The Role of the Interfacial Intermetallic in Lead-Free Solder

Keith Howell & Keith Sweatman
Nihon Superior Co., Ltd.
Osaka, Japan

ABSTRACT
The formation during the soldering process of the layer of intermetallic compound Cu_6Sn_5 at the solder substrate interface provides the essential evidence that a metallurgical bond that is the basis of a solder joint has been established. Although the importance of this interfacial intermetallic was long recognized in tin-lead solders the implications of the change to lead-free solders on this layer and its impact on solder joint reliability are yet to be fully understood. An obvious and important difference is that the copper required to form that intermetallic that for tin-lead solder joints could come only from the substrate is now a constituent of all of the commonly used lead-free solders. It has recently been found that the allotropic transformation of the Cu_6Sn_5 from the hexagonal close packed form to the monoclinic form as the temperature falls below 186°C appears to have implications in lead-free solders that it did not have in tin-lead solders. This paper reports the discovery that the inclusion of a specific level of nickel in the formulation of a tin-copper solder has the effect of stabilizing the hexagonal close packed form of the intermetallic at normal operating temperatures. The consequences of this stabilization on the mechanical integrity and three-dimensional structure of the intermetallic layer will be described and the implications for solder joint reliability reviewed.

INTRODUCTION
Alloys of metals which have limited solid solubility may form during solidification new phases which differ from the more common solid solutions to the extent that the constituent elements are in a particular stoichiometric ratio. These phases, known as intermetallic compounds (IMC) typically have a crystal structure that is different from the constituent metals. Because of that different crystal structure these IMC have mechanical, electrical and chemical properties that can be very different from those of their constituent elements and that has implications for behavior of the solder of which they are a part.

Possibly the most significant difference between tin-lead alloys and most of the alloys now considered suitable as lead-free solders is that in addition to occurring at the solder substrate interface IMC are an unavoidable part of the microstructure formed during solidification even on an inert substrate. These IMC are ideally in the form of a finely dispersed secondary and sometimes tertiary phase of a eutectic but also sometimes in the form of primary crystals in hypereutectic alloys, which if they are large in relationship to the joint dimensions, as can be the case with the plate-like crystals of Ag_3Sn can compromise the reliability of the joint

An indication of how ill-prepared the electronics industry was to deal with these IMC dispersed within the solder is that when they occurred in tin-lead solder as a result of a build up of copper in a wave solder pot they were considered so undesirable that the recommendation was to reduce the copper level by completely or partially draining the solder bath and refilling with fresh copper-free solder. And although an IMC layer is a useful indicator of proper wetting of joints substrates (Figure 1) in tin-lead solder a thick layer at the solder substrate interface was seen as an area of weakness that could jeopardize the reliability of the solder joint in service, particularly under conditions of impact loading.

However, the industry now has to come to terms with the fact that the two elements chosen as the primary replacement for lead in solder, copper and silver, have virtually no solubility in tin in the solid state and appear in the microstructure only as IMC.

During soldering there are two interactions between the molten solder and the substrate. There is a tendency for the substrate to dissolve in the molten solder and a tendency for the substrate to react with the tin in the solder to form an IMC at the solder/substrate interface. When the solder solidifies the dissolved substrate elements will precipitate within the bulk solder as a primary or eutectic phase or at the solder/substrate interface with the basis for determining which alternative predominates still not fully understood.

Whether or not a liquid will wet a solid substrate is dependent on the balance of surface free energies and does not require the formation of an intermetallic at the interface. However, the presence of an interfacial IMC does provide useful visual evidence that wetting has occurred. The chemical reaction between the tin in the solder and the metal in the substrate cannot occur unless the solder has wet.

For the two most common substrates, copper and nickel the interfacial IMC formed are, respectively, Cu_6Sn_5 and Ni_3Sn_4. On an electroless nickel substrate the situation is complicated by presence of phosphorus which also forms compounds with the metallic elements present in the system.

In this paper, only the interaction between solder and a copper substrate will be considered.

In the tin-lead system the active element is the tin since lead does not form IMC with any of the elements usually present in solder joints. The only IMC present in a tin-lead joint is that formed by reaction between the tin and the substrate.

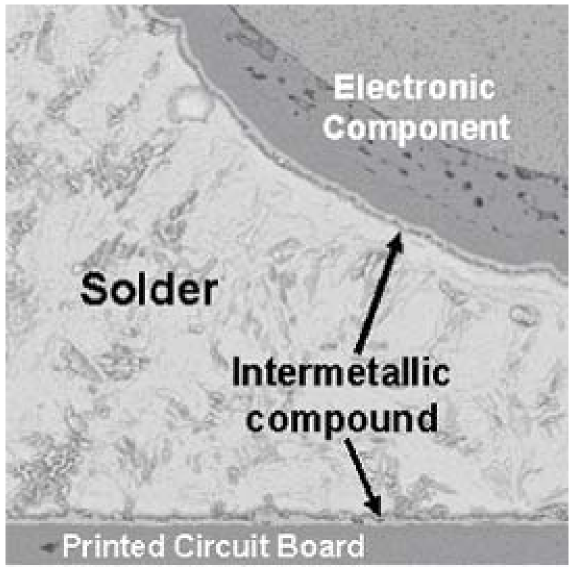

Figure1. The Intermetallic Layers in a Solder Joint

STABILITY OF INTERMETALLIC GROWTH

While the addition of silver to the tin-copper system seems to accelerate growth of the interfacial IMC nickel appears to act as an inhibitor (Figure 2). In the Sn-0.7Cu alloy this inhibition seems to be greatest at a nickel level of 0.05% [1]. As can also be seen in Figure 4 the morphology of the IMC is also affected by the tertiary addition to the tin-copper system. Although initially thicker the IMC in the tin-copper-nickel system remains smooth and compact while in other alloy systems it develops a pronounced columnar form (Figures 2 and 3)

Since the a thick layer of the relatively brittle interfacial IMC is considered to provide an easy path for crack propagation its stability in the tin-copper-nickel system is expected to have beneficial consequences for the reliability of this alloy in service.

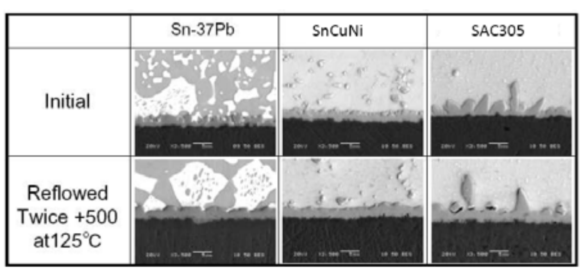

Figure 2. Change in the Interfacial IMC at Elevated Temperature.

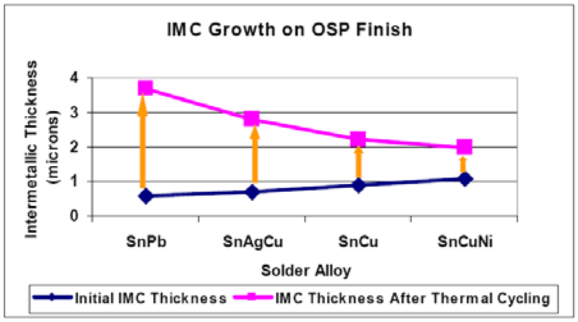

Figure 3. Intermetallic growth after 4000 cycles (-40°C / +125°C)

THE EFFECT OF NICKEL

That Cu_6Sn_5 exists in two allotropic forms with a transformation from the hexagonal η to the monoclinic η' at 186°C [2] (Figure 4). The hexagonal crystal (Figure 5) has symmetry as a right prism with a hexagonal base while the monoclinic crystal structure forms a rectangular prism with a parallelogram base (Figure 6). For a solder joint that change from η to η' has two significant consequences. There is a 2.15% increase in volume and the mechanical properties of the η' phase are different from those of the η phase.

It has been established [3] that when nickel is added to a tin-copper alloy it incorporates preferentially in the Cu_6Sn_5 substituting for copper in the crystal structure. It has now been found [4] that the nickel stabilizes the higher temperature hexagonal close packed (hcp) form down to room temperature (Figure 7).

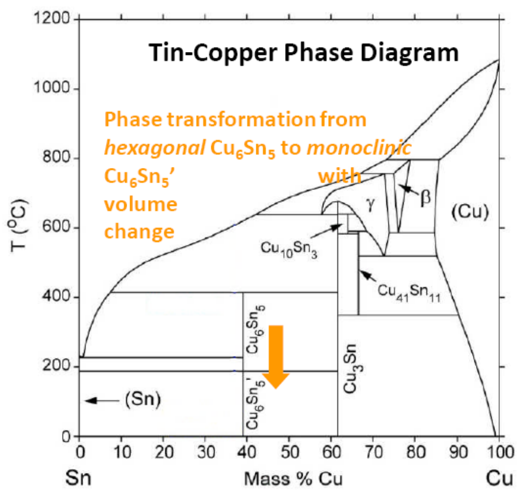

Figure 4. Tin-Copper Phase Diagram.

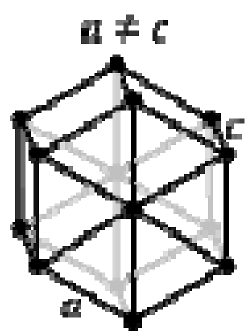

Figure 5. Hexagonal crystal, Ref. Gia.Cossa.

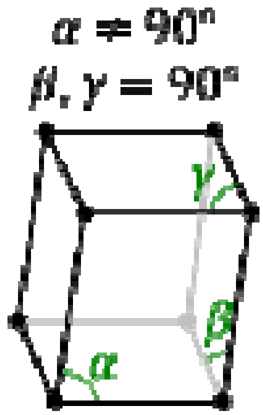

Figure6. Monoclinic crystal, Ref. Gia.Cossa.

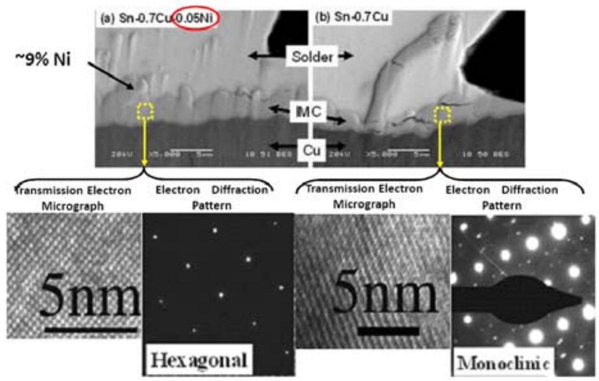

Figure7. Room Temperature Crystal Structure of $(Cu,Ni)_6Sn_5$ and Cu_6Sn_5 and their Morphology in a Solder Joint.

INCIPIENT CRACKING IN THE IMC LAYER

There is evidence [5] that there is less cracking in the interfacial IMC when the hcp form has been stabilized by the presence of nickel (Figures 7, 8, 9, 10) It is presumed that one reason that there is less cracking is that avoidance of the stress that would otherwise be generated by the volume increase in the solid state. Difference in the mechanical properties of the hcp form could also be a factor and this is something that is currently being investigated

Table 1. Alloys Tested

Alloy	Composition
Sn-Pb	Sn-37Pb
Sn-Cu	Sn-0.7Cu
Sn-Cu-Ni	Sn-0.7Cu-0.05Ni+Ge
Sn-Ag-Cu	Sn-3.0Ag-0.5Cu

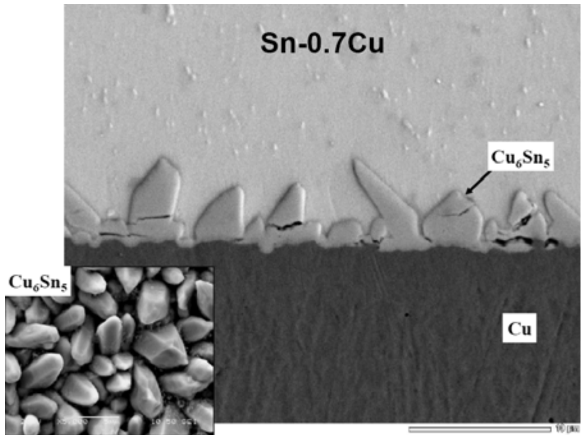

Figure8. IMC Layer in Sn-Cu

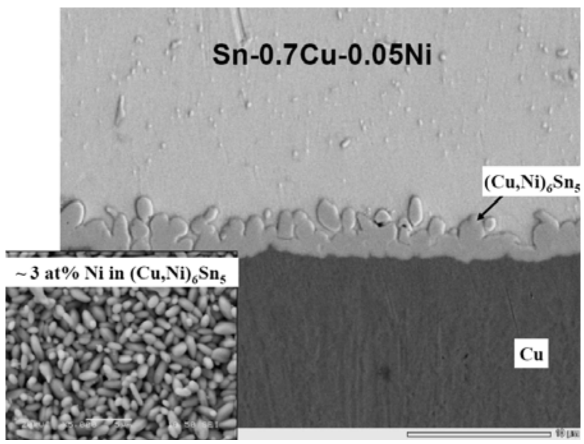

Figure9. IMC Layer in Sn-Cu-Ni

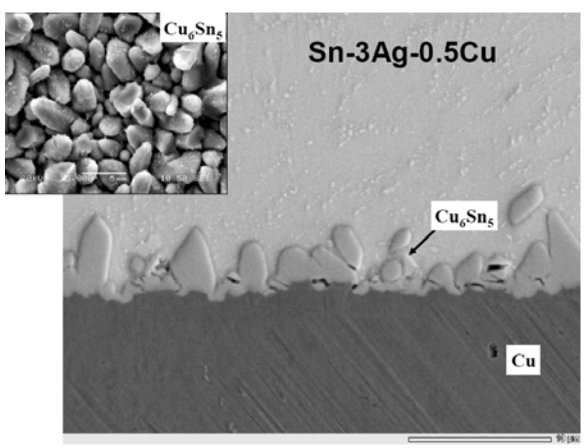

Figure10. IMC layer in Sn-Ag-Cu

SHEAR IMPACT PROPERTIES

0.5mm solder balls of the compositions listed in Table 1 were reflowed onto fluxed solder-mask-defined pads on 1.6mm FR-4 copper laminate which had an OSP finish. These were subjected to shear impact at speeds of 10, 100, 1000, 2000, and 4000 m/s in a Dage HS4000 bond tester and from the force-displacement plot a peak force and fracture energy were determined. The failure mode was also noted from examination of the fracture by scanning electron microscopy of the fracture surfaces and cross-sections through the fracture.

