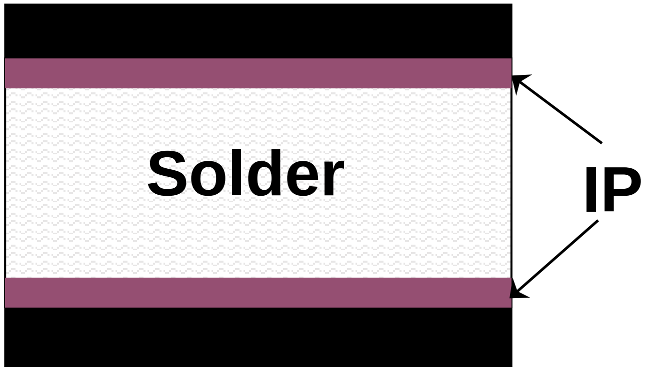
Diffusion soldering fundamentals and application

Conventional soldering



<u>Soldering:</u> joining process below 425 ^{o}C using filler metals (solders) having melting temperatures below those of base metals

Solders act by:

- wetting the metal surfaces forming the joints,

- flowing between these surfaces filling the space between them,

- metallurgically bonding to the surfaces when solidified.

Conventional soldering

Directive 2002/95/EC - New electrical and electronic equipment should be free of lead and other hazardous substances by July 1st, 2006.

WEEE 2002/96/EC - Waste Electrical and Electronic Equipment (WEEE) – deadline 2008

Substitutes for Sn-Pb solders

Sn-based multicomponent alloys with alloying elements such as Bi, In, Ag and Zn

Challenges for new joints

Limitation

Service temperature: 60-100 °C below soldering temperature (220-260 °C for Sn-Pb solders)

Operating temperature of many electronic devices built on silicon carbide and III-V compound semiconductors exceeds 350 ^{o}C (jet engines, nuclear reactors, geothermal walls, automotive electronics, industrial robots, and space electronics).

Miniaturization of components and contact areas in electronic packaging increase the specific load of contacts due to heat dissipation (chip resistors and resistant heating elements).

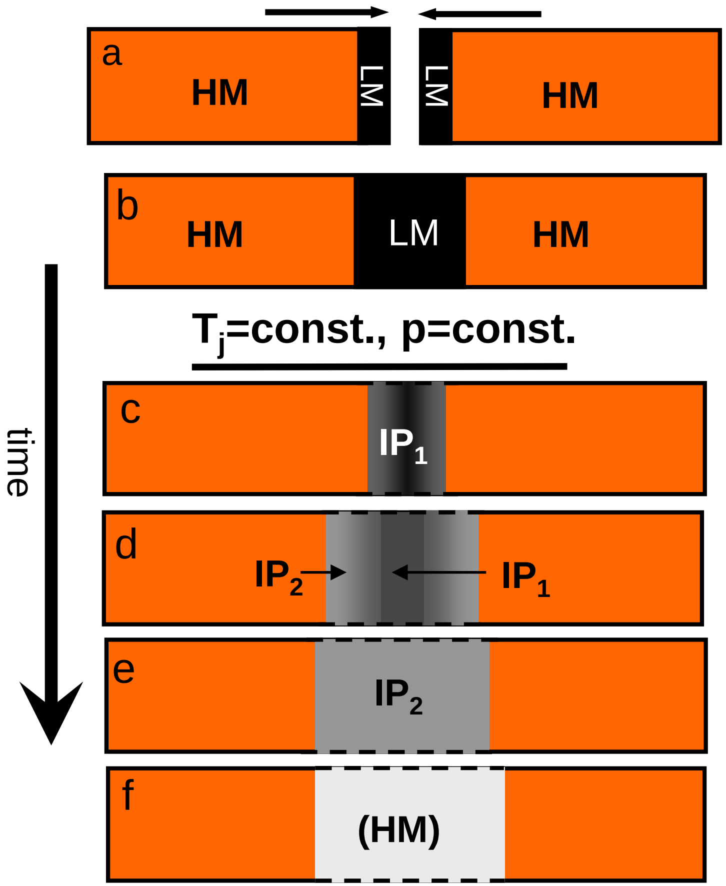
IBM: First a solution of the interconnection problem;
Then everything else

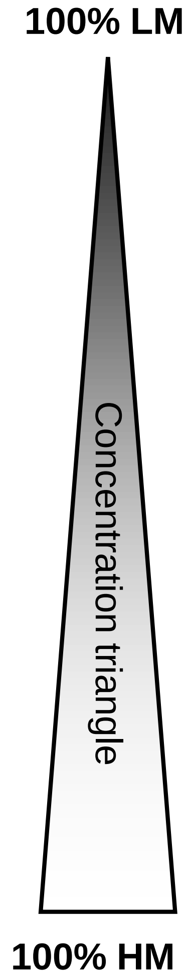
Need for a new lead-free joining technology

- High temperature stability: ~2 to 3 fold higher than the fabrication temperature
- High mechanical strength
- Small energy consumption due to low fabrication temperature
- Environmentally friendly
- Reduction in size and cost
- No high temperature exposure of other circuit elements

- High temperature stable contacts of resistive heaters for thick-film hot plates, resistive elements for gas sensors
- Selective-area sealing and complete package sealing of microcircuits
- Development of packages for optoelectronics and other microcircuit application
- Wafer-to-wafer joining, flip-chip joining, 3D integration etc.
- Producing metal-polyethylene interconnection

Diffusion Soldering





HM- high-melting component (**substrate**)

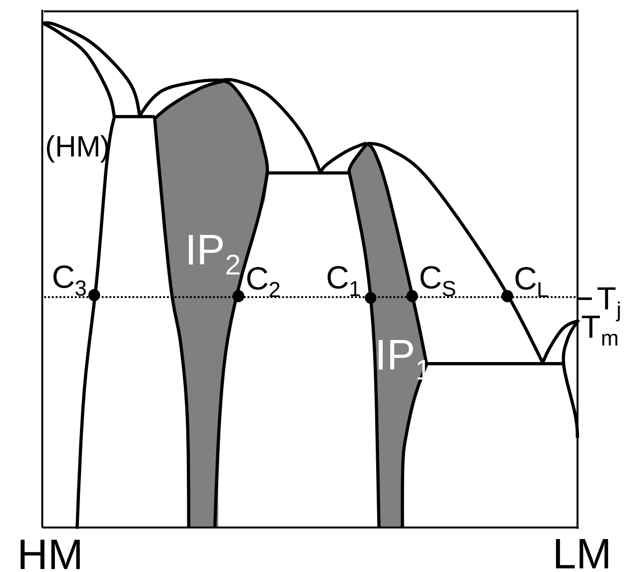
LM- low-melting component (**solder**)

IP- intermetallic phase

(HM)- solid solution of LM in HM

T_j- joining temperature

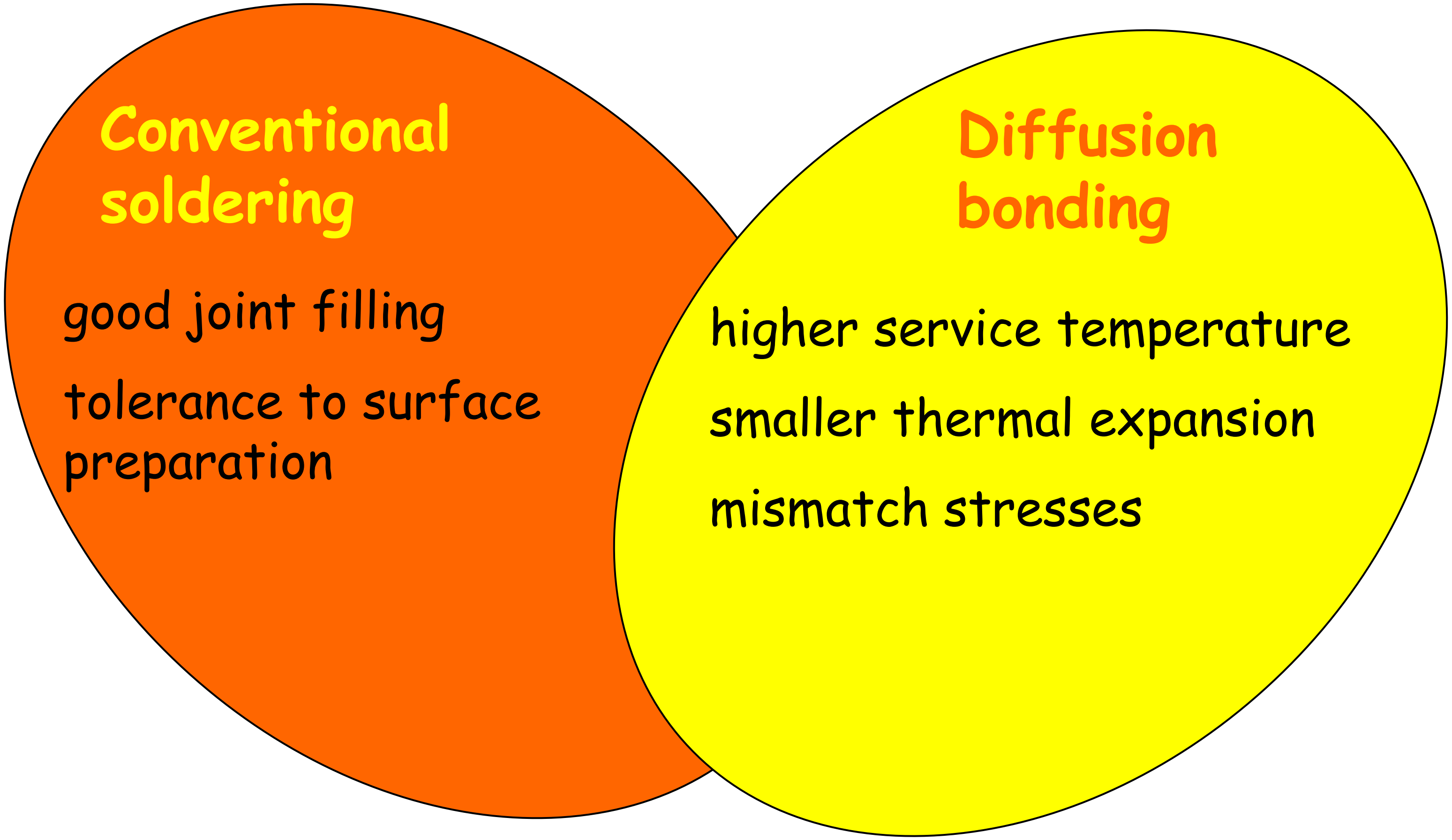
T_m- melting temperature of LM



The *diffusion soldering* should be distinguished from the *diffusion brazing.* Although both processes involve the same bonding mechanism, the solid solution of LM in HM is ultimately formed during *brazing* in the interconnection area instead of the intermetallic phase. It also means that proces is performed at such temperatures or for such systems where there is no intermetallic phases.

The term *transient liquid phase diffusion bonding* (TLP) is also frequently used to describe the joining process involving isothermal solidification. However, it is also claimed, that no interface remains after the TLP bonding operation, which resembles the diffusion brazing rather than diffusion soldering.

