Chapter 8
Impact of Black Pad and Intermetallic Layers on the Risk for Fractures in Solder Joints to Electroless Nickel/Immersion Gold

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8.1 Introduction

When frequent fractures were observed in solder joints to ball grid array (BGA) components in the late nineties, these were first associated with a plating defect in electroless nickel/immersion gold (ENIG) finishes called “black pad”. The inclination for fractures is then caused by a poorly developed intermetallic layer on solder lands affected by the black pad defect. Later, it has been realised that fractures to ENIG finishes may occur even when a proper intermetallic layer is formed. The fractures then occur as fractures in the intermetallic layer or between two intermetallic phases in the intermetallic layer. However, it may often be difficult to determine whether a fracture to an ENIG surface is caused by the black pad defect or by a fracture in the intermetallic layer. Since the two failure mechanisms cannot be completely separated from each other, both will be described. The characteristics of fractures due to the black pad defect and the mechanisms causing black pad defects will first be discussed. The mechanism for fractures in the intermetallic layer will then be discussed.

8.2 Failure Mechanisms

8.2.1 Fractures Due to “Black Pad” Defects

The defect “black pad” on an ENIG finish was first reported in 1990 for flip chips soldered to electroless nickel/immersion gold-coated substrate pads [1]. When the flip

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G. Grossmann and C. Zardini (eds.), *The ELFNET Book on Failure Mechanisms, Testing Methods, and Quality Issues of Lead-Free Solder Interconnects*,
DOI: 10.1007/978-0-85729-236-0_8,

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 Ni_3P present on the nickel surface and it was concluded that it was this phase that caused the dewetting. Therefore, it was initially believed that the black pad defect was caused by the phosphorus content 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 in the phosphorus content rather increases the risk for the black pad defect [2–4]. In fact, Cordes and Huemoeller obtained very poor shear strength for solder joints to surfaces with immersion gold on electrolytic nickel, i.e. a phosphorus-free nickel, but also excellent shear strength of solder joints to surfaces with electrolytic gold on electroless nickel [3]. These results indicate that the enrichment of phosphorus on the nickel surfaces is not the cause of the increased risk for solder joint failures. Instead, the enrichment is a consequence of the mechanism causing the increased risk for failures.

Very large efforts have been made to understand what causes the black pad defect and how to prevent it. Although the frequency of the black pad defect has been reduced due to various actions performed, black pad defects still occurs and there are differing opinions of what causes it and how it should be prevented.

The known characteristics of the black pad defect give important clues to the mechanisms causing the defect but also for identifying when a fracture is due to the black pad defect. The most typical characteristics are as follows:

- poorly developed and/or locally missing intermetallic layer in the 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 the black pad defect 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 then 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 occur mainly on boards coated with solder masks

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

8.2.1.1 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:

$$\mathrm{Me(1)}^{n+} + ne^- \rightarrow \mathrm{Me(1)} \tag{8.1}$$

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

$$\mathrm{Me(2)} \rightarrow \mathrm{Me(2)}^{n+} + ne^- \tag{8.2}$$

where Me(2) may be the same metal as Me(1) or it may be another metal. The anodic reaction may, for example, also be oxidation of water:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{8.3}$$

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 more indirectly affect them. 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:

$$\mathrm{Me}^{n+} + \mathrm{Red} \rightarrow \mathrm{Me} + \mathrm{Ox} \tag{8.4}$$

where Red is the reducing agent and Ox the oxidised form. In an autocatalytic process, the deposit metal catalyses the reaction 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. Plating processes for electroless (autocatalytic) nickel use almost exclusively hypophosphite as reducing agent. The reaction when hypophosphite is used is very complex but it can be simplified and written as: [5]

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+ \tag{8.5}$$

In addition, the following reaction occurs simultaneously:

$$3H_2PO_2^- \rightarrow H_2PO_3^- + H_2O + 2OH^- + 2P \tag{8.6}$$

As a result of the latter reaction, phosphorus is co-deposited in the nickel coating. The phosphorus content may vary from 1 to 13 wt%.

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 conditions do not change.

Another non-electrolytic plating process is *immersion plating*, which 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:

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu \tag{8.7}$$

The total reaction is the same as occurs 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 anodic and cathodic reactions occur on the same surface.

