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Tin pest issues in lead-free electronic solders

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Abstract Tin pest is the product of the $\beta \rightarrow \alpha$ allotropic transition at 13.2°C in pure tin. It is a brittle crumbly material, often responsible for the total disintegration of the sample. The transformation involves nucleation and growth, with an incubation period requiring months or years for completion. Experimental observations reveal a substantial inconsistency and an incomplete understanding of the process. Some alloy additions promote tin pest by reducing the incubation time, whereas others retard or inhibit its formation. Traditional solder alloys have generally been immune to tin pest in service due to the presence of lead, and bismuth and antimony as common impurities. However, the new generation of lead-free solders are more dilute—closely resembling tin. A much debated question is the susceptibility of these alloys to tin pest. Bulk samples of tin-0.5 copper solder undergo the transition at – 18°C although not at – 40°C after five years exposure. Other lead-free alloys (Sn–3.5Ag, Sn–3.8Cu–0.7Cu and Sn–Zn–Bi) are immune from tin pest after a similar period. Large scale model joints exhibit tin pest but it appears that actual joints may be resistant due to the limited free solder surface available and the constraint of intermetallic compounds and components. It seems likely that impurities are essential protection against tin pest, but for long term applications there is no certainty that tin pest and joint deterioration will never occur.

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1 Introduction

The World's largest industrial sector, Electronics, is currently facing two major challenges. The first concerns the demand for continuing miniaturisation of equipment and the associated increase in density of component packing and in functional efficiency. In this case, maintenance of overall structural integrity and avoidance of electrical contact (shorting) between adjacent component parts are key criteria to be achieved. The nature of the materials involved is of secondary concern. In contrast, the second challenge is material-centred, and relates to existing and proposed legislation to remove toxic lead from solder alloys. The damage to health from lead in items, such as paint and piping, is well known and its presence has been eliminated many years ago. Considerably more debate has surrounded the possible hazards associated with the disposal of goods containing lead in their electronics systems, largely because of the much reduced volumes involved. Nevertheless, the Environmental Lobby has prevailed and, with the additional driver of potential commercial profit, adoption of lead-free solder technology is well underway [1]. For example, in the European Community, after 1st July 2006, lead-containing solders were prohibited in the vast majority of applications. This ban involved purchasers as well as producers, so the ramifications for a global industry, such as Electronics, are clear.

Soldering is the preferred method of joining components to printed circuit boards (PCBs) in electronics. It is generally a relatively low temperature (< 250°C) process, so avoiding thermal damage to the polymeric materials of the PCB or the component. The process involves the formation of an intermetallic

compound (IMC) between the metallic materials being joined. Unlike welding, no melting occurs. The fundamentals and practicalities are described briefly in Ref. [2].

Since antiquity, the most common forms of solder have been based upon alloys of tin and lead—notably Sn–37 mass per cent Pb, which is the eutectic composition and possesses the lowest melting point of the tin–lead system. Further advantages associated with this alloy are good fluidity, wettability, mechanical properties and a pleasant shiny appearance. It is an almost perfect alloy for its purpose, and it was no surprise that it assumed a dominant role in the production of interconnections in electronics. Some two decades ago, the toxicity problem surfaced, but the removal of lead was resisted by commercial/industrial intransigence and the highly satisfactory nature of the current Sn–37Pb alloy. Irrespective of this, the search for new solder alloys without lead had been triggered. Details of the investigations are reviewed elsewhere [3, 4], but the principal outcome was that there was no direct (or drop-in) replacement of Sn–37Pb. The favourites were again tin-based systems with a eutectic, and containing silver, copper or zinc. More precisely, Sn–3.5Ag, Sn–0.5Cu, Sn–3.8Ag–0.7Cu, Sn–8Zn–3Bi were popular amongst those proposed. Small variations in composition from those cited above may be found due to patent restrictions or producer preference. While these new alloys have been found to have properties at least equal to those of Sn–37Pb [5, 6], all of them suffer the disadvantage of a higher melting point (i.e. up to 223°C as compared with 183°C for the Sn–37Pb alloy). This can impose significant constraint on processing and PCB assembly. Another area of potential vulnerability of lead-free solders is the possibility of forming tin pest on prolonged exposure to low temperatures. The present review examines the available information on tin pest in pure tin and its alloys, with particular emphasis upon the new generation of lead-free solder alloys and the likelihood of its appearance on actual joints in service.

2 Tin and its alloys

For an engineering metal, tin has an uncommon crystal structure which varies according to the temperature. Between its melting point (232°C) and 161°C, γ Sn occurs with a rhombic crystalline configuration. Below 161°C and at room temperature, it exists in a body centred tetragonal (bct) form as β, or 'white' tin. However, it undergoes an allotropic transition at 13.2°C to a diamond cubic structure, known as α, or 'grey' tin which is a non-ductile semiconductor (Fig. 1). The lattice parameters are: for β Sn, a = 5.831 and c = 3.181 × 10^{-10}m, and for α Sn, a = 6.489 × 10^{-10} m [7], and a considerable volume change (~ 27 percent) is associated with the transition. Consequently, localised rupture occurs which is normally observed on surfaces or corners of samples where constraint is a minimum. The surface spots or eruptions (warts) are known as tin pest or tin plague. The transition occurs by a process of 'nucleation and growth', and the incubation period may be prolonged, ranging from a few months to several years [8].

Tin pest was first reported more than 150 years ago [9] and the vast majority of work on the $\beta \rightarrow \alpha$ transition was performed over 50 years ago. In most studies, the long and uncertain period of incubation was substantially eliminated by *inoculation*, or seeding, with grey tin particles, simply pressed into the white tin surface. For example, by this approach it was possible to achieve 100 per cent transformation in a few days, as compared with the decades required in the original

Fig. 1 The allotropic transformation in tin

condition [10]. Consequently, the majority of the available literature on tin pest relates to the *growth* phase of grey tin following artificial nucleation. Its relevance to the present day service situation is therefore somewhat limited.

