New Lead Free Solder Composition and Physical Properties of Printed Wiring Board Laminate Material To Suppress Lift-Off and Improve Reliability

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Abstract
Lift-off (fillet-lifting) and land-lifting phenomena, which occur in wave soldering with Sn-Ag-Cu (SAC) solders, depend on the physical properties of the solder and the laminate material used. A new Sn-Ag-Cu-Ni-Ge (SACNG) solder and two types of printed wiring board (PWB) laminate materials with higher glass transition temperatures (Tg), lower coefficients of thermal expansion (CTE) and higher peel strengths at high temperatures have been developed to suppress fillet- and land-lifting. The SACNG solder and laminate materials have shown excellent reliability in the wave soldering process and thermal cycling evaluation. Moreover, the valid physical properties of laminate materials for suppressing fillet- and land-lifting have been investigated by FEM analysis.

Introduction
With increasing global interest in environmental protection, Lead Free solder is expected to be used for PWBs in electronic equipment. Among Lead Free solders, the ternary SAC solders were expected to be a substitute for Sn-Pb eutectic solders, and have spread in manufacturing electric devices. However, advanced Lead Free solder having higher reliability than the SAC solder is required from the viewpoint of adaptability to various joint methods, with lower stress change, longer term heating stability, and higher heat conductivity as solder joint parts. On the other hand, the substrate (laminate) materials are required to have higher Tg and heat resistance, and lower water absorption due to the higher melting point of the Lead Free solder. Lift-off (fillet-lifting) and land-lifting phenomena, occurred in wave soldering with SAC solders, depend on the physical properties of the solder and the laminate material used. In this study, a new SACNG solder and two types of laminate materials will be introduced, and also the relationship between the lift-off phenomena and material properties will be investigated.

Lift-Off and Mechanical Properties
The root cause of lift-off is considered to be the stress concentration at the fillet area. Two main factors of the stress concentration are the z-axis direction of thermal expansion of the laminate material and the solidification shrinkage of the solder [(1)]. The lower the shrinkage in cooling from the melting point of the solder to room temperature, the lower is the stress at the land area. The shrinkage of the substrate (laminate) material depends on its CTE and Tg. Therefore, according to the report by Ishizuka and Kono [(2)], using a laminate material with a lower shrinkage rate (defined as the Contraction index: W) and higher Tg, can suppress land lifting with the laminate material showing a lower total CTE.

Laminate Materials
3.1 Halogen-free laminate materials
High Tg, low CTE, low water absorption, high heat resistance and high peel strength of the laminate materials are presumed to suppress lift-off and land lifting. From the viewpoint of dioxin or furan problems after combustion, major OEMs will demand halogen-free laminate with flammability level of UL 94 V-0. Two kinds of laminates have been developed to meet these requirements.

Halogen-Free Laminate Material A
Bis phenol-A (BPA) type epoxy resin is generally used as the base resin of the conventional FR-4. This type of epoxy resin itself is somewhat flammable. Therefore, the conventional FR-4 needs to contain a large volume of flame retardant compounds. A new base resin system having a highly cross-linked structure with a nitrogen rich feature has been developed, which proved to be highly flame retardant as well as having higher Tg, higher modulus, and lower water absorption. The comparison of the new resin and the conventional BPA type epoxy both without flame retardant is shown in Table 1.

Table 1 - Comparison of The Laminate with The New Resin and The Conventional Epoxy

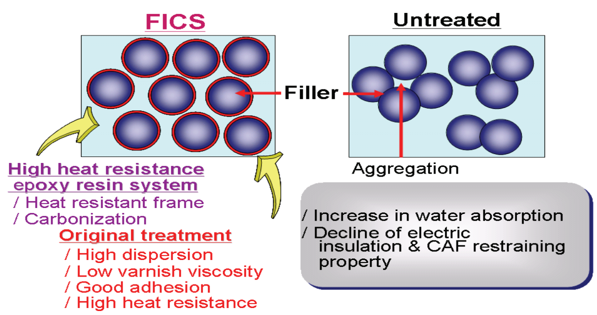
Items		Condition	Properties of laminate	
			New resin	BPA type epoxy
Volume of aromatic components in skeleton (wt%)		---	60-70	40-50
Flammability	Flame retardant level	UL94	V-1	HB
	Maximum combustion time(s)	UL94	24	>60
Tg.(K)		TMA	423	393
Flexural modulus (GPa)		298 K	5.9	3.4
Water absorption (wt%)		PCT 20 h	1.1	3.8

(1.6mm thickness, without flame retardant)

Flammability of the new resin itself is UL 94 V-1. A certain kind of flame retardant compound is added to the new resin to attain the same UL94V-0 as the laminate.

