附表

表 1.1 日本無鉛銲料時程表[8]

Year	Activity
1999	First mass production using lead-free solders
2000	Adoption of lead-free components
2000	Adoption of lead-free in wave soldering
2001	Expansion of lead-free components
2001	Expansion of lead-free products
2002	General use of lead-free solders in new products
2003	Full use of lead-free solders in all new products
2005	Lead-containing solders used only exceptionally

表 1.2 歐洲無鉛環境時程表[9]

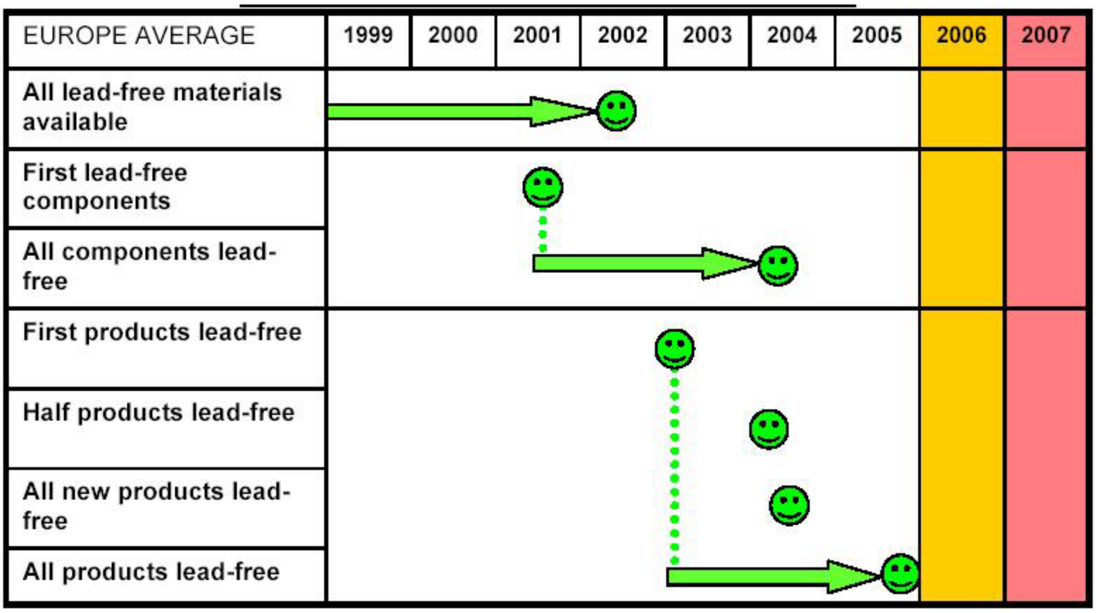

表 1.3 鉛在各產品中的消耗量[10]

Product	Consumption %
Storage batteries	**80.81**
Other oxides (paint, glass, ceramic, pigments, chemicals)	**4.78**
Ammunition	**4.69**
Sheet lead	**1.79**
Cable covering	**1.40**
Casting metals	**1.13**
Brass, bronze billets and ingots	**0.72**
Pipes, traps, extruded products	**0.72**
Solder (excluding electronic solder)	**0.70**
Electronic solder	***0.49***
Miscellaneous	**2.77**

表1.4 主要的無鉛銲料組成[11]

Alloy	Melting Range (C)	Metal Cost/Lb (as of 2/3/99)	Density at 25C (lbs/cubic in)	Metal Cost per in^3	Patent (Yes/No)
63Sn/37Pb	183	$2.37	0.318	$0.75	No
42Sn/58Bi	139	$3.44	0.316	$1.09	No
77.2Sn/20In/2.8Ag	179-189	$30.06	0.267	$8.02	Yes
91Sn/9Zn	199	$3.23	0.263	$0.85	No
91.8Sn/3.4Ag/4.8Bi	208-215	$6.24	0.272	$1.70	Yes
90Sn/7.5Bi/2Ag/0.5Cu	186-212	$5.09	0.273	$1.39	No
96.2Sn/2.5Ag/0.8Cu/0.5Sb	213-219	$5.48	0.267	$1.46	Yes
95.5Sn/4Ag/0.5Cu*	217-218	$6.55	0.269	$1.76	No*
95Sn/3.5Ag/1.5In	218	$8.15	0.268	$2.18	No
93.5Sn/3.5Ag/3Bi	216-220	$5.92	0.269	$1.59	No
96.5Sn/3.5Ag	221	$6.32	0.368	$2.33	No
99.3Sn/0.7Cu	227	$3.48	0.264	$0.92	No
95Sn/5Sb	232-240	$3.37	0.263	$0.88	No

* Some Sn/Ag/Cu alloy compositions are covered by patents; however, this composition can generally be considered free and clear.