Although immersion plating can be achieved with many combinations of substrate and plating metals, the depositions 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 under the plated metal may lead to that the latter lose adhesion. Second, and perhaps most important, the deposition rate is basically determined by the difference in electrochemical potential for the substrate and the plated metal (difference in nobility) and thus is difficult to control. If the difference in electrochemical potential is large, the initial plating rate will 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 diminish immersion plating. 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 the addition of complexing agents to the bath and, by this means, the plating rate can 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.

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 per unit area at 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 per unit area at anodic surfaces will increase as more of the 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 and 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 exposes new surfaces beneath the plated metal layer. The best solution to avoid this type of over-etching 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.

8.2.1.2 Immersion Gold Plating on 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 since 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 were affected by the phosphorus content in the electroless nickel [3]. 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 8.1). It was not described how the deposition rate was determined but obviously it must have been measured as the average value of deposition rate 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

Table 8.1 Effect of nickel composition on the deposition rate and adhesion of the gold deposit [3]

Phosphorus content (%)	Deposition rate (μm/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

correlation; the higher the deposition rate, the poorer the adhesion. Poor adhesion indicates that over-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 [5]. These results clearly show that it is not the phosphorus in the nickel coating that is the cause of the black pad defect.

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. These residues will make it difficult to wet the surface by a solder. They may also 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 the black pad defect [6]. If this film is thick enough, it may prevent wetting the gold layer by solder. However, it is usually no problem to wet the gold layer on surfaces affected by the black pad defect. Thus, this film is normally too thin for preventing wetting. It is residues and corrosion products beneath the gold layer that hinder good wetting on electrolytic nickel. However, the thin nickel oxide film offers an opportunity to non-destructively detect surfaces affected by the black pad defect.

On electroless nickel, the dissolution of nickel during the immersion plating causes an enrichment of phosphorus at the surface. Chan et al. have reported that phosphorus is enriched in the uppermost 150 Å of the nickel layer when 0.7–0.8 μm immersion gold is deposited on electroless nickel with 8–10 wt% phosphorus [4]. The phosphorus content in the enriched layer was maximum 20 wt%. This is in agreement with the results from other investigations that have shown that the phosphorus content in the enriched layer is usually 2–3.5 times higher than in the electroless nickel [4, 7–10].

The enrichment of phosphorus has a negligible effect on the wettability of the nickel surface in a soldering process. However, when the black pad defect occurs, extensive etching of the nickel may take place leading to a much thicker layer with enriched phosphorus. This increase in thickness of the layer with enriched phosphorus may be the reason for the difficulties to properly wet surfaces with black pad defects. However, entrapped bath residues and the oxidation of exposed nickel surfaces are probably the main reasons. This is supported by the finding of higher oxygen content associated with black pad regions [11].

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. Microsections of solder pads with the black pad defect often show gold spikes that penetrate downward from the surface along the nickel nodule boundaries [7, 9, 10, 12]. 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 [13]. 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 time. This type of corrosion damages can probably only be prevented by assuring that there are no crevices between the nickel nodules. That can be achieved by a slow rate of nickel deposition which reduces the sizes of the crevices [13]. It can also be achieved by increasing the phosphorus content in the nickel. According to Lamprecht et al., a smoother surface without crevices between the nickel nodules is achieved if the phosphorus content is increased to 11.2 wt% [14]. The extent of the corrosion damages during immersion gold coating will also be affected by the plating time and by the chemistry of the plating bath.

In other cases, corrosion of the nickel is observed as a more or less continuous black band beneath the gold coating [7, 9]. The black band may be confined to a few nodules or cover a large area of the pad and have a thickness of 1 μm. When 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 [7]. 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 if the phosphorus content is high. Eslambolchi et al. noted a correlation between phosphorus content and immersion gold thickness where higher phosphorus content led to a thinner gold layer [2]. A thinner gold layer indicates that it is less porous.