Halogen-Free Laminate Material B

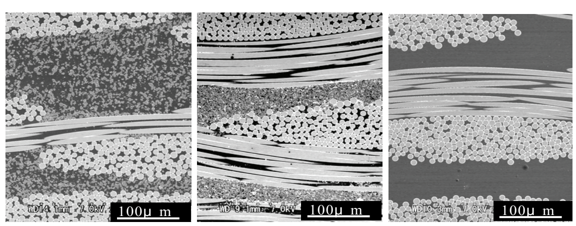
FR-4 with Tg higher than 170C is widely used for motherboards and package substrates. However, lower CTE is required of this type of material to improve reliability. It is effective to use inorganic filler to reduce CTE. When a large volume of filler is mixed with the resin, aggregation of fillers will occur in the resin impairing reliability. A new filler interphase control system (FICS), shown in Figure 1, has been developed with the advantages of both higher filler volume content and better dispersion characteristics of the filler. These are obtained by using an original treatment at the interphase between the matrix resin and fillers.



(CAF: Conductive Anodic Filament)

Figure 1 - Schematic Diagram of Filler Interphase Control System

With this technology, halogen-free type material B has been developed which has far lower CTE than material A. Cross sections of the laminate Materials A and B, and the conventional FR-4 (material C) are shown in Figure 2.



(a) Material A (b) Material B (c) Material C

Figure 2 - Cross Sections of The Three Laminates Differing in Inorganic Filler Content

Thermal-Mechanical Properties

The comparison of the basic physical properties of the conventional and the two newly developed halogen-free FR-4s is shown in Table 2.

Table 2 - Comparison of Basic Physical Properties of The Conventional and Two Newly Developed Halogen-Free FR-4s

Item			Middle Tg halogen-free FR-4	High Tg, low CTE halogen-free FR-4	Conventional FR-4
Laminate			Material A	Material B	Material C
Tg-TMA(K)			413(140 degC)	448(175 degC)	408(135 degC)
Tg-DMA(K)			465(192 degC)	490(217 degC)	423(153 degC)
CTE(ppm/K)	Z	< Tg	48.0	32.8	52.2
		>Tg	206.0	161.0	322.0
Young's modulus at R.T. (GPa) ; Static methods			27.5	29.5	23.6
Poisson's ratio			0.15	0.20	0.15
Thermal conductivity(W/m･K)			0.67	0.82	0.28
Specific heat(J/kg･))			800-900	880-980	800-1000
Water absorption	E-24/50+D-24/23		0.02-0.04	0.03-0.05	0.05-0.07
Contraction index W(%)			2.17	1.22	3.28

The Tg of material A is 140Cº by TMA and is higher than that of material C. Material A has a lower CTE (Z direction), a higher thermal conductivity and a lower water absorption than material C. Material B has the highest Tg (175Cº by TMA), highest modulus, and lowest water absorption, resulting in the best heat resistance. The CTE (Z direction) of material B is nearly half that of material C. The value of the contraction index, W is, lowest for material B. The correlation of the kind of solder (SAC or SACNG) with the lift-off and land-lifting phenomena was then investigated using these three materials.

Experimental Material and Solder Condition

The chemical composition of two kinds of lead free solders is shown in Table 3. The Specifications of the PWBs and the component are shown in Tables 4 and 5 respectively. HC40-39NF made by Tamura was used in a mass production line. The wave soldering conditions are shown in Table 6.

