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Microstructure gradient in 60Sn40Pb solder joints annealed under an external electric field

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Prior work [1–13] has shown that an electrostatic field of the order of a kV/cm can have an influence on solid-state reactions in metals and alloys. Since no prior studies have been reported on the influence of an external electric field on phase coarsening in a dual-phase alloy, this topic was of interest in the present investigation. Near-eutectic 60Sn40Pb solder joints were employed, because of their extensive use in the electronics industry. Moreover, an investigation of microstructure coarsening in this alloy without and with a field had previously been performed [14, 15]. Of special interest in the present work was the influence of the electric field on the difference in the microstructure at the perimeter (surface) compared to the center of the circular solder disk.

The specimens consisted of 60Sn40Pb solder joints approximately 0.2 mm thick between two 20 mm long × 6.4 mm dia. Cu rods. Details regarding the preparation of the joints and metallographic procedures are given elsewhere [14]. The microstructure of the as-reflowed solder was typical of solder joints in electronic packages, consisting of occasional Pb-rich dendrites in a matrix of a fine, globular, degenerate Pb-Sn eutectic with a relatively uniform distribution of the Pb-rich and Sn-rich phases. The solder-joint specimens were annealed without and with an electric field for 70 h in a silicone oil bath at $150 \pm 0.2\,^\circ\text{C}$. The electrical arrangement for the tests with field is presented elsewhere [15]. The specimen was connected to the positive terminal of the dc power supply and the anneals were performed with an applied voltage $V = 5$ kV/cm, which gave a nominal external electric field $E = 25$ kV/cm with an electric current $I = 3.1\ \mu\text{A}$. Duplicate tests were performed to indicate the reproducibility and accuracy of our results. The as-reflowed and annealed specimens were sectioned in half longitudinally, metallographically polished and etched. Optical photomicrographs were taken at 1000× at three locations: (a) the center of the cylindrical solder disk, (b) within 0.2 mm of the right circumference and (c) within 0.2 mm of the left circumference along the same diagonal. The mean sizes of the individual Pb-rich and Sn-rich phases of the eutectic were determined at each location by measuring the linear intercepts (200–500) of each phase on randomly-drawn lines on the photomicrographs.

The mean sizes of the Pb-rich and Sn-rich phases in the *as-reflowed condition* were 0.65 and 1.38 μm, respectively, independent of the location within the solder joint, giving an average combined phase size $\bar{D}_\text{o} \approx 1\ \mu\text{m}$. These values are similar to those for solder joints in electronic packages. The effect of an electric field on the coarsening of the Pb and Sn phases (given by their respective mean size $\bar{D}$ at the *center* of the solder disk) at $150\,^\circ\text{C}$ has been presented previously [15]. The field *retarded coarsening at this location*, the degree of which increased with field strength.

The mean phase sizes resulting form the anneal of 70 h at $150\,^\circ\text{C}$ without and with the electric field here are presented in Fig. 1 as a function of distance from the center of the solder joint. Included is the volume fraction of Sn given by $f_\text{Sn} = \bar{D}_\text{Sn}/(\bar{D}_\text{Sn} + \bar{D}_\text{Pb})$ [15]. It is seen that both the Pb and the Sn phase sizes are smaller when a field is applied than without a field at all three locations. *However, the retarding effect of the field is greater near the specimen surface compared with the center.* In addition, the field has affected the volume fractions f of the respective phases, with f_Sn at the center being increased by the field, while f_Sn at surface is decreased. Conversely, f_Pb is decreased at the center and increased near the surface, in keeping with $f_\text{Pb} + f_\text{Sn} = 1$. The equilibrium value was calculated from the phase diagram for the Pb-Sn system considering the density of each constitutent.

To explain the effects of an external electric field on phase coarsening in 60Sn40Pb shown in Fig. 1 two generally-accepted physical conditions are considered: (a) upon application of an external electric field there occurs an *excess surface charge, but no overall electric field exists in the interior of a metal specimen* and (b) with no applied field there exist two main sources of *local* electric field inside the 60Sn40Pb specimen, namely: (1) charged vacancies, solutes or vacancy-solute complexes and (2) contact potential between the Pb and Sn phases.

The decrease in rate of coarsening observed here for the 60Sn40Pb alloy is in keeping with the retarding effect of an external electric field on the rates of precipitation in Al and Fe alloys [6–8]. Since these phenomena are diffusion-controlled, it appears that a major effect of a field is to reduce the governing diffusion rate. In the prior work [14] it was determined that the coarsening rates of the Sn and Pb phases in 60Sn40Pb *without field* were given by $\bar{D}^\text{n} - \bar{D}_\text{o}^\text{n} = A_\text{o} D_\text{b} t$, where $n \approx 4$ and $A_\text{o} = B\gamma c_\text{o}\Omega w$. D_b is the grain boundary or interfacial boundary diffusion coefficient and t is the time. B is a parameter which depends on the volume fraction and the geometry of the phase, $\gamma \approx$ the grain boundary energy, $c_\text{o} = \exp(-\Delta H/RT)$ the equilibrium solute concentration near the grain boundaries,

