

Recrystallization Principles Applied to Whisker Growth in Tin

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Tin whiskers found in electroplated deposits are known to be single crystals which spontaneously grow. Thus whisker growth can be regarded as a grain growth phenomenon. In this paper we examine whisker grain growth in the context of the well-developed principles of recrystallization process as applied to bulk metals that have undergone deformation and annealing. As a grain grows in whisker form, recrystallization process must take place as tin atoms rearrange in to the lattice structure of the elongating grain. Peculiarities of tin deposit structure that may cause whisker growth are discussed. Frank-Read source of dislocations is proposed as a possible mechanism for whisker formation. The effect of various factors on whiskering is analyzed.

Recrystallization theory postulates that shear strain introduced by plastic deformation is stored in the metal in the form of dislocations (lattice defects). In bulk metals, produced metallurgically from the molten phase, these lattice defects usually are not present in noticeable quantity unless the material is subjected to cold work (plastic deformation at temperatures significantly below melting point). In electroplated tin, however, the metal is formed at the temperatures much below melting point. During plating, energy is stored in the deposit in the form of crystal defects such as vacancies and dislocations. This causes the crystal structure of metal deposits to resemble the structure of cold worked metals, and thus forms the starting point for application of recrystallization principles.

The second important factor that justifies the application of recrystallization/grain growth principles to whisker formation is related to the low recrystallization temperature of tin. Recrystallization temperature is defined as the temperature at which a particular metal with particular amount of cold deformation will completely recrystallize within one hour. Typically, it can be estimated as between 0.4 and 0.7 T_m (where T_m is the melting temperature). It is a well-known fact that in most metals, recrystallization occurs at elevated temperatures. For tin, however, the recrystallization temperature is approximately 30°C, which means that recrystallization will spontaneously occur around room temperature (above and below 30°C), reforming a strain-free structure¹.

These two factors – strain stored in the deposits in the form of dislocations and recrystallization at room temperature, substantiate the application of recrystallization process principles to whisker formation. But before we elaborate on this hypothesis, let us briefly summarize the principles of recrystallization process.

Recrystallization process/Annealing cycle

The recrystallization process consists of three principal stages: recovery, recrystallization, and grain growth. Together, the three stages of the recrystallization process describe the formation of a new microstructure of lower free energy due to reaction in the solid state^{1,2,3}. To clarify the terminology in the text, when “recrystallization process” is mentioned, it means all three stages; when “recrystallization” term is used, it means just recrystallization stage alone.

Recovery

In recovery, the density and distribution of lattice defects within a deformed crystal change, resulting in release of energy. This freeing of strain energy begins immediately at the start of annealing cycle and at the temperatures much below those at which recrystallization occurs. Recovery is associated with annihilation of excess dislocations which can occur via the reaction between dislocation segments of opposite signs (negative and positive edge dislocations; left-hand and right-hand screw dislocations).

Another process that takes place during recovery stage is called polygonization. It is associated with reorganization of dislocations to form low energy grain boundaries and small crystalline areas with low strain (subgrains). During this process, edge dislocations move either by slide in the direction parallel to their slip plane or by climb in the direction perpendicular to their slip plane. The driving force for these movements comes from strain energy of the dislocations which decreases during polygonization. As the result of recovery, no new grains are formed but the final crystal structure affects the recrystallization.

The recovery process is responsible for the very sharp decrease in internal stress of tin electrodeposits observed within minutes after plating. It is interesting to note that this fast stress release occurs regardless whether initial stress in the deposit is compressive or tensile. In both cases, the absolute value of stress drops to very low numbers but remains of the same type as the initial value (i.e., higher initial tensile stress reduces its absolute value but remains tensile).

Recrystallization

During the recrystallization stage, an entirely new set of grains is formed. The kinetics of recrystallization differ from that of the recovery stage, resembling nucleation and growth mechanism. In the first slow step of recrystallization, nucleation occurs in the regions of severe localized deformation. Those new nuclei are not formed in the classical sense as totally new sites, i.e. atom by atom addition to the embryo until the stable nucleus is formed that then grows into newly formed recrystallized grain. The origin of recrystallized grains is always pre-existing regions that are highly misoriented in relation to the material surrounding them. This high degree of misorientation gives the region from which the new grains originate the needed growth mobility. The second fast step of recrystallization – growth of nuclei, occurs until the driving force for this process diminishes and at that point the recrystallization is complete. One of the conditions necessary for a small strain-free volume to grow and consume the surrounding deformed regions is that it is surrounded, at least in part, by the equivalent volume of high-energy grain boundaries. This condition is required because the mobility of low energy grain boundaries is very low and will not allow formation of a nucleus. If a difference in dislocation density exists across a grain boundary, then the portion of the more perfect grain may migrate into the less perfect grain under driving force associated with the strain energy gradient across the grain boundary. The boundary movement will sweep the dislocations in its path and thus, create a small relatively strain-free volume.

Typical nucleation sites in polycrystalline materials include:

- high energy grain boundaries and triple junctions
- deformation zones around particles
- shear bands.

Interesting statistics for nucleation sites distribution in various areas of highly deformed crystal structure are presented in Table 1. ⁴ It shows the number of nuclei formed in cold-rolled aluminum after annealing at 340°C for 10 min and 20 min. The data indicate that majority of nucleation sites occur at high energy grain boundaries and particle inclusions, the latter gaining more weight with time of annealing.

<i>Nucleation sites</i>	<i>10 minutes</i>	<i>20 minutes</i>
Grain interior	10	10
Grain boundary	60	70
Triple junction	30	20
Particle-stimulated nucleation (PSN)	30	50

Table 1. Nucleation site distribution in cold-rolled aluminum for different annealing times at 340°C.

