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DEVELOPMENT OF LEAD-FREE ALLOYS WITH ULTRA-HIGH THERMO-MECHANICAL RELIABILITY

Pritha Choudhury, Ph.D., Morgana Ribas, Ph.D., Ranjit Pandher, Ph.D., Anil Kumar, Sutapa Mukherjee,
Siuli Sarkar, Ph.D., Bawa Singh, Ph.D.
Alpha, an Alent plc Company
South Plainfield, NJ, USA
ssarkar@alent.com

ABSTRACT

Several new applications requiring solder materials that would perform for extended periods under harsh operating conditions have recently emerged. Clearly there is a need for a ROHS compliant solder with thermal and mechanical reliability better than Sn-Ag3-Cu0.5/ Sn-Ag4-Cu0.5 but with a similar melting range so that it can be a drop in replacement for these solders. In the work shown here, Alpha focused on improving the mechanical properties of the bulk solder as well a controlled growth of interfacial IMCs and alloy microstructure. Major composition additions do impact the melting behavior and the bulk mechanical properties. Minor alloy additions can also alter the diffusion kinetics and have significant impact on the long term reliability. Tensile tests and high temperature creep tests were used for initial screening of the alloys and understanding the potential impact of each addition on the reliability of the solder in final application. In this paper, a detailed study of the effect of small composition changes (major additions) and of micro additions is presented. Improvements in thermal, mechanical and metallurgical properties of the new alloys are discussed and compared to Sn-Ag3-Cu0.5. We show that the newly developed Pb-free solder alloy Maxrel Plus performs better than Sn-Ag3-Cu0.5 in high strain rate tests such as drop shock and vibration tests as well as in thermal fatigue tests.

Key words: Lead-free solder, ultra-high reliability, drop shock, thermal cycling, vibration test

INTRODUCTION

Tin-Silver-Copper alloys became the most popular solders when the electronics industry transitioned from Sn-Pb to lead-free solders [1-4]. Among all Sn-Ag-Cu alloys Sn-Ag3-Cu0.5 (SAC305) and Sn-Ag4-Cu0.5 (SAC405) were commonly used initially. As technology developed, low Ag SAC alloys became more popular as they were better suited for portable electronics because of their better resistance to drop shock as compared to SAC305/SAC405 [5-7]. However, these low-silver SAC alloys did not have as good thermal fatigue life as SAC305/405. So there was a need for solder materials with good drop shock performance as well as good thermal fatigue life.

In addition to that, in some fields, such as automotive, high power electronics and energy, including LED lighting, it is desirable for solder alloys to operate at higher temperatures, for example 150°C or higher. The SAC305/SAC405 alloys do not perform well at such temperatures.

There are a number of requirements for an alloy to be used as a solder in processes such as alloy wave soldering, surface mount and ball grid arrays. First, the alloy must exhibit good wetting characteristics in relation to a variety of substrate materials, such as copper, nickel, nickel-gold, in order to form an adequate bonding. Such substrates may be coated to improve wetting, for example by using tin alloys, gold or organic coatings (OSP). Good wetting also enhances the ability of the molten solder to flow into a capillary gap, and to climb up the walls of a through-plated hole in a printed wiring board, to thereby achieve good hole filling.

Among other standard requirements for electronics packaging and assembly, are long-term stability. The solder joint mechanical properties should be stable over time. Solder alloys tend to dissolve the substrate to form an intermetallic compound at the interface with the substrate. For example, tin in the solder alloy may react with the substrate at the interface to form an intermetallic compound (IMC) layer. If the substrate is copper, then a layer of Cu_6Sn_5 may be formed. Such a layer typically has a thickness varying from a fraction of a micron to a few microns. At the interface between this layer and the copper substrate an IMC of Cu_3Sn may be present. The interfacial intermetallic layers will tend to grow during aging, particularly where the service is at higher temperatures, and the thicker intermetallic layers, together with any voids that may have developed may further contribute to premature fracture of a stressed joint. So, it is very important to have a controlled intermetallics growth.

