Pb-Free Solders and Aerospace/Defense (A&D) High Performance Considerations

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ABSTRACT

The Aerospace & Defense (A & D) industries maintain a high level of interest in the expansive amount of work performed in developing and qualifying Pb-free solder alloys. The three main areas of interest continue to be thermal cycle, mechanical shock, and vibration. The past twenty years have seen an unprecedented increase in alloy development such that the concepts of "generations of solders and "families of solders" have been coined to help manage the numerous individual alloys on the market today. This paper will discuss work done with Pb-free solder alloys, many with the addition of constituents focusing on varying property enhancements. The purpose is to provide a "snap shot" summary of progress to date and relate perspectives both as advantages and concerns solely in a constructive manner to aid researchers in planning their next steps in development and qualification of these alloys.

INTRODUCTION

The European Union RoHS (Restriction on the use of hazardous substances) Directive was the driving force in the electronics industry for the conversion from manufacturing with eutectic tin-lead (63Sn37Pb) solder to manufacturing with Pb-free solder [1]. The initial implementation for the high volume, consumer electronics market was mandated in 2006. As the high-volume market segments transitioned to Pb-free manufacturing, high reliability electronic equipment suppliers continued to manufacture and support tin-lead (SnPb) electronic products by using the European Union Pb-in-solder exemption. In parallel, considerable research was being conducted to evaluate the quality and reliability of Pb-free electronic assemblies. As exemptions neared expiration, high reliability manufacturers in telecom, medical, and automotive markets developed the confidence to convert many of their products successfully to Pb-free manufacturing. However, the aerospace & defense (A & D) industries that have characteristically stricter mission critical reliability requirements, continue to widely use SnPb solder manufacturing processes.

The A & D industries recognized the worldwide supply chain implications imposed by implementation of the RoHS Directive. They have been engaged in a joint endeavor to survey all technological aspects of Pb-free solder manufacturing in anticipation of a measured and systematic conversion to Pb-free manufacturing. The overall objective is to develop strategies for reliability risk assessments and supply base challenges specific to the industries' rigorous requirements and unique environmental service and storage conditions. Most of these conditions and requirements consist of various combinations of thermal cycling, thermal shock, vibration, and high strain rate mechanical shock.

These efforts have resulted in a technology assessment and gap analysis of the most widely used Pb-free materials to enable development of strategies and tools needed for risk mitigation. A considerable amount of supporting information can be found in the open literature on identification of the risks, potential failures and shortfalls if the risks are realized. Many of the technical papers, handbooks, standards, and specifications that are referenced in this paper can be used as comprehensive guidance and recommendations to mitigate these risks [2-5].

Designs continue to evolve in complexity which increases reliability risks in aggressive A & D operating environments. The technology assessment cites solder joint fatigue as an important and increasing area of risk. Thermal fatigue requirements always have been a priority for the products of many high reliability end users [6]. Pb-free solder alloy development is continuing to evolve to address the changing requirements. The so-called third generation family of commercial solder alloys has emerged mostly driven by the dramatic increase in electronic content in automobiles [6-9]. The goal of these solders is to provide alternatives to the ubiquitous second generation SnAgCu (SAC) alloys such as SAC305. While many of these new alloys are known to have exceptional performance in thermal cycling, very little is known about their performance in thermal shock, vibration, and mechanical shock. None of these Pb-free alloys, including SAC305, have been proven to satisfy all the complex A & D requirements. Furthermore, with the number of high-performance Pb-free alloy offerings continuing to increase, assessing and managing their performance is a challenge.

The purpose of this paper is to summarize the current status of alloy development and performance in relation to A & D requirements. Advantages and concerns are discussed to aid researchers in planning next steps in development and qualification of these alloys in high-performance products and systems.