The recovery and recrystallization stages may proceed simultaneously, and for the tin plating process, which occurs close to or above the recrystallization temperature, it may be assumed that these processes are completed during and shortly after the deposit is created. In the recrystallization stage, whiskers do not

grow but the crystalline structure is created that defines the potential for whisker formation. Analysis of this structure along with projection of how strain/stress will build-up over time (which will be discussed later) may allow modeling and prediction of whisker propensity.

Grain growth.

The last stage of recrystallization process – grain growth, is the most important step for understanding the whisker mechanism. This is the stage where whiskers actually appear and grow. And that's where whisker formation deviates from the classical recrystallization processes. During normal grain growth as a part of classical recrystallization process, the driving force for grain growth is reduction of the interfacial energy of grain boundaries. As the grains grow in size and their numbers decrease, the grain boundary area diminishes and the total surface energy is lowered. After the recrystallization stage is complete, certain grains continue to grow at the expense of other crystals, which become consumed. The most common mechanism of grain growth in bulk polycrystalline materials is called geometrical coalescence. During this process, the specimen maintains its original shape as grains grow internally.

In this regard, whisker growth is different from normal grain growth because it occurs outside of the original boundaries of the deposit. Whisker growth may be regarded as “abnormal grain growth” in which two conditions must be met. First, that normal grain growth is inhibited, and secondly that structural conditions nevertheless allow some grains to grow². Typical tin deposits, being often only one grain thick, may satisfy the first condition for “abnormal” grain growth. This may be attributed to the increasing effect of the surface grooves in the deposits where each grain occupies the whole cross-section of the deposit and is bounded by the grain boundaries that emerge to the deposit surface. It is well known that the normal grain growth is inhibited and even stopped when the average grain diameter approximates the specimen thickness. Grain boundaries near any free surface of a metal specimen tend to lie perpendicular to the specimen surface, which has the effect of reducing the net curvature of the boundaries next to the surface and thus decreasing the surface energy. This results in the formation of grooves where the boundaries emerge. Freeing a grain boundary from its groove requires additional work and, as a result, the groove restrains the movement of the boundary. Grooves act as pinning points for grain boundaries, restricting grain boundary movement and normal grain growth. Thus, tin deposits represent a special case in which classic grain growth is inhibited by surface effects and the first condition for the “abnormal” grain growth is met².

To satisfy the second requirement for “abnormal growth”, the grains that *do* grow as whiskers must possess attributes which are unique to those grains. The simple observation that not all grains in a deposit grow as whiskers suggests that there is a structural requirement which has a statistical likelihood of occurring in any given deposit. The driving force for grain growth is reduction of interfacial energy, therefore it may be predicted that the structural requirement is an orientation relationship at the grain base resulting in a low energy condition which favors diffusion of atoms from a high to low energy state. In whisker growth, new surface area is created which increases the surface energy of the system. However, it is also known that grains having low surface energy will grow preferentially, thus, reducing overall energy of the system. The surface energy of the grain is determined by the packing order of the atoms in the exposed lattice. As tin has a tetragonal structure (more complex than most metals), it is anisotropic and therefore, grains with different orientation will have different lattice structure exposed at the surface and will be expected to have different surface energies. Thus, certain combinations of orientations for neighboring grains may create conditions favorable for one of those grains to grow as a whisker. The energy released by whisker growth must be greater than that required for creating additional surface area, as proven by the very fact that whiskers do grow. However, the whisker may have a growth orientation which is energetically favorable.

Figure 1 is an image of a cross-sectioned 10 micron thick tin deposit which has been chemically etched. Due to the tetragonal anisotropic structure of tin, the etchant has revealed structure on the grain surfaces which results from the crystallographic orientation. There are four grains visible, each having a different orientation as shown by the surface structure. The deposit is one grain thick, even at this upper range of typical plating thickness. The boundaries between the grains are roughly aligned perpendicular to the deposit surface.

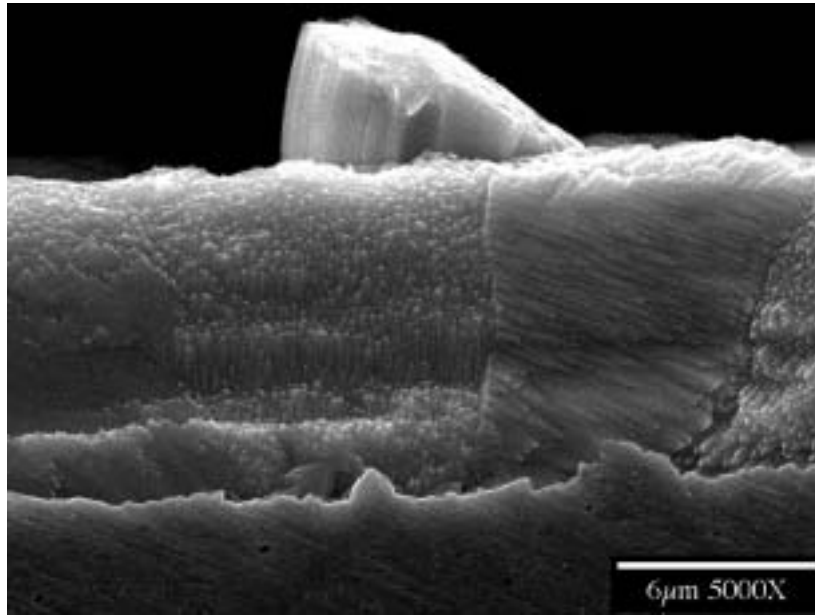


Figure 1. Etched cross section of 10 micron matte tin deposit.

