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

Effect of Ternary Addition
on Discontinuous Precipitation Kinetics in Pb–Sn Alloys

By

I. Manna and S. K. Pabi

An attempt is made to identify the precise origin of the effect of alloying additions on the discontinuous precipitation kinetics with trace additions of Sb (0.26 at%) and Cd (0.16 at%) to a Pb–9.87 at% Sn alloy. Extensive resistometric measurement of the precipitation kinetics, duly substantiated by microstructural observations at appropriate stages, evidences that the drastic reduction (> 50%) in the reaction rate can be attributed neither to the atomic size nor the valence electron difference caused by the Sb or Cd addition. Segregation of the ternary elements at the sweeping reaction fronts appears to retard and ultimately terminate the discontinuous precipitation process at a premature stage.

Es wird versucht, die genaue Ursache für den Einfluß von Legierungszusätzen auf die diskontinuierliche Präzipitationskinetik der Pb 9,87 At% Sn-Legierung mit Zusätzen von Sb (0,26 At%) und Cd (0,16 At%) aufzufinden. Ausführliche Widerstandsmessungen zusammen mit entsprechenden Mikrostrukturuntersuchungen zeigen, daß die drastische Reduktion (> 50%) der Reaktionsrate weder auf die Atomgröße noch auf die Valenzelektrondifferenz infolge Sb- oder Cd-Zusatz zurückgeführt werden kann. Möglicherweise wird durch die Segregation des dritten Elements an der fortschreitenden Reaktionsfront der diskontinuierliche Präzipitationsprozeß in einem frühzeitigen Stadium zuerst verzögert und schließlich gestoppt.

1. Introduction

Discontinuous precipitation (DP) is deleterious to the mechanical, physical, and chemical properties of a large number of commercially important alloys [1, 2]. Addition of alloying element has been one of the most effective means for complete or partial suppression of such undesirable reaction [1]. Alloying additions may interfere with the nucleation event by changing the precipitate characteristics and/or boundary properties. On the other hand, segregation of the added element at the reaction front (RF) or interlamellar spaces may significantly alter the DP growth kinetics. Earlier studies have attempted to correlate the influence of alloying additions on DP with the segregation behaviour of the ternary element [1, 3 to 5]. In this connection, the difference in atomic size [1, 4, 6 to 8] and valence electron number [1, 8 to 11] between the solvent and ternary vis-a-vis that between the solvent and solute elements have also been considered to be important factors. However, a systematic effort to identify the precise origin of the effect of ternary addition on DP is still wanted [1].

Pb–Sn is one of the earliest and most well-documented systems for the DP studies [12 to 18]. However, no investigation on the role of a ternary element in Pb–Sn alloys has been reported so far. Addition of trace amounts of Sb and Cd to a Pb–Sn alloy may significantly change the valence electron difference (in opposite senses) without effecting any considerable atomic size mismatch in the ternary alloys. Effects of such Sb and Cd

[1]) Kharagpur 721 302, India.

additions, if any, should indicate whether the valence electron difference alone may change the DP kinetics provided Sb and Cd exhibit opposite influences. On the other hand, absence of any noticeable effect would clarify that the atomic size difference is essential to control the DP reaction by ternary addition. Therefore, the present study aims to investigate which of the existing theories may adequately explain the effect of ternary addition on the DP kinetics.

2. Experimental

A Pb–9.87 at% Sn alloy was prepared from high purity Pb and Sn by melting and casting in an evacuated pyrex tube. Measured amounts of a Pb–17.5 at% Sb master alloy and pure Cd were remelted separately with the Pb–9.87 at% Sn alloy in a similar manner to prepare the Pb–Sn–Sb and Pb–Sn–Cd ternary alloys containing 0.26 at% Sb and 0.16 at% Cd, respectively. The alloys were homogenized at ˙523 K for 50 h. About 1 m long wires, hot extruded at 433 K from 8 mm diameter ingots, were mounted on bakelite sheets to form four-probe samples for the resistivity measurements. Thin strips of approximately 1 mm thickness were also prepared by rolling with intermediate annealing at 343 K for metallographic studies. Prior to every isothermal precipitation at the temperature T_p, the samples were solution treated in oil bath at 433 K for 12 h, quenched in distilled water (298 K), and transferred to a water bath controlled within ± 0.5 K. After precipitation at $T_p \geqq 298$ K for time t_p, the instantaneous resistance R_t was recorded with a General Radio 1666 DC Kelvin bridge to yield the fractional change in resistivity, $\Delta R_t/R_0$, as follows:

