On the Spontaneous Growth of Soft Metallic Whiskers

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***Abstract-* The room temperature spontaneous growth of low melting point metal whiskers, such as Sn, poses a serious reliability problem in the semiconducting industry; a problem that has become acute with the introduction of Pb-free solder technology. Recently it was shown that the driving force is most probably a reaction between oxygen and the sprouting metal. [1] The resulting volume expansion creates a compressive stress that pushes the whiskers up. The model proposed explains observations on In and Sn whiskers as well as many past observations. Herein further evidence is presented for, and discussion of, the proposed model. Stresses, calculated using finite element modeling, are reasonable and in line with measured values. Based on this work, a potential solution to the whisker problem is in principle simple: either slow or prevent the diffusion of oxygen into the soft metal or, more practically and effectively, work with larger grained solder, which should reduce the magnitude of the compressive stresses.**

Keywords-metal whisker, oxidation

I. INTRODUCTION

Electrical failure due to metallic whisker formation was first discovered in 1948 by Bell telephone laboratories [2]. Individual whiskers grow several microns to millimeters long. Such lengths have been shown to cause damage to microelectronics. Whiskers form from low melting or soft metals, SM, such as tin, zinc, lead and cadmium [3-7]. Furthermore, aluminum has been known to form whiskers at elevated temperatures [8-10]. For reasons that are not entirely clear, the presence of Pb in the solder mitigates whisker growth. With the rising use of Pb-free solder, whisker growth has become an increasing challenge in electronics.

It is generally agreed that whiskers grow to relieve compressive stresses. [11] The source of which had not been identified. Recently, the origin of the stress was proposed to arise from a reaction between the metal and oxygen. [1] In other words, the compressive stresses arise from the formation of an oxide layer at grain boundaries forming the interface between the substrate and the soft metal (Fig. 1).

This work focuses on whisker growth in two distinct systems: a Sn-Al system that results in Sn whiskers and an In-Zr_2InC system that results in In whiskers. Zr_2InC is a ternary carbide from a family of ternary compounds with a $M_{n+1}AX_n$ chemistry, where n=1, 2, or 3, M is an early transition metal, A is an A-group element, and X is either carbon and/or nitrogen [12].

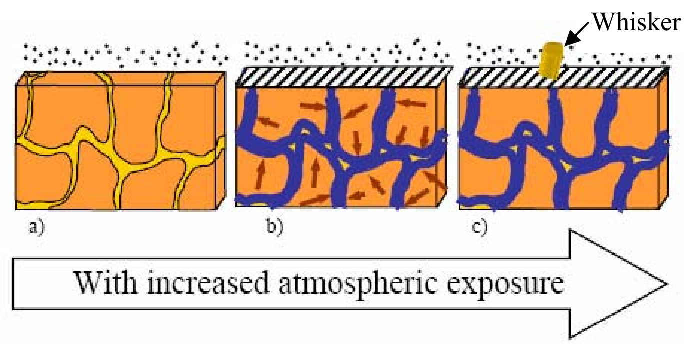

Figure 1. Model for whisker growth with the presence of a soft metal at grain boundaries of substrate material. a) oxygen interacts with material b) oxide layer forms at interface of SM and substrate grain, in addition to a thin native oxide layer at the surface (denoted by diagonal hatch marks), resulting in a compressive stress. c) compressive stress forces SM to yield and whisker forms.

II. EXPERIMENTAL DETAILS

A. In-Zr_2InC System

The Zr_2InC samples were synthesized by ball milling powders of Zr (-325 mesh, 99.9%, ProChem, Rockford, IL), In (-325 mesh, 99.99%, Alfa Aesar, Ward Hill, MA) and graphite (-300 mesh, 99%, Alfa Aesar, Ward Hill, MA). The mixed powders were vacuum sealed in borosilicate glass tubes, which, in turn, were collapsed by heating to 500 °C in air for 2 h, followed by heating to 600 °C for 9 h. The collapsed tubes were then placed in a hot isostatic press, HIP, which was heated to 750 °C in 2 h; held at temperature for ≈ 1.5 h, while the Ar gas pressure was increased to ≈ 70 MPa. Once pressurized, the temperature was increased to 1300 °C in 1 h and held at that temperature for 12 h. The pressure at temperature was ≈ 90 MPa.