Thus the observed growth of whiskers may result from a combination of circumstances; special orientation of the growing grain both with respect to the free surface as well as its neighboring grains. This would further imply that all whiskers have the same growth orientation. Confirmation of this would be required by advanced x-ray methods.

The discussion above addressed the question *why* whiskers grow. Let us now discuss *how* they grow. One assumption that can be made is that some peculiarity in the tin grain structure creates a favorable condition for Frank-Read sources of dislocations formed under shear stress in the deposit. The first attempt to apply this mechanism to whisker formation was made by Lindborg⁵. He describes whisker growth as a two-stage process. The first stage is the formation of dislocation loop in the grain boundary or recrystallized grain which becomes the foundation for growing whisker. Figure 2 illustrates various stages in the dislocation loop expansion. Under application of shear stress, an edge dislocation (xy) tends to bow (a). If the stress is sustained, it causes the curved dislocation to expand (b) until it intersects itself (c) at the point m . At this stage, the end segments, being of the opposite signs, cancel each other and it causes the loop to break into two new segments (d): a circular one that starts climbing towards the surface by one atomic distance and a new segment that begins expanding.

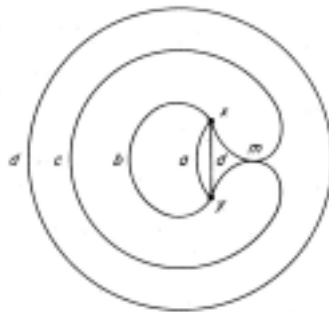


Figure 2. Various stages in the generation of a dislocation loop at a Frank-Read source³.

The process of generation of dislocation loops is also illustrated in Figure 3. As dislocation loop 1 is formed (a) and expands, other full size loops move upwards (b). As loop 1 reaches the full size, it climbs up by one atomic distance and another loop 2 is formed (c). The subsequent loop 2 will expand to full size and climb and new loop 3 will be formed (d).

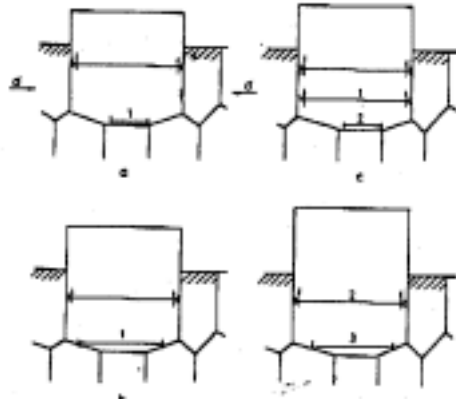


Figure 3. Lindborg's whisker growth model – dislocation loop generation mechanism ⁵.

This model gives a good explanation for the fact that whiskers have very consistent diameter along their length. The dislocation loops surrounding a plane of atoms that climb towards the deposit surface grow to the same size as the diameter of the whisker. It is commonly noticed that whisker diameters fall in the range from 2-15 μm . If the deposit grain size is much smaller than 2-3 μm (e.g., in the case of bright tin), initial grain growth (prior to whisker formation) may produce large grains of irregular shape, called eruptions or flowers. When those irregular grains reach sufficient size, a loop generation mechanism may be initiated and whiskers start growing from those larger grains. This explanation may clarify the question whether those eruptions should cause concern as pre-cursors for whiskers. To answer this question, we propose that the probability to grow whisker out of those large recrystallized grains is higher than from small-grained deposit.

Figure 4 is an electron image of a FIB-created trench at the base of a whisker on bright tin deposit. The very fine columnar grain structure of the deposit can be seen. Much larger recrystallized grains are evident extending from the deposit to the whisker base. The whisker grain originates at a grain boundary intersecting these larger grains and does not reach the substrate.

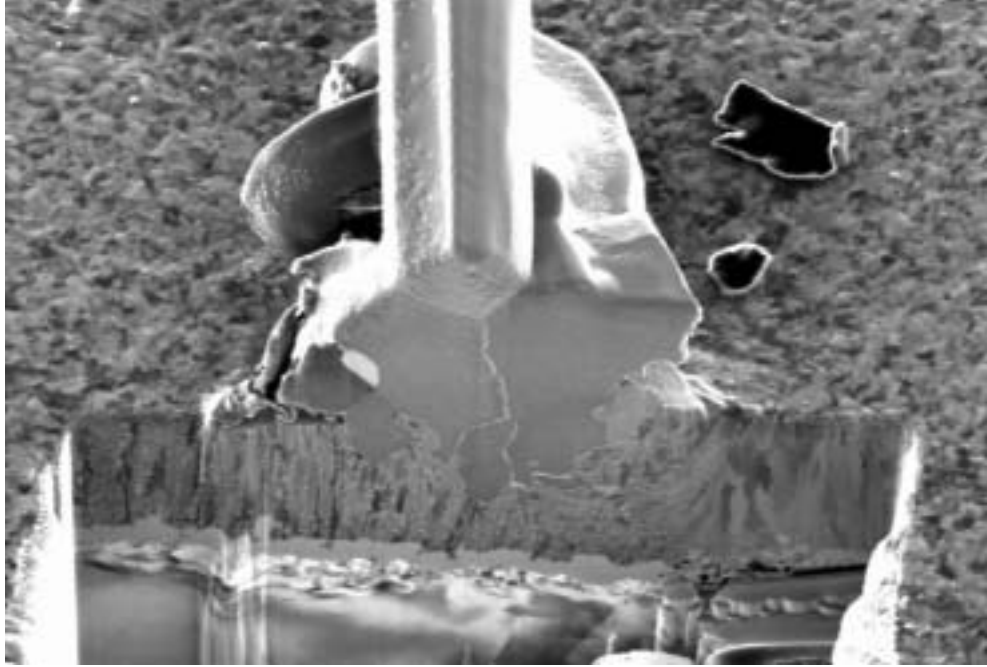


Figure 4. Electron image of FIB-created trench in bright tin. (Image courtesy G. Galyon and L. Palmer, IBM Corp./NEMI Modeling Committee, personal communication).

