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High Phosphorous Electroless Nickel Process for Mobile Phone PWBs

Masahiro Nozu, Akira Kuzuhara, Atsuko Hayashi,
Hiroshi Otake, and Shigeo Hashimoto
C.Uyemura & Co.,Ltd.
Osaka, Japan

Donald Gudeczauskas
Uyemura International Corporation Technical Center
Southington, CT

Abstract

An Electroless Nickel and Immersion Gold (ENIG) plating process with a middle phosphorous content nickel layer is currently a mainstream final finishing application for mobile phone Printed Wiring Boards (PWB). As a trend according to the worldwide market growth of mobile phones, the demand for higher resistance characteristics in corrosive environments for ENIG finished boards has increased. Although various methods have been introduced as an evaluation method for higher corrosion resistance, sulfurous acid gas (SO_2 gas) testing is a recent area of industry focus. However, because of the significant corrosive characteristic of SO_2 gas, the conventional ENIG layer cannot tolerate this testing method, and thus has become an area of major concern. As a result, a high phosphorous nickel ENIG plating process, which inhibits higher resistance in a corrosive environment compared to a middle phosphorous process, is being adopted as a final finishing method. However, several other factors of the total plating process that may influence corrosion resistance have not been verified or fully investigated. Therefore, in this study we introduce ENIG plating layer characteristics required for higher resistance in corrosive environments by investigating corrosion conditions of ENIG layers caused by SO_2 gas testing, and furthermore conduct observations on factors that influence these ENIG characteristics.

Introduction

Middle phosphorous ENIG plating has conventionally been utilized as a final finishing process for mobile phone PWB applications, however, due to concern of resistance characteristics against corrosive environments, one industry focus is the adoption of a high phosphorous ENIG process. In this study, in order to clarify ENIG characteristics necessary for higher corrosion resistance, we review corrosion conditions of various ENIG layers by conducting corrosive SO_2 gas testing, which is a key method frequently used to evaluate corrosion resistance. Evaluations were conducted by investigating corrosion conditions and also corrosion area locations. Also, in order to clarify resistance against SO_2 gas corrosion, we introduce a corrosion model case in consideration of Ni formation. Furthermore, factors that effect SO_2 gas corrosion resistance, such as corrosion resistance of Ni and immersion Au plating layer, formation of Ni plating layer, and local corrosion of immersion Au plating and OSP treatment will be discussed. Although reliability issues such as Au peeling, solder resist lift off and skip plating are also issues of concern regarding a high corrosion resistant ENIG plating process, which typically utilizes a high phosphorous electroless nickel, we have limited reports in this study to SO_2 gas corrosion characteristics in order to focus on environmental resistance issues.

As a precondition, investigation was conducted in consideration of mainstream Selective PWBs (partial plating PWBs). For Selective PWBs, dry film resist (D/F) is applied to portions where solder joint connections are necessary, and after ENIG plating is conducted, Organic Solderability Preservative (OSP) finishing is conducted on the solder joint connection portions after this D/F is removed. We will also report on the influence that OSP finishing has on SO_2 gas corrosion. Dissolution from the D/F may affect the ENIG plating process by causing phosphorous content increase in the nickel layer, skip plating and deposition rate deterioration. However, we will omit reports concerning D/F dissolution in this study because this dissolution does not significantly influence SO_2 gas corrosion results.

Test Condition

A typical ENIG finishing process for selective mobile phone PWBs is shown in Table 1. Test substrates were selective mobile phone PWBs in market distribution or SO_2 gas test evaluation boards (Cu substrate for evaluation : 1cm x 1cm) that are manufactured by the same process as selective PWBs. Unless specifically stated, the pretreatment process of the ENIG plating process is according to Table 1.

Table 1 – ENIG Plating Process for Selective PWBs

	Chemical
Cleaner	Commercial Product
Etching	SPS+ H_2SO_4
Acid rinse	H_2SO_4
Pre-dip	H_2SO_4
Activator	Commercial Product
Electroless Ni	Commercial Product
Immersion Au	Commercial Product
Remove D/F	NaOH
Pretreatment of OSP (Cleaner)	Commercial Product
Pretreatment of OSP (Etching)	SPS+ H_2SO_4 or H_2O_2+ H_2SO_4
OSP	Commercial Product

Electroless Ni (high %P) and Immersion Au plating were conducted by utilizing commercial products with various bath content concentration, pH and bath temperature in order to obtain the fixed plating thickness and characteristic. However, conventional middle phosphorous ENIG plating layers were obtained by utilizing different commercial products. Standard plating thickness for Ni was 4~5µm, and 0.04~0.08µm for Au. Phosphorous content within Ni plating layers were measured by Fluorescent X-ray analysis.