Table 3 - Compositions of The Solders

Contents	Solder(wt%)				
	Sn	Ag	Cu	Ni	Ge
SAC	Bal.	3.15	0.495	--	--
SACNG	Bal.	3.62	0.496	0.058	0.011

Table 4 - Specifications for PWBs Used

PWB design	Parameters
Thickness (㎜)	1.6
Through-hole diameter(㎜)	1.0
Land diameter(㎜)	1.4,1.6,1.8,2.0,2.2
Solder resist	Halogen-free t=50 μm
Surface finish	Heat-resistant pre-flux
Laminate	Material A,B,C
Size(㎜)	116L×140W

Table 5 - Specifications for The Component Used

Components	Pitch/Pin size(mm)	Plating	Number of pins
Connecter	2.54/0.8	Sn	5

Table 6 - The Wave Soldering Condition

Soldering condition	Parameters
Pre-heat time	323-393 K, 120 s
Soldering temperature	528 K（Solder bath）
Wave time $1^{st}/2^{nd}$	2.5 s/5.0 s
Conveyor speed	0.8 m/min
Conveyor angle	5°
Atmosphere	N_2 (O_2 :1000 ppm)
Flux type	RMA(EC-19s-8)
Flux supply	Spray :95 ml/m^2

Results and Discussion

Laminate Materials and Lift-Off, Land-Lifting Phenomena

Some small cracks were observed in the resin area close to the land area. No crack is observed at the interface between the land and the resin. In this paper, we defined these small cracks as "land-lifting". The land-lifting image and their pattern diagrams observed by FE-SEM are shown in Figure 3.

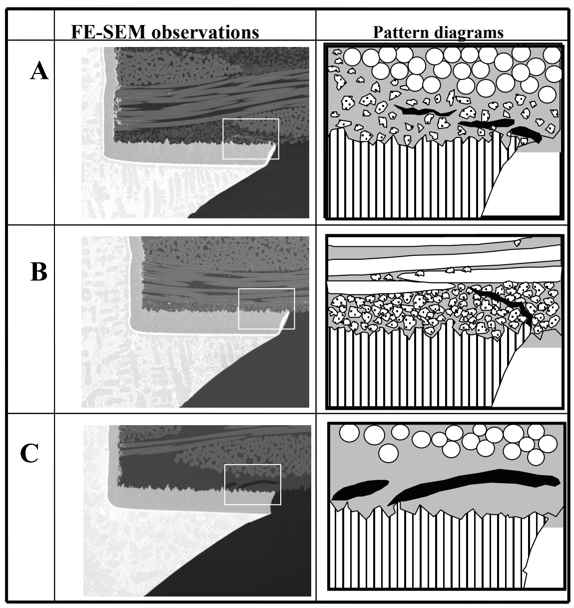


Figure 3 - FE-SEM Images of Cross-Sections of The Fillet and The Cracking Pattern Diagrams of The Laminate Materials

Land-lifting phenomenon are different for each laminate material. The length of the land-lifting cracks was 50 um for the materials A and B, but was as large as 100 -200 um for the material C. The difference is considered to be caused by the difference in the value of residual stress concentration resulting from the thermal-mechanical properties of materials.

Solder Material and Lift-Off, Land-Lifting Phenomenon

The correlation between the land diameter and land-lifting rate for various laminate materials are summarized in Figure 4.