X-ray diffraction, XRD, was used for phase identification. To accurately measure the volume fraction of unreacted In, a differential scanning calorimeter (DSC) was used. The grain size was characterized from SEM micrographs using the linear intercept method.

To determine the effect of the ambient atmosphere on whisker growth, a sample of Zr_2InC that had experienced whisker growth was sectioned in two, cold mounted in a resin (Castolite, LECO, St. Joseph, MI) and polished down to 60 nm silica. One half of the sample was sealed in an evacuated borosilicate glass tube, while the other was exposed to the atmosphere. After three months, the evacuated sample was removed from the glass tube. Both halves were then viewed in a SEM.

B. Sn-Al System

The Sn-Al samples were synthesized, using a similar method as Furuta and Hamamura [13], by combining equal weights of bulk aluminum and tin shot (~ 3mm, 99.8%, Aldrich Chem., Milwaukee, WI) in an alumina crucible. The metals were heated in a box furnace to 800 °C. Occasionally, the crucible containing the melt was shaken to encourage complete mixing. After 3 h at 800 °C, the melt was removed from the furnace and quenched by quickly pouring it into a metal dish at room temperature.

The quenched samples were sectioned using a bandsaw. The cut surfaces were then polished using a 3 µm diamond suspension. Directly after polishing, all but one sample section was sealed in vacuum in borosilicate glass tubes under a mechanical pump vacuum. Samples were subsequently removed from the glass tube at varying time intervals and compared to the samples that were held in air.

In addition to sealing samples in a vacuum environment, samples were also partially coated with a thin layer of a nylon based nail polish (Sally Hansen, Farmingdale, NY). The coated samples were exposed to the atmosphere for 65 days before the coating was dissolved with acetone prior to examining their surfaces in a SEM.

The local stresses involved in the previously proposed mechanism for whisker growth [1] were estimated using a quasi-2-D numerical method, assuming a uniform, hexagonal microstructure where the substrate, viz. Al or Zr_2InC was assumed to be semi-infinite cylinders centered within each hexagon, with the SM filling the areas between the cylinders (Fig. 2a). Boundary conditions were applied to maintain the hexagonal microstructure, preventing a shift or change in geometry. The grain size of the substrate was varied, as well as the thickness of the SM film. Due to symmetry, only 1/12 of the grain geometry was constructed in the finite element model (see Fig. 3 in reference 1 for further details).

III. Results and Discussion

The XRD, SEM and EDS analyses confirmed that the HIPed Zr_2InC samples were fully dense, predominantly single phase, with small volume fractions of zirconium carbide and unreacted In at the grain boundaries. DSC analysis indicated the In content was ≈ 3.6 vol. %. The majority of grains ranged in size between 3-5 µm.

After a period of several weeks at room temperature, In structures appeared to sprout from the surface. In whiskers were observed to grow from the grain boundaries (Fig. 3). Previous work clearly showed the effect of oxygen exposure on whisker growth (see Fig. 2 in reference 1). In one case, during sample mounting a network of intergranular cracks developed. With time, these cracks filled with In resulting in the formation of microscopic In walls (inset Fig. 3). Another sample held at room temperature for ≈ 300 days, grew a 10 µm diameter whisker that was ≈ 4.2 mm long corresponding to a growth rate of 0.8 µm/day. This exceptional length indicates that the In source is potentially the entire sample.