Solder joint reliability is another important factor. It can be indicated by shear strength, drop shock, creep resistance, thermal fatigue resistance and vibration resistance. The presence of intermetallics in the alloy itself results in improved mechanical properties, which can be achieved through solid solution, precipitate strengthening and grain refinement mechanisms. In addition to that, diffusion modifiers, i.e. alloying elements added with the purpose of modifying the diffusion at the interfacial intermetallics can also be used to design a more reliable alloy. One typical example is SACX Plus alloy (Sn-0.3Ag-0.7Cu-0.1Bi-Y1-Y2), a low-silver Pb-free solder that contains proprietary micro additives to improve soldering and mechanical properties. Apart from lower Ag content, the SACX Plus alloy uses diffusion modifiers to obtain a superior drop shock performance [7].

In this work we show the effect of major and minor alloying additions on alloy properties. Tensile tests and high temperature creep tests were used for initial screening of the alloys and understanding the potential impact of each addition on the reliability of the solder in final application. Improvements in thermal, mechanical and metallurgical properties of the new alloys are discussed as compared to Sn-Ag3-Cu0.5. In particular, results of drop shock, thermal cycling and vibration tests will be discussed.

EXPERIMENTAL DETAILS

Test Vehicles

The test vehicles used in this study were reflowed in a seven zone heater reflow machine (Ominiflo7); soaked at 150-200°C for 115sec, with 240-245°C peak temperature and 60sec TAL.

Two test vehicles were used in the study shown here. For the vibration test, various chip resistors (0402, 0603, 1206), QFP208 and BGAs were mounted on a calibrated CERF board (Figure 1). Test vehicle used in the drop shock and thermal cycling tests follows the JEDEC recommendation. A 77 x 132 mm Cu-OSP finished PCB with non-solder mask defined 0.225 mm pads was used (Figure 2). Each testing board can accommodate up to 15 CTBGA84, which are individually monitored for electrical discontinuities. These CTBGAs have Ni-Au finish and were assembled using SAC305 and Maxrel Plus 12 mil spheres.

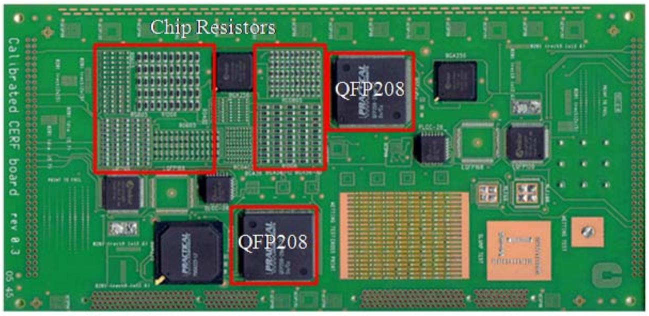
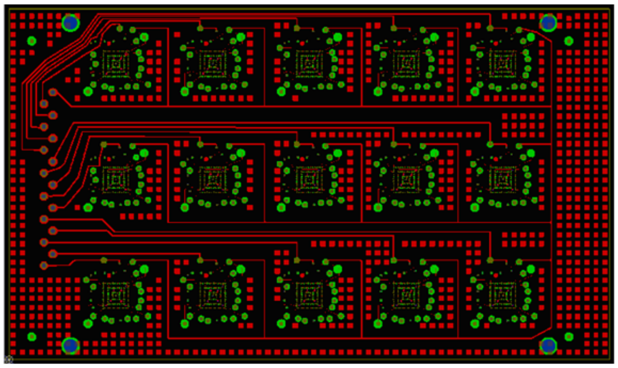


Figure 1. CERF test vehicle used in vibration test

Drop Shock & Thermal Cycling Test Vehicle



Board:
Surface finish: Cu OSP
NSMD
No. of components/board: 15
Component:
CTBGA 84 of each alloy
Pad size: 0.225mm
Surface finish: NiAu

Figure 2. Drop shock and thermal cycling test vehicle

Drop Shock Test

The JESD22-B111 standard is a usual choice for testing board level drop resistance of handheld devices, especially during development of new alloys. Other drop tests used in the electronics industry require full assembly of a device and are generally used only at final development stages.

A Lansmont M23 shock machine, shown in Figure 3 (left), is used for performing the drop tests of our customized test vehicle. By adjusting the drop height and the strike surface it is possible to achieve JEDEC's recommended service condition B (1500Gs, 0.5 msec duration and half-sine pulse), which is monitored as shown in Figure 3 (right).