表1.5 具潛力的無鉛銲料[11]

Excluded Alloys	Remaining Alloys	Melting Range (°C)	Metal Cost Per Pound (2/3/99)	Reasons for Exclusion
63Sn/37Pb (standard)		183	$2.37	Lead content.
42Sn/58Bi		138	$3.44	Bismuth content. Melting point too low for some applications
77.2Sn/20In/2.8Ag		179 - 189	$30.06	Indium content (cost and availability)
91Sn/9Zn		199	$3.23	Zinc content (poor wetting).
90Sn/7.5Bi/2Ag/0.5Cu		186 - 212	$5.09	Bismuth content. Four part alloy. Broad freezing range.
	95.5Sn/4.0Ag/0.5Cu	**217 - 218**	**$6.55**	----
95Sn/3.5Ag/1.5In		218	$8.15	Indium content.
96.2Sn/2.5Ag/0.8Cu/0.5Sb		213-218	$5.48	4 part alloy. No major benefits over binary alloys. Lower Ag content potential appeal for wave soldering.
	96.5Sn/3.5Ag	**221**	**$6.32**	----
93.5Sn/3.5Ag/3Bi		216 - 220	$5.92	Bismuth Content. Low melt point phase with Pb contamination.
	99.3Sn/0.7Cu	**227**	**$3.48**	----
	95Sn/5Sb	**232 - 240**	**$3.80**	-----

表 2.1 重要的銲料性質[5]

Properties relevant to manufacturing	Properties relevant to reliability and performance
Melting/liquidus temperature	Electrical conductivity
Wettability (of copper)	Thermal conductivity
Cost	Coefficient of thermal expansion
Environmental friendliness	Shear properties
Availability and number of suppliers	Tensile properties
Manufacturability using current processes	Creep resistance
Ability to be made into balls	Fatigue properties
Copper pick-up rate	Corrosion and oxidation resistance
Recyclability	Intermetallic compound formation
Ability to be made into paste	

表 3.1 63Sn-37Pb 與 Sn-3.5Ag 性質比較[11]

Composition	Melting Point (°C)	Density (kg/m³)	Coefficient of Thermal Expansion (ppm/°C)	Electrical Conductivity (% IACS)	Electrical Resistivity (μΩ cm)	Surface Tension (N/m)	Thermal Conductivity (W/[mK])
63Sn/37Pb	183	8400	21.4 @ 25°C	11.5	14.99	0.49	57.9 @ 32.6°C
96.5Sn/3.5Ag	221	7290	22 @ 20°C	14	12.31	0.48	55.3 @ 23.9°C

表 3.2 迴焊用合金的比例分佈[9]

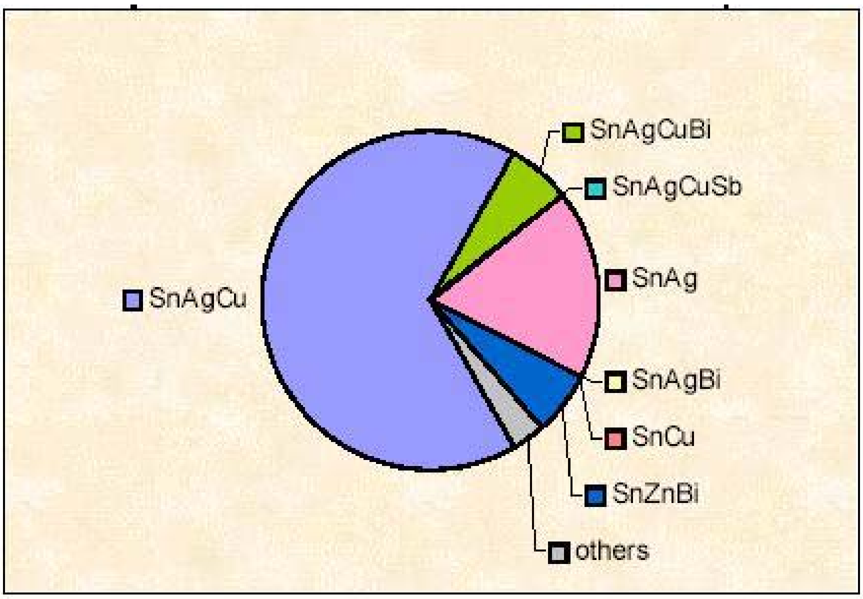

表 3.3 常用的 Sn-Ag-Cu 銲料組成[9]