SO_2 gas testing was conducted in a desiccator with the SO_2 concentration maintained within 10±3 ppm by utilizing a Na_2SO_3, K_2HPO_4 and KH_2PO_4 mixed solution as the gas source. The test boards were treated in this SO_2 gas atmosphere for 24hours at 41.5℃ before evaluation. Optical observation of appearance, surface Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) analysis, and cross section Focused Ion Beam (FIB) observation were conducted.

Investigation of Corrosion Condition

Observation of Corrosion Condition

A typical middle phosphorous nickel ENIG plating layer after SO_2 gas testing is shown in Figure 1. Spot shaped discoloration can be determined from this observation. SEM observation of these discoloration sections are shown in Figure 2, and from EDS analysis Ni,O,S was detected from the island-like corrosion sections. Cross-section FIB observation of the island-like corrosion sections showed that the corrosion areas seemed to cover the plating layer (Figure 3).

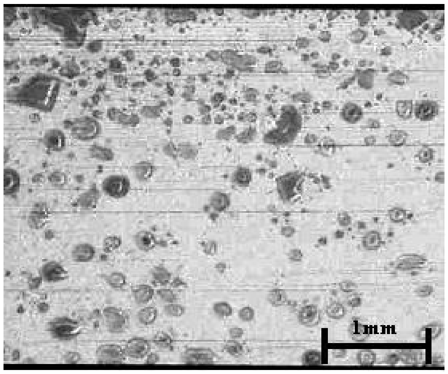


Figure 1 – Middle P ENIG Surface after SO_2 Gas Test (Pad Portions on PWB)

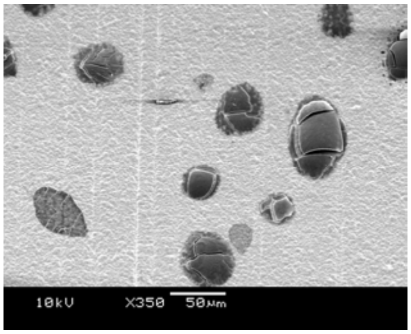


Figure 2 – SEM Observation of Corrosion

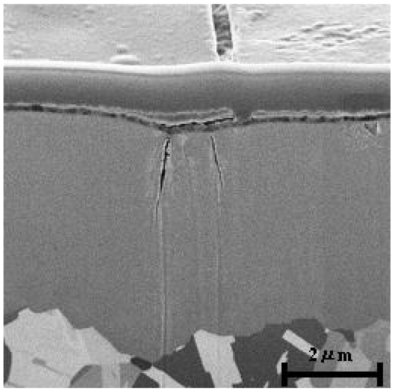


Figure 3 – FIB Cross Section Observation of Corrosion

After physically removing the corrosion areas, as shown in Figure 4, a crack suspected to be the source of corrosion was confirmed. By conducting FIB cross-section observation of this portion, it was confirmed that corrosion generating from this point extended down to the Cu surface (Figure 5). Therefore, these results demonstrate that corrosion on the ENIG surface caused by SO_2 gas extends vertically downward, and the corrosion substances (including Ni,O,S) that materialize on the ENIG surface cause a discoloration phenomenon as shown in Figure 1.

