

CRYSTALLOGRAPHICALLY-FACETTED VOID FORMATION IN THE MATRIX OF LEAD-FREE SOLDER JOINTS

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Crystallographically-faceted void (CFV) formation in lead-free solder-joints has been observed after solidification and during subsequent solid-state ageing. Such voids have not previously been reported in the literature. This paper gives a preliminary report on observations of voids which tend to be associated with, and adjacent to, intermetallic compounds in the solder bulk and near-substrate interface region. It has been observed that CFVs are correlated with β -Sn crystallographic orientation and form in a tetragonal shape. Ageing promotes the CFV clustering and growth.

Key words: lead-free solder, voiding

INTRODUCTION

As a result of environmental issues and consequent legislation, lead-free electronics manufacturing has become a global trend. Environmentally-friendly soldering alloys for the electronics industry are under further development in order to optimize their long-time stability and reliability.

One of the major aspects influencing the long-term reliability of solder joints is microstructural integrity. In addition to the formation of non-equilibrium microstructures during the solidification of lead-free solders, which results in microstructural heterogeneity compared to lead-containing solders¹, it has been reported^{2,3} that lead-free solder-joints are more likely to develop voiding than traditional lead-containing ones. Voids become troublesome when they form in large quantities, reducing the cross-sectional area of the joint². According to the IPC-610-D⁴ standard for electronic assemblies, the maximum void area should not exceed 25% of the solder-joint cross-section. Research carried out by Wickham et al.³ showed that the void level in lead-free PBGA (Plastic Ball Grid Array) solder-joints did not exceed 15% regardless of the soldering conditions.

Aspandiar⁵ proposed a classification of voids commonly detected in solder joints as follows: macro-voids; planar micro-voids; shrinkage voids; micro via voids; pin-hole voids; and Kirkendall voids. Some of those (shrinkage voids) are unique to the Sn-Ag-Cu solders, and are caused by the solidification sequence⁵. Voiding in solder-joints has also been investigated by Jang et al.⁶ who described an additional type of voids unique to lead-free assemblies and occurring during solid state ageing. Jang et al. have reported that these voids are always found to be attached to the

intermetallic particles in the solder matrix, especially to those formed during interfacial processes at the interface with the substrate.

Many studies of lead-free solders are focused on the interfacial processes during the interaction between the substrate and the molten solder, resulting in intermetallic layer formation⁷⁻⁹. Nevertheless, there is a lack of research highlighting the effect of the intermetallic precipitates on voiding within a solder-joint, especially during its ageing. The present paper reports on crystallographically-faceted voiding in lead-free solder-joints during solidification and subsequent solid state ageing. These voids could affect the long-term reliability.

EXPERIMENTAL METHOD

For solder-joint assembly, 99.98% copper plates were used. The plates were cut into coupons with dimensions of 20 x 30 x 1mm. The following lead-free alloys were used: SAC405 (Sn95.5 – Ag4.0 – Cu0.5) by Heraeus GmbH; CASTIN (Sn96.2 – Ag2.5 – Cu0.8 – Sb0.5) and SN100C (Sn – Cu0.7 – Ni0.05 + Ge) by AIM Ltd. The solder compositions are given in mass%. The joints were prepared by the following process: two pieces of polished and cleaned Cu substrates were set parallel to each other with a 0.5mm space between them. The soldering paste was filled into the gap and reflowed by means of a hot-air gun with an air flow temperature of 280°C and a time above liquidus of 30 seconds. Thermo-profiling was performed by means of a K-type thermocouple immersed into the solder and data monitoring with Labview with a signal reading rate of 4 readings per second. The measured solder-joint cooling rate in the air was about 0.7°C/sec. The soldered samples were polished again and cut into small pieces (1 x 5mm) with rectangular cross-section using a diamond cut-off saw.

All the samples were then cold mounted in epoxy resin and then the grinding and polishing was carried out with the following steps: 220 Grit SiC abrasive → 500 Grit → 1000 Grit → 2400 Grit → final polishing using colloidal silica. The prepared cross-sections were not etched. After cross-section preparation, the specimens were examined with Field Emission Gun Scanning Microscopy (FEI Sirion 200). Electron backscattered diffraction (EBSD) analysis was performed by means of a HKL Channel 5 detector. Ageing was carried out at 160°C in a Gallenkamp furnace. The specimens were not broken out of the mounts for ageing. After ageing, samples were repeatedly polished to check that the voids observed were not a surface phenomenon.

