



# Fragility of Pb-free Solder Joints

## **Abstract**

**Recent investigations have revealed that Pb-free solder joints may be fragile, prone to premature interfacial failure particularly under shock loading, as initially formed or tend to become so under moderate thermal aging. Depending on the solder pad surface finish, different mechanisms are clearly involved, but none of the commonly used surface finishes appear to be consistently immune to embrittlement processes. This is of obvious concern for products facing relatively high operating temperatures for protracted times and/or mechanical shock or strong vibrations in service.**

**While fragility problems and the associated embrittlement mechanisms have long been known for both electroless and electrolytically deposited Ni/Au coatings, soldering to Cu has been viewed as 'safer' as far as robustness is concerned. However, recent observations suggest the existence of two or more embrittlement mechanisms in Pb-free solder joints on Cu pad structures, each leading to brittle interfacial fracture at the pad surfaces. With risks of embrittlement associated with all the commonly used solderable surface finishes, the electronics industry is currently confronting very difficult problems. The variability in the manifestations of these embrittlement mechanisms does, however, lend hope that some of these problems may be avoidable or controllable.**

**While it is imperative for each company to pursue its own interests in this arena, it is also clear that there is a common interest within the electronics industry in solving the reliability problems, associated with these solder joint embrittlement problems, particularly considering the short time frames associated with the transition to Pb-free solder technology. The consortium concept may be very usefully applied to this problem, which the industry is now confronting. A consortium effort could provide insurance for the member companies against overlooking critical phenomena or understandings. A consortium could also act as a common forum for advocating the infrastructure changes which will almost certainly accompany the required solutions to these problems.**

## Introduction

The microelectronics packaging industry relies on solder joints for the robust mechanical attachment and electrical interconnection of a wide variety of components. Thermal excursions and mechanical shock or vibration often lead to substantial loads on these joints. Notwithstanding, we have a detailed technical understanding, based on decades of experience, by which to assess and predict the consequences for Sn-Pb soldering technology. Over the last few years a significant amount of work has also been done in developing Pb-free soldering technology. Although we are still far from the level of experience and understanding reached for the Sn-Pb system, the commonly preferred Pb-free (Sn-Ag-Cu) alloy system is usually claimed to offer superior or comparable thermomechanical fatigue resistance and, at worst, a minimal reduction in mechanical shock resistance. These claims are still the subjects of intensive research, notably in terms of the effects of the evolution of the solder joint microstructure in thermal cycling and with time at elevated temperatures. Recent reports do, however, suggest some unexpected embrittlement problems associated with both Cu and electrolytic Ni/Au-coated solder pad surfaces. In fact, apparently no commonly used solderable surface coating is consistently immune to embrittlement problems. This circumstance may pose a serious reliability concern and infrastructure problem for the microelectronics industry, as it moves towards the implementation of Pb-free soldering technology. However the variability in the manifestation of embrittlement mechanisms, at least in the Cu pad system, lends some insight and hope to the prospect that some of the embrittlement mechanisms can be controlled.

In simple terms, the mechanical forces on a solder joint originate from externally imposed forces on its card assembly or from mismatched thermal expansions within the structures to which the solder joint is attached. The plastic deformation properties of the solder serve to limit the stresses in the solder joint at sufficiently high stress values. Even moderate thermal cycling usually requires some joints to survive loads which induce significant plastic deformation in each cycle, making it paramount for the interfacial intermetallic compound structures in the solder pads to survive loads corresponding to the solder plastic flow stress. The solder plastic flow stress is invariably higher under externally imposed mechanical loading, in particular loads associated with system mechanical shock, because of the higher imposed strain rates.

Accordingly, even intermetallic compound structures that are strong enough for thermal cycling may still be the ultimate weakest link in a shear or pull test. However, this is not necessarily immediately critical since externally imposed mechanical loading may often be limited, by design, to a level that does not involve much plastic flow of the solder or, at least does not exceed the critical interfacial tensile load required for interfacial fracture. Still, a switch from failure through the solder to failure at a pad surface or within the intermetallics in such a test is invariably an indication of an ongoing weakening. In general, solder joints which demonstrate brittle interfacial fracture without significant plastic deformation of the solder joints, represent an inherent problem in applications, where shock loading of the solder joints can be anticipated. In such instances very little energy is dissipated in the solder joint in the fracture process and the solder joint structures are inherently prone to shock reliability problems. Some of the embrittlement mechanisms may also cause sufficient weakening to allow for premature solder joint failure even under a CTE mismatch stress in some applications. In fact, continued interfacial void growth in the intermetallics may even cause failure at very low load values.

