specimens. The velocities and elastic constants for pure Sn agree with the values reported by Anderson (Mason 1965).

The phase diagram of In-Sn taken from Smithells (1955) and reproduced in figure 1 shows that the system Sn-In consists of the following phases: (i) δ, tetragonal, Sn rich

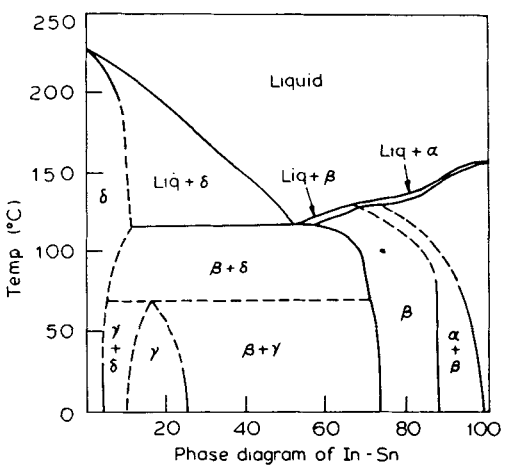

Figure 1. Phase diagram of In-Sn.

solid solution (0–4 wt% In), (ii) $\gamma + \delta$, mixed phase (4 to 10 wt% In), (iii) γ, phase $InSn_4$, which has a peritectic reaction at 205°C (Yatsenko and Golovin 1974), hexagonal (10 to 25 wt% In), (iv) $\beta + \gamma$, mixed phase (25 to 73 wt% In).

Figure 2 represents the concentration dependence of longitudinal and shear wave velocity while figure 3 presents the results on elastic constants E and n. Figures 2 and 3 reveal dips and peaks in velocities and elastic constants at specific concentrations of Indium. In the absence of phase changes in the system with increasing concentration of In, the elastic constants and the ultrasonic velocities would have decreased monotonically. The dips in V_L and V_S at 3 wt% In can be attributed to the phase changes illustrated in the phase diagram, namely, homogeneous tetragonal δ phase to intermetallic $\gamma + \delta$ phase at about 4 wt% of In. Subsequently both V_L and V_S show rapid increase until a concentration of 9 wt% of In and exhibit maxima. These maxima are followed by minima at a concentration of 12 wt% of In. From the phase diagram it is seen that a phase change is indicated at 10·5 wt% of In, from $\gamma + \delta$ (a mixed phase) to δ, a homogeneous hexagonal structured phase. Presumably, structural transformation of $\gamma + \delta$ to γ at 10·5 wt% of In is reflected as anomalies in ultrasonic velocities on either side of this concentration, namely, maxima in V_L and V_S at 9 wt%, and prominent minima at 12 wt% of In. These maxima and minima might be due to the pre- and post-transitional effects of the transformation and probably indicate the onset and completion of the structural transformation.

It is useful to compare the above results with those reported in other physical properties and correlate them. Tschirner and Wobst (1971) observed, while investigating the specific electrical resistivity and temperature coefficient of resistance in several molten In-Sn alloys, that the temperature coefficient of resistance plotted against the

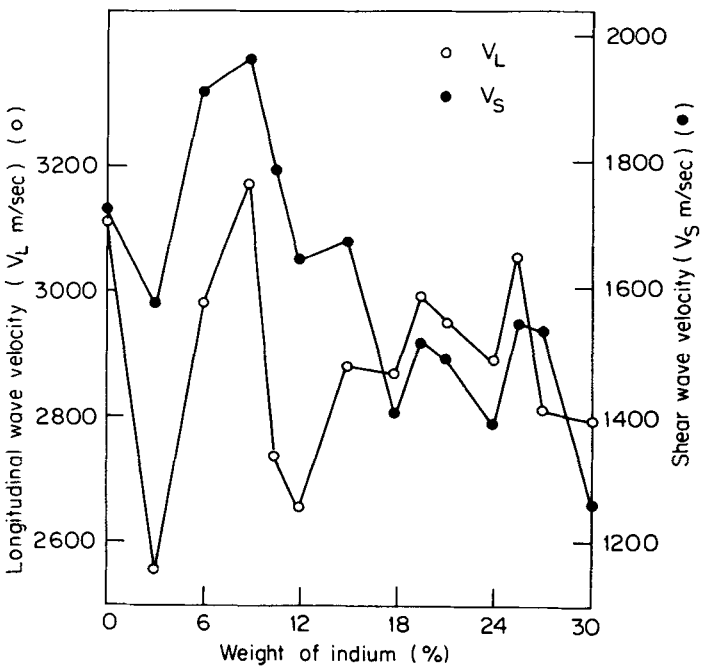

Figure 2. Concentration dependence of longitudinal wave velocity and shear wave velocity.