The electrical continuity of each component is monitored during each drop using an Analysis Tech STD event detector. Each of the BGA84 assembled in the drop shock test vehicle was tested till failure (electrical resistance discontinuity greater than 1000 Ω lasting more than 1 µsec). The BGA failures were recorded once a first discontinuity is followed by three others within five subsequent drops. Weibull curves are built for evaluating the probability distribution of the failures over a period of time.

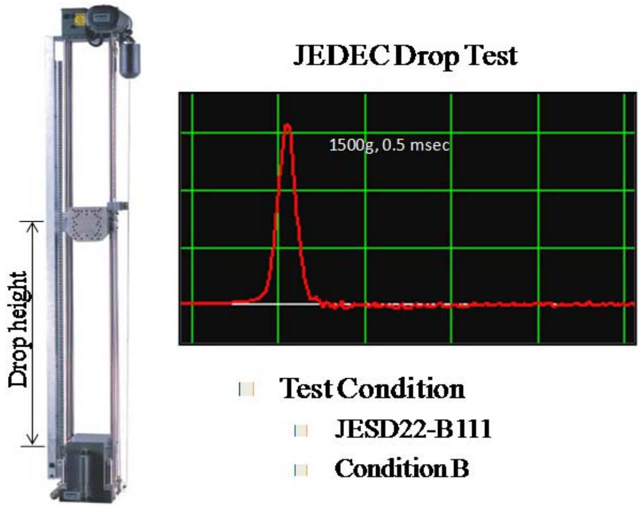


Figure 3. Lansmont drop shock testing machine (left) and half-sine shock pulse curve corresponding to JEDEC service condition B (right)

Thermal Cycling Test

Thermal cycling tests were carried out in an air to air Espec chamber (model TSA-101S) at -40°C (30min) ↔ 150°C (30min) for 2,000 thermal cycles. The test vehicles were electrically monitored for discontinuities/increase in contact resistance using an Agilent data logger (model 34980A) as described in the IPC 9701 standard. In addition to that, the effect of thermal cycling on solder joints of the new alloys was evaluated by removing CERF boards from the chamber at 500 and 1000 cycles for vibration test. A scanning electron microscope (SEM) was used to analyze solder joint microstructure features on chip resistors (0402, 0603, 1206) and QFP208.

Vibration Test

For the evaluation of resistance of the solder joints to vibration, CERF test vehicles were placed in a vibration shaker. The vibration shaker used has capacity of 1000 kgf and movements in x, y and z axis (Figure 5). A specially designed fixture was affixed on the vibration shaker and four test vehicles were tested at a time.

The test vehicles were tested as per the IEC 60068-2-64 standard, conforming to the automobile category 2 (i.e., engine compartment; attached to body or on the radiator). A detailed description of the test conditions used is shown in Table 1. The total vibration test duration is 24 hrs, 8 hrs in each axis.

Test vehicles were evaluated as soldered, and after 500 and 1000 thermal cycles. After completion of the test, chip resistors (0402, 0603, 1206) and QFP208 were evaluated for any damage, deformation and cracks through visual inspection and SEM analysis.

Equipment

- Espec thermal cycling chamber (Air-Air) TSA-101S
- Agilent 34980A datalogger

Test Conditions

- IPC 9701-A standard
- -40°C ↔ +150°C (30 min dwell time)