While issues with soldering to Ni/Au coated pads have long been recognized, recent observations appear to involve new phenomena, as outlined below. In contrast, until now Cu pads coated with OSP, immersion Ag, immersion Sn, or solder have been viewed as 'safer' in this respect. This does not mean that degradation mechanisms are completely absent, even for Sn-Pb soldering. In fact, rapid diffusion of Cu through both the Cu<sub>3</sub>Sn and the Cu<sub>6</sub>Sn<sub>5</sub> intermetallic layers commonly leads to the growth of Kirkendall voids at the Cu/Cu<sub>3</sub>Sn interface [1], [2] and/or the Cu<sub>3</sub>Sn/Cu<sub>6</sub>Sn<sub>5</sub> interface [3]. However, these voids often remain very low in density and too small to be visible by optical microscopy [1], [2]. They are therefore usually not considered to be of practical concern.

Recent reports of rapid mechanical weakening of Sn-Ag-Cu solder joints on Cu pads in thermal aging have caused considerable stir in the microelectronics packaging community [4], [5]. The effect appeared to be caused by the growth of Kirkendall voids along the Cu<sub>3</sub>Sn/Cu interface (*Figure 1*). Extensive voiding was observed after only moderate aging (20-40 days at 100°C) making it an obvious practical concern, at least for products facing elevated operating temperatures and mechanical shock or vibrations in service. In fact, the apparent temperature dependence might suggest a

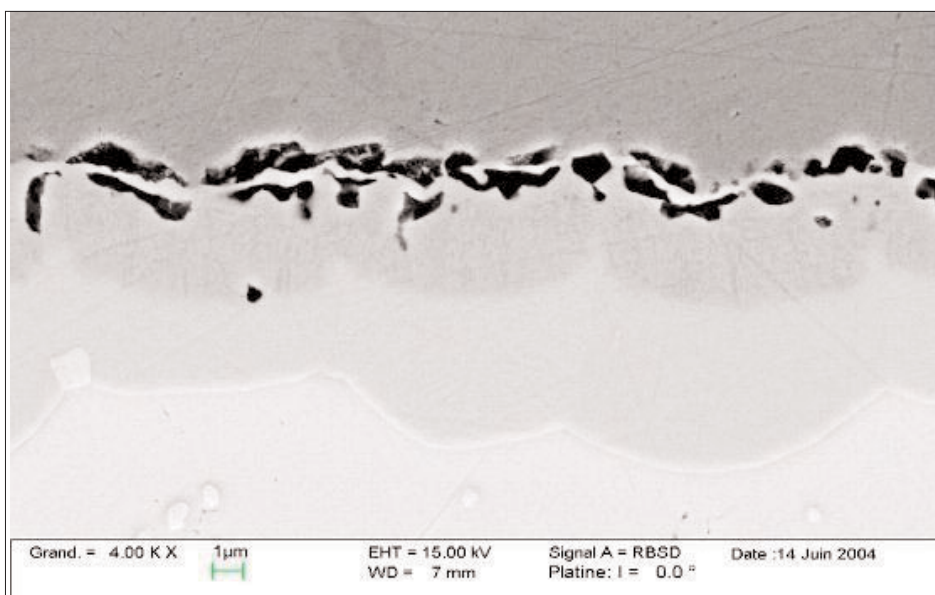


Figure 1: Interface between Sn-Ag-Cu solder ball and Cu pad after 1000 hours at 150°C. Kirkendall voiding is, typically, found within the  $Cu_3Sn$  phase at the Cu -  $Cu_3Sn$  interface. Micrograph shows worst case condition at the end of the aging process.

risk of failure within a few years under even quite mild operating conditions. The behavior was confirmed independently by others [5], [6], but fortunately this embrittlement problem may be avoidable. Initial experiments by UIC did not reproduce the voiding [7], and work by IBM [6], suggests a dependence on plating lot (Figure 2). These findings may suggest an effect of impurities. In some instances contamination has been shown to strongly enhance Kirkendall voiding, as impurities are less soluble in the intermetallic phases and thus may be 'swept' ahead of the transformation front and precipitate to act as heterogeneous nucleation sites for voids [8]. It can, however, also not be excluded that sub-microscopic voids or bubbles were somehow incorporated at the Cu-surface during reflow and subsequently serve as sinks for vacancies.