RESULTS

During microstructural investigations of the lead-free solder-joints, CFVs have been constantly observed in the β -Sn matrix in the ‘as soldered state’. For example, Figure 1 shows an SN100C alloy solder-joint cross-section in the region near the interface with the substrate. EBSD analysis showed that the CFV orientation is always correlated with the β -Sn grain crystallographic

orientation; the CFVs form in a tetragonal shape. Depending on the cross-section plane, they have been observed as triangles, rectangles, squares or triangles with cut ends. The red tetragonal unit cell in Fig. 1 is from the EBSD analysis and shows the crystallographic orientation of the β -Sn grain in this area.

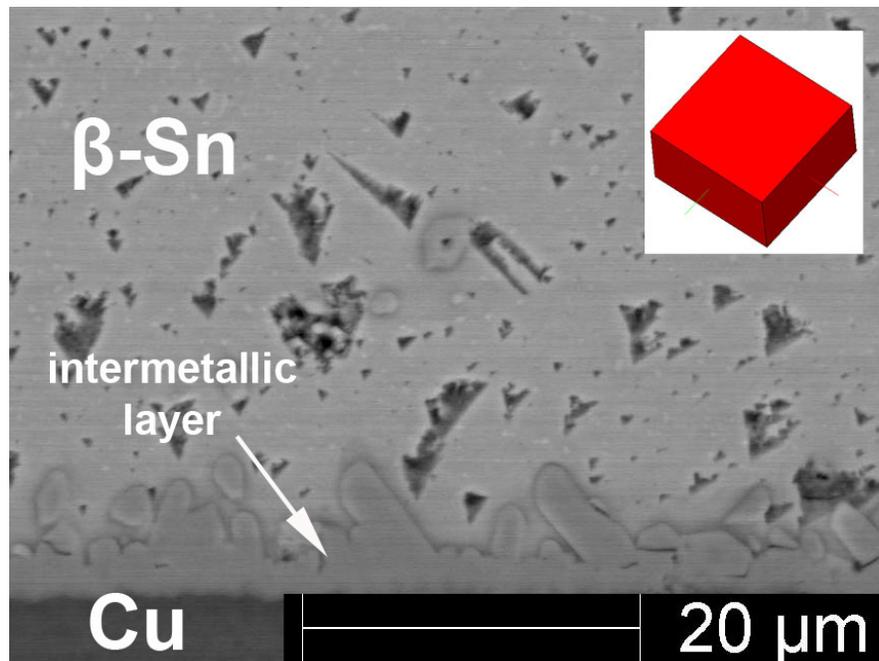


Figure 1. Correlation between the orientation of the voids and the crystallographic orientation of the β -Sn (shown inset in the top right and corner and derived from EBSD). The cross-section is unetched and is in the 'as soldered state'; Sn100C alloy.

The CFVs were observed to be preferentially located near the substrate-solder interface, i.e. near the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ intermetallic (IMC) layers, and in the solder bulk close to the IMC particles Cu_6Sn_5 and Ag_3Sn . Ageing at a relatively high temperature of 160°C resulted in CFV clustering and growth (Figures 2A, B). Figure 2B shows what appears to be a layer-by-layer growth mechanism of the CFV.