Three fracture modes were recognized (Figure 11). In Type I the fracture propagates through the interfacial IMC (Figures 12 & 13). In Type II failure the fracture propagates through the body of the solder sphere (Figure 14). In Type III there is no crack propagation ahead of the impact head and the sphere is simply sheared by the impact head (Figures 15).

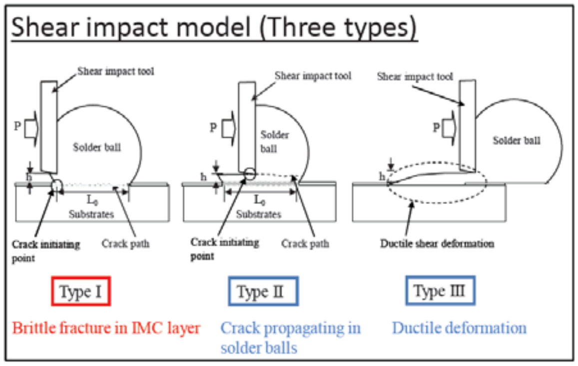

Figure11. Shear Impact Model Defining Failure Modes.

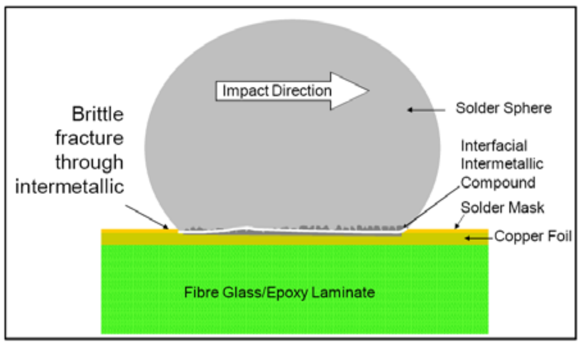

Figure12. Schematic Representation of Type I Fracture.

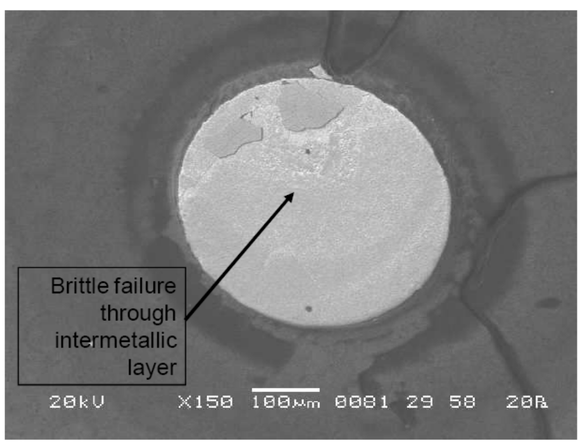

Figure13. Example of Type I Fracture

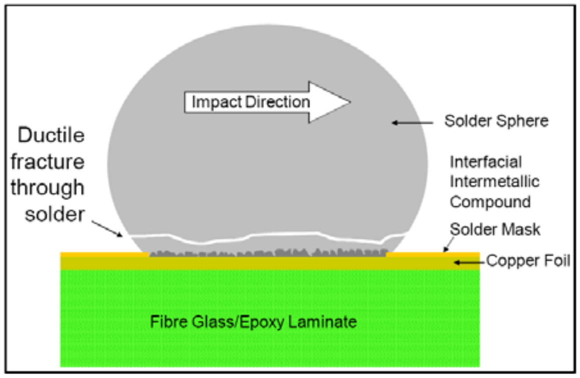

Figure14. Schematic Representation of Type II failure

The fracture energy and maximum force were plotted as a function of the shear speed for the four alloys tested (Figures 16-19). In these plots a distinction is made between the fracture energy up to the peak force and the fracture energy thereafter through to failure. The peak force is taken at the force required to initiate crack propagation so that the energy absorbed in the completion of the fracture is a measure of the ease of crack propagation.

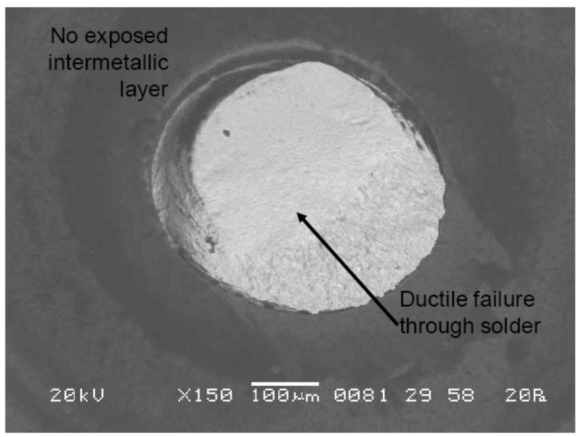

Figure 15. Example of Type III Fracture.

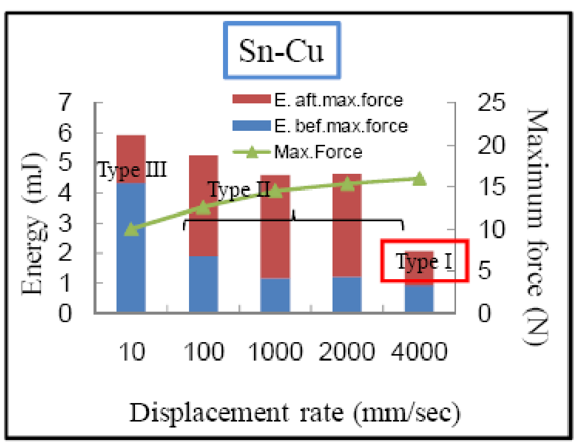

Figure 16. Sn-Cu Shear Failure Modes, Peak Force and Fracture Energy.

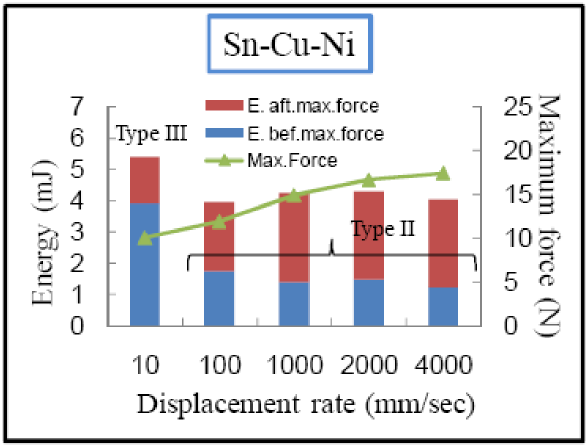

Figure 17. Sn-Cu-Ni Shear Failure Modes. Peak Force and Fracture Energy

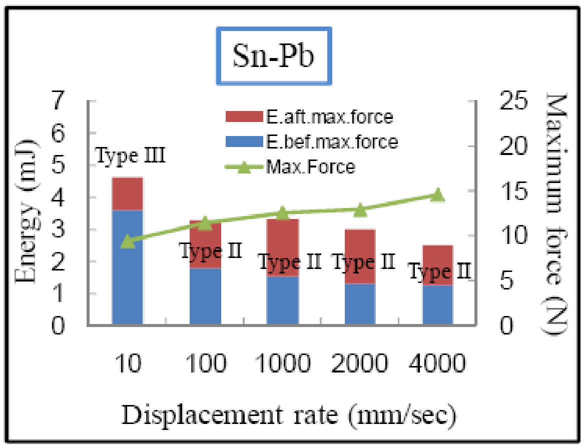

Figure 18. Sn-Pb Shear Failure Modes, Peak Force and Fracture Energy.

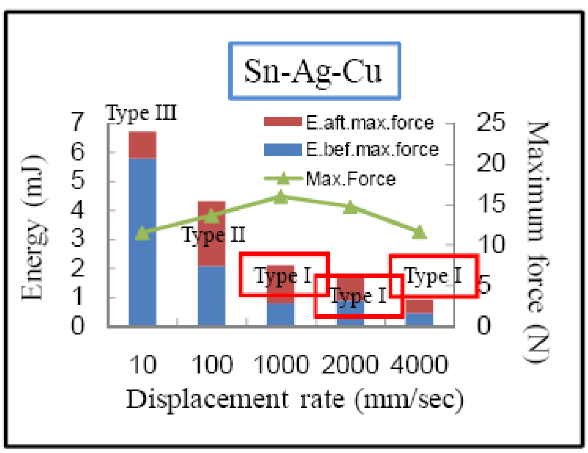

Figure 19. Sn-Ag-Cu Shear Failure Modes, Peak Force and Fracture Energy.

CONCLUSIONS

Sn-Pb and Sn-Cu-Ni do not exhibit Type I failure at any of the shear speeds tested (Figures 17 & 18). Sn-Cu exhibits Type 1 failure at the maximum shear speed of 4000 m/s (Figure 16) whereas Sn-Ag-Cu fails in the brittle manner at shear speeds of 1000mm/s and above (Figure 19). All of the alloys exhibit Type III ductile shear failure at the lowest shear speed of 10 mm/s. The fracture modes of Sn-Pb, Sn-Cu-Ni, and Sn-Ag-Cu are shown schematically in Figure 20. Sn-Ag-Cu BGAs exhibited a low resistance to shear impact loading over the whole range of shear speeds tested.

The deformation energy after the peak load of the shear testing of Sn-Ag-Cu BGAs is very low which indicates that crack propagation is easy through the already-cracked IMC phase

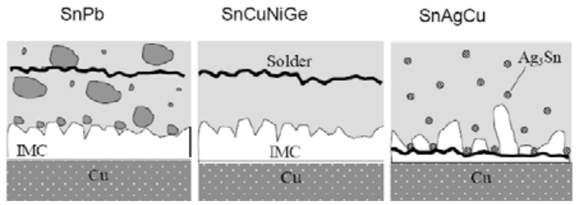

Figure 20. Apparent Fracture Modes on Cu substrate.

SUMMARY

1. Nickel stabilizes the hexagonal close packed form of Cu_6Sn_5 at temperatures below the 186°C transformation temperature of the unstabilized phase
2. The nickel stabilization of the Cu_6Sn_5 reduces the incident of initial cracking in the IMC layer in the as-soldered condition.
3. Stabilizing the interfacial intermetallic has a beneficial effect on the resistance of a solder joint to impact loading.
4. Sn-Cu-Ni BGAs exhibited superior properties in shear impact tests comparable with those of Sn-Pb and significantly superior to those of Sn-Cu and Sn-Ag-Cu BGAs.
5. Sn-Ag-Cu BGAs exhibited a low resistance to shear impact loadings at all the shear speeds tested.
6. The low deformation energy after the maximum load of in the Type I failure of Sn-Ag-Cu suggests that crack propagation is easy in the unstabilized IMC layer.

ACKNOWLEDGMENTS

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Nihon Superior Co., Ltd.
Osaka, Japan

2009 IPC Midwest Conference

IPC MIDWEST CONFERENCE & EXHIBITION

your partner for soldering solution

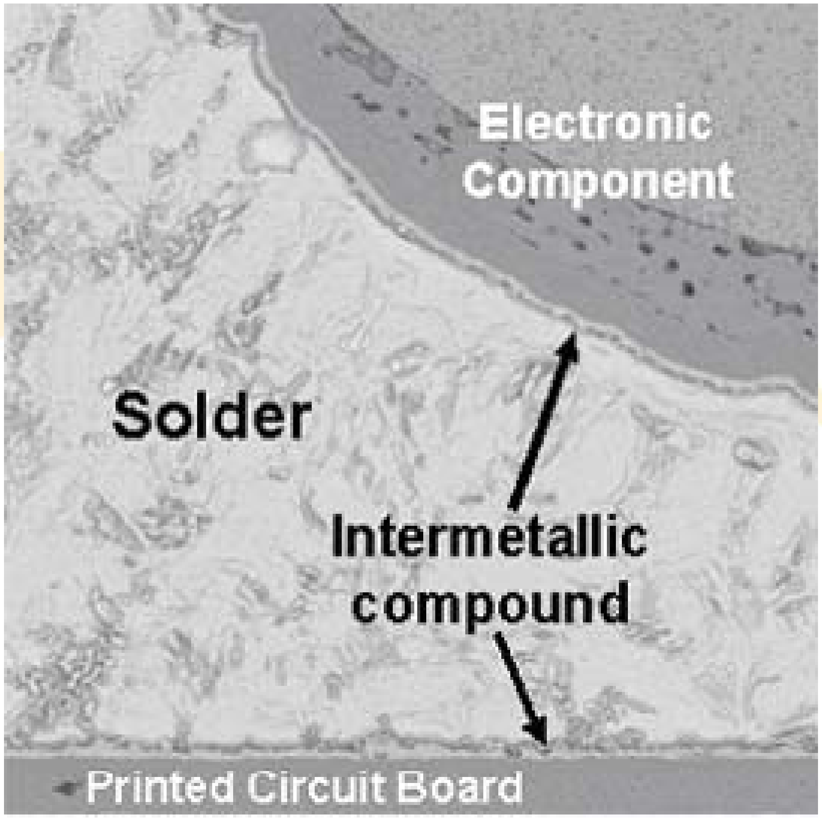
NIHON SUPERIOR

Intermetallic Compounds

- New phases form in metal alloys
  - During the solidification
  - By reactions with substrates
- These phases are classified as intermetallic compounds (IMC) rather than alloys because the constituent elements are present in specific stoichiometric proportions
- The crystalline structure is typically different than the constituent metals resulting in different:
  - Mechanical properties
  - Electrical properties
  - Chemical properties

Role of IMC in Solder Joints

- The IMC layer formed at the solder/ substrate interface play a critical role in the mechanical behavior solder joints.



