

A COLLABORATIVE INDUSTRIAL CONSORTIA PROGRAM FOR CHARACTERIZING THERMAL FATIGUE RELIABILITY OF THIRD GENERATION PB-FREE ALLOYS

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ABSTRACT

Development of the first generation of current commercial Pb-free solder alloys was based on, high Ag content, near-eutectic Sn-Ag-Cu (SAC) compositions. Subsequently, second generation, lower Ag alloys were developed to address the shortcomings of near-eutectic SAC, particularly poor mechanical shock performance. The development of third generation Pb-free solder alloys is proceeding along two prominent paths. In one case, high-Ag content alloys are being modified with various major alloying additions to improve thermal fatigue performance in aggressive use environments and increase resistance to damage from high strain rate mechanical loading. In the other case, alloys with Ag content lower than SAC305 are being developed to address needs for better drop/shock resistance, lower processing (melting) temperature, and lower cost. This paper describes the planning and progress of an experimental program for evaluating the thermal fatigue performance of a number of third generation alternative Pb-free solder alloys. The program is being developed and executed through a collaboration of several major industrial consortia that includes membership from high reliability end

users, solder suppliers, and electronic contract manufacturers.

Key words: Lead-free alloys, alternative alloys, low and high silver alloys, third generation Pb-free alloys, microalloying, thermal fatigue reliability

INTRODUCTION

In the decade since the implementation of the RoHS Directive [1], there have been a number of significant innovations in Pb-free solder alloy formulations. Alloy development continues to be driven primarily by experience gathered through volume manufacturing and increased deployment of a variety of Pb-free products of increasing complexity. This experience has resulted in an increased number of Pb-free solder alloy choices beyond the first generation near-eutectic Sn-Ag-Cu (SAC) alloys that were established initially as replacements for eutectic SnPb [2]. Second generation, lower Ag alloys have been developed and introduced to address the shortcomings of the first generation near-eutectic SAC, such as poor mechanical shock performance, higher cost, and a variety of technical

and logistical risks. Third generation commercial alloys are emerging as additional alternatives as Pb-free manufacturing becomes pervasive, designs continue to evolve in complexity, and operating environments become increasingly more aggressive.

Thermal fatigue requirements always have been a priority for the products of many high reliability end users [3]. Solder joints age and degrade during service and eventually fail by the common wear out mechanism of thermally activated solder fatigue (creep fatigue) [4]. Solder fatigue is the major wear-out failure mode and major source of failure for surface mount (SMT) components in electronic assemblies [5].

Since 2008, the Pb-Free Alloy Alternatives Characterization Program sponsored by the International Electronics Manufacturing Initiative (iNEMI) has been working to fill the gap in knowledge associated with thermal fatigue resistance of first and second generation, Sn-based, Pb free solder alloys [2, 3, 6-19]. With the emergence of third generation Pb-free solder alloys, high reliability end users have recognized the need to characterize and understand the long-term attachment performance of solder joints made with these Pb-free solders.

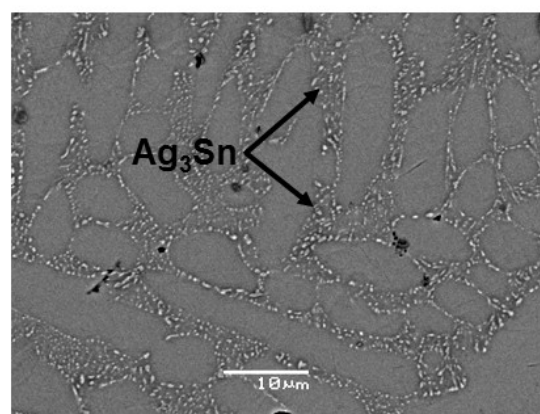
The current program uses the basic approach of the previous iNEMI Alloy study to enable development of similar data for third generation Pb-free solders. The Alloy evaluation team, which already includes participation from the CALCE (Center for Advanced Life Cycle Engineering), and AREA (Universal Advanced Research in Electronic Assembly) consortia, has been expanded through a collaboration with another major industrial consortia, the High Density Package User Group (HDPUG). These consortia collectively are supported by members from high reliability telecom, automotive, avionics, and military/defense end users, solder suppliers, and electronic contract manufacturers. This paper describes the planning and progress of the collaborative experimental program for evaluating the thermal fatigue performance of a number of third generation alternative Pb-free solder alloys.