Figure 4. Equipment and test conditions used in thermal cycling test

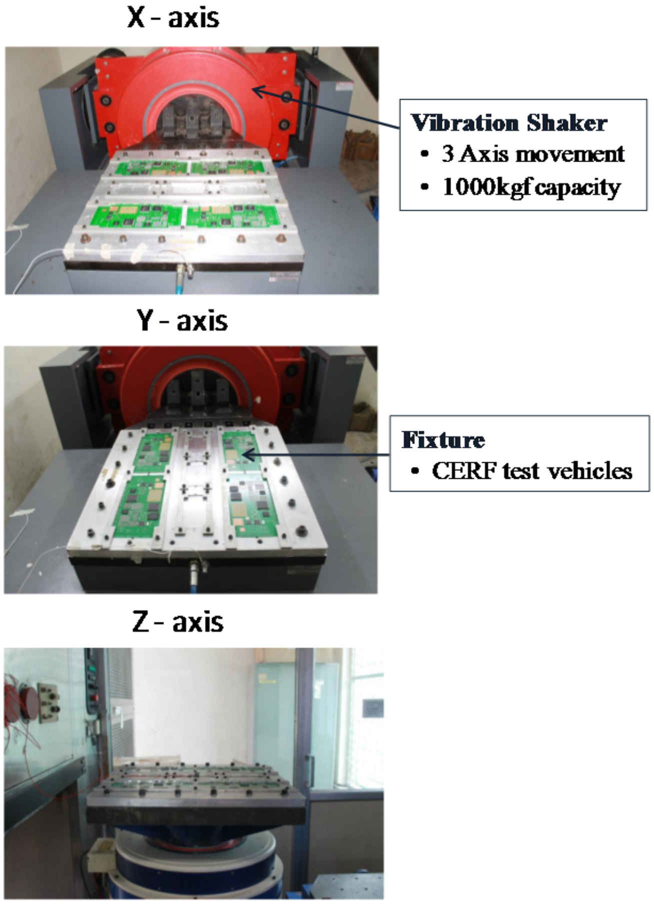


Figure 5. Vibration shaker used for the vibration test with three axis movement

Table 1. Vibration test conditions as per IEC 60068-2-64 standard

Frequency Range			5 Hz to 200 Hz		
X axis		**Y axis**		**Z axis**	
Frequency (Hz)	**PSD (g2/Hz)**	**Frequency (Hz)**	**PSD (g2/Hz)**	**Frequency (Hz)**	**PSD (g2/Hz)**
5	0.01500	5	0.01500	5	0.004
10	0.00900	10	0.01900	10	0.004
20	0.00900	15	0.01900	15	0.04
200	0.00070	200	0.00150	200	0.001
Grms = 0.6952		**Grms = 0.9503**		**Grms = 1.1223**	
Test Duration			8 hrs each axis		
Ambient Temperature			24.1°C		

RESULTS AND DISCUSSION

A summary of some key physical properties of the alloys evaluated here is shown in Table 2, but for a complete discussion of this data please refer [8].

Maxrel Plus (Sn-3.8Ag-0.8Cu-3Bi-X1-X2) is a lead-free, antimony-free solder alloy that contains multiple additives in order to achieve ultra-high thermo-mechanical reliability. It is a drop in replacement for common Pb-free solders because its melting temperature of this alloy is similar to SAC305/405. This new alloy has lower solidus and liquidus temperatures than SAC305, which permits lower soldering temperatures. However, its differentiation from SAC305 is really visible in its mechanical properties. Maxrel Plus has almost twice the hardness of SAC305, but its Young's modulus, and consequentially its stiffness, is similar to SAC305. The ultimate tensile strength (UTS) is a good indication of how solid solution, precipitate strengthening and grain refinement mechanisms act reinforcing the new alloy. At room temperature Maxrel Plus UTS is 70% higher than SAC305. High temperature (150°C) UTS of Maxrel Plus is also 42% higher than SAC305.

Table 2. Physical properties of the alloys

Property	**SAC305**	**Maxrel Plus**
Solidus Temperature (°C)	217.3	210.9
Liquidus Temperature (°C)	221.2	215.9
Vickers Hardness (HV-1)	15	28
Young's Modulus (GPa)	49.9	49.7
Poisson's Ratio	0.36	0.36
UTS 25°C (MPa)	48.7	83.0
UTS 150°C (MPa)	15.7	22.3

Creep properties at high temperature give a very good indication of the thermal cycling performance of an alloy. This is particular important during alloy development since thermal cycling testing takes time and requires resources such as the powder of these experimental alloys. Maxrel Plus and SAC305 were tested at 150°C, under constant load of 200N and the results are shown in Figure 6. Creep strength is evaluated by measuring the total time taken for the rupture of the sample, whereas the creep elongation is given by the creep strain. The results show that Maxrel Plus creep strength and creep elongation are 140% higher and 200% higher, respectively, than SAC305.