Once nucleated, subsequent growth is relatively rapid [8, 11]. It was considered to be a diffusionless transformation but the observational methods available at the time were insufficiently sensitive to confirm this [8]. The maximum rate of transformation is reported to be at around – 40°C, associated with a maximum linear growth rate of the grey tin phase of 0.06 mm per day [10]. At – 18°C, the growth rate is about one third of this [8]. The process rarely goes to completion [12, 13] and partial reversal can be achieved by heating to about 60°C or above. A potentially worrying scenario to the designer of equipment likely to operate in conditions conducive to tin pest formation is that of *'self inoculation'* i.e. during thermal cycles in service, if tin pest is nucleated during the cold phase of one cycle, and the process is incompletely reversed during the following warm phase, the requirement for a prolonged incubation period in the next cold phase will disappear. The tin is said to be '*activated*' and significantly more tin pest will form—and so on. No such event in service has been reported to date, but as with most disasters, it is not impossible that a combination of circumstances could contrive to set up such conditions.

A key point emerging from a survey of the literature from that period is the lack of consistency in the findings—both in terms of the occurrence, or not, of the transformation and the rate at which it proceeds when it does. In particular, any quantitative observation is entirely specific to the conditions of the experiment being described. This is in no way a criticism, but rather a recognition of the enormous challenges involved—the precise roles of composition, impurity levels, strain effects and microstructure are not clearly understood. This is well illustrated by an extensive study at Battelle Laboratories [14, 15] on non-inoculated tin samples stored at – 40°C. Twenty one varieties of a commercially pure tin, with small amounts of Pb, Sb, Bi, Cu, As, Fe as impurities, were exposed for ten years and examined periodically. Only in one batch did the majority (22 out of 24) cast samples transform in periods of between 5 and 114 months, but following cold rolling, 11 out of 12 of identical samples from that batch did not transform after 10 years exposure. Similar erratic behaviour was exhibited by four other brands when less than 20 per cent of identical samples transformed within the 10 year period. No tin pest formed at all in any of the remaining brands. Chemical analysis failed to resolve the matter. Further, subsequent work indicates that cold work promotes rather than retards the transformation [14, 16, 17].

It has been suggested that stress relaxation in the white tin ahead of the interface plays an important role in the growth of tin pest [18]. The high stresses that are generated by the large volume change form a zone of plasticity in front of the β/α interface, the rate of migration of which is controlled largely by the average stress level in its vicinity. Relaxation via point defect creation, dislocation motion, twinning or crack formation reduces these stresses and more rapid growth occurs. This hypothesis can account for an observed thickness effect on tin pest growth. With reduced thickness, below 500μm, the plastic zone size is less but the dislocation density within it is higher. This hinders relaxation, maintains a higher local stress level and favours slow growth of the interface. For foil thicknesses above 500μm, stress relaxation occurs quite rapidly and the thickness effect is not apparent (Fig. 2). The controlling plastic zone size is generally much smaller that the grain dimensions, so no grain size effect is observed. A steady state balance between work hardening and recovery is envisaged in the zone ahead of the interface, and the activation energy for growth is most closely associated with diffusion along dislocation cores. Naturally, the balance between core and bulk diffusion varies with temperature, and it is not unusual for either mechanism to dominate according to the temperature.

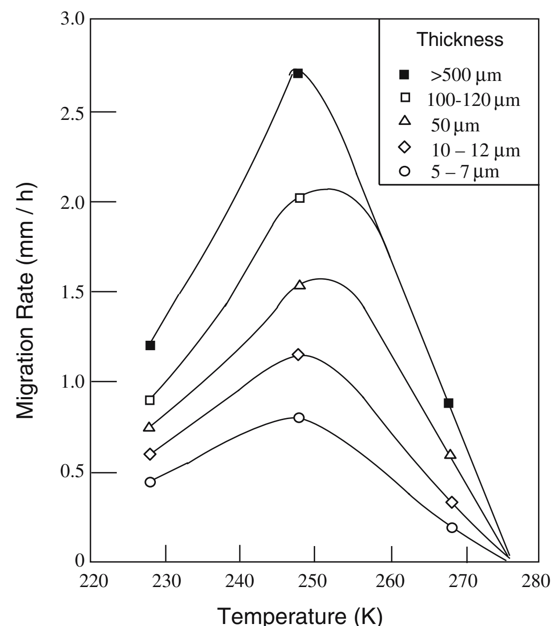

Fig. 2 Effect of sample thickness on migration rate of the β/α interface in pure tin (18, modified)

TEM studies of the transformation are limited due to the brittle nature of grey tin and the large volume change involved. Some success has been achieved by performing the transformation in samples preprepared for TEM examination. Observations of the $\beta \rightarrow \alpha$ transition in pure tin reveal a preferred orientational relationship between the two phases [19, 20]. The (111) plane of grey tin is parallel to the (001) plane of white tin, and the [211] direction is nearly parallel to the [010] of white tin. The absence of grey tin in foils thinner than 130 nm was attributed to surface energy effects [19]. Overall, the available evidence—the curved nature of the β/α interface, the lack of a three-dimensional crystallographic relationship between the phases and the retention of Xenon cavities in both phases [21] —suggested that the transformation was massive [22] rather than martensitic [19]. It is suggested that the transformation occurs partly by mass transformation and partly by atom motion that is massive in nature. There is a hysteresis effect between the directions of the reaction, with the $\alpha \rightarrow \beta$ transformation occurring about 20°C above the $\beta \rightarrow \alpha$ transition [23].