THIRD GENERATION PB-FREE SOLDER ALLOYS

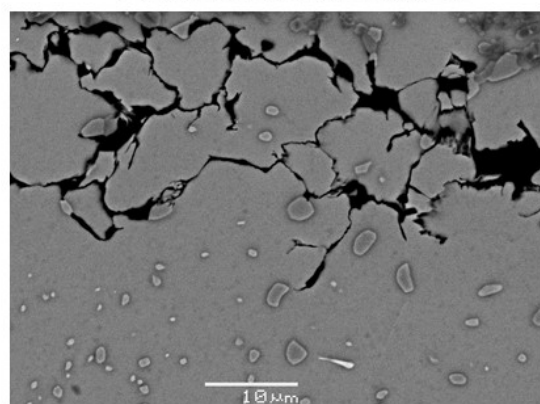
The genesis for development of third generation Pb-free solders has been the increased reliability requirements resulting from the dramatic increase in electronic content in automobiles. Many automotive control modules, sensors, and components are mounted in areas that experience high operating temperatures, and rapid thermal and power cycling, in combination with vibration and shock.

Although SAC alloys have better fatigue life than eutectic SnPb solder, their reliability is limited at higher operating temperatures [20]. During solidification of SAC solders, the Ag and Sn react to form networks of Ag_3Sn precipitates at the primary Sn dendrite boundaries [21, 22]. These intermetallic precipitates are recognized as the primary strengthening mechanism in SAC solders [21-25]. During

thermal or power cycling and extended high temperature exposure, the Ag_3Sn precipitates coarsen and become less effective in inhibiting dislocation movement and slowing damage accumulation. This pattern of microstructural evolution is characteristic of the thermal fatigue failure process in these Sn-based Pb-free alloys and was described originally in detail by Dunford et al more than a decade ago [26]. Figure 1 shows scanning electron micrographs illustrating coarsening of the Ag_3Sn precipitates in SAC305 solder caused by thermal cycling.



SAC305 as solidified



SAC305 after thermal cycling

Figure 1. Scanning electron micrographs illustrating Ag_3Sn intermetallic precipitate coarsening due to thermal cycling.

In response to the need for higher temperature performance and a lack of a suitable commercial Pb-free solder alloy formulation, a working group of solder suppliers, end users, and academic researchers was formed to develop an alloy solution [27, 28]. The outcome of the work of this group was the initial third generation, commercial Pb-free alloy identified as Innolot or 90iSC [e.g., 29]. The Innolot alloy is based on the ternary SAC387 formulation, but contains significant alloying additions of bismuth (Bi) and antimony (Sb), along with a microalloy addition of nickel (Ni).

The introduction of solute atoms into solid solution of a solvent-atom lattice invariably produces an alloy that is stronger than the pure metal [30]. Figure 2 shows a simplified schematic illustration of substitutional solid

solution strengthening. Dislocation movement or deformation is inhibited by distortion in the β -Sn lattice caused by solute atoms such as Bi incorporated into the Sn lattice. The development of Innolot provides some evidence that substitutional solid solution strengthening can improve resistance to creep and fatigue at higher temperatures in Sn-based, Pb-free solders. The working hypothesis is that solid solution strengthening not only supplements the Ag_3Sn precipitate hardening found in SAC solders, but continues to be effective once precipitate coarsening reduces the effectiveness of the intermetallic Ag_3Sn precipitates [31].

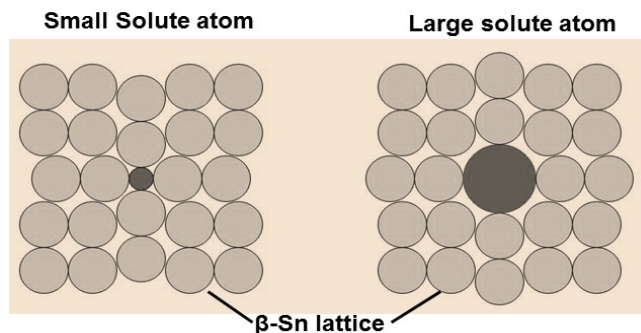


Figure 2. A simple schematic illustrating lattice distortion due to substitutional solute atoms.

Consistent with the Innolot approach, the elements proposed most commonly for solid solution strengthening in Sn-based, third generation solders are Bi and Sb. The element indium (In) also is used but to a lesser extent, due to its high cost. Bi and In, when used as a major alloying elements, also reduce the melting point of most solder alloy formulations, while the addition of Sb tends to increase the melting point [27]. These modified SAC alloys are off-eutectic compositions and are characterized by non-equilibrium solidification and often significant melting ranges [32-34].

