A study of high Cu behavior on electrolytic Ni and electroless Ni pad finish

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Abstract

It has been used various pad finish materials to enhance the reliability of solder joint and Electroless Ni Immersion Gold (the following : ENIG) pad has been used more than others.
This study is about reliability according to being used in commercial Electrolytic Ni pad and ENIG pad, and was observed behavior of various Cu contents.
After reflow, the inter-metallic compound (IMC) between solder and pad is composed of Cu_6Sn_5 (Ni substituted) by using EDS, and in case of ENIG, between IMC and Ni layer was observed the dark layer (Ni_3P layer).
Additional, it could be controlled the thickness of dark layer according to Cu contents.
Investigated the different fracture mode between electrolytic Ni and ENIG pad after drop shock test, in case of soft Ni, accelerated stress propagated along the interface between 1st IMC and 2nd IMC, and in case of ENIG pad, accelerated stress propagated along the weaken surface such as dark layer.
The unstable interface exists through IMC, pad material and solder bulk by the lattice mismatch, so that the thermal and physical stress due to the continuous exterior impact is transferred to the IMC interface. Therefore, it is strongly requested to control solder morphology, IMC shape and thickness to improve the solder reliability.

Key words : High Cu, ENIG, drop, IMC, Ni3P

1. Introduction

With increasing use of portable appliances such as PDA and cellular phone, changing environment of application requires higher solder joint reliability. The various pad finished material is being used to enhance the reliability of solder joint. Advantages and disadvantages of common pad finish materials are as shown in table 1.[1]

Ni plating method is to make the metal film on desired material by using reduction metallic ions from metallic salt solution such as electroplating (to use electrical current), chemical plating (to use reduction by chemicals), immersion plating (to use ionization).[2] Chemical plating is called electroless plating without the use of external electrical power. Electroless plating is not using mask, it can be chose the plating and the price of electroless plating is low-cost. Also, it had a good solder joint and performance by solder diffusion prevention layer.[2] Electroless Ni plating is deposited by using various reductant, and is widely using in PCB industry[3] and it has a selective coating and good solder-ability and corrosion resistance.[4~5]

However, electroless Ni(P) has a problem, black the commercial expansion, one of the problem is brittle failure between electroless Ni(P) layer and solder.[6~13] A brittle failure mode was often found BGA under ENIG pad finishes PCB, it is hard to foresee the brittle failure on ENIG PCB and is announced to observe with a relatively small amount.[10] The causes are P segregation on the solder interfacial reaction,[7] void and crack in electroless Ni(P) crystallization process,[12] Ni(P) plating layer corrosion during immersion gold plating,[8] etc. However, the exact reason of the brittle failure is under investigation. After soldering, it was formed Ni-Sn IMC layer between Ni-P and solder. At the same time, it was formed thin P-rich crystalline layer between Ni-P and interfacial IMC. During this crystallization process, stress is generated in the crystalline P-rich layer which leads to fracture and eventually a weak layer was formed in between the IMC and Ni-P. Moreover, we easily found the fracture is along P-rich layer on external impacts.

Based on P-rich crystalline layer and brittle fracture relation, though the relationship between P contents and solder joint reliability has been reported by many companies, there is no clear and noticeable trend.[14~19]

In this study, we investigated interfacial reaction between a Cu level solder ball (Sn1.0Ag, SAC105, SAC1010, SAC1015) and Ni pad. The purpose of this study is to understand how SA alloy and different Cu doped SAC solder react with Ni finish during reflow.