3 Effect of alloying additions to tin

The difference between an impurity and an alloy addition is a matter for academic debate, but there is strong evidence that the presence of elements soluble in tin, such as Pb, Bi, Sb suppresses the $\beta \rightarrow \alpha$ transition by raising the transition temperature [10, 12, 16, 24] and that Cd, Au and Ag retard it [16, 25–27]. Extremely low levels of solute can be effective—as low as 0.0035 mass per cent in the case of bismuth [28]. In contrast, insoluble elements, such as Zn, Al, Mg and Mn accelerate the transformation by lowering the temperature at which it occurs [16, 29] while Cu, Fe and Ni are reported to have little influence [16]. However, later work suggests that Cu and Zn promote grey tin formation [27, 30] and it was suggested that the influence of any alloy addition could be changed by the presence of other elements [27] i.e. an element could either promote or inhibit the transformation according to the other elements present. From the application perspective, consideration of the amounts of second element addition reported in the literature indicates that an overlap with commercial forms of 'tin' is possible (commercially pure tin contains typically up to 0.2 mass per cent impurities). This range of compositions suggests one possible explanation for the inconsistent and sometimes conflicting findings reported.

The presence of copper (0.8 mass per cent) and heavy cold work (up to 90 per cent) promotes tin pest formation at – 30°C [17]. Incubation times are reduced to less than 10 days and the transformation is complete after 40 days. The effect was more marked as the degree of cold work increased (Fig. 3). Tensile pre-strain, rather than compressive, has been found to promote tin pest on tin-coated steel [27]. Even in the absence of prior deformation, as-cast samples transformed in about six months—which is much more rapid than generally observed. The composition of that alloy was (mass per cent);

Cu, 0.8; Pb, 0.001; Fe 0.0003; Sb, 0.0002, As 0.0002; Bi 0.0001.

In dilute Sn–Ge alloys, the temperature, T_c, of the reverse transformation from grey to white tin is raised by increasing the Ge content, according to the expression [31]

$$T_c = 32.0 + 51.8C^{0.33}$$

where C is the amount of Ge in atomic per cent. For example, the transition temperature for a Sn–0.5Ge alloy is about 75°C. This effect is attributed to the reduced mobility of the β/α interface. In Sn–0.6Si alloys, grey tin remains stable on heating to 90°C [32].

The role of solute (or impurity) atoms was investigated using germanium (0.1–0.3 at per cent) [18]. Within this range, the migration rate of the β/α interface slowed with increasing Ge content (Fig. 4). This was attributed to the solute atoms impeding dislocation climb—the less mobile the solute, the stronger the effect. Hence, stress relaxation was restricted and the advance of tin pest retarded.

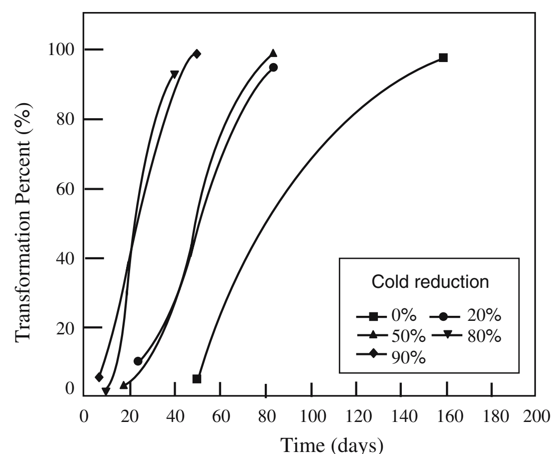

Fig. 3 Influence of cold work on the transformation in a Sn-0.8 mass per cent Cu alloy at – 30°C (17, modified)

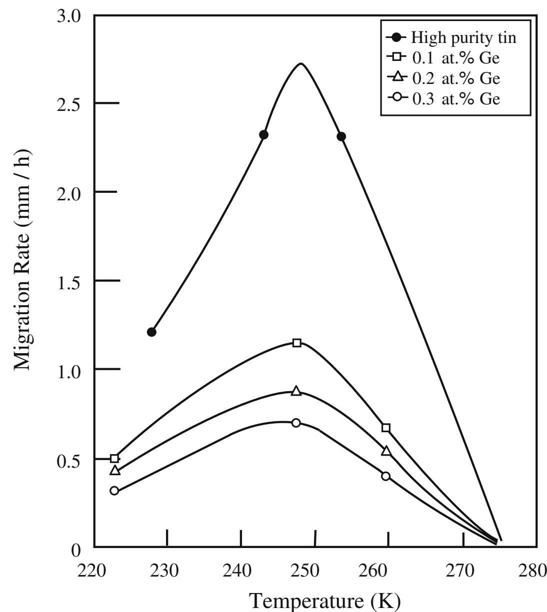

Fig. 4 Effect of solute concentration on the migration rate of the β/α interface in dilute Sn–Ge alloys (18, modified)

External pressure has a significant effect on the temperature of transformation and the rate at which it occurs [23, 33, 34]. For example, in dilute Sn–Ge alloys (0.1 to 0.5 mass per cent) the transition temperature is reduced by 50 K per kbar.

