

# **Review of the Impact of Intermetallic Layers on the Brittleness of Tin-Lead and Lead-Free Solder Joints**



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## Preface

This review has been funded by Vinnova (Swedish Governmental Agency for Innovation Systems) and Swerea. It is a part of the work done in ELFNET Sweden to assess how the transition to lead-free soldering will affect the risk for brittle fractures in solder joints.

Mölnadal, March 2006

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## Summary

Brittle fracturing in solder joints is a rather rare cause of failures but it is an increasing problem and the results from several investigations indicate that lead-free soldering will increase the risk for brittle fractures. One reason for that is the higher elastic modulus of lead-free solders compared to tin-lead solder. Another reason is that thicker and more complex intermetallic layers may form when lead-free solders are used.

Brittle fractures are caused by a high level of applied strain and strain rate. The most common situation causing brittle fractures is bending of assemblies. Bending causing brittle fractures can occur during assembly, testing, and shipping but also if a product is exposed to mechanical chock, for example by dropping it to the ground. Other causes of strain-induced fractures are fast temperature changes and vibration. A failure due to brittle fracturing may be the result of one single high-strain event or many consecutive events at a lower strain level. After soldering, there are residual stresses in the solder joints that slowly decline as a result of creep in the solder. Due to these residual stresses, solder joints are more inclined to brittle fractures the first days after soldering and they are especially vulnerable directly after soldering. Solder joints to area array components, especially large BGA components, are more inclined to brittle fractures than solder joints to other types of components.

The brittle fracture takes place in the layer of intermetallic compound (IMC) that is formed at the solder/metal interface during soldering. While the IMC layer is necessary for achieving a reliable solder joint, it is usually hard and brittle. The composition, structure, and brittleness of the IMC layer are affected by the composition of the solder and the metal finish on the soldered surface. Although many different types of surface finishes are used on solder lands and component leads and terminations, the IMC layers are almost exclusively formed to one of three metal surfaces; copper, electrolytic nickel, or electroless nickel. Other finishes plated on top of these are normally completely dissolved in the solder.

The IMC layer formed on copper when soldering using tin-lead solder consists of  $\text{Cu}_6\text{Sn}_5$ . A second layer consisting of  $\text{Cu}_3\text{Sn}$  forms at the  $\text{Cu}_6\text{Sn}_5/\text{Cu}$  interface during high temperature aging. The IMC layer formed on electrolytic nickel consists normally of  $\text{Ni}_3\text{Sn}_4$ . This compound is also formed on electroless nickel but the IMC layer formed on this finish contains other intermetallic compounds as well.

Brittle fractures on assemblies soldered using tin-lead solder have mainly been reported to occur when the PCBs or the components have solder lands with electroless nickel/immersion gold (ENIG) finish. Some of these brittle fractures have been caused by a plating defect on the ENIG finish called "black pad". However, solder joints formed on ENIG have been found to be prone to brittle fractures also in the absence of this defect.

Electroless nickel contains phosphorus. During both immersion gold plating and soldering, nickel is selectively dissolved from the surface. This results in an

enrichment of phosphorus and the formation of a  $\text{Ni}_3\text{P}$  layer at the uppermost nickel surface. The black pad defect is caused by too extensive dissolution of nickel during immersion gold plating. The extensive dissolution of nickel leads to the formation of a thick  $\text{Ni}_3\text{P}$  layer but also to etching of the nickel underneath the gold coating. Due to this over-etching, nickel surfaces are exposed to oxidation, and plating residues may be trapped beneath the gold coating. Enrichment of  $\text{Ni}_3\text{P}$  at the nickel surface combined with oxidation of exposed nickel surfaces and entrapment of plating residues renders wetting and the formation of a proper IMC layer during soldering more difficult. As a result, the solder joint will be weaker than normal and, when exposed to stress, a fracture may occur at the  $\text{Ni}_3\text{P}/\text{Ni}_3\text{Sn}_4$  interface. The defect is called black pad since the nickel surface that is exposed when a crack occurs is usually dark grey to black due to the enrichment of  $\text{Ni}_3\text{P}$ . Although it was at first believed that a high phosphorus content in the nickel promoted the formation of black pad defects, it is today generally considered that a high phosphorus content decreases the risk for black pad defects.

Results from recently performed investigations indicate that the brittleness of solder joints to electroless nickel in the absence of black pad defects is caused by a very thin IMC layer containing Ni, Sn and P formed between the  $\text{Ni}_3\text{Sn}_4$  and  $\text{Ni}_3\text{P}$  layers during soldering. There are different opinions on how the phosphorus content in electroless nickel affects the risk for brittle fractures in this layer. Results from some investigations indicate that the risk increases with increasing phosphorus content whereas results from other investigations indicate the opposite.

Electrolytic nickel does not contain phosphorus and solder joints to electrolytic nickel are therefore less inclined to brittle fractures. However, electrolytic nickel is normally coated with a rather thick layer of gold. The gold is dissolved in the solder during soldering but may form a second IMC layer consisting of  $(\text{Au},\text{Ni})_4\text{Sn}$  on top of the  $\text{Ni}_3\text{Sn}_4$  layer when the solder joint is aged. Severe embrittlement of solder joints has been observed after high temperature aging due to formation of this dual IMC layer.

Brittle fracturing in the IMC layers formed on copper has hardly ever been reported to occur in the field for solder joints with tin-lead solder. Nevertheless, it may become a problem for lead-free products used at high temperatures for a long time. Extensive formation of Kirkendall voids may occur in the  $\text{Cu}_3\text{Sn}$  layer or at the  $\text{Cu}_3\text{Sn}/\text{Cu}$  interface when exposed to temperatures above  $100^\circ\text{C}$ , perhaps even at lower temperatures. The formation of Kirkendall voids results in a significantly increased risk for brittle fractures. Impurities in the copper and the higher soldering temperature used for lead-free soldering seem to be the main causes for the formation of Kirkendall voids.

When soldering to nickel surfaces using lead-free solders, the copper content in the solder will be important for the composition, structure and brittleness of the IMC layers formed. With SnAg solder,  $\text{Ni}_3\text{Sn}_4$  will form, just as it does for SnPb solder. On electroless nickel, spalling (detachment) of this layer may occur leading to a thicker NiSnP layer being formed at the  $\text{Ni}_3\text{Sn}_4/\text{Ni}$  interface and thereby probably an increased risk for brittle fractures. If the solder contains more

than 0.6% Cu,  $(\text{Cu,Ni})_6\text{Sn}_5$  will form instead of  $\text{Ni}_3\text{Sn}_4$ . At lower copper concentrations, a dual IMC layer may form consisting of  $(\text{Cu,Ni})_6\text{Sn}_5$  and  $(\text{Ni,Cu})_3\text{Sn}_4$  with the latter phase closest to the nickel surface. This dual layer may also form when solder joints with more than 0.6% Cu are aged. Very few studies have been performed of how this dual IMC layer affects the risk for brittle fractures but the results from one study indicate a significantly increased brittleness. Copper-containing IMC layers may also form when soldering to nickel using SnAg solder if an opposite solder pad or component lead/termination has a copper surface.

Dissolution of nickel from a nickel surface into the solder may affect the IMC layer formed on an opposite copper surface. Copper atoms in  $\text{Cu}_6\text{Sn}_5$  may be substituted with nickel atoms, i.e. the composition will be  $(\text{Cu,Ni})_6\text{Sn}_5$ , and the IMC layer may become 2-3 times thicker compared to when no nickel is present. Some reports indicate that  $(\text{Cu,Ni})_6\text{Sn}_5$  are more brittle than  $\text{Cu}_6\text{Sn}_5$ . Since  $(\text{Cu,Ni})_6\text{Sn}_5$  are formed also on nickel surfaces when the solder contains copper, a higher brittleness of this phase may affect the reliability of solder joints to nickel as well.

The dual IMC layer formed during high temperature aging of SnPb solder joints to electrolytic nickel/gold is less likely to form when using SnAg solders and especially when using SnAgCu solders. Nevertheless, it has been reported to cause brittle fractures in SnAgCu solder joints during combined exposure to temperature cycling and vibration.

Traditional shear and pull tests are not adequate for assessing the risk for brittle fractures. The shear and pull rates used in these are too low in order to get high enough strain and strain rate. Test equipment that can utilise higher shear and pull rates or other test approaches are needed for evaluating the risk for brittle fractures. Standards for characterising the fracture strength of solder joints using bend and drop tests of assemblies have been developed by JEDEC and IPC. A standard has also been developed for measuring the strain and strain rates solder joints are exposed to during PCB assembly, test and operation using strain gages.

# 1 Introduction

During soldering, some of the metal to which the solder joint is formed is dissolved into the molten solder. As a result, the solder becomes supersaturated with the dissolved metal and a layer of an intermetallic compound (IMC) is precipitated on the metal surface. In some cases, the intermetallic layer may consist of two or more intermetallic compounds. This reaction is necessary to achieve wetting to the metal surface. The composition of the intermetallic compound(s) depends on the combination of metal surface and solder used. The intermetallic compounds that may form are generally much harder and more brittle than solders and can, therefore, cause brittle fractures in the interface between the solder and the metal surface.

Intermetallic compounds may also form within the bulk solder. They may then reinforce the solder joint. However, it has been known for a long time that soldering to surfaces coated with a too thick layer of gold may cause embrittlement of the solder joint, so called gold embrittlement. Gold dissolves very rapidly in molten tin-lead solder, about 1  $\mu\text{m/s}$ . Thus, no gold will remain on the metal surface unless the gold coating is very thick. Since the solubility of gold in solid solder is low, about 0.3-0.4% (percentages are given as wt-% if not otherwise specified) at 150°C [1, 2] it will be precipitated as intermetallic crystals in the bulk solder joint at higher gold concentrations. If the gold content in the solder joint exceeds 3-5%, the precipitated intermetallic crystals may cause brittle fractures in the solder joint when exposed to large stress [3, 4, 5, 6, 7, 8]. Thus, in this case it is intermetallic crystals formed in the solder joint that cause the embrittlement and the fracture occurs in the bulk solder.

Brittle fractures in the intermetallic layers formed on solder lands and components leads have rarely been a problem in the past when soldering was done primarily to copper surfaces. The IMC layer formed on a copper surface during soldering will increase in thickness during aging; the higher the temperature, the faster the growth of the layer. In laboratory tests, it has been shown that brittle fractures may occur during pull testing of solder joints that have been exposed to temperatures above 100°C for a long time [9, 10].

During the last five years, it has become apparent that solder joints to nickel are more prone to brittle fractures in the intermetallic layer than solder joints to copper. The fracture happens between the nickel surface and the nickel-tin intermetallic layer under a high level of both applied strain and strain rate [11]. Especially solder joints to area array components have been found to be prone to brittle fractures. Fracturing due to high strain and strain rate has been reported to occur under several conditions. It may occur already during the soldering process under the cooling phase or under the heating phase in a second soldering process (see Section 4.4). After reflow, brittle fractures may be caused by assembly operations that could result in bending, for example [12, 13]:

- in-circuit testing,
- depaneling or breaking of end tabs,

- insertion or removal of boards in chassis,
- attachment or removal of fasteners, press-fit connectors, and spring loaded heat sinks,
- shipping or handling with insufficient mechanical support.

Fracturing may also occur when products are exposed to temperature cycling [14], mechanical shock [15, 16, 17] and vibration [18, 19]. Dropping a product to the ground is probably the most common situation causing brittle fractures.

BGAs have been soldered to nickel surface for more than 10 years, but it is only during the last five years that it has been realised that the solder joints are prone to brittle fractures. Lead-free soldering may increase the risk for brittle fractures. Firstly, the soldering temperature is higher which will cause a faster growth of the intermetallic layer during the soldering process and a larger stress of the solder joint during cooling. Secondly, the creep rates of lead-free solders are generally considerably lower which also will cause a larger stress on solder joints when exposed to temperature changes. Thirdly, the lead-free alloys contain new alloying elements giving rise to numerous new material combinations that may affect the composition and growth of the intermetallic compounds, both at the metal surfaces and within the solder joints. Some reports have shown that lead-free solder joints are actually more prone to brittle failures than tin-lead solder joints [15, 17, 20, 21, 22]. Therefore, a literature review has been performed in order to elucidate how a change from tin-lead to lead-free soldering may affect the risk for brittle fractures. The study has been limited to the lead-free solders tin-silver, tin-copper, and tin-silver-copper. In solder joints to flip chips, electromigration due to high current density may have a large impact of the growth of the intermetallic layers [23, 24] but that will not be covered in this survey.

The numbers of papers presented in this field during the last 10 years are huge. I have read about 400 papers but that are probably less than half of all papers published. The descriptions of the experimental work performed are meagre in many papers and the results presented in some papers are contradictory. This makes it difficult to draw definite conclusions of how the composition of the IMC layer affects the brittleness of solder joints.

## 2 Growth of Intermetallic Compounds in Solder Joints

Although a large number of finishes can be found on surfaces that will be soldered, the intermetallic layer is almost always formed either on copper or nickel surfaces. Due to the poor corrosion resistance of copper and nickel, they need to be protected against corrosion by an organic solderability preservative coating (only on copper) or a corrosion resistant metal finish such as tin, solder, gold, silver, palladium, or bismuth. The four latter finishes are thin and normally completely dissolved in the solder during soldering. An exception is palladium, which sometimes may be too thick to be completely dissolved in the solder. Exceptions are also gold and silver/palladium used in thick film applications. Intermetallic layers formed on thick film surfaces will not be covered in this review.

### 2.1 Intermetallic Compounds Formed with Tin-Lead Solders

#### 2.1.1 Copper Surfaces

##### *Growth of Intermetallic Compounds during Soldering*

When tin-lead solder melts on copper surfaces, copper will start to dissolve into the solder. The solder closest to the copper surface will within a few seconds be supersaturated with copper and intermetallic crystals with the composition  $\text{Cu}_6\text{Sn}_5$  are precipitated on the copper surface [25, 26]. These crystals, which usually have a scallop-like appearance, will grow and after a normal soldering process they will completely cover the surface. The IMC layer formed has an uneven thickness, normally in the range 0.5 to 2  $\mu\text{m}$ . Thermodynamically, there should also be a layer of  $\text{Cu}_3\text{Sn}$  between Cu and  $\text{Cu}_6\text{Sn}_5$  but it is usually very thin making it difficult to detect.

Due to the relative high dissolution rate and solubility of copper in molten solder, not all copper dissolved in the solder is precipitated in the scallop-like IMC layer. When the solder solidifies, this surplus of dissolved copper often forms relative long  $\text{Cu}_6\text{Sn}_5$  tubes or rods protruding from the copper surface. The zone with protruding  $\text{Cu}_6\text{Sn}_5$  can be described as a two-phase layer. Such two-phase layers are typically formed on metal surfaces with high solubility in molten solder.

##### *Growth of Intermetallic Compounds during Aging*

The intermetallic layer continues to grow after the soldering process, the higher the temperature the faster the growth of the IMC layer. According to Lea, after 100 days aging, the thickness has increased with about 3  $\mu\text{m}$  at 70°C, 5  $\mu\text{m}$  at 100°C, 13  $\mu\text{m}$  at 135°C, and 20  $\mu\text{m}$  at 170°C for Sn40Pb [27]. Furthermore, the

growth rate is more or less proportional to the content of tin in the solder. Thus, the growth rate in Sn40Pb (40% lead) is about 60% of that in pure tin. The growth of the IMC layer in solid solder results in a more even thickness of the intermetallic layer.

At temperatures above 60°C, crystals with  $\text{Cu}_3\text{Sn}$  form at the  $\text{Cu}_6\text{Sn}_5/\text{Cu}$  interface [5, 9, 25, 27, 28]. As already mentioned, a layer with  $\text{Cu}_3\text{Sn}$  is likely formed already during the soldering process but it is then so thin that it is difficult to detect. After aging at temperatures above 100°C, 30-50% of the intermetallic layer may consist of  $\text{Cu}_3\text{Sn}$  [5, 10, 29, 30]. When the total thickness of the intermetallic layer exceeds 5-7  $\mu\text{m}$ , a continuous thick layer of  $\text{Cu}_3\text{Sn}$  can be observed.

### ***Effect of Alloying Elements in Copper and Elements Dissolved from an Opposite Surface***

The composition of copper lead frames used in components may vary. Some lead frame materials contain about 2% of iron. Martin et al. have reported that the iron brings a tremendous acceleration of the IMC growth at temperatures above 140°C [31]. After 1000 hours aging at 150°C of Sn36Pb2Ag solder joints to a copper lead frame with 2% Fe, the IMC layer had a thickness of 32  $\mu\text{m}$ . The acceleration was even larger for SnAgCu and SnAg lead-free solders. For these solders, the IMC thicknesses after 1000 hours were 40  $\mu\text{m}$  and 45  $\mu\text{m}$ , respectively. For comparison, the thickness of the IMC layer in SnAgCu solder joints to a pure copper lead frame was about 12  $\mu\text{m}$  after 1000 hours aging at 150°C.

