Black Pad and Revisiting Methodologies

Joel Flumerfelt
Tom Schleisman
Aspen Research Corporation

Abstract:
Society today relies on electronic devices that influence every aspect of our lives, such as communication, transportation, computing, home appliances, and recreation. The reliability of any electronic device depends on the design and quality of the printed circuit board (PCB) assembly. The origin of the PCB begins with a design concept followed by its verification for the desired output. The development of a manufacturing process subsequently occurs with the production of a small volume of prototype PCBs, and scale up to full production takes place once the manufacturing process is established. At each manufacturing scale up, it is advisable to evaluate and verify the quality of PCBs to appropriate material and/or performance specifications. The first part of this paper describes how we use both types of specifications to perform investigations at first article unpopulated and populated PCBs with the intent of assisting our customer's selection of a board manufacturing process, and possibly a board manufacturer. A similar methodology is applicable to raw components and geometrical design changes to characterize product process control and/or identify soldering issues. The second part of this paper covers some studies of solder connection reliability, such as Black Pad, and a developing methodology for analysis and control.

Introduction, Printed Circuit Boards:
Interconnects in electronic packages have become more complex in recent years as, for example, densities have increased, powers have decreased, and materials costs and materials restrictions have become important factors. In addition, reliability factors have impacted certain materials usages and cleanliness levels associated with them.

Soft solders, at one time chiefly tin-lead alloys, have been a mainstay in this field and there is no reason to assume that this importance will not continue. Gold ball and wedge thermo-compressive bonds are also widely used.

Extensive studies have been made of the mechanisms and reactions that occur during the soldering process. Among these have been those that have focused on the formation of various intermetallic compounds, and their affects on solder joint integrity and reliability. These are covered extensively in the literature and will not be addressed in this paper. It should be kept in mind however, that the increasing use of lead-free solders and the higher temperatures that many of these require may result in higher levels of intermetallic compounds than was the case with, for example, eutectic tin-lead solders.

One factor that seems to be overlooked at times, for all solder connections, is the necessity for thorough wetting by the solder to the mating surfaces. Without such intimate contact, mechanical strength after solder solidification can be severely impacted and the formation of bonding intermetallics is impeded.

The restrictions on lead in solders have also had an impact by, in many cases, necessitating the use of higher melting point solders. Material costs, chiefly precious metals, have also had an impact and their lower usage (mainly thinner deposits) has impacted solderability issues. In addition, the desire to minimize processing steps and/or use less costly or laborious steps has had an impact.

Introduction, Black Pad and Electroless Nickel Immersion Gold:
In recent years Electroless Nickel (EN) has been found to be a viable replacement for electroplated nickel over copper for a number of reasons. First, depositing EN does not require electrical connections, and secondly, EN has superior "throwing power" over electroplated nickel offering superior coverage in, for example, plated through holes. To facilitate soldering to EN it has become customary to coat it with a very thin layer of "Immersion Gold" (IG) with the resultant configuration termed ENIG. It is this system that has been associated with solder joint failures given the name "Black Pad".

Failures attributed to Black Pad have been analyzed by investigators for some time with results indicating that a variety of factors may contribute to the failure mechanism. These include void formation(s) in the solder in and adjacent to the solder-nickel interface, intermetallic compounds which impart brittleness to the joint, etching of the nickel surface immediately prior to and during the deposition of IG leading to interfacial tarnishing and bond separation, and phosphorus compounds at the interface of the IG and EN.

PCB Methodology:

Printed Circuit Boards (PCBs) and other components are routinely evaluated at Aspen much as they are in numerous other similar facilities. Among the routinely performed evaluations to determine component and assembly quality are: dimensional measurements, contamination analyses, metallographic cross sectioning and evaluations, materials analyses, porosity determinations, artificial aging studies, and solderability tests. All of these tests and evaluations are performed, when applicable, in accordance with industry accepted standards and specifications such as those detailed in ASTM, IPC, IEC, and ISO standard test methods., along with a number of government Military Standards, Federal Specifications, and Material Specifications.

In addition to these rote type evaluations, when the situation calls for it, modifications to the above listed test and evaluation methods are employed. Such methods include, for example, selective power being applied, both continuous and cyclical, while devices or assemblies are being exposed to certain environments.

Black Pad Methodology:
Because the occurrence of Black Pad has been predominantly occurring in systems that utilize ENIG on copper arrays and separation is most often at the solder to nickel interface, an experiment was developed to attempt to determine how the ENIG interface could impact solder joint integrity. By design, plated copper printed circuit board configurations were not processed. Instead wrought copper sheet coupons were selected to eliminate or lessen the possible affects of electroplated copper on the final configuration. This portion of the investigation is presented as a “Phase I” effort centering on the as-plated condition of the ENIG interface on a relatively thick and rigid wrought copper surface.

Materials Evaluated and Analyzed:
1. Copper Coupons, 2.5 cm X 5 cm X 0.15 cm thick; Copper Development Association (CDA) Oxygen Free Electronic (OFE) Copper 101, Unified Numbering System (UNS) Copper C10100.

2. Nickel Plating: 10 samples of each phosphorus level.
3.

- High Phosphorus EN
- Medium Phosphorus EN
- Low Phosphorus EN

The nickel was deposited using freshly prepared MacDermid VAND-ALLOY 4100 and NIKLAD 767 baths. X-ray thickness measurements were made on all samples to assure thicknesses in the range of 3 - 5 µm on all sample surfaces, Table 1.

3. Gold Plating:
IG was applied immediately after the EN application process using a freshly prepared OMG-FIDELITY 9027SG/ST-25 bath. Only thorough deionized water rinsing preceded the gold application with no surface activation chemicals used. Gold was applied to 8 coupons of each phosphorus level leaving two of each phosphorus level type for analysis unaffected by the gold application process. X-ray thickness measurements were made on all coupons and are listed in Table 1.

