Tin pest in lead-free solders

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Abstract
Considers the effect of low temperatures on the characteristics of lead-free alloys based upon tin, which is the most popular basis for the new alloys.

Introduction

Increased environmental and health concerns regarding the toxicity of lead have stimulated much research into alternative lead-free solders. These new alloys have to satisfy stringent requirements relating to toxicity, material availability and cost, manufacturability, and long-term reliability (Napp, 1996). The last of these, long-term reliability, is a key issue for lead-free implementation. In surface mount technology, the solder joint is an integral structural member of the board-track-joint-chip assembly.

During service, electronic components may be exposed to wide environmental and temperature variations which may affect reliability of the solder joint. On experiencing a temperature change (normally within the range 218K to 398K), strain is imparted to the assembly and is concentrated within the solder joints, and failure eventually occurs due to thermomechanical fatigue. These strains arise from a difference in thermal expansion coefficients between the materials of each component. To ensure reliability, the new generation of lead-free solders will require mechanical characteristics (monotonic and cyclic strength, creep resistance, rigidity and ductility) capable of withstanding the range and extremes of temperatures encountered in-service. This note considers the effect of low temperatures on the characteristics of lead-free alloys based upon tin, which is the most popular basis for the new alloys.

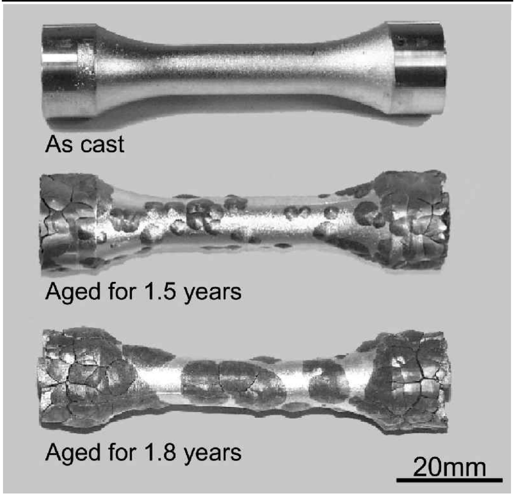
Tin undergoes an allotropic transformation of β-tin (body centred tetragonal) into α-tin (diamond cubic) at temperatures below 286K. The transformation product is termed "tin pest", and the change is accompanied by an increase in volume of 26 per cent (Hedges, 1960). Clearly, if this transformation occurred in solder joints whose principal ingredient is tin, there could be serious repercussions on performance. Before any widespread implementation of lead-free solder alloys can commence, a fundamental understanding of their allotropic transformation behaviour will be required. This note reports the findings on the effects of prolonged exposure of a Sn-0.5 Cu alloy and a Sn-37Pb alloy to low temperatures, well below that of the allotropic transition.

Results

The alloys were held at 20K above their melting point and cast into an aluminium mould in air. The mould and ingot were immediately water quenched and then aged at 255K (–18°C) for up to two years. The specimens were intermittently observed under an optical and scanning electron microscope.

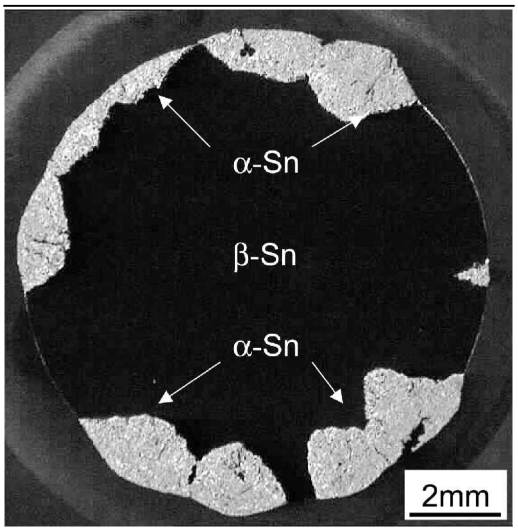
Figure 1 shows the transformation of β-tin (white tin) into α-tin (grey tin) occurring in Sn-0.5Cu, aged at 255K

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



for 1.5 and 1.8 years. Some 40 per cent of the specimen surface was transformed into grey tin (having a "wart-like" appearance) after ageing for 1.5 years, and this proportion had increased to about 70 per cent after exposure for 1.8 years. The transformation appears to require an incubation period since only a superficial film of grey tin is found after exposure for a year at 255K. Since grey tin is fairly brittle,

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



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it cracks in order to accommodate changes in the volume. This result indicates that tin pest could lead to total disintegration of real joints. No change was observed in the Sn-37Pb specimen.

It is evident that the transformation into grey tin initiates at the surface, and then expands on it. Nucleation is not uniform since the surface of the grip section (the end of the specimen) was completely transformed, whereas only 30 per cent of the gauge section was transformed. The grip sections had been machined whereas the gauge of the specimen was as-cast. This suggests that residual stress or strain might accelerate the transformation. Macroscopic bowing of the heavily transformed specimens was apparent.

Figure 2 shows a cross-section, at the grip, of a sample after exposure for 1.5 years at 255K. It can be seen that transformation had begun to expand into the material bulk from the surface. There was no visible evidence of nucleation within the bulk. EDX analysis confirmed that there was no segregation in the specimen.

Preliminary findings indicate that tin pest may also be formed on Sn-3.5Ag and Sn-9Zn alloys within areas that are work hardened. The incubation period in Sn-3.5Ag is much longer than that of Sn-0.5Cu. In contrast, that for Sn-9Zn is much shorter. Further details of these transformations are underway and will be reported in the near future.

The absence of a transformation in the Sn-37Pb alloy may be attributable to soluble impurities (such as lead, bismuth and antimony) suppressing the transformation into grey tin (Hedges, 1960).

The results indicate that tin pest has the potential to become a major hazard in applications which involve prolonged exposure to low temperatures and the use of certain tin-based lead-free solders.

References

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