IMC in Tin-Lead Solder Joints

- Lead does not form IMCs
- The only IMC present are those that result from reaction of the tin with substrate

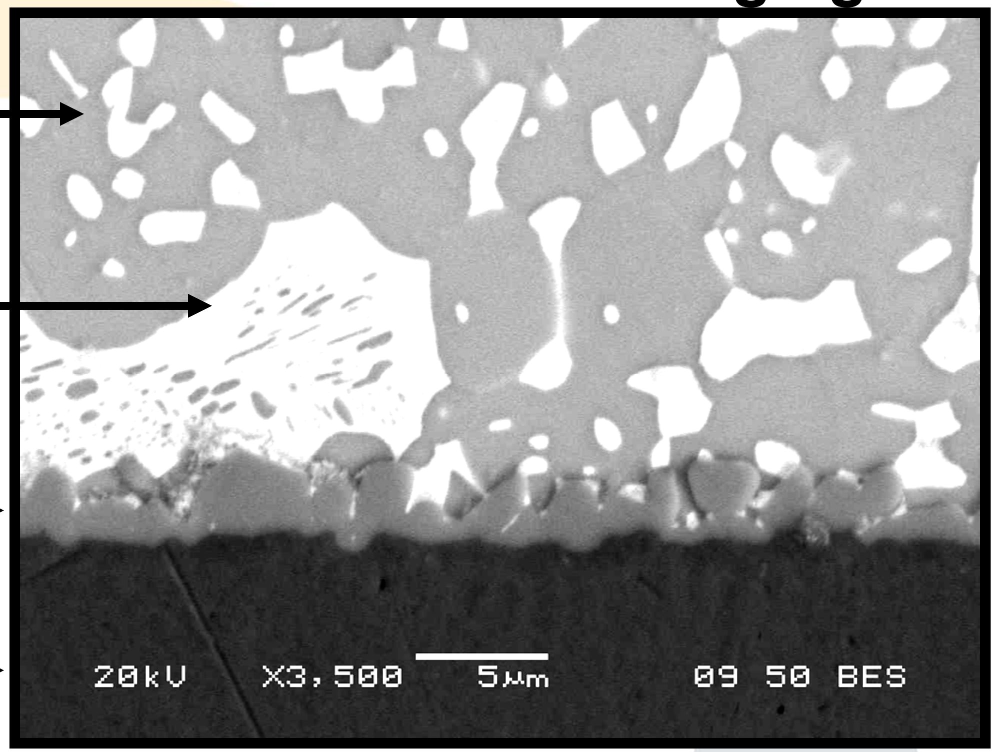
Interface of Tin-Lead solder and Substrate after Aging

Lead-rich phase
(solid solution of Sn in Pb)

Tin-rich phase
(solid solution of Pb in Sn)

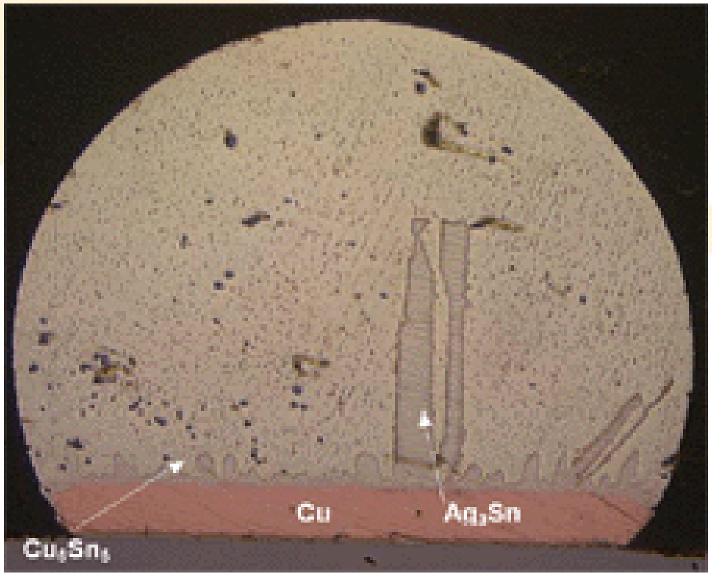
Interfacial IMC
(Cu_6Sn_5)

Copper



Lead-free

- Copper and silver replaces lead in solder
- Copper and silver have no solubility in tin in the solid state and appear in the microstructure only as IMC
  - Ag_3Sn
  - Cu_6Sn_5



Pb-Free Solders for Flip-Chip Interconnects
DR Frear, JW Jang, JK Lim & C Zhang,
JOM 53 (6) (2001) pp. 28-32

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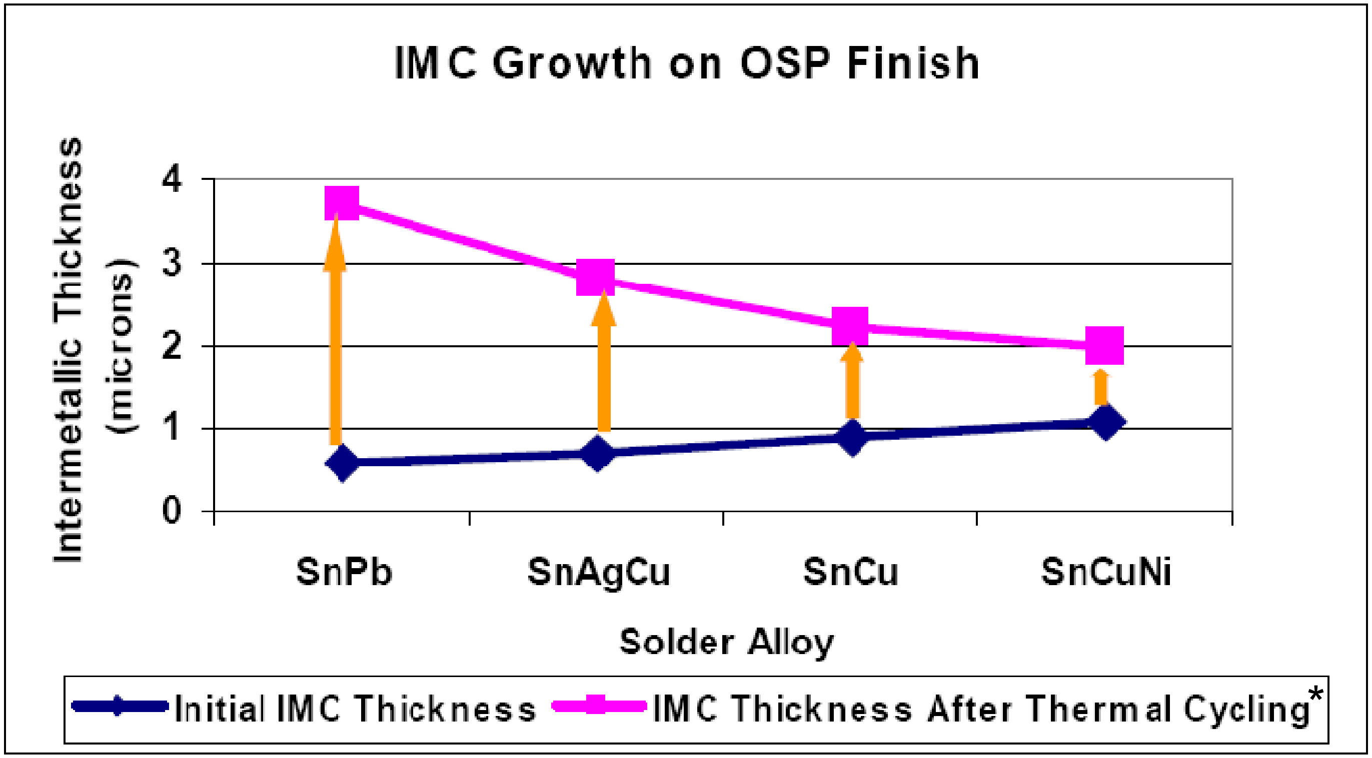
Intermetallic Growth

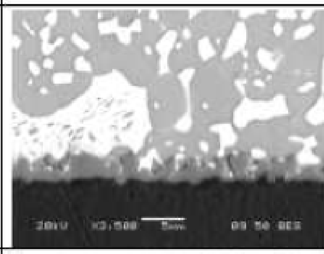
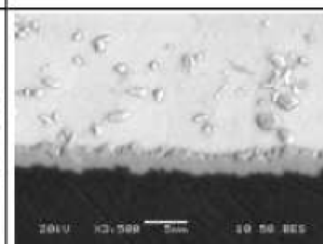
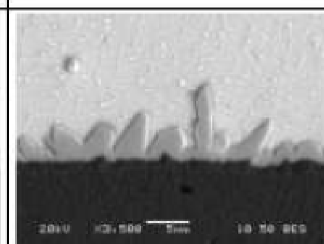
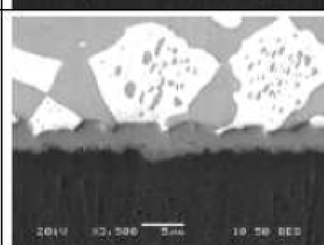
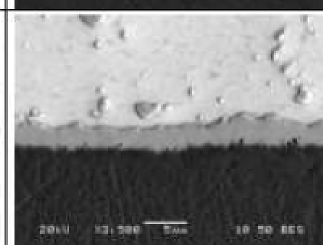
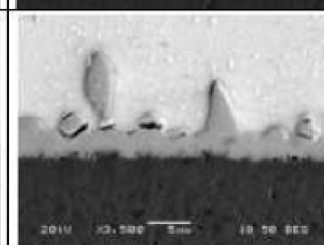
- Addition of silver to the tin-copper system seems to accelerate interfacial IMC growth
- Nickel appears to inhibit interfacial IMC growth



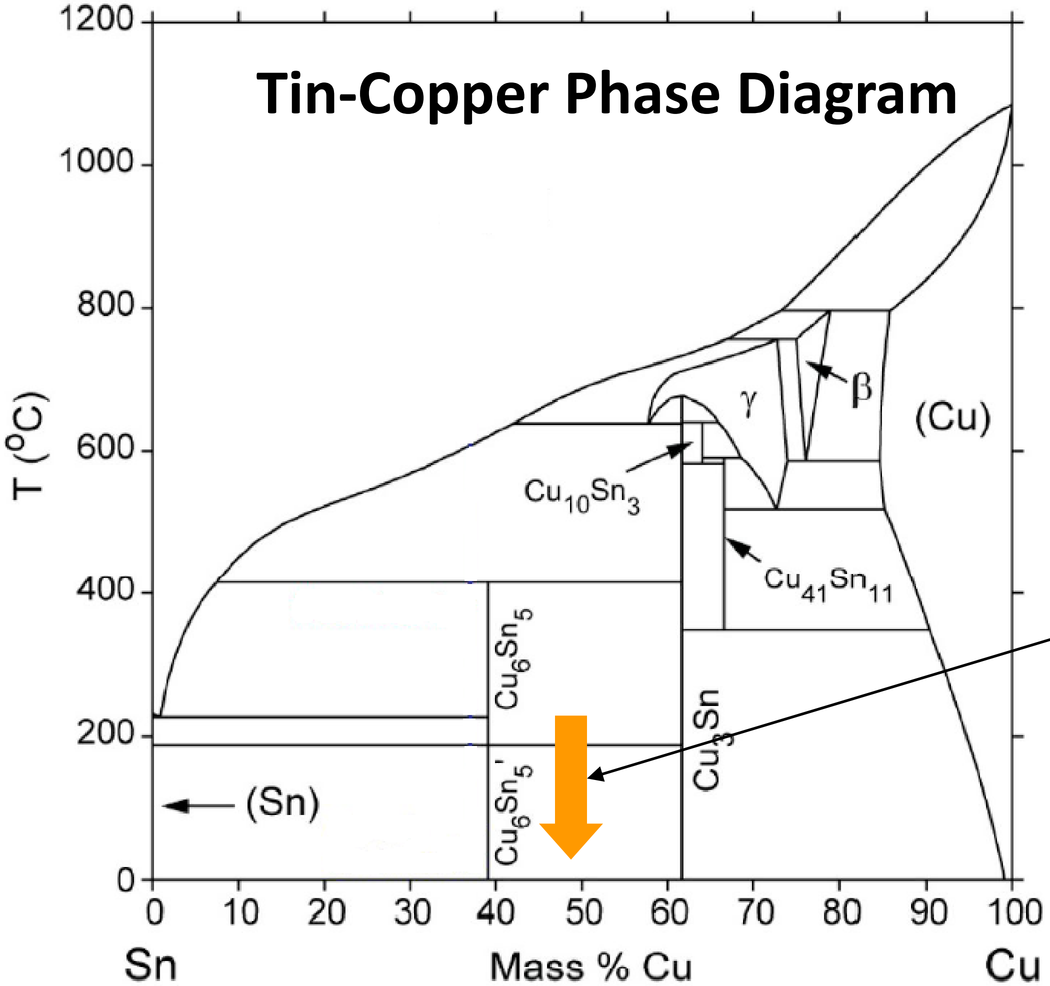
* 4000 Cycles -40 - + 125° C

Stability of Intermetallic Growth

- Thick layer of relatively brittle interfacial IMC is considered an easy path for crack propagation
- The SnCuNi system is expected to be beneficial for reliability
- The nickel in the intermetallic has the effect of suppressing columnar morphology, stabilizing the hexagonal close packed form of the Cu_6Sn_5 and slowing its growth

	Sn-37Pb	SnCuNi	SAC305
Initial			
Reflowed Twice +500 at125°C			

Stability of Intermetallic



Phase transformation from *hexagonal* Cu_6Sn_5 to *monoclinic* Cu_6Sn_5'