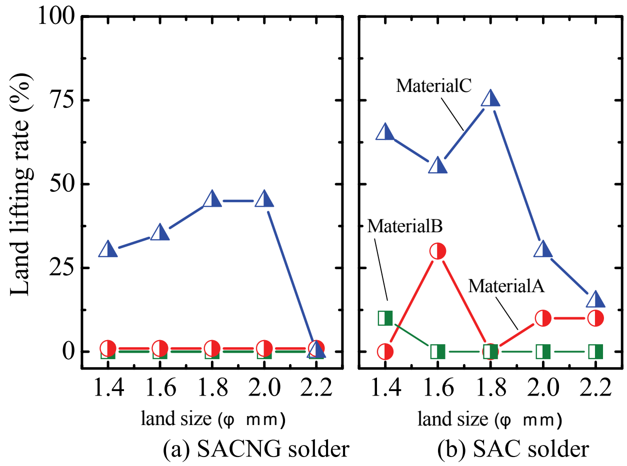


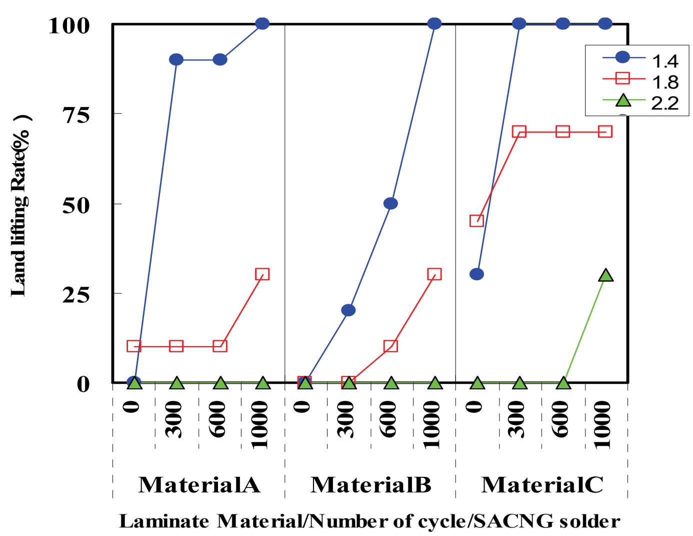
Figure 4 - Correlation between Land Diameter and Land Lifting Rate After Soldering for Various Laminate Materials

Here, we show the 'land lifting rate' as number of small cracks that occurred in the through-holes divided by the number of the total through-holes tested. Regarding the land-lifting rate, there was no significant difference between component side and soldering side. Moreover, shrinkage cavities were observed in all of the test conditions, but filet lifting was not observed in the testing.

Regarding the laminate materials, filler containing boards had much lower land-lifting rates than the non-filler containing boards. In particular, the material B with the highest filler content and the lowest W (1.22) demonstrated the best result in the three kinds of the laminate materials. For the SACNG solder, no land lifting was observed in land size 2.2 mm independent of the laminate materials. However, the land-lifting did occur in the SAC solder The root cause appears to be the β-Sn phase branch growth and the segregated solidification in the SAC solder due to the amount of Ag content of the SAC solder. This is 0.5% lower than that of Sn3.5Ag0.5Cu eutectic solder during the cooling process [(3)(4)]. Because of this, it was difficult for the SAC solder to suppress land lifting for land diameters from 1.4 to 2.2 mm.

Reliability after Thermal Cycling Test

The relationships between the land-lifting rate and thermal cycle number for the SACNG solder and various laminate materials are summarized in Figure 5. Regarding the laminate materials, the same tendency shown in Figure 4 was demonstrated.



TCT -40Cº to 125Cº, 1 h/cycle

Figure5 - Land-Lifting Rates after Thermal Cycling Test (TCT) for Various Laminate Materials

6. Influence of the laminate material properties on the land lifting

6.1 Finite Element Methods (FEM) analysis model and physical properties of the materials

To clarify the influence of the laminate properties on land lifting, stress analysis was carried out using FEM. The schematic diagram of the stress analysis model is shown in Figure6.

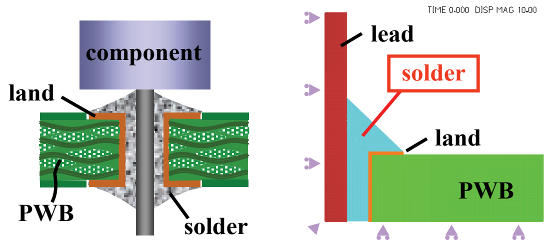


Figure – 6 - Schematic Diagram of Stress Analysis Model

The FEM analysis model was based on the sample size in the above experiments and a land size of 1.8 mm in diameter.

The thermal expansion of the preheat process in wave soldering has been considered. Physical properties and stress-strain curve, shown in Table 7 and Figure7 respectively, were used in the analysis. A modulus of 1/10000 that of the solid state was used as the modulus in the molten state. The mechanical testing was performed according to JIS Z 3198-2, and the diameter of the specimen is 6mmφin parallel part. To consider the cooling speed of the wave soldering and the shrinkage of the laminate material, the tensile strain rate of the laminate deformation was chosen to be 0.002 s^{-1}. The physical properties of the laminate materials shown in Table 8 were also used in the analysis.

