High Reliability Lead-free Solder SN100C（Sn-0.7Cu-0.05Ni＋Ge）

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Introduction

While the situation varies from country to country, nearly one year after the EU RoHS Directive came into force implementation of lead-free solder is progressing steadily. For lead-free soldering to be considered successful it is not sufficient just to have dealt with the challenges of mass production. It is also necessary to establish that the soldered joints produced are at least as reliable as those made with Sn-37Pb alloy. In this context “reliability” means the length of time in service that the initial functionality of the joint can be maintained. In this paper we will discuss some of the issues involved in solder joint reliability through a comparison of the properties of two alloys that are widely used for lead-free wave soldering, SAC305 (Sn-3.0Ag-0.5Cu) and the Sn, Cu, Ni, Ge alloy SN100C.

Measuring the Reliability of Lead-Free Solder

1. Development of Shrinkage Cavities into Crack

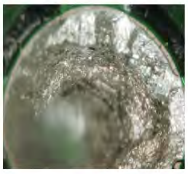
Solder Alloy	As Soldered	After 1000 cycles (-40/+125℃ 30 mins dwells)
SN100C		
Sn-3.0Ag -0.5Cu		

Figure1 Examples of shrinkage effects

Shrinkage cavities develop into a crack.

Figure 1 shows SN100C and SAC305 joints in the as soldered condition (right) and after 1000 thermal cycles (-40/+125°C, 30 minute dwells).

In the case of the SN100C, because it solidifies nearly isothermally as a eutectic at 227°C there is no shrinkage cavities and the surface is smooth and bright After thermal cycling the surface of the SN100C is disturbed by slip bands but there is no evidence of cracking. By contrast shrinkage cavities are apparent in the as-soldered SAC305 and after thermal cycling cracks have developed from these cavities. Here we will explain the mechanism of shrinkage occurrence (Figure 2).

The way in which shrinkage cavities form can be explained by reference to Figure 2. Solidification begins with the growth of primary tin dendrites in areas where the temperature of the molten solder has fallen below the liquidus (2). These tin dendrites continue to grow (3) until the remaining liquid starts to freeze as a eutectic, shrinking away from the network for dendrites to leave cavities (4). As the now solid solder cools it continues to contract further opening up the shrinkage cavities ⑸

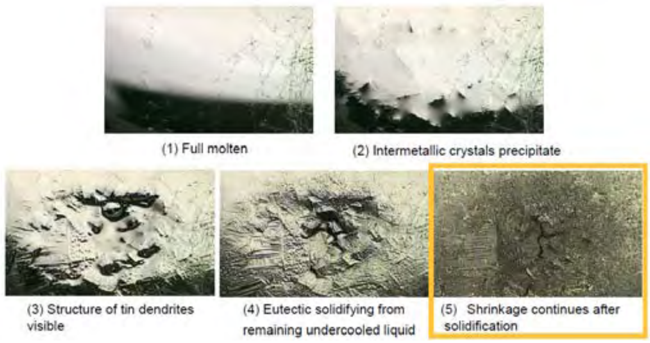


Figure 2 Mechanism of Shrinkage Occurrence

As a measure to reduce shrinkage occurrence, you can improve by shortening solidification time but caution is required because there is a concern that reliability lowered by the accumulation of strain on components at the time of solder solidification.

In addition, it is important to refine intermetalic and solidify at a stretch by selecting an eutectic solder whose solidus and liquidus temperature is same in order to reduce shrinkage. Since SN100C is nearly eutectic almost no shrinkage occurs.

2. Long Service Life under Conditions of Cyclic Strain

Good elongation

	Tensile Strength (MPa)	Elongation (%)	Time to creep strength fracture (Load 1kg) 145℃, 150℃, 180℃
SN100C Sn-0.7Cu-0.05Ni+Ge	32	48	300hrs.< , 300hrs.< , 300hrs.<
Sn-3.0Ag-0.5Cu	50	32	300hrs.< , 300hrs.< , 300hrs.< (Sn-3.8Ag-1.0Cu)
Sn-37Pb	44	25	14hrs. , 3hrs. , 7min.

Tensile Test 10mm/min. 25℃

Figure 3 Comparison of elongation of each solder

In Figure 3 the tensile strength, elongation and creep strength are plotted.