註：Sn-3.7Ag-0.7Cu 包括了 Sn-3.8Ag-0.7Cu

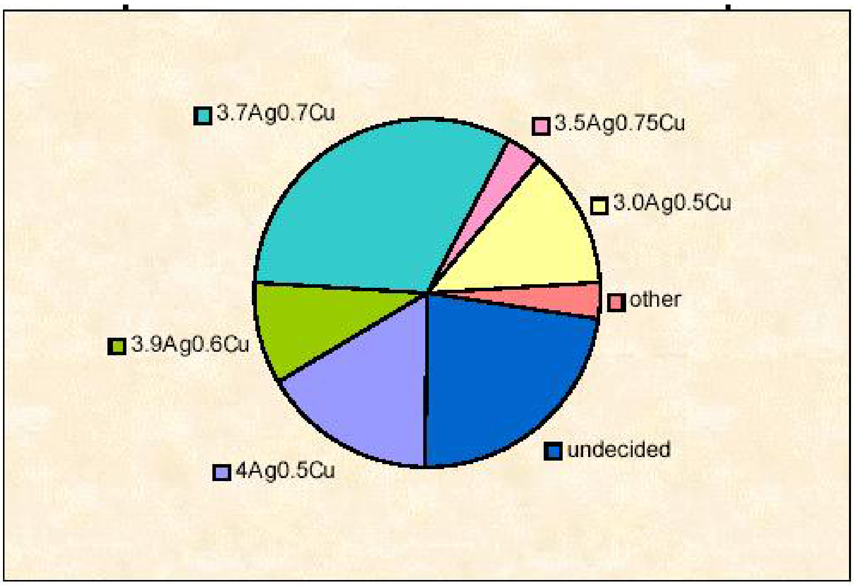

表 3.4 Sn-Ag-Cu 的專利問題[21]

Solder	Range	Solder Patented in Pure Form	Patent Covers Finished Solder Joint	Finished Solder Joint Could Potentially Infringe on Ames Patent	Comment
Sn/Ag2.5/Cu0.7	Sn / Ag0.005-3 / Cu0.5-0.7	No	No	No	Engelhard and Harris let their patents run out, now **patent free**
Sn/Ag2.5/Cu0.8/(Sb0.5)	Sn90.3-99.2 / Ag0.5-3.5 / Cu0.1-2.8 / Sb0.2-2	Yes	Yes	No	CASTIN alloy. Licensed to Cookson (Alpha Metals, Fry, etc.,), Indium Corp., Bow Solders, Senju, Koki, Nihon Handa
Sn/Ag3/Cu0.8	Sn / Ag3-5 / Cu0.5-3 / Sb0-5	Yes	Yes	No	Patented by Senju in Japan only
Sn/Ag3/Cu0.5	Sn / Ag3-5 / Cu0.5-3 / Sb0-5	Yes	Yes	No	Alloy recommended by JEIDA; Patented by Senju in Japan only
Sn/Ag3.2/Cu0.5	Sn / Ag3-5 / Cu0.5-3 / Sb0-5	Yes	Yes	No	Patented by Senju in Japan only
Sn/Ag3.5/Cu0.7	Sn / Ag3.5-7.7 / Cul-4*	No	No	Yes	Finished joint covered under Ames' patent if copper is picked up during processing.
Sn/Ag3.8/Cu0.7	Sn / Ag3.5-7.7 / Cul-4*	Yes	Yes	Yes	Finished joint covered under Ames' patent if copper is picked up during processing.
Sn/Ag4/Cu.5	Sn / Ag3.5-7.7 / Cul-4*	No	No	Yes	Finished joint covered under Ames' patent if copper is picked up during processing.
Sn/Ag4.7/Cul.7	*Sn / Ag3.5-7.7 / Cul-4**	*Yes*	*Yes*	*Yes*	*Ames' alloy*
Sn/Ag3.5	N/A	No	No	No	221°C m.p., potential phase change problems.
Sn/Cu0.7	N/A	No	No	No	227°C m.p., poorer wetting and mechanical reliability.

