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A pre-precipitation phenomenon in the Pb–Sn alloy

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Clustering or zone formation has been observed in a number of binary systems which also undergo discontinuous precipitation, e.g. Al–Zn [1–3], Al–Cu [4–6] and Cu–Be [7, 8]. Extensive studies on discontinuous precipitation in the Pb–Sn alloys [9–12], however, do not report any clustering phenomenon in this system. While the electrical resistivity of a supersaturated solid solution decreases due to the precipitation of a solute-rich phase, formation of the clusters causes an initial increase in resistivity [13] due to the scattering of electrons by the clusters [14, 15]. The present study investigates an anomalous increase in isothermal resistivity observed by us prior to discontinuous precipitation in the Pb–Sn system.

A Pb–8.82 at % Sn alloy was prepared from high-purity lead (99.99%) and tin (99.999%). The cast billet was homogenized at 250° C for 50 h and extruded at 150° C to wire of 1 mm diameter. About 1 m length of this wire was mounted on a Bakelite sheet for resistivity measurements by the four-probe method. In all the experiments the specimen was solution-treated at 170° C for 12 h, quenched within 1 sec in a water bath at room temperature ($\sim 22°$ C), and transferred within 30 sec to water or oil baths held at the precipitation temperature T_P ($\geqslant 25°$ C) controlled to $\pm 0.5°$ C. A General Radio 1666 d.c. Kelvin bridge measuring up to $10^{-6}\,\Omega$ with an accuracy of $\pm 0.01\% + 10$ p.p.m. was used to measure the fractional change in resistivity, $\Delta\varrho/\varrho_0 = (R_t - R_0)/R_0$, where R_0 and R_t are the resistances measured after holding at T_P for the time $t = 0$ and $t = t$, respectively. In each experiment, these measurements were taken at the measuring temperature $T_M = T_P$, as well as at $T_M = -196°$ C, and naturally the isothermal treatments at T_P were interrupted from time to time by transferring the specimen into a liquid nitrogen bath for about 5 min.

An earlier resistivity study by Turnbull and Treaftis [12] on the kinetics of isothermal precipitation in the Pb–Sn alloys did not reveal any significant incubation period prior to the discontinuous precipitation. A recent investigation [16] on the present alloy has, however, shown that water quenching to room temperature ($\sim 22°$ C) prior to isothermal treatment at T_P results in an incubation period t_{incub}, the magnitude of which depends on T_P. In the resistometric study, t_{incub} at any particular T_P can be defined as the t marking the outset of R_t falling below R_0. Careful measurements of R_t at $t < t_{incub}$ reveal a small ($< 1\%$) increase in $\Delta\varrho/\varrho_0$ which reaches a maximum at $t = t_{peak}$ and then drops to zero at $t = t_{incub}$. This pre-precipitation resistivity anomaly, which is similar to those in a number of other binary systems [1–8], can be attributed to the clustering of solute atoms [13] in the present Pb–Sn alloy. Fig. 1 illustrates the typical variation of $\Delta\varrho/\varrho_0$ with time for different T_P, measured both at $T_M = T_P$ (Fig. 1a) and at $T_M = -196°$ C (Fig. 1b). In either case, the peak height $(\Delta\varrho/\varrho_0)_{peak}$, which is related to the cluster density [17, 18], decreases due to the increase in T_P, possibly due to the lower solute supersaturation at higher T_P. Moreover, t_{peak} diminishes at higher T_P due to the enhanced diffusivity at higher temperatures which quickens the rate of clustering.

For any given T_P, a comparison between the magnitude of t_{peak} measured at $T_M = T_P$ (Fig. 1a) and at $T_M = -196°$ C (Fig. 1b) shows that the former is always higher. For example at $T_P = 25°$ C, $t_{peak} = 225$ min for $T_M = T_P$, and 100 min for $T_M = -196°$ C, although the state of the sample remained identical, because the measurements were