Diffusion Soldering



Potential candidates for diffusion soldering

interlayer → substrate

In-22 at.%Bi → Cu

In → Cu, Ag

In-48 at.%Sn → Cu

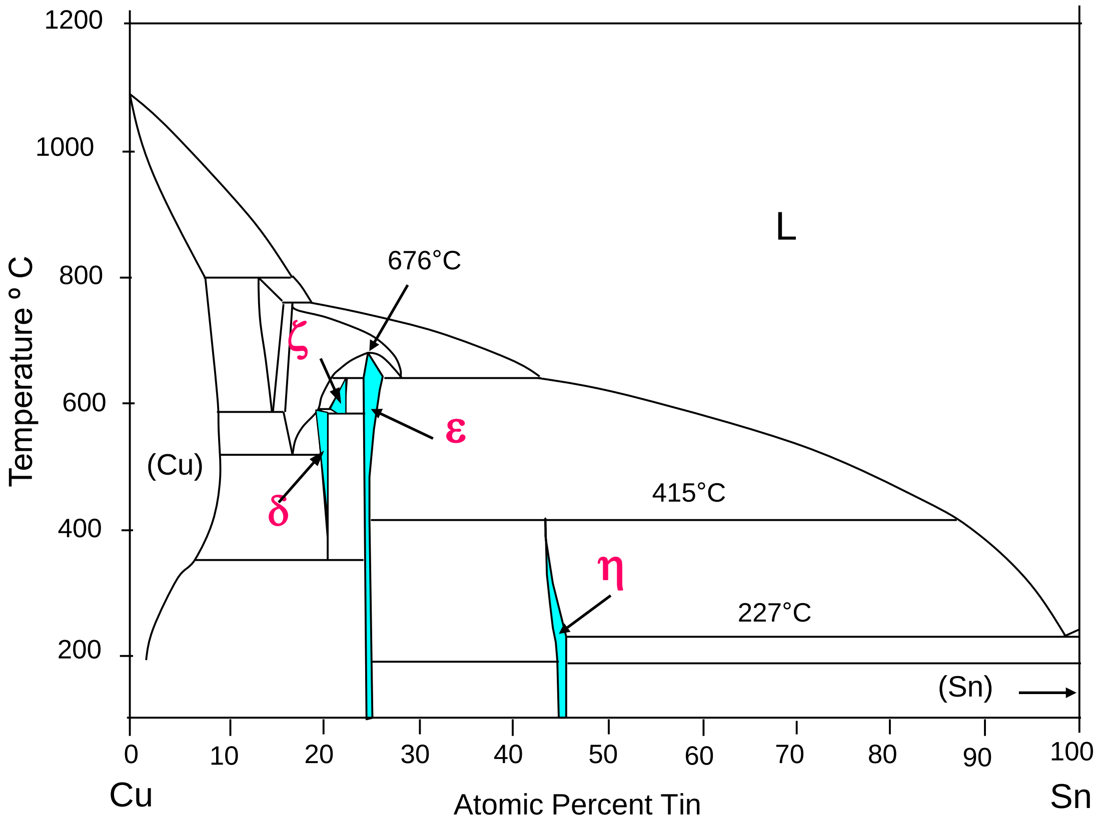
Sn → Ni,Cu,Ag

Al → Ni

solder's materials

No.	Element (at.%)			T_M [^oC]
	A	B	C	
1	In(60.3)	Bi(21.4)	Sn(18.3)	61
2	In(78)	Bi(22)	---	72
3	In(52)	Sn(48)	---	118
4	In	---	---	156
5	Sn(84.8)	Zn(15.2)	---	199
6	Sn	---	---	232
7	Al	---	---	660

Cu/Sn/Cu interconnection



η(Cu_6Sn_5)-hexagonal – 415 ºC

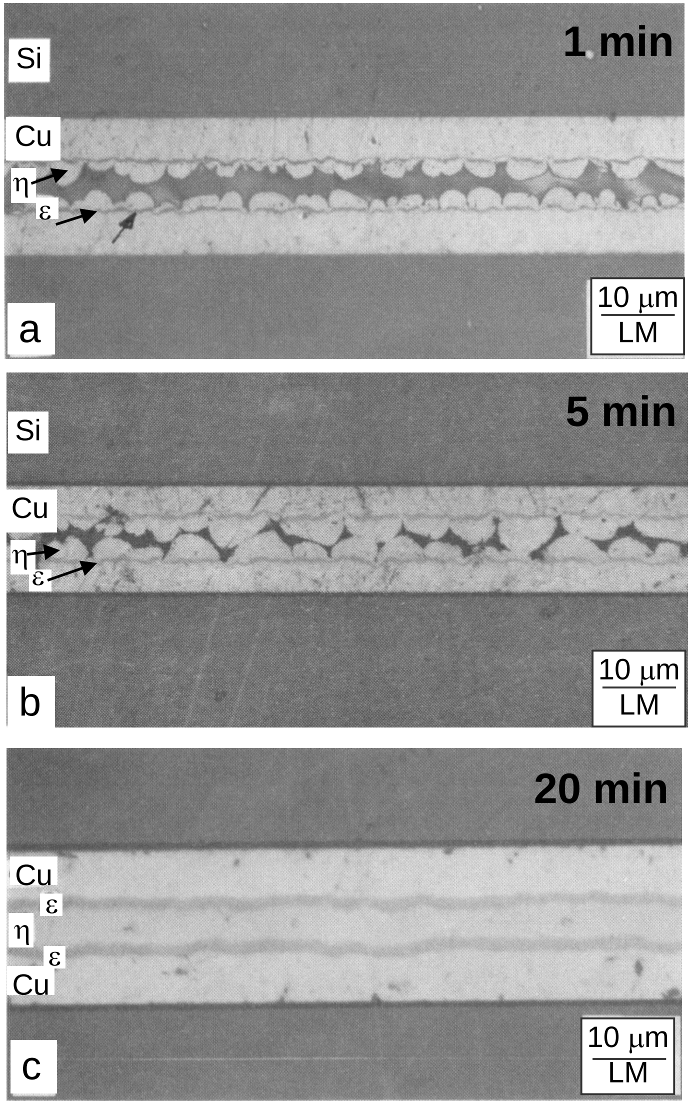
ε(Cu_3Sn)-orthorombic - 676 ºC

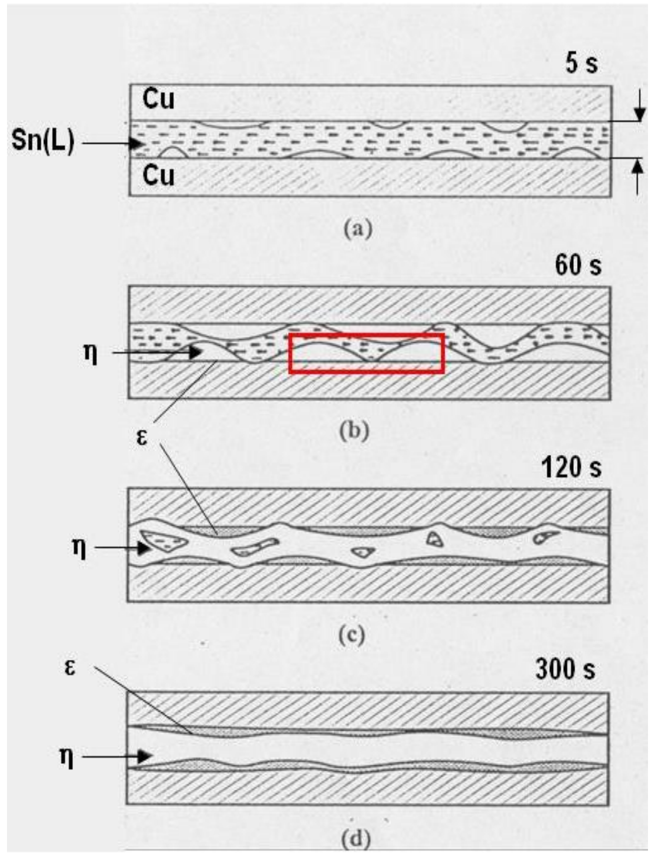
ζ($Cu_{10}Sn_3$)-hexagonal – 642 ºC

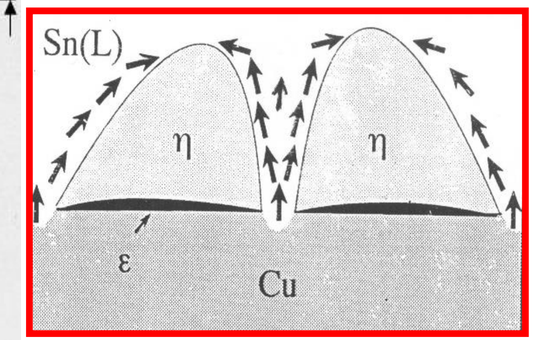
δ($Cu_{41}Sn_{11}$)-cubic – 586 ºC

Cu/Sn/Cu interconnection

240 °C ***eutectic Pb-Sn- 183 °C***







$6Cu + 5Sn(l) \rightarrow Cu_6Sn_5$
$Cu_6Sn_5 \rightarrow 5Sn(l) \rightarrow Cu_3Sn$
$Cu_6Sn_5 + 9Cu \rightarrow 5\ Cu_3Sn$

S. Bader, W. Gust, H. Hieber, Acta Metall. Mater. ***43****, 329 (1995)*

Cu/Sn/Cu interconnection

Tensile test

When both IPs present ➔ strength twice larger than for pure Sn (18 MPa)

DEMAND FOR ELECTRONIC INDUSTRY: R_m = 3-5 MPa

Thermal cycling

$$
\begin{tikzcd}
\text{-45 °C/0.5 h} \arrow[r, bend left, "\text{5 s}"] & \text{+125 °C/0.5 h} \arrow[l, bend left, "\text{5 s}"]
\end{tikzcd}
$$