Table 1. Concentration dependence of ultrasonic velocities, internal friction and elastic constants in Sn-In alloys.

Weight % of In	Density ρ (g/cc)	Longitudinal wave velocity V_L (m/sec)	Shear wave velocity V_S (m/sec)	Young's modulus $E \times 10^{-11}$ (dynes/cm^2)	Rigidity modulus $n \times 10^{-11}$ (dynes/cm^2)	Internal friction $Q^{-1} \times 10^{+3}$	Bulk modulus $K \times 10^{-11}$ (dynes/cm^2)	Poisson's ratio σ
0	7·298	3112	1725	7·068	2·172	0·754	4·172	0·278
3	7·564	2552	1580	4·926	1·888	1·157	2·408	0·189
6	7·288	2981	1915	6·477	2·673	0·769	2·913	0·149
9	6·880	3170	1966	6·914	2·659	0·524	3·368	0·188
10·5	7·442	2735	1790	5·567	2·385	2·605	2·388	0·125
12	7·516	2649	1645	5·274	2·034	2·923	2·562	0·186
15	7·182	2877	1675	5·945	2·015	1·186	3·258	0·244
18	7·033	2866	1400	5·777	1·379	1·405	3·939	0·343
19·5	7·529	2987	1516	6·717	1·730	0·658	5·564	0·359
21	7·335	2944	1491	6·357	1·631	0·862	4·183	0·328
24	7·080	2882	1384	5·881	1·356	1·314	4·073	0·350
25·5	7·478	3049	1542	6·952	1·778	1·730	4·581	0·328
27	7·300	2807	1529	5·752	1·707	2·183	3·476	0·289
30	7·375	2790	1254	5·741	1·160	2·654	4·195	0·373

Temperature 34·5°C

concentration showed anomalies at concentrations of 30 at % of Sn and 90 at % of Sn. These anomalies in temperature coefficient of resistance of the molten In-Sn alloys at the above specified concentrations are presumably due to the phase transitions in the solid state namely, $\gamma+\beta$ to β (30 at % of Sn) and $\gamma+\delta$ to δ (90 at % of Sn). Further, Predel and Sandig (1970) studied the electrical conductivity in molten alloys of In-Sn system and observed anomalies in conductivity coefficients at 46 at % and 90 at % of Sn at which the intermetallic phases $\gamma+\beta$ and $\gamma+\delta$ exist in the solid state.

The measurements of thermo-EMF of alloys of the indium-tin in the liquid phase at 300, 400, 500, 600 and 630°C (Yatsenko and Golovin 1974) showed that it increased in the concentration range of 0 to 3 at % of In, exhibited a kink around 3 at % remained steady in the range of 3 to 10 at % and showed a minimum around 10 at % of In and then increased until a concentration of 70 % In. Obviously the kink around 3 at % In must be due to the transition from δ to $\delta+\gamma$ and the minimum at 10·5 at % In can be correlated to the transition $\gamma+\delta$ to γ. These workers have also investigated the viscosity and electrical resistance of these alloys and observed anomalies in these parameters around 10 % In. The peak in electrical resistance around 90 % of Sn or 10 % In is attributed to the reduction in free electron concentration. These anomalies in viscosity and electrical resistance at 10 % In concentration presumably correspond to $\gamma+\delta$ to γ transition.

The ultrasonic velocities V_L and V_S exhibit different behaviour in the concentration range of 12 to 19·5 wt % of In where V_L increases with increasing concentration of In, shows a maximum at 19·5 wt % of In, while V_S decreases initially goes through a minimum at 18 wt % and then rises to a maximum at 19·5 wt % of In. This maxima in V_L and V_S at 19·5 wt % of In are small compared to those at 9 wt % of In and 25·5 wt % of In. These anomalies in ultrasonic velocities could be due to the presence of peritectic at high temperature (205°C) at 17·4 wt % of In. It is interesting to compare this anomaly with the results of Osipenko (1970), who has investigated thermal conductivities of these alloys in the solid state as well as in liquid state at different concentrations. He has reported that an alloy containing 74·4 wt % of In exists in the solid solution region and that an alloy with 19·5 wt % of In is a two-phase mixture that becomes a homogeneous phase below 60°C. Perhaps the existence of this alloy at high temperatures, above 60°C, must have produced maximum in each of the ultrasonic velocities.