If the scope of this discussion is limited to the Defense "subset" of A & D products, the four major performance/ service conditions are thermal cycle, thermal shock, vibration, and mechanical shock. Most real-life applications consist of varied combinations of these conditions, e.g combined thermal shock/vibration in a jet aircraft, combined thermal shock/vibration/mechanical shock in a rocket, combined vibration/mechanical shock in a HMMWV (High Mobility Multi-purpose Wheeled Vehicle), etc. Specific requirements for these individual conditions originate from multiple sources: military, federal, and industry specifications/standards.

The following sections provide information to help the reader understand the challenges of implementing Pb-free technology into high performance electronics. First to be discussed is the three current categories or generations of Sn-based Pb-free solders. This will also include an extended discussion on the effects of various alloying elements and high-performance reliability test results. In the next section, a summary of high-performance test data is presented to comparing the new alloys with benchmarks. In the third section, the sources of the stringent defense service conditions are presented along with comparisons of solder alloys against the defense requirements. A final section will combine all information and provide a summary of concerns as well as potential advantages to these solder alloys.

EVOLUTION OF PB-FREE SOLDER ALLOYS

Since the implementation of the RoHS Directive in 2006 [1], there have been significant commercial Pb-free solder alloy developments. Alloys have evolved predominantly through experience gathered in volume manufacturing and the deployment of a variety of Pb-free products of increasing complexity. This has resulted in an increased number of Pb-free solder alloy offerings in addition to the first generation, high Ag content, near-eutectic Sn-Ag-Cu (SAC) alloys that replaced the eutectic SnPb solder alloy [10]. Second generation, lower Ag alloys were developed and introduced to address the shortcomings of first-generation SAC alloys, such as poor mechanical shock performance, higher cost, and other technical risks. Third generation, high-performance commercial alloys are emerging as Pb-free manufacturing becomes pervasive, designs continue to evolve in complexity, and operating environments become increasingly more aggressive [11].

Thermal fatigue requirements are a priority for the products of many high reliability end users [12]. Solder joints age and degrade during service and eventually fail by the well-known wear out mechanism of thermally activated solder fatigue (creep fatigue) [13]. Solder fatigue is recognized as the major wear-out failure mode and major source of failure for surface mount (SMT) components in electronic assemblies [14].

There are limited reliability test data in the literature for the family of third generation, high-reliability or high-performance solder alloys. A comprehensive study of the thermal fatigue performance of third generation solder alloys was initiated in 2015 by high reliability end users and solder suppliers from the International Electronics Manufacturing Initiative (iNEMI) consortium [3]. This group started working in 2008 to fill the gap in knowledge associated with thermal fatigue resistance of first and second generation, Sn-based, Pb free solder alloys [10, 12, 15-26]. The emergence of third generation Pb-free solder alloys provided the opportunity to apply the methods and experience from the earlier study to evaluate thermal fatigue performance of this new family of high-performance alloys. Findings from this current study began to emerge in 2018 [6, 7, 27, 28].

Alloy Development, Requirements, and Metallurgy

The Sn-based, SAC alloys are more resistant to thermal fatigue than the eutectic SnPb alloy, but they have reliability limitations at higher operating temperatures [29]. During solidification of SAC solders, the Ag and Sn react to form networks of Ag_3Sn precipitates at the primary Sn dendrite boundaries [30, 31]. These intermetallic precipitates are the primary strengthening mechanism in SAC solders [30-32]. During thermal or power cycling and extended high temperature exposure, the Ag3Sn precipitates coarsen and become less effective in inhibiting dislocation movement and slowing damage accumulation. Precipitate coarsening leads to local recrystallization, crack initiation, global recrystallization, and crack propagation. 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 in 2004 [33]. Figure 1 shows scanning electron micrographs illustrating coarsening of the Ag_3Sn precipitates in SAC305 solder caused by thermal cycling.