Obviously, it is possible to balance an immersion gold process for electroless nickel coatings with different phosphorus content. Thus, it is only possible to specify optimal phosphorus content in the electroless nickel for a defined gold-plating bath. If the chemistry of the immersion gold bath is changed, the optimal phosphorus content in the electroless nickel may also be changed. Furthermore, a changed reactivity of the plating bath or of the electroless nickel with time may put the balance out of order. Whereas it was previously recommended that the phosphorus content was in the range 6–10 wt% [3, 4, 15], it has during the last years been recommended to increase the phosphorus content to 9.5–13 wt% [8, 14]. According to Johal et al., the maximum thickness of the gold layer that can be achieved on high-phosphorus electroless nickel is 0.06 μm [14].

In contrast to the findings by most others, Roepsch et al. have reported that they found an increased risk for the black pad defect with increasing phosphorus content in the electroless nickel [11]. In their investigation, they compared samples from different batches from various printed circuit board manufactures. 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) in the plating bath but also the reactivity of the nickel increases with the number of MTO [5, 16]. Thus, increased phosphorus content in the samples may have been due to that they have been plated in baths with a high MTO, which has caused a higher reactivity of the nickel. This may explain the correlation between increased risk for the black pad defect and a high phosphorus content.

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 [5, 13, 15]. The main stabilisers used are sulphur-containing compounds and lead [12]. Although they are added to concentrations of only 0.5–1.0 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 in the concentration of the sulphur compound from 0.3 to 1.0 ppm will cause a decrease in the phosphorus content and, more important, a considerable increase in the reactivity of the nickel. Also an increase in 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 have control of the reactivity of the nickel coating.

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 [12]. By soaking a solder mask in deionised water and then using this water for making up an electroless nickel bath, they could prove that the solder mask leached substances that caused increased plating rate and increased reactivity of the nickel coating and even caused black pad defects when it was followed by immersion gold plating. Solder masks are often intentionally under-cured when applied to PCBs in order to increase the pliability and reduce the risk that they crack or detach during ENIG processing. Under-curing makes it easier for compounds to leach out. Crouse and Cullen showed that the impact of contaminants leaching from solder masks could be reduced by additional curing and by more effective cleaning of them. Since the black pad defect has been reported to occur mainly on solder mask-coated PCBs [12], 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 [11] supports this conclusion.

The black pad defect is often stated to be due to a hyperactive corrosive immersion gold process [4, 7, 8]. A too high temperature of the gold bath or a too high gold concentration can cause a too aggressive attack [13]. It can be noted that when the black pad defect was first observed, the problem was dissolved by increasing the thickness of the gold layer [1]. 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. The thicker gold coating was achieved by using a loosely complexed gold bath, i.e. a more aggressive bath.

However, in most cases, it is probably not an increased activity of the gold-plating bath but an increased reactivity of the nickel surface that causes the excessive corrosion. 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 [2]. Even if the phosphorus content is kept constant, the reactivity of the nickel may vary significantly as discussed. 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 s [12]. Another method is to measure the time it takes before the nickel surface turns black when it is dipped in nitric acid [16].

To achieve an even gold coating, it is important that the nickel surface is clean and has a minimum of oxides. 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. Chan et al. has shown that the number of corrosion defects increases with increasing hold time between electroless nickel and post-rinse steps [4]. Contamination and oxide layers may cause poor adhesion of the gold layer and that it becomes porous. 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 and other areas will be predominantly anodic areas during the gold-plating process. 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 and 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 localised to specific pads on a PCB [7]. Surfaces affected by the black pad defect are often connected to larger surfaces not affected by the black pad defect [17] and usually they are found on boards with complex circuitry [12]. The fact that black pad defects appears to occur more frequently on finer pitched parts with smaller pads than on larger pads [18] may also be caused by leakage from the solder mask which could have a 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 [2, 7, 9, 19], typically about twice as thick as normal [11]. This increase in gold thickness is not large enough to be used as an indication of black pad defects. 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 used but the gold coating will then likely have less protective properties [5].

8.2.1.3 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 [2]. The defect will then not be discovered until a failure occurs which may happen when the assembly is exposed to stress. A fracture will then take place between the intermetallic layer and the nickel surface. Little to no remaining Ni–Sn intermetallic phases are observed on the nickel surface [2, 7, 8].

When a solder joint with the black pad defect is 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 the black pad defect but according to Chan et al., there is no evidence that such spikes have any effect on solder joint strength [4]. Corrosion damages in the form of a band at the surface are 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 [10].

