Stress analysis of spontaneous Sn whisker growth

K. N. Tu · Chih Chen · Albert T. Wu

Abstract Spontaneous Sn whisker growth is a surface relief phenomenon of creep, driven by a compressive stress gradient. No externally applied stress is required for the growth, and the compressive stress is generated within, from the chemical reaction between Sn and Cu to form the intermetallic compound Cu_6Sn_5 at room temperature. To obtain the compressive stress gradient, a break of the protective oxide on the Sn surface is required because the free surface of the break is stress-free. Thus, spontaneous Sn whisker growth is unique that stress relaxation accompanies stress generation. One of the whisker challenging issues in understanding and in finding effective methods to prevent spontaneous Sn whisker growth is to develop accelerated tests of whisker growth. Use of electromigration on short Sn stripes can facilitate this. The stress distribution around the vicinity and the root of a whisker can be obtained by using the micro-beam X-ray diffraction utilizing synchrotron radiation. A discussion of how to prevent spontaneous Sn whisker growth by blocking both stress generation and stress relaxation is given.

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1 Introduction

Whisker growth on beta-tin (β-Sn) is a surface relief phenomenon of creep. It is driven by a compressive stress gradient and occurs at ambient. Spontaneous Sn whiskers grow on matte Sn finishes on Cu [1–15]. Today, due to the wide application of Pb-free solders on Cu conductors used in electronic packaging of consumer electronic products, Sn whisker growth has become a serious reliability issue since Pb-free solders are Sn-based and very rich in Sn. Typically, the Cu leadframe used on surface mount technology of electronic packaging are finished with a layer of solder for surface passivation and for enhancing wetting during joining the leadframe to printed circuit boards. When the solder finish is eutectic SnCu or matte Sn, whiskers of Sn are observed. Some whiskers can grow to several hundred microns, which are long enough to become electrical shorts between neighboring legs of a leadframe. The trend in electronic packaging technology is to integrate systems in packaging, so that elements of devices and parts of components are getting closer and closer together and the probability of shorting by whiskers is becoming much greater. Hence, how to suppress Sn whisker growth, and how to perform systematic tests of Sn whisker growth in order to understand the driving force, kinetics, and mechanism of growth are challenging tasks in electronic packaging industry today.

Due to the very limited temperature range of Sn whisker growth, from room temperature to about 60°C, accelerated tests are difficult. If the temperature is too low, there is insufficient kinetics due to slow atomic diffusion and if the temperature is too high, there is not enough driving force because of stress relief.

The whisker growth is spontaneous, indicating that the compressive stress behind the growth is self-generated; no external applied stress is required. Otherwise, one can expect a whisker to slow down and stop when the applied stress that is not applied continuously is exhausted. Therefore it is of interest to ask where is the self-generated driving force coming from, how can the driving force maintain itself to achieve the spontaneous whisker growth, and also how large is the compressive stress gradient needed to grow a whisker?

Spontaneous whisker growth is a unique creep process in which both stress generation and stress relaxation occur simultaneously at room temperature. The three indispensable conditions of Sn whisker growth are (1) The room temperature diffusion in Sn, (2) The room temperature reaction between Sn and Cu to form Cu_6Sn_5 and induce the compressive stress in Sn, and (3) The stable surface oxide on Sn. The last condition is needed in order to produce a stress gradient for creep. When the oxide is broken, the exposed free surface is stress-free, so a compressive stress gradient is developed for creep or the growth of a whisker to relax the stress.

Reviews obtained from examining Sn whiskers by using cross-sectional scanning and transmission electron microscopy of samples prepared by focused ion beam thinning will be discussed in this paper [16]. Use of X-ray micro-diffraction by synchrotron radiation to study the structure and stress distribution around the root of a whisker grown on eutectic SnCu will be discussed later [17].

The growth of a Sn whisker is from the bottom, not from the top, since the morphology of the tip does not change [12]. Many Sn whiskers have been found to grow at room temperature and some of them are long enough to short two neighboring legs of the leadframe as shown in Fig. 1a. It is possible that when there is a high electrical field across the narrow gap between the tip of a whisker and the point of contact on the other leg, just before the tip of the whisker touching the other leg, a spark may ignite fire. The fire may result in failure of the device or a satellite [18–21]. Even when a whisker breaks, it could fall between two neighboring conductors and bridge them.

2 Morphology of spontaneous Sn whisker growth

In Fig. 1b, an enlarged SEM image of a long whisker on the eutectic SnCu finish is shown. The whisker in Fig. 1b is straight and its surface is fluted. The crystal structure of Sn is body-centered tetragonal with the lattice constant "a" = 0.58311 nm and "c" = 0.31817 nm. The whisker growth direction, or the axis along the length of the whisker, has been found mostly to be the "c" axis, but growth along other axis such as [100] and [311] has also been found.

On the pure or matte Sn finish surface, short whiskers or hillocks were observed as shown in Fig. 1c. The surface of the whisker in Fig. 1c is faceted. Besides the difference in morphology, the rate of whisker growth on the pure Sn finish is much slower than that on the SnCu finish. The direction of growth is more random too.

Comparing the whiskers formed on SnCu and pure Sn, it seems that the Cu in eutectic SnCu enhances Sn whisker growth. Although the composition of eutectic SnCu consists of 98.7 atomic % of Sn and 1.3 atomic % of Cu, the small amount of Cu seems to have caused a very large effect on whisker growth on the eutectic SnCu finish.

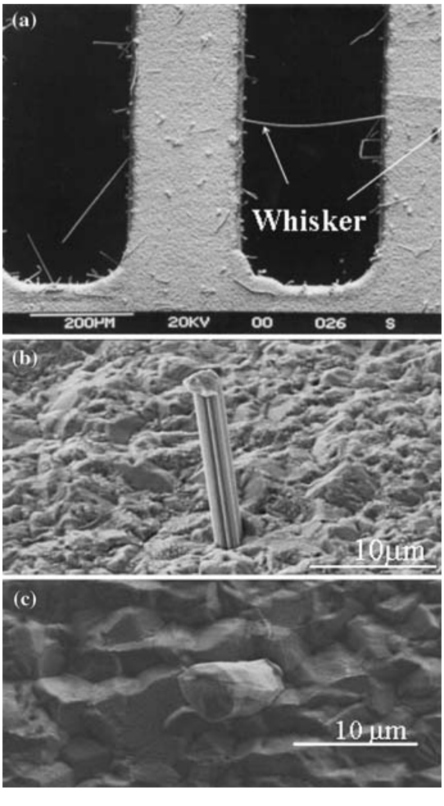


Fig. 1 (**a**) Many Sn whiskers have been found to grow at room temperature and some of them are long enough to short two neighboring legs of the leadframe. (**b**) An enlarged SEM image of a long whisker on the eutectic SnCu finish is shown. (**c**) On the pure or matte Sn finish surface, short whiskers or hillocks were observed

In Fig. 2a, a cross-sectional SEM image of a leadframe leg with SnCu finish is shown. The rectangular core of Cu is surrounded by an approximate 15 μm thick SnCu finish. A higher magnification image of the interface between the SnCu and Cu layers, prepared by focused ion beam, is shown in Fig. 2b. An irregular layer of Cu_6Sn_5 compound can be seen between the Cu and SnCu. No Cu_3Sn was detected at the interface. The grain size in the SnCu finish is about several microns. More importantly, there are Cu_6Sn_5 precipitates in the grain boundaries of SnCu. The grain boundary precipitation of Cu_6Sn_5 is the source of stress generation in the CuSn finish. It provides the driving force of spontaneous Sn whisker growth [21, 22]. The critical stress issue will be addressed later.