IBM also reports another brittle interfacial intermetallic compound failure phenomenon which does not appear to be associated with Kirkendall voiding [6]. Ball pull testing demonstrated interfacial failure within the intermetallics on Cu pads immediately after assembly, and this phenomenon was invariably enhanced by thermal aging. It remains to be ascertained whether this is a practical concern as continued aging did not necessarily, unlike in the case of voiding, lead to a further reduction in pull strength. Again, plating lot variability in the phenomenon was found.

The only mature alternative to soldering to Cu would be nickel, usually coated with a layer of Au to protect it from oxidation. There have been reports [9]

that prolonged reaction between electroless Ni(P) and Sn-Pb may also lead to the formation of Kirkendall voids near the Ni surface, but this appears to be a less likely problem than for Cu. A more complex mechanism is observed when the package includes a Cu-pad on the opposite side of the Sn-Pb joint, and thus a ready supply of Cu to the solder. In this case, a build-up of a ternary  $(Cu,Ni)_6Sn_5$  layer is observed on top of the  $Ni_3Sn_4$  (which was formed on a nickel surface). In this instance aging has been seen to lead to void growth at the  $Ni_3Sn_4/(Cu,Ni)_6Sn_5$  interface [10]. A similar problem might be expected with Sn-Ag-Cu solder on nickel, because of the ready supply of Cu in this solder alloy.

A unique and widely recognized concern, specifically associated with electroless nickel immersion gold (ENIG), is the so-called 'black pad' phenomenon. This is, in fact, a somewhat ubiquitous term which encompasses a number of phenomena related to failure at or near the Ni(P)/ $Ni_3Sn_4$  interface. Most generally it refers to a lack of solderability of the Ni(P) surface due to a high amount of corrosion, during the immersion gold process, but often the effects of various alloys or combinations of alloys near the interface are included as well. 'Black pad' usually refers to a 'time zero' phenomenon, whether reflected in obvious fragility or just reduced mechanical fatigue resistance at/within the contact pad structure. However an alternative mechanism by which a seemingly perfect intermetallic structure may degrade over time may also be related to the corrosive 'black pad' effect. This second mechanism appears to involve the growth of  $Ni_3Sn_4$ , a resulting enrichment in P and formation of  $Ni_3P$  underneath and the growth of a ternary phase in between. In either case the problem seems exacerbated by a transition from Sn-Pb to Sn-Ag-Cu solder [11], [12].

Electrolytic nickel is usually coated with an electrolytically deposited layer of gold. The problem with this approach is that manufacturing tolerances do not allow for the control of electroplated gold thicknesses to much less than 25-50 micro-inches (0.63-1.3 m). Depending on, among other things, the maximum load in service this may present a concern. Extensive research [13-19] has shown the gold to dissolve into Sn-Pb solder during reflow only to gradually return to the nickel surface during subsequent aging and contribute to the build-up of a  $(Ni, Au)Sn_4$  layer on top of the  $Ni_3Sn_4$  intermetallic at that surface. The resulting interface is mechanically unstable with a strength that continues to decrease with increasing  $(Ni, Au)Sn_4$  thickness. Indications are that the increased dissolution