More stress is imposed on components when soldering with lead-free solders than with Sn-37Pb because their higher melting point requires that the joints are formed at higher temperatures. And any stress in Sn-37Pb joints tends to be relieved by flow of the solder itself. Because of their higher yield point the residual stress is not so easily relieved in lead-free solder joints. Therefore if the stress imposed on boards and components is to be minimized ductility is a more important property in a solder than strength.

Since SAC305, which has a high silver content has a high yield point any stress that builds up on components as the assembly cools remains unreleased. We can see from Figure 3 that the elongation of SAC305 at 32% is lower than the 48% value for SN100C. To confirm the effect of this lower ductility we subjected a test piece to cyclic strain until fracture occurred.

Test conditions:

1. Solder alloy

- SN100C
- Sn-3.0Ag-0.5Cu
- Sn-37Pb

2. Manufacture of the test piece

Cut solder bar into 7x20x50mm pieces to ensure equal volumes for each alloy, melt at 400°C and pour into a mould with cavity dimensions 160mm long, 12mm wide and 10mm deep

3. Tensile tester set up and test method (see Figure 4).

Clamp the test piece in the tester with a distance of 60mm between chucks.

Strain rate: 20mm/minute
Strain: ±5mm
Measure the peak load in the tensile part of each cycle until fracture occurs.

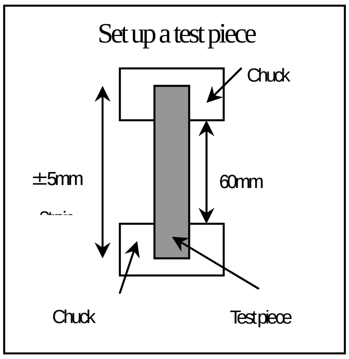


Figure 4 Set up a test piece

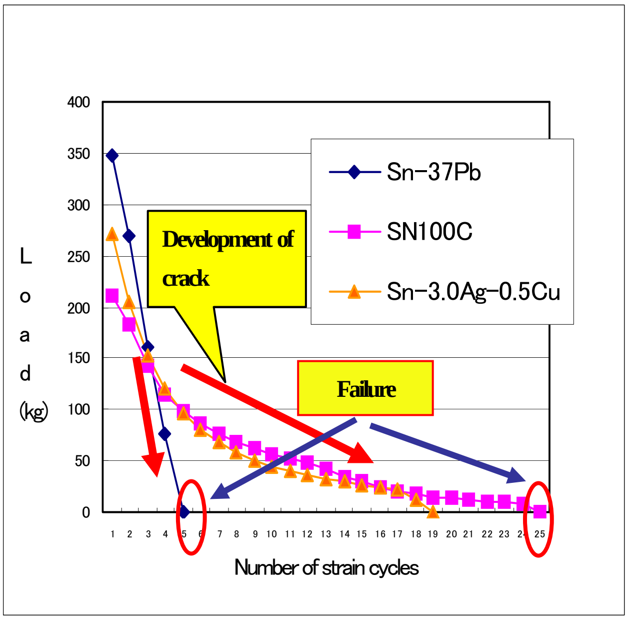


Figure 5 Peak stress at point of strain reversal

Figure 5 shows the peak stress at each cycle with the number of cycles to failure noted. The load required to achieve the specified strain decreases with each cycle because of the reduction in the effective test piece cross-section due to necking and crack propagation.

Alloy	Load required for first tensile strain (Kg)	Cycles to failure (Numbers)
SN100C	212	25
Sn-3.0Ag-0.5Cu	272	19
Sn-37Pb	347	5

Figure 6 test result cycles to failure

As shown in Figure 6, the ranking of the alloys on the

basis of the peak load required to achieve the initial 5mm deformation was, in ascending order:
SN100C (212kg)<Sn-3.0Ag-0.5Cu (272kg) Sn-37Pb (347kg). By contrast the ranking of the alloys in terms of the number of cycles to failure was, in ascending order, Sn-37Pb(5 cycles)<Sn-3.0Ag-0.5Cu (17 cycles) <SN100C(25 cycles). Although requiring a lower load to achieve the initial 5mm strain the SN100C has a greater capacity for accommodating cyclic strain than Sn-37Pb or Sn-3.0Ag-0.5Cu. SN100C survives five times as many strain cycles as Sn-37Pb before failure.

3. Excellent Resistance to Thermal Fatigue

Figure 7. Cross-sections showing incidence of cracking in surface mount components

Figure 7 shows the changes that occur in SN100C, Sn-3.0Ag-0.5Cu joints as a result of thermal cycling carried out under the following conditions.