Table1. Advantages and disadvantages of common surface finishes

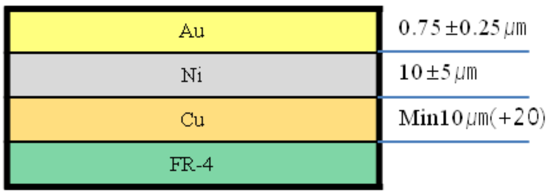
Finish	Advantage	Dis-advantage
Electro-lytic Ni/Au	-. Installed capacity, legacy process; excellent WB capability and solderability. -. Growth kinetics of Sn-Ni IMC is slower than Cu-Sn IMC. -. Better stability of the pad prior to soldering.	-. Au embrittlement when Au>3 wt% - Not an issue for flash packages
ENIG	-. Widely & generally used -. Good shelf life(-months) -. Handling tolerance	-. Industry variations due to different process chemistries. -. The most challenging PCB process requiring sophisticated controls. -. Requires disciplined process control or optimization
ENEPIG	-. Excellent solder-ability. -. Good shelf life (~12 months). -. Ni & Pd are oxidation barriers; E-less Pd is not corrosive to Ni. -. Excellent solder-ability.	-. Solder joint strength is dependent highly upon Pd thickness. -. Much more complex Manufacturing process than that of ENIG.
OSP	-. Good surface planarity. -. Strongest solder joint through Cu-Sn inter-matallic. -. Cheapest finish -. Higher drop reliability than others	-. Short shelf life (~6 months) -. Very narrow time process window for multiple assembly-hours. -. Cannot detect the cause of quality issues -. Solder joint issues due to interaction with assembly process by thermal damage.

2. Experimental procedure

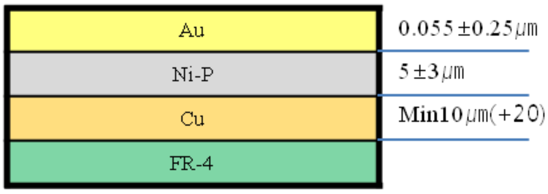
Among the most advanced microelectronic packages, ball-grid-array (BGA) technology are expected to have increasing applications because of their higher input-output connection density achieved through area-array solder joints. In this study, we used a ternary phase alloy (Sn-Ag-Cu alloy), lower silver content solder ball (Sn-1.0Ag-0.5Cu), and a various Cu contents solder balls (Sn-1.0Ag, Sn-1.0Ag-1.0Cu, Sn-1.0Ag-1.5Cu), the size is 450um. Pad finishes are Electroless Ni immersion Au (the following: ENIG), Electrolytic Ni/Au (the following: Ni/Au) on the ball grid array (BGA). SR open size is 500um, pitch is 2mm. Schematic illustration of surface finish is as shown Fig.1.

Reflow temperature profile carries out with 240℃, and a time above the liquidus of approximately 40sec (over 220℃ or higher). After reflow process, the flux cleaning is around 10 min with 60℃ distilled water. The flux type is WS. We found the IMC using cross-sectionla SEM image. Specimens were cold mounted and cross-sectioned through a row of solder balls. The specimens were then ground with 2000-grit SiC paper, and mechanical polished using 0.3 & 0.05um Al_2O_3 powder. We used Sn stripper, 95 vol% C_2H_5OH, 4 vol% HNO_3, with 1 vol% HCL, to find the intermetallic compound (IMC) and Ni_3P layer thickness. And then, we observed the cross-section of the Ni_3P layer thickness with transmission electron microscope (TEM) by raising the magnification.

A Dage 4000 tester was used for the low-speed ball shear test. A constant shear speed of 0.3mm/sec was applied. The gap between the substrate surfaces and the shear tool was kept at 20um. This test with low-speed shear test is to find the mechanical strength change with Cu contents level solder ball according to JEDEC (JESD22-B117). The board level test samples are formed 4 boards and test condition of 1500±10%G, 0.5mm/s was applied according to JEDEC (JESD22-B111).



(a) Ni/Au (Electrolytic Ni/Au)



(b) ENIG(Electroless Ni immersion Au)

Fig. 1. Schematic illustration of surface finish.

3. Results and discussion

3.1. Microstructures comparison

To find the interfacial reaction between the various Cu content solder and Ni pad after 1 time of reflow – Top view image and section image as shown Fig.2 and Fig.3.