According to Laurila et al. [25], Ohriner has reported an increase in IMC growth rate when copper is alloyed with nickel. The maximum growth rate was achieved with 6-9% of Ni. On the other hand, according to Wu et al. the addition of nickel to tin-lead solder increases the activation energy for solid-state growth of both  $\text{Cu}_6\text{Sn}_5$  (from 0.8 eV to 2.17 eV) and  $\text{Cu}_3\text{Sn}$  (from 1.69 eV to a very large value) [32]. That is, the growth rate of both phases ought to decrease when nickel is added to the solder. This conclusion is partly supported by work done by So et al. [33] and Mei et al. [34]. So et al. found that dissolution of nickel from the terminations on passive components suppressed the growth of  $\text{Cu}_3\text{Sn}$  on the printed board solder land when aged for 12 days at 155°C but, however, the total thickness of the IMC layers was not much affected. Mei et al. compared the IMC layers formed on copper pads coated with an organic solderability preservative (OSP) in solder joints to BGA components with either nickel/gold or copper pads after aging at 125°C for 20 days. The IMC layer on the OSP pads contained less  $\text{Cu}_3\text{Sn}$  when the BGA had nickel/gold pads although no nickel was found neither in the solder nor in the IMC layer. On the other hand, the  $\text{Cu}_3\text{Sn}$  layer on the BGA with copper pads, which had passed two soldering processes, was rather thin despite the fact that the opposite pad also consisted of copper (and had a rather thick layer of  $\text{Cu}_3\text{Sn}$ ). No explanation was given why the  $\text{Cu}_3\text{Sn}$  layer was thin on the BGA with copper pads. Mei et al. observed that almost no  $\text{Cu}_3\text{Sn}$  was formed when a Cu2.5Ni0.5Si leadframe with 10  $\mu\text{m}$  electroplated SnPb was aged at

145°C for 5 days. This result also supports that Ni may suppress the formation of  $\text{Cu}_3\text{Sn}$ .

If the solder contains gold (usually from dissolution of gold from an opposite solder land plated with electrolytic nickel-gold) the  $\text{Cu}_6\text{Sn}_5$  layer will dissolve some gold, at least after having been exposed to high temperature aging. Ratchev et al. performed temperature cycling between  $-40$  to  $+125^\circ\text{C}$  of Polymer Stud Grid Array (PSGA) packages with Ni/Au coated polymer studs soldered on a PCB with OSP finish [35]. On the PCB pads,  $\text{Cu}_3\text{Sn}$  was found closest to the copper and on top of that a dual IMC layer. Next to the  $\text{Cu}_3\text{Sn}$  layer, a layer of  $(\text{Cu,Au})_6\text{Sn}_5$  with 7 at-% Au was found and on top of that a layer of  $(\text{Cu,Au})_6\text{Sn}_5$  with 13 at-% Au. In both these phases, gold atoms had replaced some of the copper atoms in the  $\text{Cu}_6\text{Sn}_5$  structure.

### ***Formation of a Layer with Lead-Rich Phase***

Solid tin-lead solder consists of two phases, one tin-rich and one lead-rich. Since the intermetallic layer does not contain any lead, the growth of the intermetallic layer in solid solder joints will cause a depletion of tin in the solder closest to the intermetallic layer. As a consequence, a layer with the lead-rich phase will form between the intermetallic layer and the bulk solder. This layer with lead-rich phase does not prevent further growth of the intermetallic layer [5, 6, 29, 36] and, probably, it does not significantly affect the mechanical properties of the solder joint [3].

## **2.1.2 Nickel Surfaces**

### ***Growth of Intermetallic Compounds during Soldering***

The dissolution rate of pure nickel in molten solder is more than one decade lower than that of copper [6, 37, 38, 39]. Therefore, nickel is often used as a diffusion barrier between Cu and Sn in order to limit the dissolution of under bump metallisation on flip chips.

Although reported thicknesses of the IMC layer on nickel are normally thinner than that on copper, the difference is in many cases not large [40]. Since the solubility of nickel in molten solder is very low, most of the dissolved nickel will be found in the IMC layer. A two-phase layer is normally not formed although it can sometimes be observed but it is then usually very thin [25]. The fact that almost all dissolved nickel is precipitated in the IMC layer may explain why the thickness of this layer on nickel is not much thinner than that formed on copper despite the higher dissolution rate of copper.

Moreover, the formation of IMC layers on nickel finishes is more complex than on copper surfaces. This is partly due to the fact that the properties of nickel finishes may vary considerably and partly due to that the composition and structure of the IMC layer may vary more. Nickel finishes on component leads and solder lands on area array components usually are electrolytic finishes but

may also be electroless (autocatalytic) finishes on area array components. Nickel finishes on printed boards are almost exclusively electroless coatings. Electroless nickel finishes contain varying amounts of phosphorus whereas electrolytic nickel finishes do not contain any phosphorus. To preserve the solderability of nickel finishes, they are almost always coated with a thin corrosion resistant metal coating. The most common coatings used to protect nickel coatings on component leads and terminations are tin, tin-lead solder, palladium and gold. On area array components, electrolytic nickel is usually coated with 0.5 to 1.5  $\mu\text{m}$  electrolytic gold whereas electroless nickel on both area array components and printed boards is coated with 0.02 to 0.2  $\mu\text{m}$  immersion gold. However, since all coatings plated on nickel are either melted during soldering or dissolved very rapidly in the molten solder, final wetting is almost always to the nickel surface.

Frear et al. [10] have reported a growth rate of the IMC layer on electrolytic nickel during soldering which is of about the same order of magnitude as that reported on copper by Tu et al. [41]. However, the reactivity of the nickel may vary considerably. Harman has reported that the growth rate of the IMC layer in molten solder is ten times higher on bright nickel than on sulphamate nickel, two different types of electrolytic nickel [42]. Kang et al. found that the growth rate on electroless nickel was two to three times higher than on electrolytic nickel for SnAg and SnAgCu solders at 250°C [43]. Thus, the properties of the nickel finish have a large influence on the growth rate of the IMC layer.

### ***Growth of Intermetallic Compounds during Aging***

Anhöck et al. have reported that the IMC growth is faster on electrolytic nickel than on electroless nickel in solid Sn37Pb solder during high temperature aging [44]. The electroless nickel had about 9% P. At 150°C, the growth rate was proportional to the square root of time on electroless nickel but not on electrolytic nickel. On the latter coating, the growth rate was instead linearly proportional to time. Whereas the IMC layer had increased in thickness with about 1.5  $\mu\text{m}$  after 900 hours on the electroless nickel, it had increased with about 12  $\mu\text{m}$  on the electrolytic nickel. Furthermore, on the electroless nickel the IMC layer consisted of  $\text{Ni}_3\text{Sn}_4$  whereas it consisted of two phases on the electrolytic nickel;  $\text{Ni}_3\text{Sn}_2$  closest to the nickel and  $\text{Ni}_3\text{Sn}_4$  on top of that phase. At 85 and 125°C, the growth rate of the IMC layer was proportional to the square root of time also on the electrolytic nickel and only  $\text{Ni}_3\text{Sn}_4$  was formed. The growth rate at 85°C on the electrolytic nickel was of about the same order of magnitude as the growth rate at 150°C on the electroless nickel, i.e. a much faster growth of the IMC layer on the electrolytic nickel also at lower temperatures. Similar results have been reported by Nieland [45]. Islam et al. have reported that the growth rate of the IMC layer on electrolytic nickel compared to electroless nickel (with about 6.6% P) is higher also for Sn3.5Ag solder [46].

The contradictory results reported by Kang et al. and Anhöck et al. may be due to the fact that Kang et al. studied the growth rate in molten solder whereas Anhöck et al. studied the growth rate in solid solder, but it may also be due to varying properties of the electroless nickel layers. The content of phosphorus in the

electroless nickel affects the microstructure of the finish [45, 47, 48]. Finishes with less than 7-8% P have a micro- or nanocrystalline structure whereas finishes with more than 7-8% P have an amorphous structure. The microstructure may have an impact on the growth rate of the IMC layer. The phosphorus content in electroless finishes has previously usually been in the range 6-11% [49, 50]. In recent years, there has been an increased use of electroless nickel with up to 13% P [51]. That is, the microstructure may be either nanocrystalline or amorphous, which may explain why some have observed faster IMC growth on electroless nickel compared to electrolytic nickel whereas others have observed the opposite. However, according to some investigations, the growth rate of the IMC layer is lower on high-phosphorus nickel than on low-phosphorus nickel [45, 51] whereas other investigations indicate the opposite [48, 52, 53, 54]. Thus, the effect of the phosphorus content on the growth rate of the IMC layer may vary for reasons not known.

The temperature may also be important for the relative growth rates of the IMC layers. He et al. compared the growth rates of the IMC layers for Sn37Pb and Sn3.5Ag solder joints to electroless nickel and sputtered nickel [55]. For both solders, a thinner and more fine-grained IMC layer was formed on the sputtered nickel during soldering. Whereas the growth rate of the IMC layer was also lower on the sputtered nickel compared to the electroless nickel for both solders during aging at 150 and 170°C, it was higher at 130°C.

#### ***Tin-Nickel Intermetallic Compounds Formed during Soldering and Aging***

Most investigations of the composition of the IMC layer formed on nickel in molten solder have shown only one intermetallic phase and it has been identified as  $\text{Ni}_3\text{Sn}_4$  [25, 26]. However, Dunford et al. have reported that they have found  $\text{Ni}_3\text{Sn}$  on electroless nickel [56]. Lin and Jang claim that  $\text{Ni}_3\text{Sn}$  together with  $\text{Ni}_3\text{Sn}_2$  may be formed on very rough nickel surfaces or at a soldering temperature of 240°C for more than 10 minutes [57]. Thus, maybe the microstructure of the electroless nickel is not only important for the growth rate of the IMC layer but also for its composition. A faster growth, i.e. a faster dissolution of the nickel, would promote the formation of the nickel-rich intermetallic compounds.

In solder joints on electrolytic nickel aged at 150°C, Anhöck et al. found  $\text{Ni}_3\text{Sn}_2$  in addition to  $\text{Ni}_3\text{Sn}_4$  as already mentioned [44]. The growth rate of the IMC layer was in that case very fast. Also Tu et al. found  $\text{Ni}_3\text{Sn}_2$  at the  $\text{Ni}_3\text{Sn}_4/\text{Ni}$  interface when aging solder joints to electrolytic nickel at 120°C for 36 days [19]. They reported that also  $\text{NiSn}$  was formed at the  $\text{Ni}_3\text{Sn}_4/\text{bulk}$  solder interface. The solder joints were formed between CSP components having copper pads coated with 1  $\mu\text{m}$  gold (no nickel) and a PCB having pads coated with nickel (probably electrolytic) and less than 1  $\mu\text{m}$  flash gold.

### ***Coupling Effect when Solder Joints are Formed between Nickel and Copper Surfaces***

When a solder joint is formed between a nickel surface and a copper surface,  $(\text{Cu,Ni})_6\text{Sn}_5$  may be formed on top of the  $\text{Ni}_3\text{Sn}_4$  layer or as the only layer on the nickel surface [58, 59, 60, 61, 62]. The ternary phase is the same phase that is formed on copper but with some of the copper atoms substituted with nickel atoms. The copper in this phase originates from the copper surface. This “coupling effect” is more pronounced if the distance between the soldered surfaces is short as for flip chips. Under certain conditions, which are poorly understood, it may promote formation of a thick IMC layer on the nickel surface during soldering with a thickness of up to  $8\ \mu\text{m}$  [62]. During high temperature aging, the coupling effect is reported to cause reduced consumption of nickel at the same time as the consumption of copper on the opposite pad is increased [60]. Furthermore, the formation of  $(\text{Cu,Ni})_6\text{Sn}_5$  on the nickel surface may cause the nickel surface to become porous during high temperature aging, resulting in decreased reliability [59].

### ***Effect of Phosphorus in Electroless Nickel on Intermetallic Compounds Formed***

The phosphorus in the electroless nickel is generally considered to not dissolve in the solder although Vandeveld et al. have reported that some phosphorus may be incorporated into the IMC layer when soldering using SnAgCu solder [18]. They found 3 at-% of P in the NiSn IMC layer. Due to the selective dissolution of the nickel, the uppermost nickel becomes enriched with phosphorus and it is usually claimed to consist of  $\text{Ni}_3\text{P}$ . When soldering using lead-free solders, the  $\text{Ni}_3\text{P}$  layer has been reported to have a fine columnar structure with some tin that have diffused through the column boundaries deep into the layer [25, 63]. This is probably also the case when soldering using SnPb solder. Recent investigations using TEM (transmission electron microscopy) have revealed that the IMC structure at the interface may be very complicated and may consist of several layers, especially after high temperature aging [25, 48, 52, 64, 65, 66]. Most notably, a layer with a thickness less than  $0.3\ \mu\text{m}$  containing Ni, Sn and P (composition may vary) has been found at the  $\text{Ni}_3\text{P}/\text{Ni}_3\text{Sn}_4$  interface. Other phases have also been found, for example  $\text{Ni}_{48}\text{Sn}_{52}$  between the  $\text{Ni}_3\text{Sn}_4$  and NiSnP layers and  $\text{Ni}_{12}\text{P}_5$  in the phosphorus-enriched nickel layer.

### ***Effect of Dissolved Gold from Nickel/Gold Platings***

As mentioned before, nickel surfaces to be soldered are often coated with gold to preserve the solderability. The gold dissolves rapidly in molten solder and all gold will therefore be found in the solder after the soldering process. If the gold concentration exceeds 0.3-0.4%, the solubility of gold in solid solder [1, 2], it is precipitated in needle-like crystals with the composition  $\text{AuSn}_4$ . It has been known for a long time that if the gold content exceeds 3 to 5%, the solder joint will become brittle due to the  $\text{AuSn}_4$  crystals, so called gold embrittlement [3, 4, 5, 6, 7, 8]. It may occur for leaded components with electrolytic gold finish when

the solder volume is rather small. It is not a problem for electroless nickel/immersion gold (ENIG) plated printed boards since the gold finish is too thin on these boards, normally less than  $0.125\ \mu\text{m}$  [67]. Nor is it a problem for BGAs with electrolytic finish on the solder lands since the gold content will then be well below 3% due to the large solder volume in the solder balls.

However, a new type of gold embrittlement has been found at much lower gold content when soldering to nickel surfaces [2, 7, 8, 68, 69, 70, 71]. When a gold-containing solder joint on a nickel surface is aged, the gold is redistributed in the solder joint. The gold migrates to the nickel surface and a new AuNiSn intermetallic layer is formed on top of the  $\text{Ni}_3\text{Sn}_4$  layer. The composition of this new layer is  $\text{Au}_x\text{Ni}_{1-x}\text{Sn}_4$  with  $x = 0.4-0.5$  [1, 7]. It has the same structure as  $\text{AuSn}_4$  but with 55-60% of the gold atoms substituted with nickel atoms. It is believed that the reason why  $\text{Au}_x\text{Ni}_{1-x}\text{Sn}_4$  is formed is that it is thermodynamically more stable than  $\text{AuSn}_4$  [71, 72]. Since gold has much higher solubility and mobility in solid solder than nickel, it is gold that migrates to locations where nickel can be found and not the opposite [1]. Therefore, the new phase is formed on top of the  $\text{Ni}_3\text{Sn}_4$  layer where nickel atoms can be found. Ratchev et al. found also some crystals of  $(\text{Au},\text{Ni})_3\text{Sn}_4$  at the  $(\text{Au},\text{Ni})\text{Sn}_4/\text{Ni}_3\text{Sn}_4$  interface [14]. The lower the gold content in the solder joint, the slower the growth of the AuNiSn intermetallic layer. It has been claimed that a gold concentrations of more than 0.2-0.3%, which is the solubility limit of gold in solid tin-lead solder, is required for it to form [7, 71]. However, Zribi et al. have reported that it may form even at gold concentrations of 0.031 to 0.1 at-% (0.04-0.14 wt-%) [73, 74].