Cu/1.5 μm Sn/Cu – 5 min at 330 °C

For more than 300 cycles and p=0.8 MPa

R_m = 27 MPa

S. Bader, W. Gust, H. Hieber, Acta Metall. Mater. ***43****, 329 (1995)*

Cu/In-Sn/Cu interconnection

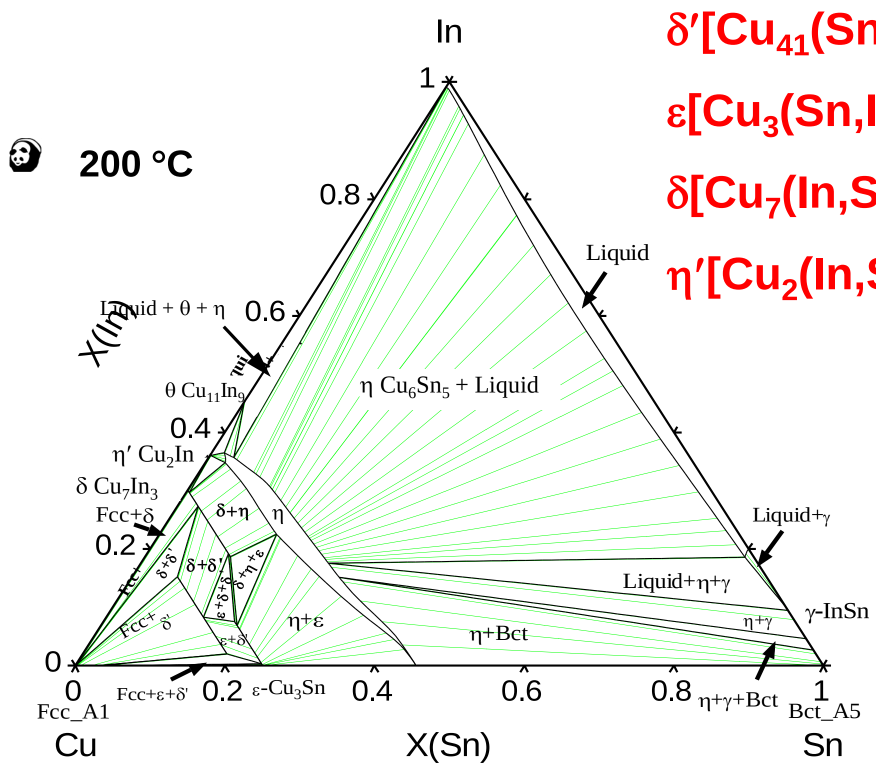
$\eta[Cu_6(Sn,In)_5]$

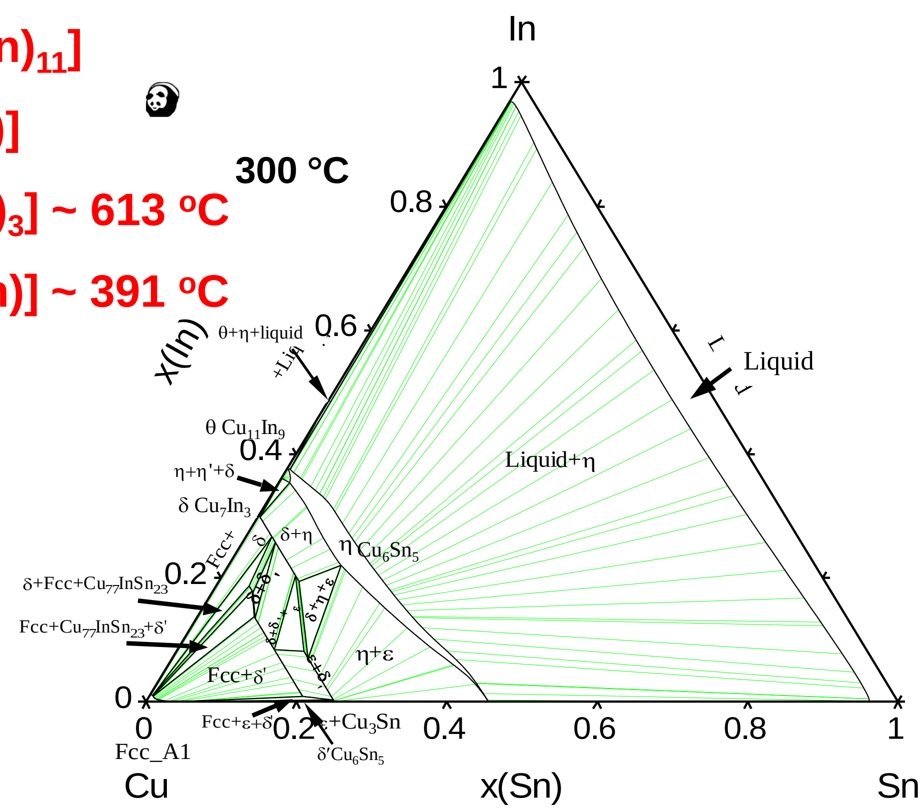
$\delta'[Cu_{41}(Sn,In)_{11}]$

$\varepsilon[Cu_3(Sn,In)]$

$\delta[Cu_7(In,Sn)_3]$ ~ 613 °C

$\eta'[Cu_2(In,Sn)]$ ~ 391 °C

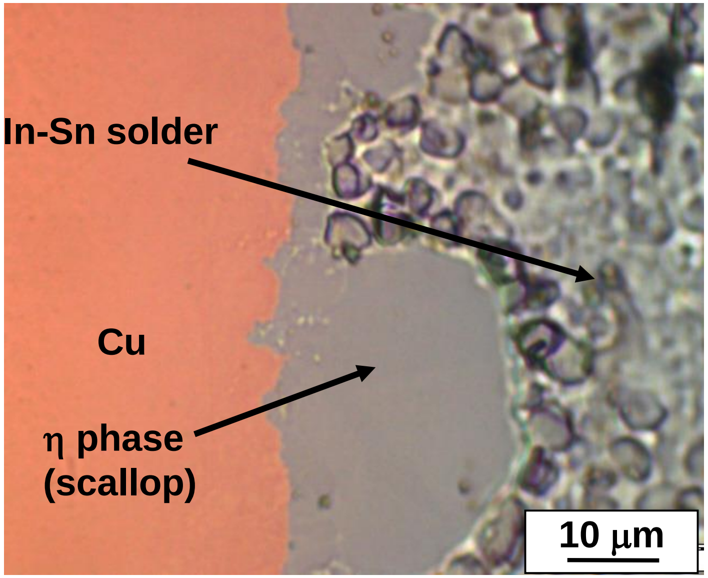


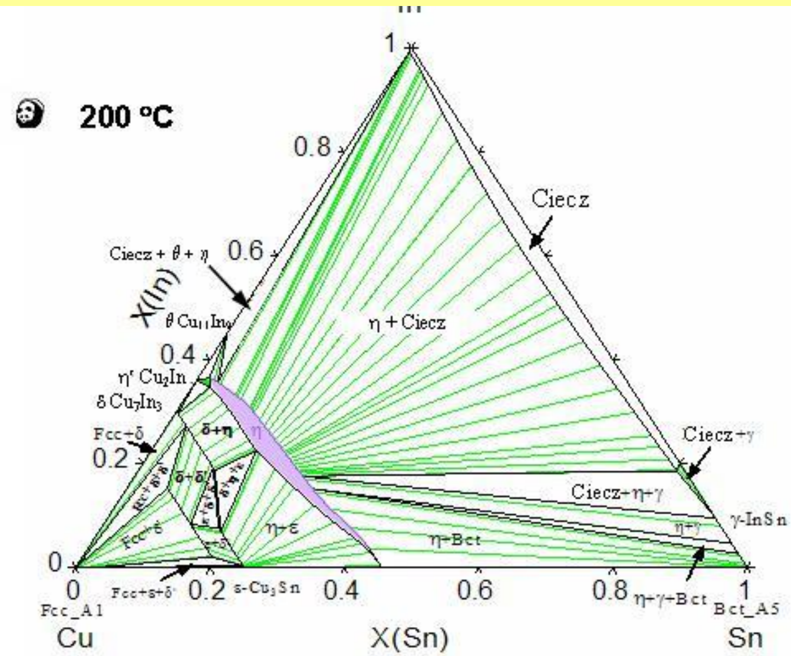


X.J. Liu, H.S.Liu, I. Ohnuma et. al.
Experimental determination and thermodynamic calculation of the phase equilibria in the Cu-In-Sn system
J. Electronic Mater. 30 (2001) 1093-1103

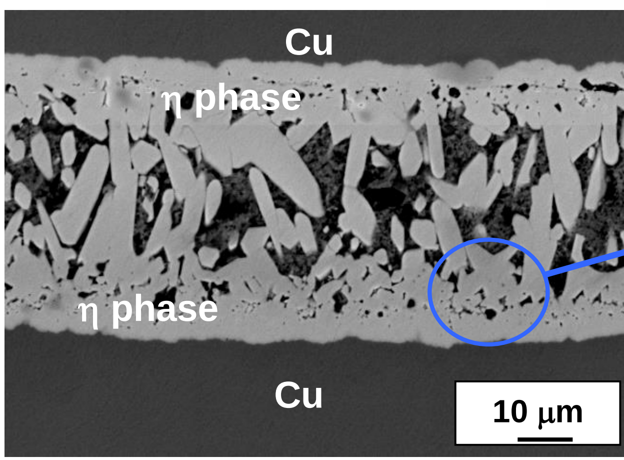
Cu/In-48Sn/Cu interconnection - η[$Cu_6(Sn,In)_5$] phase