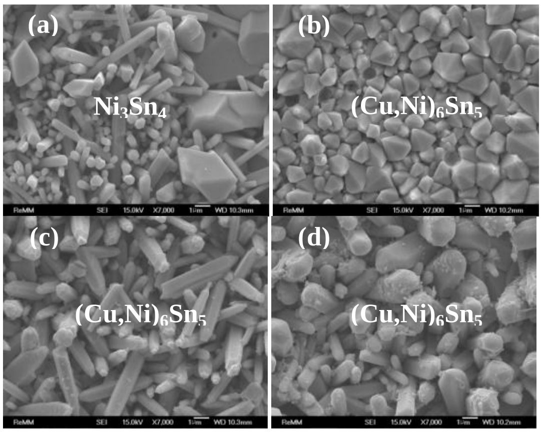


Fig. 2. Top view SEM image of the various Cu contents solder on the electrolytic Ni pad finish as reflowed. (a) Sn-1.0Ag (b) Sn-1.0Ag-0.5Cu (c) Sn-1.0Ag-1.0Cu (d) Sn-1.0Ag-1.5Cu

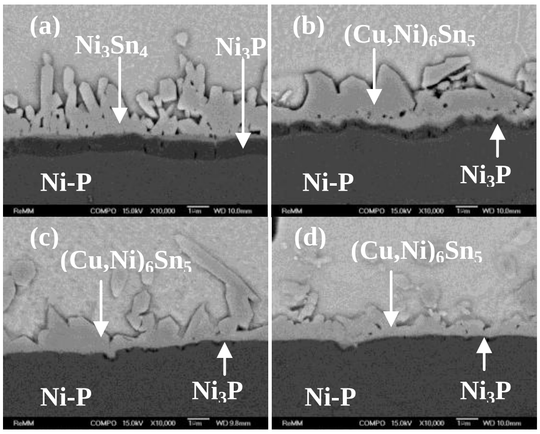


Fig. 3. X-section SEM image of the various Cu contents solder on the ENIG pad finish as reflowed. (a) Sn-1.0Ag (b) Sn-1.0Ag-0.5Cu (c) Sn-1.0Ag-1.0Cu (d) Sn-1.0Ag-1.5Cu

A reaction Sn-Ag solder and Ni layer were formed Ni_3Sn_4 IMC and Sn-Ag-Cu and Ni layer were formed $(Cu,Ni)_6Sn_5$ IMC. As well known, $(Cu,Ni)_6Sn_5$ IMC was faster than Ni_3Sn_4 about growth speed.[20] The SEM is equipped with an energy dispersive spectrometer (EDS) to analyze the intermetallic compound (IMC) and phase composition. The result is as shown Table.2. As a EDS result, Non-detected Cu solder was formed Ni_3Sn_4 IMC, but detected Cu solder was formed Cu_6Sn_5. Also, Cu_6Sn_5 was changed to $(Cu,Ni)_6Sn_5$ by Ni substitution. It was observed relatively more Cu contents with increasing Cu contents and was typical formed hexagonal system. Also, hexagonal system in the Cu content of 1.0wt% higher was soft. In reflow process, a form speed of Cu_6Sn_5 IMC is increased. So, Cu and Ni, it had enough time to be substitution reaction and a gap between $(Cu,Ni)_6Sn_5$ IMC and bulk solder by difference of thermal expansion. In case of difference of thermal expansion was made compression stress in bulk solder and formed many needle-shaped.