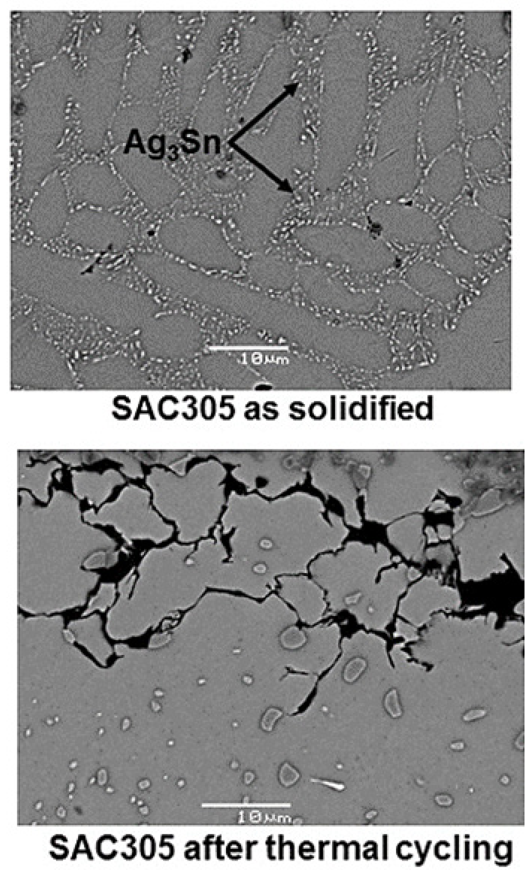


Figure 1: Scanning electron micrographs illustrating Ag_3Sn intermetallic precipitate coarsening that precedes recrystallization and crack propagation during thermal cycling of SAC305. [Copyright SMTA]

The motivation for development of third generation Pb-free solders is 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 [11]. SAC alloys cannot satisfy the reliability requirements for these use environments.

To address the requirement for higher temperature performance in a commercial Pb-free solder alloy formulation, a working group of solder suppliers, end users, and academic researchers was formed to develop an alloy solution [34, 35]. The output of this working group was the initial third generation, commercial Pb-free alloy identified as Innolot or 90iSC [36]. The Innolot alloy is based on the ternary SAC387 alloy but contains major alloying additions of bismuth (Bi) and antimony (Sb), along with a microalloy addition of nickel (Ni).

The need for solder alloys with better higher temperature performance alloys has resulted in the development of many new commercial Pb-free solder alloys. These alloys are based on the SAC system but have major and micro alloying alloy additions to promote better high temperature performance. Many higher temperature applications have requirements for increased resistance to damage from high strain rate mechanical loading, in addition to providing superior resistance to thermal fatigue damage. These alloys are referred to as high-performance solders because they are targeted for applications with aggressive or harsh use environments.

A partial list of high-performance alloys is provided in Table 1. Many of these alloys are included in the iNEMI consortia investigation [11]. That test matrix also contains SAC305 as the performance baseline alloy. The table shows that Bi is the alloying element used most pervasively, which is consistent with the attention given to Bi in the Pb-free alloy literature [29, 34, 37, 38-44]. The metallurgical fundamentals for alloying are discussed in the subsequent paragraphs.

Table 1: Nominal solder compositions for high-performance solder alloys.