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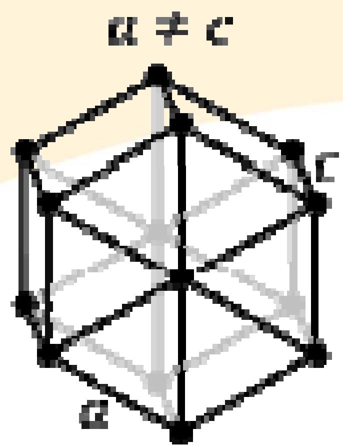
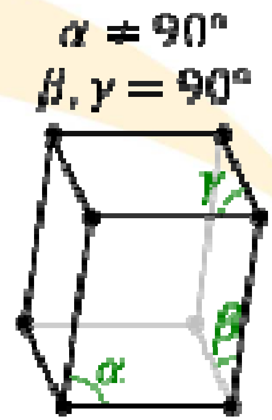
Crystal Structure

- Transformation from hexagonal to monoclinic at 186° C with 2.15% volume increase



Hexagonal



Monoclinic

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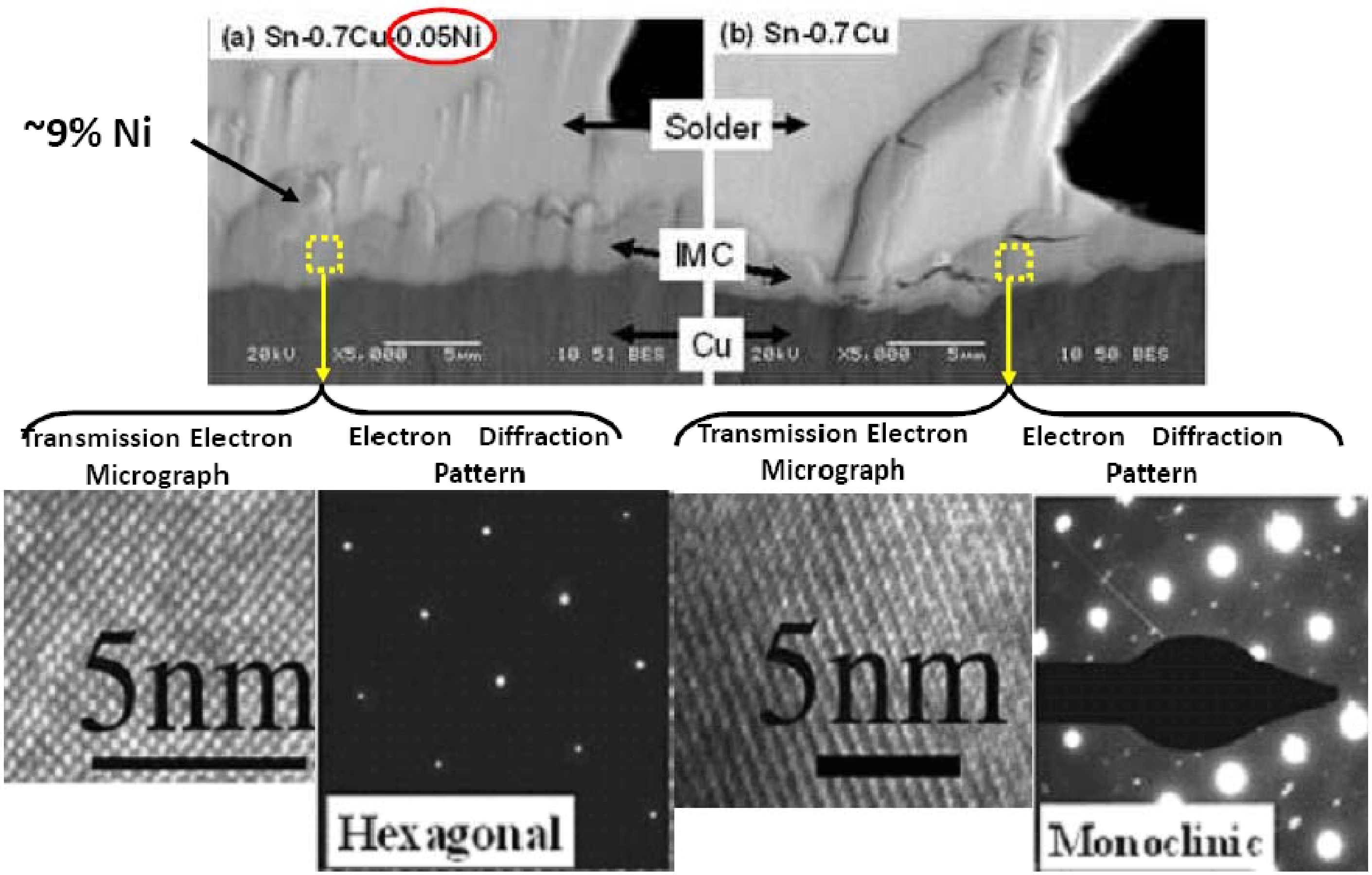
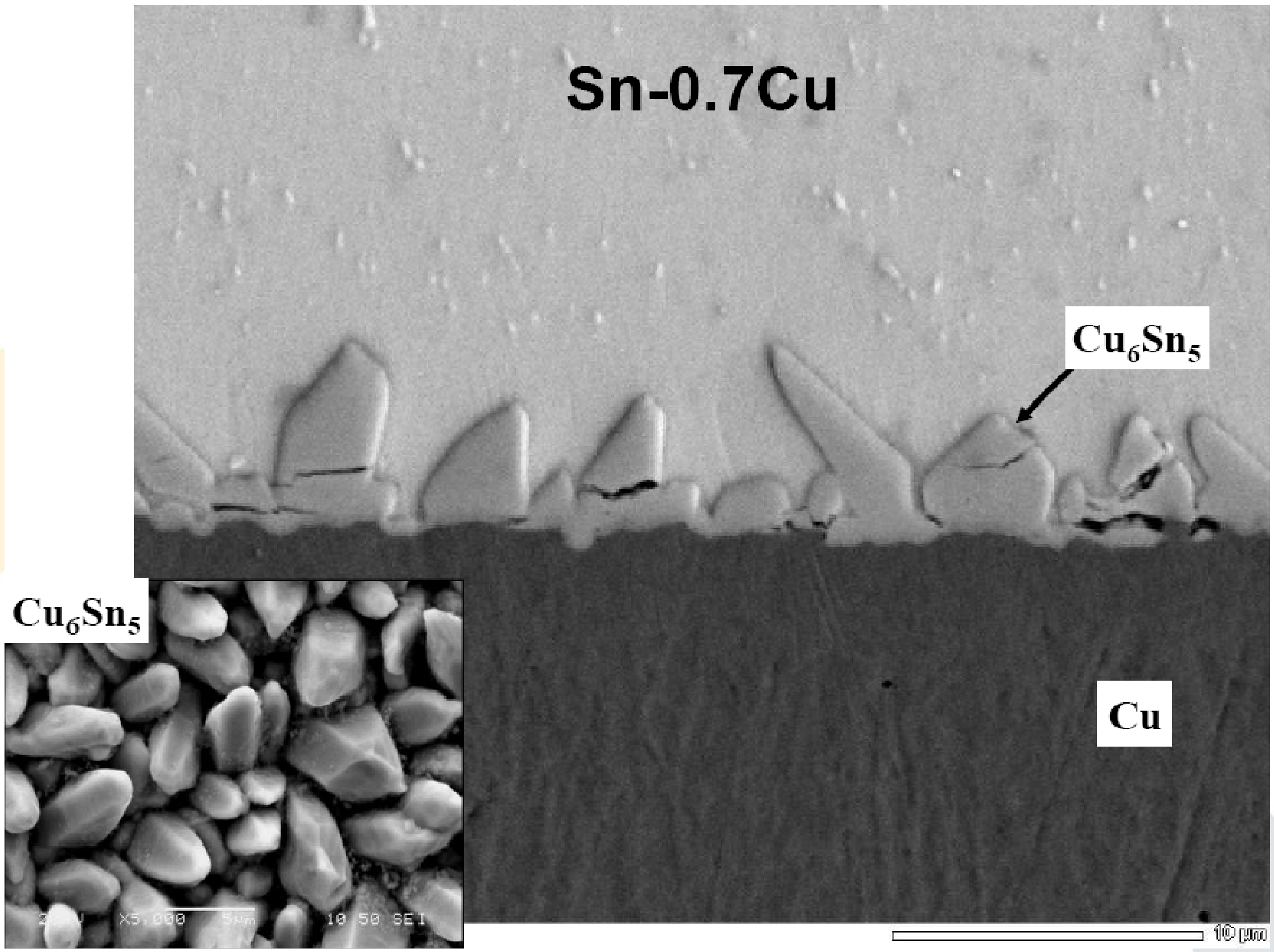
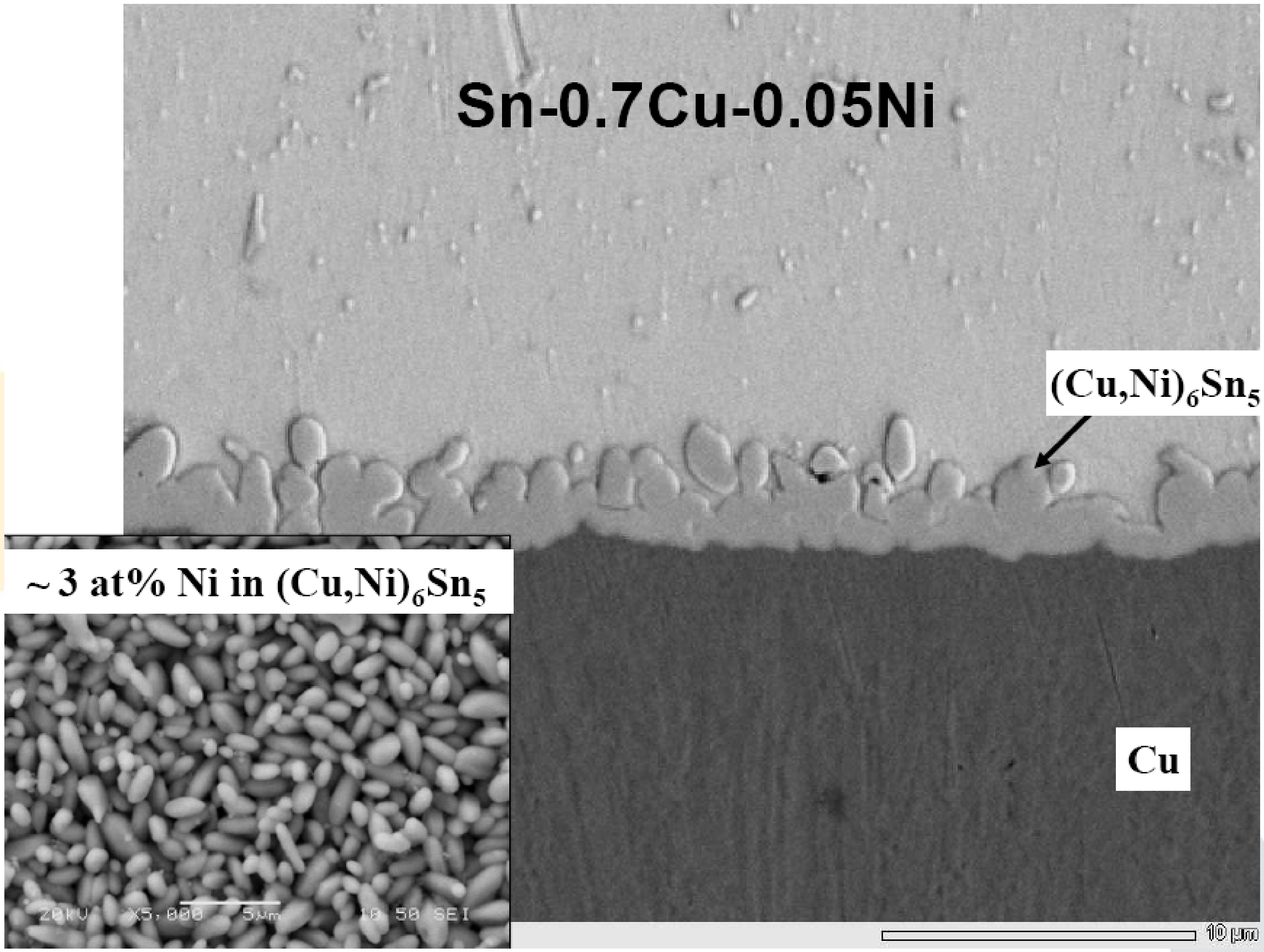
Crystal Structure