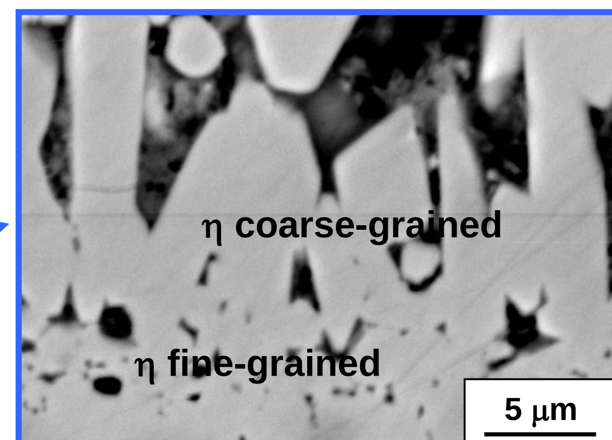
180 °C / 3 h



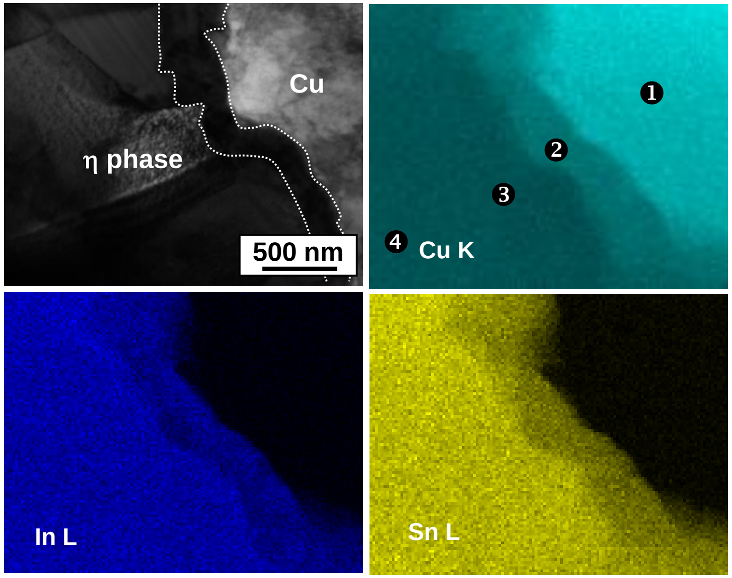


200 °C / 10 h

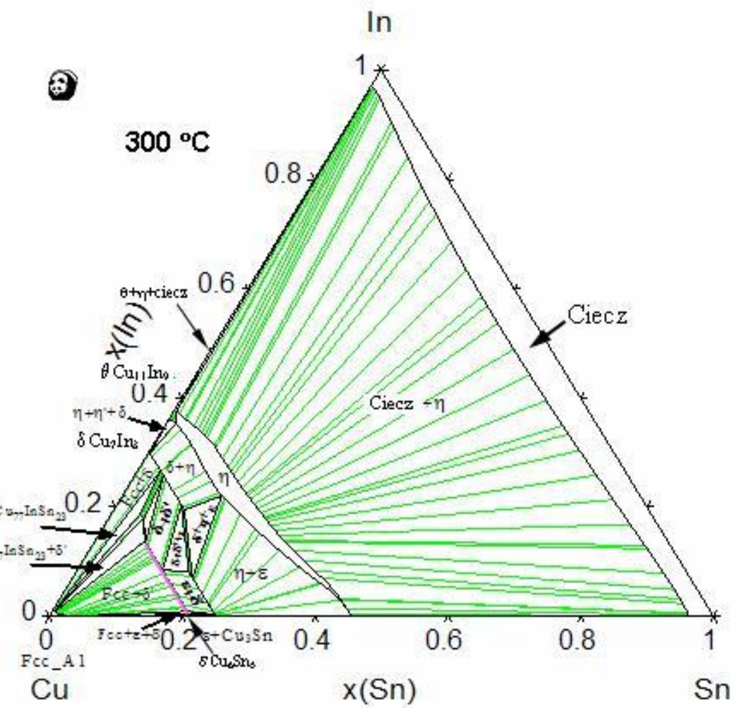


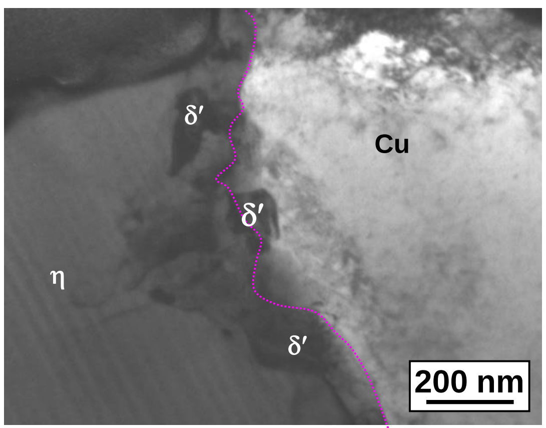


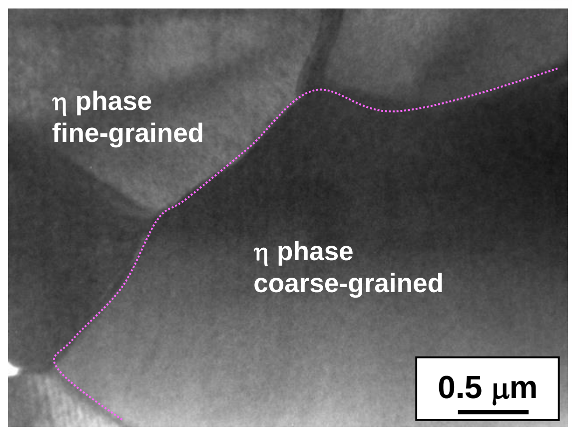
Cu/In-48Sn/Cu interconnection- η[$Cu_6(Sn,In)_5$] and δ′[$Cu_{41}(Sn,In)_{11}$] phases



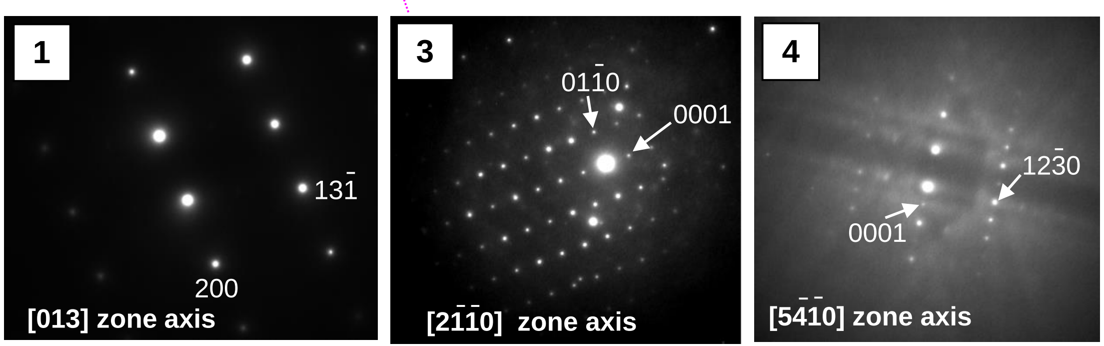
200 °C / 60 h





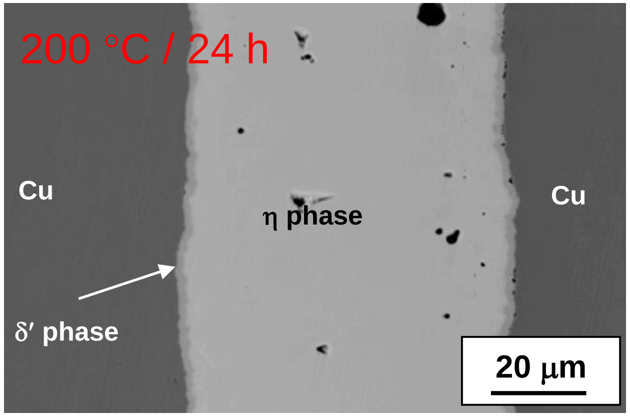


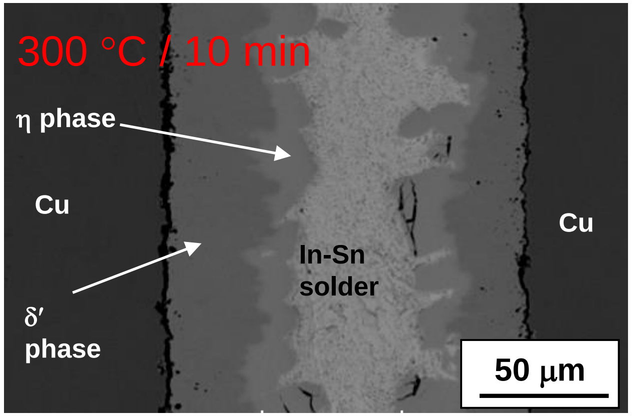
Lp.	Cu	In	Sn	phase
1	99.4	0.2	0.4	*Cu*
2	71.6	16.6	11.8	*δ′*
3	53.4	21.4	25.3	*η (fine)*
4	55.8	19.7	24.6	*η (coarse)*

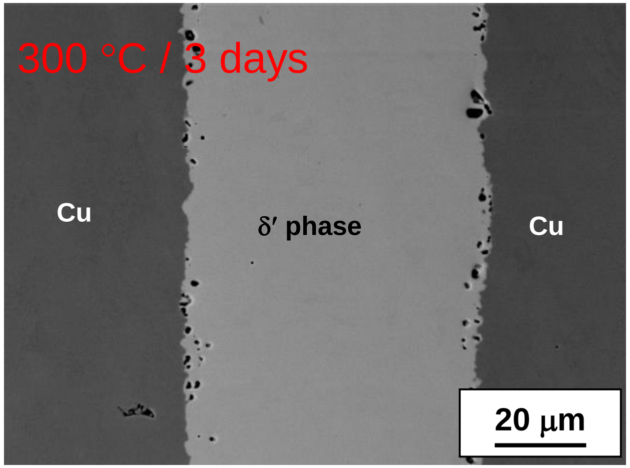


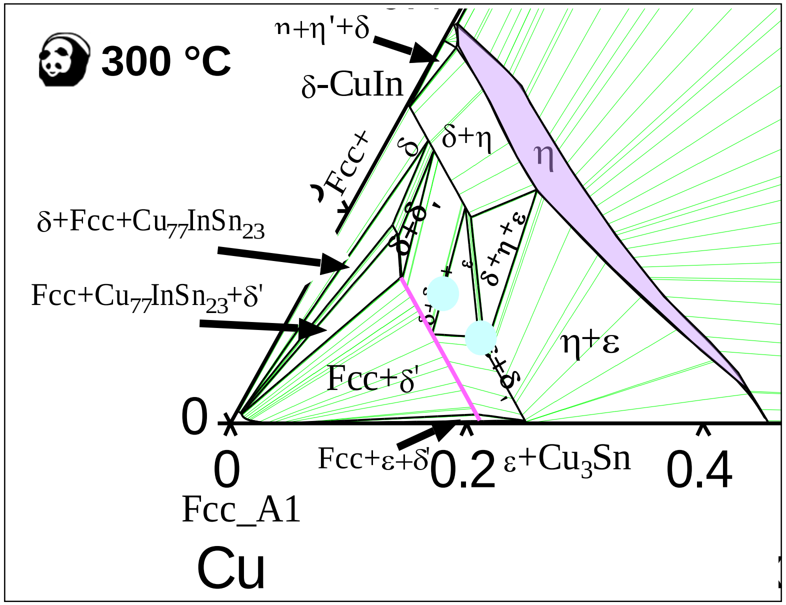
δ′[$Cu_{41}(Sn,In)_{11}$]