表 3.5 SnAgCu 合金製造時允許的公差範圍[22]

Alloy	Alloy Ragne
Sn96.5/Ag3/Cu0.5	Sn96 to 97/Ag2.8 to 3.2/Cu0.3 to 0.7
Sn95.5/Ag3.8/Cu0.7	Sn95 to 96/Ag3.6 to 4/Cu0.5 to 0.9
Sn95.5/Ag4/Cu0.5	Sn95 to 96/Ag3.8 to 4.2/Cu0.3 to 0.7

表 5.1 PCB 基材的主要特性[3, pp.629]

Resin/Filler	**T_g(℃)**	**Lateral CTE (ppm)**	**Max. Water Absorption (%)**
Phenolic/Paper	125	14~18	0.75
Epoxy/Glass (FR-4)	130	14~18	0.15
Polyimide/Glass	250	12~16	0.35
Polyimide/Quartz	280	6~8	0.35
Epoxy/Aramid	180	7~9	0.44
BT-Epoxy	185	13~14	0.19

表 6.1 63Sn-37Pb (Au-Ni-Sn)的厚度成長(μm)

時間/溫度	125℃	150℃	175℃
120 小時	-	-	-
240 小時	-	-	-
480 小時	2.25	5.12	5.73
720 小時	2.32	6.18	7.5
1000 小時	2.78	8.15	10.72

註：”-”代表尚未形成連續層

表 6.2 63Sn-37Pb (Ni-Sn)的厚度成長(μm)

時間/溫度	125℃	150℃	175℃
120 小時	~	1.19	4.96
240 小時	~	1.73	6.22
480 小時	~	0.88	5.87
720 小時	0.87	2.51	4.37
1000 小時	0.68	1.34	4.16

註：”~”代表厚度小於 0.5μm (因誤差大而不列入)

表 6.3 63Sn-37Pb (Au-Ni-Sn)+(Ni-Sn)的總厚度(μm)

時間/溫度	125℃	150℃	175℃
120 小時	-	1.19	4.96
240 小時	-	1.73	6.22
480 小時	2.25	6	11.6
720 小時	3.19	8.69	11.87
1000 小時	3.46	9.49	14.88

表 6.4 Sn-3.5Ag (Ni-Sn)的厚度成長(μm)

溫度 / 時間	125℃	150℃	175℃
120 小時	~	1.33	1.63
240 小時	~	1.24	1.89
480 小時	~	1.63	3.36
720 小時	1.86	2.39	4.08
1000 小時	2.18	3.03	4.98

註：”~”代表厚度小於 0.5μm (因誤差大而不列入)

表 6.5 Sn-4Ag-0.5Cu (Cu-Ni-Au-Sn)的厚度成長(μm)

溫度 / 時間	125℃	150℃	175℃
120 小時	0.98	1.75	3.47
240 小時	1.52	2.32	4.08
480 小時	2.01	3.16	4.75
720 小時	3.19	4.53	5.43
1000 小時	3.47	5.24	8.75

表 6.6 擴散係數(D)與溫度的關係($\mu m^2/hr$)

IMC \ 溫度	125℃	150℃	175℃
$(Au,Ni)Sn_4$ (63Sn-37Pb)	0.002959	0.097101	0.263385
Ni_3Sn_4 (Sn-3.5Ag)	0.004464	0.007398	0.028761
Cu-Ni-Au-Sn (Sn-4Ag-0.5Cu)	0.015848	0.030300	0.049662

表 6.7 IMC 之致動能與擴散常數

IMC	Q (KJ/mol)	D_0 ($\mu m^2/hr$)
$(Au,Ni)Sn_4$ (63Sn-37Pb)	134.8	1.96×10^{15}
Ni_3Sn_4 (Sn-3.5Ag)	54.65	5.58×10^{4}
Cu-Ni-Au-Sn (Sn-4Ag-0.5Cu)	33.96	4.55×10^{2}

表 6.8 銲點原始剪力強度(0 小時) (gf)

銲點 / 溫度	63Sn-37Pb	Sn-3.5Ag	Sn-4Ag-0.5Cu
25℃	2077.42	1845.93	2245.7

表 6.9 銲點經時效作用 120 小時後之剪力強度(gf)

銲點 / 溫度	63Sn-37Pb	Sn-3.5Ag	Sn-4Ag-0.5Cu
125℃	1728.34	1731.49	1863.85
150℃	1568.71	1793.91	1860.94
175℃	1500.25	1855.80	1995.20

表 6.10 銲點經時效作用 480 小時後之剪力強度(gf)

