Department of Metallurgical Engineering,[1]
Indian Institute of Technology, Kharagpur[1]

A Resistometric Study of Migrating Boundary Characteristics

in Pb-Sn Alloys

By

I. MANNA and S.K. PABI

The structure and diffusivity of mobile boundaries (MBs) vis-a-vis static boundaries (Sbs) have evoked considerable controversy in recent times. While metallographic observations on few boundaries at the reaction temperatures (say, method M1) report diffusivity in the MBs 2 to 4 orders of magnitude higher than in the SBs /1, 2/, measurements of the boundary velocities at ambient temperature following periodic freezing of the reaction front by quenching (method M2) usually indicate identical diffusivities in both /3 to 6/. Investigations by method M1 are relatively poor in statistics and the boundaries under observation can be intrinsically faster moving or having higher diffusivity /7, 8/. On the other hand, periodic arrest of the boundary movement in M2 may change its (postulated) mobile configuration into a static one /9/.

In the present investigation, the effects of periodic arrest of the MBs (by pulse heating/cooling) on the isothermal discontinuous precipitation kinetics have been studied by a bulk-averaging technique, namely, electrical resistivity. This would be a test for the validity of method M2 and also it may point out whether MBs, on an average, have different structural characteristics than SBs.

Two Pb-Sn alloys containing 8.82 (alloy A) and 14.65 (alloy B) at% Sn were prepared from high purity Pb(99.99%) and Sn(99.999%). Cast billets were homogenized at 523 K for 50 h and extruded at 433 K to wires of 1 mm diameter. For resistivity measurements 1 m long wires were mounted on bakelite sheets, solution treated at 443 K for 12 h, quenched in water, and isothermal precipitation at $T_p \gtreqless 298$ K was carried out in oil and water baths controlled to ± 0.5 K. After precipitation at T_p for time t, the resistance (R_t)
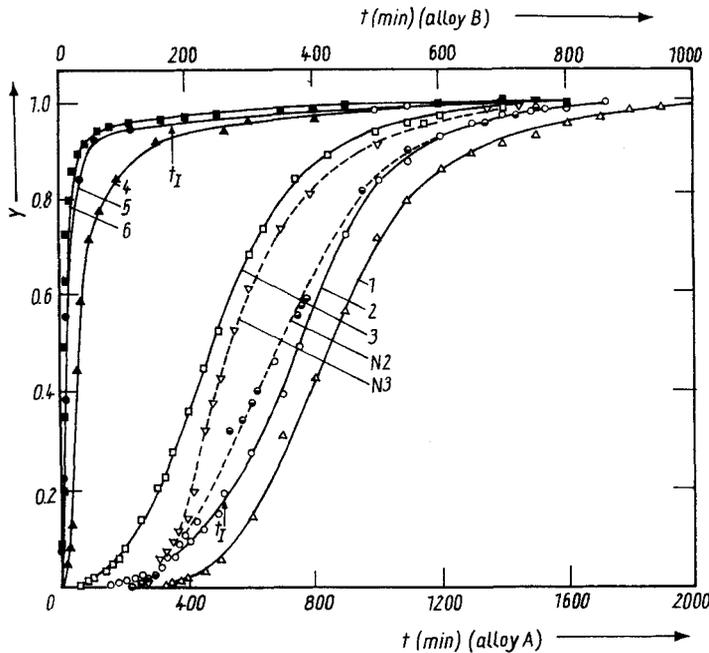
1) Kharagpur 721302, India.

Fig. 1. Precipitation isotherms of alloy A at T_p = (1) 318 K, (2) 308 K, (3) 298 K, and alloy B at T_p = (4) 363 K, (5) 308 K, (6) 298 K. Curves N2 and N3 are precipitation isotherms of alloy A at T_p = 308 K and 298 K, respectively, but measured at T_M = 77 K. Arrows on (2) and (5) indicate t_I for pulse treatments (see text)

measured at a temperature T_M by a General Radio 1666 dc Kelvin bridge yields the fraction transformed Y from the relation /10/

$$Y = \frac{\Delta R_t}{\Delta R_{max}} \; ; \quad \Delta R_t = R_o - R_t \; ; \quad \Delta R_{max} = R_o - R_f \, , \qquad (1)$$

where $R_o = R_t$ at t = 0, and $R_f = R_t$ when $(dR_t/dt) < 0.04 \, (dR_t/dt)_{max}$.

