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IMMERSION PLATING OF BISMUTH ON TIN-BASED ALLOYS TO STABILIZE LEAD-FREE SOLDERS

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ABSTRACT

Bismuth was deposited on tin and tin-copper alloys by immersion plating, with the purpose of protecting lead-free solder balls from a destructive sub-ambient phase transformation ("tin pest"). Deposition in aqueous solutions, or in non-aqueous solutions at $\leq$130 ^{o}C, yielded dark, poorly adhering deposits which could not be reflowed. By contrast, use of a glycerol solution above the Sn-Bi eutectic temperature (139 ^{o}C) yielded reflective deposits with good adhesion to the substrate and amenable to fluxless reflow. The concentration of Bi in the reflowed solder ball could be controlled by changing the immersion time. Unlike usual exchange processes, the rate of deposition did not decrease markedly with time. Extensions of this "immersion eutectic plating" process are suggested.

INTRODUCTION

There is an imminent need to eliminate the use of lead from electronics packaging, and in particular to develop lead-free solders that can replace the old lead-tin ones. This necessity is due to environmental concerns and pending regulatory changes, in particular in the European Community:

- Waste Directive on Electrical and Electronic Components – manufacturer pays recycling expenses (beginning in 2005)
- Reduction of Hazardous Substances (RoHS) – phasing out of lead in electronic components (beginning in 2006)

The new alloys making their way into development and manufacturing are tin-based, usually containing >90% Sn with small amounts of copper, silver and/or bismuth added; for instance: SnAg (~3.5% Ag), SnAgCu (~3.5%Ag, ~0.7% Cu), SnCu (~0.8% Cu), SnBi (~3-4% Bi), SnZnBi (8% Zn, 3% Bi).

Tin and high-tin alloys of the lead-free type are susceptible to a destructive low-temperature phase transition known variously as "tin pest", "tin disease" or "tin plague"

(1). This phenomenon was apparently first studied in the late 19th century when tin organ pipes in Northern Europe were observed to deteriorate after cold winters. Antique collectors and museum curators are familiar with the problem, which often affects old pewter objects. An oft-quoted (though apparently not well documented) story even attributes the failure of Napoleon's Russian campaign partly to the degradation, in the harsh cold of the Russian winter, of the tin buttons with which his soldiers' coats were equipped.

The "tin pest" makes its appearance below 13 ^{o}C, as tin undergoes a very sluggish phase transformation from the room-temperature tetragonal beta-tin structure ("white tin") to the diamond-like alpha-tin ("gray tin"). The phase transition is accompanied by a large volume increase and consequent loss of mechanical integrity or even crumbling into gray tin dust.

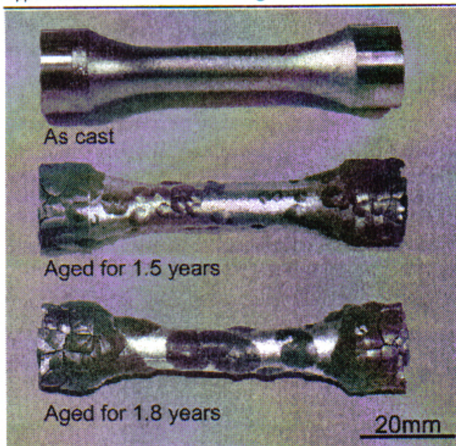


Figure 1
Appearance of Sn-0.5mass%Cu ingot at 255K

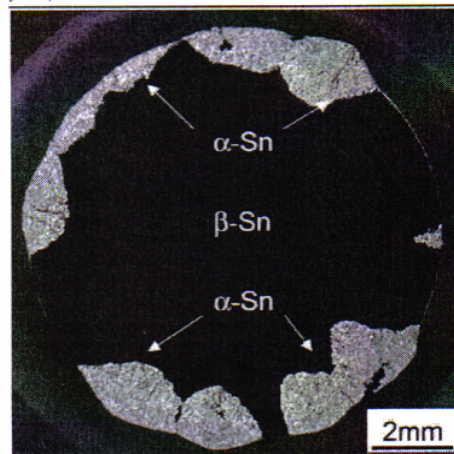


Figure 2
Cross-section of the sample at a grip end (aged for 1.5 years)

Figure 1. (Left) ingots of Sn – 0.5%Cu aged at 255K; (right) cross-section through a grip end of the sample aged for 1.5 years. (From ref. 5, with permission.)