Although a number of third generation Pb-free solders now are being commercialized, the concept of using major element alloying to improve mechanical properties or to alter melting behavior is far from novel. Formulations incorporating Bi, Sb, and In into basic Sn-Ag or Sn-Ag-Cu eutectics were studied by the NCMS consortium of industrial partners in 1997 [32] and the properties were documented by NIST and the Colorado School of Mines beginning in 2002 [33]. At the time the NCMS study was conducted, it was considered comprehensive, but the thermal fatigue aspect of the work ultimately was limited because the study predated the widespread introduction of area array technology. A more recent, updated discussion of the effects of alloying on solidification, melting behavior, and properties can be found in reference [34].

For the purposes of this study, third generation Pb-free solder alloys are grouped into two general categories based on targeted performance requirements and Ag content. In both cases, significant modifications to SAC alloy

properties are achieved through both major and micro alloying additions. In one case, the common high-Ag SAC formulations are being modified with various combinations of major and microalloy additions to enhance thermal fatigue performance under conditions of elevated temperature exposure and severe thermal cycling. An additional goal is to increase resistance to damage from high strain rate mechanical loading, while maintaining superior resistance to thermal fatigue damage. These alloys often are referred to as high reliability solders because they are targeted for applications with aggressive or harsh use environments. In the second case, lower-Ag SAC formulations (Ag content less than 3%) are being modified with major and micro alloying additions, but here the objective is to provide better drop/shock resistance, lower processing (melting) temperature, and lower cost, while maintaining acceptable fatigue reliability [20].

The alloys included currently in this investigation are listed in Table 1. The test matrix is dominated by higher-Ag, high reliability alloys, but also contains several lower-Ag alloys. SAC305 and SAC105 are included as baseline alloys. The table shows that Bi is the alloying element with the strongest level of interest, which is consistent with the attention given to Bi in the Pb-free alloy literature [e.g., 20, 27, 31, 35-41].

Table 1. Nominal solder compositions and estimated melting ranges for the alloys included in the study.

Alloy	Nominal Composition (wt. %)							Melting Range, °C
	Sn	Ag	Cu	Bi	Sb	In	other	
SAC305	96.5	3.0	0.5					217-221
Innolot	91.3	3.5	0.7	3.0	1.5		0.12 Ni	206-218
HT	95.0	2.5	0.5			2.0	Nd	206-218
MaxRel Plus	91.9	4.0	0.6	3.5				212-220
M794	89.7	3.4	0.7	3.2	3.0		Ni	210-221
M758	93.2	3.0	0.8	3.0			Ni	205-215
SB6NX	89.2	3.5	0.8	0.5		6.0		202-206
Violet	91.25	2.25	0.5	6.0				205-215
Indalloy 272	90.0	3.8	1.2	1.5	3.5			216-226
Indalloy 276	89.3	3.8	0.9		5.5	0.5		221-228
Indalloy 277	89.5	3.8	0.7		3.5	2.5		214-223
LF-C2	92.5	3.5	1.0	3.0				208-213
SN100CV	97.8		0.7	1.5			0.05Ni	221-225
405Y	95.5	4.0	0.5				0.05 Ni; Zn	217-221
SAC105	98.5	1.0	0.5					215-227
SACm	99.0	0.5	1.0				50 ppm Mn	217-227
SAC1205+Ni	98.3	1.2	0.5				Ni	218-227

The Pb-Free Alloy Characterization team has developed an experimental program to provide the industry with an initial assessment of the thermal fatigue performance of multiple third generation commercial Pb-free alloys. The test matrix includes high and low Ag alloys developed to satisfy a number of design targets such as improving high temperature fatigue resistance, and addressing needs for better drop/shock resistance, lower processing (melting) temperature, and lower cost.

The thermal fatigue test plan incorporates a number of thermal cycling profiles used by high reliability end users in telecom, military/defense, and avionics markets. The program is being developed and executed through a collaboration of several major industrial consortia that includes membership from high reliability end users, as well as solder suppliers, and electronic contract manufacturers.

TEST VEHICLE

Component and Test Board Description

This study utilizes the components and printed circuit board (PCB) developed as the test vehicle for the second generation iNEMI Alloy Alternatives study [2]. The two daisy-chained ball grid arrays (BGA), a 192 I/O chip array BGA (192CABGA) and an 84 I/O thin core chip array (84CTBGA) are shown in Figure 3 [42]. The parts were purchased as land-grid arrays (LGA) to enable subsequent attachments of the various Pb-free-alloy balls included in the scope of the program (Table 1).