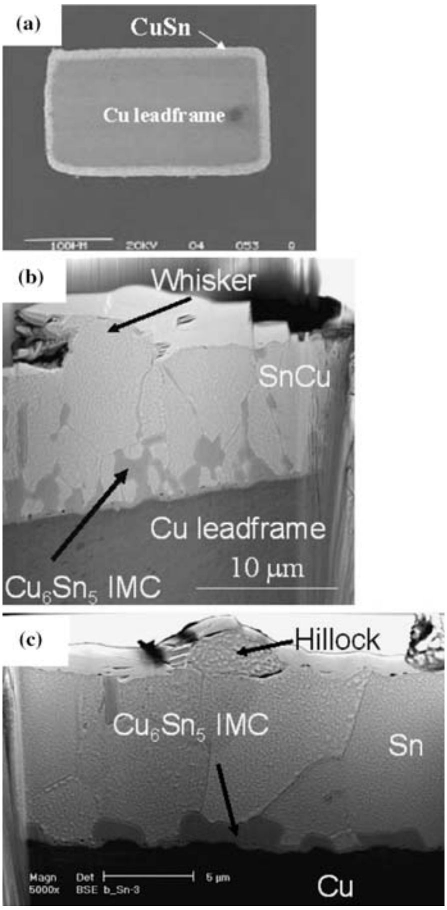


Fig. 2 (**a**) A cross-sectional SEM image of a leadframe leg with SnCu finish is shown. The rectangular core of Cu is surrounded by an approximate 15 μm thick SnCu finish. (**b**) A higher magnification image of the interface between the SnCu and Cu layers, prepared by focused ion beam, is shown. An irregular layer of Cu_6Sn_5 compound can be seen between the Cu and SnCu. No Cu_3Sn was detected at the interface. The grain size in the SnCu finish is about several microns. More importantly, there are Cu_6Sn_5 precipitates in the grain boundaries of SnCu. (**c**) A cross-sectional SEM image, prepared by focused ion beam, of matte Sn finish on Cu leadframe is shown. While the layer of Cu_6Sn_5 compound can be seen between the Cu and Sn, there is much less Cu_6Sn_5 precipitates in the grain boundaries of Sn

In Fig. 2c, a cross-sectional SEM image, prepared by focused ion beam, of matte Sn finish on Cu leadframe is shown. While the layer of Cu_6Sn_5 compound can be seen between the Cu and Sn, there is much less Cu_6Sn_5 precipitates in the grain boundaries of Sn. The grain size in the Sn finish is also about several microns. The lacking of grain boundary Cu_6Sn_5 precipitates is the most important difference between the eutectic SnCu and the pure Sn finish with respect to whisker growth.

TEM images of the cross-section of whiskers, normal to their length, are shown in Fig. 3a, b together with electron diffraction pattern. The growth direction is the c-axis. There are a few spots in the images which might be dislocations.

3 Stress generation (driving force) in Sn whisker growth by Cu–Sn reaction

The origin of the compressive stress can be mechanical, thermal, and chemical. But the mechanical and thermal stresses tend to be finite in magnitude, so they cannot sustain a spontaneous or continuous growth of whiskers for a long time. The chemical force is essential for spontaneous Sn whisker growth, but not obvious. The origin of the chemical force is due to the room temperature reaction between Sn and Cu to form the intermetallic compound (IMC) of Cu_6Sn_5. The chemical reaction provides a sustained driving force for spontaneous growth of whiskers as long as the reaction progresses with unreacted Sn and Cu.

Stress is generated by interstitial diffusion of Cu into Sn and the formation of IMC in the Sn; it generates a compressive stress in the Sn. When the Cu atoms from the leadframe diffuse into the finish to grow the grain boundary IMC, as shown in Fig. 2b, the volume increase due to the IMC growth will exert a compressive stress to the grains on both sides of the grain boundary. As shown in Fig. 4, for a fixed volume V in the Sn finish that contains an IMC precipitate, the growth of the IMC due to the diffusion of a Cu atom into this volume to react with Sn will produce a stress,

$$\sigma = -B\frac{\Omega}{V} \tag{1}$$

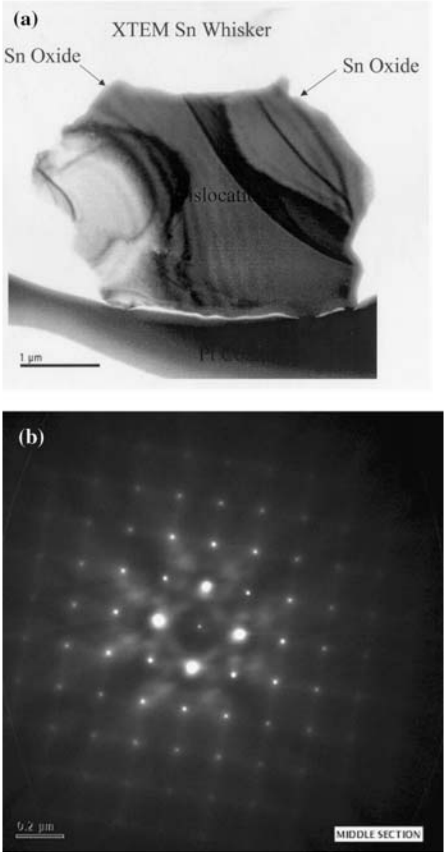


Fig. 3 TEM images of the cross-section of whiskers, normal to their length, are shown in (**a**) and (**b**) together with electron diffraction pattern

where σ is the stress produced, B is bulk modulus, Ω is the partial molecular volume of a Cu atom in Cu_6Sn_5 (the molar volume change of Sn atoms in the reaction for simplicity is ignored). The negative sign indicates that the stress is compressive. In other words, an atomic volume into the fixed volume is added. If the fixed volume cannot expand, a compressive stress will occur. When more and more Cu atoms, say n Cu atoms, diffuse into the volume, V, to form Cu_6Sn_5, the stress in the above equation of σ increases by changing Ω to $n\ \Omega$.