The formation of those large irregular grains in the matrix of bright tin is a direct evidence of recrystallization process prior to the whisker growth and is very common for bright tin deposits. For matte tin deposits, this grain enlargement is not frequent because the initial deposit grain size is comparable with the common whisker diameter range. Initial grain growth may be rarely observed for matte tin deposits with unusually small grains. Figure 5 shows a whisker on matte tin 5 micron-thick deposit. The deposit has very fine grains and the whisker is growing from a surface nodule of larger recrystallized grains.

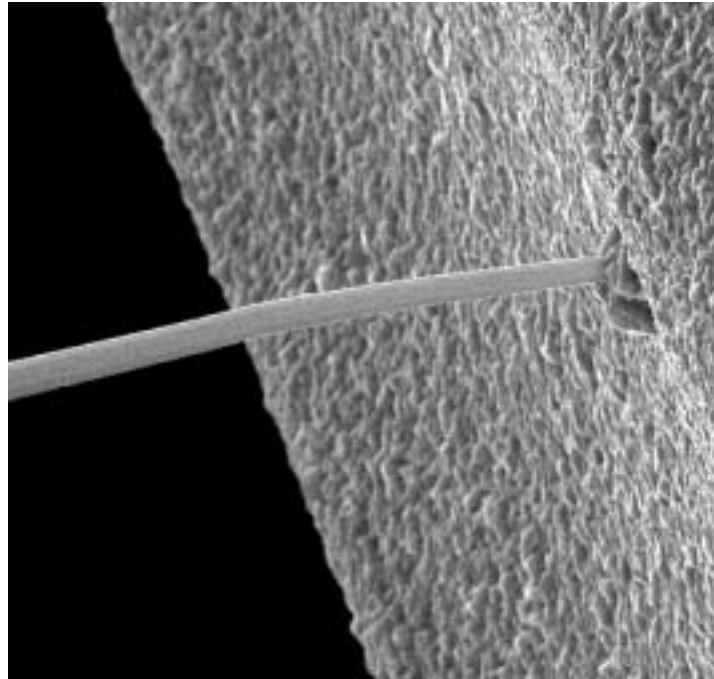


Figure 5. Whisker growing from surface nodule of large recrystallized grains on small grain size matte tin deposit.

Thus, deposit grain size is one of the factors that needs to be satisfied before loop generation and whisker growth occurs.

The preceding is related to the first stage of Lindborg's model for whisker growth – dislocation loop expansion. The time before this process is initiated may be identified as an incubation or dormancy period. To estimate the length of incubation period, one needs to understand what factors initiate the loop generation mechanism and measure/evaluate those factors.

The second stage of Lindborg's model – the upwards movement of the dislocation loop, is associated with long-range diffusion of tin atoms towards the whisker. For each atom climbing up, a vacancy is formed behind it. Those vacancies diffuse into the bulk of the deposits via grain boundaries/dislocations while tin atoms move at the same time towards the growing whisker. Eventually those vacancies are absorbed in high energy grain boundaries, dislocation loops, or at the surface. If significant numbers of vacancies are absorbed in some areas of the deposit, this may result in voids, depletion of surface grain boundaries or consumption of grains. In Figure 6a, whisker growth is accompanied by evidence of material depletion around the whisker base and in surrounding grain boundaries. In Figure 6b, in addition to the grain boundaries depletion, "sinking" grain can be observed next to the whisker. Note that the surface of the receding grain is similar in texture to the surrounding grains and is tilted with respect to the surface. This shows that diffusion of atoms from this grain is taking place subsurface, either by lattice or grain boundary diffusion. In classic grain growth, coalescence of grains is accomplished by reduction in grain boundary area. In this case, the grain boundaries are pinned and the original "shell" shape of grain is retained, while atoms move by diffusion into a more energetically favored state and the grain is sinking below the surface as it is being consumed. The horizontal striations on the walls of the "sinking" grain and in the depleted grain boundaries provide the evidence that this phenomenon is related to whisker growth and not to the plating process (plating defects).

The depletion of tin atoms can alternatively be interpreted as sites of accumulation of vacancies during whisker. These features are often observed in tin deposits and provide the proof of long-range diffusion from high energy areas (grains with certain orientation, high energy grain boundaries) to low energy sites (whiskers). The consumption maybe less evident if large volume fraction of tin deposit has high degree of misorientation (high energy grain boundaries). In this case, vacancies maybe distributed more evenly within larger number of sites and the depletion will be less noticeable.