Fig. 3 shows a typical SEM image of the cross-section of an electroless Ni layer. From this cross-sectional micrograph, it is seen that a thin dark layer was formed in between IMC and Ni-P. This is the P-rich Ni-layer(Ni_3P), due to the reaction of Ni and Sn on ENIG pad, it was left with excess P accumulates at the interface between ENIG and the intermetallic compound. P-rich Ni-layer is to comprise – Ni(3):P(1) rate with a little Sn (~7 at%).[21] Tiny crystals of Ni_3P were formed in this P-rich Ni layer from the amorphous electroless Ni. During this crystallization process, stress is generated in the crystalline P-rich Ni layer which leads to fracture and eventually a weak layer is formed in between the IMC and the Ni-P layer. Moreover, Kirkendall voids also generate due to the excessive depletion of Ni in the P-rich Ni layer. The condensation of the Kirkendall voids result a continuous crack along the interface of the P-rich Ni layer the underneath IMC layer.[21] Ni_3Sn_4 on Electroless Ni layer was formed first needle shaped. And then, it was changed to lump. However, Cu-Ni-Sn, ternary system, it was formed layer shaped. A layer type IMC worked as diffusion prevention layer and down electroless Ni reaction.

We found that Cu contents higher in solder, P-rich Ni layer thickness was decreased.$(Cu,Ni)_6Sn_5$ IMC was faster than $(Ni,Cu)_3Sn_4$ about interfacial reactions with the electroless Ni-P. Cu in bulk was influenced to form $(Cu,Ni)_6Sn_5$ IMC.

In other words, the small Ni contents were consumed the Cu-Ni-Sn IMC, then P-rich Ni-layer was formed thin layer. In conclusion, Cu contents in solder with ENIG pad finish were controlled P-rich Ni-layer's growth by Ni diffusion control.

Table 2. The IMCs composition of various Cu contents solder

Solder	Cu (at%)	Ni(at%)	Sn(at%)
Sn 1.0Ag		39~40	59~60
Sn 1.0Ag 0.5Cu	30~31	22~23	46~47
Sn 1.0Ag 1.0Cu	40~42	11~14	42~46
Sn 1.0Ag 1.5Cu	47~48	4~5	47~48

3.2. Mechanical strength of solder joints

Fig. 4 shows ball shear test on various Cu contents solder with Ni layer. In this study, total 20 pads, we used 10 pads out of 20 pads. And this strength was average value.

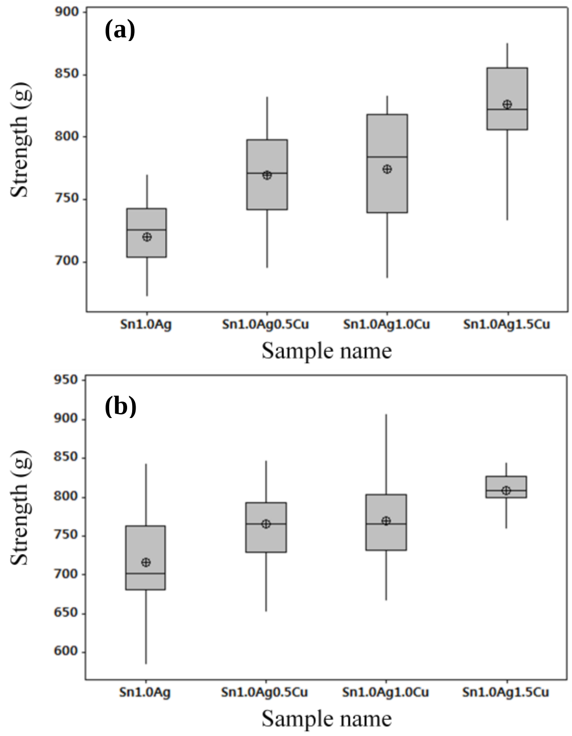


Fig. 4. Shear strength of the joint with various Cu contents solder. (a) Electrolytic Ni pad (b) Electroless Ni pad

If Cu content in solder was increased, shear strength tended to be increased. As you know the IMC layer with a high Cu contents, there are many IMC of needle-shaped, formed generally network structure. Also, it was increased combination surface area in an interface. A bulky IMC in solder interfered crack spread.

During shear test, if a pure interfacial shear stress was lower than interfacial combination strength, it was inside fracture in solder.
But, the opposite was interfacial joint. It means that interfacial combination strength was lower than pure interfacial shear stress. It was fractured in IMC.
In this study, we was found the spalling of IMC and brittle fracture with thick P-rich Ni-layer in Sn-1.0Ag and others were shown ductile fracture.

