Resistometric determination of the metastable solvus for discontinuous precipitation

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The formation of solute-depleted matrix phase and precipitates, as a duplex product, behind a boundary advancing into a supersaturated matrix is termed discontinuous precipitation (DP) [1]. The chemical driving force provided by the solute supersaturation has a profound influence on the kinetics of DP [2–5]. A critical amount of solute supersaturation seems to be necessary to keep the reaction fronts in motion and to sustain the discontinuous reaction [6–8]. Consequently, for any given alloy composition there must be a temperature T_{DP} ($< T_E$, the equilibrium solvus temperature) above which DP should cease to occur. The conventional method of determining the metastable solvus for DP from microstructural observations [9–11] is usually well suited to systems in which the transformations can be frozen at the viewing temperatures. An alternative method based on a resistivity technique has been applied in the present study on the Pb-Sn system for determining its metastable solvus for DP. The Pb-Sn system has certain attractive features. The lead-rich alloys in this system undergo DP at about room temperature [10, 12, 13]. The formation of one-dimensional lamellar product through repeated nucleation on dislocations in these alloys has not yet been detected [1, 14]. Moreover, the discontinuous transformation in this system does not seem to encounter any significant competition from the continuous mode of precipitation [13]; although clustering before discontinuous reaction in Pb-Sn alloys has recently been reported [15, 16].

The compositions of three binary alloys (A, B and C) prepared from high-purity lead (99.99%) and tin (99.999%) are listed in Table I. The as-cast alloy billets (diameter 10 mm) were homogenized at 250° C for 50 h. Wires of diameter 1 mm were extruded at 160° C for the resistivity measurements. Plates about 25 mm × 20 mm × 1 mm needed for the metallographic studies were cut from hot rolled alloy strips. In all of the experiments the alloys were solution treated in an oil bath at 170° C for 12 h, quenched in water at about 22° C within 1 sec, and transferred within 30 sec into water or oil baths held at the precipitation temperature T_P controlled to within ± 0.5° C. The instantaneous resistance R_t of the alloy specimens precipitated for time t was measured at T_P by means of a General Radio 1666 d.c. Kelvin bridge measuring up to $10^{-6} \, \Omega$. The change in resistance caused by the transformation at T_P is $\Delta R_t = R_0 - R_t$, where $R_0 = R_t$ at $t = 0$. The ΔR_t was monitored until the resistance diminished to R_f, which is defined in a manner similar to that of Turnbull and Treaftis [12], i.e., $R_f = R_t$ when $(dR_t/dt) \leqslant 0.04 \, (dR_t/dt)_{max}$. The DP seems to terminate at $R_t = R_f$ and, accordingly, the maximum change in fractional resistance caused by the transformation is $\Delta R_f/R_0 = (R_0 - R_f)/R_0$.

For metallographic examinations the plate samples were transferred to liquid nitrogen immediately after the isothermal treatment at T_P. The specimens were then electropolished at $-40° C$ in a solution of 6% perchloric acid in ethanol, using a stainless steel cathode at a d.c. potential of 30 V.

At any given T_P, ΔR_t approaches its limiting value ΔR_f, the magnitude of which depends on the extent of
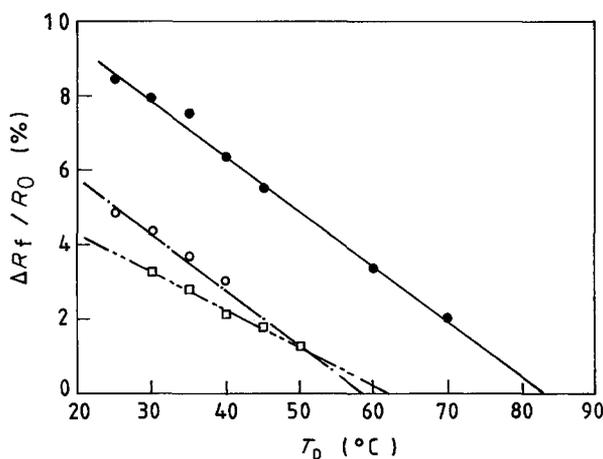

Figure 1 Plots of $\Delta R_f/R_0$ against T_P for alloys (O) A, (□) B and (●) C. Extrapolation of these plots to $\Delta R_f/R_0 = 0$ yields T_{DP} for each alloy.
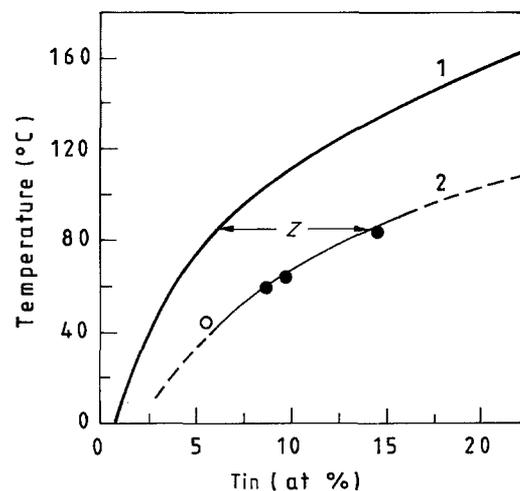