An extensive and systematic study by Boremann [35] confirmed the variability in the duration of the incubation period for pure tin (99.9944 mass per cent) at – 100 F (– 73.3°C). One of four samples in the non-inoculated condition transformed after six months exposure, but the remainder were unaffected after four years. Cold worked pure alloys, after inoculation, exhibited tin pest in Sn, Sn–40Pb and Sn–50Pb but this could usually be prevented for at least four years by the addition of 0.1 Bi or Sb. Dilute binary and ternary alloys (Sn + Pb, Sb and Bi), without inoculation were also studied. Unfortunately, their initial condition differed from that employed previously (a 2 h homogenisation anneal was applied after cold working). However, it did indicate the critical amounts of solute necessary to prevent tin pest formation after 14 months at exposure at – 100 F. These were 0.18, 0.047 and 0.27 mass per cent for Pb, Bi and Sb respectively. The existence of intermediate ranges of solute content below these levels in which the transformation did occur highlights the difficulties associated with this topic but nevertheless the study provides an valuable source of experimental detail. It was concluded that Pb, in the amounts generally found in solders, will not prevent the transformation from occurring. Small amounts of Bi or Sb are effective inhibitors—more so when they are in combination.

It seems that the strength of the β Sn phase plays a significant role, as the α Sn warts expand into it [18]. With increase in strength, tin pest growth is slowed. For similar amounts, it is likely that elements soluble in tin will make a greater contribution to solid solution strengthening than insoluble atoms will enhance particle strengthening. This suggestion is in line with the experimental observations. Elements soluble in tin, such as Pb, Bi and Sb, suppress the transition by producing a stronger β matrix around the tin pest warts. Conversely, insoluble elements, such as Zn, Al, Mg and Mn, have little effect on strength and appear to promote the transformation. The role of prior deformation is less clear, and this is probably due to it having opposing effects on the initiation and growth stages. In Sn–0.8Cu at – 30°C, it has been clearly demonstrated that cold work reduces the incubation period by up to an order of magnitude [17] whereas the transformation rated is increased by around threefold. With the exception of the Battelle study [14, 15], most previous investigations concur that the transition is promoted by cold work.

Tin pest has also been observed by Ogden (R. Odgen, Private Communication) in a reputedly Sn–3.0Cu solder alloy after low temperature storage in a domestic freezer (typical temperature a – 18°C approx) for 21 months. None was apparent after 15 months.

4 Tin pest in modern electronics?

There are numerous applications in which the electronics systems enter the domain of tin pest formation. From the IPC categories of operating conditions [37] aeronautical, aerospace and automobile are obvious candidates. However, because lead and impurities, such as Bi and Sb, suppress the $\beta \rightarrow \alpha$ transition and because the vast majority of traditional solders to date contain these elements, tin pest has not been a problem. But the emerging generation of lead-free solders are rather different; they are much more dilute—up to a 70 × in the case of Sn–0.5Cu. Microstructurally, they comprise small intermetallic particles, as opposed to substantial proportions of second phases in the conventional Sn–Pb solder alloys, together with a tin-rich solid solution. In other words, they resemble pure tin more closely than traditional lead-containing solders, so the key question is whether tin pest is more likely to form in the new lead-free alloys?

Studies by the Solder Research Group at the Open University, UK, were commenced about a decade ago as a spin off from their evaluation of the mechanical behaviour of solder alloys [38]. Due to their low

melting point, room temperature represents a significant homologous temperature (~0.65) for solders which are microstructurally unstable under ambient conditions. Common practice to preserve stability was to store the as-cast test pieces in a freezer at – 18°C prior to testing. After extended periods, tin pest warts were observed on certain samples, and these findings sparked more systematic investigations which are now described [39, 40].

A range of lead-free alloys, including Sn–3.5Ag, Sn–0.5Cu, Sn–3.8Ag–0.7Cu, and Sn–8Zn–3Bi, with Sn–37Pb as a comparator, has been exposed to sub-critical temperatures, (between – 18°C and – 40°C) for periods up to 10 years. Details of their compositions are given in Table 1. Most samples were in the form of tensile test pieces (diameter 11.1, gauge length 60 mm) in the as-cast condition and cooled by water quenching, air or furnace cooling (cooling rates 20, 0.2 and 0.02°C s^{-1} respectively). They were removed from storage and examined periodically. Some specimens were aged or subjected to monotonic or cyclic strain prior to low temperature storage.

Of the alloys investigated, only Sn–0.5Cu aged at – 18°C regularly exhibited tin pest formation. Surface spotting occurred after a few months, followed by surface eruptions, the development and growth warts, severe cracking and eventually total disintegration of the sample. Figures 5 to 8 show this sequence. Both the individual warts and the transformation interface are clearly visible (Fig. 5). The effect of surface strain, induced in this case by machining the specimen heads for gripping purposes, in promoting the transition is clear. The head regions of the sample are virtually covered with tin pest, whereas the specimen gauge length which retains its original cast surface exhibits isolated warts (Fig. 6). Spread of tin pest is largely a surface event, although penetration into the interior of the sample does gradually occur (Fig. 7). Electron Backscatter Diffraction Analysis (ESBD) confirmed that growth of tin pest occurred at the interface of the α/β phases and also the absence of grey tin in the interior of the sample (Fig. 8). Complete disintegration of the sample eventually occurs as shown in Fig. 9. Eventually, the sample fragments would become powder. It is important to note that the above observations pertain to a single sample; while a substantial proportion of Sn–0.5Cu specimens revealed tin pest formation, they did so at different rates under identical conditions. Moreover, in other samples of this alloy, no tin pest was observed although their history was identical. This observation applied to all three cooling rates. Tin pest was not formed after ageing at – 40°C in the Sn–0.5Cu alloy, nor in any of the other alloys examined, irrespective of prior treatment, after storage at either temperature.

5 Discussion

The allotropic transformation from β to α at 13.2°C in pure tin is well established, and there is substantial evidence that a similar transition occurs in many dilute tin alloys. Also mirroring the findings on tin, is the inconsistency and variability of the process in the alloy, with nucleation as the critical event. While acknowledging that the exact mechanism of the transition is unclear, the salient questions from the electronics viewpoint are; (1) *will tin pest form in other lead-free solders?* and (2) *will tin pest form in actual solder joints?* These possibilities are now considered further.