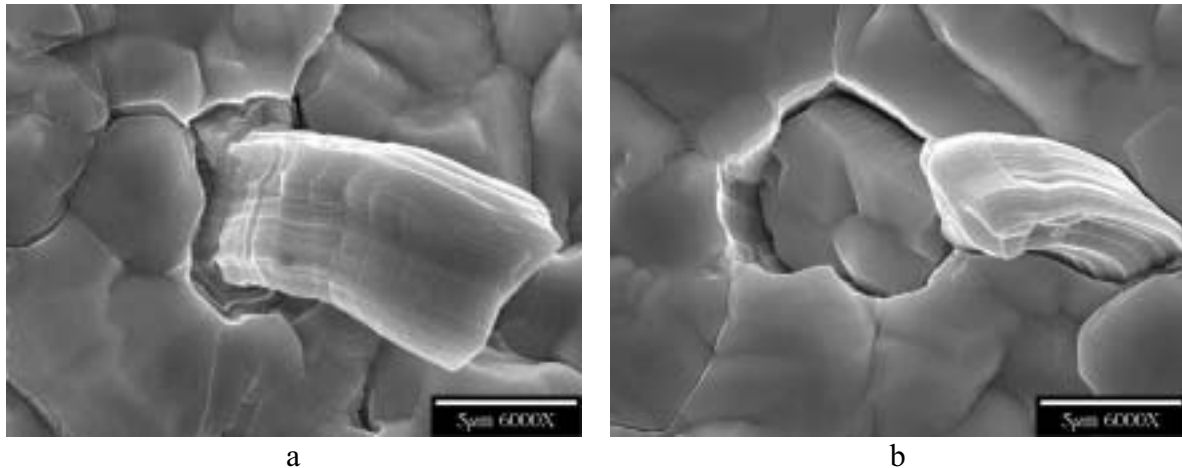


Figure 6. Depletion of material at base of whisker and in surrounding surface grain boundaries.

Whiskers have been observed of lengths many times that of the thickness of the originating deposit. The volume of atoms in these whiskers is thus very large. Inspection of the deposit surrounding the whiskers often shows no appreciable thinning and thus we can conclude that the growth is fed by long-range diffusion (see Figure 5).

Kinetics of whisker growth

To describe the contribution of each stage of Lindborg's model into whisker growth kinetics, the following equations may be utilized:

- for the dislocation loop expansion, the whisker growth rate – h_1 , can be determined as following

$$h_1 = k_1 \frac{\sigma}{R_w T} \quad (1)$$

where σ is stress, R_w is a whisker radius, and T is temperature

- for the dislocation loop climb upwards, the whisker growth rate - h_2 , can be determined as following

$$h_2 = k_2 \left(\sigma - \frac{k_3}{L_w} \right)^n \quad (2)$$

where σ is stress, L_w is space between dislocations and n is a constant that depends on dislocation density and temperature; usually $n \gg 1$. k_1 , k_2 and k_3 are constants related to material properties of the deposit. The space between dislocations, L_w , is higher for low energy grain boundaries, thus, according to this equation, whisker growth rate is higher for low energy grain boundaries which supports the assumption made earlier that whiskers grow preferentially from low energy grain boundaries.

These two equations may help to interpret some experimental data for the temperature effect on whisker growth. For deposits under high stress, σ (internal or external), $h_2 \gg h_1$ (because h_2 is proportional to σ^n where $n \gg 1$ and h_1 is proportional to σ) so the first stage becomes a speed-limiting factor and whisker growth maybe described by equation (1). In this case, the whisker growth rate is reverse proportional to temperature meaning faster whisker growth at lower temperatures. This may explain why in some experiments more whiskering is observed at room temperature (highly stressed deposits) and in others – at elevated temperatures (low stress). Also in this case, whisker growth rate is linearly proportional to stress.

For deposits under moderate stress which covers the majority of cases for tin deposits, the second stage (climbing) becomes rate-controlling and whisker growth can be described by equation (2). In this case, the effect of temperature on growth rate becomes more complex which makes the attempt to design an accelerated whisker test by applying high temperatures somewhat ambiguous. On the other hand, whisker growth rate becomes more dependent on the stress because unlike linear relation for the first stage, h_2 is proportional to σ^n . This may explain significant effect of IMC formation (increasing macrostress) on whisker growth. These considerations maybe useful when accelerated whisker tests are designed and their results are interpreted.

Lindborg's model explains the vertical direction of whisker growth as well as the uniform diameter of a whisker along its length and provides the correlation between various physical parameters and whisker growth rate. His work also supports the concept of a special orientation relationship requirement. With recent advances in the technique of micro-x-ray diffraction it may soon be possible to investigate such orientation relationships. In this paper, we show for the first time direct evidence of diffusion and dissipation of vacancies associated with whisker growth. This also supports the conclusions of Lindborg and substantiates the application of recrystallization principles.

Grain Boundaries

In polycrystalline materials, grain boundaries are the areas with highest concentration of defects (vacancies and dislocations). A grain boundary is the region between two grains having different lattice orientations. The misorientation of the two adjacent grains is an essential attribute of a grain boundary - it makes the grain boundary an interface defect containing high concentration of dislocations. The concentration of dislocations in grain boundaries depends on the angle between misoriented grains. Low angle boundaries have fewer dislocations and considered low energy boundaries.

The higher the angle between misoriented grains, the higher the energy of the grain boundary. As the angle increases, the dislocation spacing becomes so small that individual dislocations overlap and can no longer be identified. The boundary becomes a random high angle boundary. Those boundaries have very poor fit with lots of free volume and highly distorted interatomic bonds. Diffusion of atoms along high angle grain boundaries is fast compared to low angle grain boundaries.

In addition to the two types of grain boundaries - low and high angle/energy boundaries, there are other types of special high angle boundaries that allow good fitting of the atoms across the boundary and consequently have low boundary energy. Two examples of high angle/low energy boundaries are coherent twin boundaries and symmetrical tilt boundaries. For example, for Aluminum, the rotation along $\langle 110 \rangle$ axis (Figure 7) may produce good fit at high angles (38.2° , 70.8° , and 130°) and those boundaries may be considered as high angle/low energy.