The rate of transformation is apparently increased by a variey of factors:

- Lower temperature (maximum rate around -40 deg C) (2);
- Presence of gray tin "seeds", or contact with gray tin or with compounds of similar structure (e.g. InSb (3, 4)); this infection-like behavior is thus the etymological source of the phenomenon's common names.
- Surface area exposed (transformation tends to start at the surface (5, 6));
- High ambient humidity (contact with ice crystals, possibly in the metastable cubic ice form) has been implicated (7);
- Mechanical stress (6, 8);
- Purity (common impurities reduce the temperature and rate of transformation)

Clearly tin pest poses a potential risk to electronic devices stored or operated in cold environments. Until recently this problem did not manifest itself, since the solders in use have been high in lead, which is an effective suppressor of tin pest. With the elimination of lead, other suppressors have become necessary. Unfortunately, copper and silver – the two most popular alloying elements added to tin in lead-free solders – are not effective

transformation suppressors. Sn-Cu alloys containing 0.5% (5, 6*),* 0.7% (present work), and even 0.8% Cu (9) transformed after long aging at sub-zero temperatures. Silver is sometimes reported to help, but in at least one case many Sn-3.5%Ag samples transformed (9). Bismuth and antimony, however, are known to suppress the beta-to-alpha transformation very effectively (1, 6, 8). Therefore the solution seems to be to add a small amount of Bi or Sb to SnCu/SnAg/SnCuAg alloys.

Plating is a major manufacturing method of producing the C4-type solder balls used to attach patterned silicon chips to electronic packages. Adding another element, such as Bi, to one of the existing alloy baths is likely to make process control and optimization much more difficult. Specifically, at IBM it was desired to add a defined concentration of Bi to an electroplated Sn-0.8%Cu alloy. The electroplating process of this binary alloy was already difficult to control, partly because of anodic reactions: using a tin anode leads to Cu(2+) losses through cementation, while using an inert anode leads to massive oxygen evolution and irreversible Sn(4+) formation. A ternary alloy plating process was expected to be even less manageable.

It was decided therefore to plate the bismuth in a separate step, on the pre-plated SnCu alloy. To make this step as simple and economical as possible, immersion plating was chosen since it can be performed using simple equipment. The immersion (or exchange) plating was expected to work well, for the following reasons:

- Bismuth (E^o_{red} = 0.29 V) is much more noble than tin (E^o_{red} = -0.14 V)
  - Therefore, in typical aqueous media, $2Bi^{3+} + 3Sn \rightarrow 2Bi + 3Sn^{2+}$
- Immersion plating often gives low quality deposits, but here the deposit would be melted (reflowed) anyway. Little is required:
  - The deposit needs to survive rinses;
  - The deposit needs to dissolve in Sn-Cu melt upon reflow.