Precipitation of  $(\text{Au},\text{Ni})\text{Sn}_4$  on top of  $\text{Ni}_3\text{Sn}_4$  can be prevented by increasing the amount of nickel dissolved in the solder.  $(\text{Au},\text{Ni})\text{Sn}_4$  will then form in the bulk solder when the solder solidifies. Minor and Morris observed that longer reflow times increased the amount of nickel dissolved into the solder leading to the formation of the ternary phase in the bulk solder [71]. Repeated soldering processes have the same effect [1, 70, 71]. When Zribi et al. observed a dual IMC layer to form from solder containing only 0.14 wt-% Au, the soldering peak temperature had only been  $191^\circ\text{C}$ , i.e. very little nickel was dissolved in the solder [73]. When the peak temperature was increased to  $235^\circ\text{C}$ , the dual layer no longer formed during high temperature aging. Crystals of  $(\text{Au},\text{Ni})\text{Sn}_4$  were observed in the bulk solder after the soldering process which proved that an increased amount of dissolved nickel reduces the risk for a dual IMC layer to later be formed. According to Zeng and Tu [69], the saturation solubility of nickel in eutectic SnPb is estimated to be 0.052 at-% at  $220^\circ\text{C}$  but due to the low dissolution rate of nickel it is unlikely that it is reached during a soldering process. Therefore, dissolved nickel can only be expected to stabilise  $\text{AuSn}_4$  in the bulk solder when the gold concentration is low. By adding nickel to the solder,  $\text{AuSn}_4$  can be stabilised in the bulk solder at higher gold concentrations [69, 75].

The formation of a  $(\text{Au},\text{Ni})\text{Sn}_4$  layer during aging can also be prevented by adding 0.5% Cu to the SnPb solder [25, 76]. When Cu is added to the solder, the intermetallic layer formed on the nickel surface during soldering will have the composition  $(\text{Cu},\text{Au},\text{Ni})_6\text{Sn}_5$ . No second IMC layer is formed on top of this layer during high temperature aging. Furthermore, less nickel is consumed during high

temperature aging when 0.5% Cu is added to the SnPb solder [76]. Formation of a (Au,Ni)Sn<sub>4</sub> layer may also be prevented if the opposite solder pad has a copper finish. Evans et al. have reported that a Sn-Ni-Cu-Au intermetallic layer formed on the nickel pads when BGAs with electrolytic Ni/Au pads were soldered to printed boards with copper pads [77]. The (Au,Ni)Sn<sub>4</sub> phase was not formed during high temperature aging. Lin et al. studied the IMCs formed when flip chips were soldered to substrates [61]. The pads on the flip chip had 0.8 μm copper plated on nickel and the substrate pads had Ni/Au finish with two different thicknesses of the gold, 0.1 and 0.65 μm, respectively. During soldering, Cu<sub>6</sub>Sn<sub>5</sub> formed on the pads on the flip chip and (Cu,Ni)<sub>6</sub>Sn<sub>5</sub> on the substrate pads. When aged at 150°C, a layer of (Ni,Cu)<sub>3</sub>Sn<sub>4</sub> was formed next to the nickel surface on the pads on both the substrate and the flip chip (the copper layer was completely consumed on the latter pads). The (Cu,Ni)<sub>6</sub>Sn<sub>5</sub> layer on the flip chip pads were converted to (Cu,Ni,Au)<sub>6</sub>Sn<sub>5</sub> whereas the (Cu,Ni)<sub>6</sub>Sn<sub>5</sub> layer on the substrate gradually converted to (Ni,Cu)<sub>3</sub>Sn<sub>4</sub>. (Au,Ni)Sn<sub>4</sub> particles were found near the surfaces but no continuous layer was formed. The major differences between the samples having different gold thicknesses on the substrate pads were that the nickel consumption rate was lower and no (Au,Ni)Sn<sub>4</sub> was formed in the solder joints for the samples with thin gold coating. Thus, gold dissolved in the solder joint may promote a faster growth of the IMC layer.

### 2.1.3 Palladium Surfaces

Palladium is used as a corrosion resistant finish on both components and printed boards, sometimes with a very thin gold or gold alloy layer on top in order to improve the corrosion resistance. It is applied to both copper and nickel surfaces. Palladium is most commonly used as surface finish on components. It is then applied as a very thin electrolytic coating, usually with a thickness of less than 0.1 μm [3, 78, 79]. Newly developed palladium coatings may be as thin as 0.005-0.015 μm [80]. Only recently has palladium been used as surface finish on printed boards but only to a limited extent [3, 81, 82]. Due to the difficulty to apply electrolytic coatings on printed boards, palladium coatings on printed boards are usually electroless coatings containing 2-7% phosphorus but phosphorus-free coatings also exist [3, 81]. The thickness may vary between 0.15-1.5 μm but is usually within the range 0.25-0.5 μm [3, 36, 81].

There are quite contradictory data in the literature about the solubility rate of palladium in molten solder. According to Wassink [6], Abbott et al. [78], and Hwang [39], the dissolution rate is rather low. At 215°C and 250°C, the dissolution rate is 0.02 μm/s and 0.03-0.08 μm/s, respectively. That is lower than for copper but higher than for nickel. On the other hand, Tu and Zeng have reported that the growth rate of PdSn<sub>3</sub> on thick palladium in molten eutectic tin-lead at 250°C is higher than 1 μm/s and constant for at least five minutes [37]. After five minutes, the IMC layer had a thickness of 360 μm with a lamellar structure of PdSn<sub>3</sub> lamellae grown perpendicular to the palladium surface. Solder, probably consisting of lead-rich phase, was found between the PdSn<sub>3</sub> lamellae. At temperatures below 245°C, PdSn<sub>4</sub> is formed. This phase had also a lamellar structure and a rather high growth rate. After 50 s at 220°C, a 6 μm thick

intermetallic layer was formed. Klein et al. reported that a 15  $\mu\text{m}$  thick layer of  $\text{PdSn}_4$  formed after reflow at 220°C with Sn40Pb [83]. Lead was enclosed in the intermetallic layer. When aged at 150°C for 25 h, a closed layer of  $\text{PdSn}_2$  with a thickness of less than 1  $\mu\text{m}$  was formed on the Pd surface. On top of the  $\text{PdSn}_2$  layer, a mixture of  $\text{PdSn}_3$  and  $\text{PdSn}_4$  crystals were found, some of them 50  $\mu\text{m}$  long.

Thin palladium coatings with a thickness less than 0.1  $\mu\text{m}$  is dissolved quickly in molten solder [37]. For thicker palladium coatings, the palladium may not be completely dissolved in the solder during soldering [81, 82]. A palladium layer with a thickness of 0.2-0.5  $\mu\text{m}$  is not dissolved during a soldering process at 205°C but it is at 225°C [82]. Coatings with a thickness of 0.76  $\mu\text{m}$  or more may not be completely dissolved in a soldering process with a peak temperature of 220°C [81]. If the palladium coating is not completely dissolved, the intermetallic layer may become quite thick (7-8  $\mu\text{m}$ ) and consists of  $\text{PdSn}_4$  [81].

## 2.2 Intermetallic Compounds Formed with Lead-Free Solders Based on Tin, Silver and Copper

### 2.2.1 Copper Surfaces

#### *Growth of Intermetallic Compounds during Soldering*

The IMC layer formed on copper surfaces using lead-free solders based on tin, silver, and copper is similar in structure and composition to that formed using eutectic tin-lead solders. The main intermetallic phase formed during soldering is  $\text{Cu}_6\text{Sn}_5$  but a very thin layer of  $\text{Cu}_3\text{Sn}$  has been observed at the Cu- $\text{Cu}_6\text{Sn}_5$  interface [84]. The reported thicknesses of the IMC layer formed on copper may seem contradictory. Usually, the IMC layer is reported to be slightly thicker than that formed with eutectic SnPb [5, 28, 40, 85] but it may even be thinner when SnAg solder is used [5]. However, in some cases it has been found to be 2-3 times thicker compared to the IMC layer formed with eutectic SnPb [86, 87, 88]. In an investigation performed by Korhonen et al., it was shown that the thickness of the IMC layer depends on the solder volume [89]. First, they dipped fluxed copper foils in solder baths of pure Sn, Sn3.5Ag, Sn3.8Ag0.7Cu, and Sn37Pb for various immersion times. The temperatures of the solder baths were 30°C above the melting temperature of the solders. In these experiments, there is practically infinite amount of solder available. Then they reflowed 16 mil (400  $\mu\text{m}$ ) diameter solder balls on fluxed Cu substrate. The solder balls had the same composition as the solder baths except that pure tin was excluded. The reflow temperature was 250°C for the lead-free solders and 230°C for the SnPb solder and the time at the reflow temperature was 1 minute. After reflow, the height of the solder was about 150  $\mu\text{m}$ . Thus, there was a limited amount of solder available in these experiments.

The dissolution rates of copper measured after immersion in the solder baths were more than 10 times higher in pure tin and SnAg and about 5 times higher in

SnAgCu compared to SnPb. On the other hand, the IMC layers formed after 1 minute were about twice as thick for the SnPb solder compared to all lead-free solders. That is, whereas the fraction of the dissolved copper that was precipitated in the IMC layer was high for the SnPb solder, it was very low for the lead-free solders. Furthermore, the thicknesses of the IMC layers obtained by pure tin and SnAg did not increase significantly after 30 seconds whereas they continued to increase with time for SnAgCu and SnPb.

The intermetallic layers found after the reflow experiments were significantly thicker than in the immersions tests for the lead-free solders but of about the same thickness for the SnPb solder. Very little of the copper substrate was consumed with all solders. Thus, whereas the available amount of solder did not seem to significantly affect the amount of copper consumed and the thickness of the IMC layer for SnPb solder, it had a very large impact for lead-free solders. This finding may explain the seemingly contradictory results reported for IMC thicknesses obtained with lead-free solders. Furthermore, Cu added to SnAg decreases the dissolution rate of copper but increases the growth rate of the IMC layer.

### ***Growth of Intermetallic Compounds during Aging and Formation of Kirkendall Voids***

The layers of both  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  continue to grow during high temperature aging. Comparatively more  $\text{Cu}_3\text{Sn}$  is formed when SnAgCu and SnCu solders are used compared to SnAg solder, although the total IMC thickness is not affected much [90].

According to Tu and Thompson, the dominant diffusing element through both the  $\text{Cu}_3\text{Sn}$  and the  $\text{Cu}_6\text{Sn}_5$  phases is copper [91]. This leads to a depletion of copper at the Cu-Cu<sub>3</sub>Sn interface and in the Cu<sub>3</sub>Sn layer resulting in the formation of Kirkendall voids. Kirkendall voids have been observed both at the Cu-Cu<sub>3</sub>Sn interface and within the Cu<sub>3</sub>Sn layer [25, 34, 58, 84, 92]. According to Mei et al., the size of the voids is about 0.1 to 0.2  $\mu\text{m}$ . Due to the small size, they are smeared during mechanical polishing and therefore not possible to observe after traditional polishing [34]. If it shall be possible to observe the Kirkendall voids, the surface needs to be prepared using methods such as Focused Ion Beam (FIB) or sputtering with  $\text{Ar}^+$  ions. Therefore, Kirkendall voids may be more common than reported.

Impurities in the copper seem to be a major factor for the formation of Kirkendall voids. Laurila et al. did not observe voids for high purity copper soldered with pure Sn or pure SnAgCu but they did for electrolytic and electroless deposited copper soldered with both Sn and SnAgCu [25]. They concluded that the voids might not be formed due to a true Kirkendall effect but to redistribution of impurities or to volume changes upon formation of the IMCs. The amount of Kirkendall voids formed seems to vary for various plating lots supporting the conclusion that their formation is affected by impurities [58]. Furthermore, according to Laurila et al., Kirkendall voiding increases with increasing temperature and becomes extensive above 320°C [25]. Thus, the higher peak

temperature used for lead-free soldering may contribute to an increased nucleation of Kirkendall voids compared to soldering with tin-lead.

### ***Effect of Surface Finishes on the Intermetallic Compounds Formed***

The composition and morphology of the IMC layer formed on bare copper and on copper coated with HASL, OSP, immersion tin, and immersion silver are basically the same with only small variations. Zheng et al., found that one of two tested immersion tin coatings gave a more smooth and uniform IMC layer than the other when soldered with Sn<sub>3.8</sub>Ag<sub>0.7</sub>Cu [93]. Furthermore, Cu<sub>3</sub>Sn was less readily formed during aging and only when aged at very high temperatures (168°C) [94]. Possibly, the differences were due to the fact that a thicker intermetallic layer was formed between the tin-plating and the underlying copper in storage prior to soldering of the immersion tin coating that gave a smooth and uniform IMC layer.

When soldering to copper surfaces coated with immersion silver, large Ag<sub>3</sub>Sn needles or platelets may form just above the Cu<sub>6</sub>Sn<sub>5</sub> layer [93, 94]. According to Zheng et al. [94], the Ag<sub>3</sub>Sn crystals disappear from the interface during high temperature aging. Furthermore, the growth of the intermetallic layer on silver coated surfaces is more irregular than on OSP or immersion tin coated surfaces and it may be quite thick at some locations [94].

### ***Effect of Nickel and some other Elements on the Growth Rate of the IMC Layer***

As for SnPb solder, addition of nickel to SnAgCu solder reduces the growth of Cu<sub>3</sub>Sn during high temperature aging [95, 96]. According to Amagai et al. [95], it also reduces the formation of Kirkendall voids, whereas addition of indium reduces the formation of Kirkendall voids but not the growth of Cu<sub>3</sub>Sn. Addition of cobalt and iron to SnAgCu solder has also been reported to both decrease the growth of Cu<sub>3</sub>Sn and the formation of Kirkendall voids [92]. Li et al. report that addition of antimony to Sn<sub>3.5</sub>Ag<sub>0.7</sub>Cu decreases the growth rate of the IMC layer and the grain size during reflow but the reductions are rather small [97]. They did not report how the growth rate in solid solder was affected nor the impact on the formation of Kirkendall voids.

Nishikawa et al. have investigated how addition of up to 0.2% of Ni to Sn<sub>0.7</sub>Cu solder affect the growth of the IMC layer during reflow soldering [98]. An addition of as little as 0.05% Ni resulted in about three times more copper dissolved during 60 seconds at 250°C. At the same time, the morphology of the IMC layer changed from scallop to flat structure, but the thickness of the IMC layer was not much affected during soldering. In fact, it decreased slightly when only 0.05% Ni was added. When aged at 150°C, the growth of the IMC layer was slower for all Ni concentrations compared to no added Ni with the slowest growth for 0.05% Ni. The composition of the IMC layer formed was not specified. In contrast, Tsai et al. have reported that addition of Ni to an Sn<sub>3.5</sub>Ag solder substantially increased the growth rate of the IMC layer at 240°C [99]. The growth rate was about 5 times higher when 0.1% Ni was added and about 10

times higher when 1.0 % Ni was added. The IMC formed was  $(\text{Cu,Ni})_6\text{Sn}_5$  with up to about 25% of the Cu substituted with Ni. Although Ni is rarely added to solder, except to Sn0.7Cu used for wave soldering, Ni is dissolved in the solder when soldering is done to nickel surfaces. Thus, when soldering is done to copper and the opposite soldered surface consists of nickel, the growth rate of the IMC layer formed on the copper surface may be increased as observed by Dunford et al. [86]. When they soldered BGAs with ENIG pads to printed boards with OSP pads, the IMC layer formed on the OSP pads was up to 9  $\mu\text{m}$  thick. An influence of dissolved nickel on solder joint reliability was observed also by Zhang et al. [100]. They found that nickel dissolved from substrate pads caused faster degradation of solder joints to flip chip pads with Ni(V)/Cu finish.

Korhonen et al. have reported that alloying copper with 10-45% nickel decreases the dissolution rate in baths of melted SnAg and SnAgCu significantly [89, 101]. The higher the nickel content, the lower the dissolution rate of the alloy. At levels of 10 and 45% Ni, the dissolution rate was reduced with about 50 and 90%, respectively, compared to pure copper. However, the intermetallic layer formed during reflow soldering increased in thickness. The thickest IMC layer was achieved for the alloy with 10% Ni. For this alloy, the IMC layer had a thickness of 15  $\mu\text{m}$  after reflow for 1 min at 250°C. The IMC layer formed on all CuNi alloys had a composition of  $(\text{Cu,Ni})_6\text{Sn}_5$ .

Also the addition of cobalt to Sn3.5Ag increases the IMC growth on copper [102]. An addition of as little as 0.1% Co increases the growth rate threefold.

Gold dissolved in the solder may also affect the composition and structure of the IMC layer formed on copper. Park et al. have reported that an IMC layer with a composite-like structure consisting of small  $(\text{Au,Cu})_6\text{Sn}_5$  grains and finely dispersed tin islands is formed if the Au concentration in the solder exceeds 0.25% [103].