Precipitation isotherms (1) to (6) in Fig. 1 measured at $T_M = T_P$ support the two stage reaction mechanism in Pb–Sn alloys /10/. It is known that the rapid reaction rate in stage I (Y $\lesssim$ 0.75) is caused by the discontinuous mode of precipitation, while the residual supersaturation between the interlamellar spaces is relieved by volume diffusion in stage II /11/. Due to its higher degree of supersaturation, precipitation rates in alloy B are faster, the transition from stage I to stage II is more well defined, and the incubation period

is nearly zero as compared to those in alloy A (Fig. 1). Precipitation rates in both alloys decrease with increasing T_P ($\gtrsim 298$ K). The temperature T_{DP}, above which discontinuous precipitation ceases, has been determined by extrapolating the ΔR_{max} versus T_P plot to $\Delta R_{max} = 0$. T_{DP} is 333 K for alloy A and 381 K for alloy B. It may be pointed out that the degrees of solute supersaturation ΔC_{DP} at T_{DP} calculated from the equilibrium solubility data /12, 13/ are nearly identical for alloys A and B, which are 4.72 and 4.65 at% Sn, respectively. Perhaps, the driving force ($\sim \Delta C_{DP}$) required to keep the discontinuous reaction fronts in motion /14/ is not markedly dependent on the alloy composition.

The isothermal precipitation kinetics in alloy A measured with the same specimen at $T_M = 77$ K show significant divergence from those recorded at $T_M = T_P$ (cf. isotherms N2 versus 2, N3 versus 3; Fig. 1), which casts some doubt over the validity of method M2. In order to simulate M2 type measurements in resistometric studies, the isothermal precipitation at (T_P=) 308 K has been interrupted in a number of experiments at a given instant $t = t_I$ by means of pulse heating/cooling for a short while (t_D) to another temperature T_I, as per following schedule: $T_I = 348$ K ($t_D = 1, 2$ min), 333 K (1, 2, 3 min), 318 K (1, 2, 5 min), 233 K (10 min), 77 K (15 min) for alloy A; and $T_I = 383$ K ($t_D = 1, 2$ min), 343 K (1, 2, 3 min), 318 K (1, 2 min), 274 K (1, 5 min), 77 K (10 min) for alloy B. For alloy A precipitation has been interrupted in stage I at $t_I \approx 510$ min, while alloy B has been pulse treated in stage II at $t_I \approx 180$ min (cf. curves 2 and 5, Fig. 1). Further, for $T_I < T_{DP}$, t_D is short enough to preclude any precipitation at T_I, that requires fresh nucleation of lamellae /15/. These experiments essentially manifest that (i) the precipitation rates just before and after pulse treatment are identical and (ii) the resistance of the specimen increases by an amount δR (i.e. ΔR_t in (1) diminished) due to such pulse treatments (e.g. in Fig. 2). Perhaps, the deviation of curves N2 from 2 or N3 from 3 in Fig. 1 can be attributed to δR, which affects Y via equation (1). The results also reveal that δR is more pronounced in stage I (i.e. in alloy A) than in stage II (i.e. in alloy B) and its magnitude usually increases with $\left| T_I - T_P \right|$ (cf. Fig. 2). It may be postulated that δR originates from the thermal stresses in pulse treatments, e.g., the stress can bring about decohesion at some precipitate-matrix interfaces.
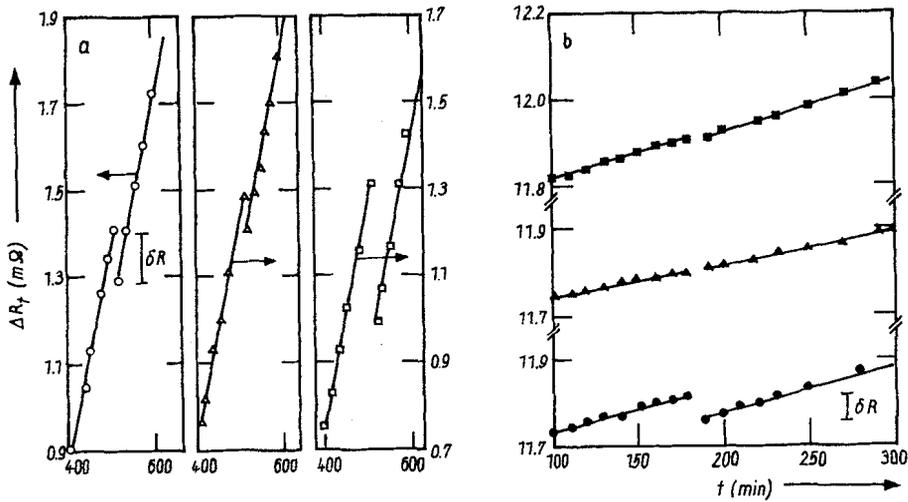
Fig. 2. Effect of pulse heating/cooling on precipitation isotherms; a) alloy A: T_I = 348 K, t_D = 1 min (O); T_I = 318 K, T_D = 5 min (△); T_I = 77 K, t_D = = 15 min (▣); b) alloy B: T_I = 383 K, t_D = 1 min (●); T_I = 318 K, t_D = = 1 min (▲); T_I = 77 K, t_D = 10 min (■)