Cu/In-48Sn/Cu interconnection - δ′[$Cu_{41}(Sn,In)_{11}$] phase

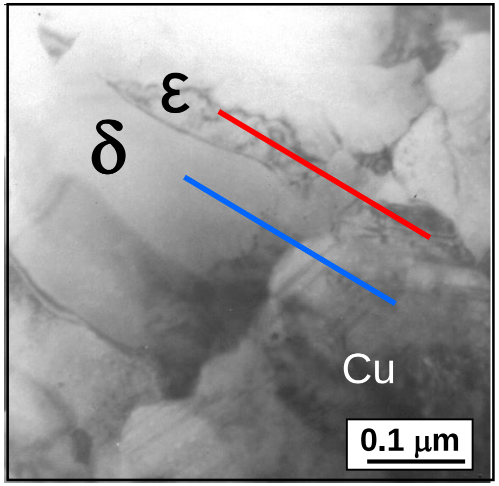


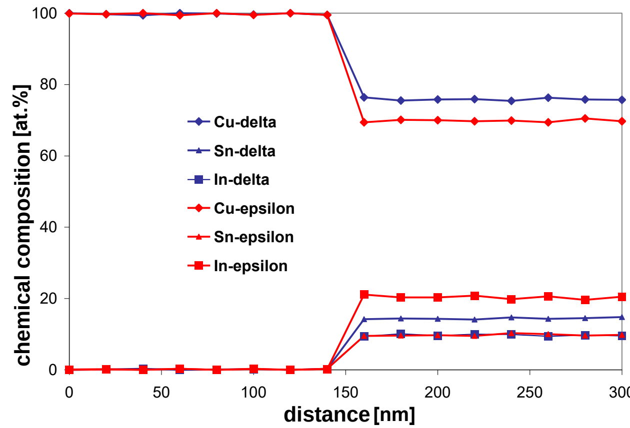




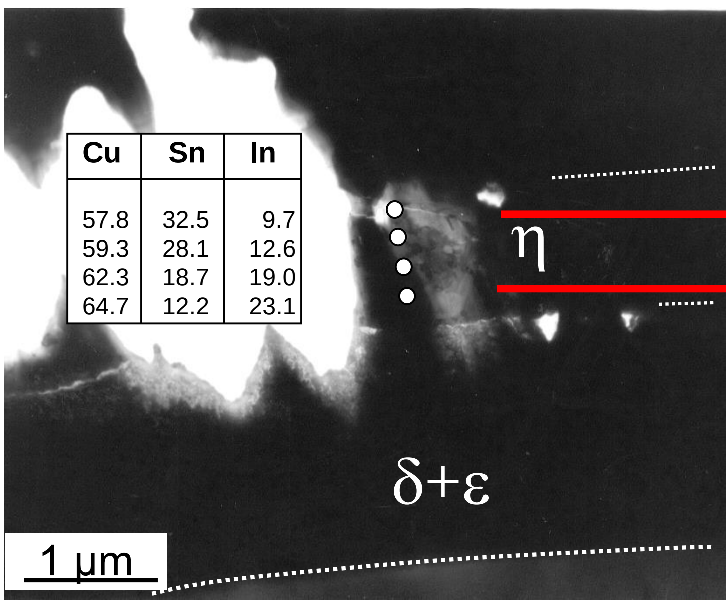


Cu/In-48Sn/Cu interconnection - ε[$Cu_3(Sn,In)$] and δ[$Cu_7(In,Sn)_3$] phases





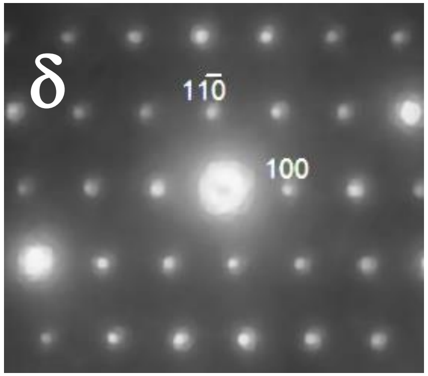
220 °C / 243 h



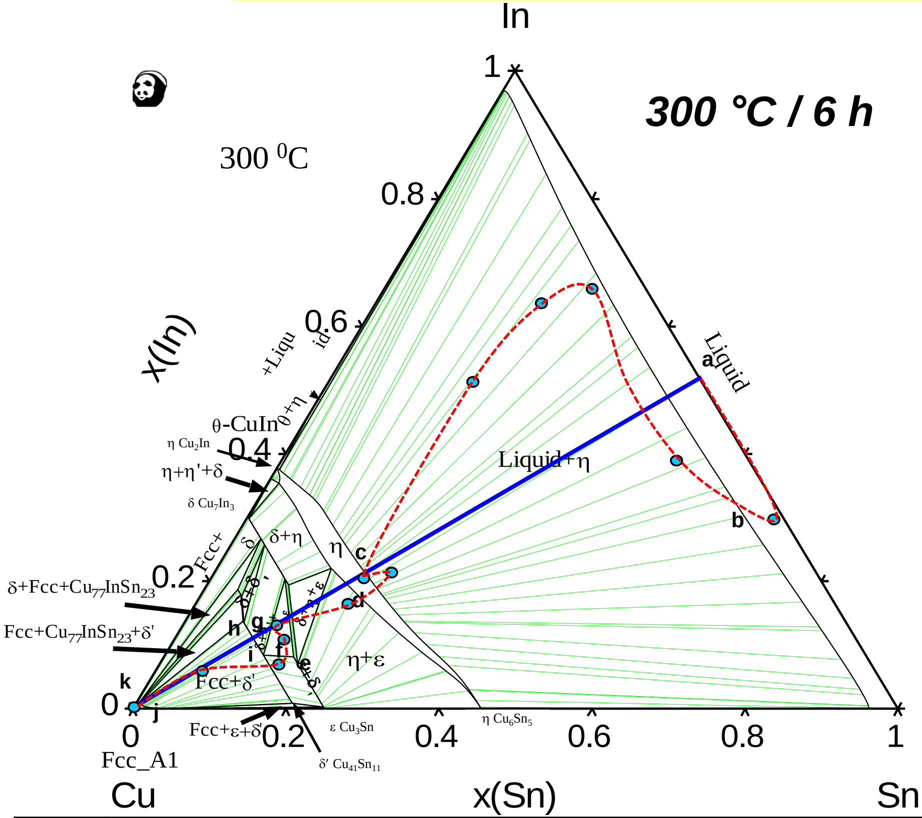
Cu	Sn	In
57.8	32.5	9.7
59.3	28.1	12.6
62.3	18.7	19.0
64.7	12.2	23.1

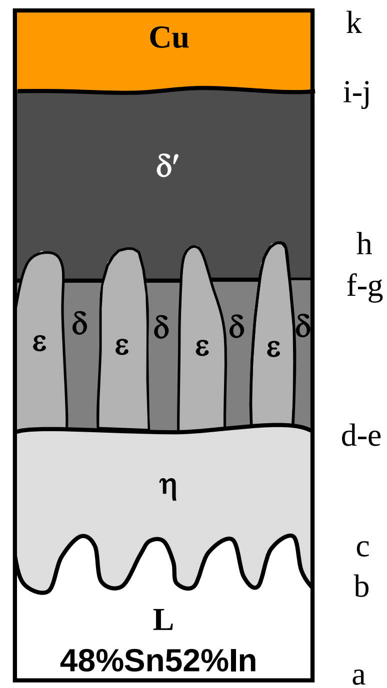
$Cu_6(Sn,In)_5$

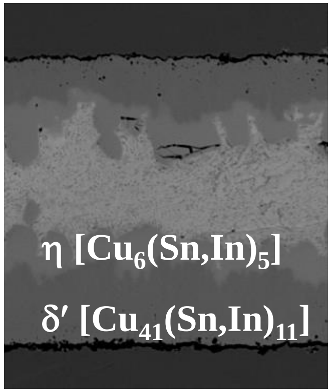
$Cu_2(In,Sn)$

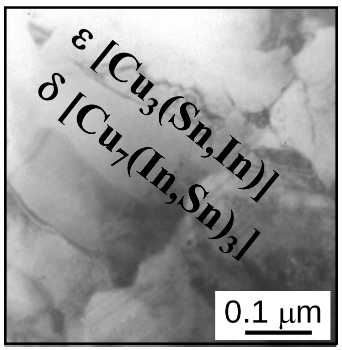


Cu/In-48Sn/Cu interconnection - diffusion path







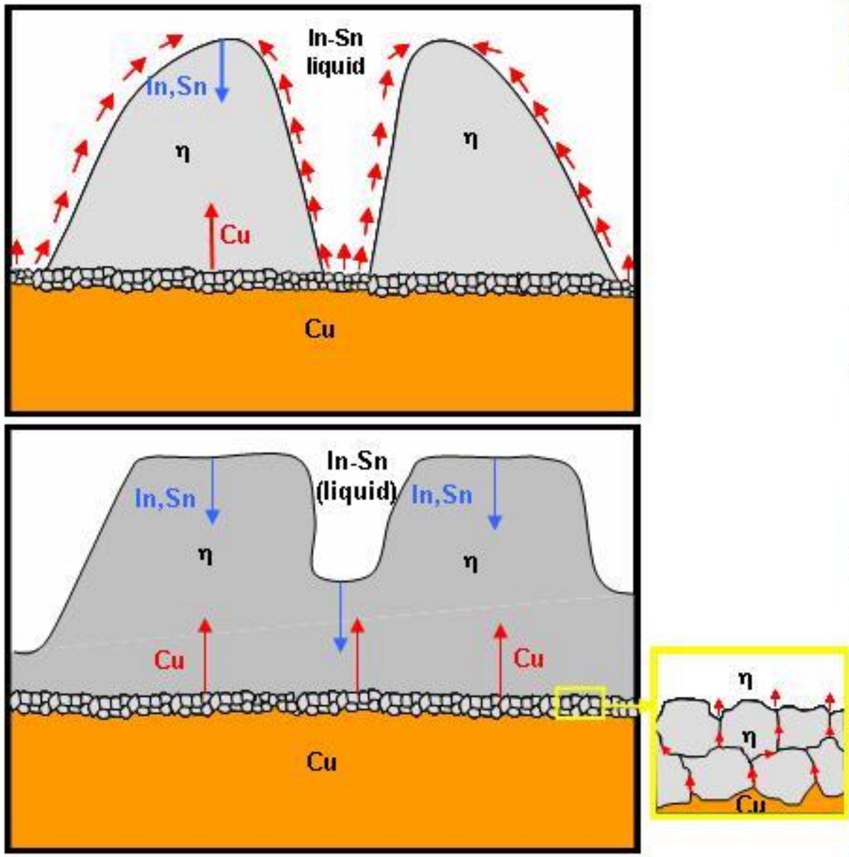


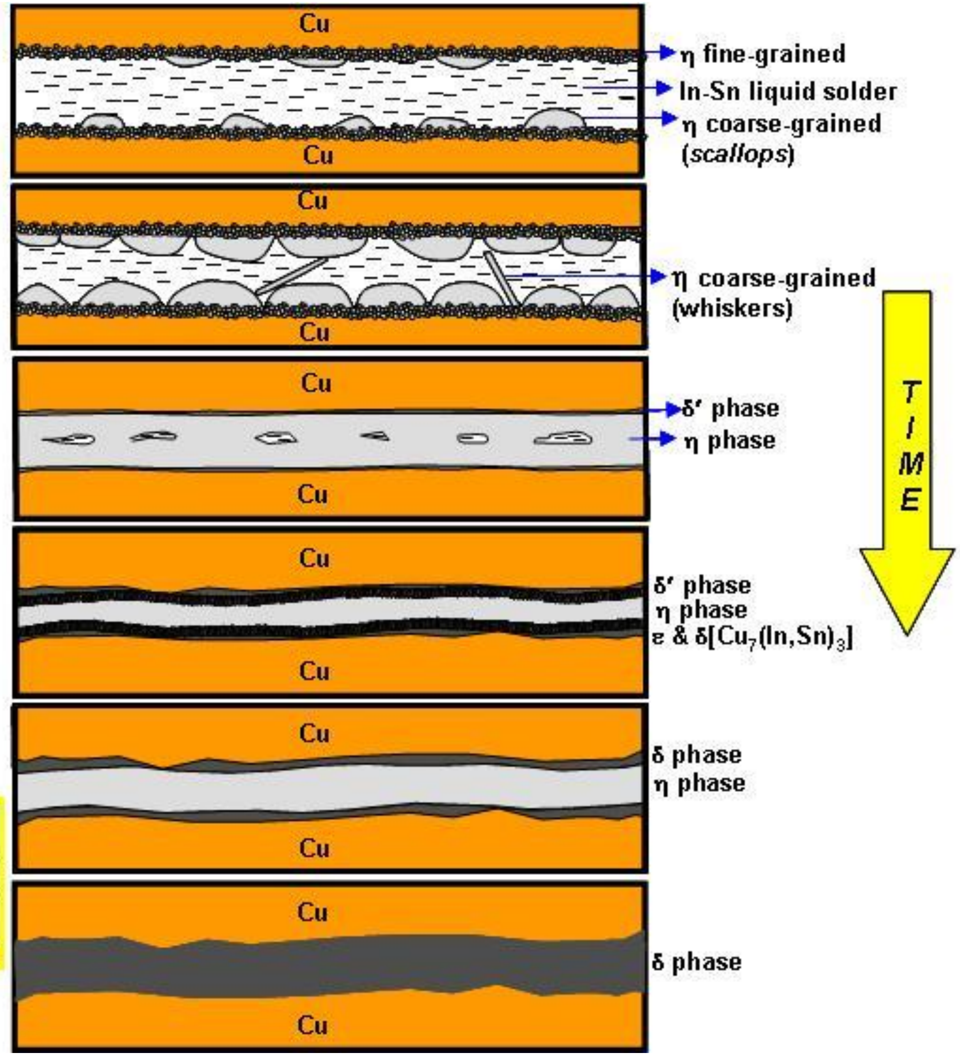
	Concentration of elements at points 1-13 across the joint [at.%], SEM (EDX)												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Cu	2	8	7	15	31	60	56	66	74	74	76	91	100
In	32	39	64	62	51	20	22	17	13	10	6	5	0
Sn	66	53	29	23	18	20	22	17	13	16	18	4	0

Clark J.B.: *Conventions for plotting the diffusion paths in multiphase ternary diffusion couples on the isothermal section of a ternary phase diagram*, Trans. Metal. Soc. AIME 227, (1963) 1250-1251.