## **2.2.2 Nickel Surfaces**

### ***Growth of Intermetallic Compounds when Soldering using SnAg Solder***

The intermetallic phase formed on nickel surfaces when soldering using tin-silver solders is usually reported to be the same as when soldering using tin-lead solders, i.e.  $\text{Ni}_3\text{Sn}_4$  [25, 43, 52, 104]. Sharif et al. have reported that also  $\text{Ni}_3\text{Sn}$  and/or  $\text{Ni}_3\text{Sn}_2$  are formed when soldering at 250°C [105]. In contrast to soldering with tin-lead, quite large amounts of  $\text{Ni}_3\text{Sn}_4$  are frequently reported to form when soldering with SnAg solders and spalling of the IMC layer may occur [45, 48, 52, 53, 106, 107]. The IMC layer then often has a needle-type structure. Kang et al. reported that rather large amounts of  $\text{Ni}_3\text{Sn}_4$  are formed at 250°C on electroless nickel, of which the majority is separated or spalled away from the interface, but no spalling occurred on electrolytic nickel [43]. Also Sohn et al. [48, 52] and Paik et al. [53] have found that  $\text{Ni}_3\text{Sn}_4$  is spalled off during soldering on electroless nickel at 250-260°C. Spalling increased as reflow time increased and it also increased the consumption of nickel and growth of the  $\text{Ni}_3\text{P}$  layer. They claimed

that spalling was caused by the growth of a nanocrystalline Ni-Sn-P layer at the  $\text{Ni}_3\text{Sn}_4/\text{Ni}_3\text{P}$  interface. A thin intermediate layer of Sn or Cu deposited on the electroless nickel suppressed spalling of the IMC layer. Furthermore, the propensity for spalling when soldering with Sn3.5Ag was affected by the phosphorus content in the electroless nickel; the higher the phosphorus content, the larger the risk for spalling. This is in accordance with the observation by Alam et al. that the dissolution rate of electroless nickel in molten Sn3.5Ag increases with increasing phosphorus content in the nickel [54]. Nieland has reported that the  $\text{Ni}_3\text{Sn}_4$  crystals are formed in a matrix of metastable  $\text{NiSn}_3$  when soldering at 260°C [45].

### ***Impact of Copper in the Solder on the Intermetallic Compounds Formed***

If the lead-free solder contains copper but less than about 0.4%,  $\text{Ni}_3\text{Sn}_4$  will still form but with some Ni substituted with Cu [25, 52, 76, 94]. If the copper concentration is higher than about 0.6%,  $(\text{Cu,Ni})_6\text{Sn}_5$  will instead form [25, 26, 53, 63, 76, 94, 108]. At intermediate Cu concentrations, a dual layer of  $(\text{Ni,Cu})_3\text{Sn}_4$  and  $(\text{Cu,Ni})_6\text{Sn}_5$  may form with  $(\text{Ni,Cu})_3\text{Sn}_4$  closest to the nickel surface [52, 53, 76, 94, 108, 109].  $\text{Ni}_3\text{Sn}_4$  may also precipitate inside  $(\text{Cu,Ni})_6\text{Sn}_5$  [16]. This transition from  $(\text{Ni,Cu})_3\text{Sn}_4$  to  $(\text{Cu,Ni})_6\text{Sn}_5$  as the copper concentration increases, occurs both for SnAgCu and SnCu solders [53, 76, 110]. As for soldering using SnPb solder,  $(\text{Cu,Ni})_6\text{Sn}_5$  may also form on nickel surfaces with SnAg solder if an opposite solder land consists of copper (coupling effect), either as a single layer [111] or as  $(\text{Cu,Ni})_6\text{Sn}_5$  needles protruding from the  $\text{Ni}_3\text{Sn}_4$  layer [86].

A dual layer was also observed when soldering to electrolytic nickel coated with 1  $\mu\text{m}$  electrolytic gold using Sn4Ag0.5Cu solder but in this case, the upper layer consisted of  $(\text{Cu,Au,Ni})_6\text{Sn}_5$  [104]. This layer was detached from the underlying IMC layer with solder filling the space between the layers. A dual layer of IMCs may also form if solder joints with more than 0.6% Cu is aged at 150-180°C [26, 53, 104, 110]. Again,  $(\text{Ni,Cu})_3\text{Sn}_4$  is formed at the  $(\text{Cu,Ni})_6\text{Sn}_5/\text{Ni}$  interface.

However, a dual layer is not always formed after prolonged soldering or high temperature aging. Zeng et al. have reported that  $(\text{Ni,Cu})_3\text{Sn}_4$  did not form when soldering with Sn3.8Ag0.7Cu, neither after five reflows nor after aging at 170°C [63]. Furthermore, the growth rate of the  $(\text{Cu,Ni})_6\text{Sn}_5$  layer was slow both during soldering and aging. This has also been reported by Zheng et al. [94]. Mattila et al. observed that the growth of  $(\text{Cu,Ni})_6\text{Sn}_5$  on electroless nickel was reduced when the opposite solder land consisted of nickel compared to when it consisted of copper [112]. Zeng et al., Zheng et al., and Mattila et al. all concluded that the limited access of copper in the solder was the reason for the reduced growth rate. Also Sohn et al. reported slower growth of  $(\text{Cu,Ni})_6\text{Sn}_5$  (or  $(\text{Cu,Ni})_3\text{Sn}_4$  at low copper concentration) with Sn3.5Ag0.5Cu compared to  $\text{Ni}_3\text{Sn}_4$  with Sn3.5Ag [52]. However, they concluded that it was due to a more layer-type precipitation for  $(\text{Cu,Ni})_6\text{Sn}_5$  in contrast to a needle-like structure for  $\text{Ni}_3\text{Sn}_4$ . On the other hand, Alam et al. have reported higher growth rate of  $(\text{Cu,Ni})_6\text{Sn}_5$  with Sn3.5Ag0.5Cu compared to  $\text{Ni}_3\text{Sn}_4$  with Sn3.5Ag in both molten and solid solder

[113, 114]. Li et al. reported twice as high growth rate of the IMC layer on nickel during soldering with SnAgCu compared to SnAg [115] and Sharif et al. reported 3-4 times higher growth rate in solid solder at 190°C [105] but in both these latter cases it were on electrolytic nickel whereas the others used electroless nickel. Cotts et al. have reported that with a relative large supply of Sn3.5Ag1.0Cu, the growth rate of  $(\text{Cu,Ni})_6\text{Sn}_5$  on nickel at 150°C was about twice as high compared to the growth rate of  $\text{Ni}_3\text{Sn}_4$  from pure tin [26]. The type of nickel used was not specified. For small solder joints, they observed that the thickness of  $(\text{Cu,Ni})_6\text{Sn}_5$  did not increase significantly when the solder had been depleted of copper. Thus, the supply of copper may be important for the growth rate of the IMC layer.

The addition of copper to Sn and SnAg solders not only affects the composition of the intermetallic layer. The consumption of nickel is reduced, both during soldering and high temperature aging, and there is less risk for spalling of the IMC layer [53, 105, 106, 116]. However, in an investigation done by Alajoki et al., CSP components with ENIG under bump metallisation were soldered to a board with OSP pads using a Sn4Ag0.5Cu solder [117]. Although not discussed in the paper, figures in the paper showed extensive spalling of the  $(\text{Cu,Ni})_6\text{Sn}_5$  layer and a rather thick Ni-Sn-P layer on the nickel surface that was in direct contact with the solder at many locations. The electroless nickel had an exceptional high phosphorus content of 16-17%, which may have been the cause of the spalling.

If  $(\text{Ni,Cu})_3\text{Sn}_4$  forms at the  $(\text{Cu,Ni})_6\text{Sn}_5/\text{Ni}$  interface during soldering, spalling may occur of the  $(\text{Cu,Ni})_6\text{Sn}_5$  layer [108]. As mentioned previously, a porous nickel plating has been reported to form when  $(\text{Cu,Ni})_6\text{Sn}_5$  is grown on nickel from SnPb solder [59]. In that case, the Cu originated from an opposite copper pad. If pores are formed in the nickel, it will be detrimental for the reliability of the solder joint even if the nickel consumption is reduced.

### ***Effect of Gold and Palladium Dissolved in the Solder***

If the solder contains small amounts of gold from an immersion gold layer, the uppermost region of  $(\text{Cu,Ni})_6\text{Sn}_5$  may be transformed to a layer with the composition  $(\text{Cu,Ni,Au})_6\text{Sn}_5$  when aged at temperatures above 125°C the [53]. When the nickel surface is plated with both palladium and gold, the IMC layer formed on the nickel surface when soldered with Sn3.9Ag0.6Cu may consist of  $(\text{Cu,Ni,Pd})_6\text{Sn}_5$  [118].

The risk for formation of dual IMC layers during high temperature aging of solder joints containing gold is reduced for lead-free solders [104, 115, 119]. When SnAg solders are used,  $(\text{Au,Ni})\text{Sn}_4$  are formed on top of the  $\text{Ni}_3\text{Sn}_4$  layer during aging but not as a homogenous layer. The  $\text{AuSn}_4$  crystals formed in the solder joints do contain some nickel after soldering. That is, the higher soldering temperature results in more dissolved nickel compared to tin-lead soldering, enough to stabilise the  $\text{AuSn}_4$  crystals in the bulk solder and reduce the migration of gold to the solder/ $\text{Ni}_3\text{Sn}_4$  interface. Thereby, the risk for that a continuous  $(\text{Au,Ni})\text{Sn}_4$  layer shall form is reduced. Liu et al. have suggested that  $\text{Ag}_3\text{Sn}$  particles somehow hinder the diffusion of gold back to the interface [119]. In any case, if the gold concentration in the solder is high enough, the dual layer will still

form [72, 120]. Therefore, peak temperature and time in molten phase during soldering, reactivity of the nickel finish and gold concentration in the solder joint will all be crucial for the risk that a dual layer is formed during aging.

When soldering is done using SnAgCu solder, contradictory results are reported regarding the IMC layer formed. Several investigations have shown that a single gold containing layer,  $(\text{Cu,Au,Ni})_6\text{Sn}_5$ , is formed during soldering if the copper concentration is 0.5-0.75% [25, 104, 115]. This is the same phase that is formed when soldering on copper finish with both tin-lead and lead-free solders and on nickel with copper-containing solders, but with some copper atoms substituted with gold atoms. At lower copper concentration (<0.5%) or if the solder joint is aged at high temperature,  $(\text{Ni,Cu})_3\text{Sn}_4$  is formed underneath the  $(\text{Cu,Au,Ni})_6\text{Sn}_5$  layer [104]. According to Shiau et al. [104] and Laurila et al., [72]  $(\text{Au,Ni})\text{Sn}_4$  is not formed on top of the  $(\text{Cu,Au,Ni})_6\text{Sn}_5$  layer during high temperature aging, not even at very high gold concentrations in the solder joint. However, Vandeveldt et al. found a dual layer of  $(\text{Ni,Cu})_3\text{Sn}_4/(\text{Au,Ni})\text{Sn}_4$  after a combined temperature cycling/vibration test of BGAs soldered with a SAC solder paste, probably Sn4Ag0.5Cu [18]. The composition of the solder balls on the BGAs was not specified. The  $(\text{Au,Ni})\text{Sn}_4$  layer was almost continuous. Similar results were obtained for flip chip assemblies except that  $(\text{Au,Ni})\text{Sn}_4$  did not form a continuous layer. The  $(\text{Cu,Au,Ni})_6\text{Sn}_5$  layer was missing both for the BGA and the flip chip assemblies. Zribi et al. reported that  $(\text{Cu,Ni})_6\text{Sn}_5$  formed on the nickel surface when they soldered flip chips on Ni/Au coated copper pads with Sn3.5Ag1.0Cu [73]. That is, the layer did not contain gold. The gold was instead found in  $(\text{Au,Ni,Cu})\text{Sn}_4$  crystals in the bulk solder. The copper content in this phase was low, less than 1 at-%, but it was proposed that lack of Ni to form  $(\text{Au,Ni})\text{Sn}_4$  was compensated by Cu. Also Ratchev et al. found a dual layer after temperature cycling of polymer stud grid array packages between -40°C to 125°C, but consisting of  $(\text{Ni,Cu})_3\text{Sn}_2$  and  $(\text{Au,Ni})\text{Sn}_4$  [14]. The  $(\text{Au,Ni})\text{Sn}_4$  layer was not continuous.

### 2.2.3 Intermetallic Compounds with Silver

Silver in solder joints is always found as  $\text{Ag}_3\text{Sn}$  crystals except for a very small amount dissolved in the solder. The intermetallic layers formed on copper and nickel surfaces do not contain any silver and a continuous layer of  $\text{Ag}_3\text{Sn}$  is never formed. The  $\text{Ag}_3\text{Sn}$  crystals are formed in the bulk solder and sometimes take the shape of large platelets that may be attached to the intermetallic layer formed at copper and nickel surfaces. According to Dunford et al., large  $\text{Ag}_3\text{Sn}$  platelets may form when Cu is present in the solder [56]. The large  $\text{Ag}_3\text{Sn}$  platelets contain up to 7% Cu and a more correct composition is therefore  $(\text{Ag,Cu})_3\text{Sn}$ . Park et al. have reported that also Au dissolved in the solder may promote the formation of large  $\text{Ag}_3\text{Sn}$  platelets [103]. According to Kim et al., the formation of large platelets of  $\text{Ag}_3\text{Sn}$  increases the risk for brittle fractures [121]. They recommend that the Ag content in solders should be less than 3.2% in order to prevent that large platelets are formed in the solder joints.

If soldering is done to immersion silver coated surfaces, the silver will dissolve in the solder and increase its content of silver. Immersion silver is available in two

very distinctive versions. One that gives a thin silver deposit and one that gives a thicker silver deposit. In IPC's standard for immersion silver, IPC-4553 [122], it is stated that *“Excessive thickness of immersion silver combined with lead free silver bearing solder, have the potential to create an embrittled solder joint. The committee (for developing the standard) is working to define the upper wt% silver content in a solder joint at which the long tem reliability remains acceptable.”*

### 3 Impact of Intermetallic Compounds on the Risk for Brittle Fractures

Brittle fractures in the intermetallic layer to soldered surfaces were hardly ever a problem before area array components were used in combination with nickel finishes. It had previously been reported, mainly from laboratory tests, that brittle failures could occur in solder joints to copper surfaces if they are aged at high temperatures. The brittle fractures occurred during pull testing when the intermetallic layer had reached a thickness of 5-7  $\mu\text{m}$  [9, 10]. At this thickness, a continuous layer of  $\text{Cu}_3\text{Sn}$  had formed at the  $\text{Cu}_6\text{Sn}_5/\text{Cu}$  interface and the brittle fractures occurred between the two IMC layers.

When frequent brittle fractures were observed for BGAs in the late nineties, these were first associated with a plating defect on electroless nickel/immersion gold finishes called “black pad”. The brittleness of the solder joints is then caused by a poorly developed intermetallic layer on solder lands affected by the black pad defect. Later, it has been realised that brittle fractures to ENIG finishes may occur even when a proper intermetallic layer is formed but also that brittle fractures may occur when soldering to other finishes. However, it is often difficult to determine whether a brittle fracture to an ENIG surface is caused by the black pad defect or by a brittle intermetallic layer. Therefore, the characteristics of brittle fractures due to black pad and the mechanisms causing black pad will first be described. The impact of various intermetallic compounds on the risk for brittle fractures will then be discussed.

#### 3.1 Brittle Failures due to “Black Pad”

The defect “black pad” on ENIG finish was first reported in 1990 for flip chips soldered to ENIG-coated substrate pads [123]. When the flip chips were soldered to the substrate pads, dewetting of the nickel surfaces was observed. Since the exposed nickel surfaces had a dark grey to black appearance, the defect was referred to as the “black pad” condition. It was determined that the dark colour was due to  $\text{Ni}_3\text{P}$  present on the nickel surface and it was concluded that this phase caused the dewetting. Therefore, it was initially believed that black pad was caused by the phosphorus in the electroless nickel and that a remedy would be to decrease the phosphorus content. However, most investigations that later have been performed indicate that a decrease of the phosphorus content rather increases the risk for black pad [68, 124, 125]. In fact, Cordes and Huemoeller obtained very poor shear strength for solder joints to surfaces with immersion gold on electrolytic nickel, i.e. phosphorus-free nickel, but excellent shear strength of solder joints to surfaces with electrolytic gold on electroless nickel [124]. These results indicate that the enrichment of phosphorus on the nickel surfaces is not the cause of the embrittlement. Instead, the enrichment is a consequence of the mechanism causing the embrittlement.

Very large efforts have been made to understand what causes black pad and how to prevent it. Although the frequency of black pad has been reduced due to

various actions performed, black pad defects still occur and there are differing opinions of what causes it and how it should be prevented.

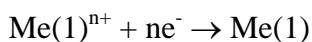
The known characteristics of black pad give important clues to the mechanisms causing the defect but also for determining whether a brittle fracture is due to black pad or not. The most typical characteristics are;

- poorly developed and/or locally missing intermetallic layer in solder joints,
- corrosion damages of the electroless nickel plating beneath the gold coating,
- a layer with enriched phosphorus beneath the gold coating,
- a gold coating that is slightly thicker than normal,
- a thin layer of nickel oxide on top of the gold coating,
- an increased risk for black pad when the phosphorus content is decreased in the electroless nickel,
- plating of immersion gold on electrolytic nickel may cause a similar effect (although the fractured surfaces are not black) but not plating of electrolytic or autocatalytic gold on electroless nickel,
- black pad defects are often located to certain solder pads on a specific board design and
- black pad defects mainly occur on boards with solder masks.