Note a simple mass balance shows that the ΔV due the diffusion of O into *numerous* near-surface interfaces translates into the extrusion of long whiskers from specific surface sites. [1]

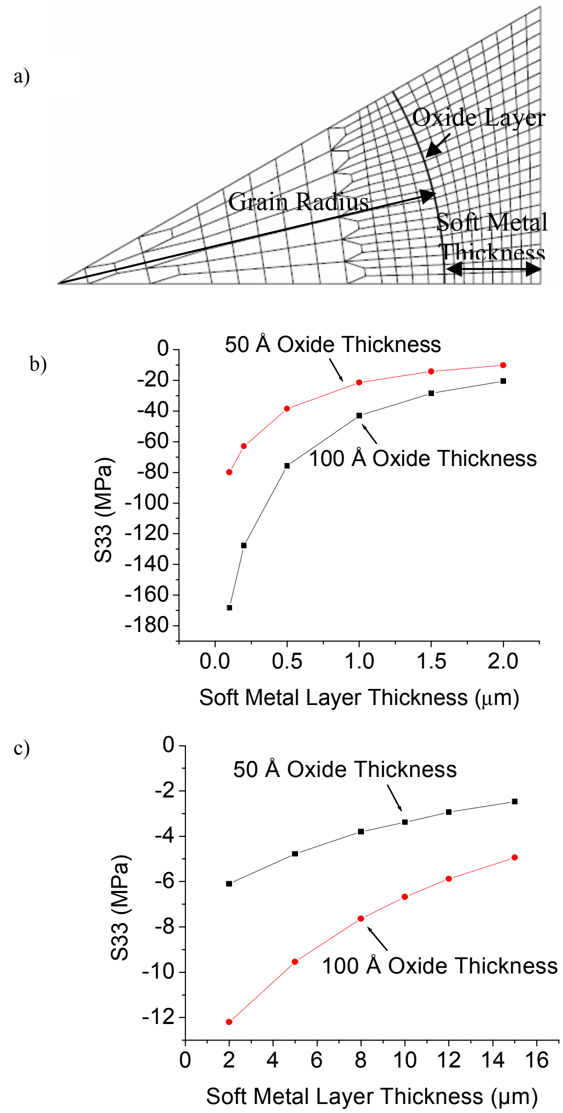

Figure 2. Finite element modeling. a) Modeling geometry. Effect of soft metal thickness on average stress for a fixed grain size and an oxide thickness of 50 Å and 100 Å. b) Zr_2InC/In system with 4 µm grain size c) Al/Sn system with 40 µm grain size. Modeling constants used include: elastic modulus, E_{Zr2InC}=200MPa, E_{In}=10 GPa E_{In2O3}=116 GPa; Poissons ratio, ν_{Zr2InC}=0.2, ν_{In}=0.445, ν_{In2O3}=0.35; E_{Al}=70MPa, E_{Sn}=50 GPa E_{SnO2}=263 GPa; Poissons ratio, ν_{Al}=0.3, ν_{Sn}=0.375, ν_{SnO2}=0.29

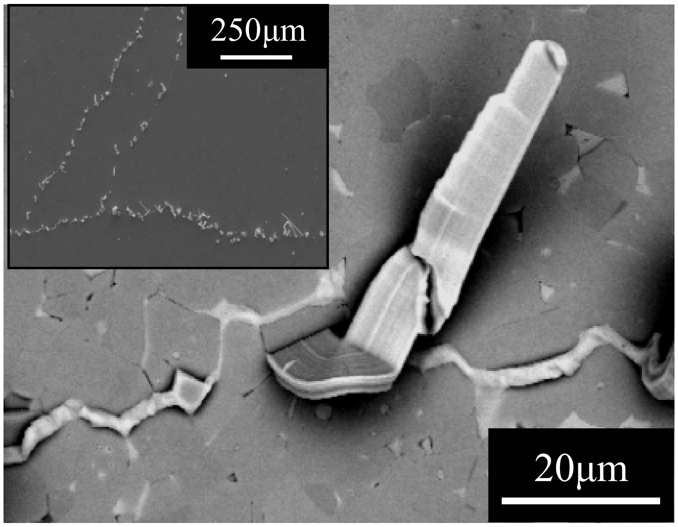

Figure 3. Indium whiskers grow from grain boundaries. Inset: Whiskers have a tendency to form along cracks creating line of whiskers.