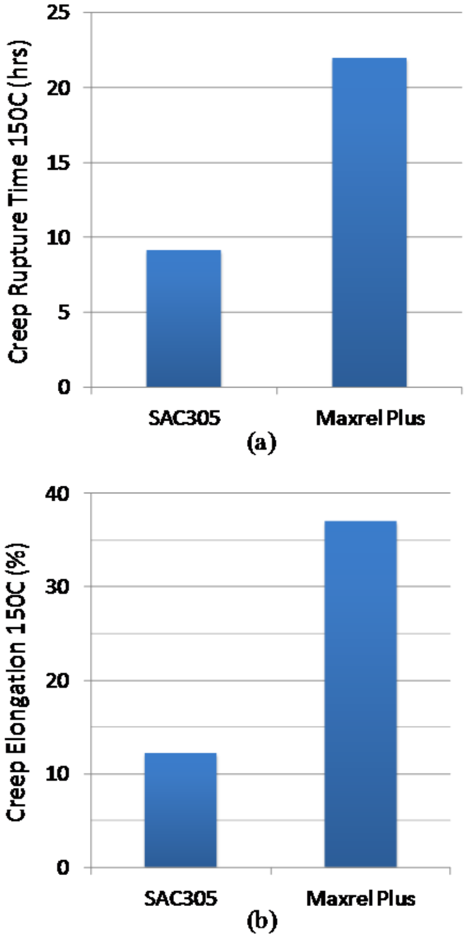


Figure 6. High temperature creep properties of the alloys

Drop Shock Performance

Conventionally, high Ag SAC alloys are known to have very good thermal reliability, but poor mechanical reliability. Their poor performance in tests such as drop shock is generally attributed to the brittleness of the interfacial IMC present on the solder joints of alloys such as SAC305/SAC405 [9]. Low Ag SAC alloys work towards minimizing this drawback by controlling interfacial IMC formation [10-12].

The drop shock results are shown in Figure 7. The drop shock characteristic life (63% failures) of Maxrel Plus alloy is about 44% higher than SAC305. These results demonstrate that mechanical reliability performance can be independent from Ag content by engineering Maxrel Plus alloy strength and interfacial IMC.

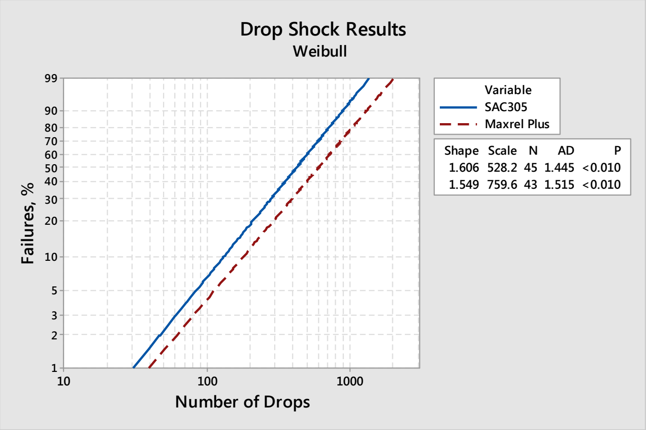


Figure 7. Weibull distribution of drop shock results

Thermal Cycling Results

Thermal cycling results were summarized at 250, 750, 1500 and 2000 thermal cycles, as shown in Table 3. As the thermal profile used is quite harsh, from -40°C to +150°C with 30 min dwell times, the initial failure in SAC305 was seen within the first 250 thermal cycles. The initial failure in Maxrel Plus was observed between 250 and 750 thermal cycles. However, as these test vehicles are assembled under experimental conditions, such early failures before 1000 cycles may be just outliers. At 1500 thermal cycles, 49% of SAC305 had failed, whereas only 31% of Maxrel Plus had failed. At the end of the thermal cycling test, at 2000 thermal cycles, 100% of SAC305 had failed, whereas only 60% of Maxrel Plus had failed.

As 40% of the components assembled using Maxrel Plus survived the test, data was censored at 2000 cycles in order to plot the Weibull distribution curves (Figure 8). The thermal cycling characteristic life of Maxrel Plus is 28% higher than SAC305. In addition to that, crack initiation (onset) in the CTBGA84 components using Maxrel Plus alloy started at 1000 cycles, whereas for SAC305 it started at 500 cycles (images not shown here). As one more evidence of Maxrel Plus superior solder joint strength, shear force after 2000 cycles is 97% higher than SAC305.