By understanding the chemistry of the plating reactions, all these characteristics and the mechanism causing black pad can be explained.

### 3.1.1 Chemistry of Metal Plating

The plating process of a metal can be divided into two reactions, one cathodic and one anodic reaction. The metal is deposited by the cathodic reaction in which metal ions dissolved in the plating bath are reduced to metal on the surface to be plated. The reaction can be written:

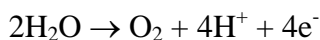


The anodic reaction may vary. It may be a reversed cathodic reaction:



where Me(2) may be the same metal as Me(1) or another metal.

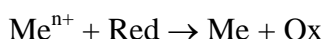
The anodic reaction may, for example, also be oxidation of water:



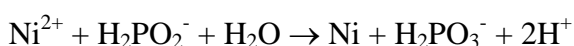
At **electrolytic plating**, the plating is achieved by applying a voltage between the surface to be plated (cathode) and a counter electrode (anode). Since the applied voltage is the driving force for the plating process, the plating rate is mainly

determined by its magnitude. The quality of the plating is to a part determined by the applied voltage but primarily by various compounds added to the plating bath. Some added compounds directly affect the plating reactions whereas others affect them more indirectly. Examples of the latter type are salts that are added to increase the electric conductivity and buffer systems that are added to stabilise the pH. Additives that directly affect the plating reactions are compounds that form strong complexes with the metal ions and/or are co-deposited in the plating. Compounds that form strong complexes with metal ions are often negatively charged inorganic or organic ions, for example halides, cyanide, and organic acids, but may also be non-charged organic compounds, for examples amines. Other metal ions may also be added to be co-deposited in the plating. The additives affect the crystal structure of the deposit and are divided into groups depending on the dominating effect. Brighteners give a more mirror-like surface, grain refiners give a more fine-grained structure, and stress reducers reduce the stress in the plating.

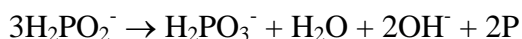
Plating may also be achieved by non-electrolytic plating, i.e. without an applied voltage. The most common process is **autocatalytic plating** or electroless plating as it is also called. The plating is then achieved by adding a reducing agent to the plating bath. The reaction can be written [126]:



where Red is the reducing agent and Ox its oxidised form. In an autocatalytic process, the deposit metal catalyses the reaction. The reaction only occurs on the metal surface and it will continue as long as the metal surface is exposed to the solution. Common reducing agents are hypophosphite, formaldehyde, borohydride, hydrazine, and thiourea. The most used reducing agent for plating of electroless (autocatalytic) nickel is hypophosphite. The reaction is very complex but it can simplified be written [49]:



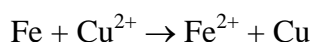
In addition, the following reaction occurs simultaneously:



As a result, phosphorus is co-deposited in the nickel coating. The phosphorus content may vary from 1% to 15% depending on the composition and temperature of the bath.

The plating rate of an autocatalytic process, which is determined by the temperature and composition of the plating bath, is essentially constant as long as the plating continuous.

Another non-electrolytic plating process is **immersion plating**. Immersion plating is caused by a galvanic displacement reaction. When the substrate metal is less “noble” than the plating metal, the uppermost metal layer of the substrate metal may be substituted with the plating metal. A well-known example is immersion plating of copper on iron in an acidified copper sulphate solution [126]:



The total reaction is the same as occur when copper is electroplated with a counter electrode made of iron. The main differences are that during immersion plating, it is the difference in electrochemical potential (galvanic cell) for the two metals that is the driving force for the reaction and that the anodic and cathodic reactions occur on the same surface.

Although immersion plating can be achieved with many combinations of substrate and plating metals, the deposits are usually porous and have poor adhesion as the example with immersion plating of copper on iron. There are two reasons for this. First, since the plating is achieved through a displacement reaction, the dissolution of the substrate metal may lead to that etching occurs beneath the plated metal, which thereby lose adhesion. Second, the deposition rate is basically determined by the difference in electrochemical potential for the substrate and the plated metal (difference in nobility) and thus difficult to control. If the difference in electrochemical potential is large, the initial plating rate may be too high to get a well-structured and adherent metal coating. In fact, it is often necessary to perform a strike plating during electrolytic plating in order to prevent that an initial immersion plating ruins the adhesion of the electroplated coating. The strike plating is performed in a bath with low activity of the plated metal (low concentration of the metal and high concentration of complexing agents) to reduce immersion plating reactions. Therefore, good adhesion of immersion platings can usually only be achieved if the difference in electrochemical potential is small.

The electrochemical potential of the substrate and plating metals can to some extent be affected by addition of complexing agents to the bath, and by this means can the plating rate be affected. Compounds that form strong complexes with the plated metal will reduce the activity of the plating metal which will decrease the plating rate whereas compounds that form strong complexes with the substrate metal will enhance the dissolution of it and thereby increase the plating rate. Addition of complexing agents may even change the order of "nobility". Tin is normally less noble than copper but by adding for example thiourea, which forms very strong complexes with copper, tin can be immersion plated on copper [127].

Nevertheless, it is a difficult balance act to optimise the bath composition. When the displacement reaction starts, the plated metal will be deposited as small islands on the substrate metal. These islands will be cathodic surfaces whereas the rest of the substrate metal will be anodic surfaces. That is, initially the anodic surfaces will be much larger than the cathodic surfaces. As more and more of the surface is coated with the plating metal, the cathodic areas increase in size and at the end of the process they are much larger than the anodic areas. As a consequence, the plating rate on the cathodic surfaces will decrease with time since the amount of metal reduced at the cathodic areas must balance the amount of metal oxidised at the anodic areas. This also means that the oxidation rate of the anodic areas will increase as more of the total area is coated with the plated metal and may finally become very high.

Ideally, an immersion plating process will lead to a completely coated substrate metal and, in contrast to autocatalytic plating, the plating process will cease by itself when the coating is completely covering. In reality, it is difficult to achieve a completely coated surface. If the electrochemical potentials are balanced to give a low initial plating rate, the coating may become very thin but it will be difficult to achieve complete coverage. On the other hand, if the initial plating rate is too fast, the coating may become porous. Since the anodic reaction is an etching process and the plated metal will function as an etch resist, a porous coating and an aggressive plating solution may lead to over-etching. The effect will be that the surface of non-coated substrate metal will reach a minimum and then increase again when over-etching expose new surfaces beneath the plated metal layer. The best solution to avoid this would probably be to perform a sort of strike plating. That is, start the plating in a bath balanced to give slow initial plating in order to get a low-porous layer and then continue in a bath balanced to give faster plating reactions to get a high final coverage.

### 3.1.2 Immersion Gold Plating of Electroless Nickel

Usually, there is a large difference in the electrochemical potentials for gold and nickel. Thus, it is difficult to get good adhesion of immersion gold on nickel. However, electroless nickel offers a possibility to decrease the plating rate of immersion gold. The reactivity of electroless nickel is very much affected by the phosphorus content; the higher the phosphorus content the lower the reactivity of the nickel coating.

Cordes and Huemoeller have examined how the deposition rate of gold and the adhesion of the gold deposit are affected by the phosphorus content in the electroless nickel [124]. They found a clear correlation between the phosphorus content and the deposition rate; the higher the phosphorus content, the lower the deposition rate (see Table 1). It was not described how the deposition rate was determined but obviously it must have been measured as an average value for a defined time period. The initial deposition rates were probably much higher. The adhesion of the gold layers was tested by a tape test. Again, they found a clear correlation; the higher the deposition rate, the poorer the adhesion. Poor adhesion indicates that etching beneath the gold layer has occurred. The effect of the phosphorus content on the shear strength of reflowed solder balls was also investigated. Concurrently with the decreased adhesion of the gold layer when the phosphorus content was decreased, the shear strength of reflowed solder balls degraded.

It can be noted that the deposition rate was highest on electrolytic nickel, i.e. a nickel coating containing no phosphorus. The adhesion of the gold layer was also worse to the electrolytic nickel and the shear strength of reflowed solder balls to this coating was very poor. On the other hand, excellent ball shear results were obtained for samples with electrolytic gold on electroless nickel. These results clearly show that it is not the phosphorus in the nickel coating that causes black pad.

*Table 1 Effect of nickel composition on the deposition rate and adhesion of the gold deposit [124].*

Phosphorus content (%)	Deposition rate ( $\mu\text{m}/\text{min}$ )	Adhesion – tape test (% peeling)
0 (electrolytic Ni)	0.025	75
3	0.019	5-10
5	0.015	1-2
7	0.010	0
9	0.005	0

On electrolytic nickel, over-etching beneath the gold coating may degrade the solderability in several ways. Exposed nickel surfaces will be oxidised. Residues from the plating bath may be trapped beneath the gold coating and contribute to more extensive oxidation of the exposed nickel surfaces. Corrosion products may also migrate through the porous gold coating and deposit on top of the gold surface. McFaddin has reported that, by using low-vacuum scanning electron microscope (LVSEM) and energy dispersive X-ray spectroscopy (EDS) with a low electron beam voltage, a very thin film of nickel oxide often can be detected on top of the gold layer on surfaces affected by black pad [128]. If this film is thick enough it may prevent wetting of the gold layer. However, it is usually no problem to wet the gold layer on surfaces affected by black pad. Thus, this film is normally too thin for preventing wetting but it offers an opportunity to non-destructively detect surfaces affected by black pad. Most likely, it is the corrosion products and bath residues trapped beneath the gold layer that prevent good wetting on electrolytic nickel.

Over-etching during immersion plating of electroless nickel will also expose the nickel surface to oxidation and bath residues may be trapped beneath the gold coating. In addition, the dissolution of nickel during the immersion plating will cause an enrichment of phosphorus at the surface, just as soldering does. Chan et al. have reported that phosphorus is enriched in the uppermost 150 Å of the nickel layer when 0.07-0.08  $\mu\text{m}$  immersion gold is deposited on electroless nickel with 8-10% phosphorus [125]. The phosphorus content in the enriched layer was 20% at maximum. This enrichment of phosphorus has a negligible effect on the solder wettability of the nickel surface. However, when the black pad defect occurs, extensive corrosion of the nickel may take place leading to a much thicker layer with enriched phosphorus. The phosphorus content in the enriched layer is usually 2-3.5 times higher than in the electroless nickel [125, 129, 130, 131, 132]. This enrichment of phosphorus is likely the main reason for the difficulties to properly wet surfaces with black pad defects but higher oxygen content associated with black pad regions [133] indicates that plating and corrosion residues probably also contribute.

An autocatalytic nickel coating consists of nickel nodules that have been growing upward from the underlying copper surface. The nodules can be described as closely packed columns. Micro-sections of solder pads with black pad often show gold spikes that penetrate downward from the surface along the nickel nodule boundaries [129, 131, 132, 134]. The gold spikes are associated with corrosion damages that can be seen as dark spikes that penetrate even deeper along the nickel nodule boundaries than the gold spikes. In worst case, they may penetrate through the nickel coating down to the underlying copper. This type of corrosion damages is probably caused by crevices present between some nickel nodules prior to the coating with immersion gold [47]. The bath solution that fills a crevice will not contain enough gold ions to completely coat the sides of the nickel nodules. When the solution has been depleted with gold ions, the non-coated surfaces will be anodic surfaces through the remainder of the plating process. This type of corrosion damages can probably only be prevented by assuring that there are no crevices between the nickel nodules. A slow rate of nickel deposition reduces the sizes of the crevices [47]. According to Johal et al., a smoother surface without crevices between the nickel nodules can be achieved with a phosphorus content of 11.2% [51]. The extent of the corrosion damages during immersion gold coating will be affected by the plating time and probably also by the chemistry of the plating bath.

In other cases, corrosion of the nickel is observed in micro sectioning as a more or less continuous black band of the uppermost nickel beneath the gold coating [129, 131]. The black band may be confined to a few nodules or cover a large area of the pad and have a thickness of 1  $\mu\text{m}$ . If the gold layer is stripped away from areas with a thick dark band, the nickel surface has an appearance of cracked mud. If a cross-section is made using FIB, many very narrow voids perpendicular to the surface can be observed in the black band [129]. This type of corrosion damages is probably caused by a porous gold deposit, i.e. a too fast initial gold deposition rate. To prevent this type of corrosion damages, the chemistry of the immersion gold bath must be balanced to give the optimum plating rate with respect to the reactivity of the electroless nickel coating. As discussed previously, it is probably easier to balance an immersion gold bath for electroless nickel with high phosphorus content. Eslambolchi et al. noted a correlation between phosphorus content and immersion gold thickness where higher phosphorus content led to a thinner gold layer [68]. Thus, a thinner gold layer indicates that it is less porous.

Obviously, it is possible to balance immersion gold processes for electroless nickel coatings with different phosphorus content. Thus, it is not possible to specify an optimal phosphorus content in electroless nickel. It will depend on the chemistry of the immersion gold bath used. Furthermore, a changed reactivity of the plating bath or the electroless nickel with time may put the balance out of order. Whereas it was previously recommended that the phosphorus content was within the range 6-10% [124, 125, 135], it has during the last years been recommended to increase the phosphorus content to 9.5-13% [51, 130]. According to Johal et al., the maximum thickness of the gold layer that could be achieved on high-phosphorus electroless nickel was 0.06  $\mu\text{m}$  [51].

In contrast to the finding by most others, Roepsch et al. have reported that they found an increased risk for black pad with increasing phosphorus content in the electroless nickel [133]. In their investigation, they compared samples from different batches from various PCB manufacturers. That is, the phosphorus content was not purposely varied in the samples. The phosphorus content in electroless nickel normally increases with the number of metal turn over (MTO) but also the reactivity of the nickel increases with the number of MTO [49, 136]. Thus, an increased phosphorus content in the samples evaluated by Roepsch et al. indicated that they had been plated in baths with high MTO. Thus, a higher reactivity of the nickel can be expected despite a higher phosphorus content and, consequently, also an increased risk for black pad defects.

Various compounds are added to the electroless nickel bath. They have a number of functions, for example to stabilise the bath against spontaneous nickel reduction and to control the quality of the plating at edges [47, 49, 135]. The main stabilisers used are lead and sulphur-containing compounds [134]. Although they are added to concentrations of only 0.5 to 1.0 ppm, they have a significant impact on the plating rate and the properties of the plated nickel coating including the phosphorus content. Even an increase of the concentration of the sulphur compound from 0.5 to 1.0 ppm will cause a decrease of the phosphorus content and, more important, a considerable increase of the reactivity of the nickel. Also an increase of the lead concentration will increase the reactivity of the nickel but the effect is not as large as it is for the sulphur compound. Thus, it is very important to assure a constant concentration of the stabilisers in order to control the reactivity of the nickel.

According to Crouse and Cullen, solder masks may leach sulphur-containing compounds (photo-initiators) that have the same effect as the stabilisers added to nickel baths [134]. By soaking a solder mask in deionised water and then using this water for making an electroless nickel bath, they could prove that it caused increased plating rate, increased reactivity of the nickel, and even the black pad defect when the nickel coating was immersion gold plated. Solder masks are intentionally under-cured when applied to PCBs in order to increase their pliability and thereby reduce the risk for that they crack or detach during ENIG processing. This makes it easier for compounds to leach out. Crouse and Cullen showed that the impact of contaminations leaching from solder masks could be reduced by additional curing and by more effective cleaning. Since the black pad defect has been reported to occur mainly on solder mask coated PCBs [134], leaching of sulphur compounds from the solder mask is probably one of the major causes of black pad defects. The fact that black pad defects tend to appear more frequently and more severely at the corners and edges of pads versus the centre of the pad [133] also support this conclusion.

The black pad defect is often stated to be due to a hyperactive corrosive immersion gold process [125, 129, 130]. A too high temperature of the gold bath or too high gold concentration can cause a too aggressive attack [47]. It can be noted that when black pad was first observed, the problem was dissolved by increasing the thickness of the gold layer [123]. Thereafter, the ceramic substrate was heat treated at 600-650°C to convert the gold coating into an alloy region

with nickel, which eliminated the black pad defect. A thicker gold coating was achieved by using a loosely complexed gold bath, i.e. a more aggressive bath. Without the heat treatment, this would have worsened the black pad defect.

However, usually it is more likely that the excessive corrosion is caused by an increased reactivity of the nickel surface. It is difficult to maintain constant phosphorus content in electroless nickel. The phosphorus content is affected not only by additives to the bath but also by temperature, pH, MTO, and loading factor [68]. Even if the phosphorus content is kept constant, the reactivity of the nickel may vary significantly due to changed concentrations of stabilisers, as discussed previously. Hence, it may be necessary to regularly check the reactivity of the nickel to assure that the immersion gold process will not cause a too fast plating rate. This may be done by testing the corrosivity of the nickel coating. One method used is to measure the weight loss after immersion in concentrated nitric acid for 30-60 seconds [134]. Another method is to measure the time it takes before the nickel surface turns black when it is dipped in nitric acid [136].