3.3. Drop test of solder joint strength

The result was as shown Fig. 5. This is weibull distribution for drop strength of various Cu contents solder on Ni pad. In case of non-detected Cu contents solder, it had the worst drop strength. But, when Cu contents were increased, drop strength was also increased. However, if excessive Cu contents in solder was not good drop performance. The Cu above the limited solubility caused to increase the precipitation hardening and this behavior interrupts to dissipate more energy during plastic deformation on drop impact test.

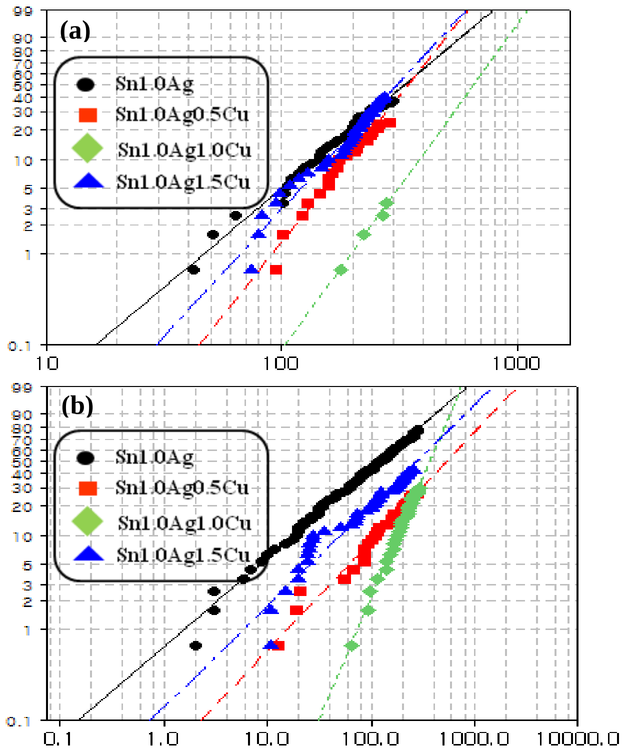


Fig. 5. Weibull distribution for drop strength of various Cu contents solder on Ni pad. (a) Electrolytic Ni pad (b) Electroless Ni pad

3.4. Cross-section observation with SEM

Fig. 6 shows fracture mode definition after drop test. Regardless of SAC composition and Ni pad, it was shown all IMC fracture mode as shown Fig. 7. Also, Fig. 8 shows IMC fracture mode was investigated by EDS line to see more.

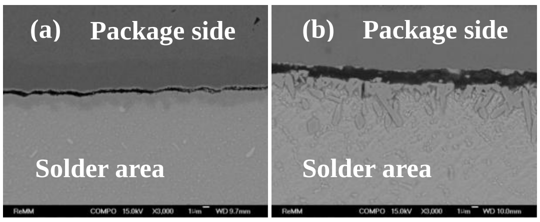


Fig. 6. Fracture mode after drop strength on Ni pad. (a) Electrolytic Ni pad (b) Electroless Ni pad

In case of Electrolytic Ni pad, it was shown the crack propagation was from between $(Cu,Ni)_6Sn_5$ IMC and $(Ni,Cu)_3Sn_4$. Crystal structure of Ni and Cu is FCC. And reformed IMC on Ni and Cu layer is HCP system. In case of cell volume, Cu and Ni is $0.04666nm^{-3}$ and Ni_3Sn_4 , Cu_3Sn , Cu_6Sn_5 is 0.24999, 1.141331, $0.779368nm^{-3}$.[22] It has the lattice mismatch between IMC and substrate by difference of cell volume. If the shock wave from