Table 3. Thermal cycling results

% Failures	SAC305	Maxrel Plus
0 – 250 Cycles	2	0
0 – 750 Cycles	4	2
0 – 1500 Cycles	49	31
0 – 2000 Cycles	100	60

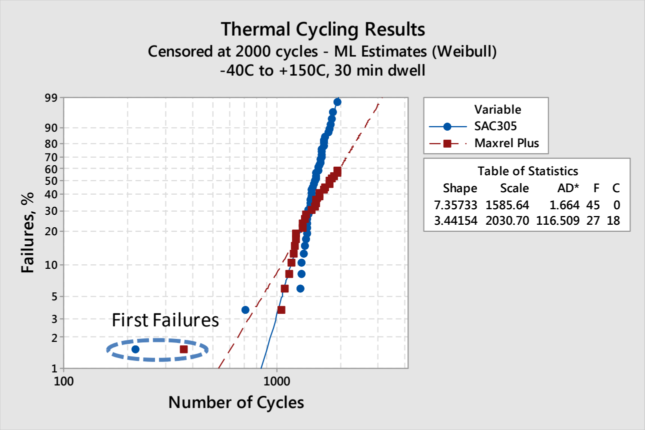


Figure 8. Thermal Cycling Weibull distribution

Vibration Test Results

After the vibration tests, we observed that the leads of the QFP208 were damaged, so they were not considered in the evaluation of the alloys. Upon visual inspection of the chip resistors, cracks were observed only on the test vehicles that were subjected to thermal cycling test. Figure 9 shows SEM images of 1206 chip resistors cross-sections after vibration test.

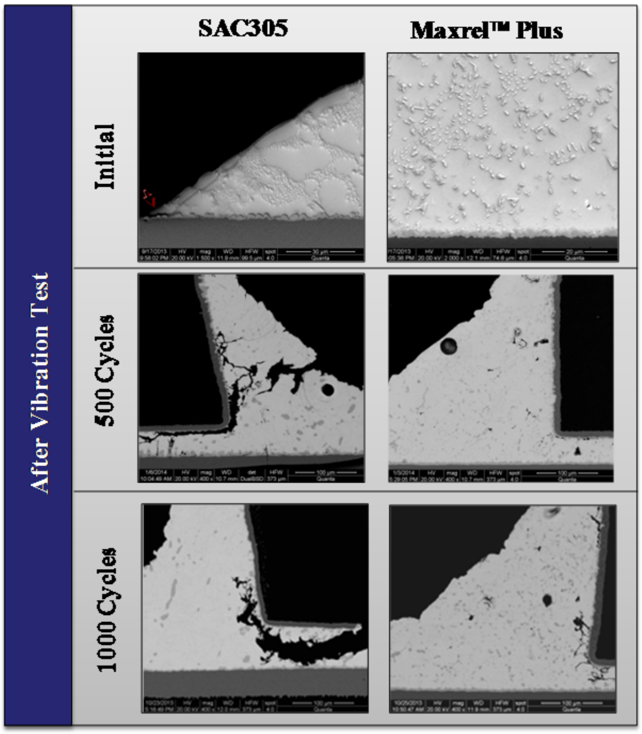


Figure 9. Cross-sections after thermal cycling and vibration test

The cross-section images indicate that the solder joint of both alloys resisted quite well to the stress generated during the vibration test. No cracks were observed on Maxrel Plus, whereas small cracks on the interfacial IMC were observed for SAC305. However, after 500 thermal cycles the solder joints using SAC305 were found to be severely damaged, whereas no cracks were observed in Maxrel Plus. At 1000 thermal cycles, larger cracks were observed in SAC305 and smaller cracks in Maxrel Plus.

CONCLUSIONS

A new Pb-free solder alloy has been developed which performs better than industry standard Pb-fee solder SAC305 in high strain rate tests such as drop shock and vibration tests as well as in thermal fatigue tests. A large number of alloys were designed, prepared and tested. To screen the alloys, basic mechanical properties of the bulk alloy have been measured and used to predict its performance in the final real life application. Final selected candidate alloy, Maxrel Plus, has been extensively tested side by side with SAC305. Maxrel Plus performs better than SAC305 in drop shock, vibration and thermal cycling tests.

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