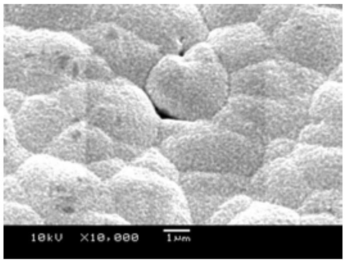


Figure 4 – SEM Observation of Corrosion Spot Existing in Corrosion Area

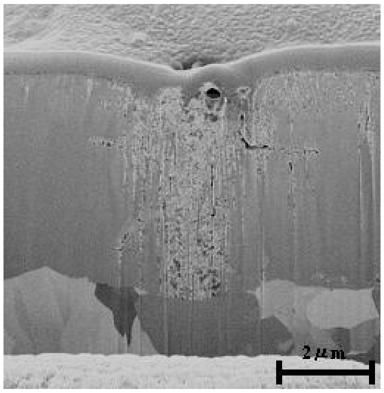


Figure 5 – FIB Cross-Section Observation of Corrosion Spot

Corrosion Area Locations

By observing the corrosion area locations of high phosphorous and middle phosphorous nickel ENIG layers, it was determined that a major portion of these corrosions could be confirmed at the grain boundaries of the nickel layer, as shown in Figure 4. Furthermore, there were cases when corrosion areas concentrated to specific portions on the board surface. Figure 6 shows an example of SO_2 gas corrosion occurring accordingly to the brush scratch marks on the surface after SO_2 gas testing. This phenomenon was caused by Ni surface form transformations, as shown in Figure 7, and will also occur due to scratches caused by manual handling. Also, if discoloration (cloudy marks) occurs after the ENIG plating process, as shown in Figure 8 (a), this area will be significantly corroded {Figure 8(b)}. Microscopic observation, as shown in Figure 9, reveals that cloud-like discoloration is caused by a concentration of nodules. We consider that these nodules significantly transform the Ni surface and therefore become the cause of serious SO_2 gas corrosion.

Furthermore, the cross section SEM observation shown in Figure 10 demonstrates corrosion considered to be caused by contamination on the Cu substrate surface. Pinholes created within the Ni plated layer because uniform deposition was denied by this contamination on the Cu surface are considered to be the cause of SO_2 gas corrosion. This contamination is assumed to have adhered to the Cu surface during the scrubbing process.

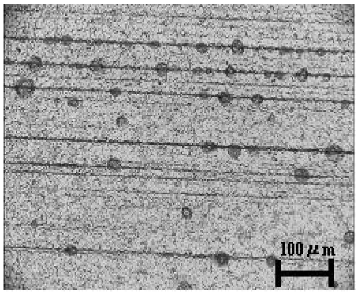


Figure 6 – SO_2 Gas Corrosion on High P ENIG Surface According to Brush Marks of Board

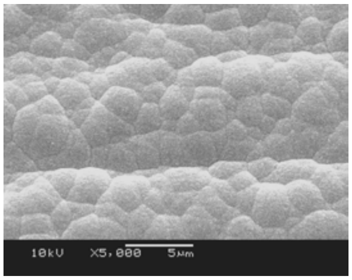


Figure 7 – Surface SEM Observation of Brush Mark Areas

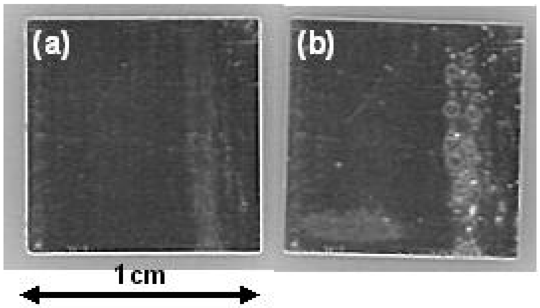


Figure 8 – SO_2 Gas Corrosion Occurring at Discoloration areas (a) as Plated; (b) After SO_2 Gas Testing

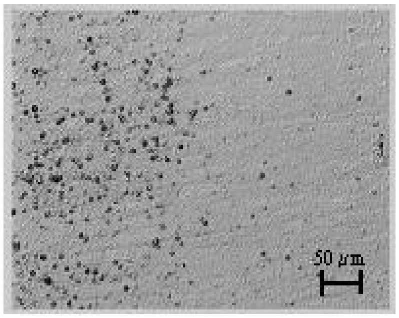


Figure 9 – Optical Microscopic Observation of White Discoloration Areas (Black Spots are Nodules)