Motion of the MBs in stage I (i.e. in alloy A) is arrested during the pulse heating interval t_I /15/, when MBs can relax (except at T_I = 77 K) /7/ to their perceptible static configurations. In this case, a decrease in the rate (dR_t/dt) following pulse treatments is expected /15/, if the incoherent reaction fronts have to revive their mobile configurations /9/. Since this is not borne out by the experiments, the present study does not evidence any diversity between the structure of MBs and SBs. Finally, these results also indicate that the metallographic measurements (which are insensitive to thermal stress effects) of the discontinuous reaction kinetics in a Pb–Sn alloy by method M2 may not be in error; although some structural changes (evident from δR) may result due to repeated quenching in M2.

References

/1/ K. SMIDODA, W. GOTTSCHALK, and H. GLEITER, Acta metall. 26, 1833 (1978).

/2/ M. HILLERT and G.R. PURDY, Acta metall. 26, 333 (1978).

/3/ J. OBERSCHMIDT, K.K. KIM, and D. GUPTA, J. appl. Phys. 53, 5672 (1982).

/4/ C.R.M. GROVENOR, Scripta metall. 16, 317 (1982).

/5/ W. GUST, M.B. HINTZ, R. LUCIC, and B. PREDEL, in: Phase Transformation in Solids, Ed. T. TSAKALAKOS, Mater. Res. Soc. Symp. Proc. 21, 513 (1984), North Holland Publ., Co. Amsterdam 1984.

/6/ W. GUST, J. BEUERS, J. STEFFEN, S. STILTZ, and B. PREDEL, Acta metall. 34, 1671 (1986).

/7/ R.W. BALLUFFI, in: Diffusion in Crystalline Solids, Ed. G.E. MURCH and A.S. NOWICKI, Academic Press, New York 1984 (p. 319).

/8/ W. GUST, M.B. HINTZ, A. LODDING, H. ODELIUS, and B. PREDEL, Acta metall. 30, 75 (1982).

/9/ R. WIRTH and H. GLEITER, Acta metall. 29, 1825 (1981).

/10/ D. TURNBULL and H.N. TREAFTIS, Acta metall. 3, 43 (1955).

/11/ W. GUST, Phase Transformations, Vol. 1, Inst. Metallurgists, London 1979 (p. II).

/12/ J.W. CAHN and H.N. TREAFTIS, Trans. AIME 218, 376 (1960).

/13/ Y.C. LIU and H.I. AARONSON, Acta metall. 16, 1343 (1968).

/14/ M. HILLERT, Mechanism of Phase Transformation in Crystalline Solids, Inst. of Metals, London 1969 (p. 231).

/15/ K.N. TU and D. TURNBULL, Acta metall. 15, 1317 (1967).