5.1 Formation of tin pest in other solder alloys

The efficacy of solute additions in inhibiting or promoting the $\beta \rightarrow \alpha$ transition in tin was described earlier. In terms of *global composition*, Pb, Bi and Sb suppress the allotropic transformation whereas elements insoluble in tin promote it. Much of the published work involved very low solute concentrations which could be effective in their actions. From this, two aspects merit further consideration; the level and type of impurities, and compositional variations i.e. *local composition* effects.

A wide variation exists in the purity levels of commercial lead-free solder alloys and few agreed limits apply. Typical ranges for elements commonly found are, in mass percent, R. Bilham (Private Communication);

Table 1 Composition of SRG alloys

Sn	Pb	Ag	Cu	As	Bi	Fe	Al	Sb	Zn	Others
Balance	37	–	< 0.08	< 0.02	0.25	< 0.02	0.005	0.2	0.005	0.08
Balance	0.014	0.008	0.55	< 0.001	< 0.001	0.001	< 0.0002	0.012	< 0.001	< 0.003
Balance	0.04	3.47	0.003	< 0.001	< 0.001	0.007	< 0.0002	0.025	< 0.001	< 0.003
Balance	< 0.1	3.8	0.7	< 0.03	< 0.1	< 0.02	< 0.001	< 0.1	< 0.001	< 0.2
Balance	0.081	–	0.006	0.001	2.92	0.002	–	0.005	7.89	–

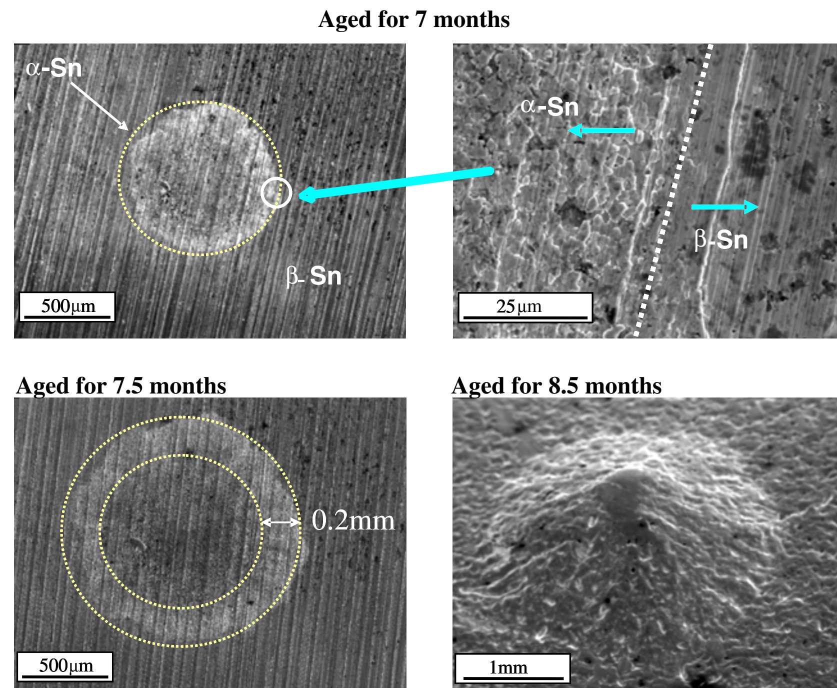

Fig. 5 Early stages of tin pest formation in a Sn–0.5Cu alloy during storage at − 18°C

Fig. 6 Development of tin pest over a test piece, exposed at 18°C, showing a higher concentration of warts on machined areas

$$\text{Pb }(0.03\text{–}0.07); \text{Bi}(0.003\text{–}0.030); \text{Cu}(<0.01)$$
$$\text{Zn, Cd, Al}(\leq 0.001); \text{Fe, As, Ni}(0.003\text{–}0.01).$$

The extreme values are roughly 0.04 to 0.12 mass per cent when alloys have either a minimum amount or a maximum amount of each impurity. These levels overlap with compositions of the intentional alloys made up to study the $\beta \rightarrow \alpha$ transition. For comparison, in the classic Batelle study [14, 15] of 'pure' tin, the impurity levels of individual batches ranged from 0.002 to 0.246 mass per cent. The composition of the Sn–0.5 Cu alloy described previously (Table 1) coincides well with the above bands, and in its entirety would be regarded as a relatively pure alloy (total impurity content ~ 0.04 mass per cent). Notably, the lead content appears low. The significant point is the similarity in levels of intentional addition in the published work on tin pest in 'pure' tin and typical amounts of impurity likely to be encountered in commercial lead-free alloys. So, in present day commercial alloys, the impurity levels could play a vital role in determining the susceptibility to tin pest formation.

A dichotomy arises between the scientific requirement for total understanding and the engineering need to evaluate the probability of tin pest formation in service. The studies described previously on Sn–0.5Cu involved a commercial alloy, the composition of which was given in Table 1. Despite the presence of three established tin pest inhibitors (Pb, Bi and Sb) the transition occurred eventually in the majority of samples. Detailed chemical analysis of individual specimens has yet to be performed.