8.2.2 Brittle Failures in Intermetallic Layers

It has been recognised that also a second failure mode may cause fractures to ENIG [20, 21]. 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 [20]. However, for properly formed solder joints, it may be difficult to clearly distinguish this failure mechanism from that caused by black pad defects and it is likely that the two failure mechanisms interact.

Since these fractures have appearances of brittle fractures, they are often referred to as brittle fractures. In some cases, they are true brittle fractures but in other cases, they are rather interfacial fractures between two layers with different compositions.

According to Sohn et al. [22] and Mattila and Kivilahti [23], the interfacial cracking in solder joints on electroless nickel not having a black pad defect occurs in a very thin Ni–Sn–P layer formed on top of the layer with enriched phosphorus. That is, for both failure mechanisms, the fracture occurs between the Ni–Sn intermetallic layer and the layer with enriched phosphorus on the nickel surface. Thus, very little Ni–Sn intermetallic phases will remain on the nickel surface in both cases.

Neither is the presence of a nickel layer with enriched phosphorus a 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. Furthermore, 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 [4]. Thus, wetting during soldering must always occur to a nickel surface with enriched phosphorus. Hence, the formation of a nickel surface with enriched phosphorus as such does not seem to cause a non-wettable surface. Most probably, it is the over-etching beneath the gold layer leading to entrapment of bath residues and exposure of the nickel surface to oxidation that causes 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 [3]. Since the function of the gold layer is to preserve the solderability by preventing oxidation of the nickel surface, over-etching will reduce that function.

The composition of the phosphorus-enriched layer formed during soldering is usually specified to be Ni_3P which corresponds to a phosphorus concentration of 15 wt%. In comparison, the phosphorus content in the enriched layer formed during immersion gold plating is normally specified to be between 10 and 20 wt%, i.e. in the same order. Hence, the properties of the phosphorus-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 how a high phosphorus content affects the reliability of the solder joints. According to Bulwitch et al. [8] and Lee [16], high-phosphorus nickel increases the risk for brittle fractures caused by phosphorus enrichment during soldering and subsequent thermal excursions. On the other hand, Johal et al. have reported that high-phosphorus nickel not only decreases the risk for the black pad defect but also improves the reliability of the solder joints [14]. They tested how the phosphorus content affected the shear strength of Sn–Ag–Cu balls before and after 1,000 temperature cycles between –55 and +125°C. Before temperature cycling, shear tests of solder balls to nickel coatings with 8.0 and 11.2 wt% P gave consistent results with high values and little spread in shear force, whereas solder balls to a nickel coating with 4.2 wt% P showed a wide spread in shear force with considerably lower shear force for some solder balls. After temperature cycling, also the solder balls to the nickel coating with 8.0 wt% P gave a large spread in shear force, while the solder balls to the nickel coating with 11.2 wt% 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 wt% P showed partial brittle fractures, whereas the fractures to the nickel coating with 11.2 wt% P showed ductile fractures. The structures of the intermetallic layers were examined by stripping off the solder. The intermetallic layer on the nickel coating with 8.0 wt% P had a structure that was courser and less dense compared to the intermetallic layer on the nickel coating with 11.2 wt% P. They proposed that the difference in structure was due to differing dissolution rate of nickel during soldering and ageing. Less nickel should be dissolved from the more corrosion-resistant high-phosphorus nickel.

As discussed previously, recently performed investigations indicate that fractures on electroless nickel not affected by the black pad defect occur in a thin Ni–Sn–P layer between the Ni_3P and Ni–Sn intermetallic layers [22, 23]. In the investigation done by Mattila and Kivilahti, a Sn–Ag–Cu solder was used to solder chip scale packages (CSP) to ENIG and a porous microcrystalline or amorphous thin Ni–Sn–P layer with the composition $Ni_{55}Sn_{45}P_{10}$ was formed between the Ni_3P layer and a layer of $(Cu,Ni)_6Sn_5$. Cracking occurred in the Ni–Sn–P layer when the assembled CSPs were exposed to a drop test. 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 Ni–Sn–P layer for the test vehicles soldered with the Sn3.5Ag solder. The Ni–Sn–P layer in this case was formed between the Ni_3P layer and a layer of Ni_3Sn_4, it was nanocrystalline with Kirkendall voids and had a composition of Ni_3SnP. The reason why brittle cracking only occurred for the Sn3.5Ag solder was claimed to be due to spalling of the Ni_3Sn_4 layer and thereby larger consumption of nickel during soldering. This resulted in an increased growth of the Ni–Sn–P layer. The shear rate used for testing was only 0.2 mm/min. A higher shear rate may have caused brittle fractures also for the Sn3.0Ag0.5Cu solder joints.