銲點 / 溫度	63Sn-37Pb	Sn-3.5Ag	Sn-4Ag-0.5Cu
125℃	1441.53	1673.8	1800.41
150℃	1374.52	1822.73	1844.38
175℃	1355.43	1753.06	1939.85

表 6.11 銲點經時效作用 1000 小時後之剪力強度(gf)

銲點 / 溫度	63Sn-37Pb	Sn-3.5Ag	Sn-4Ag-0.5Cu
125℃	1320.40	1609.57	1852.80
150℃	1292.73	1607.75	1909.68
175℃	1222.16	1733.56	2010.19

表 6.12 63Sn-37Pb 銲點經等溫時效作用後的破壞面(EDX 分析)

	120 小時	480 小時	1000 小時
125℃	75%(延)-25%(脆)	50%(延)-50%(脆)	$(Au,Ni)Sn_4/Ni_3Sn_4$
150℃	25%(延)-75%(脆)	$(Au,Ni)Sn_4/Ni_3Sn_4$	$(Au,Ni)Sn_4/Ni_3Sn_4$
175℃	Ni_3Sn_4	$(Au,Ni)Sn_4/Ni_3Sn_4$	$(Au,Ni)Sn_4$/銲料

註: %為在銲點破壞面所佔的面積

表 6.13 各銲料之剪力模數

銲料合金	G(T) (MPa)	備註
Pure Sn [67]	16302-40.5T(℃)	3/8E
Tin [29]	17159.26-40.37T(℃)	ν =0.35 [本文]
60Sn-40Pb [43]	13100--55.85T(℃)	ν =0.35 [43]
63Sn-37Pb [30]	10703.7-39.63T(℃)	$\nu=0.35, \dot{\varepsilon}=1.92\times10^{-2}s^{-1}$ [本文]
63Sn-37Pb [64]	7000-0.0164T(℃)	ν =0.35 [43]
Sn-3.5Ag [43]	19305.33-68.95T(℃)	ν =0.35 [43]
Sn-3.8Ag-0.7Cu [42]	22233.3-92.59T(℃)	$\nu=0.35, \dot{\varepsilon}=1.92\times10^{-2}s^{-1}$ [本文]
Sn-3.9Ag-0.6Cu [64]	6888.89-0.0076T(℃)	ν =0.35 [43]

註：單位均已經過換算。Poisson's ratio 為作者給定之假設。

表 6.14 Sn-3.5Ag 銲點的穩態潛變率平均值 **($\times 10^{-6}$ s^{-1})**

	0.75	1	1.25	1.5	1.75	2	2.13	2.25	2.5	2.75
25℃	-	-	-	-	-	3.8	9.03	13.53	101	122
75℃	-	1.71	5.98	21.9	122	454	-	-	-	-
125℃	6.2	25	109	608	1046	-		-	-	-
150℃	44.79	202	480	1130	1670	-	-	-	-	-

表 6.15 Sn-4Ag-0.5Cu 銲點的穩態潛變率平均值 **($\times 10^{-6}$ s^{-1})**

	0.75	1	1.25	1.5	1.75	1.88	2	2.13	2.25	2.5	2.75
25℃	-	-	-	-	-	-	2.04	7.84	8.95	44.8	115
75℃	-	-	2.62	6.09	19.1	152	504	-	-	-	-
125℃	2.45	3.49	92.27	269	979	-	2710	-	-	-	-
150℃	38.4	237	262	509	2230	-	-	-	-	-	-

表 6.16 Sn-3.5Ag 在三種不同潛變模型下之材料參數表

Sn-3.5Ag	A-P	n=4.31~11.7	Q=44.01~74.83 KJ/mole
	Dorn	n=6.67, Q=37.5KJ/mole	
	sinh	A=0.01555, α=1400, n=4.3, Q=37.5KJ/mole	