Figure 2 (Curve 1) The equilibrium solvus of tin in lead [10]. The full portion of curve 2 shows the metastable solvus for discontinuous precipitation obtained from experiments, and the broken portion represents extrapolation of the experimental data according to $\Delta C_{DP}/C_0 = 0.55$ (see text). $Z = \Delta C_{DP}$ for alloy C. (●) Present work and (O) from [10].
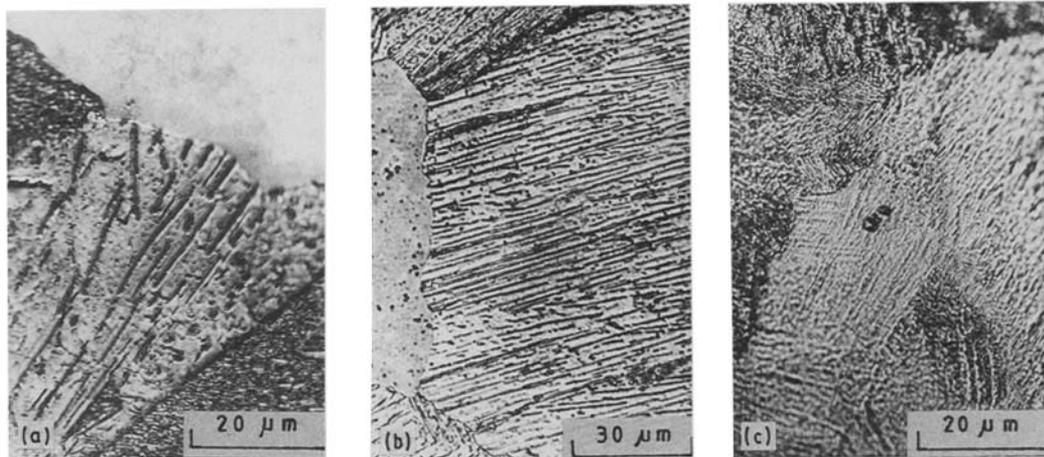
Figure 3 Microstructures of (a) alloy A, (b) alloy B and (c) alloy C, following precipitation at 35°C. The interlamellar spacing in alloy B is much smaller than that in alloy A. The spacing in alloy C is not resolved by light microscopy.

phase separation, as well as on the measuring temperature T_P. At $T_P = T_{DP}$, however, ΔR_f becomes zero irrespective of the measuring temperature. Therefore, if measurements are taken at temperatures where the phase separation takes place predominantly by a discontinuous mode, a plot of $\Delta R_f/R_0$ against T_P extrapolated to $\Delta R_f/R_0 = 0$ should yield T_{DP}. The values of T_{DP} for the present alloys obtained in this manner from the plots in Fig. 1 are summarized in Table I.

The variation of T_{DP} with the initial solute content C_0 is shown in Fig. 2, which essentially yields a portion of the metastable solvus for DP. At any given T_P the horizontal distance of separation between the equilibrium and the metastable solvus ΔC_{DP} (illustrated for alloy C in Fig. 2) signifies the minimum solute supersaturation necessary to initiate or sustain the DP. The ΔC_{DP} of alloys A, B and C are listed in Table I and reveal that its magnitude increases with C_0. Furthermore, the interlamellar spacings in the precipitate colonies become distinctly finer with tin enrichment in alloys (cf. Fig. 3). Perhaps the larger interfacial energy of the transformation product in higher-tin alloys calls for more driving force via higher ΔC_{DP}. Nevertheless, microstructural examination of the present alloys confirms the absence of DP above the T_{DP} estimated through resistivity experiments (cf. Table I).

Tu and Turnbull [10] defined a temperature T_{Cr} below which discontinuous dissolution fronts do not advance. The T_{Cr} reported in [10] for a Pb–Sn alloy is shown in Fig. 2. Theoretically, T_{Cr} should be slightly higher than T_{DP}, due to the transformation hysteresis. If this hysteresis is small, $T_{Cr} \approx T_{DP}$, and then the ΔC_{DP} of the alloy used in [10] can be readily estimated. The results for alloy T in Table I obtained in this

manner also manifest a reduction in ΔC_{DP} with lowering of C_0. It is interesting to note that the $\Delta C_{DP}/C_0$ of all of the alloys in Table I lie within the close range 0.53 to 0.57. The broken curve in Fig. 2 represents the extrapolation of experimentally determined metastable solvus according to $\Delta C_{DP}/C_0 = 0.55$.

The statistical nature of the proposed method can make it relatively free from experimental errors compared with the conventional metallographic method of estimating T_{DP} [9–11], especially when the discontinuous reaction is complete within a few minutes (e.g. in alloy C [16]). For determination of T_{DP}, the use of the dimensionless parameter $\Delta R_f/R_0$ (see Fig. 1) is preferred over ΔR_f, particularly where the reaction does not reach completion due to some trace additions [16]. In Fig. 1, however, why the magnitude of $\Delta R_f/R_0$ for alloy B is smaller than for alloy A at several T_P is not fully understood, because alloy B is richer in tin. It is possible that R_0 is influenced by the cluster formation [15, 16] during quenching. Nevertheless, theoretical considerations suggest that there is a range of temperature beyond which the continuous mode of precipitation may compete with the discontinuous reaction in alloys [17]. The present extrapolation method attempts to minimize the uncertainty in the evaluation of T_{DP} caused by such overlapping transformation processes.

TABLE I C_0, T_{DP}, ΔC_{DP} and $\Delta C_{DP}/C_0$ for the Pb–Sn alloys

Alloy	C_0 (at % tin)	T_{DP} (°C)	ΔC_{DP} (at % tin)	$\Delta C_{DP}/C_0$
A	8.82	58.5	5.02	0.57
B	9.87	62	5.60	0.57
C	14.57	83	7.96	0.55
T	5.50	44*	2.64	0.55

*Obtained from the data in [10], after assuming $T_{DP} \approx T_{Cr}$.

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