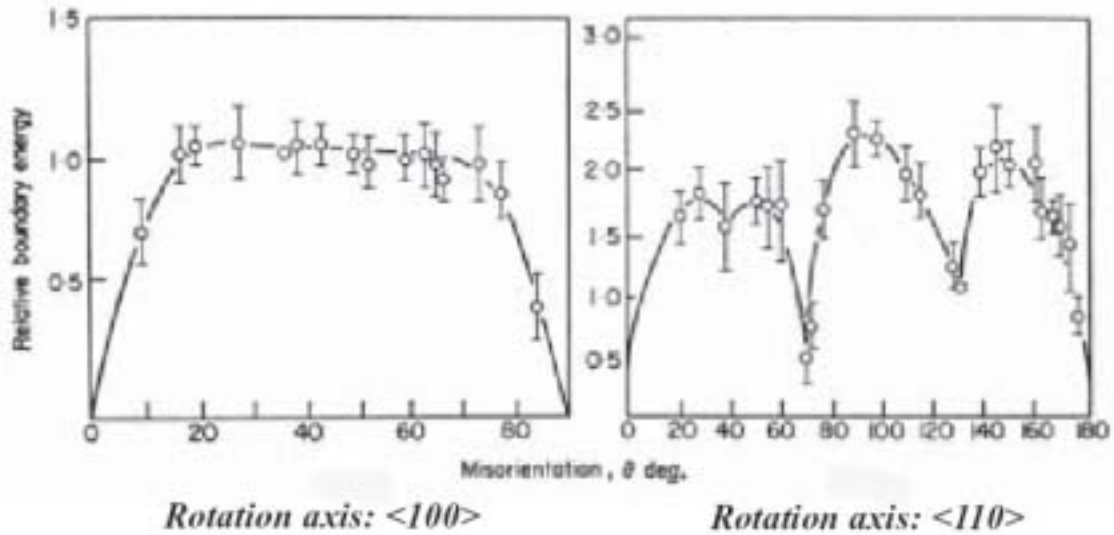


Figure 7. Measured grain boundary energies for symmetric tilt boundaries in Aluminum

These high angle/low energy boundaries are called Coincident Site Lattice (CSL) Boundaries. The difference in energy between low and high energy grain boundaries may be significant and is illustrated in Table 2 for various metals.⁴

Crystal	$\gamma_{\text{coh twin}}$ (mJ/m ²)	$\gamma_{\text{incoh twin}}$ (mJ/m ²)	γ_{gb} (mJ/m ²)
Cu	21	498	623
Ag	8	126	377
Fe-Cr-Ni (304 SS)	19	209	835

Table 2. Grain boundary energies for different orientations in various metals.

Two aspects of crystal orientation should be considered to estimate potential for whiskers: deposit texture and the fractions of high and low energy boundaries. The texture of the deposit may be defined as the degree of random orientation of grains relative to each other. If deposit has strong preferred orientation, most of the grains have nearly identical orientation and their boundaries are low energy ones. As the orientation of grains becomes more random the probability of high and low grain boundaries co-existing in

the deposit increases accordingly. For polycrystalline tin deposits, the propensity to form whiskers will be determined by the presence of both high and low energy grain boundaries with the maximum probability of whiskers occurring where high and low energy grain boundaries are present in comparable quantities.

Low energy grain boundaries as well as recrystallized grains may become the sites for whisker growth as proposed by Lindborg. However, as whiskers start growing, the transport of atoms to feed whiskers is provided by diffusion that is associated with vacancy formation and dissipation away from growing whiskers, while tin atoms migrate at the same time towards the whisker. Thus, high-energy grain boundaries play an important role in sustaining whisker growth by providing pathways for diffusion. If only low energy grain boundaries are present in the deposit, it may result in creating favorable conditions for whisker initiation, but whisker growth will be slow.

If on the other hand, most of grain boundaries in tin deposits are high energy ones, the probability to create a site for whisker formation is low (occasional low energy grain boundaries) but when a whisker starts growing, the diffusion of atoms to feed the whisker will be fast and almost unlimited. In this case, fewer but longer whiskers may be formed. When both high and low energy grain boundaries are present in comparable amounts, large numbers of whiskers of significant length could be formed.

Other factors affecting grain growth in tin deposits

Impurities have significant effect on whisker growth both negative and positive, lead being the example of the impurity that prevents whiskering. Diffusion can occur either as lattice or grain boundary diffusion, the latter being a faster mechanism. Diffusion also occurs more rapidly in high angle grain boundaries. However the presence of impurity elements can dramatically change diffusion rates in grain boundaries, and for this reason also has a significant effect on the temperature of recrystallization, even when the impurities are present at very low levels^{1,2,3}.

In the case of bulk materials subjected to plastic deformation, a certain amount of strain energy is stored in the material which does not change with time unless the material is annealed. There are no additional sources of strain during storage. Unlike bulk materials, deposits of metals have two additional sources of strain energy that exist right after plating but more importantly, create additional strain during storage. Those two sources are the substrate-deposit interface and the deposit surface. The substrate-deposit interface has a dual effect on strain. On one hand, some deformation of the deposit occurs due to misalignment of substrate and deposit lattices. This component is present right after plating and does not change with time. Another factor is the formation of intermetallic compounds (IMC) which is minimal initially but grows with time. Both factors at the substrate-deposit interface are responsible for the uneven distribution of strain through the deposit thickness which in combination with anisotropic structure of tin may create high localized stresses. We believe that the increase in stress due to IMC formation should be considered as a macrostress that increases the potential for whisker growth but is not a direct cause for whisker formation. This judgment is based on two facts:

1. The structure of IMC's at the bottom of the whisker is no different from neighboring grains where no whiskers are formed
2. Whiskers originate not from substrate-deposit interface but within the bulk of the deposit.