Of all the candidate lead-free solder alloys, Sn–0.5Cu is the most dilute, i.e. it should resemble pure

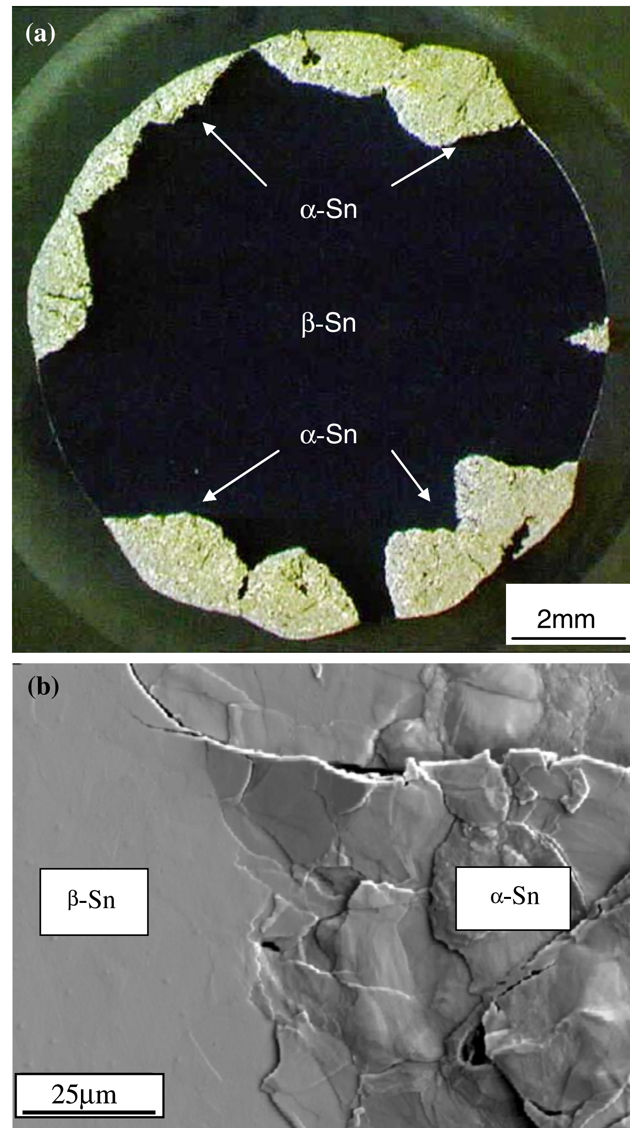

Fig. 7 Penetration of α tin (tin pest) into the interior of the gauge head, and the interface region between the α and β phases

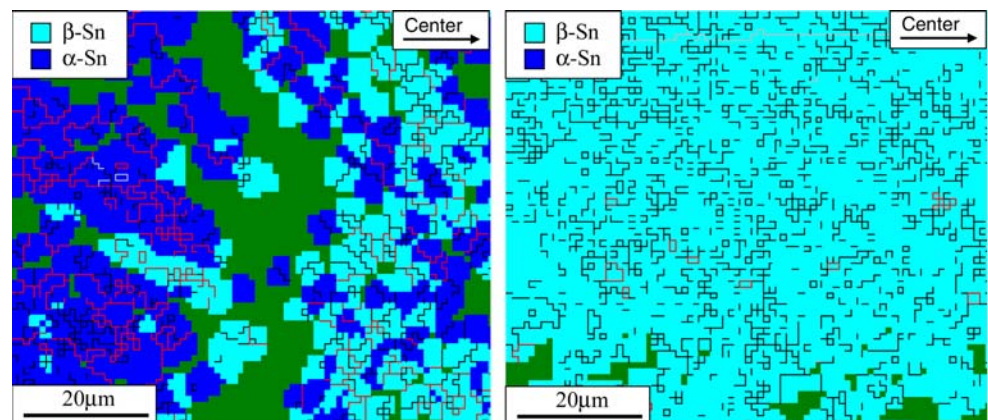

Fig. 8 Electron backscatter diffraction image of α/β interface and the region ahead of it

tin more closely than other selected systems. This is borne out by its propensity for tin pest formation. Approximately, one atom in every 100 in Sn–0.5Cu is a copper atom; in the ternary Sn–3.8Ag–0.7Cu, one in twenty is a solute atom, while in Sn–37Pb, one atom in five is lead. In the case of tin pest formation in alloys, two criteria are worthy of consideration; the proximity of the solid solution composition to pure tin (*the*

Fig. 9 Total disintegration of a Sn–0.5Cu test piece after prolonged exposure at – 18°C

proximity hypothesis), and the *excess solute* situation. From the available evidence, additions that suppress tin pest are soluble, thus affecting the solid solution with little or no excess solute atoms. Elements insoluble in tin are likely to be associated with excess solute atoms which may cluster or form precipitates (IMCs) and the conditions of instability conducive to the $\beta \rightarrow \alpha$ transition. The solid solution will contain a limited amount of solute, will approximate more closely to pure tin and hence be more susceptible to tin pest formation.

The discussion so far has largely focussed upon global composition considerations, but the possibility of local variations should also be considered. There will be regions in the microstructure that more closely resemble pure tin than indicated by the overall composition. Microstructure and local composition depend upon initial cooling rate and any subsequent heat treatment. For solders, room temperature represents a significantly high homologous temperature for thermal instability and continued changes in microstructure and local composition—so storage periods should be included. The equilibrium solid solubilities of Ag and Cu in tin at the respective eutectic temperatures are 0.04 mass per cent (0.042 atomic per cent and 0.0063 mass per cent (0.012 atomic per cent) respectively [42]. Considerably higher values have been found in a commercial version of the ternary Sn–3.8Ag–0.5Cu alloy (0.1 mass per cent Ag and 0.16 mass per cent Cu) [43], and this has been attributed to supersaturation during non-equilibrium cooling during the casting process [44]. This level of supersaturation was retained subsequently, even after prolonged annealing at 150°C and above [44]. In addition to the extent of solute atoms in solution, the volume fraction of 'tin' dendrites is likely to be sensitive to the cooling rate, if the findings for the family of Sn–3.8Ag–0.7Cu [45] apply to Sn–0.5Cu. With the eutectic composition, the volume fraction of 'tin' regions (containing less than 0.1 mass per cent Ag and 0.006 mass per cent Cu) varied from 5 per cent under slow cooling (1°C s^{-1}) to 65 per cent after rapid cooling (100°C s^{-1}). The situation was further complicated by sensitivity to the Ag and Cu content—for hypoeutectic concentrations, an increase in cooling rate increased the volume fraction of 'tin' dendrites, whereas the opposite occurred for hypereutectic amounts of Cu and Ag. However, no effect of cooling rate was observed in the study of tin pest in Sn–0.5Cu described earlier.