In diffusional processes, such as the classic Kirkendall effect of interdiffusion in a bulk diffusion couple of A and B, the atomic flux of A is not equal to the opposite flux of B. Assuming that A diffuses into B faster than B diffuses into A, a compressive stress in B will be expected since there are more A atoms diffusing into it than B atoms diffusing out of it. However, in Darken's analysis of interdiffusion, there is no stress generated in either A or B or no analysis of stress was given. Since Darken has made a key assumption that vacancy concentration is in equilibrium everywhere in the sample [23, 24]. To achieve vacancy equilibrium, one must assume that vacancies (or lattice sites) can be created and/or annihilated in both A and B as needed. Hence, provided that the lattice sites in B can be added to accommodate the incoming A atoms, there will be no stress. The addition of a large number of lattice sites implies an increase in lattice planes if one assumes that the mechanism of vacancy creation and/or annihilation is by dislocation climb mechanism. It further implies that lattice plane can migrate, which means Kirkendall shift, in turn it implies marker motion if markers are embedded in the moving lattice planes in the sample. In some cases of interdiffusion in bulk diffusion couples, vacancy may not be in equilibrium everywhere in the sample, so very often Kirkendall void formation has been found due to the existence of excess vacancies [25].

To absorb the added atomic volume due to the in-diffusion of Cu by the fixed volume of V in the finish as considered in Fig. 4, it requires addition of lattice sites in the fixed volume. Furthermore, allowance of Kirkendall shift or addition of lattice plane to migrate is necessary. Otherwise, compressive stress will be generated. Since Sn has a native and protective oxide on the surface, the interface between the oxide and Sn is a poor source and sink for vacancies and furthermore the protective oxide ties down the lattice planes in Sn and prevents them from moving. Therefore, this is the basic mechanism of stress generation. It is worth noting that creep is driven by a stress gradient, not by a stress. Typically creep is defined as a time-dependent deformation under constant load. Actually the driving force

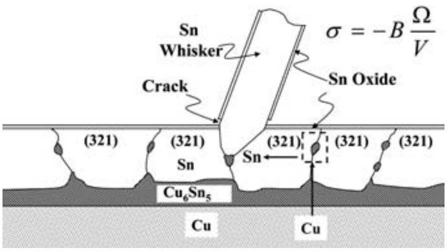


Fig. 4 We consider a fixed volume V in the Sn finish that contains an intermetallic compound (IMC) precipitate, the growth of the IMC due to the diffusion of a Cu atom into this volume to react with Sn will produce a stress

of atomic migration in creep is stress gradient as given in the Nabarro–Herring model. Under a hydrostatic tension or compression, there may be random walk of atoms, but no creep. A uniform compressive stress will not lead to creep, so we need a mechanism to produce a compressive stress gradient in the Sn finish. It will be discussed in next Section.

For the oxide to be effective in tying down lattice plane migration, the finish cannot be too thick. In a very thick finish, say over 100 µm, there are more sinks in the bulk of the finish to absorb the added volume of Cu. Whiskers is a surface relief phenomenon. When bulk relief mechanism occurs, whisker will not grow. There is a dependence of whisker formation on the thickness of finish. Since the average diameter of whiskers is about a few microns, whisker will grow more frequently on a finish having thickness of a few microns to a few times of its diameter.

Sometimes it is puzzling to find that Sn whiskers seem to grow on a tensile region of a Sn finish. For example, when a Cu leadframe surface was plated with SnCu, the initial stress state of the SnCu layer right after plating was tensile, yet whisker growth was observed. Consider the cross-section of a Cu leadframe leg coated with a layer of Sn as shown in Fig. 2a, that experienced a heat-treatment of reflow from room temperature to 250°C and back to room temperature. Since Sn has a higher thermal expansion coefficient than Cu, the Sn should be under tension at room temperature after the reflow cycle. Yet with time, Sn whisker grows, so it seems that Sn whisker grows under tension. Furthermore, if a leg is bent, one side of it will be in tension and the other side in compression. It is surprising to find that whiskers grow on both sides, whether the side is under compression or tension. These phenomena are hard to understand until one recognizes that the thermal stress or the mechanical stress, whether it is tensile or compressive, is finite. It can be relaxed or overcome quickly by atomic diffusion at room temperature. After that, the continuing chemical reaction will develop the compressive stress needed to grow whiskers. So the chemical force is dominant and persistent. In other words, the compressive stress needed for the spontaneous whisker growth on Sn is induced by chemical reaction between Sn (or SnCu) and Cu at room temperature. Room temperature reaction between Sn and Cu was studied by using thin film samples for detection sensitivity [14, 21].

The idea of compressive stress induced by the growth of a grain boundary phase has a few variations. One is the wedge model proposed by Lee et al. [26] that the Cu_6Sn_5 phase between the Cu and Sn has a wedge shape in growing into the grain boundaries of Sn. The growth of the wedge will exert a compressive stress to the two neighboring Sn grains, same as splitting a piece of wood with a wedge. So far, no such wedge-shape IMC has been observed in XSEM, for example, see Fig. 2b.

4 Effect of surface Sn oxide on stress gradient generation and whisker growth

To discuss the effect of surface oxide, one can refer to the effect on Al hillock growth. In an ultra-high vacuum, no surface hillocks were found to grow on Al surface under compression [27]. Hillocks grow on Al surfaces only when the Al surface is oxidized, and Al surface oxide is known to be protective. Without surface oxide, the free surface of Al is a good source and sink of vacancies, so a compressive stress can be relieved uniformly on the entire surface or the surface of every grain of the Al based on Nabarro–Herring model of lattice creep or Coble model of grain boundary creep. In these models, as shown in Fig. 5, the relaxation can occur in each of the grains by diffusion to the free surface of each grain. The free surfaces are effective source and sink of vacancies. Therefore, the relaxation is uniform over the entire Al film surface; all the grains just thicken slightly. Consequently, no localized growth of hillocks or whiskers will take place.