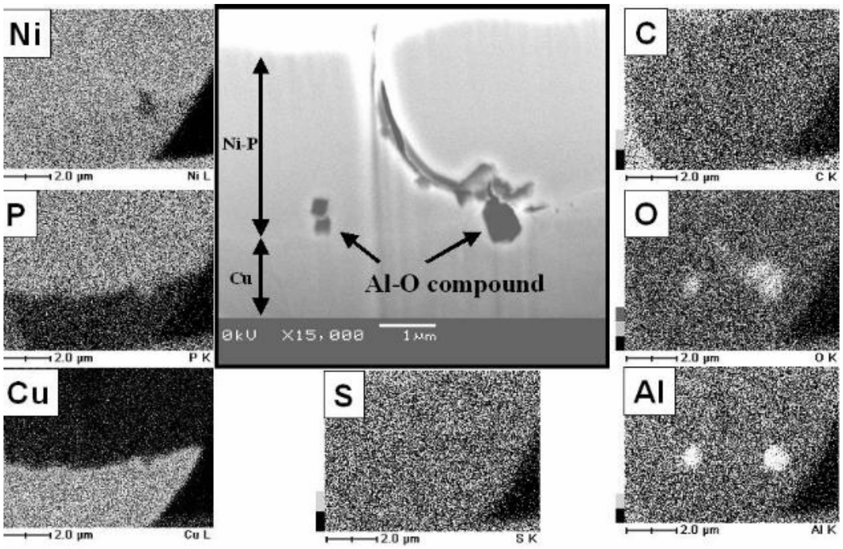


Figure 10 – Contamination of Cu Surface Existing Inside the High P ENIG Layer at SO_2 Gas Corrosion Areas (Cross Section SEM and EDS)

Corrosion Model Case

From the observations and studies we conducted, our understanding is that in order to clarify SO_2 gas resistance characteristics, it is necessary to investigate a corrosion model case in consideration of a formation factor also and not only a planar structure corrosion model based on Ni/Au galvanic corrosion. On one hand, the corrosion resistance characteristic of the Ni layer and also the immersion Au plating coverage characteristic are critical when Ni/Au galvanic corrosion is considered. On the other hand, Ni layer surface uniformity and reduction of local corrosion caused by immersion Au plating and OSP treatment are critical when the formation factor is considered. Furthermore, the Ni layer formation is influenced by not only the Ni plating bath performance, but also by the Cu substrate formation and surface conditions such as wettability and contamination, and also pretreatment processes.

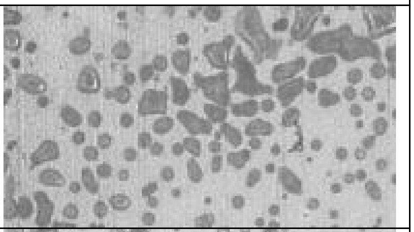
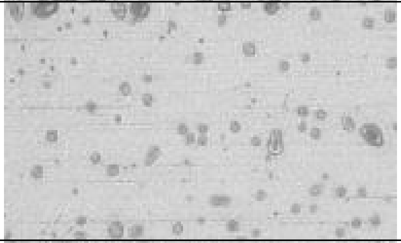
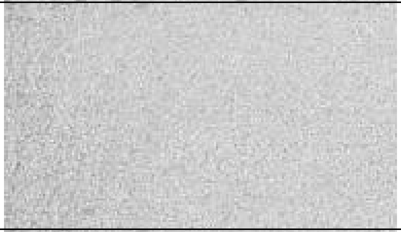
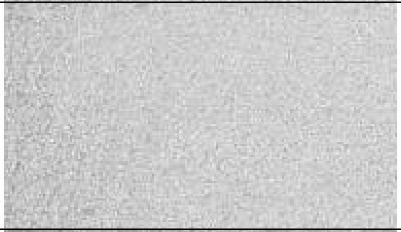
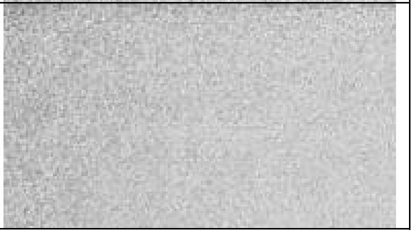
Factors that Effect SO_2 Gas Resistance Characteristics

Corrosion Resistance of Ni layer

The corrosion resistance characteristic of the Ni layer is significantly influenced by the phosphorous content percentage (P%) within the Ni layer.