The absence of tin pest on samples of Sn–0.5Cu aged at – 40°C for up to five years is in contrast to the earlier work on pure tin which suggested that the maximum rate of formation was around this temperature. While the thermodynamic driving force will undoubtedly be greater at the lower temperature, irrespective of any change in transition temperature induced by copper, the associated kinetics of the transformation could be slowing the process to timescales beyond those in the present investigation. Alternatively, this finding might be attributable to differences between 'pure' tin and the Sn–0.5Cu alloy, but since the latter comprises only one copper atom in a hundred, such a key difference is not immediately apparent. The absence of tin pest after exposure at very low temperatures, when it forms at higher temperatures, has been reported for Cd and Bi additions to tinplate [27].

6 Tin pest in solder joints

The possibility if tin pest formation in solder joints was suggested by Bornemann [35] and by Williams [30] about half a century ago. Model joints, comprising samples of copper soldered with pure tin, a high purity Sn–Pb solder or a commercial solder, were exposed at – 40°C *after inoculation*. No tin pest was observed in the sample made using the commercial solder alloy—a fact attributed to the Bi an Sb impurities present.

In addition to the compositional effects which themselves may be distorted by conditions within the joint, the dimensions, geometry and scale of an actual interconnection may play a role in the formation of tin pest. From a geometrical and mechanical perspective, a soldered joint can be regarded a very thin layer of soft material (the solder) covered on its upper and lower surfaces by much harder materials (the intermetallic layer and the component/substrate surfaces). As miniaturisation proceeds, the solder layer is becoming

almost a plane, and the significance of the IMC layer increases. Unlike the bulk solder samples described earlier, the proportion of free surface area in a joint is considerably limited.

Although tin pest forming on actual joints in service is unknown to the Author, it has been observed on relatively large *model* Cu/Sn/Cu joints in which the degree of constraint is much less (Y. Kariya, Private Communication). Figure 10 again demonstrates the propensity for tin pest to form at free surfaces. A soldered interconnection could contain several, if not all, classes of material (metal, ceramic, polymer and composite) each possessing quite disparate properties [47]. The mechanical response is then determined by the entire structure rather than simply by the behaviour of a single component in it. The constraint emanating from the surface layers is likely to restrict the large volume expansions associated with tin pest formation. Some of the initial studies on pure tin showed that the growth rate of the transformation product was halved at high pressure (90 atmospheres) [33, 34], suggesting perhaps that investigations of tin pest for aerospace applications should involve a vacuum? Simple physical constraint has been shown to inhibit the transformation in regular-shaped samples of tin [48].

Returning to chemical factors, regions throughout a soldered joint may experience quite different cooling rates, either between different joints or within a single unit. This will result in both microstructural and local compositional variations as discussed previously, but in a more complex manner. Similarly, initial or service-induced stress or strain (e.g. thermomechanical cycling) can also produce compositional changes which might affect the propensity for tin pest formation.

With the transition to lead-free solders, it should not be forgotten that other sources of lead (e.g. finishes and terminations) exist and may constitute over half of the lead available [49]. Implementation of lead-free technology involves more than simply changing the solder alloys.

It is hoped that the scenario envisaged by Lasky [50] that 'purification' of solder alloys (i.e. reducing Sb, Bi and Pb levels) might promote tin pest formation with dire consequences will never take place. However, this approach might be a valuable exercise in 'closing the door *before* the horse has bolted!

7 Areas for future investigation

Studies of phase transformations, such as the white-to-grey in tin, are generally associated with the heyday of X-ray crystallography and dilatometry. More than 70 years have elapsed since the fundamentals of the α/β