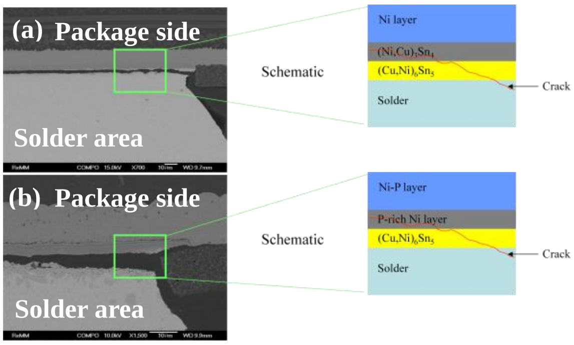


Fig. 7. Schematic of crack propagation after drop strength. (a) Electrolytic Ni pad (Crack propagation along the between pad and IMC layer on package side: Interfacial fracture mode) (b) Electroless Ni pad (Crack propagation along the P containing IMC on package side: Interfacial fracture mode)

outside is higher than the critical stress on intermetallic compound's boundary surface generated each of the difference stress, the crack is propagated along the weakest interface composed of $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$. Therefore it is necessary to control the $(Ni,Cu)_3Sn_4$ IMC formation for minimization purpose of lattice mismatch.

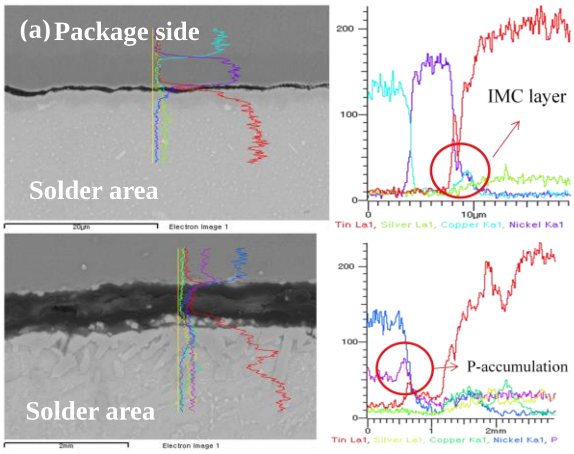


Fig. 8. EDS line pro-file after drop strength on Ni pad. (a) Electrolytic Ni pad (b) Electroless Ni pad

In case of electroless Ni pad, result of fracture mode after drop test, the crack was formed P-rich Ni layer between IMC and electroless Ni layer. Electroless Ni was formed amorphous status on Cu plating. But, during reflow process, Ni of UBM was reacted with solder (Tin), and then Ni(P) was changed phase transformation such as Ni-Sn-P through Ni_3P. It made a volumetric shrinkage.[23] Ni_3P was weak performance and we found from this study the crack was propagated quickly through inside. Therefore, Ni_3P thickness must be controlled.

Fig. 5 shows, Sn-1.0Ag1.0Cu solder had the best drop performance regardless pad materials. We observed the $(Ni,Cu)_3Sn_4$ IMC , Ni_3P layer with transmission electron microscopy (TEM) as shown Fig. 9.

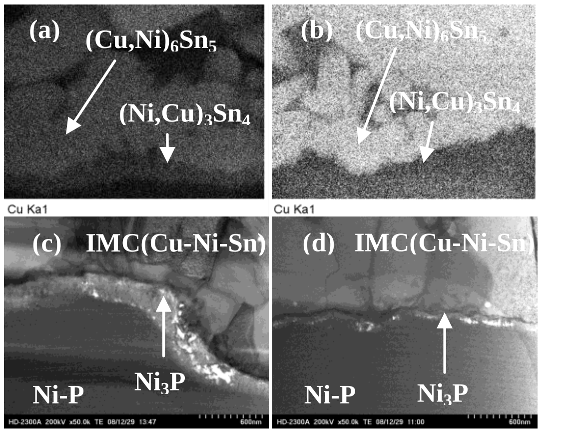


Fig. 9. TEM image of various Ni pad. (a) Electrolytic Ni pad: Sn-1.0Ag-0.5Cu (TEM mapping image) (b) Electrolytic Ni pad: Sn-1.0Ag-1.0Cu (TEM mapping image) (c) Electroless Ni pad: Sn-1.0Ag-0.5Cu (TEM image) (d) Electroless Ni pad: Sn-1.0Ag-1.0Cu (TEM image)