Table 1 – IG and EN plating thickness (µm)

EN Composition	Gold	Nickel
High Phosphorus	0.089 - 0.096	4.0 - 4.4
Medium Phosphorus	0.089 - 0.096	4.0 - 4.1
Low Phosphorus	0.089 - 0.099	3.9 - 4.3

Evaluations:
Visual light microscopy examinations of all samples, both ENIG and EN, were performed to make certain the surfaces were uniform and to help avoid subsequent analyses being compromised. One coupon from each of the three phosphorus level groups was then examined in a Scanning Electron Microscope (SEM) at 20KV accelerating voltage with an incorporated X-ray Energy Dispersive Spectrometer (EDX). Figures 1-6 are micrographs of the surfaces and elemental spectra of the blocked regions in the photos. Higher magnification photomicrographs in the figures show textures and evidence of “microporosity” in both the IG and EN surfaces. Table 2 lists the atomic and weight percent compositions of the areas shown.

One sample from each of the three phosphorus level ENIG groups was also subjected to X-ray Photoelectron Spectroscopy (XPS). Depth profiles were collected over 2mm x 2mm areas at a nominal sputtering rate of 100Å per minute relative to SiO_2, and terminated once it was clear that the IG to EN interface had been passed. Figures 7-9 are depth profile plots of the coupons.

Porosity evaluations were also made of the three EN phosphorus content levels of the ENIG coupons using the sulfurous acid vapor method described in ASTM Specification B799. Figures 10-12 are photos of the results and show significant levels of blooming indicating gold porosity on all samples. The three ENIG coated phosphorus level classes were also subjected to 1 hour of non-condensing steam aging per IPC-J-STD-002 Category 2 conditions..

Cross hatch adhesion tests of the ENIG, in accordance with ASTM Method B571, were performed on the gold surfaces of the three phosphorus content level coupons both before and after steam aging. Both scraping and tape evaluations did not reveal any adhesion failures.

Summary:

As noted earlier, this segment of the investigation into Black Pad failure and root cause mechanisms is presented as a "Phase I" effort. As such the data presented is focused on the IG to EN interface in the as applied state. None of the coupons, other than the steam aged coupons, had been exposed to elevated temperatures to result in significant levels of nickel phosphide precipitation in the EN.

Both the SEM/EDX and XPS analyses show the variations of phosphorus content in the EN below the IG top coating. At this time, with the EN being in the as-plated condition it is presumed that the phosphorus is essentially present as a supersaturated nickel phosphide in an amorphous nickel matrix nickel matrix.

The XPS depth profile plots of the gold to nickel interfaces are considered interesting in showing significant amounts of both carbon and oxygen at and below the interface in the low and medium phosphorus content ENIG coupons, while the high phosphorus content coupon shows only oxygen at the interface. The significance of these findings is not clear at this time. One presumption is that the NIKLAD 767 bath used for the low and medium EN deposits incorporates activating, stabilizing, or leveling components that become incorporated in the deposit.

The sulfurous acid vapor porosity evaluation described above is also interesting in that it shows that the very thin IG plating on the EN is ineffectively providing a continuous or low permeability barrier coating that is intended to impedes passivation of the EN under the IG. It is unclear at this time if the "blooming" that resulted from the porosity test is wholly due to microporosity or if permeation through the IG was the main cause.

If the EN is effectively protected it should provide a readily reactable, i.e., solderable, surface under the IG. The mechanism of the immersion plating process is such that, with a continuous and dense gold top layer, oxygen at the interface should be essentially absent.

At this point of this investigation a hypothesis is presented that passivation of the nickel under permeable or porous immersion gold may retard wetting of the solder as the gold is dissolved, such that, even though it appears that a continuous solder film on the nickel is present, tenacious bonding is intermittent. Fluxes that are commonly used in these processes, such as RMA and rosin mildly activated, would be marginal at best in reducing the passive film to allow the solder to react with the nickel. It is also postulated that porosity in either the IG or EN layers, or both, may emit outgassing products during the soldering heating cycles that both physically impede flux contact and solder wetting, which in turn may contain substances that react with the nickel surface.

The formation of various intermetallic compounds and nickel phosphide precipitates during the solder heating period is also admitted as playing a possible role. Conditions during soldering, e.g. air and humidity, may also impact the situation by "tarnishing" the nickel through the gold during the heat up step. Also, extended time of storage of ENIG finished surfaces before soldering is thought have an impact simply because the very thin gold is not considered to be an efficient barrier coating.

Industry experience, though, indicates that the occurrence of Black Pad is intermittent and countless connections with excellent reliability have been made with ENIG. This in itself indicates the need for additional investigations.

Table 2 - EDX Compositions of Regions shown in Figures 1-6.
Data with and without Carbon inclusion.

EN High Phosphorus

Element	Atom %	Wt %	Element	Atom %	Wt %
C -K	19.8	5.1			
P -K	11.0	7.3	P -K	14.0	7.9
Ni-K	67.9	85.8	Ni-K	84.4	90.2
Cu-K	1.3	1.8	Cu-K	1.6	1.9

EN Medium Phosphorus

Element	Atom %	Wt %	Element	Atom %	Wt %
C -K	18.0	4.4			
P -K	5.5	3.5	P -K	6.8	3.7
Ni-K	75.7	90.9	Ni-K	92.1	95.0
Cu-K	0.9	1.2	Cu-K	1.1	1.3

EN Low Phosphorus

Element	Atom %	Wt %	Element	Atom %	Wt %
C -K	18.9	4.6			
P -K	3.4	2.2	P -K	4.3	2.3
Ni-K	75.4	90.3	Ni-K	92.9	94.6
Cu-K	2.3	2.9	Cu-K	2.8	3.1

ENIG High Phosphorus

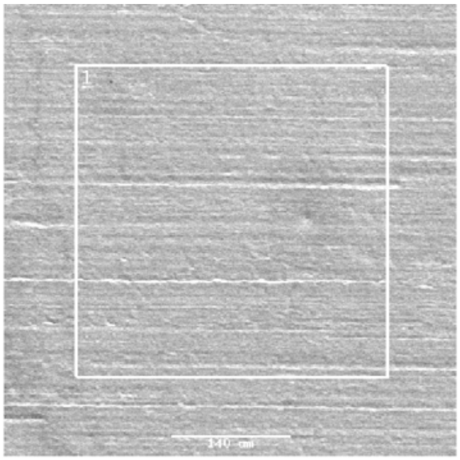
Element	Atom %	Wt %	Element	Atom %	Wt %
C -K	19.3	4.4			
P -K	10.6	6.3	P -K	13.3	6.7
Au-M	4.0	14.7	Au-M	5.0	15.6
Ni-K	64.6	72.7	Ni-K	79.8	75.7
Cu-K	1.6	1.9	Cu-K	1.9	2.0