$$\frac{\Delta R_t}{R_0} = \frac{R_0 - R_t}{R_0}, \tag{1}$$

where $R_0 = R_t$ at $t_p = 0$. R_t values have been monitored till $R_f = R_t$ when $(dR_t/dt_p) \leqq 0.04 \ (dR_t/dt_p)_{max}$ so that R_f signifies the practical end of the DP process [16].

For metallographic studies at appropriate stages of the isothermal precipitation, thin strips were electropolished with a 6 vol% solution of $HClO_4$ in ethanol at 233 K with 30 V (dc). The volume fraction transformed, Y_M, was estimated by the point counting method on more than 15 fields of observation with a Versamet-2 microscope.

3. Results

Fig. 1a reveals the variation of $\Delta R_t/R_0$ as a function of t_p at $T_p = 308$ K for both the binary and ternary alloys. Microstructural evidences (i.e. volume fraction transformed, Y_M), superimposed on the reaction isotherms in Fig. 1a, substantiate that the reaction kinetics determined by resistivity are truly representative of the DP rate in the present alloys. The reaction rates in both the Sb and Cd added alloys are considerably lower than that in the binary Pb–Sn alloy. The reduction in precipitation kinetics assumes a significant proportion with the progress of the reaction. Similar features have also been observed at $T_p = 323$ (Fig. 1b), 318, 313, and 303 K. Fig. 2 provides a direct comparison of the extent of the DP reaction in terms of the factor $\Delta R_f/R_0$ as a function T_p, indicating perhaps that the effect of ternary addition is more pronounced at lower T_p. It has already been noted that DP in the ternary alloys remains incomplete by more than 50% in comparison to that in the binary alloy (Fig. 1). The extent of retardation and ultimately suppression of the precipitation
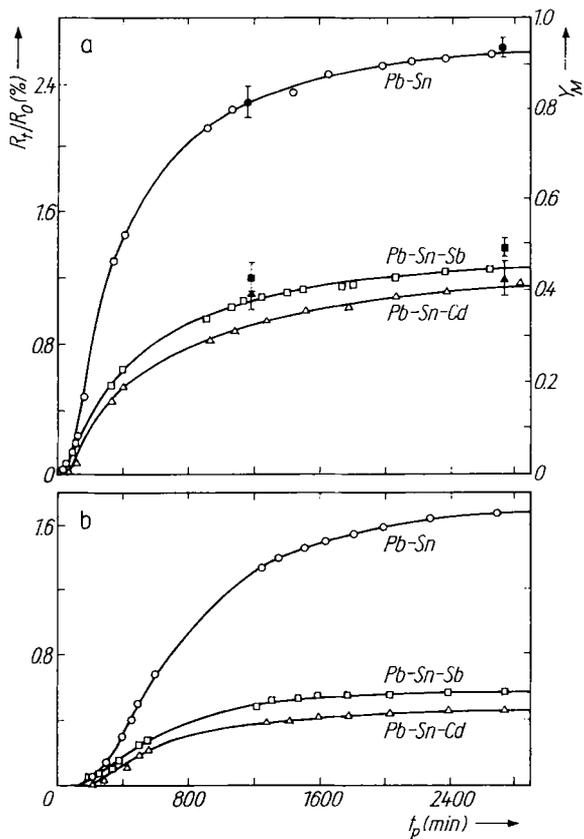
Fig. 1. Variation of $\Delta R_t/R_0$ as a function of t_p (open symbols) for the binary Pb-Sn and ternary Pb-Sn-Sb and Pb-Sn-Cd alloys at a) $T_p = 308$ and b) 323 K. Filled symbols represent the metallographic estimation of the volume fraction transformed (Y_M) at predetermined t_p