A whisker or hillock is a localized growth on a surface. To have a localized growth, the surface cannot be free of oxide, and the oxide must be a protective oxide so that it effectively blocks all the vacancy sources and sinks on the surface. Furthermore, a protective oxide also means that it pins down the lattice planes in the matrix of Al (or Sn), so that no lattice plane migration can occur to relax the stress in the volume, *V*, considered in Fig. 4. Only those metals

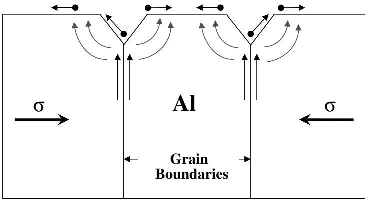


Fig. 5 Nabarro–Herring model of lattice creep or Coble model of grain boundary creep. A schematic diagram to show that when the surface has no oxide, the relaxation of stress can occur in each of the grains by atomic diffusion to the free surface of each grain

which grow protective oxides, such as Al and Sn, are known to have serious hillock or whisker growth. When they are in thin film or thin layer form, the surface oxide can pin down the lattice planes in the near-surface layer easily. On the other hand, it is obvious that if the surface oxide is very thick, it will physically block the growth of any hillock and whisker. No hillocks or whiskers can penetrate a very thick oxide or coating. Thus, a necessary condition of whisker growth is that the protective surface oxide must not be too thick so that it can be broken at certain weak spots on the surface, and from these spots whiskers grow to relieve the stress.

In Fig. 6a, a focused ion beam image of a group of whiskers on the SnCu finish is shown. Figure 6b has the image of the same area after the oxide on a rectangular area of the surface of the finish was sputtered away by using a glancing incidence ion beam to expose the microstructure beneath the oxide. In Fig. 6c, a higher magnification image of the sputtered area is shown, in which the microstructure of Sn grains and grain boundary precipitates of Cu_6Sn_5 are clear. Due to the ion channeling effect, some of the Sn grains appear darker than the others. The Cu_6Sn_5 particles distribute mainly along grain boundaries in the Sn matrix, and they are brighter than the Sn grains due to less ion channeling. The diameter of the whiskers is about a few microns. It is comparable to the grain size in the SnCu finish.

In ambient, one can assume that the surface of the finish and the surface of every whisker are covered with oxide. The growth of a hillock or whisker is an eruption from the oxidized surface. It has to break the oxide. The stress that is needed to break the oxide may be the minimum stress needed to grow whiskers. It seems that the easiest place to break the oxide is at the base of the whisker. Then to maintain the growth, the break must remain oxide-free so that it behaves like a free surface and vacancies can be supplied continuously from the break and can diffuse into the Sn layer to sustain the long range diffusion of the Sn atoms needed to grow the whisker.

Figure 7 is an illustration in which the surface of the whisker is oxidized, except at the base. The surface oxide of the whisker serves the very important purpose of confinement so that the whisker growth is essentially a one-dimensional growth. The surface oxide of the whisker prevents it from growing in lateral direction, thus it grows with a constant cross-section and has the shape of a pencil. Also the oxidized surface may explain why the diameter of a Sn whisker is just a few microns. This is because the gain in strain energy reduction in whisker growth is balanced by the formation of surface of the whisker. By balancing the strain energy against the surface energy in a unit length of the whisker, $\pi R^2 \varepsilon = 2\pi R \gamma$, providing

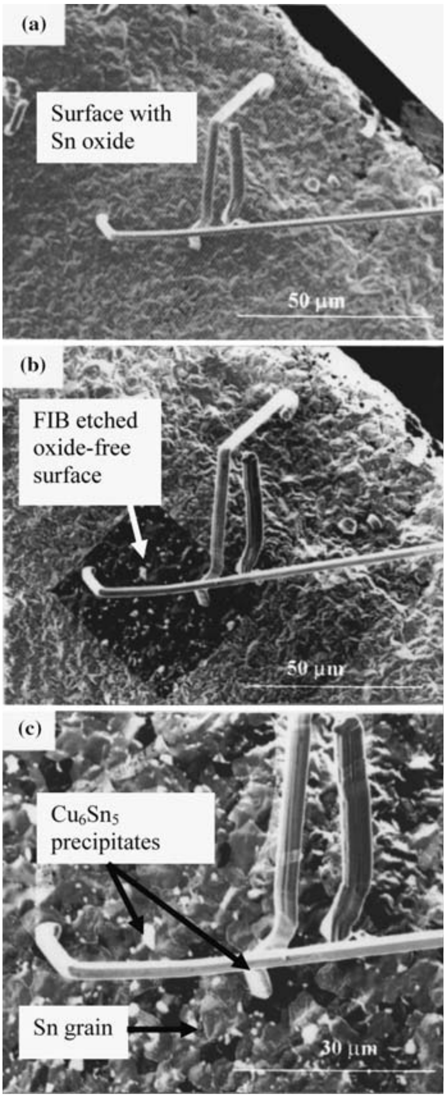


Fig. 6 (**a**) A focused ion beam image of a group of whiskers on the SnCu finish is shown. (**b**) The oxide on a rectangular area of the surface of the finish was sputtered away by using a glancing incidence ion beam to expose the microstructure beneath the oxide. (**c**) A higher magnification image of the sputtered area is shown, in which the microstructure of Sn grains and grain boundary precipitates of Cu_6Sn_5 are clear. The Cu_6Sn_5 precipitates are indicated by the arrows in the figure

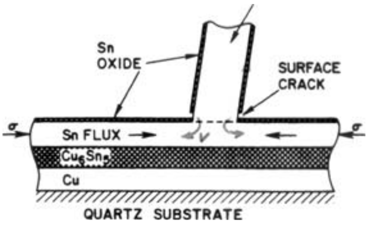


Fig. 7 A schematic diagram depicts that the surface of the whisker is oxidized, except the base

$$R = \frac{2\gamma}{\varepsilon} \qquad (2)$$

where R is radius of the whisker, γ is surface energy per unit area, and ε is strain energy per unit volume. Since strain energy per atom is about four to five orders of magnitude smaller than the chemical bond energy or surface energy per atom of the oxide, the radius or diameter of a whisker is found to be several microns, which are about four orders of magnitude larger than the atomic diameter of Sn. For this reason, it is very difficult to have spontaneous growth of nano-diameter Sn whiskers.

5 Measurement of stress distribution by synchrotron radiation micro-diffraction

The micro-diffraction apparatus in advanced light source (ALS), at Lawrence Berkeley National Laboratory, was used to study Sn whiskers grown on SnCu finish on Cu leadframe at room temperature [28]. The white radiation beam was 0.8–1 μm in diameter and the beam step-scanned over an area of 100 μm by 100 μm at steps of 1 μm. Several areas of the SnCu finish were scanned and those areas were chosen so that in each of them there was a whisker, especially the areas that contained the root of a whisker. During the scan, the whisker, and each grain in the scanned area, can be treated as a single crystal to the beam. This is because the grain size is larger than the beam diameter. At each step of the scan, a Laue pattern of a single crystal is obtained. The crystal orientation and the lattice parameters of the Sn whisker and the grains of SnCu matrix surrounding the root of the whisker were measured by the Laue patterns. The software in ALS is capable of determining the orientation of each of the grains, and displaying the distribution of the major axis of these grains. Using the lattice parameters of the whisker as stress-free internal reference, the strain or stress in the grains in the SnCu matrix can be determined and displayed. Figure 8 shows a low magnification picture of an area of finish wherein a whisker is circled and scanned.