ENIG Medium Phosphorus

Element	Atom %	Wt %	Element	Atom %	Wt %
C -K	21.3	4.1			
P -K	4.2	2.1	P -K	5.4	2.2
Au-M	10.6	33.2	Au-M	13.6	35.0
Ni-K	61.5	58.1	Ni-K	77.9	60.3
Cu-K	2.4	2.5	Cu-K	3.1	2.6

ENIG Low Phosphorus

Element	Atom %	Wt %	Element	Atom %	Wt %
C -K	18.8	3.0			
P -K	2.5	1.1	P -K	3.2	1.1
Au-M	18.3	48.0	Au-M	22.7	49.8
Ni-K	56.4	44.4	Ni-K	69.3	45.6
Cu-K	4.0	3.4	Cu-K	4.9	3.5



Sample ID : Black_Pad
Area ID : Low_Phos_a
Label : Low Phos ENIG
Date/Time: : 2006/10/31 15:05

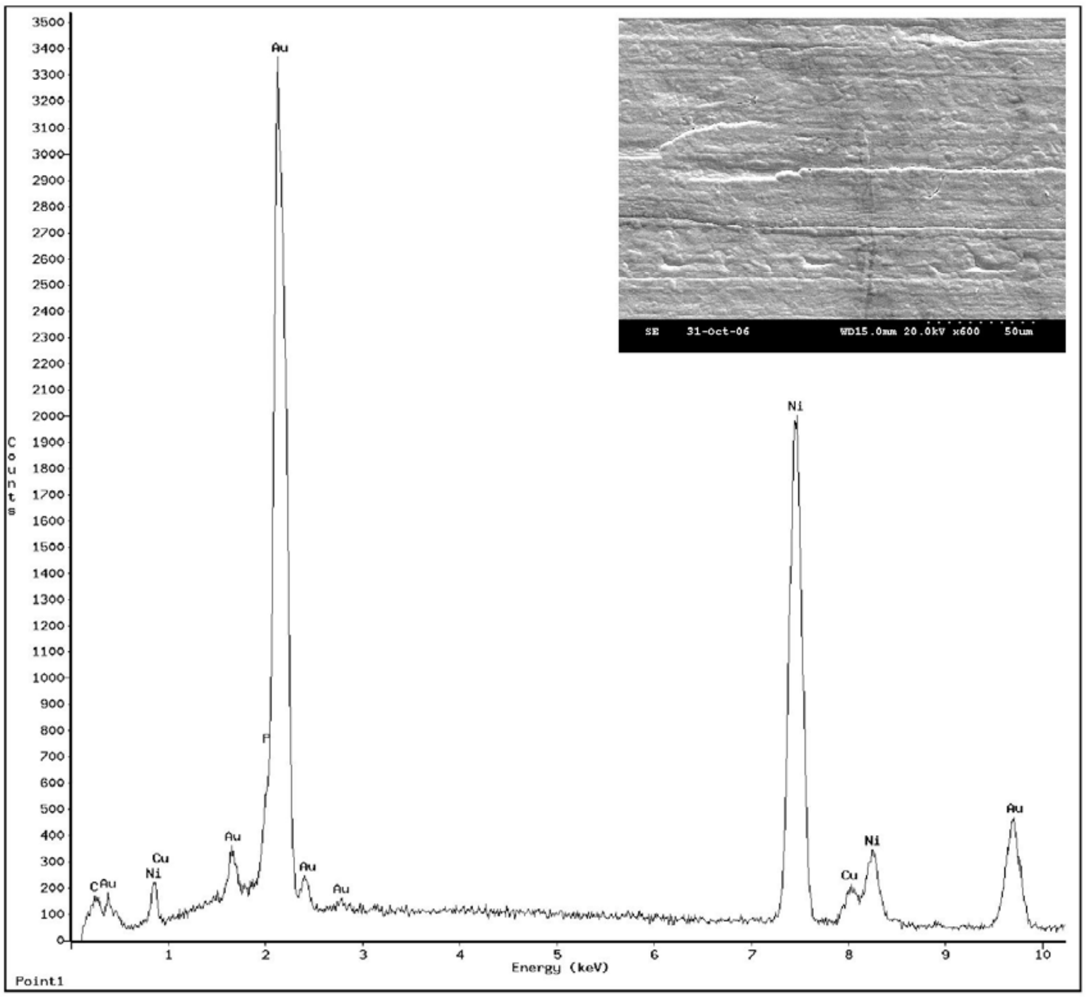
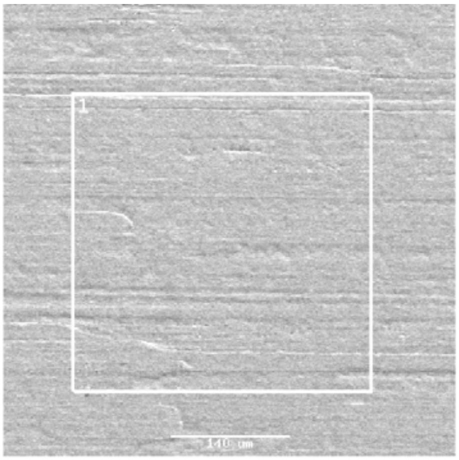


Figure 1 - SEM micrograph and EDX spectrum of IG over low phosphorus EN panel. Inset SEM micrograph shows porosity in the IG surface, 600X.



