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A rheological assessment of the effect of trace level Ni additions on the solidification of Sn–0.7Cu

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Abstract

The influence of trace level Ni additions on the eutectic solidification mode of Sn–0.7Cu has been studied using continuous torque experiments during solidification. The solid fraction at which resistance to paddle rotation at the thermal centre of the sample occurs is related to the spatial distribution of solid during solidification. The results indicate that a transition in solidification mode occurs in the range 0–300 ppm Ni. Growth occurs antiparallel to heat flow from near the mould walls in the Ni-free alloy, while equiaxed growth from distributed centres dominates in alloys containing at least 300 ppm Ni.

Keywords: Eutectic solidification; Lead-free solder; Coherency; Soldering

1. Introduction

Since the discovery that lead is a heavy metal toxin and is hazardous to health, there has been a driving force to eliminate the lead that leaches into the soil from landfill sites. Many pieces of legislation have been passed which will limit the use of Pb-containing solders. The most imminent is the European Union directive banning the use of hazardous substances, including lead, in electronic equipment from 1st July 2006.

In recent decades a concerted worldwide research effort has been underway to develop lead-free solders for the electronics industry [1,2]. One attractive lead-free solder is the eutectic Sn–0.7Cu alloy which has found application in wave, dip and iron soldering processes and is cheaper than most other candidate alloys [3,4]. It is known that the microstructure of eutectic Sn–0.7Cu can be altered by the addition of small quantities of certain alloying elements. For example, both the morphology of the β-Sn and Cu_6Sn_5 phases are affected by the addition of up to 1 wt.% Ag [4], 3 wt.% Au [5] and 0.5 wt.% RE [3], and 0.2–1 wt.% Zn is reported to refine the β-Sn phase [6].

This paper concerns the effect of trace Ni levels on the solidification and microstructure of Sn–0.7Cu. The addition of Ni at levels in the range 20–1000 ppm Ni is known to improve the soldering properties of Sn–0.7Cu [7–11]. After the Ni addition there is a reduced tendency for "bridging", the potential for webs of solder to form between adjacent terminals during wave soldering [12]. Additionally, the interface between the solder and substrate is improved [9,13] and the solder has an improved surface finish. Commercial Sn–0.7Cu solders that take advantage of this effect typically contain 600 ppm Ni.

Recently Nogita et al. studied the effect of trace Ni additions on the solidification behaviour of Sn–0.7Cu and observed three distinct changes in the solidification of Sn–0.7Cu after a 600 ppm Ni addition. First, the morphology of the Cu_6Sn_5 phase became coarser and more rounded. Second, the small volume fraction of primary β-Sn

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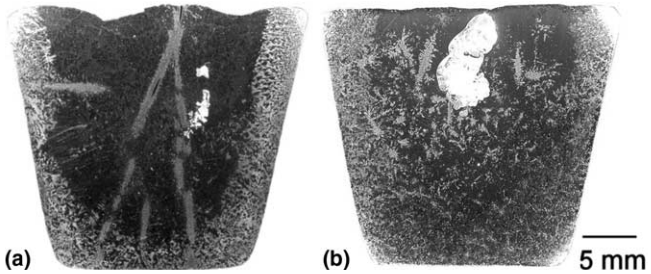

Fig. 1. Quenched macrostructures showing the effect of 600 ppm Ni on the eutectic solidification mode of Sn–0.7Cu: (a) Ni-free, (b) 600 ppm Ni [12]. Black is quenched liquid whereas white is the solid at the time of the quench.

dendrites decreased. And third, a change in eutectic solidification mode occurred: quenching experiments revealed that the eutectic solidification mode of the Ni-free alloy was by growth from near the mould walls antiparallel to heat flow with a mushy interface (Fig. 1a). In contrast, the 600 ppm Ni containing alloy solidified by equiaxed growth from numerous centres distributed throughout the sample (Fig. 1b). Furthermore, Nogita et al. found most of the Ni to be concentrated in the Cu_6Sn_5 phase, a finding consistent with past studies which have shown that Ni has extensive solubility in Cu_6Sn_5 [14,15]. It is not clear to what extent each of the changes brought about by the Ni addition contributes to the improved soldering properties.