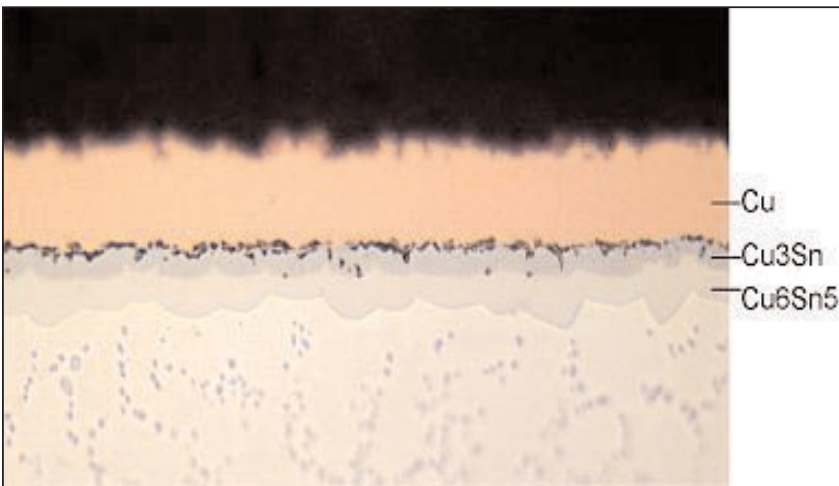
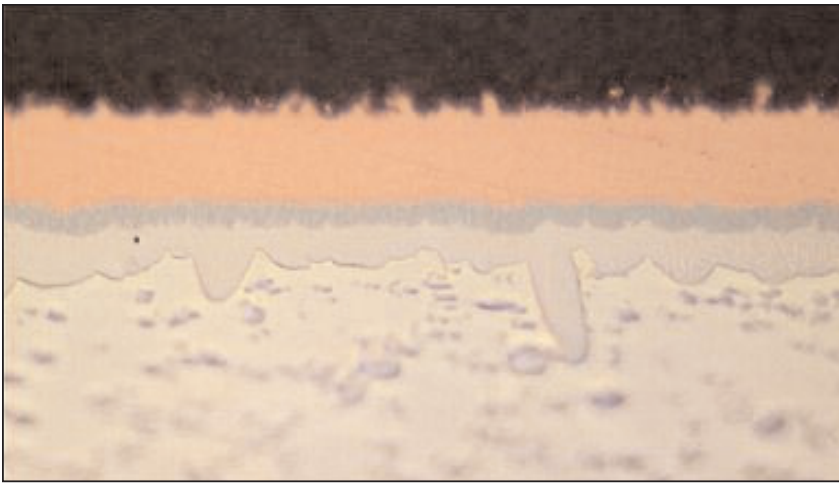


Figure 2: Experimental BGA solder joint interfaces between Sn-Ag-Cu solder balls and Cu pads on identically aged samples (1000 hours @ 150°C). The two samples were produced from two plating lots, but were reflowed using the same solder ball lot, the same flux lot, the same reflow profile and atmosphere in the same oven on the same day.

of nickel at the higher reflow temperatures associated with Sn-Ag-Cu soldering may tend to stabilize the gold within ternary Ni-Au-Sn precipitates in the bulk of the solder, but further studies may be required to quantify effects of various parameters. Qualcomm recently reported observations of 'time zero' failures of Sn-Ag-Cu CSP joints on electrolytic Ni/Au in drop testing, a problem that was reduced or eliminated by reductions in reflow temperature and time. The authors ascribed the brittle failures to a mismatch between the Ni<sub>3</sub>Sn<sub>4</sub> and an overlying (Cu, Ni)<sub>6</sub>Sn<sub>5</sub> layer [20], but similar thicknesses of (Cu, Ni)<sub>6</sub>Sn<sub>5</sub> usually appear to be stable on top of (Ni, Cu)<sub>3</sub>Sn<sub>4</sub> in other experiments. Still, the phenomenon appears to be different from the well established Au-related problem.

## Summary

Transitioning to Pb-free soldering the industry seems to be facing significant risks of solder joint fragility associated with all the commonly used solder pad surface finishes.

Well established 'black pad' effects and an alternative aging induced embrittlement of the intermetallic structure on ENIG pads appear even more critical for Sn-Ag-Cu than for Sn-Pb joints. Another mechanism associated with the greater Au-thicknesses in electrolytically deposited Ni/Au coatings may be eliminated or reduced in Pb-free soldering. However, usually soldering of Sn-Ag-Cu to Ni pads leads to the build-up of a (Cu, Ni)<sub>6</sub>Sn<sub>5</sub> layer on top of the Ni<sub>3</sub>Sn<sub>4</sub>. Some such structures have been found to be brittle immediately after Sn-Ag-Cu solder alloy assembly, and aging of a Ni<sub>3</sub>Sn<sub>4</sub>/(Cu, Ni)<sub>6</sub>Sn<sub>5</sub> structure, albeit in Sn-Pb joints, has been seen to lead to strong voiding and porosity in some instances.

Too often, extensive Kirkendall voiding may weaken Sn-Ag-Cu solder joints on Cu pads after only moderate aging, and a seemingly independent embrittlement mechanism was found to occur even without aging although it does still tend to worsen with aging. Initial results may suggest a dependence on plating lot, but other factors such as materials (solder, flux, solder paste, pad finish, plating parameters, ...) and process parameters (reflow profiles and ambient, oxidation and contamination of solder and pads, pad configuration, paste volumes, ...) are expected to be important as well.

In general, the variability of most of these embrittlement mechanisms does lend hope that at least some of them may be avoidable or controllable.