Fig. 9 shows TEM image for Sn-1.0Ag-0.5Cu solder and Sn-1.0Ag-1.0Cu. Sn-1.0Ag-1.0Cu. solder was more controlled $(Ni,Cu)_3Sn_4$ and Ni_3P layer thickness than Sn-1.0Ag-0.5Cu solder. This is already we mentioned, $(Cu,Ni)_6Sn_5$ IMC reaction speed was faster than $(Ni,Cu)_3Sn_4$ and effect of Cu was as below: Ni diffusion control, $(Ni,Cu)_3Sn_4$ IMC control, Ni_3P layer growth speed control.
Therefore, the sample which required high reliability such as drop strength must be considered to use high Cu contents solder.

4. Conclusion

We examined the relationship between the kind of Ni pad and the reliability of solder ball (various Cu content) for package substrates such as BGA. The results are shown below;

(1) Electrolytic Ni pad, we found the difference a kind of IMC depended on various Cu content. If Cu contents were increased, it was a gap between $(Cu,Ni)_6Sn_5$ IMC and bulk solder by difference of thermal expansion. In case of difference of thermal expansion was made compression stress in bulk solder and formed many needle-shaped.
In case of electroless Ni pad, it was observed P-rich Ni layer regardless Cu contents in solder. If Cu contents were increased, the small Ni contents were consumed the Cu-Ni-Sn IMC, then P-rich Ni-layer was formed thin layer.

(2) When Cu contents were increased, shear strength was also increased. And this is formed needle-shaped and had a network structure and was increased combination area in interfacial joint.

(3) As a result of drop test, we found the difference of fracture mode between the kinds of Ni pad. In case of electrolytic Ni pad, crack was propagated along the weakest interface composed of $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$. Electroless Ni pad, crack was propagated along the P-rich Ni-layer.

(4) Sn-1.0Ag-1.0Cu had the best drop performance. $(Cu,Ni)_6Sn_5$ IMC reaction speed was faster $(Ni,Cu)_3Sn_4$ and effect of Cu was as below: Ni diffusion control , $(Ni,Cu)_3Sn_4$ IMC control , Ni_3P layer growth speed control. Therefore, the sample which required high reliability such as drop strength must be considered to use high Cu contents solder.

Reference

[1] Surface Finishes: 21stCentury Challenge
–Jack Josefowicz, Ph.D.,Directorof Technology, Tyco Printed Circuit Group

[2] A. Nadai, "Theory of flow and Fracture of solids", 2,535, McGraw-Hill, NY(1967)

[3] W. M. Chen, M. McCloskey, and S. C. O, "Isothermal aging effects on the microstructure and solder bump shear strength of eutectic Sn37Pb and Sn3.5Ag solder", Microelectron. Reliab. 46, 896(2006)

[4] Glenn O. Mallory and Juan B. Hadju, Electroless plating : fundamentals and applications, (American electroplater and surface finishers society, 1990) Ch. 4.

[5] R. Achenbrenner, A. Ostmann, U. Beutler, J. Simon and H.Reichl, "Electroless nickel/copper plating as a new bump metallization", IEEE Trans. CPMT, Part B18(2), 334(1995)

[6] T. I. Eijim, D.B. Hollesen, A. Holiday, S. A. Gahr and R. J. Coyle, "Assembly and reliability of thermally enhanced high I/O BGA packages", Proc 21st IEEE International Electronics manufacturing Symposium 25 (1997)

[7] Z.Mei, M. Kauffmann, A. Eslambolchi and P. Johnson, "Brittle interfacial fracture of PBGA packages on electroless Ni/immersion Au", Proc 48th Electronic Component and Technology Conference 952 (1998)

[8] N. Biunno, "A root cause failure mechanism for solder joint integrity of electroless Ni/immersion gold surfaces", Proc IPC Printed Circuits Expo 1999 s15-5 (1999)

[9] G. M. Wenger, R. J. Coyle, P. P. Solan, J. K. Dorey, C. V. Dodd, R. Erich and A. Primavera, "Case sudies of brittle interfacial fractures in area array solder interconnects", Proc 26th International Symposium for testing and failure analysis 355 (2000).