In the concentration range 19·5 wt % of In to 24 wt % of In both V_L and V_S have shown sharp decrease and exhibited minima at 24 wt % of In followed by immediate maxima at 25·5 wt % of In. A comparative study of these results with the phase diagram shows that these anomalies could be correlated to the phase transformation of γ to $\gamma+\beta$ at 24 wt % of In. Finally, after 25·5 wt % of In both V_L and V_S have shown decrease with increasing concentration of In though the decrease in V_L is sharp compared to that in V_S.

Figure 3 describes the variation of Young's modulus and rigidity modulus with increasing concentration of indium in the concentration range of 0 to 30 wt % of In. The behaviour exhibited by E and n is analogous to those of ultrasonic velocities V_L and V_S. Initially, both Young's modulus and rigidity modulus have decreased with the addition of In impurity until 3 wt % of In and exhibited dips at the same concentration, though the dip in E is more prominent than in n. The variation of lattice spacings of the solid solution of Sn with the addition of In in small concentrations has been investigated by Lee and Raynor (1954) who reported considerable decrease in a spacing and slight decrease in c spacing. The decrease in lattice spacing decreases the elastic constants.

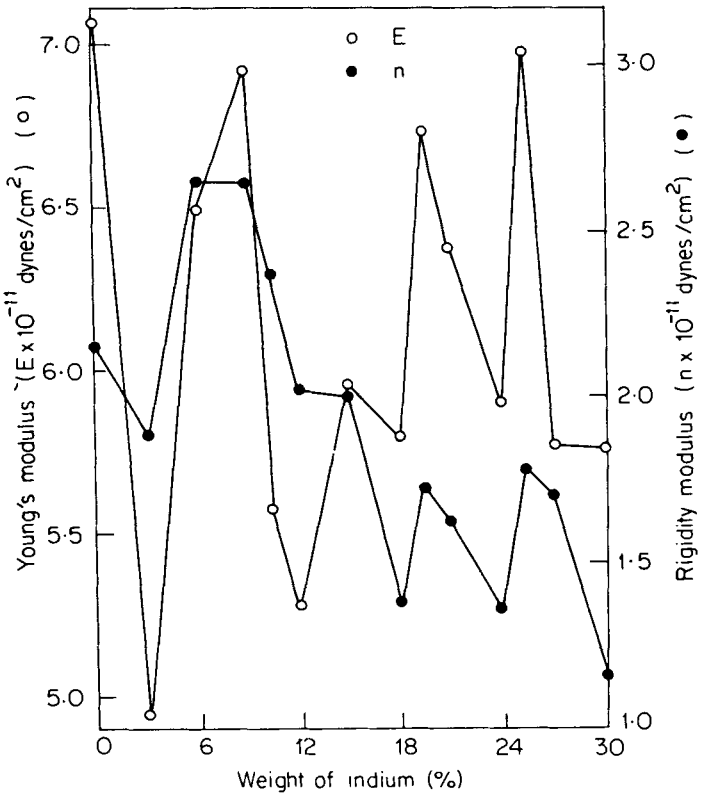

Figure 3. Concentration dependence of Young's modulus and rigidity modulus.

Further, in the solid solution range with the addition of In, the electron concentration per atom ratio decreases as In is trivalent and Sn is tetravalent; consequently the elastic constant decreases. As the atomic radii of Sn and In are nearly the same, the difference is not significant as to affect the elastic constants. Accordingly, the initial decrease of elastic constants in the concentration range of 0 to 3 wt % of In can be attributed to the combined effect of the change in lattice spacing and the change in electron concentration per atom ratio. Between 9 wt % and 12 wt % of In, both E and n have shown sharp decrease though the degree of sharpness of E is more. In the concentration range of 12 wt % to 19·5 wt % of In, E and n have shown slight increase at 15 wt % of In, but depicted prominent minima at 18 wt % of In, followed by a sharp rise at 19·5 wt % of In. This unusual minima and maxima might be attributed to the existence of this alloy as a two-phase mixture at high temperature which becomes homogeneous at temperature below 60°C. Further, in the concentration range 19·5 wt % to 25·5 wt % of In, both the elastic constants E and n have decreased and exhibited minima at 24 wt % of In followed by maxima at 25·5 wt % of In. These pairs of minima and maxima could be due to the phase transition occurring from γ to $\gamma + \beta$ around 25 wt % of In.