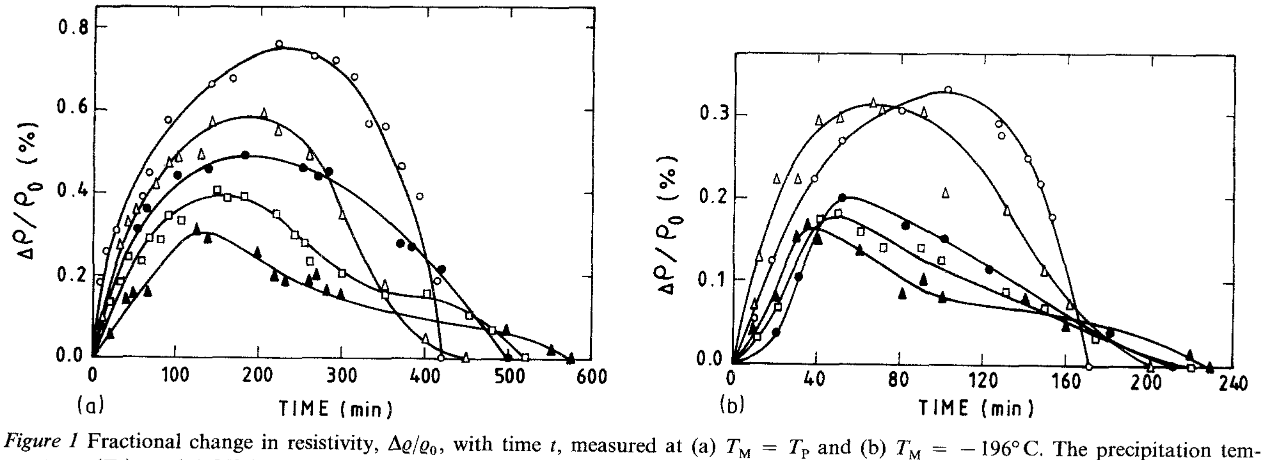

Figure 1 Fractional change in resistivity, $\Delta\varrho/\varrho_0$, with time t, measured at (a) $T_M = T_P$ and (b) $T_M = -196°$C. The precipitation temperatures (T_P) are (○) 25° C, (△) 30° C, (●) 35° C, (□) 40° C and (▲) 45° C.

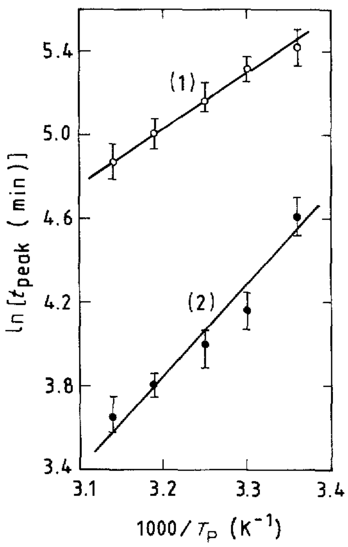

Figure 2 Plot of $\ln t_{peak}$ against $1000/T_P$. Curve 1 is obtained for $T_M = T_P$ while for Curve 2 $T_M = -196°C$.

taken in the course of the same experiment. Hence, the critical size of the clusters [14, 15, 17] associated with the resistivity peak in the present alloy seems to depend on the temperature of measurement T_M. It may be pointed out that clusters having a planar morphology (e.g in Al–Cu or Cu–Be) manifest a similar dependence of t_{peak} on T_M, while spherical clusters in Al–Zn or Al–Ag alloy do not show such interdependence [19]. The large difference (~14%) in atomic size between the lead and tin atoms may favour the planar morphology of the clusters in the Pb–Sn alloy due to strain energy considerations.

The activation energy (Q) values for the clustering in the present alloy, determined from the Arrhenius plot of t_{peak}, obtained from the measurements at $T_M = T_P$ (Curve 1 in Fig. 2) and that at $T_M = -196°C$ (Curve 2 in Fig. 2) are 22.2 and 36.5 kJ mol^{-1}, respectively. In view of the observed influence of T_M on the critical cluster size corresponding to the resistivity peak, Q derived from the measurements at a constant T_M (−196°C) gives a better estimate of the activation energy for clustering, which is 36.5 kJ mol^{-1} (Curve 2, Fig. 2). It may be noted that this value of Q is significantly lower than the lattice diffusion energy of tin in lead, i.e. 109.2 kJ mol^{-1} [11], and such a divergence is typical for the process of clustering aided by quenched-in excess vacancies [1, 20].

Finally, clustering prior to precipitation is likely to reduce the driving force for discontinuous precipitation [21]. No clustering or significant t_{incub} were observed by Turnbull and Treaftis [12], possibly due to the lower concentration of quench-in excess vacancies in their specimens, which were directly transferred to the isothermal bath at T_P following solution treatment. Further, the sensitivity of their measurements (up to $10^{-4}\,\Omega$) [12] appears inadequate for the detection of the small magnitude of $\Delta\varrho/\varrho_0$ (cf. Fig. 1) associated with clustering in the Pb–Sn alloys.

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