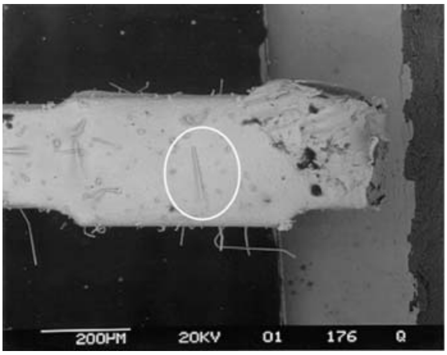


Fig. 8 A low magnification picture of an area of finish wherein a whisker is circled and scanned

Figure 9 shows the X-ray micro-diffraction analysis result of stress distribution around whisker. The whisker part is removed in order to observe the stress around the whisker root more clearly. The absolute value of stress in the whisker is higher than that in the surrounding grains. If the whisker is assumed to be stress-free, the surface of SnCu finish will be under compressive stress. The study shows that in a local area of 100 μm × 100 μm the stress is highly inhomogeneous with variations from grain to grain. The finish is therefore under a biaxial stress only on the average. This is because each whisker has relaxed the stress in the region surrounding it. But, the stress gradient around the root of a whisker does not have a radial

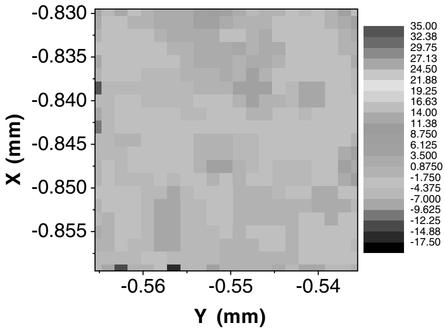


Fig. 9 In the figure, the whisker part is removed in order to observe the stress around the whisker root more clearly. The absolute value of stress in the whisker is higher than that in the surrounding grains. If we assume the whisker to be stress-free, the surface of SnCu finish is under compressive stress

symmetry. The numerical value, and the distribution of stress, are shown in Table 1, where the root of the whisker is at the coordinates of “$x = -0.8415$” and “$y = -0.5475$”. Overall, the compressive stress is quite low, of the order of several MPa, however, one can still see the slight stress gradient going from the whisker root area to the surroundings. It means that the stress level just below the whisker is slightly less compressive than the surrounding area. This is because the stress near the whisker has been relaxed by whisker growth. In Table 1, the light-colored arrows indicate the directions of local stress gradient. Some circles next to each other in Table 1 show the similar stress level, which most likely means that they belong to the same grain.

The total strain tensor is equal to the sum of deviatoric strain tensor and the dilatational strain tensor. The latter is measured from energy of Laue spot using monochromatic beam and the former is measured from deviation in crystal Laue pattern using white radiation beam.

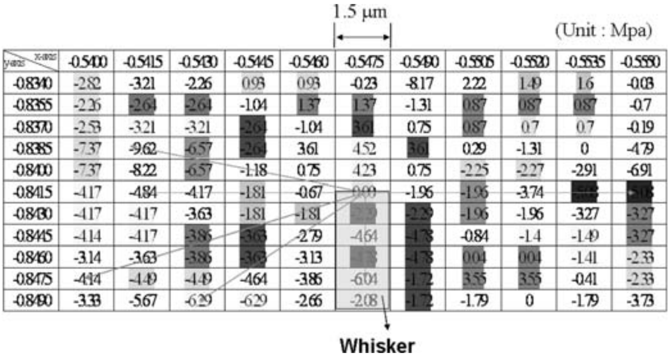
$$\begin{aligned}\varepsilon_{ij} &= \varepsilon_{\text{deviatoric}} + \varepsilon_{\text{dilatational}} \\ &= \begin{vmatrix} \varepsilon'_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon'_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon'_{33} \end{vmatrix} + \begin{vmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{vmatrix}\end{aligned} \tag{3}$$

where the dilatational strain, $\delta = \frac{1}{3}(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})$ and $\varepsilon_{ii} = \varepsilon'_{ii} + \delta$.

The measurements of these two strain tensors can be explained as follows. The deviatoric strain tensor is calculated from the deviation of spot positions in the Laue pattern with respect to their “unstrained” positions. The latter is obtained from an “unstrained” reference. By assuming that the whisker is strain-free, the Sn whisker itself can be used as the unstrained reference and to calibrate the sample-detector distance and the tilt of detector with respect to the beam. The geometry is fixed. From the Laue spot positions of the strained sample, any deviation of their positions from the calculated positions if the sample has zero strain can be measured. The transformation matrix which relates the unstrained to the strained Laue spot positions is then calculated and the rotational part is taken out. The deviatoric strain can then be computed from this transformation matrix. Presence of more spots in the Laue pattern will facilitate the deviatoric strain tensor determination. The deviatoric strain is related to the change in the shape of the unit cell, but the unit cell volume is assumed to be constant and it consists of five independent components. The sum of the 3 diagonal components should be equal to zero.

To obtain the total strain tensor, the dilatational strain tensor must be added to the deviatoric strain tensor. The dilatational component is related to the change in volume of the unit cell and it consists of a single component of expansion or shrinkage, δ, in the last equation. In principle, if the deviatoric strain tensor is known, only one addition measurement is needed, that is the energy of a single reflection is required, to obtain this single dilatational component. The monochromatic beam can be used to do this. The energy of E_0 for zero dilatational strain can be calculated from the orientation of the crystal and the deviatoric strain for each reflection. The energy can be scanned by rotating the monochromator around this energy E_0 and watch the intensity of the peak of interest on the CCD camera. The energy which maximizes the intensity of the reflection is the actual energy