In previous work, it was concluded that the compressive stresses due to the oxidation of the SM were responsible for whisker growth. [1] As noted above, these stresses were estimated using numerical methods (Abaqus v. 6.3) using the mesh shown in Fig. 2a. Assuming the oxide layer expands by 25 vol.%, the resulting average out-of-plane stress (S33) was calculated as a function of the SM layer thickness for two oxide layer thicknesses: 50 Å and 100 Å, assuming a substrate Zr_2InC grain diameter of 4 µm. Not surprisingly, relatively large compressive stresses are associated with thin SM films as compared to thicker ones (Fig. 2b). The stresses generated in the Zr_2InC system - with less than 4 vol.% excess In, contained numerous areas where the In was present in thin films, occasionally connected to thicker pockets at triple points (see Fig. 1a in Ref. 1) – were of the order of 10 MPa if the oxide film formed was 50 Å, and the SM thickness was ≈ 2 µm (Fig. 2b). For 100 Å layers the stresses were roughly doubled (Fig. 2b). These stresses are well over the reported value of the yield point of pure In (≈ 1.5 MPa). S33 was a weak function of substrate grain diameter. Similar calculations were performed for the Sn/Al system (Fig. 2c), assuming the Al grain size is ≈ 40 µm. To accurately depict the Al/Sn system, the range of SM thickness chosen for analysis was larger than that used for the Zr_2InC/In system and more in line with the microstructure observed (Figs. 4 and 5). The calculated stresses were about an order of magnitude lower for the Al/Sn system, (Fig. 2(c)). The latter are similar in magnitude to the compressive stresses measured by X-ray diffraction by Hutchinson et al. in Sn thin films. [11]

It is also worth noting here that there are no intermetallics in the Al/Sn system, and therefore their formation cannot be invoked to explain the growth of the Sn whiskers.

In order to explore whether residual stresses play a role, Berkovich and spherical nanoindenters were used to indent a polished Zr_2InC surface. Immediately after the indentation, some In was found to have been slightly extruded from between some grain boundaries in the near vicinity of the indentation. However, when the indentations were revisited several weeks later, no apparent change in the shape of the raised In was observed. Thus, other than the immediate effect of extruding some of the unreacted In, residual stresses do not appear to promote In-whisker growth in this case.

Based on the micrographs shown here and previous work [1,10,14], it is apparent the In does not exude uniformly but only in certain locations. The reason for this state of affairs is not understood at this time. However, one possibility is the extent of oxidation of the SM surface. According to the model presented in previous work [1], for the whiskers to exude, oxygen must diffuse inwards. If the surface oxide skin is too thick, the oxygen diffusional flux through it could be insufficient to cause growth of the whiskers. Consistent with this notion are two observations. First, heating the samples in air to temperatures above 300 °C destroys the ability of the surfaces to form In whiskers. Second, freshly fractured surfaces appear to be much more active than polished surfaces. A good example is the filling of cracks with In during sample mounting (inset in Fig. 3). In general most thin cracks get filled with In, in contradistinction, only very select areas on the surface exude In.

It is worth noting here that there are two oxide layers at play; a grain boundary and a surface oxide layers (Fig. 4), with the former resulting in compressive stresses. The role and nature of the surface or native oxide is less clear, but it is reasonable to assume that the surface oxide that forms on the SM is different in thickness, and certainly in composition than the oxide layer that form on the substrates, viz. Zr_2AlC or Al (Fig. 4). Thus despite the formation of an oxide layer on the SM, it is again reasonable to assume that a possible, grain boundary-like oxygen diffusion path will remain (see Fig. 4). It is this path that we believe allows for oxygen diffusion to continue to diffuse into the substrate despite the presence of a native oxide film. Note that this conjecture – that clearly needs experimental confirmation – is consistent with a situation where grain boundary diffusion of oxygen is key.