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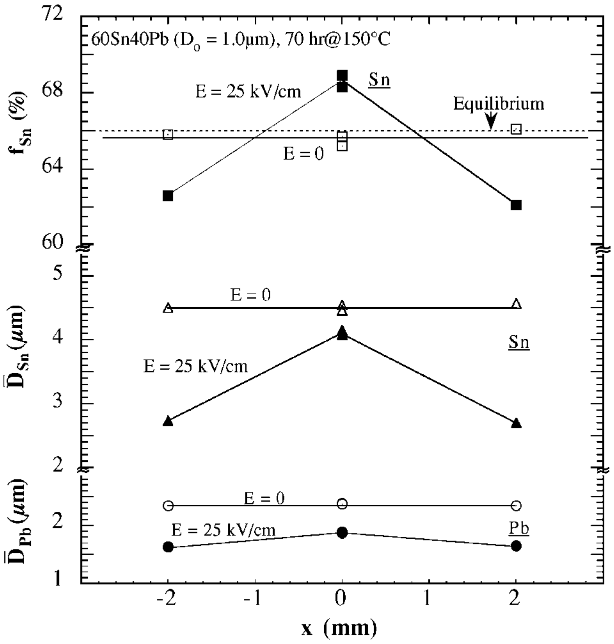

Figure 1 Mean Pb-rich phase size $\bar{D}_{\mathrm{Pb}}$, mean Sn-rich phase size $\bar{D}_{\mathrm{Sn}}$ and volume fraction f_{Sn} of the Sn phase as a function of distance from center of the 6.4 mm diameter solder disk for annealing without and with electric field E.

Ω is the atomic volume and w is the grain boundary width. Hence, the field could retard the rate of coarsening by reducing D_{b}. A reduction in D_{b} could occur from a depletion of charged vacancies due to their interaction with the charged surface or from the interaction of the field with charges at the boundaries.

The external field of 25 kV/cm is not expected to have an influence on the contact potential between the Sn and Pb phases in the specimen interior. However, whether segregated impurities or oxides at the interfaces play a role is not clear.

A gradient in the effect of an electric field on microstructure was also found for the porosity of sintered Fe powder compacts, where the reduction in porosity by the field was significantly greater near the surface of the specimen compared to the interior [9]. This was explained by assuming that the reduction in porosity resulted from the migration of negatively charged vacancies from the interior to the positively charged surface. Thus, the greater reduction in the rate of coarsening by the field at the surface compared to the interior observed here could also occur from a greater depletion of negatively charged vacancies due to their migration to the positively charged surface.

With the electrical arrangement used here, electrons flow from the positively charged surface of the solder joint to the interior and out through the Cu to the power supply. In view of the small electric current it is, however, unlikely that electromigration of the Sn will occur from an *electron wind* as observed elsewhere [17–20]. It may be possible that the migration of charged vacancies to the charged surface leads to an opposite migration of the Sn, the Sn having a higher interface diffusion coefficient than the Pb. Another possibility is that the field changed the electrochemical potential of the Sn-rich and/or Pb-rich phases and in turn the respective solid solubilities, as proposed for Al alloys [1–5]. A change in the electrochemical potential might occur if the solute solubility corresponds to a solute-vacancy complex and the vacancy concentration is altered by the field.

The above explanations suggest that the depletion of charged vacancies by their motion to the charged surface is a major factor in the effects of an external electric field on phase coarsening and separation in the 60Sn40Pb alloy. Additional work is however needed to further evaluate the physical basis for the observed effects.

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References

1. A. A. KLYPIN, *Metallovdendenie i Thermicheskaya Obrabotka Metallov* 3(12) (1979).
2. W. LIU and J. Z. CUI, *Scripta Met. Mater.* **33** (1995) 623.
3. W. LIU, K. M. LIANG, Y. K. ZHENG and J. Z. CUI, *J. Mater. Sci. Lett.* **15** (1996) 1327.
4. *Idem., ibid.* **15** (1996) 1918.
5. K. JUNG and H. CONRAD (unpublished research, 2002).
6. W. LIU and J. Z. CUI, *J. Mater. Sci. Lett.* **16** (1997) 1410.
7. H. A. LU and H. CONRAD, *Appl. Phys. Lett.* **59** (1991) 1847.
8. H. CONRAD, Y. CHEN and H. A. LU, in "Microstructures and Mechanical Properties of Aging Materials," edited by P. Law, R. Viswanathan, K. Murty, E. Simone and D. Frear (TMS, Warrendale, PA, 1993) p. 279.
9. Y. FAHMY and H. CONRAD, *Metall. Mater. Trans.* A **32A** (2001) 811.
10. H. CONRAD, W. D. CAO, X. P. LU and A. F. SPRECHER, *Scripta Mater.* **23** (1989) 697; *Mater. Sci. Engr.* A **138** (1991) 247.
11. W. D. CAO, X. P. LU, A. F. SPRECHER and H. CONRAD, in "Superplasticity in Aerospace II," edited by T. McNelley and H. Heikken (TMS, Warrendale, PA, 1990) p. 269.
12. X. P. LU, W. D. CAO, A. F. SPRECHER and H. CONRAD, *J. Mater. Sci.* **27** (1992) 2243.
13. H. CONRAD, Z. GUO and A. F. SPRECHER, *Scripta Metall.* **23** (1989) 821.
14. K. JUNG and H. CONRAD, *J. Electronic Mater.* **30** (2001) 1294.
15. *Idem., Mater. Sci. Eng.* A **356** (2003) 8.
16. R. DEHOFF and E. RHINES, "Quantitative Microscopy," (McGraw-Hill, New York, 1968).
17. G. DIGIACONO, in Proc. IEEE (1979) p. 72.
18. S. BRANDENBURG and S. YEH, in Proc. Surf. Mount Int. Conf. and Expo. (SMTA, 1998) p. 337.
19. C. Y. LIU, C. CHEN, C. N. LIAO and K. N. TU, *Appl. Phys. Lett.* **75** (1999) 58.
20. *Idem., J. Appl. Phys.* **88** (2000) 5703.

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