Table 1 Stress distribution around the root of a whisker, which is at the coordinates of “$x = -0.8415$” and “$y = -0.5475$”



y-axis \ x-axis	-0.5400	-0.5415	-0.5430	-0.5445	-0.5460	-0.5475	-0.5490	-0.5505	-0.5520	-0.5535	-0.5550
-0.8340	-2.82	-3.21	-2.26	0.93	0.93	-0.23	-8.17	2.22	1.49	1.6	-0.03
-0.8355	-2.26	-2.64	-2.64	-1.04	1.37	1.37	-1.31	0.87	0.87	0.87	-0.7
-0.8370	-2.53	-3.21	-3.21	-2.64	-1.04	3.61	0.75	0.87	0.7	0.7	-0.19
-0.8385	-7.37	-9.62	-6.57	-2.64	3.61	4.52	3.61	0.29	-1.31	0	-4.79
-0.8400	-7.37	-8.22	-6.57	-1.18	0.75	4.23	0.75	-2.25	-2.27	-2.91	-6.91
-0.8415	-4.17	-4.84	-4.17	-1.81	-0.67	0.00	-1.96	-1.96	-3.74	[illegible]	[illegible]
-0.8430	-4.17	-4.17	-3.63	-1.81	-1.81	[illegible]	-2.29	-1.96	-1.96	-3.27	-3.27
-0.8445	-4.14	-4.17	-3.86	-3.63	-2.79	-4.64	-4.78	-0.84	-1.4	-1.49	-3.27
-0.8460	-3.14	-3.63	-3.86	-3.63	-3.13	[illegible]	-4.78	0.04	0.04	-1.41	-2.33
-0.8475	-4.14	-1.49	-1.49	-4.64	-3.86	-6.04	-1.72	3.55	3.55	-0.41	-2.33
-0.8490	-3.33	-5.67	-6.29	-6.29	-2.66	-2.08	-1.72	-1.79	0	-1.79	-3.73

of the reflection. The difference in the observed energy and the E_0 gives the dilatational strain.

Since, $\sigma'_{xx} + \sigma'_{yy} + \sigma'_{zz} = 0$ by definition, $-\sigma'_{zz}$ is a measure of the in-plane stress (Note that for a blanket film, with free or passivated surface, on the average the total normal stress $\sigma_{zz} = 0$), from that σ_b (biaxial stress)=$(\sigma_{xx} + \sigma_{yy})/2 = (\sigma'_{xx} + \sigma'_{yy})/2 - \sigma'_{zz} = -3\sigma'_{zz}/2$. This relation is always true on the average. A positive value of $-\sigma'_{zz}$ indicates a overall tensile stress whereas a negative value indicates an overall compressive stress. However, the measured stress values, corresponding to a strain of less than 0.01%, are only slightly larger than the strain/stress sensitivity of the white beam Laue technique (sensitivity of the technique is 0.005% strain). No long range stress gradient has been observed around the root of a whisker, indicating that the growth of a whisker has released most of the local compressive stress in the distance of several surrounding grains.

6 Stress relaxation (kinetic process) in Sn whisker growth by creep

Whisker growth is a unique creep phenomenon in which stress generation and stress relaxation occurs simultaneously. Therefore, one must consider two kinetic processes of stress generation and stress relaxation and their coupling by irreversible processes [29]. About the two processes in whisker growth, the first is the diffusion of Cu from the leadframe into the Sn finish to form grain boundary precipitates of Cu_6Sn_5. This kinetic process generates the compressive stress in the finish. The second is the diffusion of Sn from the stressed region to the root of a whisker which is stress-free to relieve the stress. The distance of diffusion in the second process is much longer than the first and also the diffusivity in the second process is slower too, so the second process tends to control the rate in the growth of whiskers.

Since the reaction of Sn and Cu occurs at room temperature, the reaction continues as long as there are unreacted Sn and Cu. The stress in the Sn will increase with the growth of Cu_6Sn_5 in it. Yet the stress cannot build up forever; and it must be relaxed. Either the added lattice planes in the volume, V, in Fig. 4 must migrate out of the volume, or some Sn atoms will have to diffuse out from the volume to a stress-free region.

Since room temperature is a relatively high homologous temperature for Sn, which melts at 232°C, the self-diffusion of Sn along Sn grain boundaries is fast at room temperature. Therefore the compressive stress in the Sn induced by the chemical reaction at room temperature can also be relaxed at room temperature by atomic rearrangement via self grain boundary diffusion. The relaxation occurs by the removal of atomic layers of Sn normal to the stress, and these Sn atoms can diffuse along grain boundaries to the root of a stress-free whisker to feed its growth.

7 Accelerated test of Sn whisker growth

One of the most annoying behaviors of Sn whisker growth is that it does not grow when it is needed but grows when it is not needed. In order to predict the lifetime of Pb-free solder finish without whisker growth, one should conduct accelerated tests as in most reliability problems. An accelerated test can be conducted at larger driving force or faster kinetics, provided that the mechanism of failure remains the same. Typically, tests at higher temperatures are performed to obtain the activation energy of the rate controlling process, which will enable the extrapolation of the life time at the device operation temperature. For Sn whisker growth, while it is possible to conduct the tests up to 60°C, the rate of whisker growth is still quite slow due to slow atomic diffusion. When the temperature approaches 100°C, the diffusion is faster, yet the stress will be relieved due to fast atomic diffusion. Hence, competition between driving force and kinetics determines the rate of whisker growth. Although Cu can be added to Sn to have a faster whisker growth as in eutectic SnCu solder, the rate is still not fast enough. Besides, the effect of Cu on whisker growth needs to be isolated.

In 1954, Fisher et al. developed a method for accelerated growth of Sn whiskers by using a metallographic clamp [30], and they reported the maximum growth rates at clamping pressures of 7500 psi to be about 10,000 Å/s. Compared with the spontaneous growth rate of about few Å/s without external pressure [31], the growth rate for accelerated growth is much faster and the mechanism of growth might be different. Lee et al. reported that Sn whiskers grew on the Sn film plated with Cu concentration above 2% after high acceleration stress test for 300 h. Arnold published a paper in 1956 on investigating the methods to repress the growth of whiskers [32]. He found that neutron bombardment enhanced the growth of Sn whiskers. When the plated Sn film was bombarded at a neutron flux density of 10^{12} cm^{-2} s^{-1} for 30 days, dense whiskers were found in the film. He also found that electrical and magnetic fields had no effect on acceleration effect.

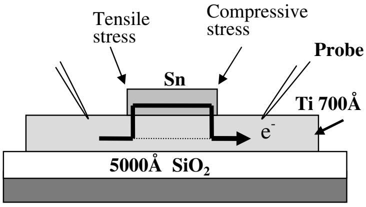


Fig. 10 The cross-sectional schematic drawing showing the structure of the Blech Sn film. Most of the electrons drift in the Sn film, as indicated by the arrow in the figure

Liu et al. demonstrated that the growth of Sn whiskers can be accelerated by electromigration [33]. When electric current is applied to leadframes or continuous Sn films, it produces no back stress. The sample that Liu et al. used was 5000 Å pure Sn film on a Ti conducting layer, which is also known as Blech specimen [34], as shown schematically in Fig. 10. The resistance of the Ti layer is much higher than the Sn film. Thus most of the electrons take a detour into the Sn film on the cathode end (left side) of the Sn stripe, and exit near the anode end (right side) of the Sn stripe. Since the Ti layer has higher electromigration resistance, the Ti atoms almost do not migrate during the current stressing. In electromigration, Sn atoms migrated from the left to the right, resulting in the formation of voids on the cathode end and hillocks on the anode end.