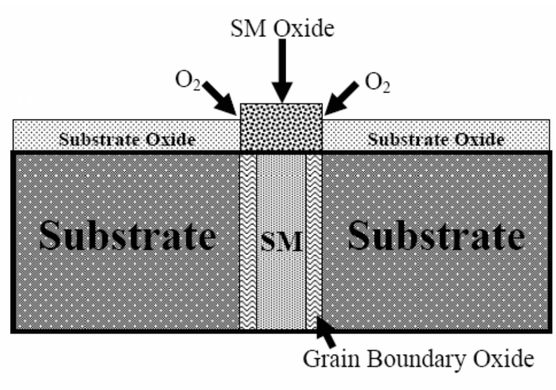

Figure 4, Oxygen potentially diffuses along the interface between SM oxide and substrate oxide, traveling down the interface of the SM and grain boundary oxide to form further grain boundary oxide and promote whisker growth.

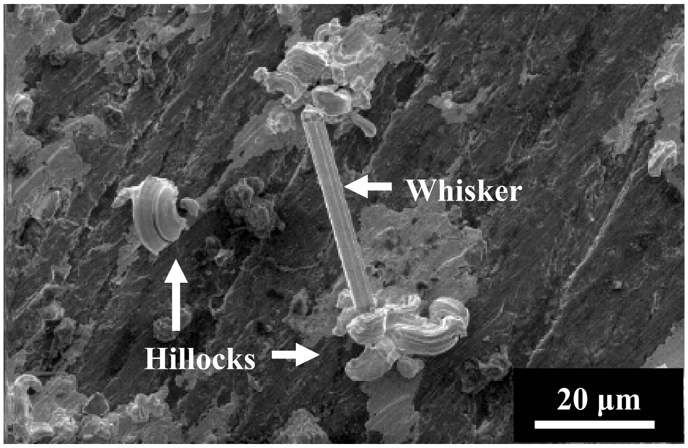

Figure 5. Sn hillocks and whiskers appear on the surface of the Sn/Al system.

Growth Mechanisms and Kinetics

The formation of whiskers is many times associated with hillocks (Fig. 5). Sn hillocks formed on a sample stored in vacuum for 30 days (Fig. 6(a)). A similar sample exposed to atmosphere for the same time period had a higher frequency of whiskers, but still formed hillocks (Fig. 6(b) and (c)). As noted in previous work, the growth in vacuum is believed to be due to residual or adsorbed oxygen [1].

The model presented herein is also consistent with the fact that atmospheric O_2 and water vapor accelerate whisker growth. [15] The model also explains why Cd thin films held in vacuum for up to 34 days, grew no whiskers, but when the same films were exposed to air short - 5 to 10 µm long - whiskers appeared after only 3 days [16]. Along the same lines, Kehrer and Kadereit, reported that when 300 Å to 1000 Å Sn films were deposited on glass in a moist oxygen atmosphere of 10^{-4} Torr and annealed at 60 °C numerous whiskers were detected within a few hours. [17] When the deposition was carried out at a pressure of 10^{-6} Torr no whiskers were observed, in the same time scale.

Based on orientation imaging microscopy (results not shown) whiskers tend to be single crystals. It is believed that whiskers grow by essentially Coble creep, viz. the SM atoms diffuse from areas of high stress to those of lower stress along the grain boundaries as proposed by Hutchinson et al. [11] The latter authors derived an expression for the linear growth rates, LGR, of the whiskers from thin Sn layers. Hutchinson et al. also showed convincingly, and confirmed herein, that bulk diffusion cannot possibly account for the growth rates observed. This work slightly alters their end result for the problem at hand, assuming grain boundary diffusion, and obtains:

$$LGR \approx \frac{4\delta D_{GB} V_m b \sigma_m}{3RTa^2 \lambda \ln(b/a)} \qquad (1)$$

where λ, δ, and D_{GB} are the grain size of soft metal, grain boundary thickness, and grain boundary diffusivity, respectively. V_m is the molar volume of the SM, *a* is the whisker radius and b, the radius around the whisker that is fueling its growth. R and T have their usual meaning. σ_m is the compressive stress driving the process. Note Hutchinson et al. did not identify the origin of σ_m, instead they used measured values.