The purpose of the present study was to further investigate the transition in solidification mode of Sn–0.7Cu with increasing Ni content in the range 0–1000 ppm Ni. Eutectic grain boundaries in Sn–0.7Cu based alloys are often difficult to define in fully solidified samples unless there is significant ternary segregation so as-cast samples contain little information about the evolution of solid during solidification. The present investigation adopted a modified version of the rheological dendrite coherency test to determine whether this in situ technique is capable of revealing changes in eutectic solidification mode in the Sn–0.7Cu system. The results of the rheological experiments were then used, in conjunction with the quenched microstructural observations of Nogita et al. [12], to further understand the effect of Ni content on the solidification of Sn–0.7Cu.

2. Experimental procedure

Sn–0.7Cu alloys containing six Ni levels in the range 0–1000 ppm were used. The mean chemical compositions of the alloys are given in Table 1. In order to study how the spatial distribution of solid differs between the alloys during solidification, a technique similar to the rheological dendrite coherency test [16,17] was employed. A physica DSR150 rheometer was used to measure the rheological response when a paddle was slowly rotated at the thermal centre of each alloy during solidification.

Experiments were carried out in boron nitride (BN) coated mild steel cylindrical cups. The cups had dimensions height = 40 mm, ID = 40 mm and wall thickness = 2 mm, and contained four ribs to prevent wall slip. For each experiment, 350 g of alloy was melted in a cup using a resistance furnace on the rheometer rig. A K-type thermocouple, calibrated against commercial purity Sn, and a 304 stainless steel paddle coated in BN were then immersed in the melt. The paddle was 20 mm tall and 10 mm wide with a 2 mm thick arm exiting the surface of the sample. Once immersed, the bottom of the paddle was 10 mm from the base of the crucible. The crucible was situated on an insulating board and another insulating board was added to the top of the crucible once the paddle had been inserted. At this point the experimental setup appeared as shown in Fig. 2. The system was then held at 300 °C (~73 K superheat) for approximately 30 min to ensure thermal equilibrium after which an experiment was started by removing the furnace and allowing the sample to cool naturally in air. The paddle was rotated from the time the furnace was removed at a rate of 0.05 rotations per minute and

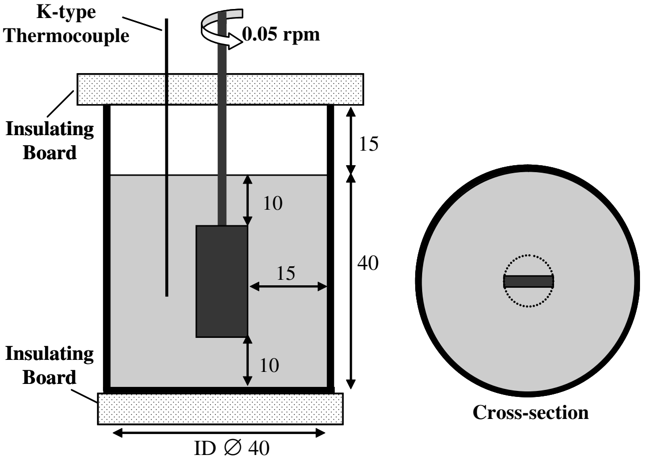

Fig. 2. A schematic of the setup used for the continuous torque rheology experiments. Dimensions are in millimetres.

Table 1
Average compositions of the six Sn–0.7Cu–(Ni) alloys (wt.%)

Sample	Sn	Cu	Ni	Pb	Sb	Ag	Zn	Al	Fe
Ni free	Bal.	0.683	0.002	0.039	0.004	0.005	<0.001	<0.001	0.004
100 ppm	Bal.	0.666	0.009	0.025	0.006	<0.001	<0.001	<0.001	0.004
200 ppm	Bal.	0.678	0.021	0.033	0.010	<0.005	<0.005	<0.005	0.023
300 ppm	Bal.	0.675	0.030	0.033	0.010	<0.005	<0.005	<0.005	0.009
600 ppm	Bal.	0.667	0.058	0.024	0.007	<0.001	<0.001	<0.001	0.005
1000 ppm	Bal.	0.657	0.092	0.024	0.006	<0.001	<0.001	<0.001	0.003