By conducting SO_2 gas tests on various P% Ni layers deposited by utilizing a Ni plating bath containing no sulfur additives, the influence of P% within the Ni layer was confirmed (Table 2). Although a P% of over 9% is acceptable when judged from the SO_2 corrosion resistance point of view, 10 to 11% is desirable when P% fluctuations, deposition speed and Au adhesion strength are considered. Furthermore, though it is typical to add various additives to the electroless Ni plating bath, specific additives types will also influence SO_2 gas resistance characteristic. For example, sulfur type additives, which are typically used for electroless Ni plating baths, have a tendency to deteriorate SO_2 gas resistance characteristics.

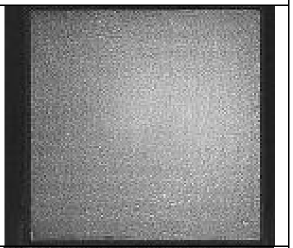
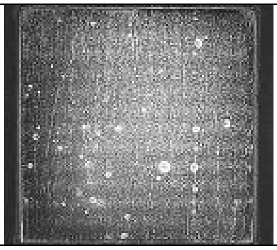
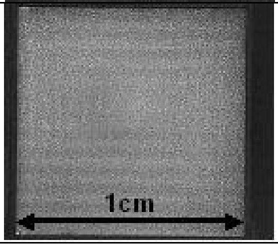
Table 2 – SO_2 Gas Results According to P Content of Electroless Ni Layer

P content	**SO_2** gas test result
6%	
8%	
9%	
10%	
12%	

Coverage of Immersion Au Plating

Immersion Au coverage can be evaluated by dipping the ENIG layer into nitric acid (61% nitric acid 500mL/L, 25□, 15min.) and observing Ni dissolution from pits in the Au plated layer. SO_2 test results will deteriorate if Au coverage is poor, as shown in Table 3.

Table 3 – Nitric Acid and SO_2 Gas Test Results According to Au Plating Type

	Bath A	Commercial Product
HNO_3 Test		
SO_2 Test		

Formation of Ni plating Layer

A uniform Ni plating layer formation is desirable in order to obtain excellent SO_2 corrosion resistance. However, there are various factors that influence the Ni plating layer formation. Concerning the substrate, Cu surface unevenness caused by processes such as brush polishing and contamination on the Cu surface will influence Ni formation (Figure 6 and 10). Concerning the pretreatment process, Cu surface wettability and etching uniformity will influence Ni formation (Figure 11). Also, activity character of the Pd activator process also has influence on Ni formation, and has correlation with the initial reaction characteristic of the Ni plating bath. Furthermore, Ni plating bath variation is also critical because the Ni layer formation uniformity will differ according to the Ni plating bath composition.

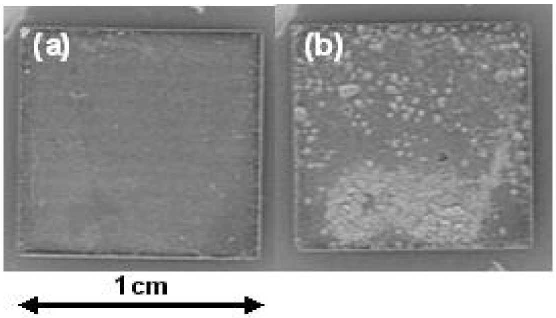


Figure 11 – High P ENIG Appearance Defect caused by Poor Wettability of Cu Surface and SO_2 Gas Test Result of this Layer (a) as Plated; (b) SO_2 Test Result

Local corrosion Caused by Immersion Au Plating

Local corrosion caused by immersion Au plating will increase if plating conditions such as bath temperature and plating time are changed, and as a result SO_2 gas corrosion will increase. For example, if plating time is extended in order to deposit a thicker plating layer, SO_2 gas corrosion will increase, as shown in Figure 12. Therefore, it is necessary to select proper plating process conditions, and an immersion gold bath composition that has a propensity to prevent local corrosion is desirable. On the other hand, there are cases when local corrosion occurs selectively at uneven Ni formation areas (Figure 13) depending on bath composition, and therefore it is critical to select plating baths properly.