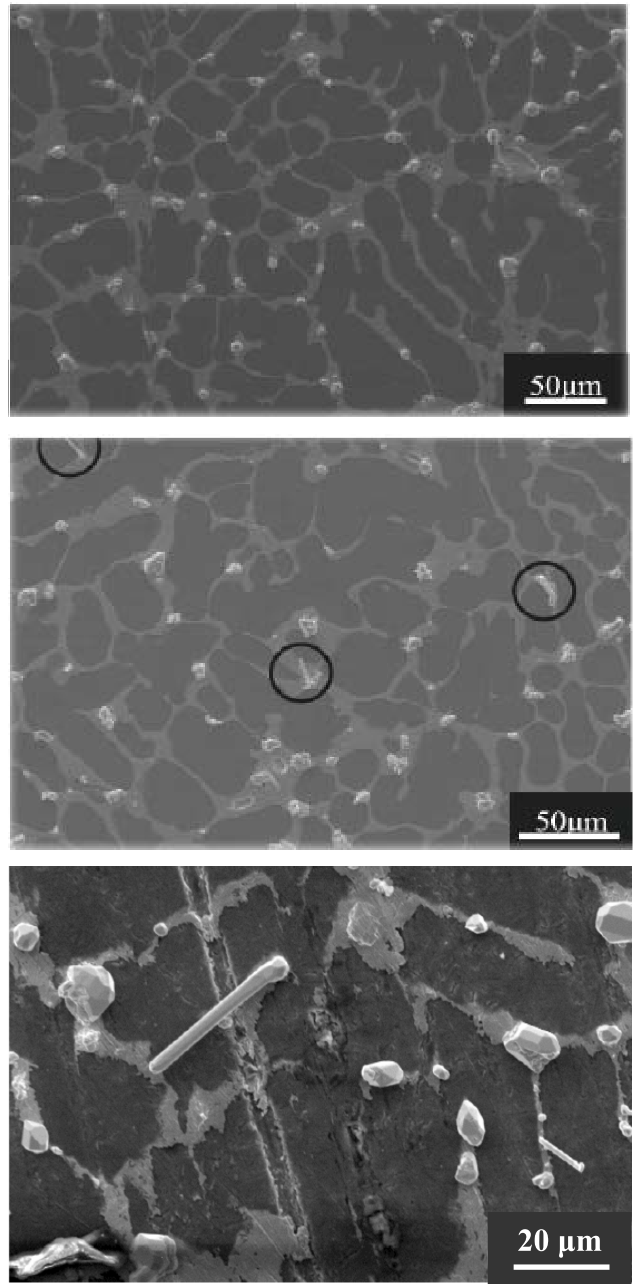

Figure 6. Effect of oxygen on Sn whisker growth in the Sn/Al system after ~30 days. (a) Only hillocks formed on sample stored in vacuum. (b) Whiskers, circled, and hillocks form on sample exposed to atmosphere. (c) Enlarged view of whiskers and hillocks

Using the values listed in Table 1 and Eq. 1, the LGR for the Zr_2InC/In and Al/Sn systems were calculated to be ≈ 6 µm/day and 1 µm/day, respectively. These values are on the same order of magnitude as experimentally measured growth rates in Sn films and typical [1,3,18].

Independent Data	Input Values for Zr_2InC/In	Input Values for Al/Sn
$V_m = 1.6 \times 10^{-5}$ m^3/mole	$\sigma = 10$ MPa	$\sigma = 10$ MPa
$D_{bulk} = 7 \times 10^{-23}$ m^2/s [20]	b = 20 μm	b = 50 μm
$\delta D_{GB} = 6 \times 10^{-22}$ m^3/s [21]	$\lambda = 5$ μm	$\lambda = 50$ μm
a=1μm	LGR ≈ 5.5 μm/day	LGR ≈ 1 μm/day

Table 1: Summary of input values used to calculate the linear growth rate, LGR, according to Eq. 1.

