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Scripta Materialia 56 (2007) 413–416
Scripta MATERIALIA
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Two-stage nonequilibrium eutectic transformation in a Sn–3.5Ag–3In solder

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Received 21 August 2006; revised 5 October 2006; accepted 28 October 2006
Available online 18 December 2006

The nonequilibrium solidification of Sn–3.5Ag–3In and the microstructure thus produced were examined in this study. Results show that In was dissolved into Sn and Ag_3Sn and reduced the melting temperature. In segregation during solidification led to an expanded melting range and a mixed normal–coarse structure with Sn and $Ag_3(Sn, In)$. This also resulted in a specific two-stage nonequilibrium eutectic solidification feature.

Keywords: Pb-free solder; Sn–Ag–In; Solidification structure; Thermal behavior

Sn–Ag alloys are considered one of the most favorable lead-free solder systems. Numerous studies have been devoted to the microstructure of Sn–Ag-based alloys [1–5]. It is known that a nonequilibrium eutectic transformation occurs during the solidification of Sn–Ag eutectic alloy and thus the β-Sn dendrites and Sn–Ag_3Sn eutectics coexist in the microstructure. Having a more complex crystal structure, the body-centered tetragonal β-Sn dendrites require a significantly great undercooling in order to induce nucleation [6] and bring about a final eutectic reaction. Such a complex solidification behavior may raise reliability concerns. Coarse Sn dendrites cause hot tearing. In some cases, Ag_3Sn, which requires minimal undercooling, grows rapidly into large plates and may induce strain localization [4].

Several reports have indicated that In can be applied to depress the melting point of Sn–Ag alloys [2,7]. Furthermore, the melting range (temperature range between solidus and liquidus) is also enlarged after In is added. Huang and Wang [2] reported that in Sn–3.5Ag–XIn alloys, the onset temperature (T_{onset}, the onset point of heat absorption upon heating) was reduced from 221.34 °C (Sn–3.5Ag) to 213.90 °C (Sn–3.5Ag–2In) and 209.28 °C (Sn–3.5Ag–5In). The effect of In on the eutectic temperature in the Sn–Ag binary system (221 °C) was also calculated [8]. Figure 1 shows that the eutectic temperature decreases gradually with higher In addition. The eutectic temperature reaches about 200 °C when the In content is 15 wt.%. For the consideration of practical applications and an in-depth insight into this alloy system, this study investigated the relationship between the microstructure and the thermal properties of a low In alloy, Sn–3.5Ag–3In.

Sn–3.5Ag and Sn–3.5Ag–3In alloys (in wt.%), designated herein as SnAg and SnAgIn, were prepared by melting pure metals in a vacuum arc melting furnace and subsequently remelting and casting into a cylindrical metal mold with an internal diameter of 30 mm. The cooling rate for the specimens, which was measured as the average value from 300 °C to 200 °C, was about 1 °C/s.

The thermal behavior of the solders was investigated using differential scanning calorimetry (DSC) and cooling curves. DSC analysis was conducted at constant heating and cooling rates of 2 °C /min. Cooling curves were obtained by inserting a thermocouple into 150 g of molten solder placed in a MgO crucible. The initial temperature of the molten solder was above 600 °C. The microstructures of the solders were investigated with a scanning electron microscope (SEM) and electron probe microanalysis (EPMA) equipped with wavelength-dispersive spectrometers (WDS).

Figures 2 and 3 show the microstructure of the specimens investigated. Compared to the SnAg sample (Fig. 2a), the solidification structure of the SnAgIn (Fig. 2b) was irregular, comprising normal structural

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doi:10.1016/j.scriptamat.2006.10.044

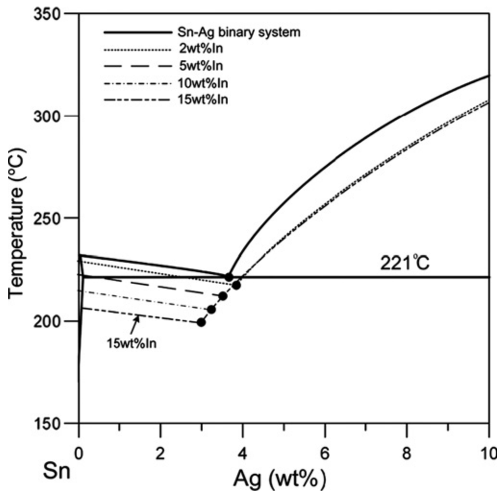

Figure 1. The effect of In on the eutectic temperature in the Sn–Ag binary system (redrawn from Ref. [8]).