[10] D. Cullen, E. Huenger, M. Toben, B. Houghton and K. Johal, "A study on interfacial fracture phenomenon of solder joints formed using the electroless nickel/immersion gold surface finish", Proc IPC works 2000 s03-2 (2000).

[11] C. H. Zhong and S. Yi, "Solder joint reliability of plastic ball grid array", Soldering and Surface Mount Technology. 11(1), 44 (1999).

[12] D. Goyal, T. Lane, P. Kinzie, C. Panichas, K. M. Chong and O. Villalobos, "Failure mechanism of brittle solder joint fracture in the presence of electroless Ni immersion gold (ENIG) interface", Proc 52nd Electronic Component and Technology Conference 732 (2002).

[13] S. Wiegele, P. Thompson, R. Lee and E. Ramsland, "Reliability and process characterization of electroless nickel-gold/solder flip chip interconnect technology", Proc 48th Electronic Component and Technology Conference 861 (1998).

[14] K. Johal, H. Robertss, S. Lamprecht and H.J. Schreirer, "Impacts of Bulk Phosphorous Content of Electroless Ni layers to solder joint integrity and their use as gold and aluminum wire bond surfaces", J. SMT, 17, 18 (2002)

[15] Martin Goosey, "Factors influencing the formation of 'black pad' in electroless nickel-immersion gold solderable finishes-a processing perspective", Circuit World, 28, 36 (2002)

[16] K. Yokomine, N. Shimizu, Y. Miyamoto, Y. Iwata, D. Love, and K. Newman, "Development of electroless Ni/Au plated build-up flip chip package with highly reliable solder joints", Proc. Elec. Comp. Tech. Conf., 1384 (2001)

[17] Goyal D, Lane T, Kinzie P, Panichas C, Chong KM, and Villalobos O, "Failure mechanism of brittle solder joint fracture in the presence of electroless nickel immersion gold(ENIG) interface", Proc. Elec. Comp. and Technol. Conf., 732 (2002)

[18] Zequn Mei; Johnson, P.; Kaufmann, M.; Eslambolchi, A., "Effect of electroless Ni/immersion Au plating parameters on PBGA solder joint attachment reliability", Proc. Elec. Comp. and Technol. Conf., 125 (1999)

[19] A. Bai, P. Y. Chuang, and C. C. Hu, “The corrosion behavior of Ni-P deposits with high phosphorous contents in brine media”, J. Mater. Chem. Phys., 82, 93 (2003)

[20] M.O. Alam, Y.C. Chan and K.N. Tu, “Effect of 0.5wt% Cu in Sn-3.5Ag solder on the interfacial reaction with Au/Ni metallization”, Chem. Mater. 49 813 (2003)

[21] Y.D. Jeon, K.W. Paik, K.S. Bok, W.S. Choi, C.L. Cho, “Study on the electroless nickel UBM-solder interfacial reaction and their effects on flip chip solder joint reliability”, J. Electron Mater., Vol 31, No 5, 520-528, (2002)

[22] Chen Xu, G.T. Galyon, S.Lai, B. Notohardjoni, Asa Frye,”tin whisker modeling committee”, INEMI (2005)

[23] J. W. Yoon, W. C. Moon and S. B. Jung, “Interfacial Reaction of ENIG/Sn-Ag-Cu/ENIG Sandwich Solder Joint during Isothermal Aging”, Micro. Eng.,83, 2329 (2006).