Thermal Cycling Test Conditions:
-45°C 15 minute dwell/+125°C 25 minute dwell.

Board: FR-4, Immersion tin finish

Cracks appeared in the Sn-3.8Ag-0.7Cu joints after 2000 cycles with complete failure after 4000 cycles. No major cracks appeared in Sn-0.7Cu until 3000 cycles and until 4000 cycles for SN100C. The conclusion is that SN100C has excellent resistance to thermal fatigue.

4. Excellent Resistance to Impact

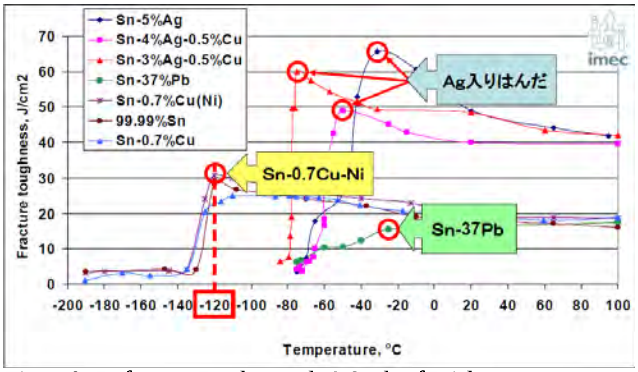


Figure 8 Reference: Ratchev et al., A Study of Brittle to Ductile Transition Temperatures in Bulk Pb-Free Solders, EMPC 2005 (IMAPs-Europe) June 12-15, Brugge, Belgium.

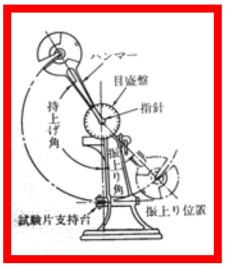
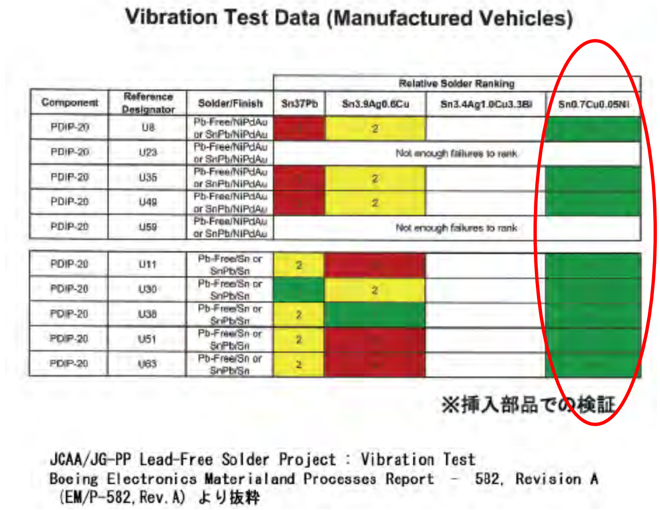


Figure 9 The hummer used for Sharpy impact test

The results of Charpy impact tests conducted by a Belgian research laboratory are shown in Figure 8. In the Charpy impact test the energy per unit of cross-sectional area required for a swinging hammer (Figure 9) to fracture a test piece is used as a measure of the property of fracture toughness. In general the smaller the impact energy the more brittle is the alloy. The results indicate that SN100C has excellent resistance to impact at temperatures as low as -120°C.

5. Excellent Resistance to Vibration

We have reported the excellent resistance of SN100C to thermal cycling and high impact strength. We will now report the results of vibration testing.



Vibration Test Data (Manufactured Vehicles)

Component	Reference Designator	Solder/Finish	Relative Solder Ranking: Sn37Pb	Sn3.9Ag0.6Cu	Sn3.4Ag1.0Cu3.3Bi	Sn0.7Cu0.05Ni
PDIP-20	U8	Pb-Free/NiPdAu or SnPb/NiPdAu		2		
PDIP-20	U23	Pb-Free/NiPdAu or SnPb/NiPdAu	Not enough failures to rank			
PDIP-20	U35	Pb-Free/NiPdAu or SnPb/NiPdAu		2		
PDIP-20	U49	Pb-Free/NiPdAu or SnPb/NiPdAu		2		
PDIP-20	U59	Pb-Free/NiPdAu or SnPb/NiPdAu	Not enough failures to rank			
PDIP-20	U11	Pb-Free/Sn or SnPb/Sn	2			
PDIP-20	U30	Pb-Free/Sn or SnPb/Sn		2		
PDIP-20	U38	Pb-Free/Sn or SnPb/Sn	2			
PDIP-20	U51	Pb-Free/Sn or SnPb/Sn	2			
PDIP-20	U63	Pb-Free/Sn or SnPb/Sn	2			