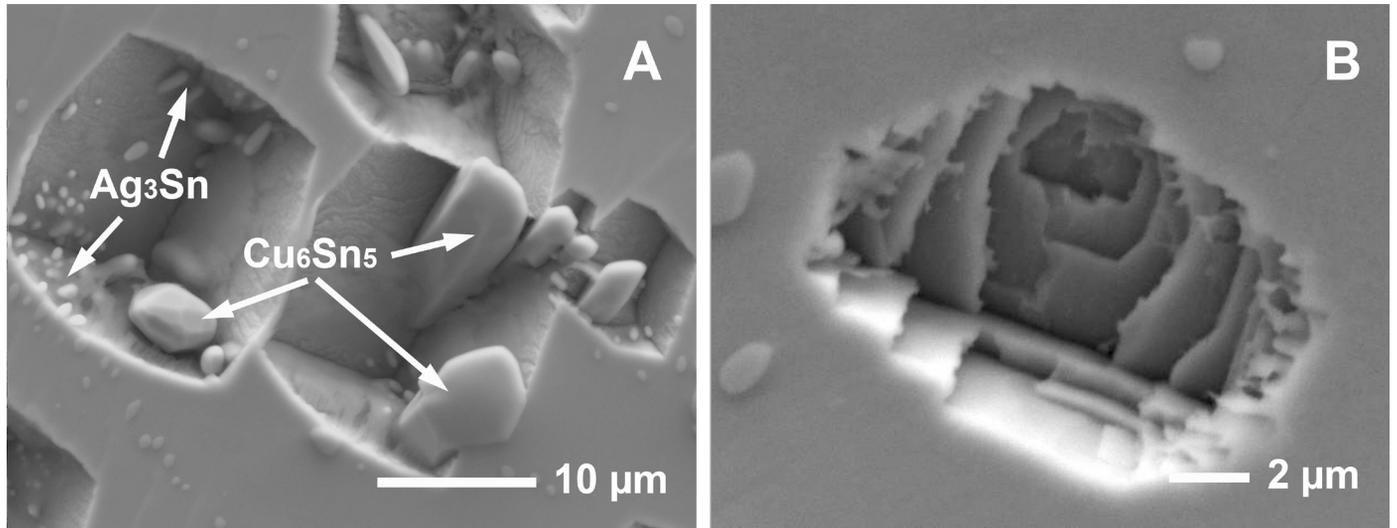


Figure 2. Scanning Electron Microscopy (secondary electron mode) images of CFVs in solder-joints assembled with SAC405 soldering paste and after soldering subjected to annealing at 160°C for 3720 hours. Cross-sections were not etched before the analysis.

Void morphology did not vary significantly between solder-joints assembled with the different solders: SAC405, CASTIN and SN100C.

In order to prove that the CF voiding is not a surface phenomenon, the specimens were repeatedly ground and polished down through the bulk. Voids were found throughout the solder volume but more copiously near the interface layer with the Cu substrate (i.e. the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ intermetallic layer).

DISCUSSION

The fact that the CFVs are faceted suggests that they must form in the solid state not the liquid state. This also suggests that they form by the condensation of vacancies in the matrix. During annealing, when the specimens were subjected to exposure at 160°C , diffusion in the Sn plays an important role in microstructural changes, since Sn is at 85% of its absolute melting point. The vacancy concentration is then high and substitutional diffusion rapid. At these temperatures, it seems feasible that vacancies could cluster and grow to form voids. This could be in response to a denser phase (the intermetallics) growing within the less dense Sn in the solid state: the coefficients of crystal lattice packing and consequently density of the intermetallic particles Ag_3Sn and Cu_6Sn_5 forming in the solder bulk are higher than those of the β -Sn matrix. During intermetallic precipitate formation from the pure components, the resulting volume of the new phase will be less than the volume of the pure components involved in the reaction. For instance, in the case of Cu_6Sn_5 precipitation, the resulting volume would be about 5.5% less than that of the two pure components (according to the rule of mixtures) and about 6% less for Ag_3Sn . This contraction upon IMC precipitation will induce a significant tensile stress in the surrounding matrix and a global shrinkage in the solder as a whole. The stress gradient directed towards the IMCs serves as a driving force for vacancy migration.

We argue here that the stress is arising because of solid state intermetallic precipitation rather than as a result of shrinkage during solidification. The phase diagram suggest that liquid forms matrix + Cu_6Sn_5 at a given temperature but this is the equilibrium state. One would expect that the solid matrix forms first from the liquid and the intermetallic then precipitates out subsequently by precipitation and growth i.e. the Cu takes some time subsequent to solidification to diffuse through the matrix to form the precipitates. Our explanation for the voids only holds if the solid matrix exists before the precipitates form. If the voids formed during solidification from the liquid state they would be likely to be rounded rather than faceted.

It is noteworthy that the IMC Cu_6Sn_5 has an allotropic transformation at 187.5°C ($\eta\text{-Cu}_6\text{Sn}_5 \rightarrow \acute{\eta}\text{-Cu}_6\text{Sn}_5$) and this transformation involves structural reorganization: hexagonal crystal lattice of η -

Cu₆Sn₅ (high temperature modification) transforms into monoclinic crystal lattice of η -Cu₆Sn₅ (low temperature modification)¹⁰. This process is associated with a volume change of the phase. It occurs in the solid state immediately after solidification (since solder joints could be super-cooled down to these temperatures) and is expected to introduce additional internal stress due to the subsequent expansion of η -Cu₆Sn₅ phase by up to 2.15%¹¹. This mitigates the 5.5% shrinkage effect identified above but the net volume change is still a contraction of 3.35%. It is possible that the specimen is, in effect, supercooled so that the η -Cu₆Sn₅ appears almost instantly followed by the formation of the voids. Alternatively the η -Cu₆Sn₅ may form first, followed by voids and followed by the η -Cu₆Sn₅ formation.

The intermetallic formation continues in the solid state during solder-joint ageing, since the time available for the transformation during soldering is not sufficient¹¹ and Cu atoms continue to diffuse from the substrates producing more IMCs within the β -Sn matrix.

In order to fully understand the phenomenon of CF void formation in Sn-rich solders, additional experiments and analysis are currently being performed.

CONCLUSIONS

Crystallographically faceted voids have been observed in lead free solder joint subjected to ageing. We argue here that these are due to stress arising as a result of the formation of intermetallics in the tin matrix in the solid state, although this stress is mitigated by the allotropic η -Cu₆Sn₅ \rightarrow η -Cu₆Sn₅ transformation.

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