event is evident in Fig. 3, where about 50% of the supersaturated matrix remains untransformed even after $t_p = 7$ days at $T_p = 308$ K for the Cd containing ternary alloy. It is relevant to mention that the highest temperatures for DP (T_{DP}) in the present alloys, derived by extrapolating $\Delta R_f/R_0$ to $\Delta R_f/R_0 = 0$ in Fig. 2 [16], are essentially the same for both the binary and ternary alloys. Apparently, the DP reaction mechanism remains
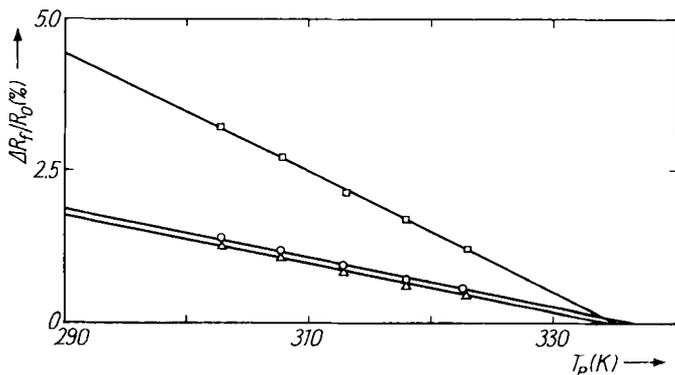

Fig. 2. Change in $\Delta R_f/R_0$ as a function of T_p for the □ Pb-Sn, ○ Pb-Sn-Sb, and △ Pb-Sn-Cd alloys. Extrapolation to $\Delta R_f/R_0 = 0$ refers to the highest temperature for DP (T_{DP}) [16]
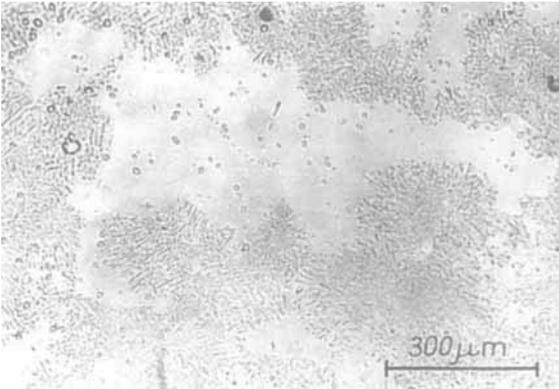
Fig. 3. Optical microstructure showing more than 50% of the matrix phase remaining untransformed at $T_p = 308$ K after $t_p = 7$ days for the Pb Sn–Cd alloy

unaltered in the ternary alloys despite the considerable reduction in the growth kinetics due to Sb and Cd additions. It is significant to note, however, under comparable conditions DP initiates at similar instances of time in both the binary and ternary alloys (Fig. 1). Therefore, the effect of the ternary addition appears to be confined mainly to the growth rather than to the nucleation stage of the reaction in the present alloys.

4. Discussion

The atomic diameters of Sn (0.3022 nm), Sb (0.2903 nm), and Cd (0.2979 nm) are nearly equal to each other and are much smaller than that of Pb (0.3499 nm) around room temperature [19]. Therefore, the matrix strain arising out of the atomic size difference due to the trace additions (<0.3 at%) of Sb and Cd to the binary alloy may be negligible. Extrapolation of the high temperature diffusion data to 298 K reveals that the bulk diffusion rate of Sb (1.36×10^{-21} m^2 s^{-1}) or Cd (9.91×10^{-21} m^2 s^{-1}) [19] is two to three orders of magnitude larger than that of Sn ($\approx 10^{-24}$ m^2 s^{-1}) [20] or Pb (1.35×10^{-23} m^2 s^{-1}) [20] in Pb matrix. Hence, redistribution of Sb or Cd through the migrating RF during DP in the ternary alloys is unlikely to be the slowest step of the precipitation process. Moreover, large scale partitioning of the trace elements between the matrix and precipitate phases is not expected, because the solubility limits of Sb or Cd in Pb as well as in Sn are about an order of magnitude larger than the amounts added in the present ternary alloys [21]. On the other hand, the valencies of Sb ($=5$) and Cd ($=2$) are different from the valency of the solvent Pb ($=2$) or the principal solute element Sn ($=4$) [19]. As a result, the ternary additions of Sb and Cd cause positive and negative deviations, respectively, in the valence electron difference with respect to the solute–solvent valence electron difference in the binary alloy. However, the drastic change in the reaction kinetics in both ternary alloys in comparison to the binary alloy is in the same direction, i.e. precipitation rates are decreased by about 50% in both ternary alloys (Fig. 1). Therefore, the present investigation appears to suggest that neither the solute–solvent atomic size mismatch factor [1, 4, 6 to 8] nor the change in valence electron difference [1, 8 to 11] could account for the observed reduction in the DP kinetics due to trace additions of Sb or Cd to the Pb–Sn alloy.