Sample ID : Black_Pad
Area ID : Med_Phos_a
Label : Med Phos ENIG
Date/Time: : 2006/10/31 15:16

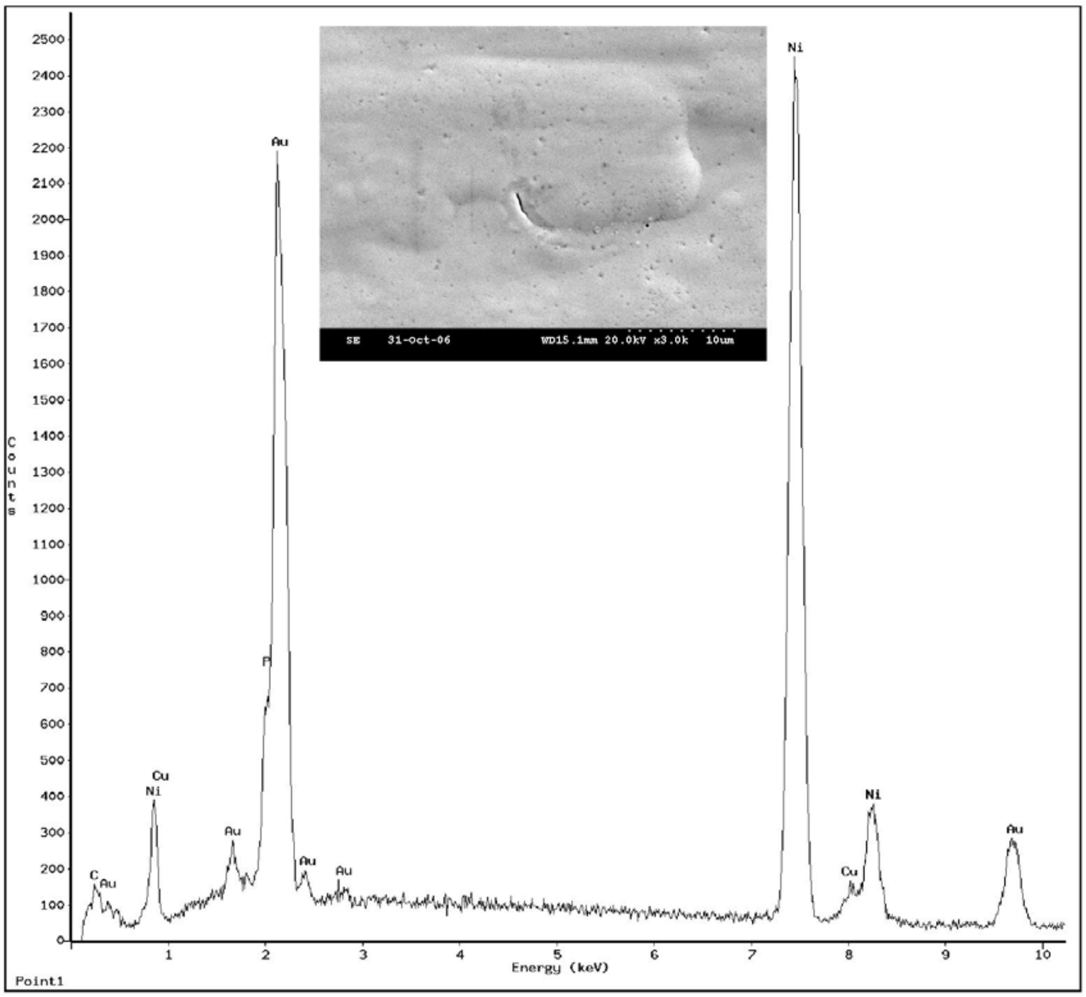
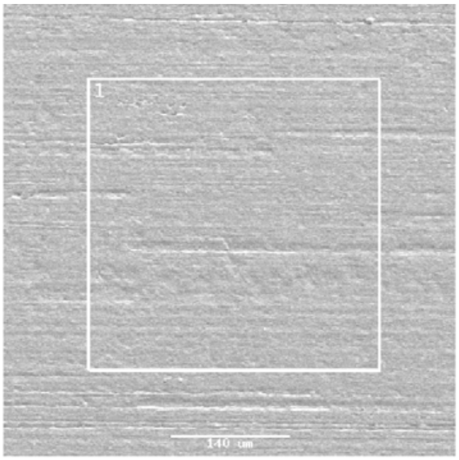


Figure 2 - SEM micrograph and EDX spectrum of IG over medium phosphorus EN panel. Inset SEM micrograph shows porosity in the IG surface, 3000X.



Sample ID : Black_Pad
Area ID : High_Phos_a
Label : High Phos ENIG
Date/Time: : 2006/10/31 15:24