Table 7 - Physical Properties of SACNG Solder

Temp. (K)	298	348	398	473
Modulus(GPa)	49.1	45.3	45.7	37.3
CTE (ppm/K)	22.3	←	←	←

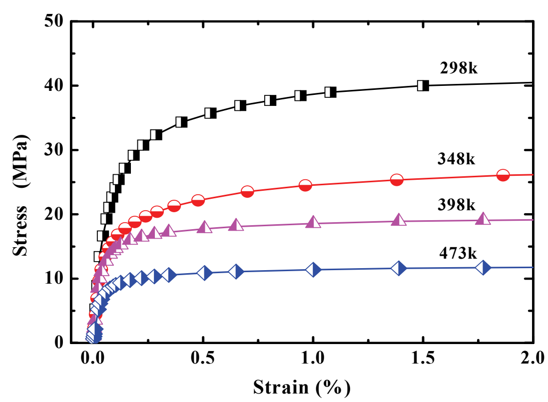


Figure 7 - Stress-Strain Curves for SACNG Solder

Table 8 - Physical Properties of Laminate Materials

Material	Temp.(K)	298	348	398	473
B	Modulus(GPa)	29.5	28.2	26.8	20.8
	Poisson's ratio	0.20			
	CTE(ppm/K)	32.8(<Tg), 161(>Tg)			
C	Modulus(GPa)	23.6	22.9	21.1	8.5
	Poisson's ratio	0.15			
	CTE(ppm/K)	52.2(<Tg), 322(>Tg)			

The melting temperature of the SACNG solder is approximately to 220 Cº. Because it is difficult to simulate the temperature distribution during soldering process; the primary temperature of the solder is defined to be 200 Cº in this paper. The stress analysis with FEM in the land area was performed in the case of the cooling process from 200 Cº to room temperature.

Analysis Result
One of the FEM analysis results is shown in Figure 8. The stress concentration was confirmed to occur primarily at the edge of the land due to the shrinkage of the PWB laminate in the cooling process after wave soldering.

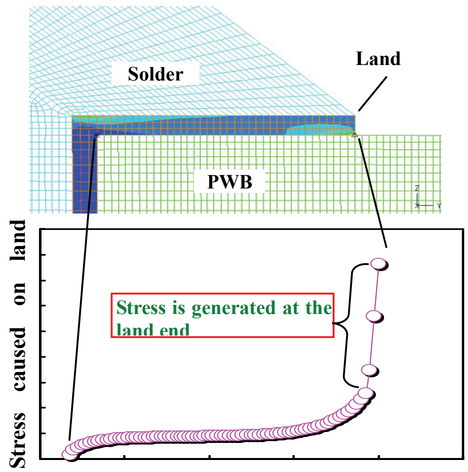


Figure 8 - FEM Analysis of The Stress Caused on Land Field

Simulation to Suppress the Land Lifting Phenomena
In the experimental results, land lifting was observed only in the resin area of the laminate materials. The main factor dominating the land lifting was considered to be the correlation between the peel strength of the copper, the resin and the strength of the laminate material. Therefore, the stress at the edge of the land and the peel strength of the laminate material were studied.