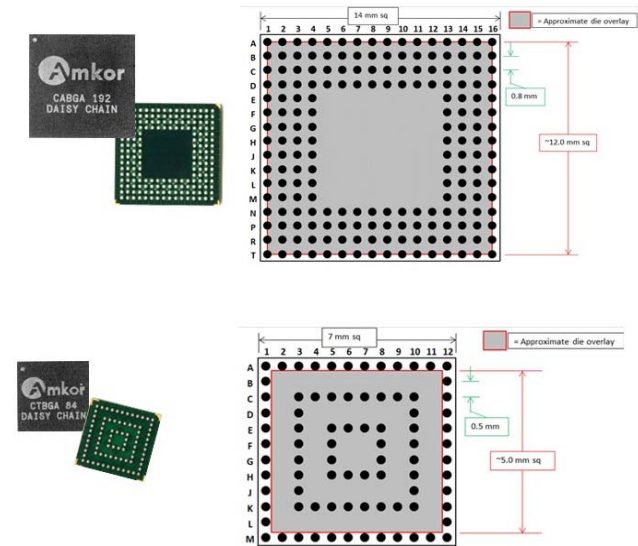
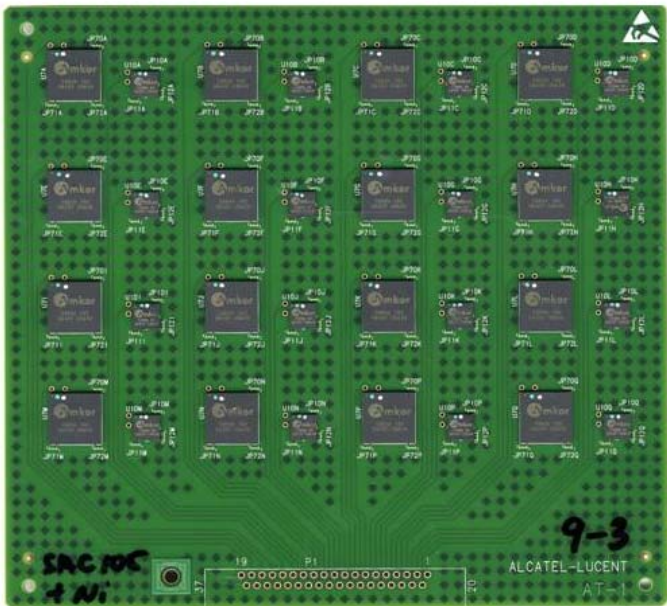


Figure 3. The 192CABGA and 84CTBGA daisy chained components and pin diagrams with die size and location.

The printed circuit board (PCB) test vehicle is 2.36 mm (93 mils) thick, with a 6 layer construction with 16 sites for the larger 192CABGA, and another 16 sites for the 84CTBGA (Figure 4). The attributes of the components and PCB are provided in Table 2. Boards have been fabricated with two different high temperature PCB laminate materials, Panasonic R-1755V and Hitachi MCL-E-679FG, and two different surface finishes, Entek HT organic solderability preservative (OSP) and electroless Ni/immersion Au (ENIG).



The CTE of the PCB was measured using a thermomechanical analyzer (TMA) and the composite coefficients of thermal expansion of the BGA packages were measured using microscopic Moiré interferometry. The data in Table 3a show a lower composite CTE for the 192CABGA package. The lower CTE of the 192CABGA results in a larger CTE mismatch with the PCB, hence the thermal cycling lifetime of the 192CABGA is shorter than that of the 84CTBGA [6]. The CTE data for the two PCB laminate materials are shown in Table 3b.

Table 3a. CTE of the BGA component test vehicles measured by microscopic Moiré interferometry.

BGA Package	Effective CTE α (ppm/°C)	
	T °C:24~130	
	x-direction	y-direction
192CABGA	8.6	10.1
84CTBGA	10.9	11

Table 3b. CTE of the PCB laminate materials measured with the TMA.

PCB Laminate	Effective CTE α (ppm/°C)	
	T °C:20~140	
	x-direction	y-direction
Panasonic R-1755V	13.5	16.1
Hitachi MCL-E-679FG	14.2	13.4

Component Ball Attachment Process

The parts were purchased as land-grid arrays (LGA) to enable subsequent attachments of the various Pb-free-alloy balls included in the scope of the program (Table 1). The ball attachment process was performed by Micros Components (<http://www.micros.com>) using the same process developed for the previous, second generation iNEMI Alloy project. The key process steps in the ball attachment process are illustrated in Figure 5 with further details available in a previous publication [2].