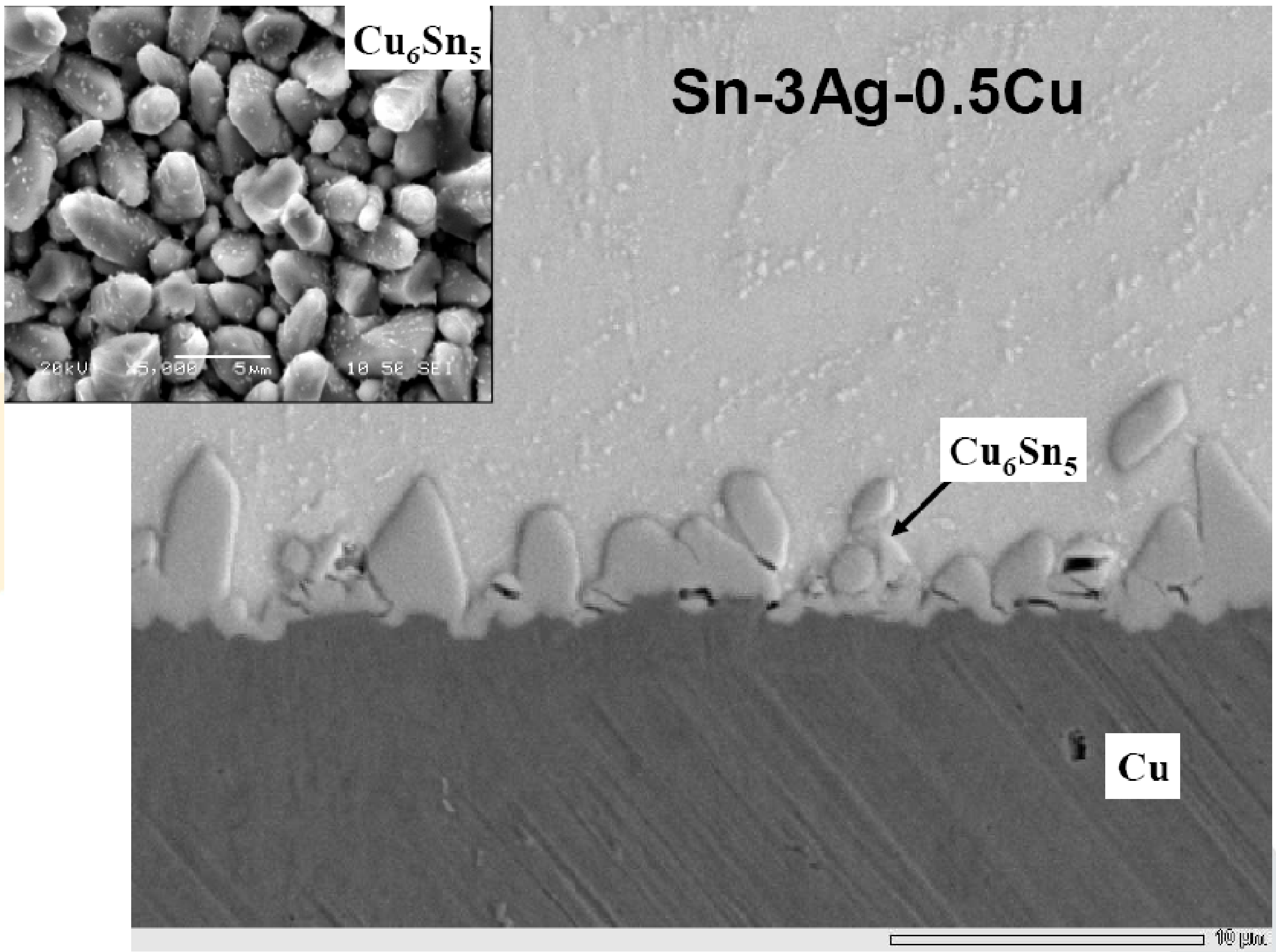
Interfacial IMC in Sn-Cu



Interfacial IMC in Sn-Cu-Ni



Interfacial IMC in Sn-Ag-Cu



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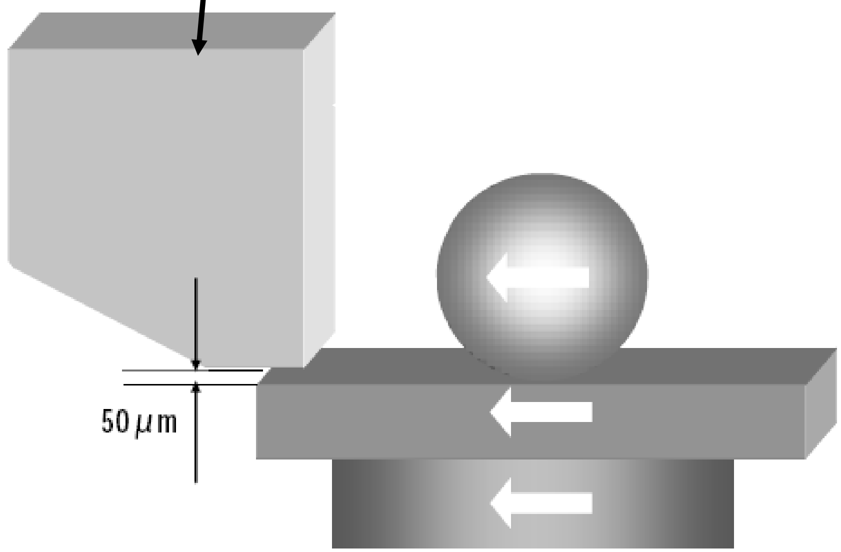
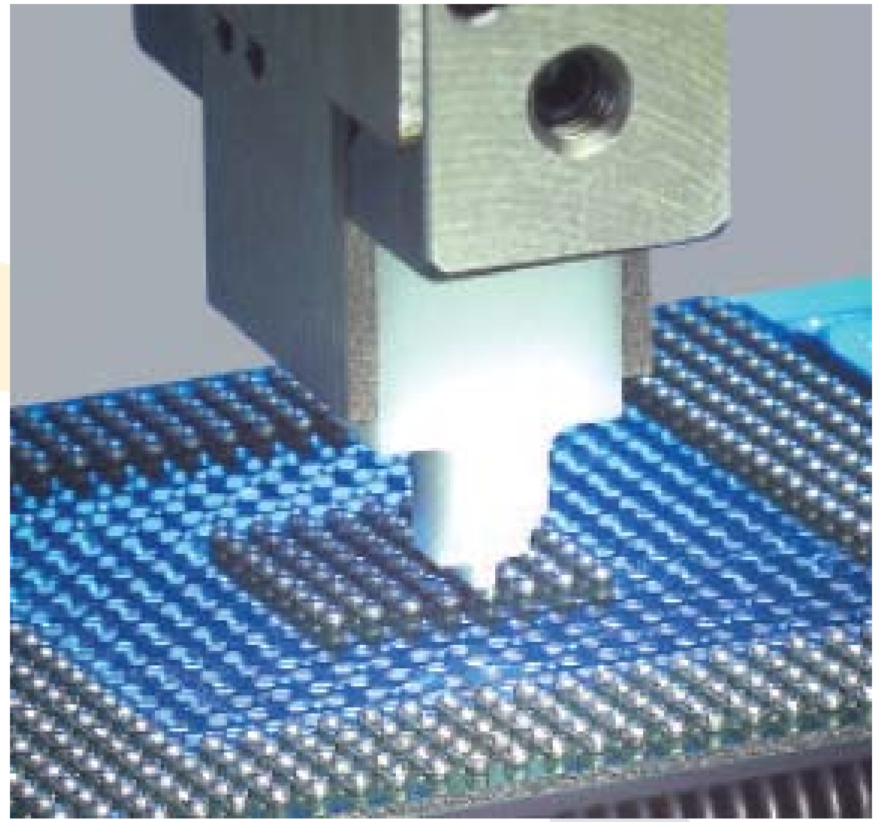
Test Apparatus

In Shear

Fixed shear tool with force measurement sensor



Test piece moves



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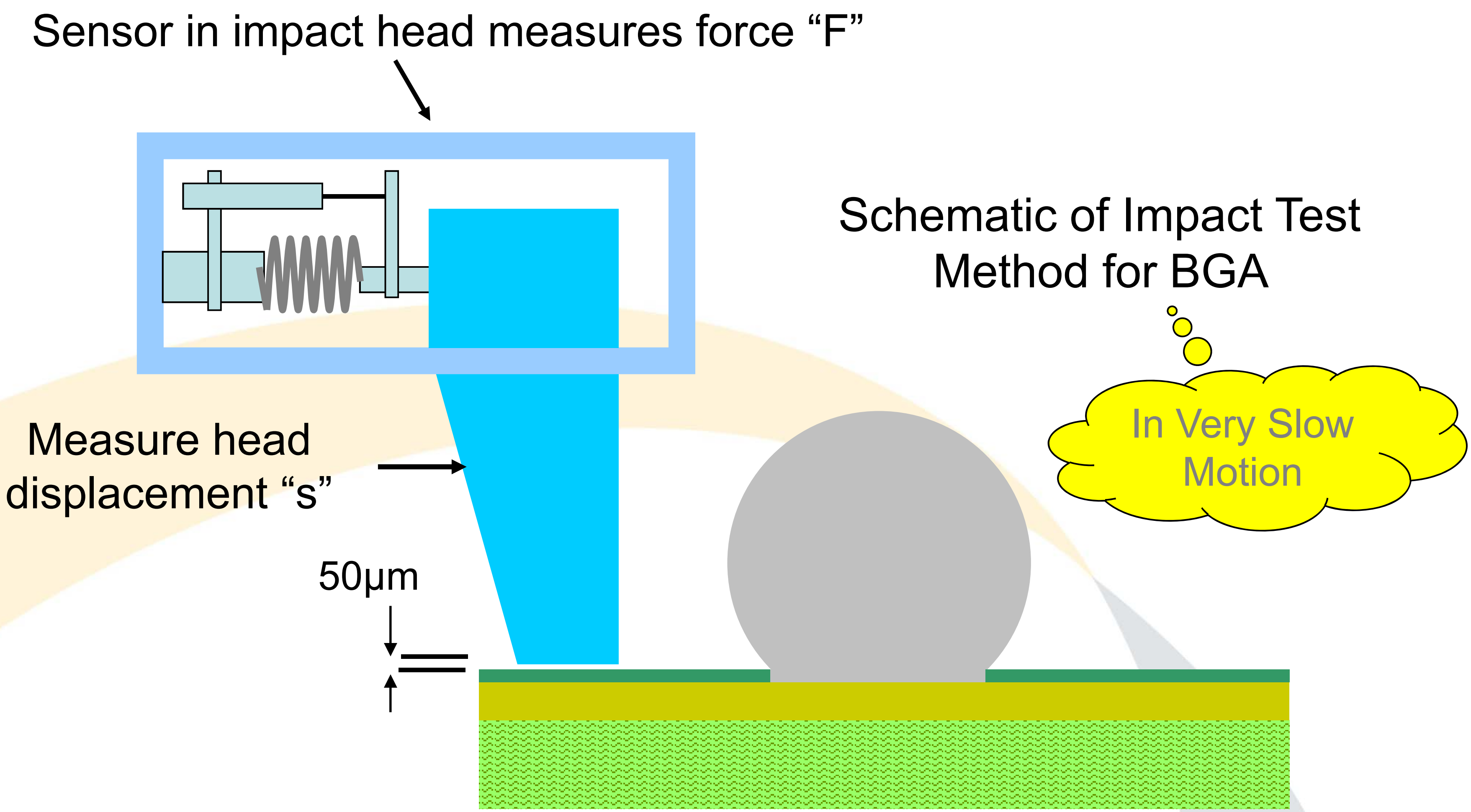
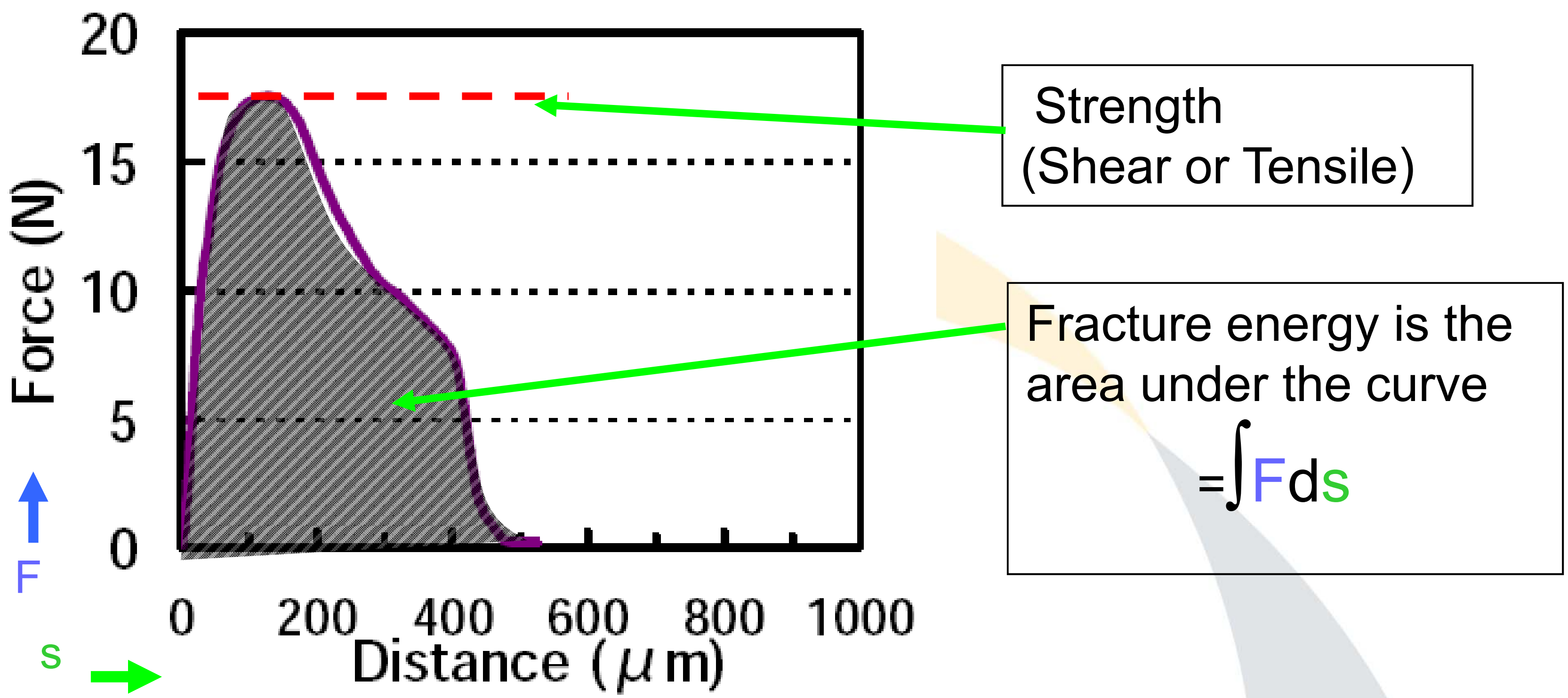
Test Apparatus