Due to current crowding induced flux divergence at the lower corner of both ends of the stripe, a compressive stress built up on the anode end and tensile stress on the cathode end during current stressing, as indicated in Fig. 10. At the anode, due to current crowding, electrons exit at the lower corner, where the compressive stress is the highest because Sn atoms will be driven there. However, at the upper corner of the anode, the compressive stress is low because of low current density. Hence a vertical compressive stress gradient is created and it will drive atoms to move up. When the oxide at the upper corner is broken, the free surface is stress-free and it enhances whisker or hillock growth. In these samples, there were no reacting layers under the Sn film, such as Cu or Ni. Thus, the driving force for the whisker growth originated mainly from the current stressing.

Figure 11 shows the plan-view SEM image for a fabricated Sn stripe after the storage at room temperature for two months. No obvious growth of Sn whiskers was observed on the Sn film. However, accelerated growth of Sn whiskers has taken place when it was applied by a high current density, as shown in Fig. 12a–f. The Sn stripe was 5000 Å thick on a Ti layer of 700 Å thick. Current density of 1.5×10^5 A/cm^2 was applied at room temperature. After 10 h of the current stressing, a whisker started to form on the anode end, as seen in Fig. 12b. As the stressing time increased, more whiskers appeared and they grew longer, as illustrated in Fig. 12c–f. The growth rate was measured to be about 3 Å/s, which was higher than that of the spontaneous growth (about 0.1–1.0 Å/s) [35]. Yet, it was much slower than that by using a metallographic clamp. However, this technique of electromigration appears to be more controllable. Sn whiskers grow on the anode end, and the growth rate can be controlled by varying applied current (driving force) and temperature (kinetics). The grow rate increased as the applied current increased, and it also increased to 7.7 Å/s at 50°C under the same current density. In addition, the growth rate was almost linear with the applied current, which is similar to that obtained by Fisher et al. using a metallographic clamp [30].

In using electromigration to conduct accelerated tests of whisker growth and by measuring the growth rate and the diameter of the whisker, the volume change per unit time of the whisker can be obtained, $V = JA\mathrm{d}t\ \Omega$, where J is the electromigration flux in units of number of atoms/cm^2-s, A is the cross-section area of the whisker, t is unit time, and Ω is atomic volume. On this basis

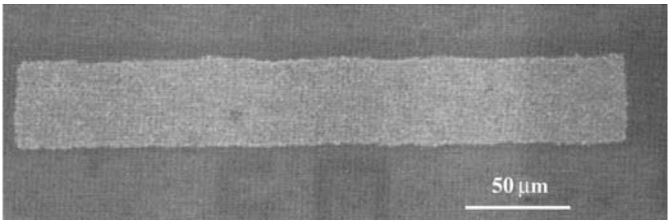


Fig. 11 Plan-view SEM image of a pure-Sn Blech sample which was stored under room temperature without current stressing for over 2 months. No obvious Sn whiskers or hillocks were found

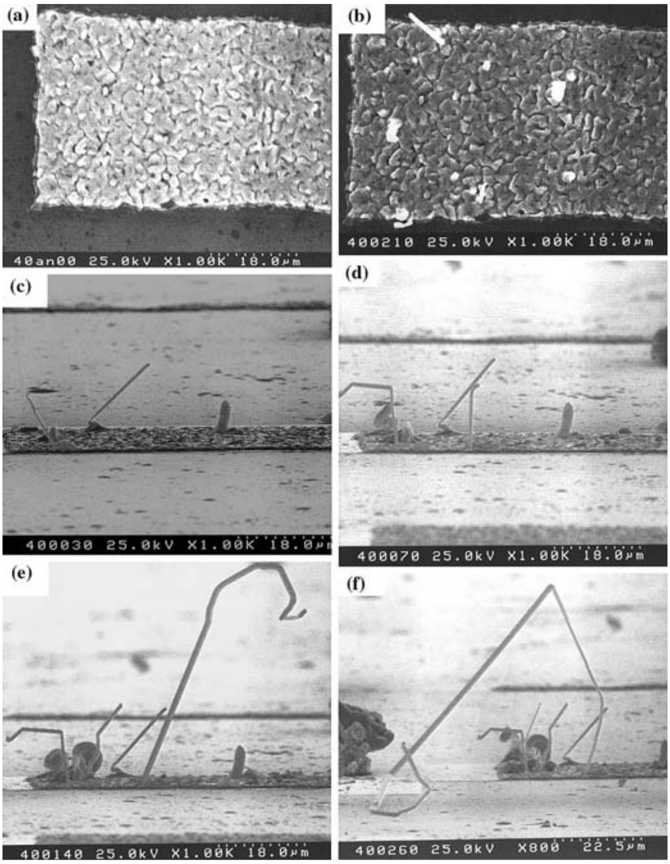


Fig. 12 SEM images showing the growth of the Sn whiskers driven by electric current. The applied current was 40 mA at room temperature, resulting in the current density of 1.5×10^5 A/cm^2 in the Sn film. (**a**) 0 h, (**b**) 10 h, (**c**) 30 h, (**d**) 70 h, (**e**) 140 h, (**f**) 260 h

$$J = C\frac{D}{kT}\left(\frac{\mathrm{d}\sigma\Omega}{\mathrm{d}x} + Z^{*}ej\rho\right) \tag{4}$$

where $C = 1/\Omega$ in pure Sn, D is diffusivity, kT is thermal energy, σ is stress at the anode, $\mathrm{d}\sigma/\mathrm{d}x$ is the stress gradient along the short stripe of Sn of length of $\mathrm{d}x$, Z^* is the effective charge number of the diffusing Sn atoms in electromigration, e is electron charge, j is current density, and ρ is resistivity of Sn at the test temperature. The stress at the cathode can be assumed to be zero. σ can be evaluated from the last equation. By keeping the stripe dimension and the applied current density unchanged, the activation energy of whisker growth when the growth as a function of temperature can be obtained.

In-situ stress distribution near the anode end of the stripe can be obtained by micro-beam X-ray diffraction in synchrotron radiation [36, 37]. The sample can be scanned by the micro X-ray beam while a high current density is passing through the sample. Furthermore, using focused ion beam, the cross-section of the sample can be prepared and studied by the micro X-ray beam diffraction.

Figure 13 shows SEM image of whiskers at the anode ends of a set of stripes of eutectic SnPb driven by electromigration. The stripes were cut by focused ion beam, and it was found that the cut has enhanced whisker growth at the anode ends. Sn whiskers grew even at temperature as high as 100°C. Thus accelerated test at higher temperature can be performed using the Blech specimens.