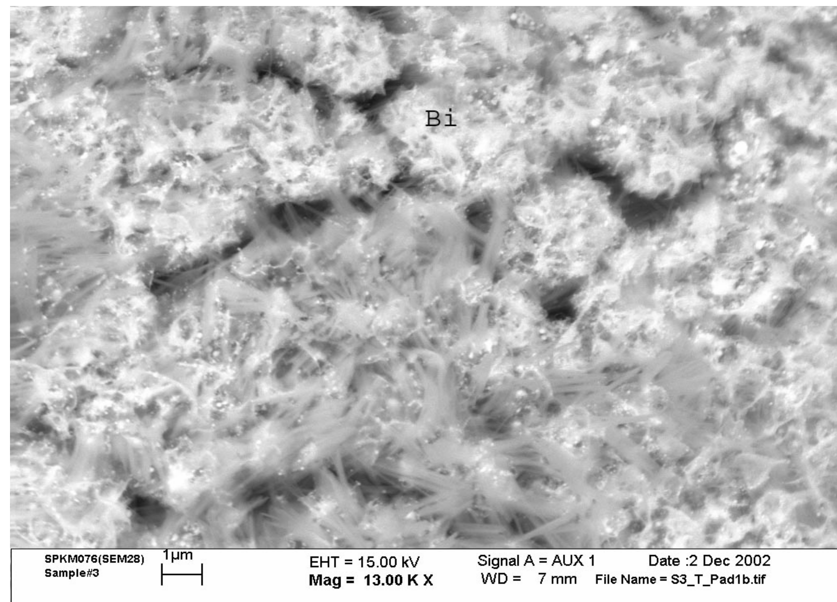
EXPERIMENTAL

The plating substrate were pure tin or Sn-0.5%Cu sheet, or electroplated Sn-0.8%Cu C4 balls. They were rinsed for 1-4 min (the longer treatment was used for older samples) in 66% methanesulfonic acid (MSA) to remove surface oxide. As expected, bismuth plated spontaneously on tin and its alloys when they contacted a Bi^{3+}-containing solution. However, the quality of the deposits was unsatisfactory:

- Aqueous solutions of Bi nitrate + HNO_3, HCl or HBr yielded powdery black deposits, partly washed away during rinsing.
- Bi nitrate or bromide in glycerol or propylene glycol (PG) with added halides at 20 or 125 ^oC yielded similar results.
- Two types of formulations using acidified Bi nitrate solutions gave somewhat better adhesion:
  - $NH_4SCN + Na_2H_2EDTA$ at 60-70 ^oC (10),
  - Water/PG/sucrose with 1.4 M KBr, up to 0.8 M HBr, and Triton x-114 or x-100 surfactant

However, even in these latter cases the deposits were black and, more importantly, could not be reflowed by the normal process. Even after reflow (2 min at 245 ^oC in

forming gas), the precipitated Bi and Bi compounds remained on the surface, as shown in fig. 2. The heat-resistant fluffy deposit indicates dendritic growth and oxide/hydroxide co-deposition, clearly not prevented by the additives used or even by the highly acid medium.



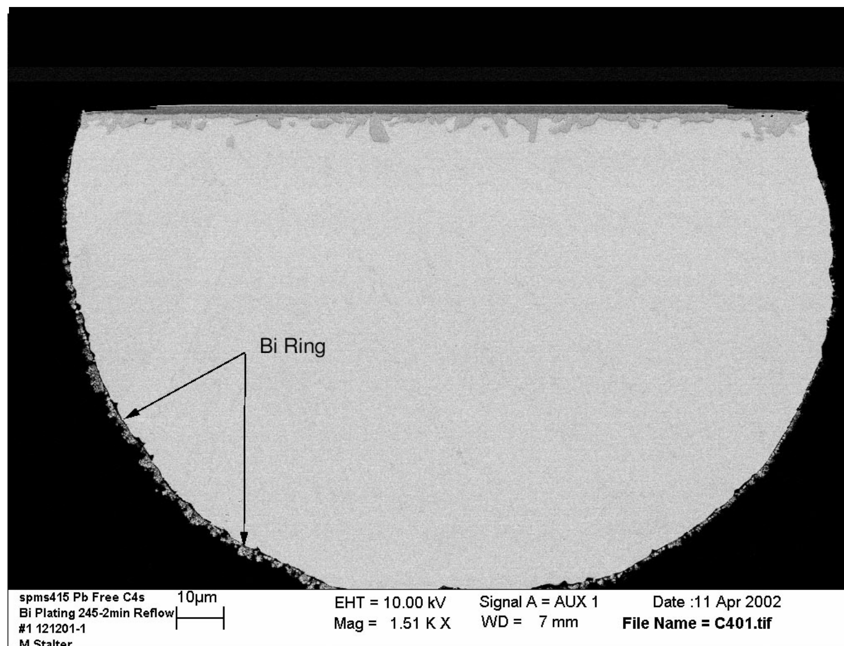


Figure 2. Aqueous-plated Bi deposit, segregated on surface of C4 ball after reflow: at high magnification (above) and low magnification (below), by SEM.