表 6.17 Sn-3.5Ag 應力指數及致動能之比較

solder alloy	Type	equation	n	Q(kJ/mol)
Sn-3.5Ag [本文]	joint	A-P	4.31~11.7	44.01~74.83
Sn-3.5Ag [本文]	joint	Dorn	6.67	37.5
Sn-3.5Ag [本文]	joint	sinh	4.3	37.5
Sn-3.5Ag [43]	joint	sinh	5.5	38.5
Sn-3.5Ag [38]	joint	A-P	3.9~11.5	N/A
Sn-3.5Ag [38]	joint	Dorn	4.5/10.6	80/75
Sn-3.5Ag [70]	joint	A-P	5~11	N/A
Sn-3.5Ag [70]	joint	Dorn	5.5[43]	60
Sn-3.5Ag [39]	FC joint	A-P	11	79.8
Sn-3.5Ag [35]	bulk	Dorn	10	50.96
Sn-3.5Ag [36]	bulk (thermal stablized)	A-P	4.5	N/A
Sn-3.5Ag [36]	bulk (fast cooled)	A-P	3	N/A
Sn-3.5Ag [72]	bulk	threshold-Dorn	7	75~83
Sn-3.5Ag [29]	bulk	A-P	11~12	46.6
Sn-3.5Ag [39]	bulk	sinh	4.75	57.1

註：sinh=hyperbolic sine function, A-P=Arrhenius Power law, Dorn=Dorn eqn.

文獻上的原始數據經過 1cal=4.187J 與 1eV=96.48kJ/mol 的換算

N/A : Not Available

表 6.18 Sn-4Ag-0.5Cu 在三種不同潛變模型下之材料參數表

Sn-4Ag-0.5Cu	A-P	n=4.19~12.3	Q=71.69~80.03 KJ/mole
	Dorn	n=7.62, Q=43.5KJ/mole	
	sinh	A=0.10559, α=1250, n=5.28, Q=43.5KJ/mole	

表 6.19 Sn-Ag-Cu 應力指數及致動能之比較

Solder alloy	type	equation	n	Q(kJ/mol)
Sn-4Ag-0.5Cu [本文]	joint	A-P	4.19~12.3	71.69~80.03
Sn-4Ag-0.5Cu [本文]	joint	Dorn	7.62	43.5
Sn-4Ag-0.5Cu [本文]	joint	sinh	5.28	43.5
Sn-4Ag-0.5Cu [39]	FC joint	A-P	18	83.1
Sn-3Ag-0.5Cu [38]	joint	A-P	4.4~11.2	N/A
Sn-3Ag-0.5Cu [38]	joint	Dorn	6.6/10.7	95/75
Sn-3.9Ag-0.6Cu [64]	joint	sinh	3.79	62.92
Sn-3.9Ag-0.6Cu [50]	joint	sinh	4.2	45
Sn-3.5Ag-0.75Cu [29]	bulk	A-P	11~12	47.3
Sn-3.5Ag-0.7Cu [36]	bulk (thermal stablized)	A-P	7.6	N/A
Sn-3.5Ag-0.7Cu [36]	bulk (fast cooled)	A-P	5	N/A
Sn-3.8Ag-1Cu [39]	bulk	sinh	3	38.7
Sn-3.8Ag-0.7Cu [40]	bulk	sinh	3.02	38.59

註：sinh=hyperbolic sine function, A-P=Arrhenius Power law, Dorn=Dorn eqn.

文獻上的原始數據經過 1cal=4.187J 與 1eV=96.48kJ/mol 的換算

N/A : Not Available

表 6.20 銲點 IMC 實驗結果之比較

IMC 實驗	63Sn-37Pb	Sn-3.5Ag	Sn-4Ag-0.5Cu
IMC layer	Ni_3Sn_4 *$(Au,Ni)Sn_4$*	***Ni_3Sn_4***	***Cu-Ni-Au-Sn***
擴散係數 受溫度的影響	敏感	不敏感	不敏感
致動能	134.8KJ/mol	54.65KJ/mol	33.96KJ/mol
IMC 厚度	最厚(≧480 小時)	最薄	次之
剪力推球強度	次之(0 小時) 最小(≧120 小時)	最小(0 小時) 次之(≧120 小時)	最大
剪力強度變化	溫度及時效作用主導	不規律變化	溫度主導
破壞模式	銲料延性破壞 界面 IMC 脆性破壞	銲料延性破壞	銲料延性破壞

表 6.21 銲點潛變實驗結果之比較

靜態及潛變實驗		Sn-3.5Ag	Sn-4Ag-0.5Cu
靜態強度(lap shear)		低	高
穩態潛變率		大	小
Arrhenius Power law	應力指數(n)	4.31~11.7	4.19~12.3
	致動能(Q)	44.01~74.83KJ/mol	71.69~80.03 KJ/mol
Dorn eqn.	n	6.67	7.62
	Q	37.5KJ/mol	43.5KJ/mol
sinh model	n	4.3	5.28
	Q	37.5KJ/mol	43.5KJ/mol
潛變阻抗		低	高