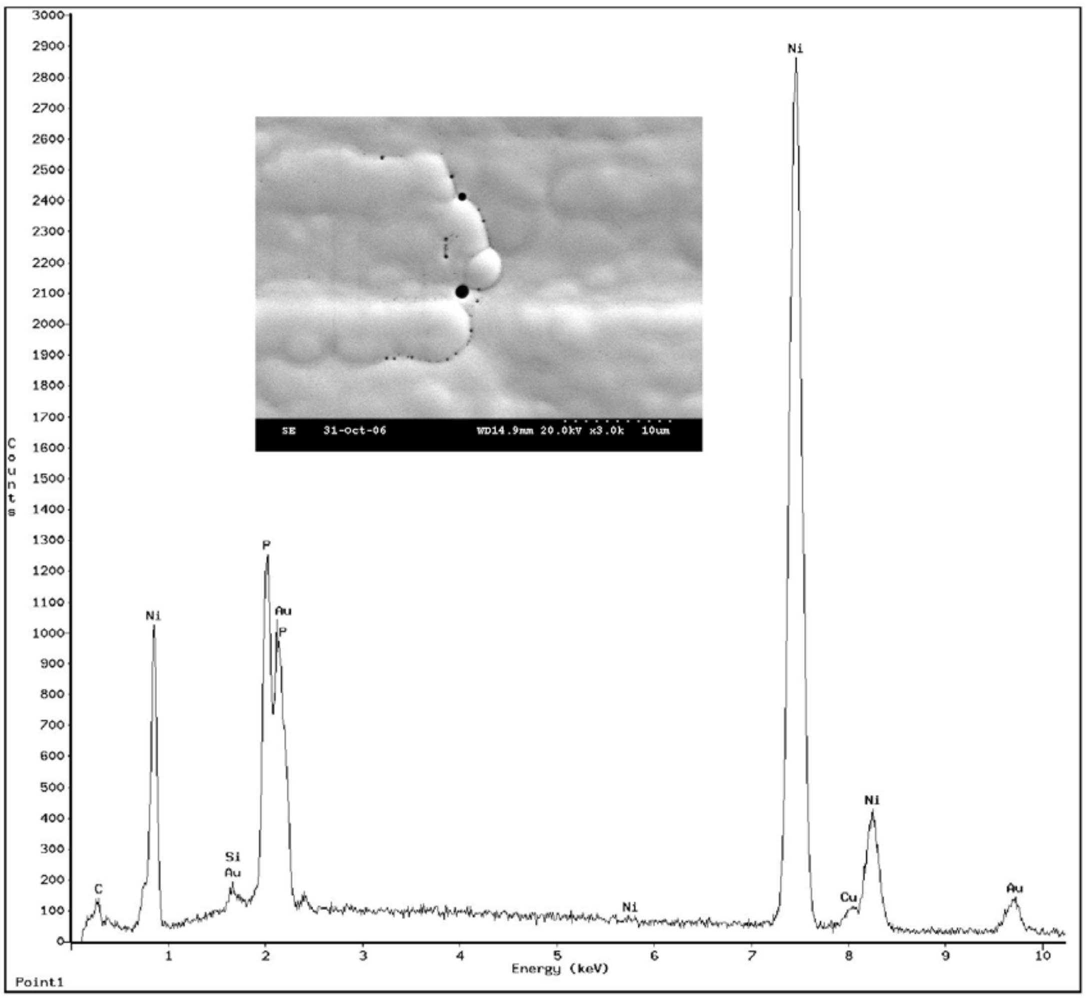


Figure 3 - SEM micrograph and EDX spectrum of IG over high phosphorus EN panel. Inset SEM micrograph shows porosity in the IG surface, 3000X.

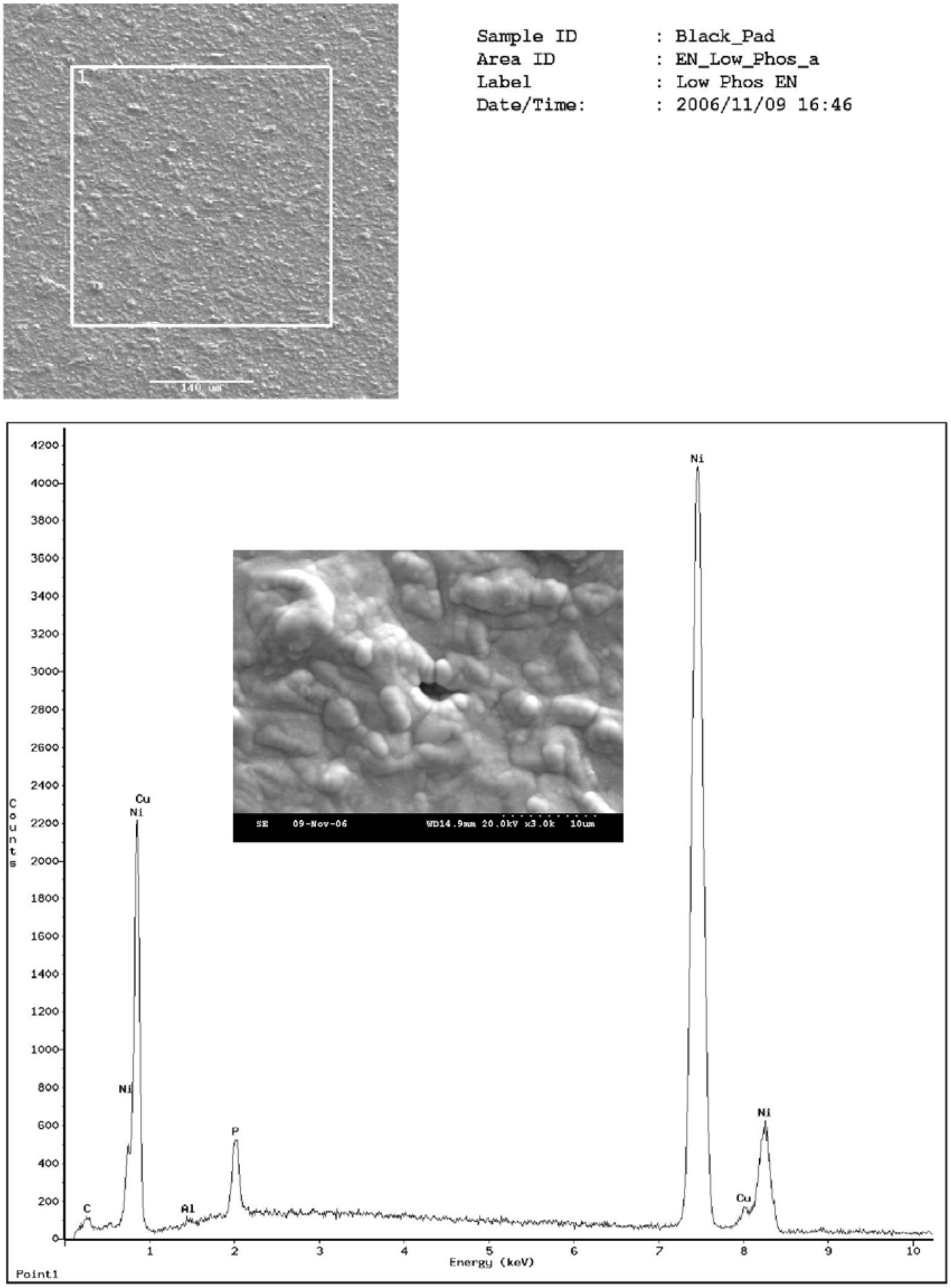
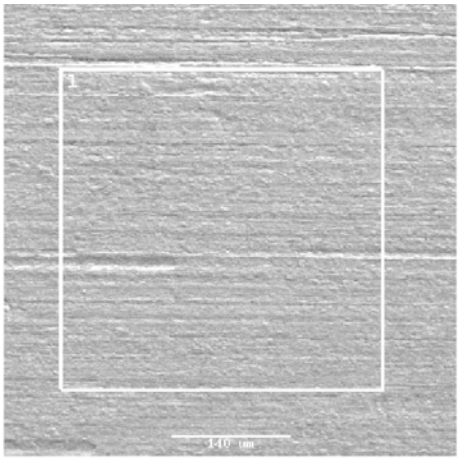


Figure 4 - SEM micrograph and EDX spectrum low phosphorus EN panel. Inset SEM micrograph shows porosity in the EN surface, 3000X.