As a possible explanation for the retardation of the precipitation kinetics due to ternary additions, it has been proposed [22] that ternary elements may segregate and tie up the potential nucleation sites like steps or ledges on the grain boundaries. This is unlikely in

the present case because the incubation period for precipitation initiation in both the binary and ternary alloys remains effectively the same at all T_p (Fig. 1). Also, extensive metallographic investigation during the growth stage does not reveal any large scale de-activation of the nucleation sites like grain boundaries in the ternary alloys. Therefore, the effect of ternary additions on the nucleation stage seems unlikely in the present case.

Fig. 1 shows that the reduction in the reaction rate due to trace addition of Sb or Cd becomes more evident with the progress of the reaction. In addition, the extent of precipitation in the ternary alloys seems appreciably lower ($<50\%$) in comparison to that in the binary alloy (Fig. 2). Careful scrutiny of the microstructures also corroborates that a considerable area of the matrix remains untransformed even after prolong (>7 days) isothermal precipitation at 308 K (Fig. 3). Hence, the increasing retardation of the reaction kinetics cannot be attributed to the edge-impingement of the advancing RFs during the growth stage of the DP colonies.

While Sb and Cd affect the overall precipitation kinetics in a similar fashion, i.e. the reaction rate (Fig. 1) as well as the extent of the precipitation (Fig. 2) are diminished by more than 50% as compared to that in the binary alloy, the effects are more pronounced at lower T_p (Fig. 2) and with the progress of the reaction (Fig. 1). It is well known that the extent of grain boundary segregation increases with the decrease in temperature due to thermodynamic reasons [23]. Grain boundary segregants may raise the activation energy, thereby, reduce the boundary diffusion rate of the solute atoms [24]. If the transformation tends to maximise the rate of decrease in free energy, a reduction in the interlamellar spacing may be expected in order to partially compensate for any reduction in the boundary diffusion rate caused by the trace addition. However, such decrease in interlamellar spacing is not evidenced in the present investigation. On the contrary, interlamellar spacing in the ternary alloys are apparently somewhat coarser (Fig. 4b and c) in comparison to that in the binary alloy (Fig. 4a) under comparable conditions of precipitation.

It is well established that the impurities in small concentration can markedly retard the boundary migration rate in high purity Pb by exerting a drag on the boundary [3, 25, 26].
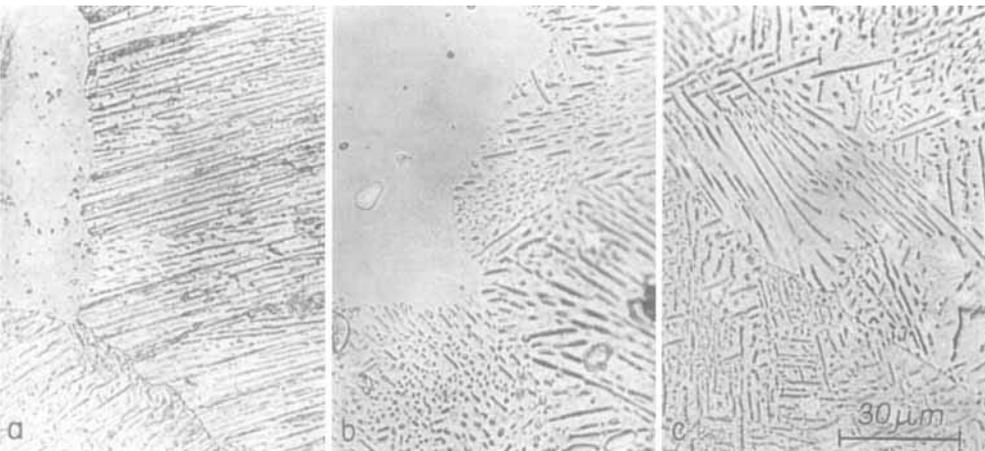