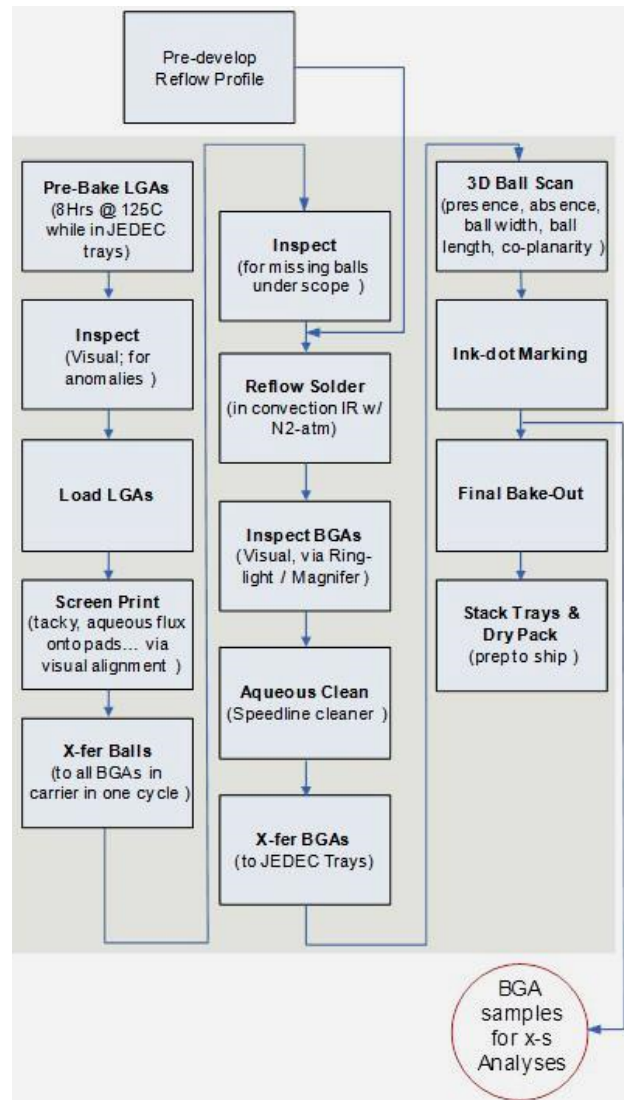


Figure 5. Flow chart illustrating the ball attachment process used to manufacture the ball grid array components.

Test Vehicle Surface Mount Assembly

The solder assembly of the test vehicles will be performed at Rockwell Collins, Cedar Rapids, IA. A pilot build using SAC305 components and paste has been performed to establish the stencil printing and reflow process parameters. A 5-mil thick stencil was used with 14 mil diameter round apertures for the larger 192CABGA and 12 mil x 12 mil square apertures for the smaller 84CTBGA. The test vehicles were reflowed in a 14 temperature zone convection oven in a nitrogen atmosphere. Type 4 no-clean solder paste will be used for all of the final assemblies. For almost all the solder compositions, the nominal peak temperature measured on the board adjacent to the solder joints will be 240 °C. The only exceptions will be the Violet and LF-C2 alloys that are designed to enable a lower reflow profile. Those two alloys will be reflowed at a peak temperature of 223 °C.

Accelerated Temperature Cycling

Accelerated temperature cycling (ATC) is the recognized technique for evaluating the thermal fatigue performance of solder attachments. The IPC-9701A document that provides guidance for assessing reliability of surface mount attachments was developed initially for SnPb solder and modified later for Sn-based Pb free solders [45].

The daisy-chained components and the test circuit boards enabled electrical continuity testing after surface mount assembly and in situ, continuous monitoring during thermal cycling. Thermal cycling was done in accordance with the IPC-9701A guideline and further, specific experimental details are provided in a previous publication [2]. The solder joints were monitored using either an event detector or a data logger set at a resistance limit of 1000 ohms, also described previously [2]. The failure data are reported as characteristic life η (the number of cycles to achieve 63.2% failure) and slope β from a two-parameter Weibull analysis.

The temperature cycling profiles for this investigation are shown in Table 4. These profiles were selected to address the requirements of four specific industries or market segments. Three of the profiles are defined in IPC-9701A with telecom represented by TC1, consumer/handheld by TC3, and military/defense by TC4. The most aggressive profile designated "auto" is included to address requirements for severe under the hood automotive applications.