$\eta[Cu_6(Sn,In)_5]$

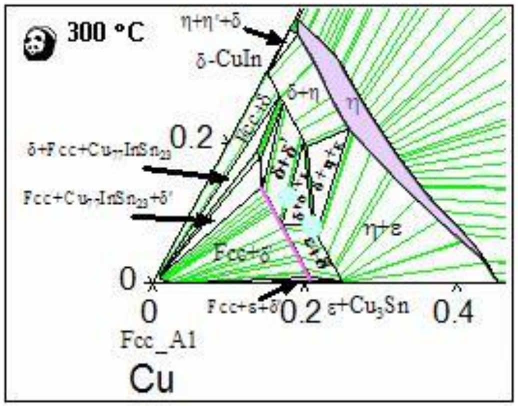
180-220 °C





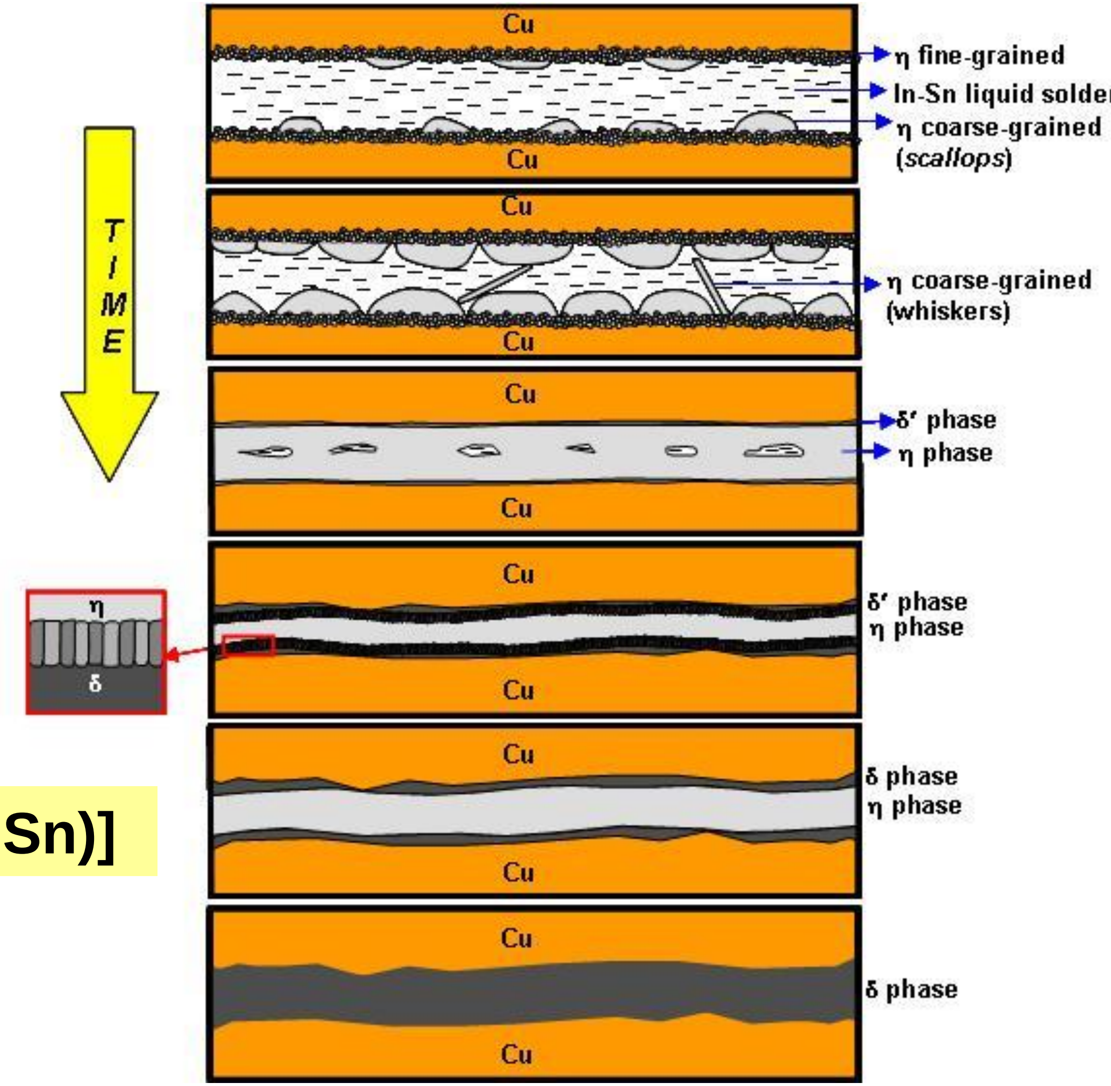
300 -350 °C

$\delta'[Cu_{41}(Sn,In)_{11}]$



$\delta\ [Cu_7(In,Sn)_3]$

$\varepsilon\ [Cu_3(In,Sn)]$



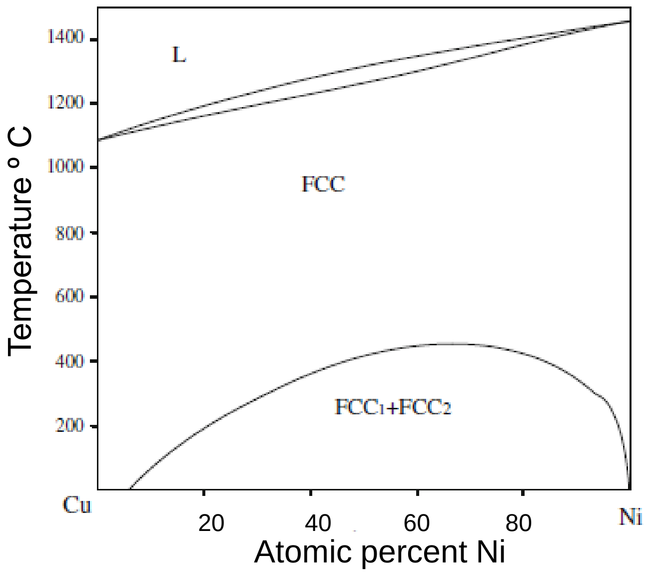
Shear test at room temperature in Cu/In-48Sn/Cu joint

Temperature and time of production	Phases present in the joined area	Shear strength [MPa]
200 °C/3 hours	η[$Cu_6(Sn,In)_5$] *and* In-Sn solder	4.6
200 °C/5 hours	η[$Cu_6(Sn,In)_5$] *and* In-Sn solder	7.1
200 °C/3 days	η[$Cu_6(Sn,In)_5$]	11.2
250 °C/3 hours	η[$Cu_6(Sn,In)_5$], δ′[$Cu_{41}(Sn,In)_{11}$], In-Sn solder	4.2
300 °C/3 hours	η[$Cu_6(Sn,In)_5$], δ′ [$Cu_{41}(Sn,In)_{11}$], In-Sn solder	4.7
300 °C/5 hours	η[$Cu_6(Sn,In)_5$], δ′ [$Cu_{41}(Sn,In)_{11}$], In-Sn solder	6.4
300 °C/3 days	δ′ [$Cu_{41}(Sn,In)_{11}$]	28.5

Shear test at elevated temperature in Cu/In-48Sn/Cu joint

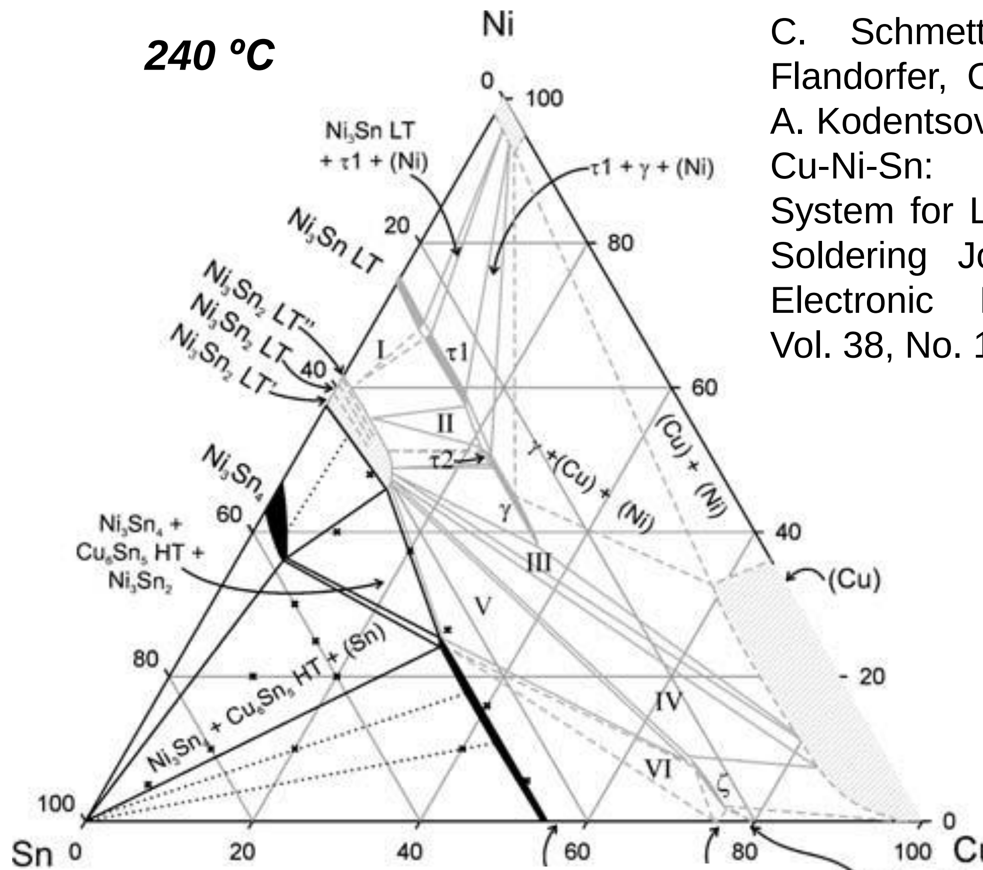
Temperature and time of production	Phases present in the joined area	Shear strength [MPa]
200 °C/3 days	η[$Cu_6(Sn,In)_5$]	9.5 (test at *100 °C*)
200 °C/2 weeks	η[$Cu_6(Sn,In)_5$] *and* δ′[$Cu_{41}(Sn,In)_{11}$]	9.8 (test at *100 °C*)
300 °C/1 week	δ′ [$Cu_{41}(Sn,In)_{11}$]	The fracture occurred in copper substrate. Joint was not destroyed at 100 and 150 °C
300 °C/2 weeks	δ′ [$Cu_{41}(Sn,In)_{11}$]	The fracture occurred in copper substrate. Joint was not destroyed at 100 and 150 °C

Cu+5at.%Ni/Sn/Cu+5at.%Ni interconnection



Cuiping Wang, Jinjin Zhu, Yong Lu, Yihui Guo, and Xingjun Liu, Journal of Phase Equilibria and Diffusion Vol. 35 No. 1, 2014.