Fig. 4. Optical micrograph presenting a comparison of the interlamellar spacing in the a) Pb Sn, b) Pb–Sn–Sb, and c) Pb Sn Cd alloys after DP at $T_p = 308$ K for $t_p = 850$ min

The remarkable effects of Sb and Cd on the DP kinetics may be explained by a similar mechanism involving gradual adsorption of the impurity atoms (i.e. trace additions) at the moving RF as it sweeps through the untransformed matrix. Under such circumstances, the RF moves at a rate at which the solute atmosphere can migrate [25, 26]. In the wake of such inhibited boundary movement, a coarser interlamellar spacing, as may be evident from Fig. 4b and c, is expected because more time is available for the solute redistribution through the boundary.

5. Conclusion

Trace addition of Sb (0.26 at%) or Cd (0.16 at%) strongly retards the DP reaction kinetics in the Pb–Sn alloy. The reason for such drastic reduction in the reaction rate cannot be attributed to the size factor or the change in valence electron difference effects. However, the effects can be best explained by anticipating marked segregation of the ternary elements giving rise to substantial solute-drag at the moving RFs, and ultimately terminating the boundary migration, and hence, the DP reaction itself, at a premature stage.

References

[1] D. B. WILLIAMS and E. P. BUTLER, Internat. Met. Rev. 3, 153 (1981).
[2] M. FRIESEL, I. MANNA, and W. GUST, J. Physique 51, Cl-381 (1990).
[3] K. LUCKE and K. DETERT, Acta metall. 5, 628 (1957).
[4] E. HORNBOGEN, Metallurg. Trans. 3A, 2717 (1972).
[5] M. CHIGASAKI and K. SEONO, J. Inst. Metals 39, 817 (1975); 40, 419 (1976).
[6] H. BÖHM, Z. Metallkd. 52, 518 (1961).
[7] B. PREDEL and H. RUGE, Z. Metallkd. 59, 777 (1968).
[8] B. PREDEL and W. GUST, Metallurg. Trans. 7A, 1925 (1976).
[9] G. KUNZE and P. WINCIERZ, Z. Metallkd. 56, 421 (1965).
[10] B. PREDEL and M. FREBEL, Arch. Eisenhüttenwesen 44, 395 (1973).
[11] B. PREDEL and W. GUST, Metallurg. Trans. 7A, 1958 (1976).
[12] D. TURNBULL and E. HORNBOGEN, Trans. MS AIME 212, 33 (1958).
[13] K. N. TU and D. TURNBULL, Acta metall. 15, 369 (1967); 15, 1317 (1967).
[14] I. MANNA, Ph. D. Thesis, I.I.T., Kharagpur 1990.
[15] I. MANNA and S. K. PABI, phys. stat. sol. (a) 108, K19 (1988).
[16] I. MANNA and S. K. PABI, J. Mater. Sci. Letters, 9, 854 (1990).
[17] I. MANNA and S. K. PABI, J. Mater. Sci. Letters 7, 1299 (1988).
[18] I. MANNA and S. K. PABI, Trans. Ind. Inst. Metals, in the press.
[19] C. J. SMITHELLS and E. A. BRANDES (Eds.), Metals Reference Book, Butterworth, London 1976.
[20] W. SEITH and J. G. LAIRD, Z. Metallkd. 24, 193 (1932).
[21] T. B. MASSALSKI (Ed.), Binary Alloy Phase Diagrams, Vol. 2, Metals Park, Ohio 1986.
[22] K. MADER and E. HORNBOGEN, Z. Metallkd. 60, 475 (1969).
[23] R. A. SWALIN, Thermodynamics of Solids, Wiley, New York 1962 (p. 221).
[24] D. GUPTA, Metallurg. Trans. 8A, 1431 (1977).
[25] K. T. AUST and J. W. RUTTER, Trans. MS AIME 215, 820 (1959).
[26] J. W. RUTTER and K. T. AUST, Trans. MS AIME 218, 682 (1960).