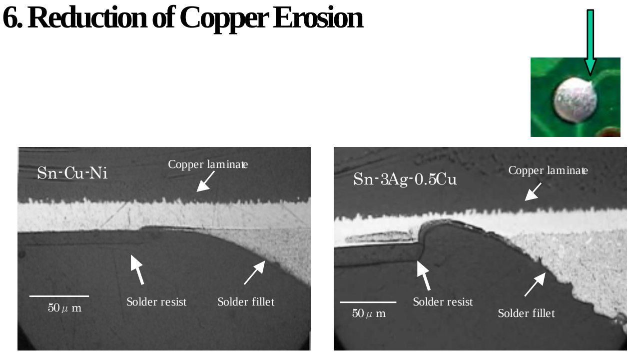
※挿入部品での検証

JCAA/JG-PP Lead-Free Solder Project : Vibration Test
Boeing Electronics Materialand Processes Report － 582, Revision A
(EM/P-582, Rev. A) より抜粋

Figure 10 JCAA/JG-PP vibration test result

Figure 10 shows the results of testing done as part of a project on lead-free solders carried out by the US Military's Joint Group on Pollution Prevention (JG-PP). According to the Joint Test Report SN100C outranks Sn-3.9Ag-0.6Cu and Sn-37Pb in vibration testing of wave soldered through-hole components. It is expected that on the basis of this performance SN100C will be selected for use in conditions of severe stress.

6. Reduction of Copper Erosion



SN100C　　Sn-3.0Ag-0.5Cu

Figure 11. Copper erosion in single-sided board

Figure 11 shows the results of a copper erosion study carried out on single-sided boards. It can be seen that the copper of the trace connecting to the land has been almost completely eroded. The effect of the solder wave is apparent in that area. SN100C erodes copper more slowly than Sn-3.0Ag-0.5Cu.

Further tests were conducted on 1.6mm thick double-sided FR-4 boards with an OSP finish..

1. Immerse the board in a rosin-based flux for 5 seconds.
2. Solder alloys: SN100C, Sn-3.0Ag-0.5Cu
3. Solder temperature: 250°C, 260°C
4. Height of solder wave above nozzle 5mm
5. Immersion depth: 2mm
6. Immersion time: 10 seconds, 20 seconds

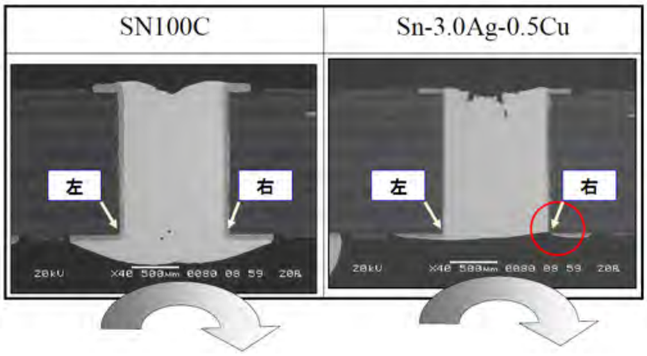


Figure 12 Erosion of the shoulder of a plated through hole on double sided board

スルーホールコーナー残部の厚み

厚みの平均(初期値)≒41. 22μm

温度	浸漬時間	残部の厚み平均(%) SN100C 左側	SN100C 右側	Sn-3.0Ag-0.5Cu 左側	Sn-3.0Ag-0.5Cu 右側
250° C	10 秒	93.47	98.59	91.53	42.46
	20 秒	87.05	86.56	77.66	3.06
260° C	10 秒	89.23	84.21	92.38	21.81
	20 秒	75.86	81.61	62.45	0

Figure 13 Thickness of remaining copper pad at the shoulder of a plated through hole

The arrow in Figure 12 indicates the direction of solder flow. Since it was found that there is a difference in the extent of erosion between the right and left sides the thickness of the remaining copper was measured separately on each side. The results are plotted in Figure 13.

Erosion by the Sn-3.0Ag-0.5Cu is substantial and increases with immersion time. After 20 seconds the copper on the right side of the hole exposed to Sn-3.0Ag-0.5Cu has eroded completely while for the hole exposed to SN100C for the same time 81.6% of the original thickness of copper remains in that location. It is clear that SN100C erodes copper more slowly even at high temperature.