To achieve a uniform gold coating, it is important that the nickel surface is clean and has a minimum of oxides. Chan et al. has shown that the number of corrosion defects increase with increasing hold time between electroless nickel and post rinse steps [125]. Since nickel oxidises very fast, it is not possible to have an oxide-free nickel surface but the time between nickel and gold plating should be kept at a minimum. Contamination and oxide layers may cause poor adhesion of the gold layer and that it becomes porous by blocking the surface. However, it may cause poor quality of the coating also in a more indirect way. Contamination and oxide layers with uneven thickness on the nickel surface may affect the chemical potential of the surface leading to that some areas will be predominantly cathodic areas whereas other areas will be predominantly anodic areas. Areas that become predominantly anodic areas will be more extensively corroded during the plating process and more likely to show black pad defects. A similar effect may be seen if areas located at different parts of a PCB are electrically connected to each other, especially if they have different sizes. Due to variation in bath agitation and consumption of bath chemicals, or temperature gradients on PCBs having a large thermal mass, a potential difference may arise between the areas that causes one area to become predominantly cathodic and the other predominantly anodic. This is probably the reason why black pad defects do not occur randomly but is often localized to specific pads on a PCB [129]. Surfaces affected by black pad are often connected to larger surfaces not affected by black pad [137] and usually they are found on boards with complex circuitry [134]. The fact that black pad defects appears to occur more frequently on finer pitched parts with smaller pads than on larger pads [138] may also be caused by leakage from the solder mask which could have larger influence on a small pad.

Since the plating process never ceases by itself when black pad defects occur, the gold coating on areas with corroded nickel is often thicker than normal [68, 129, 131, 139], typically about twice as thick as normal [133]. This increase in gold thickness is usually not large enough to be used as an indication of black pad. By interrupting the gold plating process before the surface is completely covered with gold, the extent of eventual black pad defects can probably be reduced. This is a

method that is practised but the gold coating will then likely have less protective properties [49].

### **3.1.3 Effect of Black Pad Defects on the Reliability of Solder Joints**

In cases of severe black pad defects, wetting will not occur to the nickel surface during soldering. Initially, the solder wets the gold surface but when the gold has been dissolved in the solder, dewetting will occur on parts of the solder pad or, in worst case, on the whole pad. Rework of the solder joint fails since it is not possible to wet the surface unless the surface is mechanically abraded. However, in most cases with black pad defects, solder wets the nickel surface and the solder joints look completely normal when visually inspected [68]. The defect will then not be discovered until a failure occurs which may happen when the assembly is exposed to stress. A brittle fracture will then occur in the solder joint. The fracture takes place between the intermetallic layer and the nickel surface. Little to no NiSn intermetallic phases are observed at the nickel surface [68, 129, 130].

When micro-sectioned, it is often observed that the intermetallic layer is poorly developed and is missing at areas with corrosion damages in the nickel, but this is not always observed. The presence of corrosion damages in the form of a rather thick “black band” at the nickel surface is a strong indication of a black pad defect. Corrosion damages of the nickel in the form of spikes between nickel nodules are also a clear indication of black pad but according to Chan et al., there is no evidence that such spikes have any effect on solder joint strength [125]. Corrosion damages in the form of a band at the surface are probably much more detrimental than corrosion spikes since it will result in poor wetting of a larger area. Though, if corrosion spikes extend down to the copper, copper may be dissolved in the solder and intermetallic phases with copper will be formed. According to Champaign et al., these copper-containing intermetallics create a brittle zone and the corrosion spikes act as stress risers assisting in the formation of cracks [132].

## **3.2 Brittle Failures due to Intermetallic Compounds**

### **3.2.1 Factors Affecting Brittle Fracturing**

The main factors affecting the occurrence of brittle fractures, besides black pad defects, are the type of stress a solder joint is exposed to, the compliance of the solder and the brittleness of the intermetallic layer. Of these factors, the type of stress is the most important. In most cases, a high strain rate is required to trigger a brittle fracture. High strain rate may be caused by bending of the assembly [12, 13], fast temperature changes [14], mechanical shock [15, 16, 17], and vibration [18, 19].

When a solder joint is exposed to high strain rate, the behaviour of the metallic material is dominated by elasticity [96]. Thus, when a solder joint is exposed to high strain, the stress transferred to the intermetallic layer will be determined by the strain rate and the elastic compliance of the solder. A high elastic compliance

(low elastic modulus) will reduce the stress on the IMC layer. Since the elastic modulus of Sn4Ag0.5Cu is about 33% higher than of SnPb [96], more stress will be transferred to the IMC layer in the lead-free solder joint compared to the tin-lead solder joint. Therefore, if the fracture strengths are the same for the IMC layers in a lead-free and in a tin-lead solder joint, a brittle fracture will occur at a lower strain rate for the lead-free solder joint.

In SAC solder, the primary tin phase has the highest compliance [96]. By lowering the Ag content in the solder, the amount of primary tin can be increased and thereby also the compliance. A decrease of the Ag content from 4 to 1% results in a lowering of the elastic modulus with 11%.

An increase of the elastic modulus renders the solder joint higher impact toughness. Furthermore, according to Wong et al., high strain rate tends to raise the fracture toughness of ductile materials while lowers it of brittle materials [140]. The compliance of a solder material and the brittleness of an IMC layer may, therefore, be affected by the strain rate. However, the composition, the structure, and the thickness of the IMC layer are more important for its brittleness.

### **3.2.2 Brittle Fractures in Solder Joints to Electroless Nickel**

According to IPC's standard IPC-7095A, Design and Assembly of Process Implementation for BGAs, interfacial fracture may happen between the nickel surface and the nickel-tin intermetallic layer under a high level of both applied strain and strain rate even if hyperactive corrosion does not take place [11]. However, it may be difficult to clearly distinguish between the two failure mechanisms for properly formed solder joints and it is likely that they interact.

According to Sohn et al. [52], Mattila and Kivilahti [16], and Alajoki et al. [117] the interfacial cracking in solder joints on electroless nickel not having a black pad defect occurs in the very thin NiSnP layer formed on top of the Ni<sub>3</sub>P layer. That is, for both failure mechanisms, the fracture occurs between the NiSn intermetallic layer and the layer with enriched phosphorus on the nickel surface. Thus, very little NiSn intermetallic phases will remain on the nickel surface in both cases.

The presence of a nickel layer with enriched phosphorus is no clear indication of a black pad defect. The formation of an intermetallic layer on electroless nickel during soldering causes a selective solution of nickel atoms leading to an enrichment of phosphorus in the remaining nickel, just as black pad defects do. Immersion gold plating inevitably leads to the formation of a layer with enriched phosphorus although it may be less than 20 nm thick under optimal conditions [125]. Thus, wetting must always occur to a nickel surface with enriched phosphorus. In fact, wetting and the formation of a proper intermetallic layer have in many cases been observed on immersion gold plated surfaces with much thicker layers with enriched phosphorus. Hence, the formation of a nickel surface with enriched phosphorus as such does not seem to cause a non-wettable surface. Possibly, it is the over-etching beneath the gold layer leading to entrapment of bath residues and exposure of the nickel surface to oxidation that cause the surface

to become non-wettable. The finding by Cordes and Huemoeller that immersion gold plating of electrolytic coating resulted in solder joints with very poor shear strength is hard to explain in any other way [124]. Actually, the function of the gold layer is to preserve the solderability by preventing oxidation of the nickel surface. If it is over-etched, that function will be lost.

The composition of the phosphorus-enriched layer formed during soldering is usually specified to be  $\text{Ni}_3\text{P}$ , which corresponds to a phosphorus concentration of 15%. In comparison, the phosphorus content in the enriched layer formed during immersion gold plating is normally specified to be between 10 and 20%, i.e. of the same order. Hence, the properties of the enriched layer are probably very similar regardless of how it was formed.

Whereas there seems to be consensus that electroless nickel with high phosphorus content is to be preferred in order to minimise the risk for black pad defects, there are different opinions on how a high phosphorus content affects the reliability of the solder joints. According to Bulwitsch et al. [130] and Lee [136], high-phosphorus nickel increases the risk for brittle fractures caused by phosphorus enrichment during soldering and subsequent thermal excursions. Furthermore, Sohn et al. [48, 52], Paik et al. [53], and Alam et al. [54], have reported that the growth rate of  $\text{Ni}_3\text{Sn}_4$  and the risk for spalling of the IMC layer increase with increasing phosphorus content.

On the other hand, Johal et al. have reported that high-phosphorus nickel not only decreases the risk for black pad but also improves the reliability of the solder joints [51]. They tested how the phosphorus content affected the shear strength of SnAgCu balls before and after 1000 temperature cycles between  $-55$  to  $+125^\circ\text{C}$ . Before temperature cycling, shear tests of solder balls soldered to nickel coatings with 8.0 and 11.2% P gave consistent results with high values and little spread in shear force whereas solder balls to a nickel coating with 4.2% P showed a wide spread in shear force and with considerably lower shear force for some solder balls. After temperature cycling, also the solder balls to the nickel coating with 8.0% P gave a large spread in shear force while the solder balls to the nickel coating with 11.2% P still showed high values and little spread in shear force. When examined using cross-sectioning, the fractures to the nickel coating with 8.0% P showed partial brittle fractures whereas the fractures to the nickel coating with 11.2% P showed ductile fractures. The structures of the IMC layers were examined by stripping off the solder. The structure of the IMC layer on the nickel coating with 8.0% P was coarser and less dense compared to the IMC layer on the nickel coating with 11.2% P. They proposed that the difference in structure was due to differing dissolution rate of nickel during soldering and aging. Less nickel should be dissolved from the more corrosion resistant high-phosphorus nickel.

As mentioned previously, recently performed investigations indicate that brittle fractures on electroless nickel not affected by the black pad defect occur in the thin NiSnP layer between the  $\text{Ni}_3\text{P}$  and NiSn intermetallic layers [16, 52, 117]. In the investigation done by Mattila and Kivilahti, a SnAgCu solder was used to solder CSP components to ENIG and a thin porous microcrystalline or amorphous NiSnP layer with the composition  $\text{Ni}_{55}\text{Sn}_{45}\text{P}_{10}$  was formed between the  $\text{Ni}_3\text{P}$  layer

and a layer of  $(\text{Cu,Ni})_6\text{Sn}_5$ . Cracking occurred in the NiSnP layer when the assembled CSP components were exposed to a drop test. Similar results were obtained by Alajoki et al. [117]. Sohn et al. performed shear testing of test vehicles with both Sn3.5Ag and Sn3.0Ag0.5Cu solder joints to ENIG. In their study, brittle fractures only happened in the NiSnP layer for the test vehicles soldered with the Sn3.5Ag solder. The NiSnP layer in this case was formed between the  $\text{Ni}_3\text{P}$  layer and a layer of  $\text{Ni}_3\text{Sn}_4$ , it was nanocrystalline with Kirkendall voids and had a composition of  $\text{Ni}_3\text{SnP}$ . The reason why brittle cracking only occurred for the Sn3.5Ag solder was claimed to be due to spalling of the  $\text{Ni}_3\text{Sn}_4$  layer and thereby larger consumption of nickel during soldering. This resulted in an increased growth of the NiSnP layer. No spalling occurred with the SnAgCu solder. The shear rate used for testing was only 0.2 mm/min. The low strain rate achieved with this test compared to the drop test used by Mattila and Kivilahti, and by Alajoki et al., may explain why brittle fractures occurred for SnAgCu solder joints in the latter tests but not in the shear test.

Saha et al. made samples consisting of rectangular, Cu-plated ceramic blocks soldered to organic multi-layer interposers with ENIG or Sn37Pb coating on Cu-pads using Sn3.5Ag solder [111]. The distance between the soldered surfaces was only 20-50  $\mu\text{m}$ . Therefore, the IMC layer formed on ENIG-plated pads was  $(\text{Cu,Ni})_6\text{Sn}_5$  and on Sn37Pb coated pads  $\text{Cu}_6\text{Sn}_5$ . When drop tested, brittle fractures occurred in the IMC layer on the ENIG-plated interposers but not on the Sn37Pb coated interposers (a certain number of drop tests was performed but the number was not specified). This result support that solder joints to ENIG are brittle also when the intermetallic layer consists of  $(\text{Cu,Ni})_6\text{Sn}_5$ .

According to Yee et al. [62], tin-lead solder joints to nickel become highly susceptible to brittle fracture under stress if a ternary Ni-Cu-Sn intermetallic layer is formed on the nickel surface due to a coupling effect, i.e. copper coming from an opposite copper surface. Although it was not clearly expressed in the paper to what type of nickel the solder joints were formed, figures of micro-sectioned solder joints showed a black band beneath the intermetallic layer indicating that it was electroless nickel. The coupling effect not only resulted in a change of composition of the IMC layer but also in a considerable increase of its thickness. Also Prasad has reported an increased susceptibility to brittle fractures as a result of the formation of a ternary Ni-Cu-Sn intermetallic layer on nickel due to the coupling effect, both for lead-free and tin-lead solders [141]. According to Prasad, the copper content in SAC solders is too low to significantly affect the brittleness of the IMC layer. Only when an opposite surface consists of copper is the brittleness drastically increased.

Obviously, solder joints to electroless nickel are prone to brittle fractures regardless if the IMC layer consists of  $\text{Ni}_3\text{Sn}_4$  or  $(\text{Cu,Ni})_6\text{Sn}_5$ . Also, the growth rate of the IMC layer and its thickness may be important for the brittleness of the solder joint. It will affect the thickness of the NiSnP layer and probably the extent of voids in this layer. Thus, measures that would decrease the dissolution rate of nickel during soldering ought to decrease the brittleness of the solder joints. The phosphorus content in the electroless nickel may then be important but, as already discussed, there are different opinions of how the growth rate of the IMC layer is

affected by the phosphorus content. In several papers, it is claimed the growth rate increases with increasing phosphorus content [48, 52, 53, 54], but according to Johal et al. the growth rate is decreased for high-phosphorus nickel [51]. If a low dissolution rate of nickel decreases the risk for brittle fractures, some enrichment of phosphorus in the nickel surface during immersion gold plating may in fact be beneficial for the reliability of the solder joint since it will decrease the dissolution rate of the nickel. That is under condition that proper wetting occur to the nickel surface.

Tu and Zeng [37] and He et al. [65] claim that also the  $\text{Ni}_3\text{P}$  layer has Kirkendall voids and that interfacial cracks can go through this layer.

### **3.2.3 Brittle Fractures in Solder Joints to Electrolytic Nickel**

Since electrolytic nickel does not contain phosphorus, a  $\text{NiSnP}$  layer cannot form when soldering to electrolytic nickel. Thus, the IMC layer formed on electrolytic nickel can be expected to have quite different properties regarding brittleness compared to the IMC layer formed on electroless nickel. Unfortunately, there are very few investigations performed that have studied this. Mei and Eslambolchi have reported that they got brittle fractures at the  $\text{Ni}_3\text{Sn}_4/\text{Ni}$  interface when they exposed BGA components soldered to ENIG to a four-point bending test but not when they were soldered to electrolytic nickel/gold [81]. In the investigation performed by Mattila and Kivilahti [16], CSP components with electrolytic nickel metallisation were soldered to PCBs with ENIG metallisation. Despite the fact that the solder joints on the component side had passed two soldering processes and Finite Element Model (FEM) calculations showed that the stresses at the component side interfacial region were more than two times larger than those on the PCB side, brittle cracking occurred on the PCB side during a drop test. This result indicates that solder joints formed on electrolytic nickel is considerably less brittle than solder joints formed on electroless nickel. Also Sykes claims that tin-lead solder joints to ENIG exhibits more brittle failures than to electrolytic nickel-gold or bare copper but without presenting data to support the conclusion [20].

Alajoki et al. performed drop testing of CSP packages with two different under bump metallisations: sputtered  $\text{Ni}(7\text{V})/\text{Cu}$  and ENIG. When the components were soldered to a board with OSP pads using a  $\text{Sn}4\text{Ag}0.5\text{Cu}$  solder, the IMC layer formed on  $\text{Ni}(7\text{V})/\text{Cu}$  consisted of  $(\text{Cu},\text{Ni})_6\text{Sn}_5$  (all copper was dissolved): The IMC layer formed on ENIG consisted of  $\text{Ni}_3\text{P-Sn}/\text{Ni-Sn-P}$ .  $(\text{Cu},\text{Ni})_6\text{Sn}_5$  was also formed on ENIG but was to a large extent spalled off. The number of drops-to-failure was about four times larger for the components with sputtered nickel indicating a much larger fracture strength compared to the components with ENIG.