Tradenames and Nominal Composition (wt. %) of High Reliability Solder Alloys

Alloy	Developer	Sn	Ag	Cu	Bi	Sb	In	other
405Y	Inventec	95.5	4.0	0.5				0.05 Ni; Zn
Cyclomax (SACQ)	Accurus	92.8	3.4	0.5	3.3			
Ecalloy	Accurus	97.3		0.7	2.0			0.05 Ni
HT1	Heraeus	95.0	2.5	0.5			2.0	Nd
Indalloy 272	Indium	90.0	3.8	1.2	1.5	3.5		
Indalloy 277	Indium	89.0	3.8	0.7	0.5	3.5	2.5	
Indalloy 279	Indium	89.3	3.8	0.9		5.5	0.5	
Innolot	Heraeus	91.3	3.8	0.7	3.0	1.5		0.12 Ni
LF-C2	Nihon	92.5	3.5	1.0	3.0			
M794	Senju	89.7	3.4	0.7	3.2	3.0		Ni
M758	Senju	93.2	3.0	0.8	3.0			Ni
MaxRel Plus	Alpha	91.9	4.0	0.6	3.5			
PS48BR*	Harima	Bal.	3.2	0.5	4.0	3.5		Ni, Co
REL22*	AIM	Bal.	3.0	0.7	3.0	0.6		0.05Ni; other
REL61*	AIM	Bal.	0.6	0.7	2.0			
SB6NX	Koki	89.2	3.5	0.8	0.5		6.0	
SN100CV	Nihon	97.8		0.7	1.5			0.05Ni
SN100CW1	Nihon	95.8		0.7	1.5	2.0		
Violet	Indium	91.25	2.25	0.5	6.0			
Viromet 347	Asahi	88.4	4.1	0.5			7.0	
Viromet 349	Asahi	91.4	4.1	0.5			4.0	

*Nominal values; actual composition proprietary

Metallurgical Considerations

The addition of Ag strengthens Sn and improves the creep resistance of the SAC solder by precipitation hardening (Figure 1). Other alloying elements improve the creep resistance of SAC solder by means of two other well-known metallurgical strengthening mechanisms, solid solution hardening and dispersion hardening. The introduction of solute atoms into solid solution of a solvent-atom lattice invariably produces an alloy that is stronger than the pure metal [45]. Figure 2 shows a simplified schematic of substitutional solid solution strengthening. Substitutional or interstitial solute atoms strain the lattice and dislocation movement, or deformation is inhibited by interaction between dislocations and solute atoms incorporated into the β-Sn lattice.

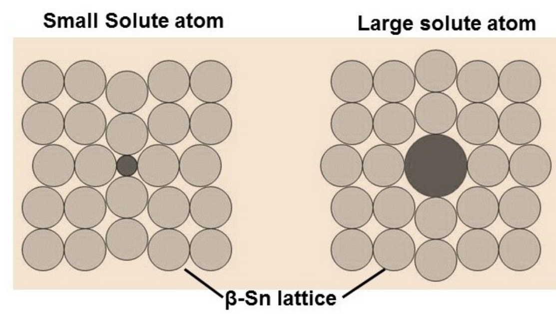


Figure 2: A simple schematic illustrating lattice distortion due to substitutional solute atoms. [Copyright SMTA]

If solute atoms precipitate from solution during thermal excursions in service, the solder alloy may strengthen by dispersion hardening. Dispersion strengthening occurs when insoluble particles are finely dispersed in a metal matrix. Typical dispersion strengthened alloys employ an insoluble, incoherent second phase that is thermally stable over a large temperature range (Figure 3) [46]. For Sn-based solder alloys, the strength could be derived from a combination of increased solid solution strengthening at higher temperatures due to increased solubility, and dispersion strengthening that would supplement the solid solution effect at lower temperatures where solubility has decreased.

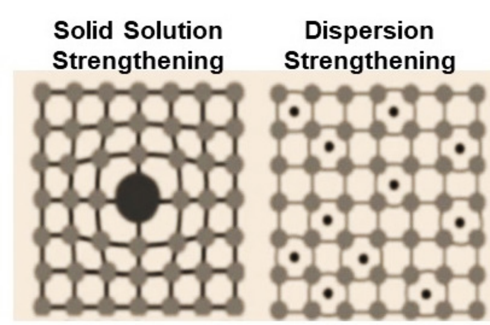


Figure 3: A simple schematic comparing solid solution (left) and dispersion strengthening (right). [Copyright SMTA]

The development of Innolot demonstrated that substitutional solid solution strengthening can further improve resistance to creep and fatigue at higher temperatures in Sn-based, Pb-free solders [34]. The hypothesis is that solid solution and dispersion strengthening not only supplement the Ag_3Sn precipitate hardening found in SAC solders but continue to be effective once precipitate coarsening reduces the effectiveness of the intermetallic Ag_3Sn precipitates [37].