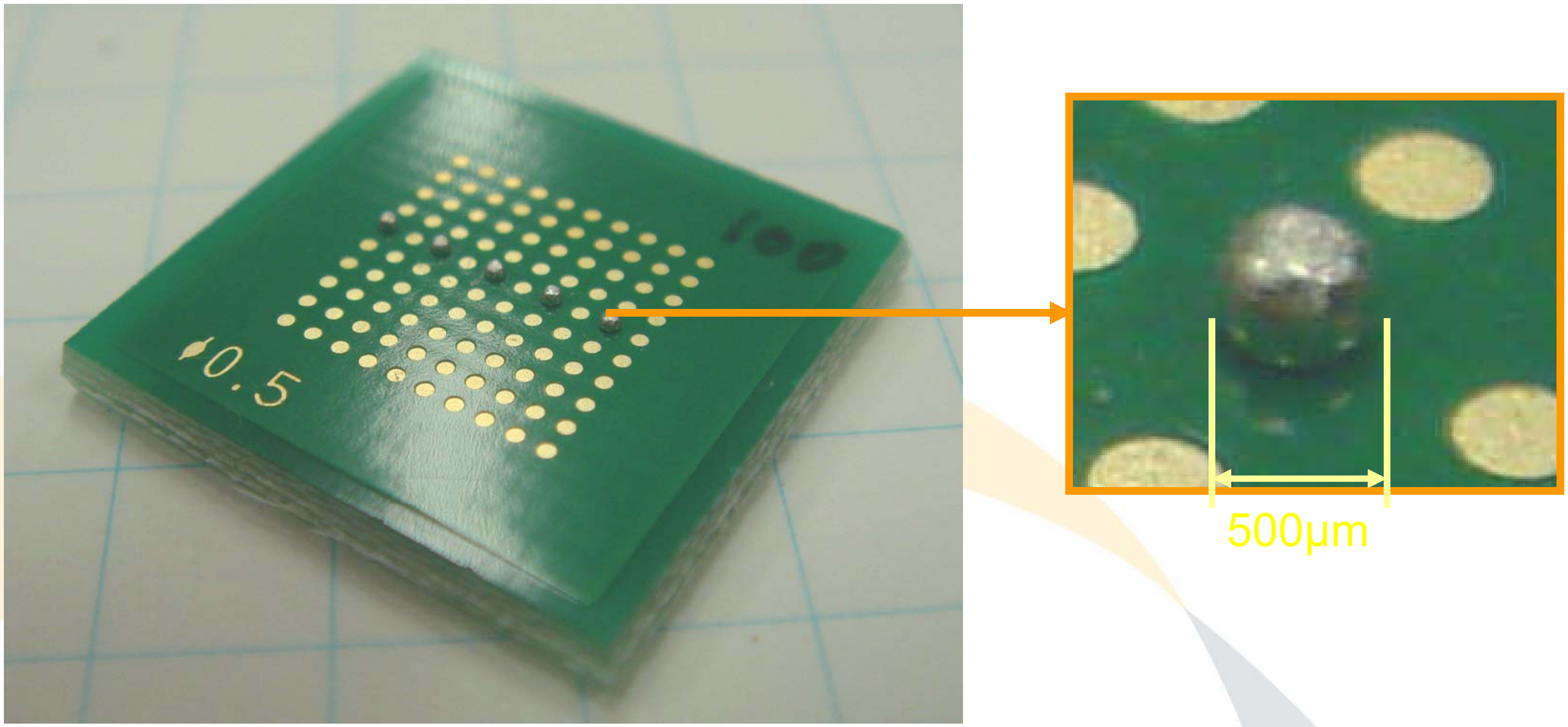


Measurement

Force is recorded as a function of the distance the test piece or the test head moves



Test Pieces



The 0.5±0.01mm diameter solder spheres were produced using the liquid drop extrusion method.

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Test Piece Specification

Laminate	FR4
Thickness	1.6mm
Solder Mask Defined Pad	0.42 ± 0.01mm diameter
Surface Finish	OSP
Solder Mask Thickness	30 – 40µm

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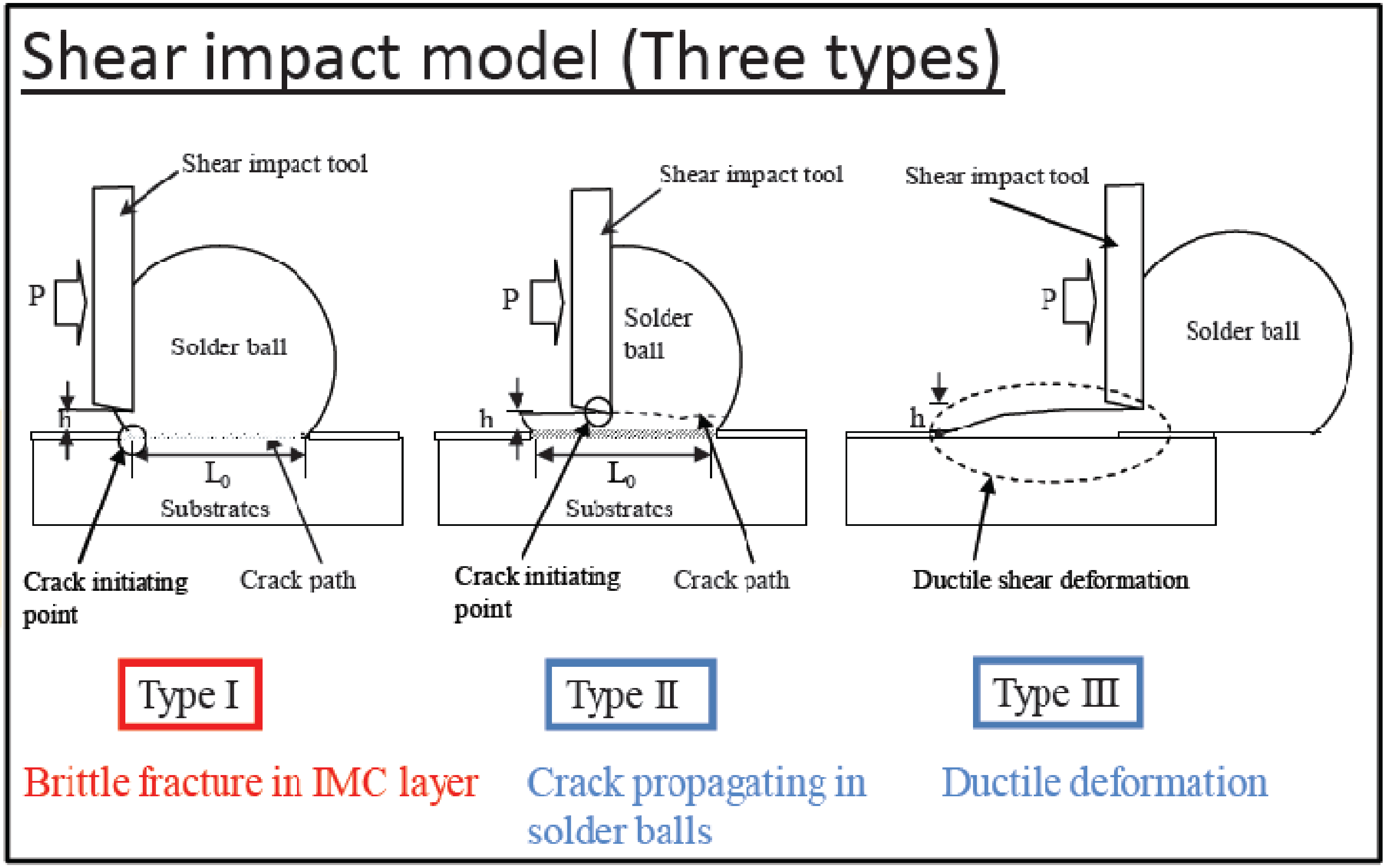
Failure Modes in Ball Impact



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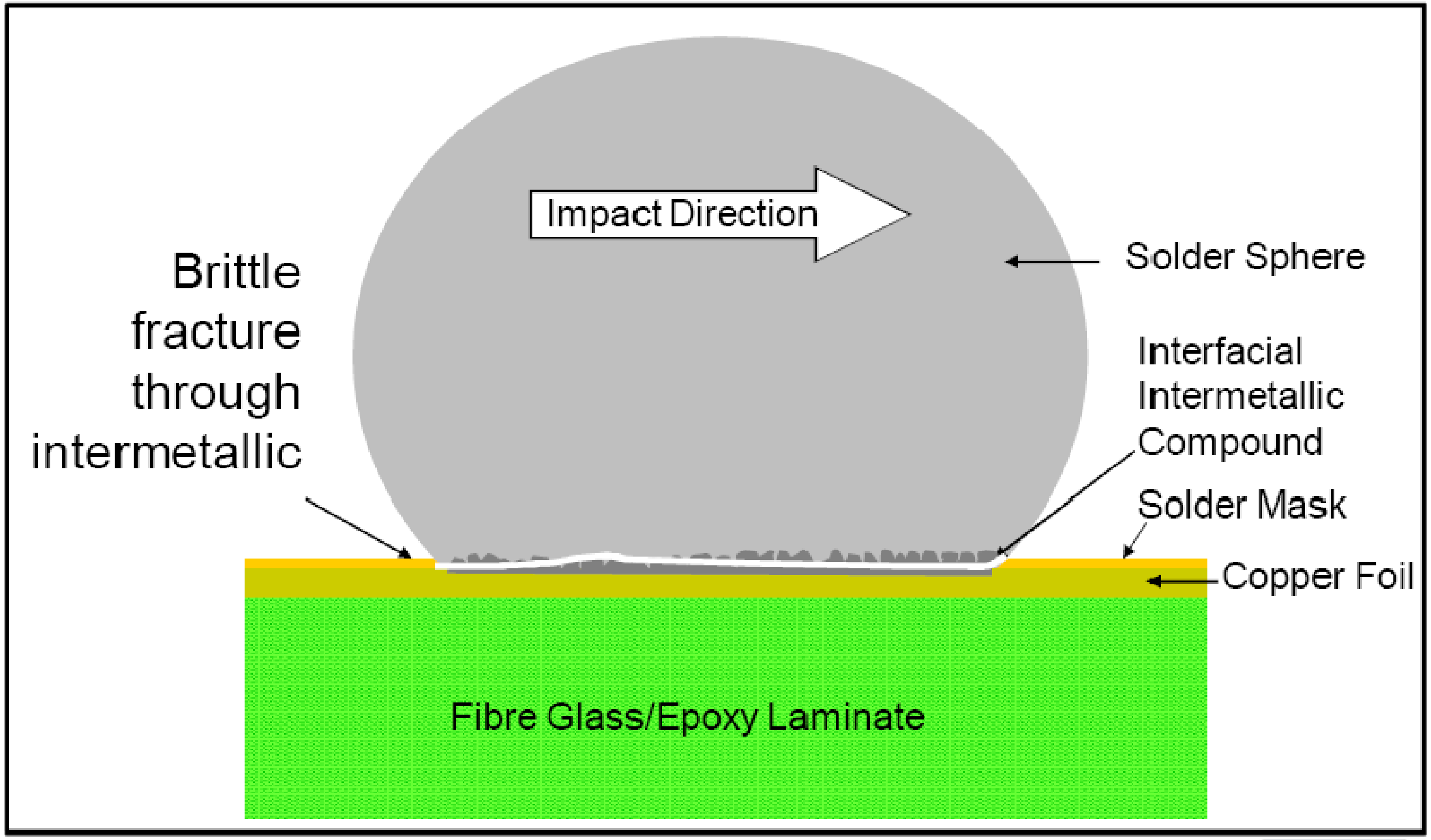
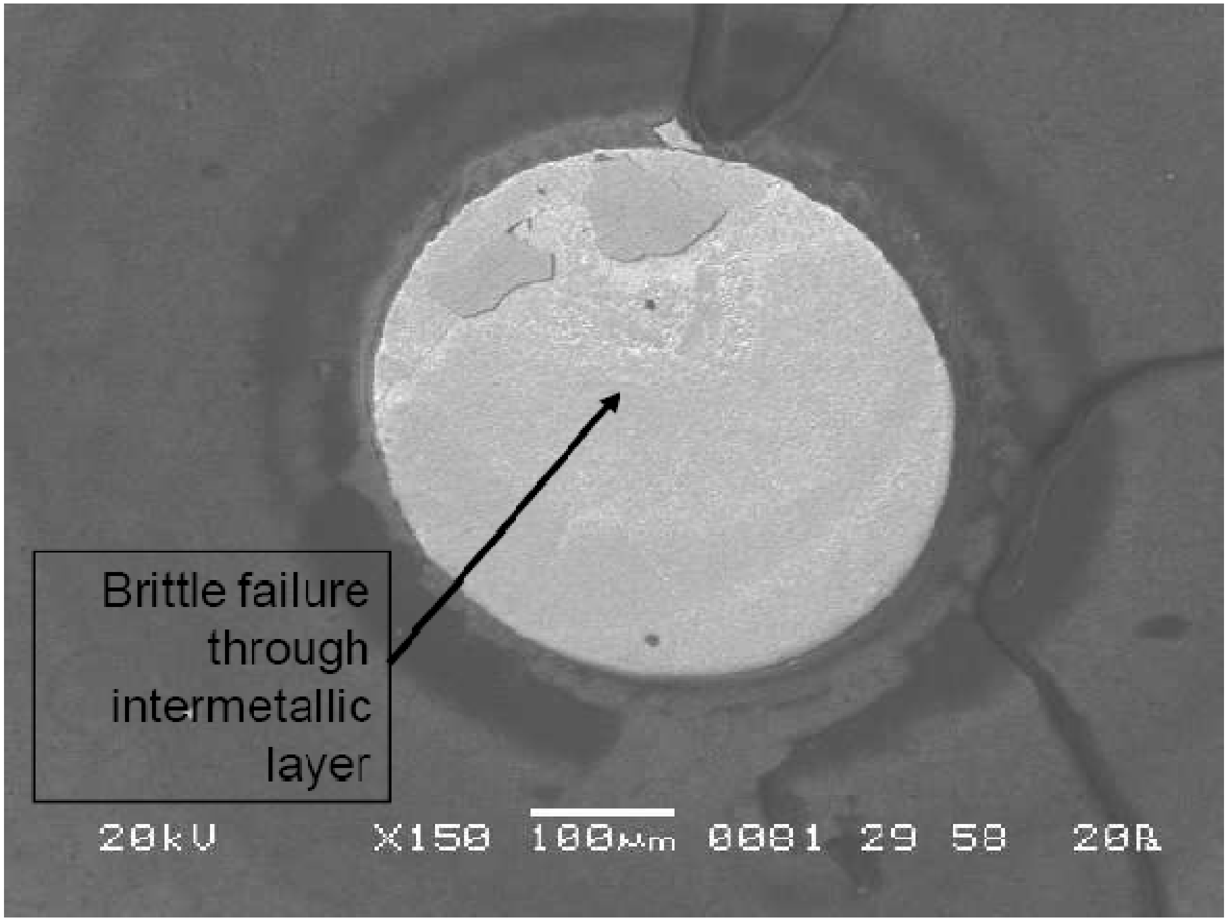
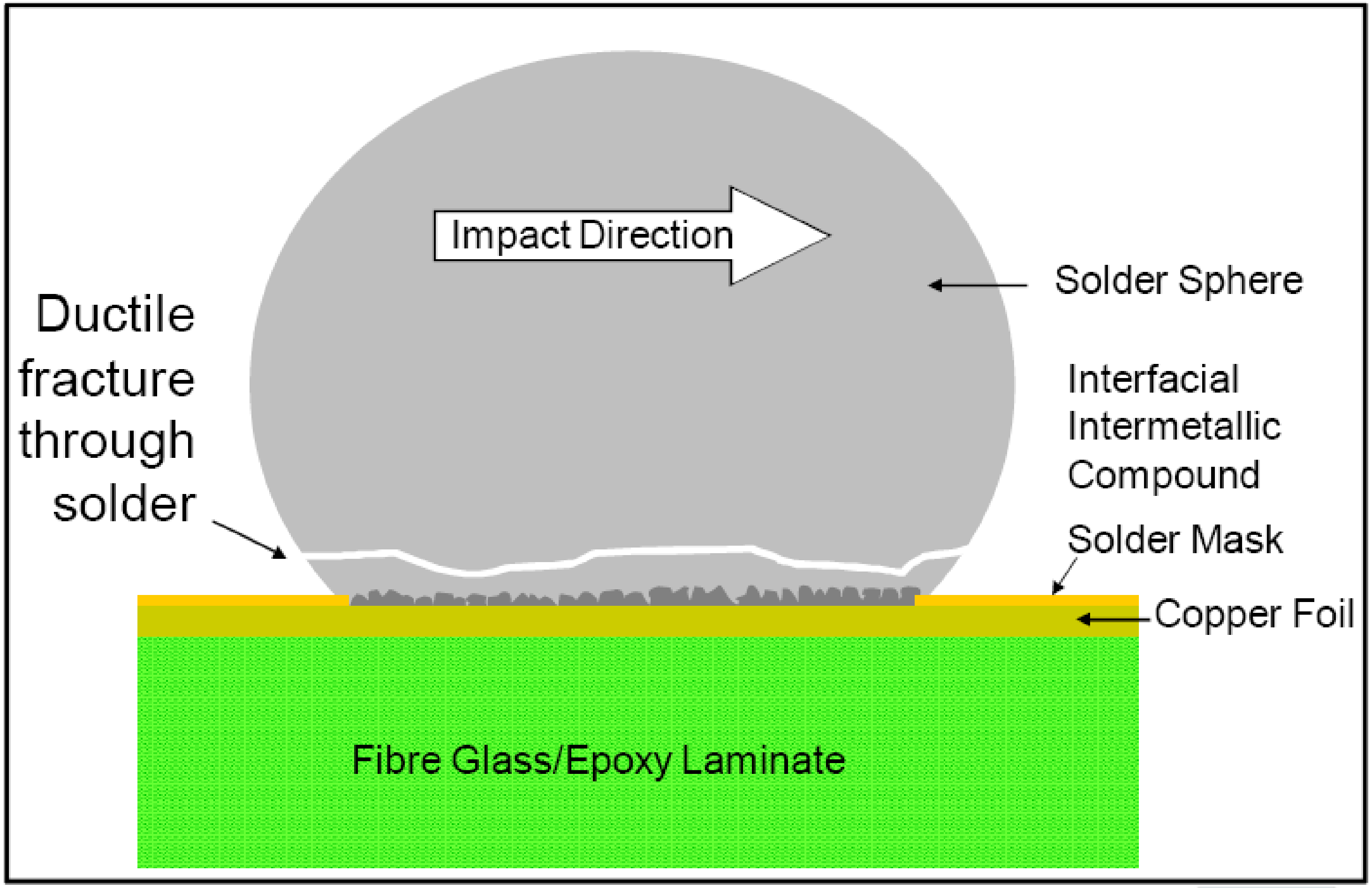
Schematic of Type I Fracture