As described in Section 2.1.2, the rather thick layer of electrolytic gold normally plated on electrolytic nickel may lead to the formation of a dual IMC layer on nickel surfaces when  $\text{SnPb}$  solder joints are aged. Between the  $\text{Ni}_3\text{Sn}_4$  layer and the solder, a layer of  $(\text{Au},\text{Ni})\text{Sn}_4$  is formed. With a gold content of 1.5% in the solder joint, it takes only about 3 hours at  $150^\circ\text{C}$  before the new phase has formed on top of the  $\text{Ni}_3\text{Sn}_4$  layer and after three weeks at this temperature, it is about 10

$\mu\text{m}$  thick [70]. This formation of two distinct intermetallic layers has been found to make the solder joint brittle with fractures occurring between the two phases. Darveaux et al. found that the time to embrittlement for a 0.76 mm solder joint formed between two nickel terminations plated with 1.25  $\mu\text{m}$  gold was 1 day at 150°C, three weeks at 100°C, and 1 year at 60°C [8]. A layer of  $(\text{Au},\text{Ni})\text{Sn}_4$  may also form during thermal cycling between  $-40$  to  $+125^\circ\text{C}$  resulting in shorter life due to brittle fractures [14].

SnAg and especially SnAgCu solders are claimed to be less prone to form a dual IMC layer when soldering to electrolytic nickel/gold (see Section 2.2.2) and thus also less prone to brittle fractures. Nonetheless, Vandeveldel et al. observed the formation of a dual IMC layer and brittle fractures when exposing BGA components soldered with a SnAgCu solder to temperature cycling and vibration [18]. Brittle fractures occurred between the layers during the vibration exposure. Their findings show that SnAgCu solders are not immune to this type of gold embrittlement.

### **3.2.4 Brittle Fractures Caused by a Dual Layer of $(\text{Ni},\text{Cu})_3\text{Sn}_4$ and $(\text{Cu},\text{Ni})_6\text{Sn}_5$**

The dual layer of  $(\text{Ni},\text{Cu})_3\text{Sn}_4$  and  $(\text{Cu},\text{Ni})_6\text{Sn}_5$  that may form on both electroless and electrolytic nickel when the solder contains copper has also been reported to increase the brittleness of solder joints. The copper may be either intentionally added to the solder or dissolved from an opposite copper surface. Gregorich et al. have reported that after final electrical testing of lead-free CSPs involving moderate mechanical stress, a small number of the components were missing one or two of the solder balls [109]. The CSPs had electrolytic Ni/Au substrate pads and Sn4.0Ag0.5Cu solder balls. Pads exposed by missing balls had a uniform matte-grey finish with little evidence of solder. Failure analysis showed that cracking had occurred between two intermetallic phases. The phase adjacent to the nickel plating contained Ni and Sn and the other phase contained Ni, Sn and Cu. The IMC phases were not identified but it was assumed that they were  $\text{Ni}_3\text{Sn}_4$  and  $(\text{Cu},\text{Ni})_6\text{Sn}_5$ , respectively. When assembled components were subjected to abrupt mechanical stress, brittle fractures sometimes occurred between the IMC layers, which proved that high strain rate could trigger brittle fractures in the dual IMC layer. Brittle fractures did not occur after the reflow profile had been changed in order to decrease the amount of intermetallic phases formed.

In the examples given so far, the brittle IMC layers have consisted of at least two intermetallic layers with different composition and the fractures have occurred between the layers or possibly through one of the layers in the case of the NiSnP layer on electroless nickel. Since most intermetallic compounds are very hard, volumetric changes during their growth will cause high residual stresses that cannot be reduced by creep as for solder. The growth of the IMCs will lead to progressive damage and weakening of the interface between the layers [84]. Furthermore, even small variations in CTE will lead to large stresses between the layers during temperature changes. These facts combined with the brittleness of the intermetallic compounds are probably the main reasons why solder joints having dual IMC layers are inclined to brittle fractures. Also, the brittleness will

increase with increasing thickness of the IMC layer. However, there are also examples of dual IMC layers that have not caused increased risk for brittle fractures. The double layer of  $(\text{Cu,Au})_6\text{Sn}_5$  with differing gold content found on copper by Ratchev et al. was not found to cause brittle fractures [35]. In this case, both phases had the same structure, which may be the reason why brittle fractures did not occur between the phases.

### 3.2.5 Substitution of Cu with Ni in $\text{Cu}_6\text{Sn}_5$

In the investigation done by Mattila and Kivilahti [16], also test vehicles with CSP components with electrolytic nickel metallisation soldered to PCBs with OSP coating were drop tested. In this case, brittle fractures occurred to the component side of the solder joint, i.e. the side with electrolytic nickel (when the components were soldered to ENIG, the fractures occurred to the board side). The crack propagated through the intermetallic layer, which consisted of a single layer of  $(\text{Cu,Ni})_6\text{Sn}_5$ . Some minor cracks were also observed in the intermetallic layer on the PCB side of the solder joint. This layer consisted of  $\text{Cu}_6\text{Sn}_5$  with a very thin layer of  $\text{Cu}_3\text{Sn}$  at the copper interface. According to Laurila et al. [25], Takemoto and Yamamoto have reported that addition of Ni to  $\text{Cu}_6\text{Sn}_5$  makes the compound more brittle. Furthermore, the hardness and elastic modulus of the CuNiSn intermetallic formed on nickel from Sn3.0Ag0.5Cu are reported to be about 20% higher than for  $\text{Cu}_6\text{Sn}_5$  [142]. However, as previously mentioned, FEM calculations showed that the stresses at the component side interfacial region were more than two times larger than those on the PCB side. Furthermore, the solder pads were solder mask defined on the component but non-solder mask defined on the PCB. Therefore, it cannot be concluded with certainty from the investigation done by Mattila and Kivilahti whether the IMC layer formed on the electrolytic nickel is more inclined to brittle fractures than that formed on copper.

### 3.2.6 Brittle Fractures in Solder Joints to Copper

Also Heaslip et al. have performed drop tests of BGA components soldered to PCBs with copper pads [17]. The pads on the BGA components had nickel plating but the type of nickel was not specified. When the solder joints consisted of Sn3.8Ag0.7Cu, ductile cracking in the solder occurred at the component side when dropping from 203 mm whereas brittle cracking in the IMC layer occurred at the PCB side when dropping from 813 mm. That is, a certain strain rate was required to get brittle fractures. Furthermore, the IMC layer contained 68.0% Sn, 31.6% Cu and 0.4% Ag but no Ni. Thus, brittle fractures may also occur in the IMC layer formed on copper and without high temperature aging. The thickness of the Sn-Cu IMC layer in the solder joints was about 5  $\mu\text{m}$  and the fracture formed close to the copper surface. Also in this case, the solder pads were solder mask defined on the component and non-solder mask defined on the PCB, but figures of micro-sectioned solder joints indicate that the solder pads were smaller in relation to the solder pads on the components on the test vehicles used by Heaslip et al. compared to the investigation done by Mattila and Kivilahti. This may explain why Heaslip et al. observed brittle failures to the copper pad and not to the nickel pad as Mattila and Kivilahti did.

In addition to drop testing BGA test vehicles having SnAgCu solder joints, Heaslip et al. drop tested also vehicles having solder joints consisting of Sn37Pb [17]. The number of drops to failure was significantly higher for these test vehicles compared to those soldered with lead-free solder. Furthermore, almost all fractures occurred at the component side but it was not specified whether the fractures were ductile or brittle. First, there may be several explanations for this finding. The higher elastic compliancy of the tin-lead solder compared to the lead-free solder results in less stress transferred to the intermetallic layer. This is perhaps the most probable explanation. Second, the higher soldering temperature for the lead-free solder and the copper content in this solder will give a thicker IMC layer. The higher soldering temperature combined with higher solubility of nickel in tin-rich solders will cause larger dissolution of nickel in the solder, which could also contribute to increased growth rate of the IMC layer on the Cu pads. An increased thickness of the IMC layer would increase the brittleness of the IMC layer. Another possibility is that more nickel is dissolved in the  $\text{Cu}_6\text{Sn}_5$  phase due to the higher nickel concentration, which could make the  $\text{Cu}_6\text{Sn}_5$  phase more brittle.

Similar results were obtained by Date et al. [143]. They compared the results from conventional shear testing of solder balls using a shear rate of 0.1-7 mm/s with the results from a miniature Charpy test having a shear rate of 0.3-1.4 m/s. In the miniature Charpy test, a pendulum smashes into the solder ball. The compositions of the balls were Sn37Pb and Sn3Ag0.5Cu (and two containing zinc) and they were reflowed three times to solder mask defined Cu-pads with either OSP or ENIG finish. Some of the samples were aged at 150°C for up to 1000 h. With the shear test, fractures occurred in the bulk solder for the Sn37Pb and Sn3Ag0.5Cu solders on both OSP and ENIG pads, even for samples that had been aged at 150°C for 1000 h. Using the miniature Charpy test, i.e. a higher strain rate, the location of the fractures in the SnPb solder started to change from the bulk to the interface after 500 h aging on the OSP pads and after 1000 h aging on the ENIG pads. In contrast, for the SnAgCu solder fractures occurred at the interface even on the samples that had not been aged on both OSP and ENIG pads. The intermetallic layer on the OSP coated pads consisted of well developed layers of  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  after 500 h aging at 150°C for both solders and the  $\text{Cu}_3\text{Sn}$  layer had a lot of Kirkendall voids. On the ENIG pads, the intermetallic layer consisted of  $\text{Ni}_3\text{Sn}_4$  for the SnPb ball and of  $(\text{Cu,Ni})_6\text{Sn}_5$  for the SnAgCu ball.

First, it is a bit surprising that the solder joints with SnPb were more brittle on OSP pads compared to ENIG pads but may perhaps be explained by the formation of Kirkendall voids on the OSP pads (see Section 3.2.7). The increased brittleness of solder joints of SnAgCu solder to OSP pads compared to SnPb solder, even on non-aged solder joints, may again be due to either higher impact toughness of the lead-free solder or larger thickness and thereby higher brittleness of the IMC layer. For the solder joints to ENIG pads, the increased brittleness may also be affected by the changed composition of the IMC layer ( $\text{Ni}_3\text{Sn}_4$  for the SnPb ball and of  $(\text{Cu,Ni})_6\text{Sn}_5$  for the SnAgCu ball).

### 3.2.7 Brittle Fractures Caused by Kirkendall Voids

When Kirkendall voids are formed within an IMC layer, as is the case for the NiSnP layer formed on electroless nickel, the fracture may occur through the IMC layer. The Kirkendall voids reduce the mechanical strength of the solder joints and increase the risk for brittle fractures in the intermetallic layer when exposed to mechanical shock or vibration. Kirkendall voids have been observed both for tin-lead and lead-free solders but the most extensive formation of Kirkendall voids has been observed for aged lead-free solder joints to copper pads, although it has been questioned if the voids are true Kirkendall voids (see Section 2.2.1). In any case, the extent of voiding may become very large when solder joints are exposed to temperatures above 100°C for extended periods.

The voids may form both within the  $\text{Cu}_3\text{Sn}$  layer and at the  $\text{Cu}_3\text{Sn}/\text{Cu}$  interface. In the latter case, the  $\text{Cu}_3\text{Sn}$  layer may be almost completely separated from the copper [84, 95]. Chiu et al. have reported an 80% reduction in drop life for an assembly of a BGA component with SnAgCu solder balls that had been aged for 10 days at 125°C [84]. Both the BGA and the printed board had Cu pads. After 40 days, an almost complete separation had occurred at the Cu- $\text{Cu}_3\text{Sn}$  interface causing a failure at the first drop. The Kirkendall voiding process was active even at temperatures as low as 100°C. It can be noted that the total thickness of the complete IMC layer was only 2-4  $\mu\text{m}$  after 40 days aging at 125°C. According to Hillman, full separation of lead-free solder joints can be experienced in 6 to 7 years for products exposed to a constant 75°C, and the time frame may sometimes even be much shorter [144]. Therefore, formation of Kirkendall voids may reduce the resistance against brittle fractures much more than formation of brittle IMC layers.

According to Garner et al. addition of nickel to a SAC solder almost eliminate the growth of the  $\text{Cu}_3\text{Sn}$  phase during high temperature aging and can therefore be used to improve the interfacial strength [96]. However, addition of nickel to lead-free solders, either intentionally or by dissolution from an opposite nickel surface, has been reported to have caused a significant increase of the growth rate of the IMC layer on copper surfaces in some cases, which could affect the interfacial strength negatively [86, 99, 100].

### 3.2.8 Other Factors Affecting the Risk for Brittle Fractures

Luan et al. have performed FEM simulations of how the drop impact life is affected by lead-free soldering [21]. The results confirmed that the higher modulus of lead-free solders compared to SnPb solders decreased the drop impact life. Furthermore, an increase of the solder ball height as well as an increase of the ball diameter decreased the impact life. A decrease of board thickness and ball pitch will also lead to reduced shock performance [96]. Since these four latter changes improve the thermomechanical fatigue life, optimising the impact life may reduce the fatigue life.

Even when temperature cycling is the dominant stress mode, poor choice of finish and solder may cause brittle fractures. Ratchev et al. temperature cycled two

versions of a Polymer Stud Grid Array (PSGA) package; one standard and one with optimised CTE that provides lower strain on the solder joint [14]. The bond pads had Ni/Au plating (thicknesses and types not specified). When soldered with SnPbAg solder, a dual layer of  $\text{Ni}_3\text{Sn}_4$  and  $(\text{Au},\text{Ni})\text{Sn}_4$  developed on the nickel surface during temperature cycling between  $-40^\circ\text{C}$  to  $125^\circ\text{C}$  but brittle fractures in this dual layer only occurred for the standard package. That is, a certain level of strain was required for brittle fractures to occur, which the standard package provided but not the optimised package. When SnAgCu solder was used, no continuous layer of  $(\text{Au},\text{Ni})\text{Sn}_4$  formed during temperature cycling and brittle fractures did not occur, neither when the standard package was used nor when the optimised package was used.

Tu et al. tested the effect of intermetallic compounds on vibration fatigue of  $\mu\text{BGA}$  SnPb solder joints [19]. The CSP components having copper pads coated with  $1\ \mu\text{m}$  gold (no nickel) were soldered to a PCB having pads coated with nickel (probably electrolytic) and less than  $1\ \mu\text{m}$  flash gold. A weight of 56 g was bonded to the top of the  $\mu\text{BGA}$  components in order to speed up the vibration fatigue testing. For non-aged test vehicles, cracks occurred at the PCB side of the joints and it propagated in the  $\text{Ni}_3\text{Sn}_4$  IMC layer or along the  $\text{Ni}_3\text{Sn}_4/\text{Ni}$  interface. For samples aged at  $120^\circ\text{C}$ , the crack site tended to move to the component side of the solder joint with increasing aging time and after 20 days it mainly occurred on the component side. The crack initiated and propagated either at the  $\text{Cu}_6\text{Sn}_5/\text{solder}$  interface or at the  $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$  interface. After aging for more than 36 days, the crack site once more moved back to the PCB side of the solder joints. A continuous layer of  $\text{Ni}_3\text{Sn}_2$  had then formed at the  $\text{Ni}_3\text{Sn}_4/\text{Ni}$  interface. Despite the rather high gold content in the solder joints, it was not reported that  $(\text{Au},\text{Ni})_4\text{Sn}$  formed on top of the  $\text{Ni}_3\text{Sn}_4$  layer during aging. Maybe copper dissolved from the pads on the CSP components stabilised this phase in the solder joints. Nevertheless, the formation of a dual IMC layer seems to increase the risk for brittle fractures on both copper and nickel surfaces.

### **3.2.9 Impact of Palladium as Surface Finish on the Risk for Brittle Fractures**

If soldering is done to palladium, an intermetallic layer consisting of  $\text{PdSn}_4$  is formed if the palladium layer is not completely dissolved. This layer has been found to be prone to brittle fractures [81, 82]. On the other hand, plating of a thin electroless palladium coating on electroless nickel may reduce the brittleness of solder joints formed to electroless nickel, but then the palladium coating needs to be completely dissolved in the solder [82]. By applying electroless, i.e. autocatalytic, palladium to electroless nickel, dissolution of nickel will be prevented during the plating process and it will be reduced during the soldering process. Thereby, black pad defects will be eliminated and the thicknesses of the layers with  $\text{Ni}_3\text{P}$  and  $\text{NiSnP}$  intermetallic will be minimised. However, electroless palladium finishes often contain phosphorus just as electroless nickel does. It is not reported in the literature what happens with the phosphorus in palladium during soldering. That may indicate that a phosphorus-enriched layer is not formed as it is for electroless nickel but that has not been clarified. Therefore, as

long as it has not been clarified what happens with the phosphorus during soldering, palladium finishes containing high levels of phosphorus may pose a risk.