It is important to note that in some cases the growth rates are much higher initially. For example, when a leaded brass sample that had a relatively thick surface oxide layer was abraded, Pb whiskers were observed to grow at rates of the order of 70 Å/s or 600 μm/day, for a relatively short period before slowing down considerably [19] This observation is important and crucial to understand some of the mechanics and subtleties of whisker/hillock growth. Since it is very unlikely that the room temperature grain boundary diffusivity of Pb is 2 orders of magnitude higher than the one listed in Table 1, one has to conclude that in the case of the Pb whiskers, the residual stresses built up were much greater than the yield point of Pb. Consequently, the growth mechanism, at least initially, must be plastic deformation or extrusion. Consistent with this interpretation is the rapid growth, and the equally rapid apparent cessation of growth – at least during the time of observation, which was of the order of hours. [19]

Based the proposed mechanism, two possible solutions to the problem of whisker growth exist. One is to totally prevent oxygen from diffusing into the SM, which is easier said than done. The second and more practical approach is to grow the SM grains (if in thin film form) and/or increase the soft metal layer's thickness if present at the grain boundaries. As Figs. 2b and 2c suggest, increasing the thickness of the SM layer reduces the buildup of stresses and consequently the growth rate of the whiskers. Even in the event that, after a prolonged time, the pressure rises sufficiently in the SM to result in growth, it is quite likely that because of the SM thickness, or grain size in the case of thin Sn layers, what forms are not whiskers but hillocks. Hillocks are not as dangerous as whiskers because they typically do not grow very long. This hypothesis still needs to be experimentally confirmed, however. Experiments with varying volume fractions of Sn are needed and should be performed.

It is worth mentioning that in addition to Zr_2InC, In or Ga were found to exude from Cr_2GaC, Cr_2GaN, Mo_2GaC, Hf_2InC, $(Zr,Ti)_2InC$ and Ti_2InC surfaces.

IV. Conclusions and Remarks

The model presented here does *not* imply that diffusion of oxygen into the grain boundaries is rate-limiting; the ingress of O and associated volume changes can occur at a faster time scale than that of whiskers growth. A useful analogy is a bicycle tire that is pumped, but slowly leaks through a fine hole over a much longer time. Consequently-linear growth rates, L_w, are possible. Nevertheless, it is not clear, why or how the compressive stresses remain more or less constant with time implicit in the calculations of LGR shown in Table 1. It is that buildup of stress over a long time that presumably resulted in the very large Pb whisker growth rates observed in leaded brass [19].

Lastly it is not claimed here that reaction with the atmosphere is the only reason for the growth of SM whiskers. It is well established that external compressive and residual stresses can enhance whisker growth rates by factors as high as 10,000. [5-7,10,22]

In summary a plausible, oxidation-based process for the spontaneous growth of soft metal whiskers is proposed. This comment notwithstanding, it is hereby acknowledged that many questions remain unresolved and the evidence presented here is circumstantial. Direct evidence will require a focused ion beam, much patience, followed by TEM observations. The presence of native oxide layers, however, could complicate the analysis. A more fruitful line of research would be to systematically study the effect of oxygen partial pressure, and possibly moisture, on whisker growth. Oxygen tracer experiments are indicated and could be extremely useful. Tracer experiments would also be invaluable in understanding why nickel barriers or Pb in Sn suppress whisker formation. Finally, it is important to realize that when, or if, intermetallic formation is ruled out, as in this and many previous papers, oxidation is the *only* possible driving force sufficient to result in the growth of whiskers. Surface energy effects or recrystallization is insufficient to result in whisker growth.

The low melting point of In, combined with its presence in excess at the grain boundaries of Zr_2InC, leads to the growth of In structures, both whiskers and hillocks. Similarly, Sn whiskers and hillocks were found to sprout from a Sn/Al alloy. In both cases, it is believed the whiskers develop due to the build up of compressive stresses resulting from the diffusion of oxygen down the soft metal/substrate interfaces and the concomitant volume expansion. Larger grained solders and/or the prevention of oxygen diffusion into the soft metal are two strategies that could be used to mitigate the problem of whisker growth.

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