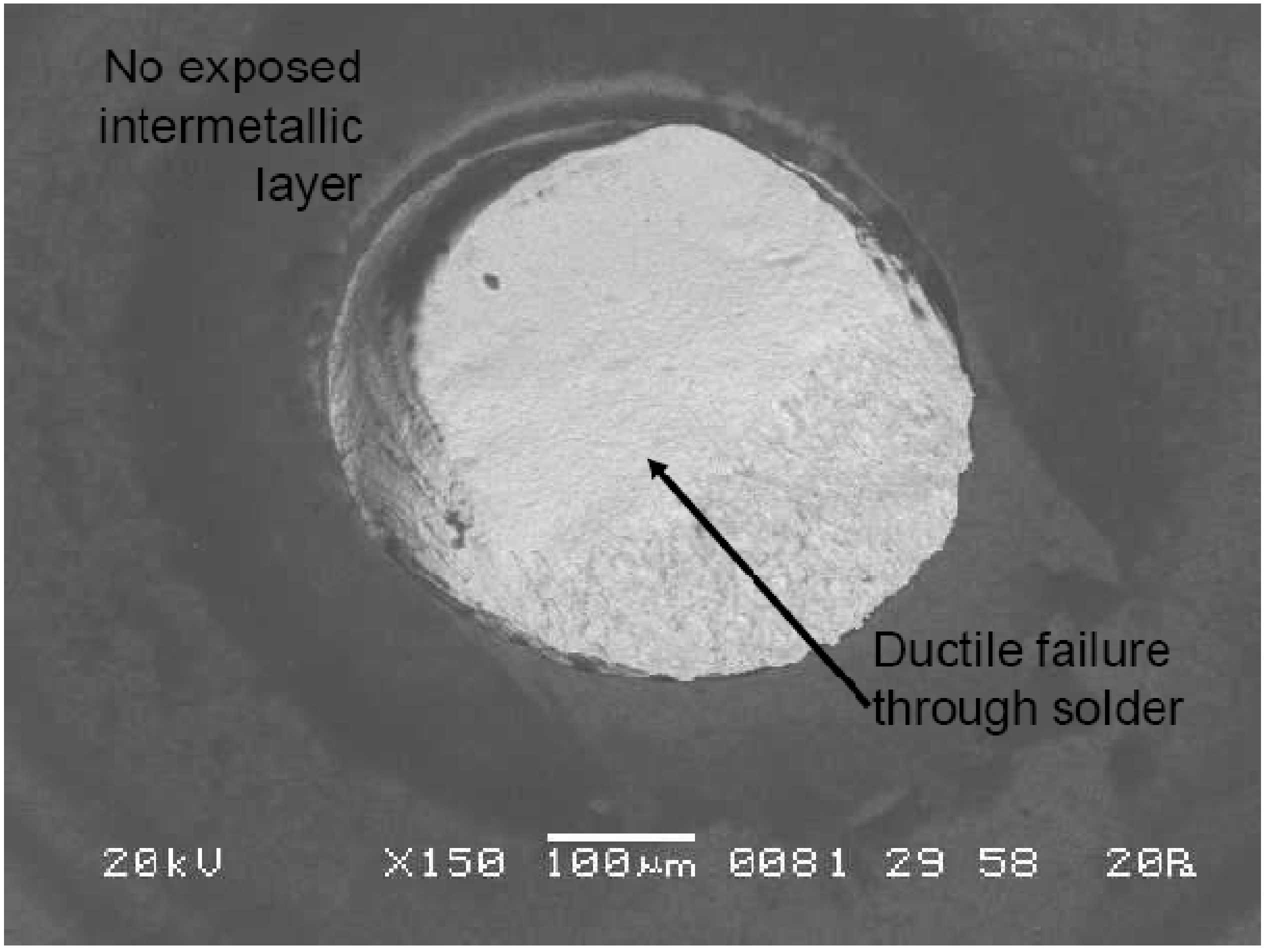
Type I Fracture



Schematic of Type II Fracture



Type III Fracture

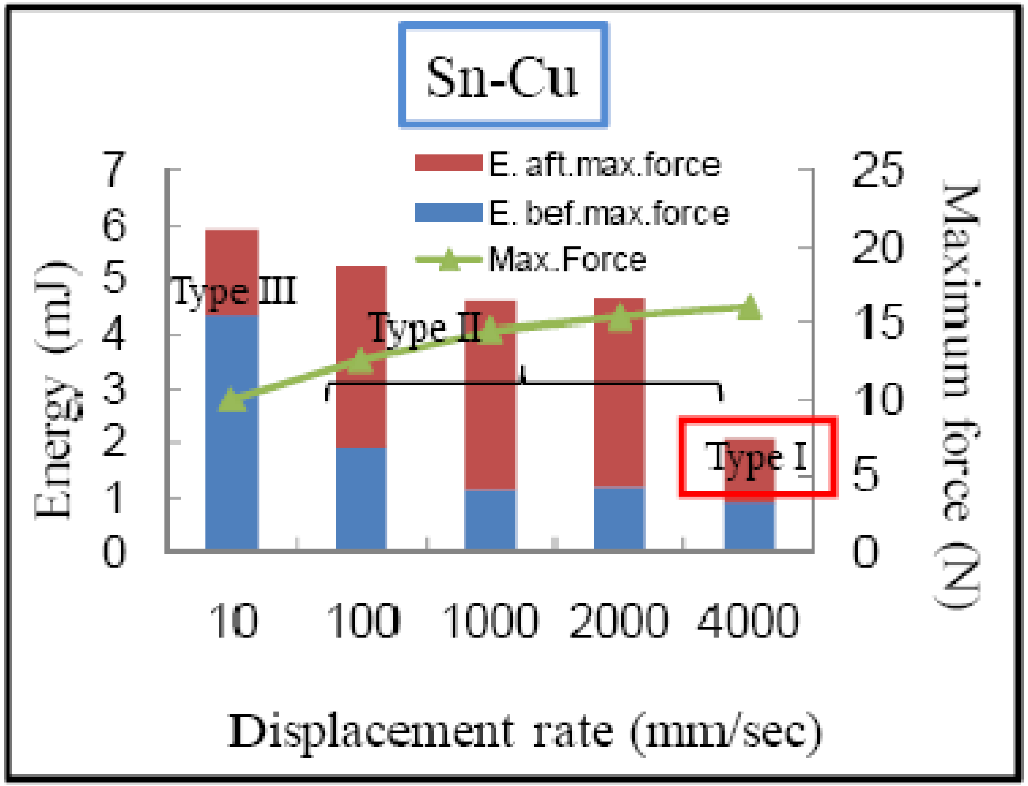


Alloys Tested

Alloy	**Composition**
Sn-Pb	Sn-37Pb
Sn-Cu	Sn-0.7Cu
Sn-Cu-Ni	Sn-0.7Cu-0.05Ni+Ge
Sn-Ag-Cu	Sn-3.0Ag-0.5Cu

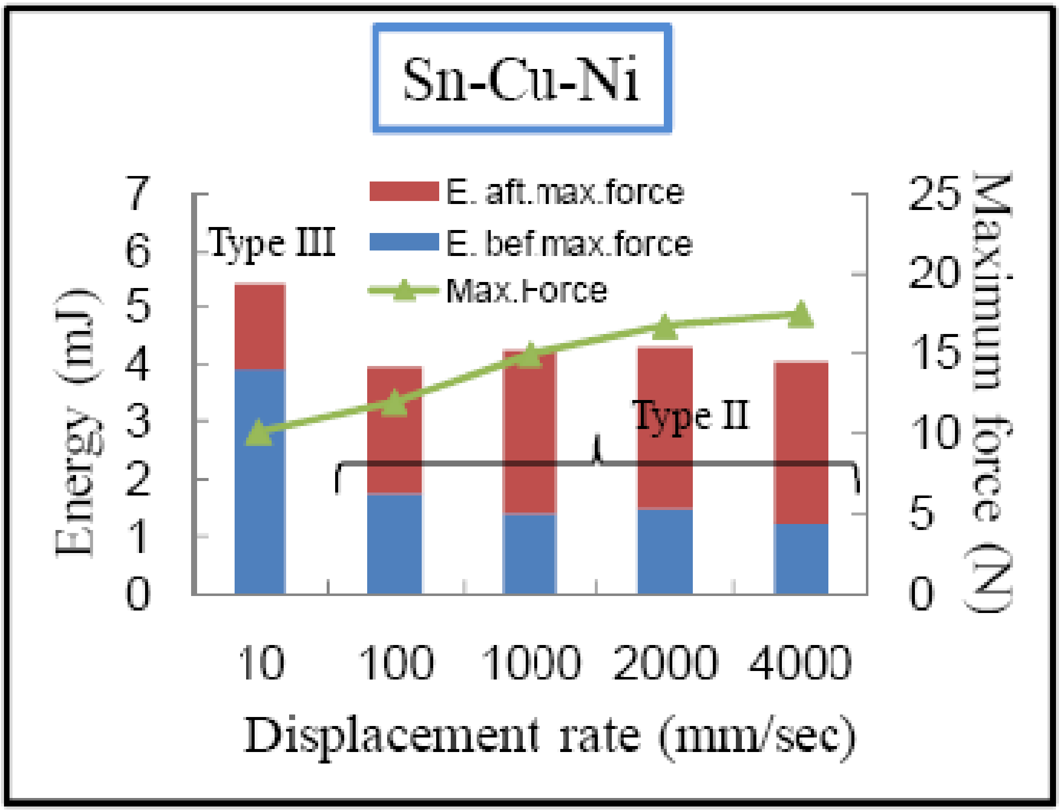
Sn-Cu

- Brittle fracture at high speed.