Arra et al. drop tested QFP components having a copper leadframe with different lead coating materials; Ni/Pd/Au, Sn15Pb, Sn2Bi, and matte tin [118]. The IMC layer on the leadframe coated with Ni/Pd/Au consisted of  $(\text{Cu,Ni,Pd})_6\text{Sn}_5$  formed on nickel whereas it consisted of  $(\text{Cu,Ni})_6\text{Sn}_5$  formed on copper in the other cases. In the latter cases, the nickel content was less than 1% and originated from the copper leadframe which contained some nickel as alloying element. The IMC layer formed on nickel, i.e.  $(\text{Cu,Ni,Pd})_6\text{Sn}_5$ , was found to be more brittle than  $(\text{Cu,Ni})_6\text{Sn}_5$  despite the fact that the latter IMC layer was almost twice as thick. That is, incorporation of Pd in  $(\text{Cu,Ni})_6\text{Sn}_5$  may make it even more brittle.

## 4 Test Methods for Assessing the Risk for Brittle Failures

If a test for assessing the risk for brittle fractures shall be adequate, there must be a clear correlation between the results from such a test and failures occurring in field conditions. Too often, tests are used because they are easy to use, inexpensive and/or give fast results, or just because they have been standardised, without considering whether they are relevant or not.

According to IPC-7095A, interfacial fracture happens on nickel surfaces under a high level of both applied strain and strain rate [11]. Nevertheless, the brittleness of solder joints is usually evaluated using shear and pull tests with low strain rate [51, 52, 53, 94, 115, 145, 146]. A few investigations have been performed where the results from tests with high strain and strain rate have been compared with results from traditional shear and/or pull tests [20, 22, 82, 84, 109, 140, 143]. They have all shown that especially traditional shear tests but also pull tests are not adequate for testing the risk for brittle fractures.

### 4.1 Comparison of Results from Traditional Shear and Pull Tests with Results from Other Tests

The results obtained by Date et al. [143] have already been discussed in Section 3.2.6. They showed that a traditional shear test failed to cause brittle fractures whereas a miniature Charpy test caused brittle failures for some combinations of solder, pad finish, and aging time. Furthermore, the solder joints obtained with SnAgCu solder to both OSP and ENIG pads were much more brittle than those obtained with SnPb solder.

Gregorich et al. tested the CSP components that occasionally had missing solder balls after final electrical testing (see Section 3.2.4) using a ball shear test, a ball pull test and a package peel test [109]. Balls were attached to the CSP components using two different reflow profiles; the original profile and one with shorter preheat time and time above liquidus and lower peak temperature. No brittle failures occurred during the shear and pull tests of any of the CSP components and the shear and pull strengths were about the same for the two groups and far exceeded the minimum performance requirements. In the peel test, components were soldered onto test PCBs and the assemblies were then manually bent until the solder joints failed. In this test, some solder joints to the CSPs soldered using the original profile showed brittle fractures with the same characteristics as observed for electrical tested components, but none to the components soldered using the modified profile. That is, propensity for brittle fractures could be detected with the peel test that apply a sudden abrupt force but not with traditional shear and pull tests.

Chiu et al. compared the results from drop tests of test boards with BGA components soldered to Cu-pads using SnAgCu solder with the results from ball shear and pull tests [84]. The test samples had been aged for various times at

125°C, which had produced Kirkendall voids at the Cu<sub>3</sub>Sn/Cu interface and within the Cu<sub>3</sub>Sn layer. After 10 days at 125°C, an 80% reduction in drop life was observed and after 40 days, an almost complete separation had occurred in the Cu-Cu<sub>3</sub>Sn interface causing a failure at the first drop. Although the shear strength decreased with aging time, the decrease was marginal after 10 days and only about 10% after 40 days. Also the decrease of the pull strength was marginal after 10 days but it was about 50% after 40 days. The failure mode was also analysed. For the shear test, no fractures occurred in the IMC layer after 10 days aging but after 40 days about 85% of the fractures occurred in this layer. The corresponding figures for the pull test were 25% and 100%, respectively. They concluded that ball shear testing and pull strength are not good indicators of shock reliability. Only the percentage of brittle failures in ball pull testing showed correlation with the results from drop testing.

Wong et al. shear tested solder balls of various compositions on organic substrates with different pad finishes: ENIG, HASL, OSP, and immersion tin [140]. The test boards had either solder mask or non-solder mask defined pads. Two shear speeds were used, 50 µm/s and 600 µm/s. With the low shear rate, fractures occurred through the bulk solder for both SnPb solder and the lead-free solders Sn3.5Ag and Sn3.8Ag0.7Cu. At the higher shear rate and solder mask defined pads, fractures still occurred in the bulk solder for the SnPb solder but mainly in the IMC layer for the lead-free solders on all finishes except HASL. For the non-solder mask defined pads, most failures were caused by pad-lifting from the substrate for all combinations of solder and finish except ENIG and lead-free solders that still fractured in the IMC layer. Again, the results indicate that a high shear rate is required to evaluate the risk for brittle fractures but also that lead-free solders are more inclined to brittle fractures than SnPb solders.

Hasegawa et al. shear tested eutectic SnPb solder balls attached to solder pads with various finishes [82]. They found that the shear speed needed to be 10 mm/min (170 µm/s) or more to cause brittle fractures for solder joints to ENIG.

According to Sykes from Dage Precision Industries, a shear rate needs typically to be greater than 1 m/s and a pull rate in excess of 0.5 m/s to test the resistance against brittle fractures [20]. Dage Precision Industries has in co-operation with many of the major manufacturers of BGA components developed equipment for high-speed shear and pull testing. Results from tests performed using this equipment has been presented by Newman [22]. Using the shear test, only at shear rates of 0.1 m/s or higher did interfacial fractures occur. For SnPb solder joints, interfacial fractures mainly occurred to ENIG surfaces. A few interfacial fractures were observed to electrolytic Ni/Au at shear rates of 1 and 4 m/s but none to copper. A considerably higher risk for brittle fractures to ENIG was observed when testing was performed within 2 days after reflow compared to testing after 1-6 months. SnAgCu solder joints had a significantly higher risk for brittle fractures at high shear rate than SnPb solder joints. For the lead-free solder, interfacial fractures dominated to both electrolytic Ni/Au and copper even at a shear rate of 0.1 m/s. No data were presented for SnAgCu solder joints to ENIG. Similar results were obtained when performing pull tests except that interfacial

fractures occurred at lower pull rates. For SnAgCu solder joints, brittle fractures occurred at a pull rate of 0.005 m/s when testing after 1-6 months.

## 4.2 Assessing the Risk for Brittle Fractures due to Dropping a Product to the Ground

Besides shear and pull tests, drop tests are often performed in order to evaluate the risk for brittle fractures. How the drop test is performed may have a large impact on the result. JEDEC has developed a standard for drop testing of components for handheld electronic products, JESD22-B111 [147]. For portable products, dropping it to the ground usually results in board bending. If a product with the assembly fixed in the corners is dropped with the assembly in a horizontal position, the interconnection stress due to board bending is 2 orders of magnitude higher than that due to acceleration according to Wong et al. [140]. For that reason, the JEDEC standard requires that the test board be mounted on a base plate with the components facing down. The board shall be fixed to the base plate in the four corners using 10 mm long standoffs to allow bending of the board. The base plate with the assembly is then dropped with the assembly in a horizontal position. The drop testing performed by Heaslip and et al. was done in a similar fashion [17].

It is stressed in the JEDEC standard that it is not meant to address drop test methods required to simulate shipping and handling related shock of electronic subassemblies. These requirements are addressed in JESD22-B110 [148]. According to this latter standard, subassemblies may be tested either in the free state or in a mounted state. If the mounted state is performed, the method of mounting to connecting member should be typical of production method. When tested in free state, shock should be applied to the assembly body in a manner to simulate expected impacts during processing, packaging, and packaged shipment. When testing in mounted state, shock should be applied to the connecting member upon which the subassembly has been mounted, using test fixturing in a manner such that the subassembly experiences the full specified test level. During the test, the connecting member should support the printed board of the assembly in a manner which best simulates usage condition of the subassembly, typically allowing the subassembly to flex during the shock test.

## 4.3 Assessing the Risk for Brittle Fractures during Manufacture and Shipping

IPC and JEDEC have developed a joint standard for characterising the fracture strength of a component's board-level interconnects when exposed to monotonic bending [149]. The monotonic bend characterisation results provide a measure of fracture resistance to flexural loading that may occur during conventional non-cyclic board assembly and test operation, and supplements existing standards that address mechanical shock or impact during shipping, handling, or field operation. The test board material, thickness, metal layer count, surface finish, and land pad design should match the actual end-use printed board. A four-point bend test is

used to characterise the fracture strength. Since storage conditions and storage duration affects the fracture resistance, it is required that testing is performed minimum eight hours and maximum 168 hours after soldering. According to Bansal et al., components tested within an hour after soldering have lower brittle fracture strength compared to components tested a few weeks after soldering [12]. Therefore, waiting too long before testing may lead to an underestimate of the risk for brittle fractures during handling directly after soldering.

In another standard developed by IPC and JEDEC, guidelines are given for how to perform strain gage testing in order to assess the strain and strain rates a Surface Mount Technology (SMT) package is subjected to during PCB assembly, test and operation [150, 151]. It is stated in the standard that *“Many board assemblers are now required to operate under strain levels specified by their customers or component suppliers”*. *“PWB strain measurement includes application of strain gages to the board at specified components, and then subjecting the instrumented board to various test and assembly operations. Test and assembly steps which exceed strain limits are deemed excessive and are identified so that corrective actions can be made. Strain limits may come from the customer, component supplier or internal best known practices”*. Examples of strain measurement criteria are given in an appendix. Manufacturing steps that can cause strain-induced failures and therefore may need to be characterized include:

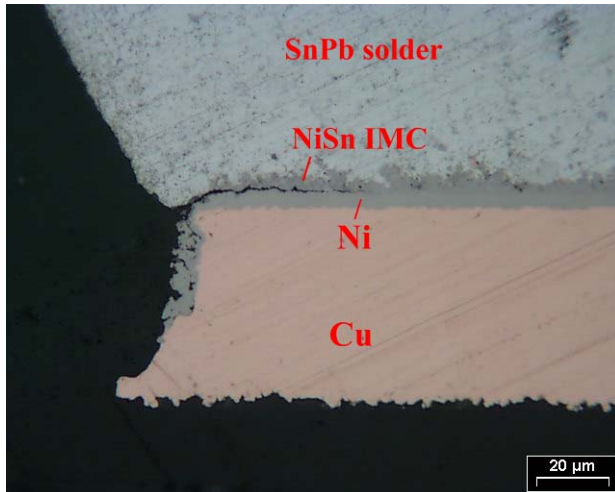
- 1 SMT assembly process: board depanelisation, all manual handling processes, all rework and retouch processes, and connector and component installation.
- 2 Board test processes: In-Circuit Test and Board Functional Test
- 3 Mechanical assembly: heat sink assembly, board support/stiffener assembly, system board integration, Peripheral Component Interconnect or daughter card installation and Dual In-line Memory Module installation
- 4 Shipping environment

The strain is measured on the PCB near the components, preferably as close as possible to all corners of a component, either on the top or underside of the board [13]. While the strain within the solder joint cannot be directly measured, results do correlate with data on brittle fractures. In order to test the ultimate strain-to-failure of a component, a board is tested at increasing strain levels until electrical failure is detected [96].

#### **4.4 Brittle Fractures Caused by Thermomechanical Stress During Soldering**

It is claimed in IPC/JEDEC-9704 that because solder joints are formed only after reflow, strain characterization is required only for assembly and test operations following SMT reflow [150]. That is not true. The solder joint is formed when the solder solidifies and, therefore, high strain and strain rate occur already in the cooling phase during soldering. It will also occur during the heating phase in a following soldering operation. I have not found anything reported in the literature

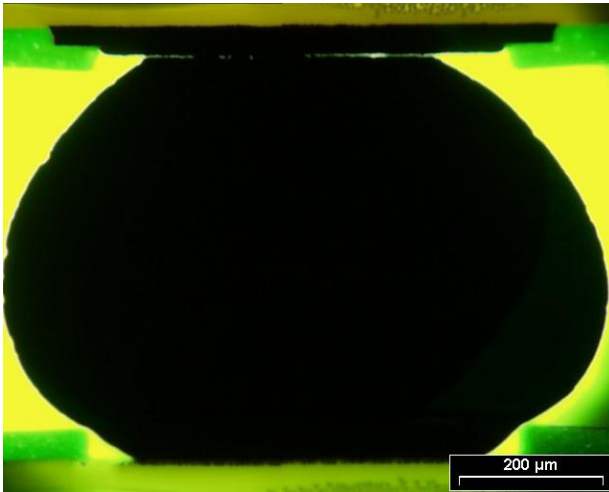
about the risk for brittle fractures during soldering but failure analyses performed at IVF have indicated that brittle fractures may occur during soldering operations. Figure 1 shows a cross-section of a corner solder joint to a large PBGA (ca 45 mm x 45 mm) after soldering. A crack has been initiated at the IMC/Ni interface, most likely during the cooling phase in the soldering process although it is also possible that it has been caused by bending of the board after soldering.



*Figure 1 Cross-section of a corner solder joint to a large PBGA showing an initiated crack formed at the IMC/Ni interface on an ENIG solder pad.*

Another example of a brittle fracture that occurred during soldering is shown in Figure 2. The figure shows a BGA that have passed a second reflow soldering process after which it displayed intermittent failures. The BGA have four peripheral rows of solder joints and the figure shows one of the solder joints in the inner row. As shown in the figure, the solder does not wet to the solder pad on the component. The shape of the solder joint indicates that it has melted during the second soldering process. Most likely, what has happened is that the outer rows of solder joints melted first and all stress caused by the increased temperature was concentrated on the solder joints in the inner row. This caused a brittle fracture at the pad interface for the solder joint shown in Figure 2. Then the solder joint melted. Since no flux was present and an intermetallic layer probably covered the surface, the molten solder failed to wet the pad surface.

In both these examples, the solder connections consisted of tin-lead solder. The creep rates of most lead-free solder are considerably lower than for tin-lead solder [152]. The lower creep rate combined with a higher peak temperature during soldering will likely increase the risk for that brittle fractures occur when soldering using lead-free solders.



*Figure 2 Cross-section of a solder joint to BGA that has passed a second reflow soldering process. The sample has been moulded in epoxy with an added fluorescent agent and has been examined using UV-light.*

## 5 Conclusions

Brittle fractures in tin-lead solder joints are mainly a problem for solder joints to ENIG finishes. For products exposed to high temperatures, embrittlement may also occur of solder joints to electrolytic nickel/gold. Solder joints to copper are not prone to brittle fractures unless the solder joints have been exposed to high temperatures for a very long time.

Lead-free solder joints are more inclined to brittle fractures than tin-lead solder joints. There are mainly two reasons for that. First, the higher elastic modulus of lead-free solders compared to tin-lead solder makes the solder joints less compliant. Second, the IMC layers formed during lead-free soldering are usually thicker and more complex compared to those formed with SnPb solder.

Most worrying is the fact that solder joints to copper no longer will be immune to embrittlement. The embrittlement of solder joints to copper is caused by extensive formation of Kirkendall voids. Fortunately, these voids are only formed at relatively high temperature. Since impurities in the copper seem to be a major cause for the formation of Kirkendall voids, a remedy may be found.

Ternary intermetallic phases,  $(\text{Ni,Cu})_3\text{Sn}_4$  and  $(\text{Cu,Ni})_6\text{Sn}_5$ , are formed on nickel surfaces when soldering using copper-containing lead-free solders. They may also form when soldering using SnAg solder and an opposite surface consists of copper.  $(\text{Cu,Ni})_6\text{Sn}_5$  may then form also on the copper surface. Under certain conditions a dual layer of  $(\text{Ni,Cu})_3\text{Sn}_4$  and  $(\text{Cu,Ni})_6\text{Sn}_5$  may form. Intermetallic layers containing the ternary phases are reported to be more brittle than layers containing the binary phases  $\text{Ni}_3\text{Sn}_4$  and  $\text{Cu}_6\text{Sn}_5$ , especially when a dual layer is formed. More research needs to be done to clarify the roles of these phases in the embrittlement of solder joints.

Assemblies having large area array components are most vulnerable to brittle fractures. Bending of these may cause high strain and strain rate in the solder joints. Due to residual stresses in the solder joints after soldering, solder joints are more inclined to brittle fractures the first days after soldering and they are especially vulnerable directly after soldering. Therefore, they need to be handled carefully during manufacture, testing and shipping in order to avoid bending. The risk for brittle fracturing under such processes can be evaluated using strain gages. Brittle fractures may also be caused by fast temperature changes, mechanical shock and vibration. It may be the result of one single high-strain event or of many consecutive events at a lower strain level. IPC and JEDEC have developed test methods for bending and drop testing of assemblies to be used for characterising the fracture strength of the solder joints.

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