It was realized that the problem might be overcome by providing "instant reflow", by generating a liquid metal phase at the interface during deposition. That approach would drastically reduce dendritic growth and oxidation. The way to do it is to perform the

exchange reaction **above the eutectic temperature** - 139 ^oC - of the binary Sn-Bi system (the presence of Cu in the alloy has little effect on the eutectic temperature).

Operation at 140-150 ^oC in an aqueous solution is difficult and it also increases the likelihood of formation of Bi hydrolysis products. A low-volatility solvent, as a (nearly) non-aqueous medium, is a more suitable choice. Glycerol stands out as the preferable choice, since it is an inexpensive polar solvent with good dissolution capability for many salts, low vapor pressure (1-2 torr) in the 140-150 ^oC range, and a flash point – 160 ^oC – higher than the reaction temperature. Acidified glycerol solutions are reasonably stable at 140-150 ^oC. Glycerol is "generally regarded as safe" (GRAS) and readily biodegradable. (Other solvents with lower flash points, e.g. propylene glycol, can be used, but then blanketing with an inert gas is needed.) In the presence of chloride or bromide ions, glycerol is a good solvent for bismuth salts such as the nitrate or the 2-ethylhexanoate. The latter salt was chosen for most experiments since it dissolves faster and raises no oxidation concerns.

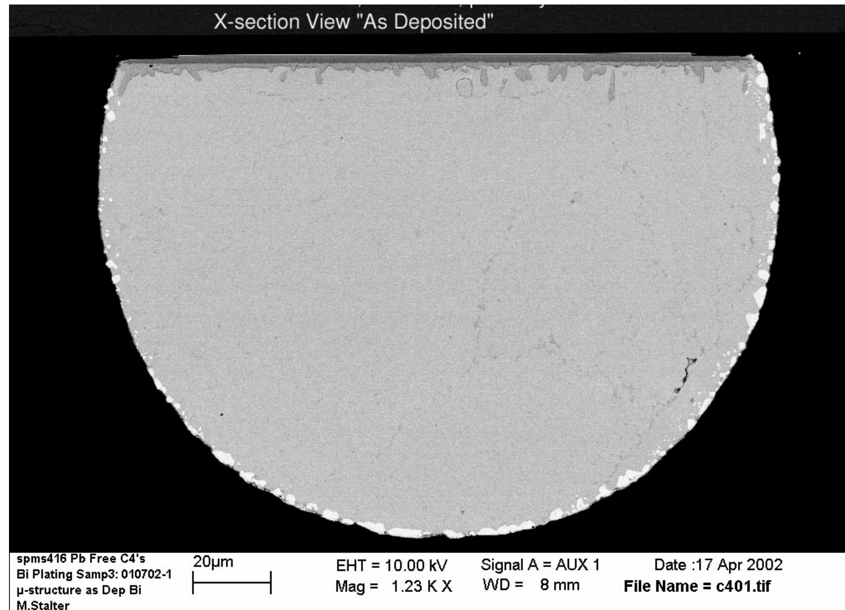
Typical working solutions contained 6-12 mmol (3.08-6.16 g) bismuth 2-ethylhexanoate, 20 g KBr and 2 ml MSA 99% in 1000 g glycerol. In a typical procedure, a sample containing plated Sn or Sn-~0.5%Cu solder balls was dipped for 1 minute in stirred 66% MSA. After rinse and blow-dry, it was dipped for 0.5-4 min into the stirred working solution at 142 ± 3 ^oC; then it was rinsed and blow-dried.