Sample ID : Black_Pad
Area ID : EN_Med_Phos_a
Label : Medium Phos EN
Date/Time: : 2006/11/09 16:57

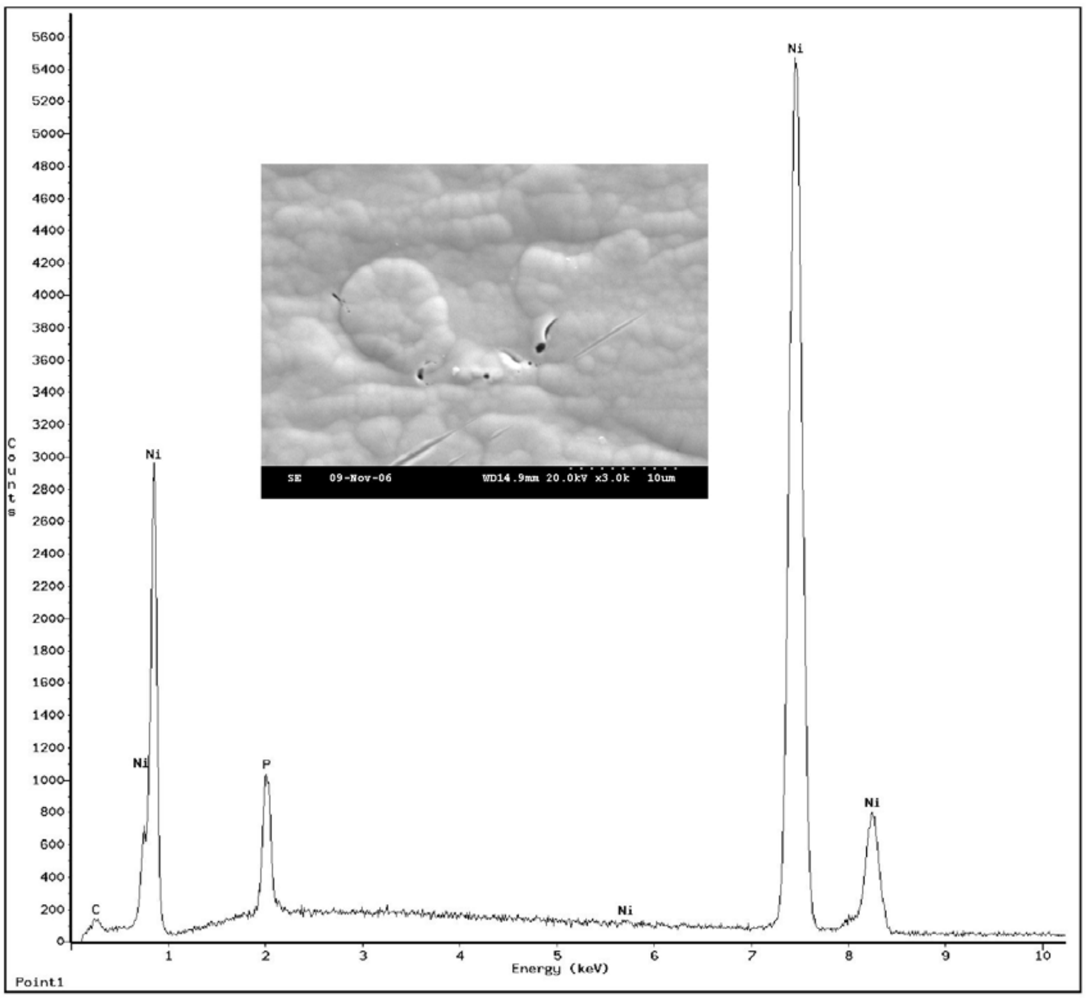
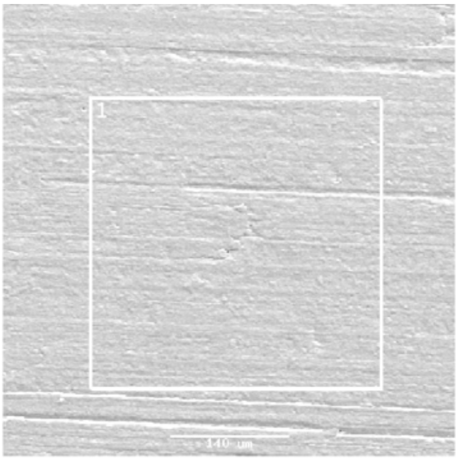


Figure 5 - SEM micrograph and EDX spectrum medium phosphorus EN panel. Inset SEM micrograph shows porosity in the EN surface, 3000X.



Sample ID	: Black_Pad
Area ID	: EN_High_Phos_a
Label	: High Phos EN
Date/Time:	: 2006/11/09 17:06