Figure 8 is an electron image of a FIB cross-section at the base of a whisker originating from a matte tin deposit. The whisker grain base can be seen to originate from a boundary in contact with two grains above the substrate; the whisker is not in contact with the substrate. The growth of IMC's at the substrate-deposit interface is relatively uniform, except somewhat larger grain in the right corner but no whisker is observed above that IMC grain. Small deposits of IMC may be seen at these grain boundaries as well.

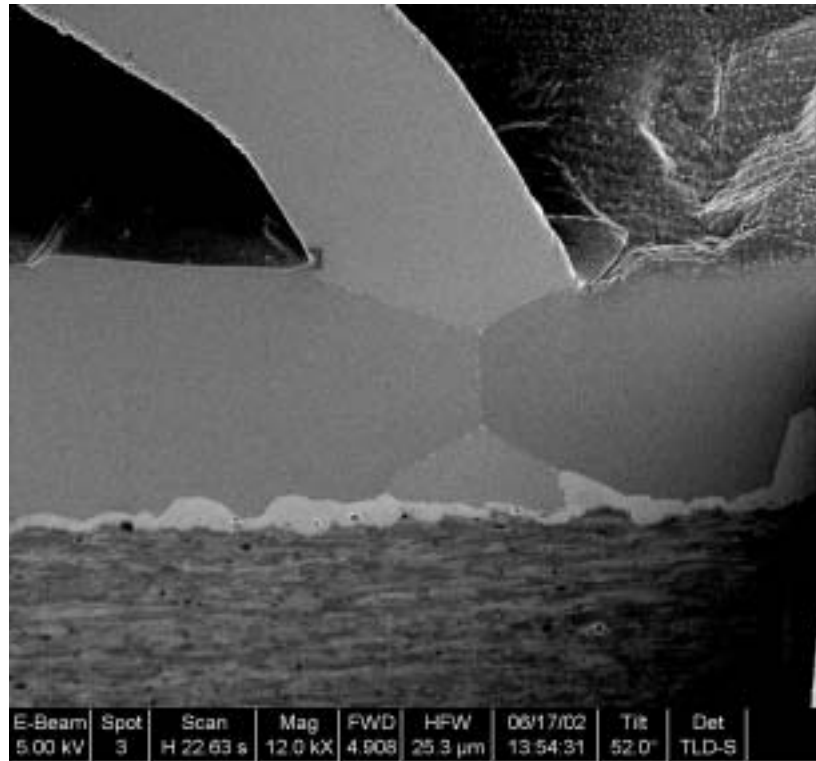


Figure 8. Electron image of FIB cross-section of whisker base in matte tin. (Image courtesy of N. Vo , Motorola ⁶)

This macrostress associated with IMC's may cause localized microstresses due to different orientation of grains and anisotropic properties of tin deposits. When considering the effect of IMC's on whisker growth, two equally important factors should be taken into account:

1. How fast and how high the stress builds up during storage (as a macrostress)
2. How susceptible the deposit is to the increased stress based on its structure (orientation, grain boundaries).

The increase of stress over time varies for different deposits subjected to the same storage conditions. However, it is well known that some deposits do not whisker under stresses higher than those causing whiskering in other deposits.

Essentially IMC's can have dual effect on whiskering. If IMC's absorbed in the grain boundaries in the atomic form or as small particles, they may act as impurities that reduce the mobility of grain boundaries and thus promote "abnormal" grain growth, i.e. whiskers. If IMC's form large particles at the substrate-deposit interface or in the bulk of the deposit, their effect is similar to the effect of any embedded particle regardless of its nature, as was discussed earlier in this paper. Some unpublished data indicate that inclusion of inert particles, e.g., Teflon and carbon, also increase whiskering. However, the presence of a particle, even if it is a tin-copper IMC, is not necessarily a prerequisite for whisker formation

Inspection of the FIB cross-sections shown here (Figures 4 and 8) indicates that the whisker base has grain boundaries that intersect with other sub-grains, that is, the whisker grain does not terminate at the substrate. Lindborg's diagram (Figure 5) also shows the growing grain intersecting with sub-grains. Thus we postulate that another prerequisite for a given grain to grow is that there must be intersecting grain boundaries at the base to fulfill the requirements of special orientation relationship and diffusion pathways.

Another factor which plays a role in whisker growth is surface oxidation. The surface oxide is sometimes described as a continuous film, which should be broken through for whisker to grow. The actual nature of the oxide film is more complex. It is well known that the grooves, or grain boundaries intersecting at the

metal surface (as discussed earlier) promote different mechanisms for surface oxide formation than over free surfaces. Impurity elements gather at grain boundaries and the oxide composition at the groove will be different from that on the grain surface. The effect of surface oxidation on deposit stress and ultimately on whisker formation is similar to the effect of IMC formation at grain boundaries where oxygen atoms behave similar to substrate atoms diffusing into the tin deposit, limiting diffusion and grain boundary mobility.

All these factors mentioned above have effects on crystal growth in tin deposits over time but no single factor can be considered as a sole cause for whisker growth. Even without any additional factors that enhance whisker formation, whiskers will grow due to grain orientation relationships in polycrystalline tin deposits. IMC formation and surface oxidation may occur in all deposits but it is the deposit structure itself that determines the degree of whiskering.