## References

- [1] Stinson-Bagby, K., "Microstructural Evolution in Thermally Cycled Large-Area Lead and Lead-Free Solder Joints", Master's Thesis, Virginia Tech, Blacksburg, VA 2002
- [2] Liu, C. Y., Tu, K. N., Sheng, T. T., Tung, C. H., and Elenius, P., "Electron microscopy study of interfacial reaction between eutectic SnPb and Cu/Ni(V)/Al thin film metallization" *Journal of Applied Physics*, 87, (2000), pp. 750
- [3] Zeng, K., Tu, K. N., "Six Cases of Reliability Study of Pb-free Solder Joints in Electronic Packaging Technology", *Mater. Sci. Eng. Reports* 38, 2002, pp. 55-105

- [4] Chiu, C., Zeng, K., Stierman, R. Edwards, D., and Ano, K., "Effect of Thermal Aging on Board Level Drop Reliability for Pb-free BGA Packages", 54th ECTC Conf., 2004
- [5] Date, M., Shoji, T., Fujiyoshi, M., Sato, K., and Tu, K. N., "Impact Reliability of Solder Joints", 54th ECTC Conf., 2004
- [6] IBM, private communication
- [7] P. Kondos, Universal Instruments Corporation, private communication
- [8] Horsting, C. W., "Purple Plague and Gold Purity", Proc. 10th Annual IEEE Reliability Symp., Las Vegas, Nevada, 1972, pp. 155-158
- [9] Goyal, P., Lane, T., Kinzie, P., Panichas, C., Chong, K. M., Villalobos, O., "Failure Mechanisms of Brittle Solder Joint Fracture in the Presence of Electroless Nickel Immersion Gold (ENIG) Interface", Proc. 52nd ECTC Conf., 2002
- [10] Zeng, K., "Influence of Solder Reaction Across Solder Joints", 6th Ann. Topical Research Conf., SEMATECH, Oct. 27-28, 2003, Austin TX
- [11] Homa, T., Kondos, P., and Meilunas, M., "Mechanical Cycling and Failure Analysis of Mixed Solder CSP Assemblies", Area Array Consortium Meeting, June 2004
- [12] Kondos, P., "ENIG Pad Finish Studies", Area Array Consortium Meeting, June 2004
- [13] Ohriner, E. K., "Intermetallic Formation in Soldered Copper-Based Alloys at 150oC to 250oC", Welding Journal: Research Supplement, July 1987, pp. 191s-202s
- [14] Mei, Z., Kaufmann, M., Eslambolchi, A., Johnson, P., "Brittle Interfacial Fracture of PBGA Packages Soldered on Electroless Ni/Immersion Au", Proc. 48th ECTC, 1998, pp. 952-961
- [15] Zribi, A., Chromik, R. R., Presthus, R., Clum, J., Zavalij, L., Cotts, E. J., "Effect of Au-Intermetallic Compounds on Mechanical Reliability of Sn-Pb/Au-Ni-Cu Joints", InterPACK Conf. Adv. in Electronic Packag. 26, no. 2, 1999, pp. 1573-1577
- [16] Zribi, A., Chromik, R. R., Presthus, R., Teed, K., Zavalij, L., DeVita, J., Tova, J., Cotts, E. J., Clum, J., Erich, R., Primavera, A., Westby, G., Coyle, R. J., Wenger, G. M., "Solder Metallization Interdiffusion in Microelectronic Interconnects", IEEE CPMT 23, 2000, pp. 383
- [17] Warburton, W. K., Turnbull, D., "Fast Diffusion in Metals", Diffusion in Solids: Recent Developments (New York: Academic Press), p. 180 (1975)
- [18] Erich, R., "Development and Implementation of Shear Testing for Surface Mount Area Array Technology", Master thesis, Binghamton University, Binghamton, NY 1998
- [19] Erich, R., Coyle, R. J., Wenger, G. M., Primavera, A., "Shear Testing and Failure Mode Analysis for Evaluation of BGA Ball Attachment", Proc. 24th IEEE Int. Electr. Manuf. Symp., Austin, TX, Oct. 18-19, 1999, pp. 16-22
- [20] Gregorich, T., Holmes, P., Lee, J., and Lee, C., "SnNi and SnNiCu Intermetallic Compounds Found When Using SnAgCu Solders", IPC/Soldertec Global 2nd Int. Conf. on Lead Free Electronics, June 2004

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