240 ºC

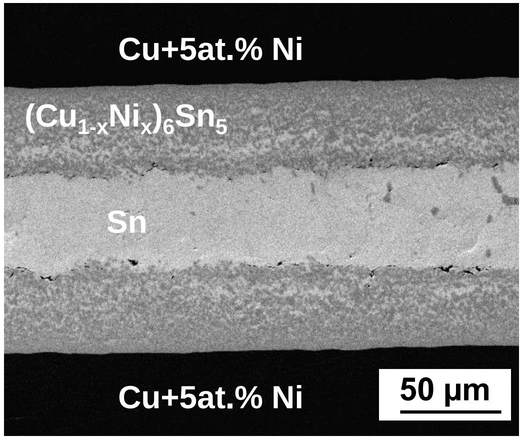


$\eta[(Cu_{1-x}Ni_x)_6Sn_5]$ $\varepsilon[Cu_3Sn]$

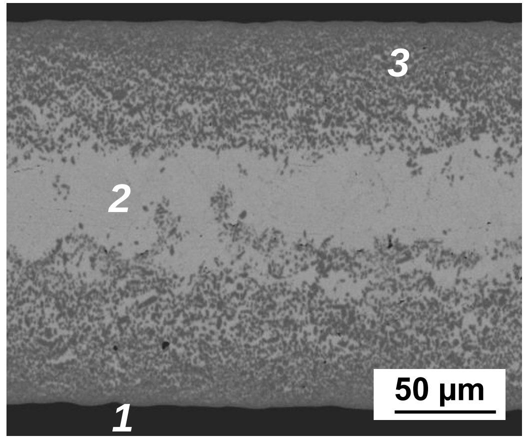
C. Schmetterer, H. Flandorfer, CH. LueF, A. Kodentsov, H. Ipser Cu-Ni-Sn: A Key System for Lead-Free Soldering Journal of Electronic Materials, Vol. 38, No. 1, 2009.

Cu+5at.%Ni/Sn/Cu+5at.%Ni interconnection η[$(Cu_{1-x}Ni_x)_6Sn_5$]

250°C / 2 min

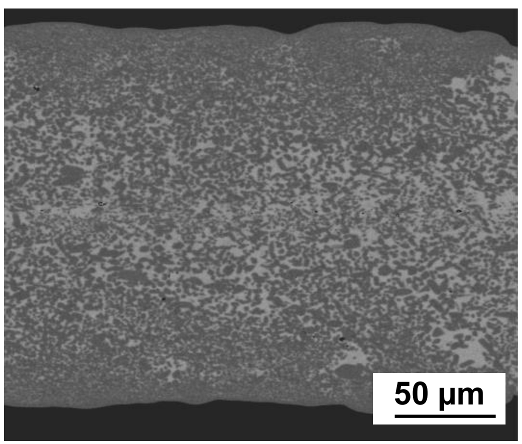


250°C / 5 min

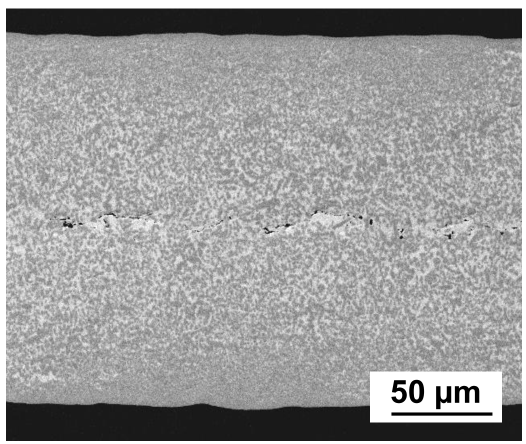


Lp.	Cu at.%	Sn at.%	Ni at.%	phase
1	95.1	0.0	4.9	***(Cu,Ni)***
2	0.0	100.0	0.0	***Sn***
3	50.7	45.1	4.2	***η***

250°C / 10 min

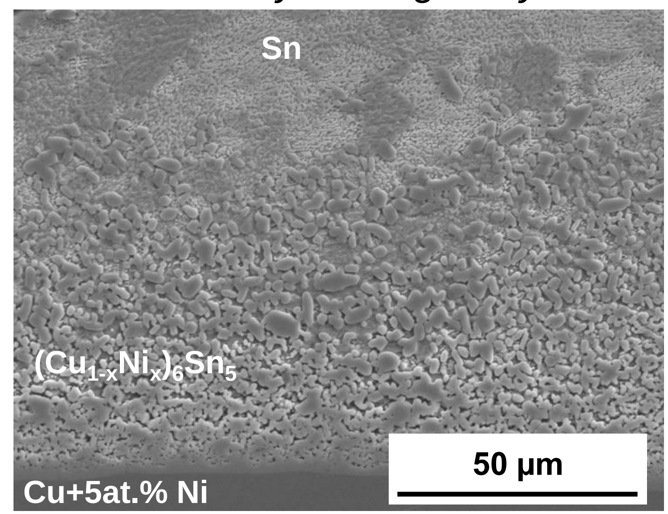


250°C / 15 min



260°C / 10 min

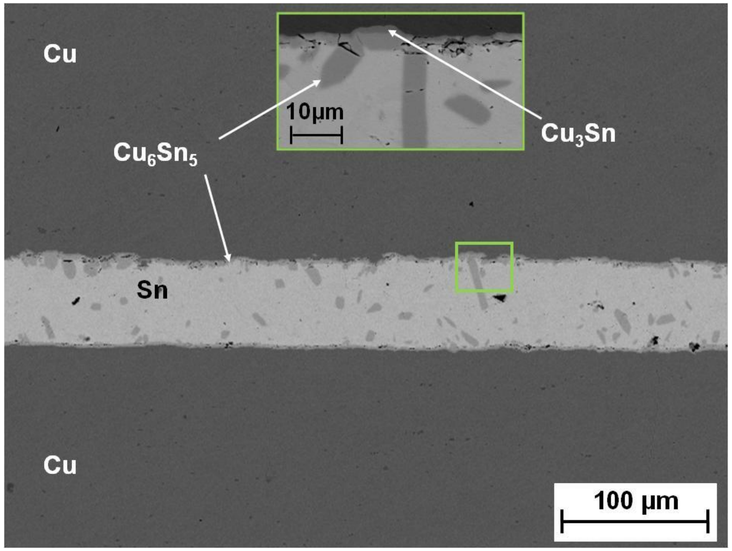
after selectively etching away the Sn



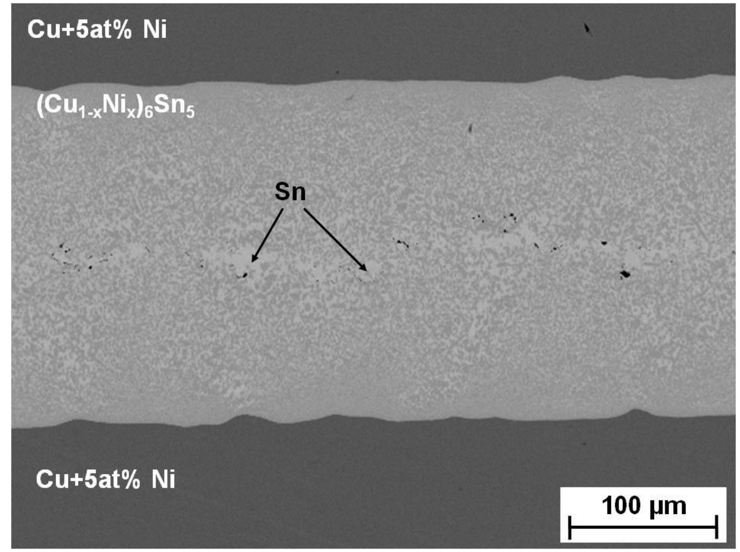
ε[Cu_3Sn] WAS NOT OBSERVED

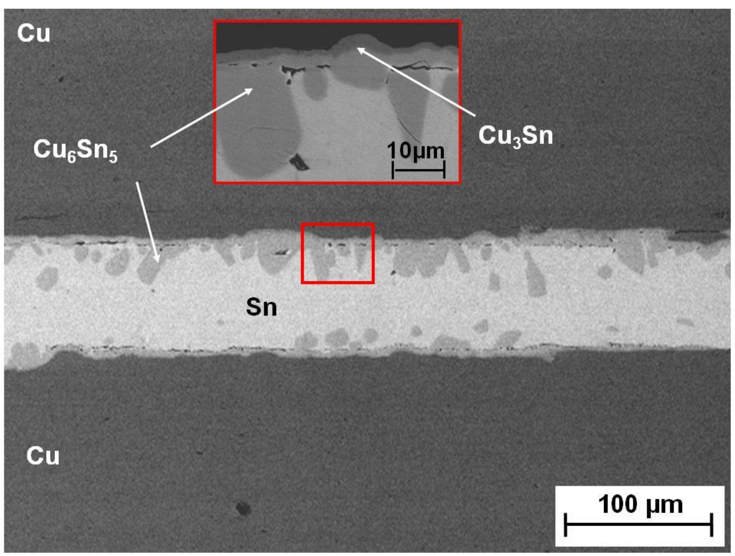
Cu/Sn/Cu vs. Cu+5at.%Ni/Sn/Cu+5at.%Ni joints