Discussion

The renewed interest in whisker growth in tin deposits is related to the recent attempt to replace lead in SnPb solders. After testing a limited number of alloying metals to prevent whiskering of tin (mainly, copper and bismuth), the conclusion was made that neither one gives any advantages in whisker prevention and pure tin has been recommended as a SnPb replacement. However, numerous data indicate that even most recent formulations for pure tin plating produce deposits with higher degree of whiskering than SnPb. The current position of electronic manufacturers is that if we understand the whisker growth mechanism and factors affecting whiskering, we will be able to control those parameters in manufacturing processes and reliably produce whisker-free pure tin deposits. Understanding and control are two different things. As we illustrated earlier in this paper, whisker growth is a very complex phenomenon. Even in simpler systems (cubic metals, normal recrystallization process), the nature of grain growth is not well understood and quantification of this process is difficult. To directly quote Haasen in Physical Metallurgy¹, “Recrystallization is one of the most complicated and, despite the numerous investigations commensurate with its technical importance, one of the least understood phenomena in metallurgy. ...the study of recrystallization depends on a complete knowledge of the defect configuration following deformation, the thermally activated movement of the defects, the interactions with solute atoms in any form, and the physics and dynamics of interfaces, which together constitute the major part of physical metallurgy.”

Despite numerous publications about whiskers, very little research has been performed in the area of physical metallurgy of tin, which should be the platform for studying whisker phenomenon. Most of the research on tin whiskers is associated with observation of whisker growth without proper characterization of the deposits under study. This creates some discrepancy in publications. No systematic approach has been proposed to address whisker phenomena. Most of the studies were done by researchers that have practical interest in tin deposits but without application of principles of physical metallurgy. On the other hand, there are numerous studies in the physical metallurgy on metals other than tin, mostly focusing on commercially important bulk metals. Tin has a more complex structure than most metals, and is consequently harder to study. All this indicates that understanding of whisker phenomena based on recrystallization principles is at its embryo stage and requires extensive work and appropriate resources. Studies should be performed in a systematic manner rather than as empirical multi-parameter matrices. This situation probably does not match the current needs of the electronic industry that is committed to switch to lead-free solders in the near future. Another difficulty of the current situation is that to gain good understanding of the whisker mechanism, fundamental research should be conducted and manufacturing companies that have high interest in this problem do not have required capabilities and resources. All this shows that a quick solution for whisker problem is not highly probable.

On the other hand, even if complete understanding of whisker growth is achieved, it probably will indicate that so many factors should be controlled to avoid whiskers that it will make it impractical for manufacturing environment. This long time required for whisker studies and low probability to find a practical solution for pure tin as a SnPb replacement most likely will reduce the interest of electronic

manufacturers to initiate fundamental research on tin whiskering. There are two other more practical options to proceed with lead-free solder program:

1. Develop mitigation strategy to deal with tin whiskers (annealing, reflow, barrier layer, conformal coating, etc.). All these options will require additional steps in the production process and thus, extra cost. They also may create new reliability concerns due to high temperature exposure and other technological difficulties.
2. Develop new materials or use existing systems besides pure tin that exhibit degree of whiskering comparable to SnPb.

Both options require some additional research. Until all those issues are resolved, pure tin probably should not be recommended for high reliability long-term applications.

Conclusions

1. Two factors justify the application of the well-developed principles of recrystallization process to the whisker growth phenomenon. One is that tin deposits contain lattice defects (dislocations and vacancies) incorporated during plating and thus, resemble bulk materials after plastic deformation. The other is the fact that the recrystallization temperature of tin is around room temperature allowing recrystallization/whisker formation to occur immediately and spontaneously.
2. The propensity of a tin deposit to grow whiskers strongly depends on its structure: grain size and the relative crystallographic orientation of grains in the deposit. The anisotropic properties of tin result in different surface energies of grains exposed at the surface. This difference and the immobility of grain boundaries pinned by surface grooves favor “abnormal” grain growth – whiskers. Low energy sites (low energy grain boundaries or recrystallized grains) become the foundation for whiskers. Whiskers originate at the intersection of grain boundaries in the bulk of the deposit, not from the substrate interface. Evidence of recrystallization and grain growth prior to whisker formation is presented for bright tin deposit – large irregular shape grains that are the precursors for whiskers.
3. Frank-Read sources of dislocations are proposed as the mechanism for whisker formation. Based on Lindborg’s hypothesis, the whisker growth mechanism consists of two stages – sliding within the deposit and climbing upwards from the deposit surface. Depending on the deposit properties, either stage may become a speed-limiting factor and determine the effect of temperature, stress and other parameters on whisker growth rate. This model explains the consistent diameter of whiskers and assists in the design and interpretation of accelerated whisker tests.
4. Grain boundaries play a significant role in the propensity of the deposit to whisker. Low angle grain boundaries may become initiating sites for whiskers due to their low energy. High angle grain boundaries are favored diffusion pathways and are critical to sustain whisker growth. The presence of both types of grain boundaries and special grain orientations are necessary for whisker growth.
5. Diffusion is the mechanism that governs whisker growth. As vacancies are emitted during whisker formation, they dissipate into high energy sites (grain boundaries or surfaces). Tin atoms simultaneously move in the opposite direction towards the growing whisker. This produces voids or depletion of surface material. For the first time, evidence of this consumption is illustrated in the form of depleted grain boundaries and receding grains.
6. IMC’s formed at the substrate-deposit interface affect whisker growth in several ways. They increase overall shear strain (macrostress). Located at the grain boundaries, they act as impurities reducing the mobility of grain boundaries and diffusion rates. If they are embedded as large particles, they create additional distortion around the particle. IMC growth may induce strain over time which causes further recrystallization and whisker growth.
7. Other factors affecting whisker growth are impurity concentration, surface oxidation and particle inclusions. These factors are important for all deposits but it is the ultimately the deposit structure itself that determines the susceptibility of the deposit to whisker growth. Additional work needs to be performed to study the orientation relationships and stress within tin deposits utilizing advanced micro-X-Ray methods.

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