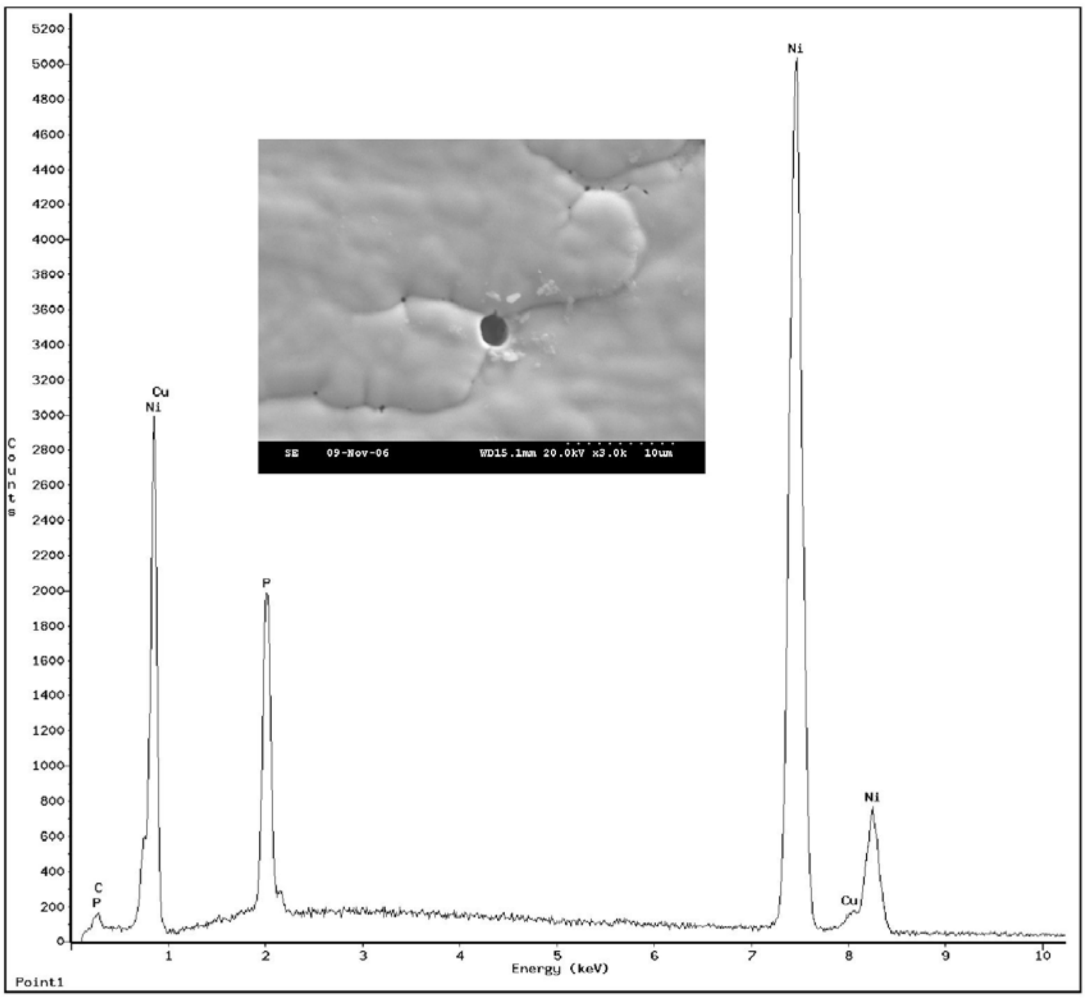


Figure 6 - SEM micrograph and EDX spectrum high phosphorus EN panel. Inset SEM micrograph shows porosity in the EN surface, 3000X.

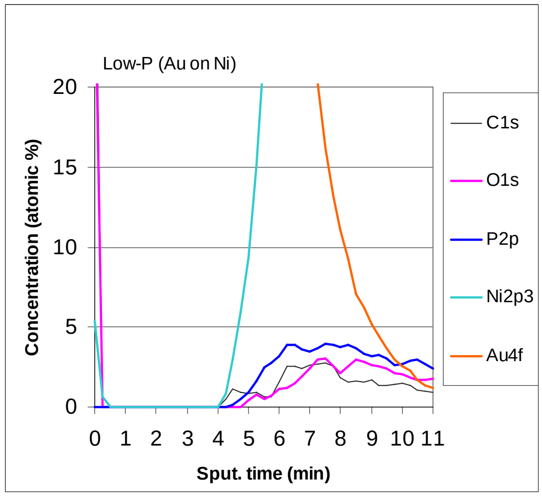


Figure 7 – XPS depth profile plot of IG over low phosphorus EN panel showing presence of oxygen and carbon at and below the gold-nickel interface.

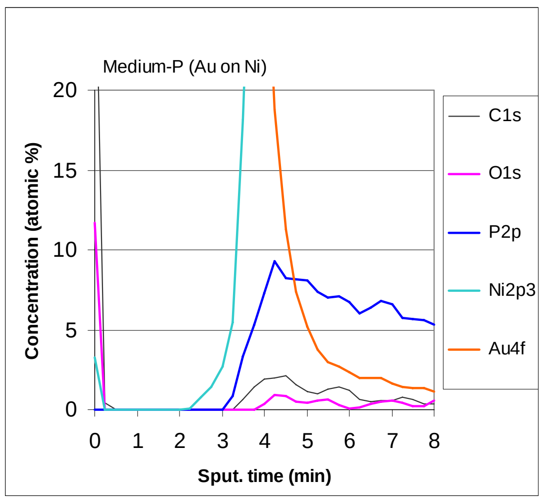


Figure 8 - XPS depth profile plot of IG over medium phosphorus EN panel showing presence of oxygen and carbon at and below the gold-nickel interface.

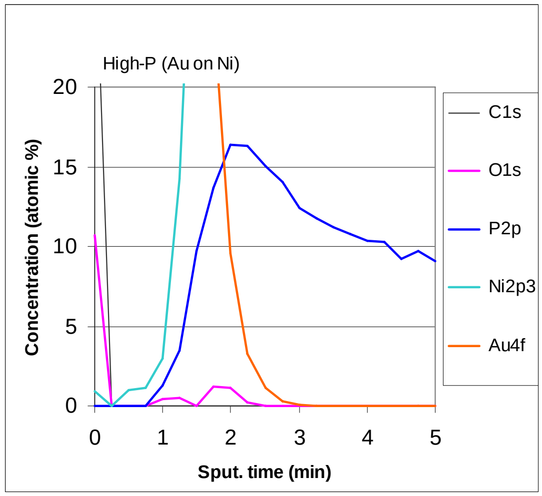


Figure 9 - XPS depth profile plot of IG over medium phosphorus EN panel showing undetectable levels of oxygen and carbon at the gold-nickel interface and in the bulk EN.

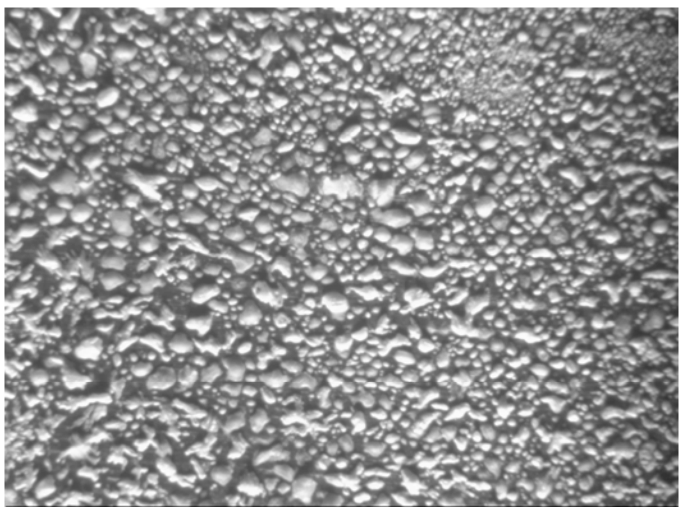


Figure 10 - Photomacrograph of sulfur dioxide porosity tested surface of IG over low phosphorus EN panel, 10X.