Cu/Sn/Cu | **Cu+5at.%Ni/Sn/Cu+5at.%Ni**

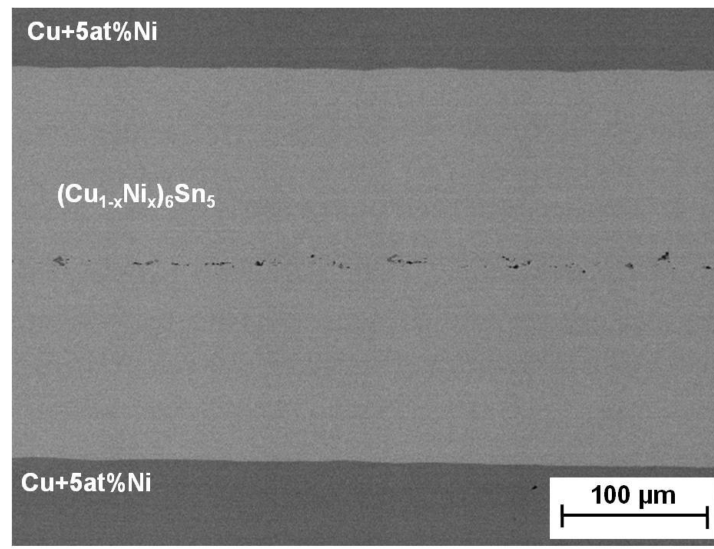


250°C / 10 min



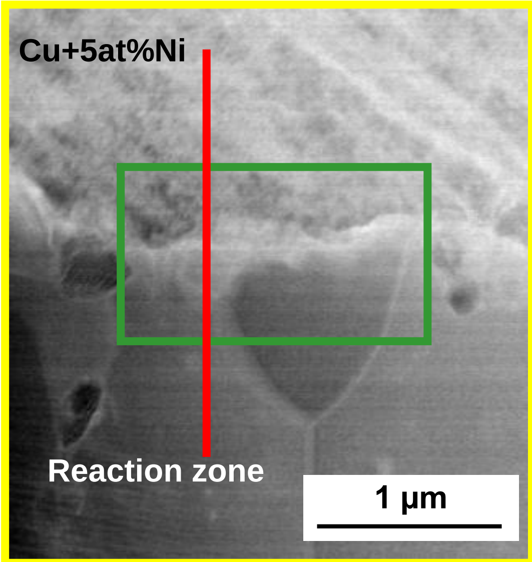


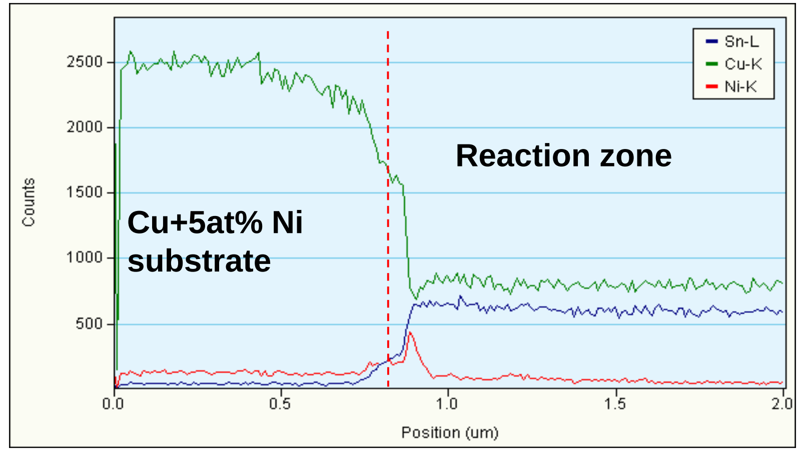
250°C / 60 min



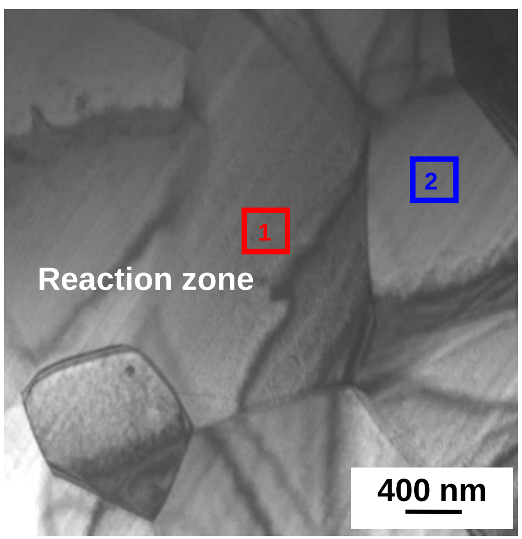
Cu+5at.%Ni/Sn/Cu+5at.%Ni interconnection η[$(Cu_{1-x}Ni_x)_6Sn_5$]

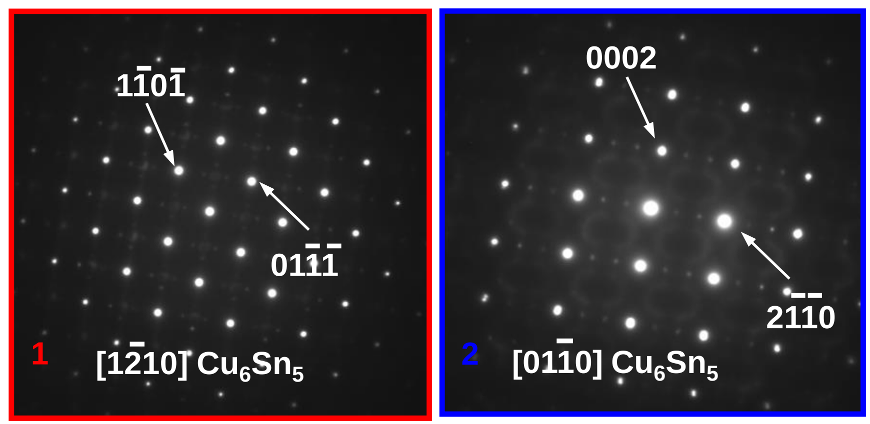
250 °C / 60 min





Ni enrichment zone-possible reason that no **ε[Cu_3Sn]** ***formed***





Rate controlling factor of IPs growth

in general:

$$x=kt^n$$

the widith of the phase interlayer

Growth rate constant

time

* for **n=0.5:** **parabolic growth**, **controlled by the volume diffusion**

* for **n=1:** **linear growth**, **controlled by the chemical reaction at the phase boundary**

There are two important advantages of linear growth from the diffusion soldering process point of view:

1. faster formation of the intermetallic phase,

2. shorter time needed to create a joint.

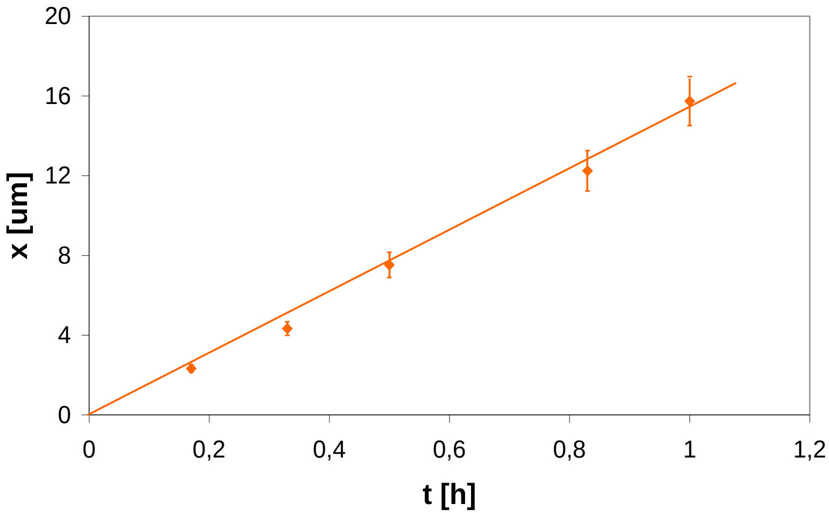
Growth kinetics η and ε phases in Cu/Sn/Cu joint

η phase	*n*
240 °C	0.21
300 °C	0.26
ε phase	***n***
240 °C	0.45
300 °C	0.49

S. Bader, W. Gust, H. Hieber, Acta Metall. Mater. ***43****, 329 (1995)*

Growth kinetics η and δ′ phases in Cu/In-48Sn/Cu joint

δ′ at 300 °C



η phase	*n*
180 °C	0.40 ± 0.02
200 °C	0.20 ± 0.03
220 °C	0.31 ± 0.09
δ′ phase	***n***
300 °C	1.08 ± 0.04
325 °C	1.10 ± 0.08
350 °C	0.91 ± 0.04

Rate controlling factor of IPs growth in Cu+5at.%Ni/Sn/Cu+5at.%Ni joints

$$S=kt^n$$

time

the area of the phase

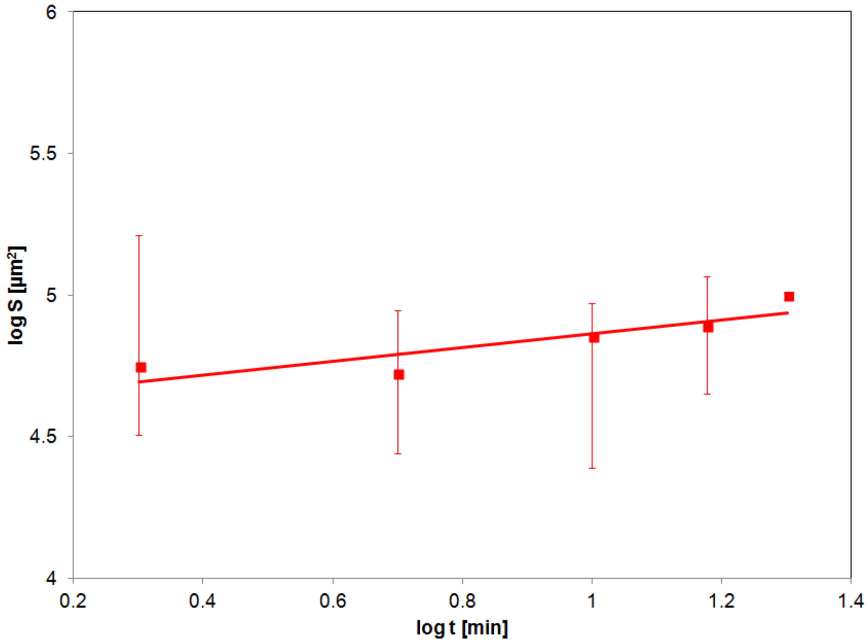
Growth rate constant

* for n=1: controlled by the volume diffusion
* for n<1: controlled by the grain boundary diffusion

Wierzbicka-Miernik A., Miernik K., Wojewoda-Budka J., Filipek R., Lityńska-Dobrzyńska L., Kodentsov A., **Zieba P.** (2013): *Growth kinetics of the intermetallic phase in diffusion-soldered Cu+5at.%Ni)/Sn/(Cu+5at.%Ni) interconnections*, Materials Chemistry and Physics 142, 682-685.

Growth kinetics η phase in Cu+5at.%Ni/Sn/Cu+5at.%Ni joint

η at 250 °C



η phase	*n coeficient*
240 °C	0.27 ± 0.08
250 °C	0.24 ± 0.08
260 °C	0.15 ± 0.09

n<1: grain boundary diffusion

Conclusions

The diffusion soldering is a novel interconnection technology. It is characterized by the low joining temperature (comparable with Pb-Sn eutectic solders) combined with the service temperature, which can be higher by several hundred degrees than the joining temperature. For these reasons, diffusion soldering is a very attractive method for certain types of electronic application.

The proces can be even more efficient if:

- the growth kinetics of IPs is controlled either by chemical reactions at the interfaces or grain boundary diffusion processes,
- The substrate is doped with other elements preventing growth of undesired IPs like ε-Cu_3Sn and accelerating growth kinetics due to change of formation mechanism of IPs (see $(Cu_{1-x}Ni_x)_6Sn_5$.