To control the diameter of a whisker growth at the anode, a thin coating of quartz can be sputtered over the entire Sn stripe with an etched hole of given diameter at the anode, as depicted in Fig. 14. Driven by an applied current density, a whisker can be pushed out from the hole at the anode. The growth rate and the volume of the whisker as a function of current

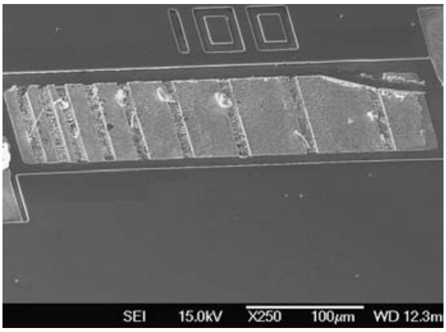


Fig. 13 SEM image showing the growth of the Sn whiskers driven by electric current in SnPb solder stripes. The applied current was 61 mA at 100°C for 65 h

density, temperature, and time in a controlled manner can be measured with this technique. At the same test condition, the Sn stripe can be replaced by an eutectic SnCu stripe or a stripe of a bilayer of Sn/Cu for comparison. However, the accelerated test may not be meaningful without a confirmation that the whisker driven by electromigration has the same growth behavior and mechanism as the whisker grown spontaneously on the Pb-free finish.

8 Prevention of spontaneous Sn whisker growth

On the basis of the analysis presented in the previous Sections, there are three indispensable conditions of spontaneous whisker growth; they are (1) The room temperature grain boundary diffusion of Sn in Sn, (2) The room temperature reaction between Sn and Cu to form Cu_6Sn_5, which provides the compressive stress or the driving force needed for whisker growth, and (3) The stable and protective surface Sn oxide. A break of the surface oxide produces the stress gradient needed for whisker growth. If we remove any one of them, in principle there will be no whisker growth. However, synchrotron radiation study has shown that it takes only a very small stress gradient to grow Sn whiskers, hence it is difficult to prevent whisker growth. National Electronics Manufacturing Initiative (NEMI) has recommended a solution to remove the condition (2) by preventing Cu from reacting with Sn. To remove the condition (3), no oxide or a very thick and unbreakable oxide or coating are necessary, such a condition is unrealistic. We propose here to remove the condition (1) by blocking the grain boundary diffusion of Sn. Furthermore, if one can remove both conditions (1) and (2), it is even better.

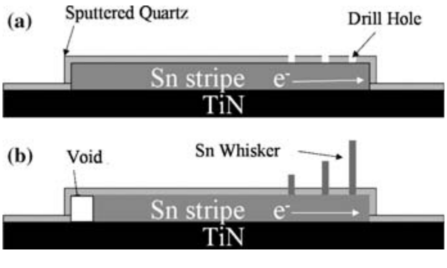


Fig. 14 Schematic drawing showing the controlled growth of Sn whiskers from the drilled holes in the anode end

Since Sn whisker growth is an irreversible process which couples stress generation and stress relaxation, it is essential to uncouple them in order to prevent Sn whisker growth. In other words, both stress generation and stress relaxation should be removed. Stress generation can be removed by blocking the diffusion of Cu into Sn. The NEMI solution is to stop the diffusion of Cu into Sn by electroplating a layer of Ni between the Cu and the Sn solder finish. Ni serves as a diffusion barrier to prevent the diffusion of Cu into Sn. One can also use Cu–Sn intermetallic compound, instead of Ni, as the diffusion barrier. An annealing of the plated leadframe above 60°C will lead to the formation of Cu_3Sn, the Cu_3Sn formed between the Cu leadframe and the Sn finish can serve as diffusion barrier.

However, up to now, no solution to remove stress relaxation is given. In other words, how to prevent the creep process or the diffusion of Sn atoms to the whiskers is unknown. This may be accomplished by using another kind of diffusion barrier to stop the diffusion of Sn. To block the diffusion of Sn atoms from every grain of Sn in the finish is non-trivial. This may be accomplished by adding several percentage of Cu or another element into the matte Sn or the eutectic SnCu solder. We recall that the Cu concentration in the eutectic SnCu is only 1.3 atomic % or 0.7 wt%. We shall add about several (3–7) wt% of Cu. We recall the cross-sectional microstructure of the eutectic SnCu as shown in Fig. 2 that Cu_6Sn_5 forms as grain boundary precipitates. The reason to add a few more percentage of Cu is to have enough precipitation of Cu_6Sn_5 in all the grain boundaries in the finish, so that every grain of Sn in the finish will be coated by a layer of Cu_6Sn_5. Thus, the grain boundary coating becomes a diffusion barrier to prevent the Sn atoms from leaving each of the grains. When there is no diffusion of Sn, there is no growth of Sn whisker since the supply of Sn is cut. Figure 15 depicts a layered structure of a Sn–Cu finish on a Ni diffusion barrier on a Cu leadframe. What is the optimal concentration of Cu in the finish requires

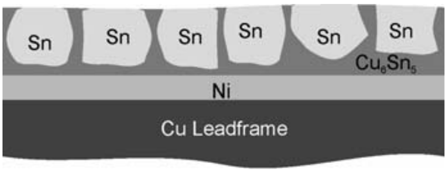


Fig. 15 A layered structure of a Sn–Cu finish on a Ni diffusion barrier on a Cu leadframe

more study. Cross-sectional SEM and focused ion beam images of the samples should be obtained to investigate the microstructure of electroplated Sn–Cu finish, especially the distribution of grain boundary phase of Cu_6Sn_5 in Sn as a function of Cu concentration from 3 to 7 wt%.

There are two key reasons of the selection of Cu (or another element) to form grain boundary precipitate in Sn. The first is that when the Sn has so much supersaturated Cu, it will not take more Cu from the leadframe. The second is that the adding of Cu will not affect strongly the wetting property of the surface of the finish. This is an important consideration since without a good property of wetting, it cannot be used as finish on the leadframe. To plate the Sn finish with a few percent of Cu is much easier than the plating of eutectic SnCu which has only 0.7 wt% Cu. It is difficult to control the concentration less than 1% in electroplating.

Whether the addition of several percent of Cu is effective and whether there are other problems must be studied. For example, whether the grain boundary precipitate is brittle or not should be investigate. Perhaps, it is the idea of how to prevent grain boundary diffusion of Sn should be explored. Whether there are other elements better than Cu for the purpose of whisker prevention also remain to be studied. It is known that the addition of several percent of Pb will prevent Sn whisker growth since Pb is soft and it tends to reduce the local stress gradients in Sn. Also because Sn–Pb is a eutectic system, the eutectic microstructure consists of two separated and intermixing phases, and they block each other in terms of long range diffusion. So, adding several percent of the other soft elements that have eutectic phase diagram with Sn, such as Bi, In, and Zn, may be good choice. If there is no Sn diffusion, we expect no Sn whisker growth.

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