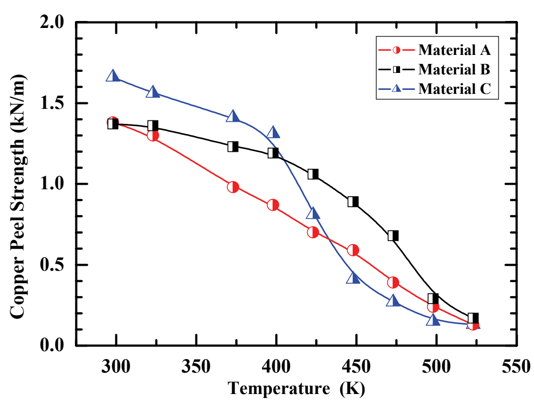
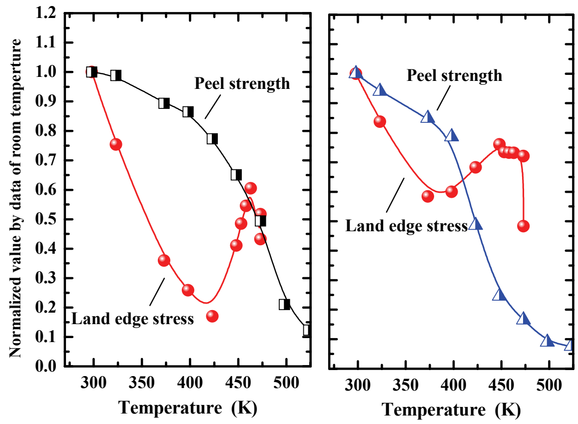


Figure 9 - Temperature Dependence of Copper Foil Peel Strength

Temperature dependence of the copper foil peel strength is shown in Figure 9. The Tg of the material B is 175 Cº, which is higher than those of the material A and C. Therefore, the peel strength of the material B at high temperatures was also higher than those of the materials A and C. Temperature dependence of the peel strength and land edge stress evaluated by FEM analysis, both normalized by the values at room temperature, is shown in Figure10. We considered that higher potential of land lifting will exist in the temperature range where normalized land edge stress exceeds normalized peel strength.



(a) Material B (b) Material C

Figure 10 - Temperature Dependence of Both Normalized Peel Strength and Land Edge Stress

In the temperature range over 150 Cº (425 Kº), land lifting occurred in material C. However, it did not occur in material B that has a lower CTE and a higher Tg. From the results, it's believed that the material B has the better ability to suppress land lifting compared to material C.

Relations of the Laminate Material Properties and The Land-Lifting

To investigate the relations between the laminate physical properties and the ability of the material to suppress land lifting, two cases were studied with material C. In the case 1 we changed the modulus of the material C; increasing it by a factor of two. In case 2, the CTE of the material C was reduced to 2/3 of its original value. The results of case 1 and case 2 are shown in Figure11.

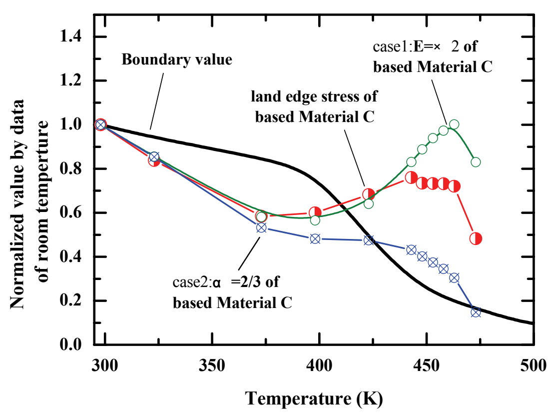


Figure 11 - Temperature Dependence of Normalized Land Edge Stress for Modified Laminate Material C

Fig 11 indicates that case 1 results in a 30 % higher stress and case 2 results in a 60 % lower stress than the original base material C in the high temperature range. Increase of filler content in the matrix resin will increase the modulus a little but decrease the CTE more, resulting in an improvement in land-lifting performance. Higher Tg will increase the modulus and decrease the CTE. However, higher Tg is especially effective in increasing the peel strength and suppressing land lifting.

The newly developed materials B and C have one-third lower CTE at higher temperatures and a 20-30 Cº higher Tg than the conventional FR-4. Experiments and analytical study by FEM demonstrated that these materials will be effective in suppressing land lifting.

Conclusion

The conclusions of this study are the following:

1. Newly developed, higher filler content laminate materials were shown to have an improved ability to suppress land lifting relative to conventional FR-4.
2. New Sn-Ag-Cu-Ni-Ge (SACNG) solder was shown to have an improved ability to suppress land lifting relative to conventional SAC (Sn3.0Ag0.5Cu) solder.
3. Laminate material having a lower CTE and a higher Tg was shown to have an improved suppressive ability against

land lifting. The former is effective in lowering land edge stress while the latter provides an improvement in peel strength.

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