７． Formation of Stable Intermetallic

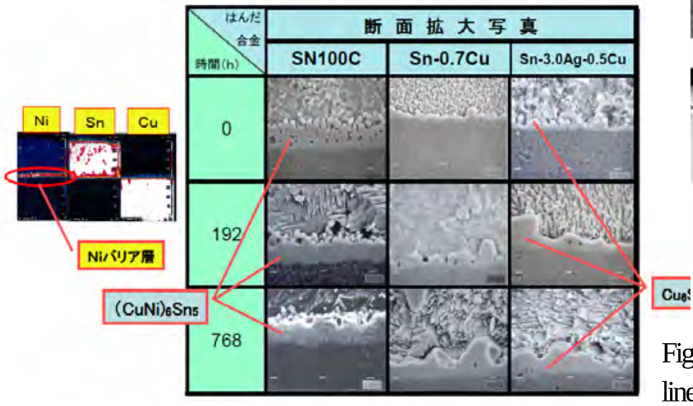


Figure14 Magnified cross section（Aging test at the high temperature）

Figure 14 shows the changes that occur in the intermetallic compound layer formed at the interface between a copper substrate and Sn-0.7Cu and Sn-3.0Ag-0.5Cu as a function of time at 120°C.

The Ni in the SN100C stabilizes the intermetallic so that it does not grow even during extended storage at high temperature (768 hours at 120°C). By contrast there is substantial growth in the intermetallic in the Sn-3.0Ag-0.5Cu alloy.

Although the intermetallic layer initially formed in the Sn-0.7Cu and the Sn-3.0Ag-0.5Cu is thinner than that formed in the SN100C, after long term aging at 120°C it has grown to a thickness greater than that of the SN100C. A thick layer of brittle interfacial intermetallic provides an easy pathway for crack propagation so that the reliability of the solder joint is compromised.

The trace addition of Ni in the SN100C incorporates in the interfacial intermetallic stabilizing it against further growth.

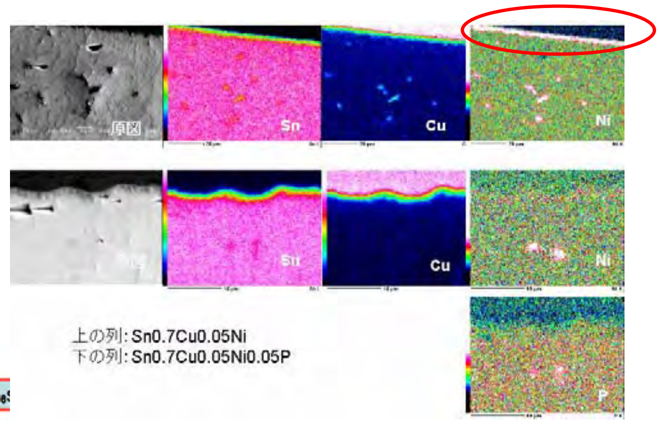


Figure15 SEM mapping (Upper line: Sn0.7Cu0.05Ni, Lower line: Sn0.7Cu0.05Ni0.05P)

The element mapping of solder joint cross-sections in Figure 15 is shows where the Sn, Cu and Ni are concentrated. When P is added to the solder as an antioxidant the Ni is dispersed throughout the joint rather than concentrating in the interfacial intermetallic so the benefit of its stabilizing effect on intermetallic growth is not obtained.

Summary

Since SN100C behaves almost perfectly as a eutectic it is possible to achieve smooth bright fillets free of shrinkage defects.

The high melting point and high creep resistance of lead-free solders means that large strain is imposed on solder joints as the result of the repeated expansion and contraction that occurs during thermal cycling. The result can be cracking of chip components and separation of the land from the laminate. To avoid overstressing of the components and the printed circuit board it is important to choose an alloy with the ductility to accommodate this strain. Although the strength of solders that contain silver, the most common of which is Sn-3.0Ag-0.5Cu, is high their low ductility means that they are not able to accommodate strain. By contract that high ductility of SN100C means that it can accommodate substantial strain without embrittlement and cracking and that is apparent in the results of the cyclic strain test, thermal cycling test, impact test and vibration test. A further advantage of SN100C is that slower growth of interfacial intermetallic during ageing. The consequence of all of these advantages is the high reliability of joints made with SN100C.