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The Solid Solubility of Ag and Cu in the Sn Phase of Eutectic and Near-Eutectic Sn-Ag-Cu Solder Alloys

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Early studies of Ag-Sn and Cu-Sn binary alloys showed very low values, 0.04 wt.% for Ag and 0.0063 wt.% for Cu, for the solid solubility of these elements in Sn at the eutectic temperature. In recent work on "as-cast" Sn-Ag-Cu solder alloys, much higher values have been reported for the Ag and Cu content of the Sn phase. In the present study, wavelength dispersive x-ray microprobe measurements made on a near-equilibrium sample confirmed the earlier solubility values. It was concluded that higher values, some of which are reported in the current paper, represent nonequilibrium, supersaturated solid solutions.

Key words: Pb-free solder, Sn-Ag-Cu solder, solid solubility

INTRODUCTION

There has been much recent interest[1] in alloys having compositions at and near that of the ternary eutectic reaction near the Sn corner of the Ag-Cu-Sn phase diagram[2] as a potential nontoxic replacement for eutectic Pb-Sn solder. This ternary eutectic reaction occurs at the composition of 3.5wt.%Ag, 0.9wt.%Cu, and 95.6wt.%Sn and temperature of 217°C,[3,4] at which the liquid decomposes on cooling to form the phases Ag_3Sn, Cu_6Sn_5, and βSn.

Early work by Homer and Plummer[5] on the binary Ag-Sn and Cu-Sn systems determined very low values for the equilibrium solid solubility of these elements in Sn at their respective eutectic temperatures and these values, 0.04 wt.% for Ag and 0.0063 wt.% for Cu were subsequently listed in handbooks, such as Hansen's book.[6] However, in a recent study[4] of a commercially available solder alloy having the composition 3.8wt.%Ag, 0.7wt.%Cu, and 95.5wt.%Sn, much higher values, 0.1wt.%Ag and 0.16wt.%Cu, have been reported in the Sn phase in as-cast material. Consequently, it is of interest to determine, in comparison with the earlier study,[5] whether these more recent values represent a supersaturated solid solution from which additional Ag_3Sn and Cu_6Sn_5 may precipitate on aging of a solder joint, and this was the purpose of the present study.

EXPERIMENTAL PROCEDURE

Four samples were prepared for study: (1) A sample that had been directionally solidified at a speed of 4.5 mm per day.[7–13] This sample had a ternary eutectic composition. (2) A sample, consisting of ball-grid array balls, having an as-cast microstructure, prepared by melting in a small tube furnace and then allowed to freeze in air at a cooling rate of approximately 11°C per second. (3) A sample, also ball-grid array balls, prepared in the same manner as sample 2, and then heated for 12 days at 203°C. (4) An as-cast sample, also ball-grid array balls, that had been aged for 1,000 h at 150°C. Samples 2, 3, and 4 were composed of a commercial alloy having the composition 3.8wt.%Ag, 0.7wt.%Cu, and 95.5wt.%Sn.

Sample 1 was selected as being closest to equilibrium because of the very low, directional freezing rate and long time spent by the solidified material at temperatures near the eutectic value after solidification. Sample 2 was selected as having a microstructure similar to that of a solder joint. Sample 3 was intended to show the effect of long-time heating at high temperature. Sample 4 was selected to show the effect of aging at a temperature that might be encountered in service.

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Table I. Results of the Composition Measurements

Sample	Ag Concentration	Cu Concentration
Unidirectionally solidified	0.024 ± 0.012 wt.%	Below detection limit
As-cast	0.093 ± 0.010 wt.%	0.022 ± 0.006 wt.%
As-cast plus 12 days at 203°C	0.089 ± 0.024 wt.%	0.019 ± 0.015 wt.%
As-cast plus 1,000 h at 150°C	0.052 ± 0.012 wt.%	0.035 ± 0.008 wt.%
Detection limit	0.012 wt.%	0.006 wt.%

All samples were mounted in an epoxy, metallographic mounting medium. They were prepared by grinding on successively finer, silicon-carbide grinding papers, with flowing water, finishing with 2,400 grit. Rough polishing was done with 6-μm diamond, followed by 1-μm diamond. The final polish was carried out using 1-μm alumina, followed by colloidal silica. This procedure revealed the microstructure without further etching.[14]

The Ag and Cu contents of the Sn phase were determined by wavelength dispersive x-ray analysis, using a Cameca SX-50 microprobe analyzer (Courbevoie, France). The pure metals were used as standards. The solder alloy freezes to form primary dendrites of the Sn phase with an interdendritic eutectic containing the Ag_3Sn and Cu_6Sn_5 phases. In making measurements on the Sn phase, care was taken to use only the largest available areas, at least 10 μm in diameter, to avoid fluorescence-excited x-rays from neighboring regions containing the Ag_3Sn or Cu_6Sn_5 phases. This diameter is at least twice that from which the x-rays are emitted for analysis. The microstructure of the slowly solidified sample was very coarse, containing large areas, approximately 200 μm in width, of the Sn phase, free of the compound phases.

RESULTS AND DISCUSSION

Results of the composition measurements are presented in Table I. Each value listed is the average of at least four determinations. The detection limits quoted correspond to a peak height of three times background. The error limits represent the standard deviations of the measurements. Detection limits are quoted at 99% confidence and are based on the standard counts and the unknown's background counts and include the magnitude of the ZAF correction factors.

As anticipated, the lowest Ag and Cu content values were obtained from the sample that was directionally solidified at very low speed. These values are essentially in agreement with those obtained in the earlier work reported by Homer and Plummer,[5] i.e., 0.04 wt.% for Ag and 0.0063 wt.% for Cu, in the binary alloys at their respective eutectic temperatures. It is concluded that these values correspond closely to equilibrium concentrations. The highest Ag and Cu concentrations were obtained from the as-cast sample. These values indicate that solidification under these conditions occurs in a nonequilibrium manner, resulting in formation of a solid solution supersaturated in both Ag and Cu. Results for the sample heated at 203°C for 12 days and for that aged for 1,000 h at 150°C, while possibly of limited accuracy because of the inhomogeneity of the samples, do indicate that heat treatment at relatively high temperature allows the Ag and Cu to precipitate out of the solution, presumably by growth on existing particles of the two compound phases.

The formation of a Sn phase supersaturated in both Ag and Cu can be accounted for in the following way. Using the solid solubility values of 0.04wt.%Ag and 0.006wt.%Cu, determined by Homer and Plummer[5] and confirmed in the present study, and the eutectic concentrations of Ag (3.5 wt.%) and Cu (0.9 wt.%) gives the following values for the distribution coefficients, k_{Ag} of Ag and k_{Cu} of Cu in Sn: $k_{Ag} = 0.04/3.5 = 0.011$ and $k_{Cu} = 0.006/0.9 = 0.007$.

As a result of these very small distribution coefficients, both Ag and Cu are strongly rejected into the liquid at the solidifying Sn interface. This results in a large buildup in concentration of these elements in the liquid adjacent to the Sn solid/liquid interface with a consequent increase in the concentrations freezing out, forming a supersaturated solid solution. The value of 0.16wt.%Cu reported by Moon et al.[4] in solution in the Sn phase of the solder alloy would constitute approximately 23 wt.% of the total Cu present in the sample and the value of 0.1wt.%Ag in solid solution, observed by Moon et al.[4] as well as the current work, would constitute approximately 2.6 wt.% of the total Ag present. It must be concluded that these values would represent substantial supersaturation of these elements in the Sn phase of the solder alloy.

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