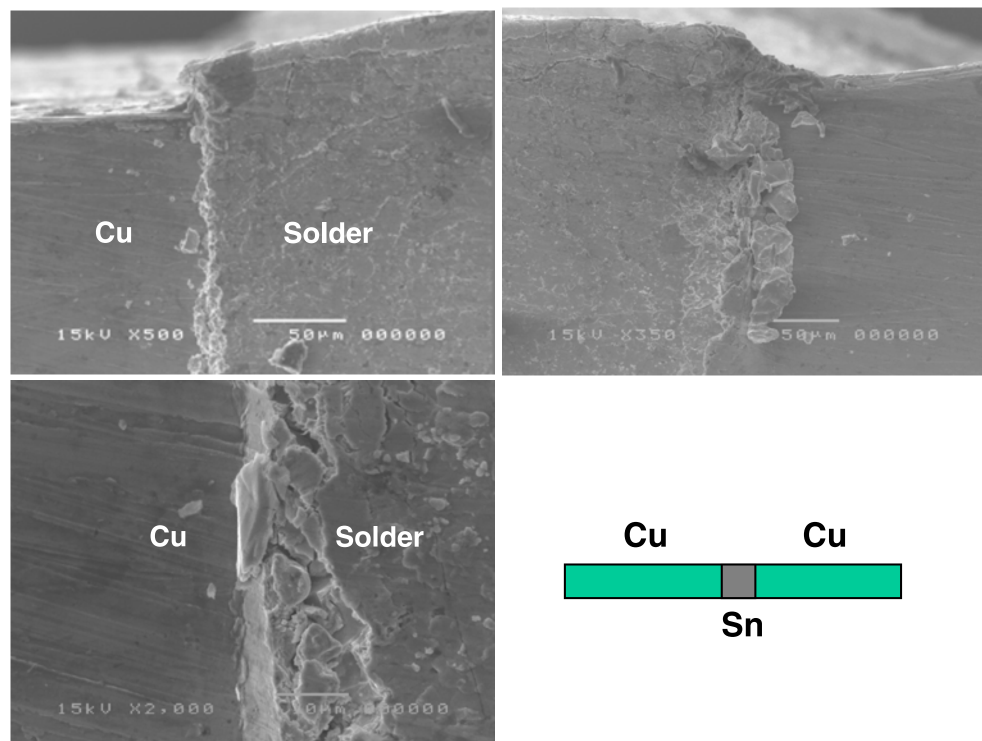

Fig. 10 Tin pest formation in a model Cu/Sn/Cu joint[46]

transition in tin, described earlier in this paper, were identified. During that period, tin pest was never a problem in solders because of the presence of lead and other inhibitors in solder alloys. However, with the advent of 'lead-free' solders and the findings of the most recent investigations, a technological driving force has been created and the subject merits re-investigation. The variety and capacity of observational methods now available (SEM, TEM, neutron diffraction, EPMA and so on) would have been unimaginable in the early days of the investigations. With this in mind, the following avenues seem worthy of further study;

- Illucidation of the precise mechanism of the transformation, particularly the nucleation stage and the criteria for its onset. Detailed crystallography, orientation relationships etc.
- Clarification of the roles of additional elements to tin—and why some retard the transition and others promote it. Considerable experimental evidence exists on this but the underlying reasons for the observed effects are unclear. Measurements of the transformation temperature.
- Examination of exposed samples with identical histories, only a proportion of which may exhibit tin pest. Identification of chemical and microstructural differences both globally and locally. Apart from near-surface regions, determination of preferable sites for nucleation.
- Evaluation of the kinetics of growth and its activation energy.
- With respect to tin pest formation in actual joints, determination of local microstructure and composition that will differ from that in bulk samples, and to some extent will be joint specific.
- The role of mechanical constraint warrants further investigation, and offers opportunity for modelling and stress analysis.

While these aspects themselves represent a formidable challenge, it is a salutary exercise to consider the potential variables involved (Table 2). Even inserting a minimal number in to the matrix produces a dauntingly large number of combinations.

8 Conclusions

A survey of tin pest formation in pure tin and tin-based alloys has indicated the following points relevant to this re-emerging and sometimes controversial topic:

- Like the pure metal, bulk samples of several dilute tin alloys experience the $\beta \rightarrow \alpha$ transition forming tin pest after prolonged exposure at low temperatures. Initial solidification rate appears to have little significance. The process involves nucleation and growth, with the former reaction being inconsistent in terms of time and its actual occurrence. Such sporadic behaviour is also found in pure tin. Due to this, the initiation stage has often been circumvented by seeding, and subsequent studies have been focused upon growth.
- A large volume change is associated with the $\beta \rightarrow \alpha$ transition, and tin pest is formed on the sample surface where constraint is a minimum. This causes eruptions (warts), cracking and eventual disintegration.
- The factors governing the allotropic change are uncertain. Elements soluble in tin, such as Pb, Sb and Bi, inhibit tin pest appearance, while insoluble additions such as Zn, Al and Mg promote its formation. Very small amounts appear to be influential, and it could be that impurities are unknowingly beneficial in suppressing tin pest. In the Sn–0.5Cu system, the addition of copper, at the level of one atom in a hundred, overrides the presence of three tin pest inhibitors, albeit in much smaller quantities.
- The exact criteria for initiation and the mechanisms by which growth occurs are not well understood. Both shear and massive transformations have been proposed, although the latter is currently in favour. Many of the experimental observations can be explained in terms of the resistance to the volume expansion emanating from either the strength of the white tin phase or the presence of a mechanical constraint.
- As well as global composition, local composition and microstructure may be important, and these are affected by cooling rate and the overall composition with respect to the associated eutectic.

Table 2 Factors affecting tin pest formation

<table>
<tr><td>Composition</td><td colspan="6">Intended</td><td colspan="6">Impurities</td></tr>
<tr><td>Condition</td><td colspan="4">As cast
(Cooling Rate)</td><td colspan="4">Cold worked
(% CW)</td><td colspan="4">CW+ Annealed
(Annealing time, temp)</td></tr>
<tr><td>Exposure</td><td colspan="3">Inoculated</td><td colspan="3">Non-Inoculated</td><td colspan="3">Temperature</td><td colspan="3">Time</td></tr>
</table>

- Tin pest formation in actual solder joints as they become even smaller is likely to be limited by the lack of free solder surface and the constraint imposed by the intermetallic layer and the adjacent component/substrate. The situation is further complicated by the possibility of variable cooling rates throughout the joint volume.
- An extensive investigation of the behaviour of lead-free solder alloys (Sn–3.5Ag, Sn–0.5Cu, Sn–3.8Ag–0.7Cu, Sn–8Zn–3Bi, with Sn–37Pb as a comparator) at – 18 and – 40°C, for periods of up to ten years, has shown that only the Sn–0.5Cu solder is vulnerable to the appearance of tin pest. To date, no tin pest has been observed in this alloy after storing at – 40°C for periods up to five years.
- The timescales over which experimental data are available are often shorter than required in some applications. Acceleration of the complete nucleation and growth process is difficult without resorting to artificial inoculation. So, perhaps the salient enquiry should not be *'Does tin pest occur...'*, but *'When does tin pest occur...'*.

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