The variation of bulk modulus with concentration (figure 4) is somewhat similar to that observed for E or n. A prominent minimum is observed at 3 wt % of In corresponding to δ to $\delta + \gamma$ transition and prominent maxima are observed at 9 wt % of

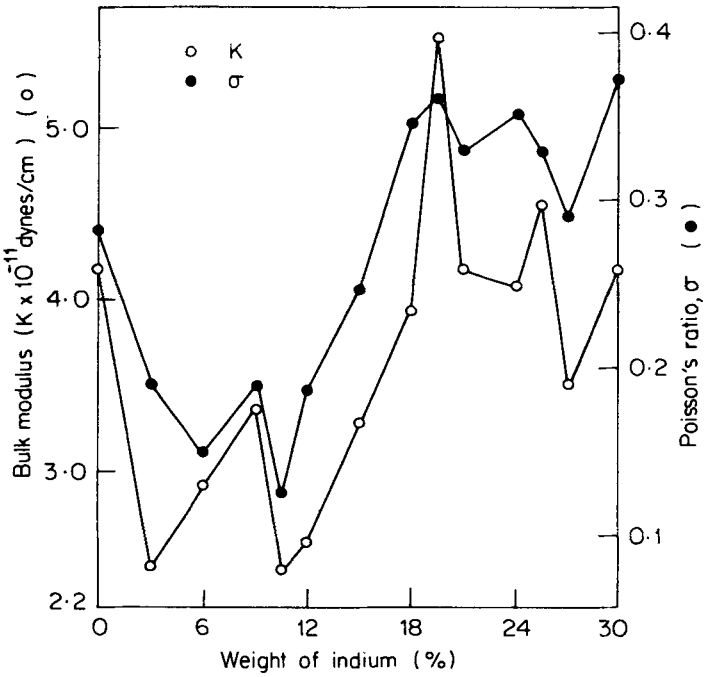

Figure 4. Concentration dependence of Poisson's ratio and bulk modulus

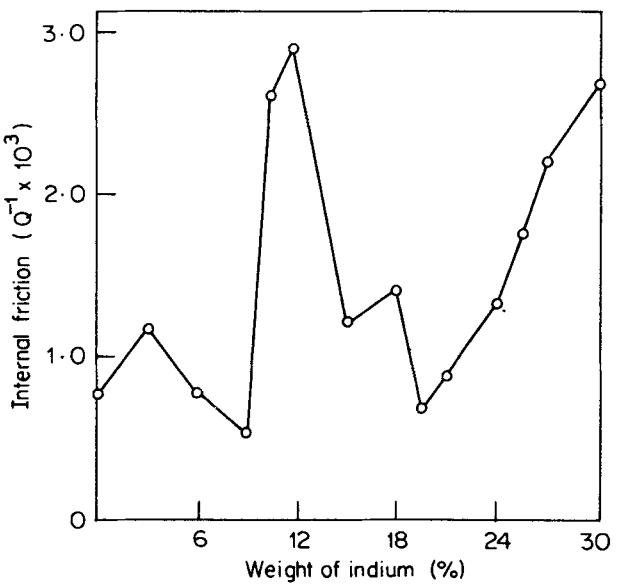

Figure 5. Concentration dependence of internal friction.

In, 19·5 wt% of In and 25·5 wt% of In corresponding to $\delta+\gamma$ to γ transition; the presence of two-phase mixture and γ to $\gamma+\beta$ transition respectively.

The variation of Poisson's ratio, also shown in figure 4, indicates a dip at 6 wt% of In instead of 3 wt% of In. Maxima in Poisson's ratio have been observed at 9 wt% of In, 19·5 wt% of In and 24 wt% of In corresponding to the already mentioned various phase changes.

Figure 5 reveals a peak at 3 wt% of In in internal friction associated with a change of phase from δ to $\gamma+\delta$. From 3 wt% of In, it decreases to a minimum at 9 wt% of In and then shows a peak at 12 wt% of In which is again associated with a phase change from $\gamma+\delta$ to γ at 12·4 wt% of In. A sharp minimum at 19·5 wt% of In could be due to the peritectic around 17·4 wt% of In. The phase change γ to $\beta+\gamma$ around 24 wt% of In did not produce any change in internal friction.

An overall study of the results definitely indicates that the ultrasonic investigations could be one of the powerful tools for investigating phase transition and hence the phase diagrams.

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