Table 4. Thermal Cycling Profiles

Thermal Cycle	Minimum Temp.	Maximum Temp. (°C)	Temp. Range ΔT	Dwell Time (min.)
TC1	0	100	100	10
TC3	-40	125	165	10
TC4	-55	125	180	10
Auto	-40	150	190	10

PCB Screening Test

The -40/150 °C thermal cycling profile is extremely aggressive due to the combined effects of the upper and lower temperature extremes and the ΔT of 190 °C. Because of concerns with PCB integrity, thermal screening tests are being conducted on bare circuit boards prior to including this thermal cycling profile in the test matrix.

The screening test plan includes four test boards of each laminate type that are being cycled from -40/150°C in a dual zone thermal shock chamber with 15 minute dwells at each temperature extreme. The test duration is 1000 cycles with one board being removed every 250 cycles for analysis. The change in the coefficient of thermal expansion (CTE) is measured using a thermomechanical analyzer (TMA), and the change in modulus is measured using dynamic mechanical analysis (DMA). Preliminary results indicate that CTE and modulus are not affected adversely by cycling in the thermal shock chamber. Metallographic cross sectional analysis is planned to determine if PCB

delamination occurs during testing. The complete results of the PCB screening test will be reported in future publications.

Experimental Test Matrix

The basic test cells for the alloy and thermal cycling experimental test matrix are shown in Table 4. Each test cell contains two fully populated test boards to provide a sample size of 32 BGA components of each type for thermal cycling and an additional partially populated test board for baseline quality and microstructural characterization. Note that the test matrix in Table 5 is not populated completely. Test cells were populated based on team member interest in specific alloys and thermal cycling profiles. Resource limitations also factored into the decisions.

Table 5. Accelerated Temperature Cycling Test Matrix showing the number of populated test boards for each cell.

Alloy	Thermal Cycling Profiles/Number of Test Boards				
	0/100 °C OSP	-40/125 °C OSP	-55/125 °C OSP	-55/125 °C ENIG	-40/150 °C OSP
SAC305	2	2	2	2	2
Innotot	2	2	2	2	2
HT	2	2	2	2	2
MaxRel Plus	2	2	2	2	2
794	2	2	2	0	2
758	2	2	2	0	2
SB6NX	2	2	2	2	2
Violet	2	2	2	2	2
Indalloy 272	2	2	2	0	2
Indalloy 276	2	2	2	2	2
Indalloy 277	2	2	2	2	2
LF-C2	2		2		
SN100CV	2		2		
405Y	2	2	2	2	2
SAC105	2	2	0	0	0
SACm	2	2	0	0	0
SAC1205+Ni	2	2	0	0	0

Alloy Compositions, Microstructural Characterization, and Failure Analysis

The actual compositions for all solder ball alloys is being measured by inductively-coupled plasma (ICP) spectroscopy. Results from that analysis will be provided in future publications.

A baseline characterization will be performed on representative board level assemblies from each of the component and alloy test cells. The purpose of the baselines is to document the solder joint quality and solder microstructure before temperature cycling to enable comparisons to samples removed from the temperature cycling chambers for failure analysis. Microstructural characterization and failure analysis will be done using optical metallography (destructive cross-sectional analysis), polarized light microscopy (PLM), and scanning electron microscopy (SEM). Using methods developed previously, the SEM operating in the backscattered electron imaging (BEI) mode has been effective for differentiating phases in the SAC microstructures [6- 12, 14-16]. Low magnification optical microscopy generally is adequate for confirming the basic solder joint quality thermal fatigue failure mode.

STATUS

The status of critical project items at the time of this writing is as follows:

- The solder ball attachment has been completed on all of the components required to populate the thermal cycling and baseline test matrix.
- The stencil printing process and surface mount reflow profile were developed using SAC305 components and solder paste during a pilot build conducted at Rockwell Collins. Multiple stencils have been ordered to facilitate the assembly of the complete test matrix.
- All but one of the solder pastes have been delivered to Rockwell Collins and are in refrigerated storage.
- The surface mount assembly of the test boards is anticipated to begin in early September 2016 depending on the delivery of the complete sets of components and solder pastes to Rockwell Collins.
- Thermal cycling will be performed at four participant sites: CALCE (-40/125 °C), i3 (-40/150 °C), Nokia Bell Labs (0/100 °C), and Rockwell Collins (-55/125 °C).

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