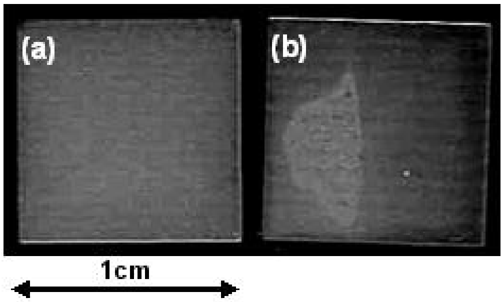


Figure 12 – High P ENIG Surface after CO_2 Gas Testing According to Immersion Au Plating Time (a) 15 min.; (b) 45 min (Au thickness (a) 0.05 μm; (b) 0.08 μm)

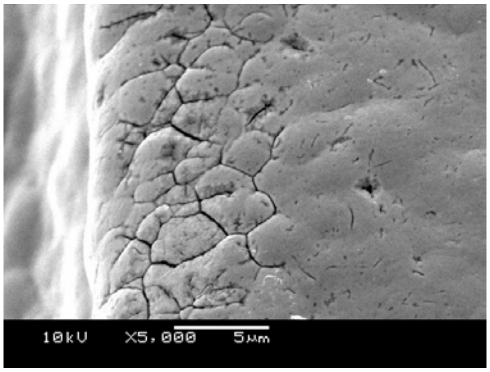


Figure 13 – SEM Observation of Local Corrosion on High P ENIG Surface caused by Immersion Au Plating (Ni Surface after Au Removal)

Local Corrosion Caused by OSP Treatment

There are cases when OSP treatment causes local corrosion selectively at the Ni formation boundary areas (Figure 14) and deteriorates SO_2 gas testing results. Therefore, it is necessary to select the proper plating solution and plating condition in order to prevent this phenomenon. Also, an effective method to improve SO_2 resistance characteristic is to utilize a direct immersion gold (DIG) plating process on Cu as an alternative process for OSP treatment. By utilizing this process, it is possible to not only avoid corrosion caused by OSP treatment, but also increase Au plating thickness without causing local corrosion on the ENIG surface, and therefore Au coverage will improve, resulting in the improvement of SO_2 corrosion resistance of the ENIG plating layer (Figure 15).

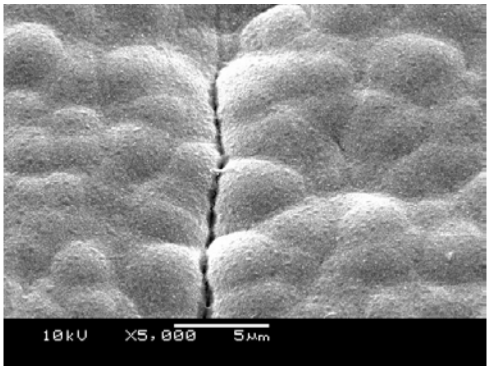


Figure 14 – SEM Observation of Corrosion caused by OSP Treatment on High P ENIG Layer

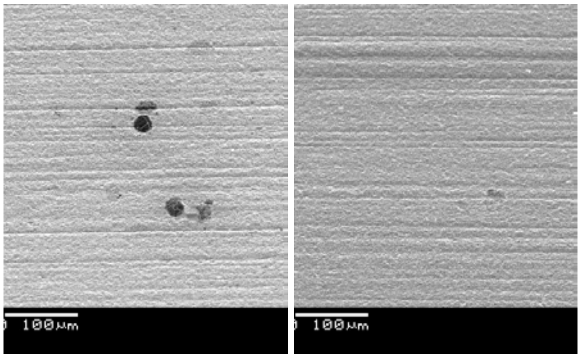


Figure 15 – SEM Observation of SO_2 Gas Test after (a) OSP Treatment; (b) Direct Au Plating on High P ENIG Layer (Au thickness (a) 0.07 μm; (b) 0.12 μm)

Conclusion

In order to improve SO_2 gas corrosion resistance characteristics, it is necessary to consider not only Ni/Au galvanic corrosion, but also the Ni surface formation factor. Board condition, pretreatment and electroless Ni plating each influence this formation factor. Furthermore, immersion Au plating and OSP treatment will negatively influence the uneven areas selectively and accelerate SO_2 gas corrosion. Because each factor mutually influences each other, in order to improve the SO_2 corrosion resistance character it is necessary to consider a corrosion model case as stated in this study, and investigate the total surface finishing process including plating line conditions. Furthermore, in circumstances which excessive SO_2 gas resistance character is required, adoption of a Au plating process directly on Cu as an alternative to OSP treatment is effective