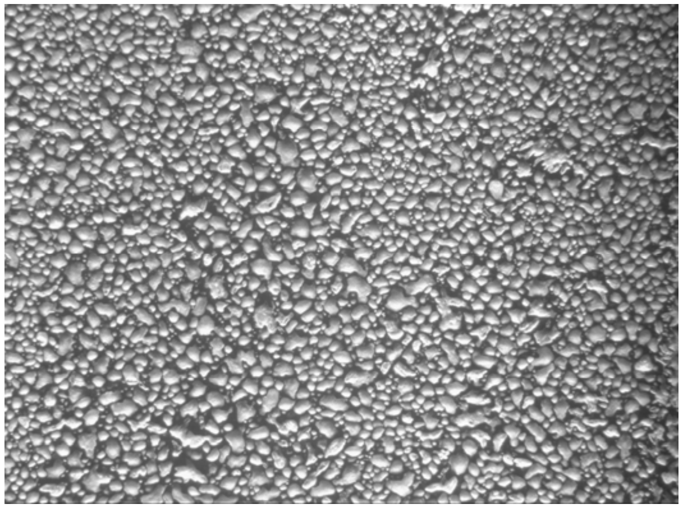


Figure 11 - Photomacrograph of sulfur dioxide porosity tested surface of IG over medium phosphorus EN panel, 10X.

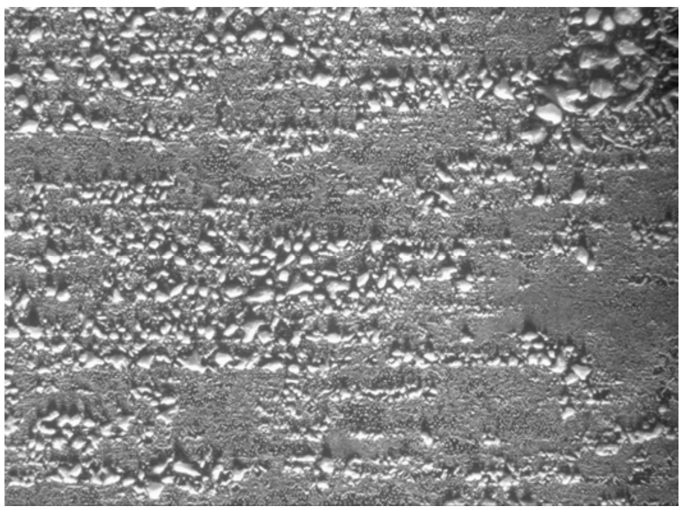


Figure 12 - Photomacrograph of sulfur dioxide porosity tested surface of IG over high phosphorus EN panel, 10X.

Contemplated Future Investigations:
Additional investigations focusing on interfacial and bulk plating layer composition(s) and the affects of plating conditions, the characteristics of differing nickel and gold plating sources, analysis of possible ENIG outgassing products, solder process heating parameters and times, flux types and application processes, and aging and storage conditions before soldering are contemplated.

References:

Emphasis, National Electronics Manufacturing Center of Excellence (U.S. Navy), Philadelphia, June 2004

Kejun-Zeng, Stierman, Abbot, and Murtuza, "The Root Cause of Failure of Solder Joints with Electroless Ni/Immersion Gold Plating", JOM (Journal of the Minerals, Metals, & Materials Society), TMS, Warrendale PA, June 2006.

Safranek W.H., The Properties of Electrodeposited Metals and Alloys, Elsevier, New York, 1974.

Manko, H.H., Solders and Soldering, McGraw-Hill, New York, 1964.

Nightingale S.J., "Tin Solders", British Non-Ferrous Metals Research Association, London 1932.

Fields, R.J. and Low, S.R., Physical and Mechanical Properties of Intermetallic Compounds Commonly Found in Solder Joints", Materials Performance Group Research Publication of the National Institute of Standards and Technology (NIST), Washington, February 2002.

Metals Handbook, Volume 6: Welding, Brazing, and Soldering; ASM International; Materials Park, OH, 1993.

Metals Handbook, 9th Edition, Volume 5; Surface Cleaning, Finishing, and Coating; American Society for Metals, Metals Park OH, 1982.

Military Standard MIL-STD-202, Test Methods for Electronic and Electrical Component Parts.

Military Standard MIL-STD-883, Test Methods and Procedures for Microelectronics.

ASTM, the American Society for Testing and Materials, Conshocken, PA.

Various metal finishing handbooks including Products Finishing and Metal Finishing.

Special Thanks to Aspen Research Corporation for funding this effort.

Additional thanks to the following individuals who provided inputs:

- John Newman, Evans Analytical Group, Chanhassen MN who provided the XPS analyses.
- Dr. John Thomas, University of Minnesota Characterization Facility, Minneapolis, MN.
- Mark Kelsey, Aspen Research Corporation, St. Paul, MN.
- Jerrid Matson, Spec Plating, Minneapolis, MN.
- Lisa Koland, Honeywell Aerospace, Minneapolis, MN.

Black Pad and Revisiting Methodologies

Joel Flumerfelt

Tom Schleisman

Aspen Research Corp

Introduction, Printed Circuit Boards:

- Solders

- Substrates

Introduction, Black Pad and Electroless Nickel Immersion Gold

PCB Methodology

Black Pad Methodology

- Nickel Passivation
- Fluxes

Material - Substrate

- Why not copper plating?

Plating System

- High, Medium, Low Phos EN
- Immersion Gold

Evaluation Methodology

- Visual
- SEM
- XPS
- Metallography
- Environmental Aging

Summary and Future Work

- Thanks
- University of Minnesota Characterization Facility
- Evans Analytical Group
- Spec Plating

- ASPEN RESEARCH corp.