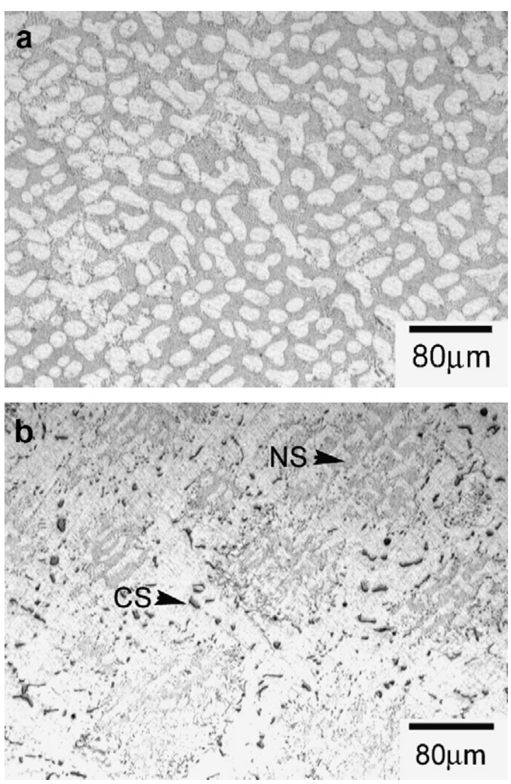

Figure 2. Microstructure of (a) the SnAg sample and (b) the SnAgIn sample. NS: normal structure; CS: coarse structure.

regions (with fine Sn dendrites and eutectics; see Fig. 3a) and coarse structural regions (with coarse Sn dendrites and intermetallic compound (IMC) particles; see Fig. 3b). It can be observed that the fine structural regions are surrounded by coarse ones. The compositional analytical results, shown in Table 1, show that the fine Sn dendrites (as indicated by point A in Fig. 3a) contained an average In content of 1.7 at.% (the data range was from 1.46 to 2.02 at.%), while 2.1 at.%In was detected in the Sn phase within the fine eutectics (as indicated by point B in Fig. 3a). The

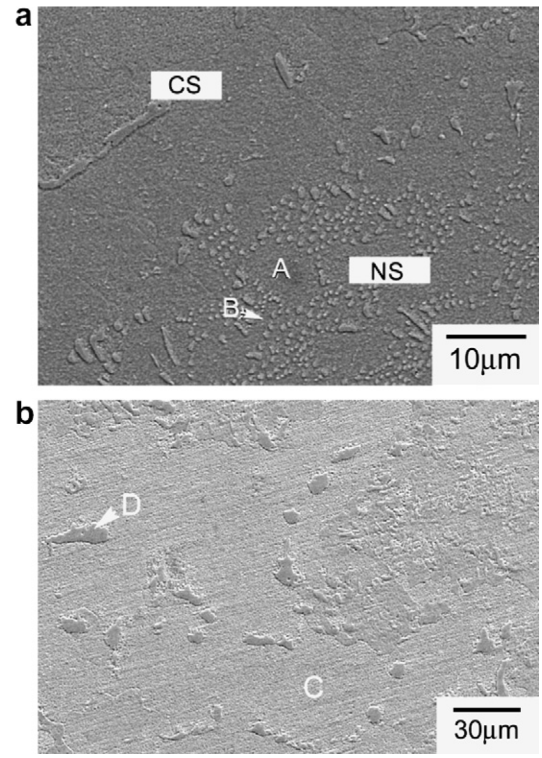

Figure 3. Magnified structure of the SnAgIn sample: (a) normal and coarse structural regions (marked by NS and CS) and (b) massive IMC particles in coarse structural regions.

Table 1. EPMA quantitative compositional results (at.%)

Phase/element	In	Ag	Sn
Fine Sn dendrites	1.7	0.1	98.2
Sn in fine eutectics	2.1	0.2	97.7
Coarse Sn dendrites	2.7	0.1	97.2
Coarse IMC	9.8	74.7	15.5

Each datum was the averaged result of five or more measurements.

average In content of coarse Sn dendrites (point C in Fig. 3b) was 2.7 at.% (the data ranged from 1.98 to 3.17 at.%). Notably, the composition of the massive compound particles (point D in Fig. 3b) was 74.7 at.%Ag–15.5 at.%Sn–9.8 at.%In, which could be identified as $Ag_3(Sn,In)$. This does not tally with the constitutional phases ($Sn + Ag_2In$) predicted in a Sn–3.66Ag–3In alloy by Ohnuma et al. [9] and ($Sn + Ag_3Sn + Ag_2In$) observed in the Sn–3.5Ag–5In by Huang and Wang [2].

In addition, such a normal–irregular structural feature was not found in Huang's Sn–Ag–In samples, the solidification rate of which ranges from 5 to 8 °C/min [2], higher than that in this study, 1 °C/min. This implies that a slower cooling rate and thus prolonged solidification period might intensify the degree of irregularity of the solidification structure.

Elemental mapping of the SnAgIn specimen (Fig. 4) reveals that the signal of In in the coarse structural regions was relatively brighter than that in the normal regions. It also illustrates that in the coarse structural regions the massive IMCs, $Ag_3(Sn,In)$, possessed a greater concentration of In than the Sn phase nearby.