The two elements used most often to improve high temperature properties in commercial, high-performance, Sn-based solders are Bi and Sb. The element Indium (In) is used to a lesser extent, in part due to its high cost. Bi and In, when used as major alloying elements, also reduce the melting point of most Sn-based solder alloys, while the addition of Sb tends to increase the melting point [33]. These additions result in modified SAC alloys with off-eutectic compositions, non-equilibrium solidification, and significant melting or pasty ranges [47-49].

Many third generation Pb-free solders are being commercialized, but the concept of using major element alloying to improve mechanical properties or to alter melting behavior is not 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 [47]. The National Institute of Standards and Technology (NIST) and the Colorado School of Mines began documenting the properties of those alloys in 2002 [48]. When the NCMS study was conducted, it was considered comprehensive, but the thermal fatigue segment of the work ultimately was limited because the work predated the development and widespread introduction of area array technology. A more recent, general discussion of the effects of alloying on solidification, melting behavior, and properties can be found in reference [49].

Antimony (Sb) Additions to Tin (Sn)

The binary Sn-Sb phase diagram in Figure 4 indicates solubility of Sb in Sn of approximately 0.5 wt. % at room temperature to 1.5 wt. % at 125 ºC [52, 53]. Thus, some contribution could be expected from solid solution strengthening of Sb dissolved in Sn-based Pb-free solders [34].

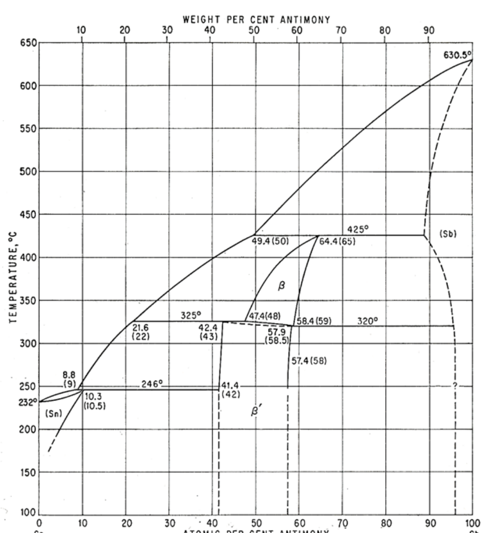


Figure 4: The Sn-Sb binary phase diagram. [Phase Diagram Credit: Max Hansen, Constitution of Binary Alloys]

Alloying with Sb may improve performance through other strengthening mechanisms. Studies by Li et al show that Sb slows the growth rate of Cu_6Sn_5 intermetallic compound (IMC) layers at attachment interfaces [52, 53]. Fast interfacial IMC growth on Cu surfaces tends to produce irregular and non-uniform IMC layers. This can lead to reduced mechanical reliability by inducing fractures at IMC interfaces or through the IMC in drop/shock loading [54].

Figure 4 also shows that Sb can form multiple different intermediate phases or IMCs with Sn (Sb_2Sn_3, SbSn, Sb_4Sn_3, Sb_5Sn_4, and $SbSn_2$) in the bulk solder [50]. Lu et al. [55] and El-Daly et al. [56] identified SbSn intermediate phase precipitates less than 5μm in size and distributed throughout the Sn dendrites. Beyer et al. show that Sn_5Sb and Sn_8Sb alloys have increased shear strength and ductility compared to conventional SAC solders and maintain their shear strength with good ductility after isothermal aging [57]. El-Daly suggests Sb also can improve creep performance and tensile strength [58]. He found SbSn precipitates within the Sn dendrites, unlike the well-known SAC Ag_3Sn mechanism, where the precipitates form at the Sn dendrite boundaries. El-Daly suggests the SbSn precipitates work to resist recrystallization by strengthening the Sn dendrites [59]. Recently Belyakov et al. have shown that SbSn forms within the Sn dendrites and at the Sn boundaries in a SAC-based alloy. They also found SbSn at recrystallized Sn boundaries after thermal cycling and assumed that the SbSn precipitates resist recrystallization by strengthening the Sn dendrites as well as strengthening the boundaries in the same manner as the Ag_3Sn precipitates [60, 61].