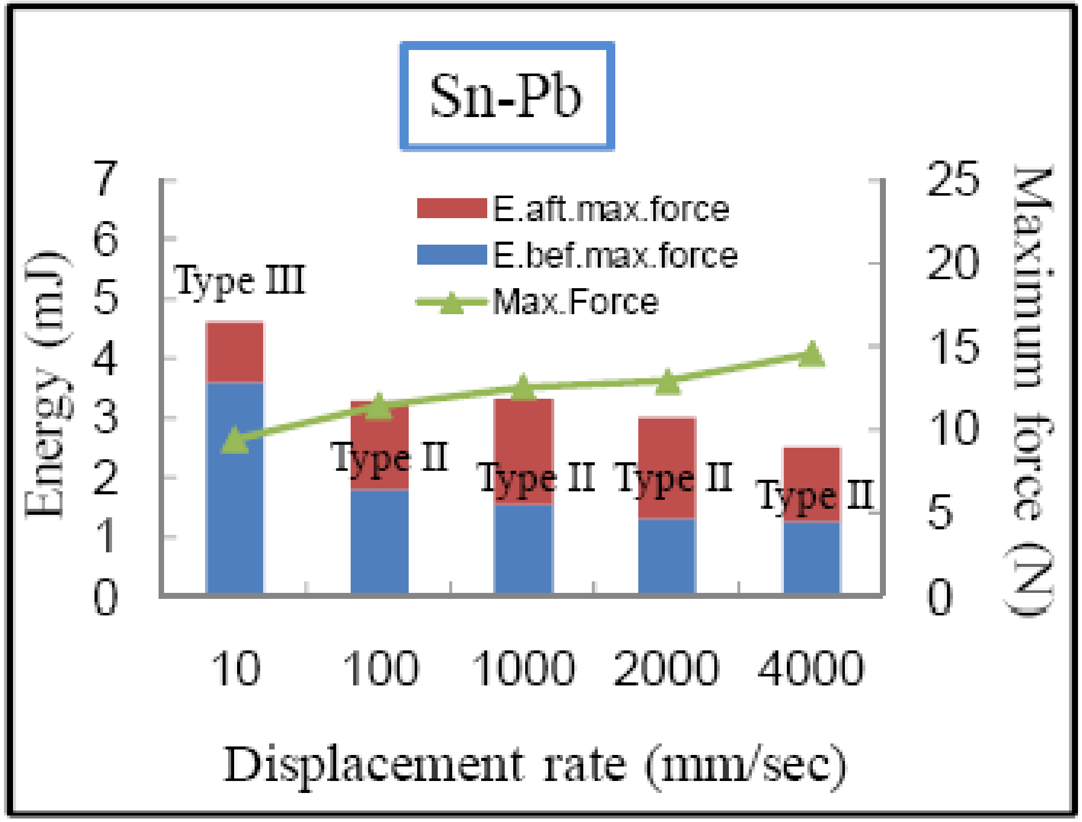
Sn-Cu-Ni

- Type II ductile fracture at high speed.



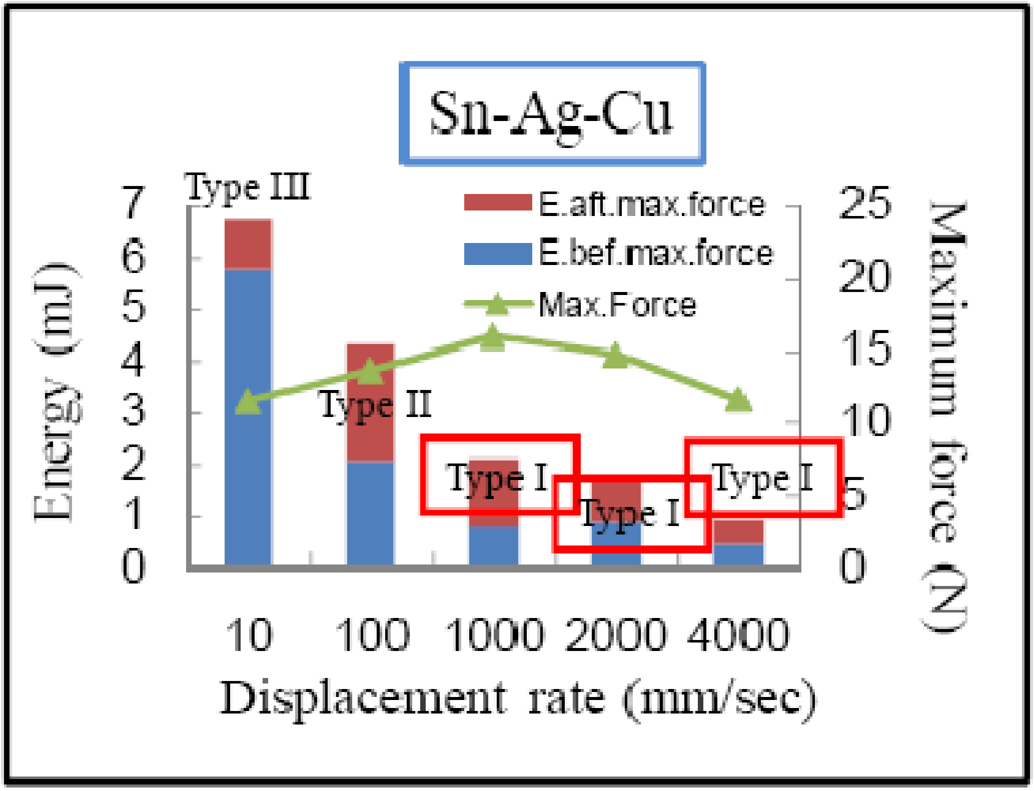
Sn-Pb

- Type II ductile fracture at high speed.



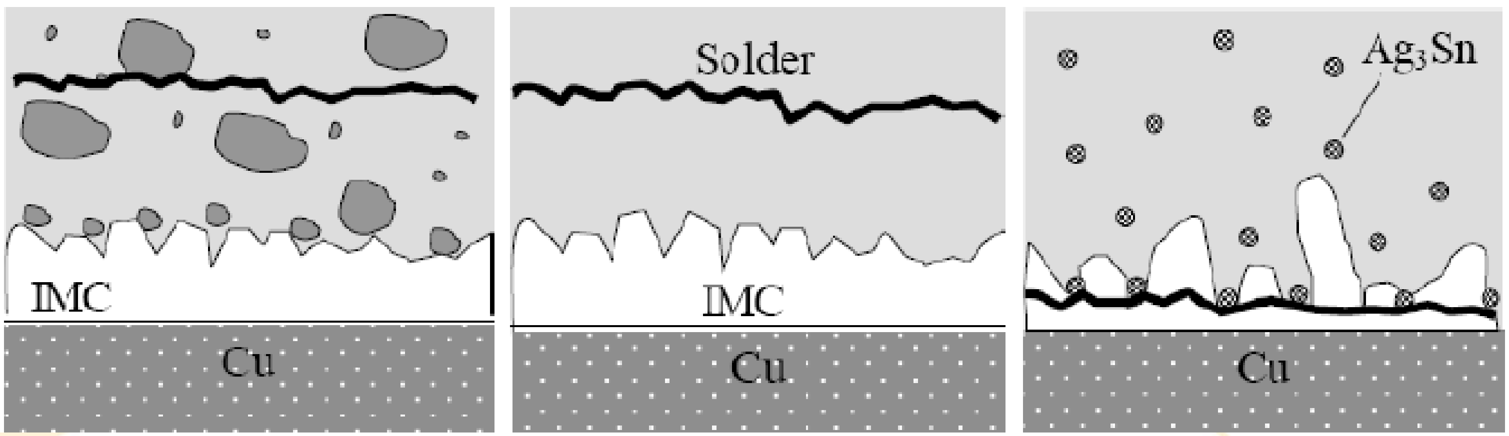
Sn-Ag-Cu

- Brittle fracture at mid and high speeds.



Apparent Fracture Modes

SnPb SnCuNiGe SnAgCu



Type II Type II Type I

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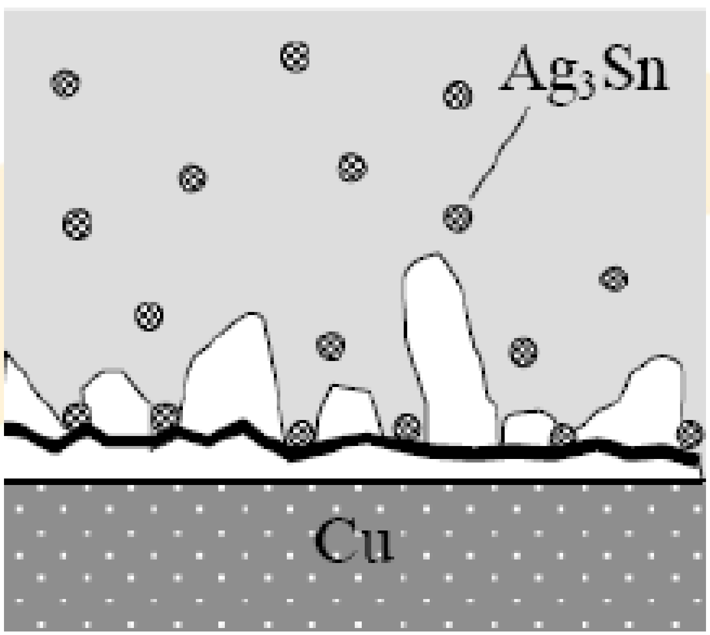
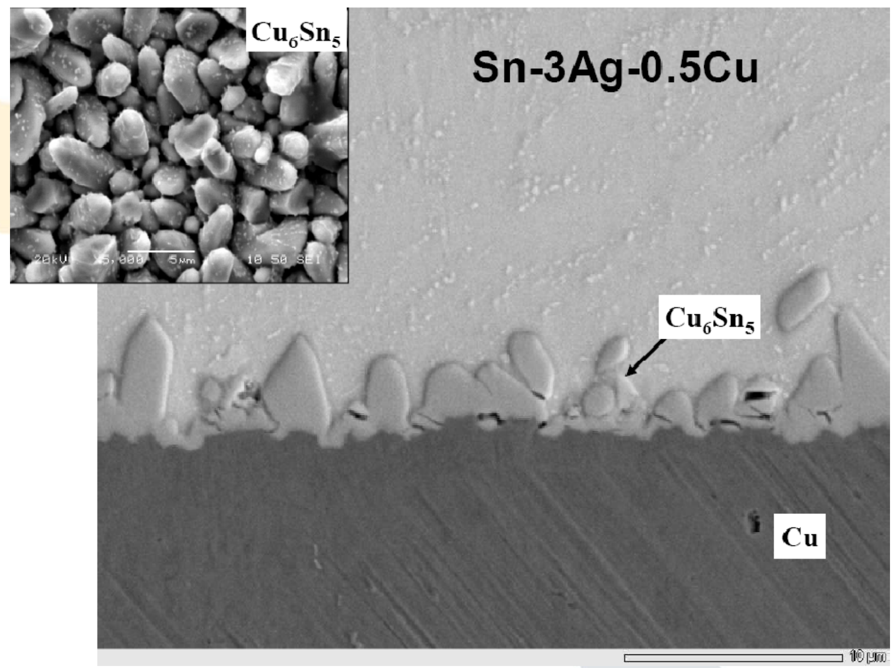
IMC Layer Cracking in Sn-Ag-Cu

- Apparent fracture mode vs cracking observed





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Summary

- Sn-Pb and Sn-Cu-Ni do not exhibit Type I brittle failure at any of the shear speeds tested
- Sn-Cu exhibits Type I failure at the maximum shear speed of 4000 m/s
- Sn-Ag-Cu fails in the brittle manner at shear speeds of 1000mm/s and above
- All of the alloys exhibit Type III ductile shear failure at the lowest shear speed of 10 mm/s

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Summary (continued)

- Sn-Ag-Cu BGA spheres exhibited a low resistance to shear impact loading over the whole range of shear speeds tested
- The deformation energy after the peak load of the shear testing of Sn-Ag-Cu BGAs is very low.

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Conclusions

- Nickel stabilizes the hexagonal close packed form of Cu_6Sn_5 at temperatures below the 186° C transformation temperature of the unstabilized phase.
- The nickel stabilization of the Cu_6Sn_5 reduces the incident of initial cracking in the IMC layer in the as-soldered condition.
- Stabilizing the interfacial intermetallic has a beneficial effect on the resistance of a solder joint to impact loading.

Conclusions (continued)

- Sn-Cu-Ni BGA spheres exhibited superior properties in shear impact tests comparable with those of Sn-Pb and significantly superior to those of Sn-Cu and Sn-Ag-Cu BGA spheres.
- Sn-Ag-Cu BGA spheres exhibited a low resistance to shear impact loadings at all the shear speeds tested.
- The low deformation energy after the maximum load of in the Type I failure of Sn-Ag-Cu suggests that crack propagation is easy in the unstabilized IMC layer.

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Thank You

k.howell@nihonsuperior.co.jp

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