RESULTS AND DISCUSSION

Under the working conditions described above, droplets of liquid Sn-Bi eutectic were generated on the Sn alloy surface. These droplets adhered well and also penetrated into the bulk along grain boundaries. The Sn-Bi eutectic solidified and stayed in place when the sample was cooled down and rinsed. Reflowing the alloy resulted in a uniform composition across the solder ball. This happened even when the reflow was done without flux, which is remarkable because it attests to the low amounts of oxidation products generated in this deposition process. The C4 balls stayed bright. Cross-sectioning and electron microprobe analysis before and after reflow showed (fig. 3) that the Bi concentrated initially at and near the ball surface, but redistributed itself uniformly throughout the solder ball after a fluxless reflow. The surface coverage is incomplete for the short exposures (and/or low Bi^{3+} concentrations) used to obtain low Bi contents of 0.15-0.6%. Thus achieving reliable protection against phase transformation at these low Bi contents necessitates the reflow of the tin-based connector, which uniformly redistributes the bismuth throughout the volume - and the surface - of the connector. However, with longer exposure (and/or higher Bi^{3+} concentration) essentially complete coverage of the surface can be achieved.

Analysis showed a solder ball content of about 0.6% Bi after plating for a 0.5 min immersion in a 12 mmol Bi^{+3} /1 L solvent composition. The amount deposited is approximately linear with immersion time, as can be seen in fig. 4; a 4%Bi content was obtained after a 4 min immersion in the same composition. Unlike in typical immersion plating, which is self-limiting, here transport of Sn^o apparently continues unimpeded

through the liquid metal phase. The nearly constant rate may be due to stable surface coverage by, and stable Sn^o activity in the eutectic melt.



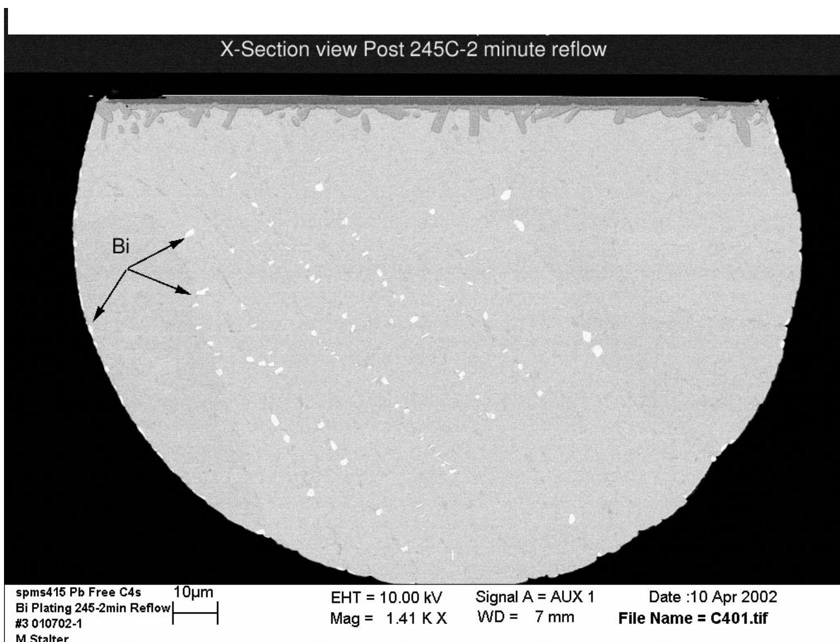


Figure 3. (above) Deposit of Bi (~2 wt%) at ~142 ^oC on cross-sectioned C4 with formation of Sn-Bi eutectic "droplets"; no dendritic deposit is visible. (below) After reflow at 245 ^oC: Most Bi has left the edge and intermixed with the SnCu. The second phase (high in Bi) is visible since Bi concentration exceeds its solubility in solid Sn.