Indium (In) Additions to Tin (Sn)

The binary Sn-In phase diagram is shown in Figure 5. While there is some disagreement over the solid solubility of In in Sn, a reasonable estimate is ~7 wt. % at room temperature and as much as 12 wt. % at 125 ºC [50]. Because of its range of solubility in Sn, In has been explored as a solid solution strengthening agent in Sn-based Pb-free solders [62, 63]. The equilibrium diagram shows that In forms two intermediate phases (β and γ) of variable composition with Sn [50] but does not appear to form any true stoichiometric compounds with Sn.

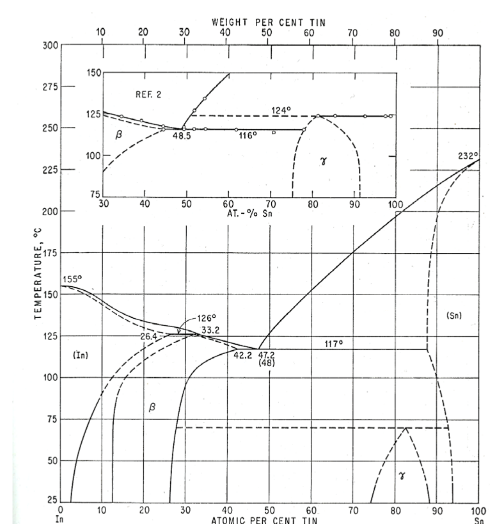


Figure 5: The In-Sn binary phase diagram. [Phase Diagram Credit: Max Hansen, Constitution of Binary Alloys]

Results from multiple solder alloy studies indicate that Indium (In) additions can improve drop and shock resistance by slowing the growth of interfacial IMC layers. Yu et al. report improved drop [64] and thermal shock [65] performance by adding as little as 0.4% In, and Amagai et al. report improved drop performance at or below 0.5 % In [66]. Hodúlová et al. show that In slows growth of Cu_3Sn and that a hybrid IMC phase $Cu_6(Sn, In)_5$ forms [67]. Sharif also observed the formation of the $Cu_6(Sn, In)_5$ IMC as well as formation of $(Cu, Ni)_3(Sn, In)_4$ on Ni substrates [68], and these IMCs also could be found in the bulk as well as the interfaces. In these hybrid IMCs, In substitutes for Sn which fundamentally is different than the common modified IMCs $(Cu, Ni)_6Sn_5$ or the $(Ni, Cu)_3Sn_4$ where Cu and Ni exchange.

Other reactions occur when In is added to SAC-based solders that complicate the ability to understand the influence of In content on reliability. Belyakov et al. reported ζ-Ag, Ag_9In_4, $AuIn_2$, γ-InSn and InSb in the bulk solder of ball grid array solder spheres and packages with Au final finishes. The spheres contained 6 wt. % In in the SAC-based alloy spheres [69] . In a study by Chantaramanee et al. additions of as little as 0.5% In or Sb in combination with In, was found to promote formation of $Ag_3(Sn,In)$ and SbSn [70]. They reported that small precipitates reduced the Sn dendrite size by 28%, but they were unable to determine the relative influence of In versus Sb on this reaction. With alloys containing In of the order of 10 %, Sopoušek et al. found that some of the Ag_3Sn transforms to $Ag_2(Sn,In)$ and Ag_2Sn [71]. These observations are consistent with the Ag-Sn binary phase diagram that shows Ag_3In, Ag_2In, and $AgIn_2$ [46]. Wang et al. reported that an addition of 1% In caused larger or coarser Ag_3Sn precipitates [72]. This is a very interesting observation, since Ag_3Sn precipitate coarsening (larger precipitates at time zero) is expected to reduce thermal cycling reliability. In principle there is a large solid solubility of In in Sn, but the effective In content in a SAC-based solder may be diminished by interactions with other elements during the formation of multiple phases.