Obviously, solder joints to electroless nickel are prone to brittle fractures regardless if the intermetallic layer consists of Ni_3Sn_4 or $(Cu,Ni)_6Sn_5$. However, the growth rate of the intermetallic layer and its thickness may be important for the brittleness of the solder joint. It will affect the thickness of the Ni–Sn–P 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. That may explain the finding by Johal et al. that high-phosphorus nickel improves the resistance against brittle fractures. Consequently, if the conclusion is correct, it will mean that some enrichment of phosphorus in the nickel surface during immersion gold plating may 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 occurs to the nickel surface.

8.3 Test Methods for Detecting Black Pad Defects and Assessing the Risk for Brittle Fractures

8.3.1 Detection of Black Pad Defects

The method using LVSEM and EDS with a low electron beam voltage to detect a thin film of nickel oxide on top of the gold layer reported by McFaddin is a non-destructive method that can be used to detect black pad defects on PCBs [6]. This is a good indication of black pad defects. However, the size of the LVSEM chamber will set a limit of the size of the PCBs that can be non-destructively analysed.

A destructive but probably more reliable method to detect black pad defects on PCBs is to dissolve the immersion gold layer using a cyanide strip and then examine the nickel surface using SEM [7, 10, 15]. Areas with black pad defects will then have a mud-cracked appearance with black regions around the nickel nodules.

Another destructive method that can also be used for assembled boards is cross-sectioning of the solder lands [6, 7, 9–11, 19]. Corrosion damages of the nickel layer in the form of spikes and black bands can then be detected and for assembled boards, poorly developed intermetallic layers, all indicators of black pad defects.

Another possibility is to expose assembled boards to environmental stress screening (ESS). By performing ESS tests utilising fast temperature changes and/or exposure to vibration, black pad defects can be stimulated to precipitate as failures. Thereby, assemblies having black pad defects can be detected.

8.3.2 Tests for Assessing the Risk for Brittle Fractures in Intermetallic Layers

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 [21]. Nevertheless, the brittleness of solder joints is usually evaluated using shear and pull tests with low strain rate [14, 22, 24–28]. 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 [29–35]. They have all shown that especially traditional shear tests but also pull tests are not adequate for testing the risk for brittle fractures.

According to Sykes, 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 [29]. Newman has presented results using equipment for high-speed shear and pull testing [30]. Using the shear test, only at shear rates of 0.1 m/s or higher did interfacial fractures occur. For Sn–Pb 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. Sn–Ag–Cu solder joints had a significantly higher risk for brittle fractures at high-shear rate than Sn–Pb 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 Sn–Ag–Cu solder joints to ENIG. Similar results were obtained when performing pull tests except that interfacial fractures occurred at lower pull rates. For Sn–Ag–Cu solder joints, brittle fractures occurred at a pull rate of 0.005 m/s when testing after 1–6 months.

8.3.3 Standards Developed for Assessing the Risk for Brittle Fractures

JEDEC has developed a standard for drop testing of components for handheld electronic products, JESD22-B111 [36]. For portable products, dropping 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. [33]. 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.

In another JEDEC standard, JESD22-B110 [37], guidance is given for how to simulate shipping- and handling-related shock of electronic subassemblies.

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 [38]. 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. 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 8 h and maximum 168 h after soldering.

In another standard developed by IPC and JEDEC, guidelines are given for how to perform strain gage testing, and in order to assess the strain and strain rates, a surface mount technology (SMT) package is subjected to during PCB assembly, test and operation [39, 40]. Manufacturing steps that can cause strain-induced failures and therefore may need to be characterised include:

- SMT assembly process: board depanelisation, all manual handling processes, all rework and retouch processes, and connector and component installation.
- Board test processes: in-circuit test and board functional test.
- 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.
- Shipping environment.

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