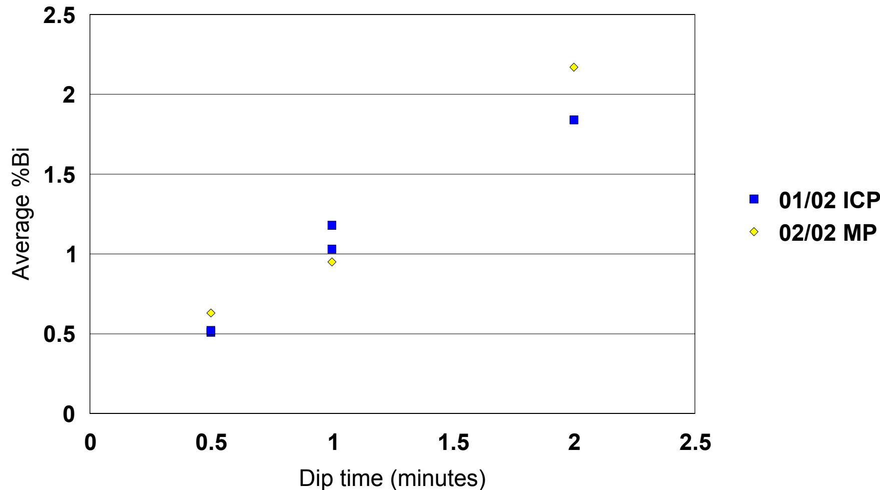


Figure 4. Kinetics of Bi deposition on C4 balls at 140 °C; data were obtained by ICP (inductively coupled plasma) after dissolution of C4 balls (squares) or by direct examination of reflowed C4 balls by electron microprobe (diamonds).

When the same conditions were employed but at only slightly lower temperatures of 125-130 °C, the resulting Bi deposit was dark, powdery and poorly adherent, proving the importance of operating above the eutectic temperature.

The Sn-Bi liquid alloy deposit wets the solid tin-based surface well, provided that the oxide-removal step before deposition is effective. A macroscopically smooth surface is generated, with reflectivity qualitatively similar to that of the original alloy. Since the nucleation of the low temperature phase is a surface-dependent process, coverage of the surface with a thin layer of Sn-Bi alloy is expected to inhibit the transformation without requiring the reflow (or remelting) of the item, which would be undesirable for, e.g., ornamental or museum artifacts. Thus the method outlined above may be useful more generally for the protection and preservation of tin-based items or devices that are exposed to cold temperatures.

The type of immersion (or exchange) plating described here is different from typical immersion plating in several ways: the deposit as formed is at least partially liquid; it is a eutectic (or near-eutectic) alloy rather than a nearly pure element; a thick deposit can be obtained since the process is not self-limiting; the deposit adheres strongly to the substrate. These differences may in fact warrant a special name for this method, such as “immersion eutectic plating” (or “exchange eutectic plating”).

While the purpose for which immersion eutectic plating was developed was to generate low-Bi solders (e.g. 0.1-0.5% Bi) for tin pest prevention, other applications are suggested by the results:

- Higher-Bi tin-based solders (e.g. 3-4% Bi)
- Preservation of tin and some tin alloy artifacts (since tin pest normally starts at the surface)

Furthermore, many other low-melting alloys should be accessible similarly. For example, the following binary systems with eutectics <200 ^{o}C come to mind ("nobler" metal being deposited is first, substrate metal being dissolved is second): Sn-Zn, Bi-Cd, Bi-In, In-Zn, Sn-Cd, In-Cd. There are many more cases for eutectics above 200 ^{o}C. Finding suitable solvents for temperatures approaching 200 ^{o}C and beyond is a challenge; however, ionic liquids, which have enjoyed much attention lately, have the requisite high temperature stability and high polarity desirable for this type of reactions.

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