It must be noted that many of the studies were conducted using laboratory bulk solder samples with microstructures atypical of microelectronic solder joints. Some of the studies also included more than one significant alloy addition [e.g., 70], which makes it difficult to isolate effects due to individual alloying elements. The work by Wada et al [62, 63], while it includes tensile testing with relatively large, bulk samples, also includes thermal cycling and drop testing with surface mount components. Their microstructural analysis included X-ray diffraction where they found $InSn_4$, In_4Ag_9, $Ag_3(Sn, In)$, and possibly α-Sn in addition to β-Sn. Wada concluded that the optimum ductility and reliability was achieved with an In content of 6 wt. %.

Bismuth (Bi) Additions to Tin (Sn)

The binary Sn-Bi phase diagram in shown in Figure 6. The solubility of Bi in Sn is approximately 1.5 wt. % at room temperature and increases to almost 7 wt. % at 100 ºC room temperature, and as much as 15 wt. % at 125 ºC [50]. There is virtually no solubility of Sn in Bi, and no intermediate phases or intermetallic compounds (IMC) are found in the Sn-Bi system.

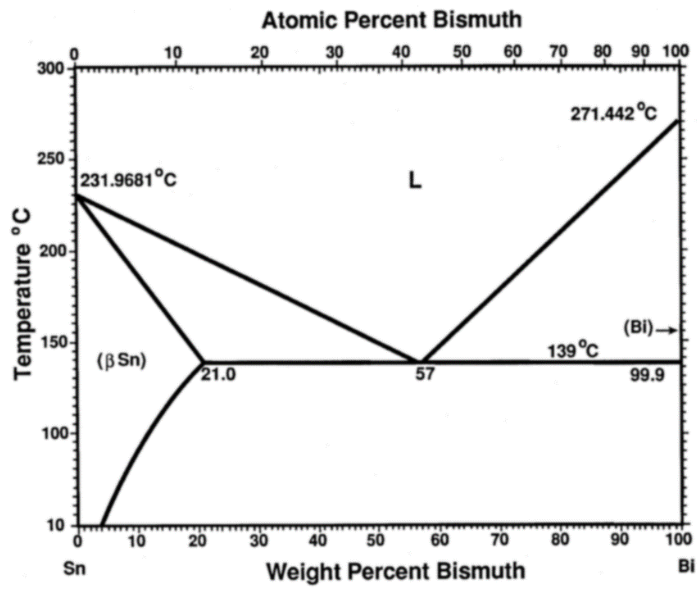


Figure 6: The Sn-Bi binary phase diagram. [Phase Diagram Credit: Max Hansen, Constitution of Binary Alloys]

Data from multiple studies show that Bi improves the mechanical properties of Sn and SAC solder [27, 34, 37-44, 73-78]. Vianco [30, 31] and Witkin [34, 66-68] did extensive mechanical testing and microstructural analysis and discussed the dual strengthening mechanisms of Bi in solid solution and Bi precipitated within Sn dendrites and at Sn boundaries. Delhaise et al. [77] reported results from their study of the effects of thermal preconditioning (aging) on microstructure and property improvement in an alloy containing 6 wt. % Bi (Violet alloy in Table 1). They hypothesize that strain from Bi precipitation induces recrystallization and increases the amount of Sn grain boundaries which in turn, become pinned by the Bi precipitates at those boundaries to resist creep deformation.

The results from fundamental studies by Vianco [38, 39] and Witkin [42, 74, 75] leave no doubt that Bi additions have a positive effect on the physical properties of Sn and Sn-based solder alloys. However, those studies used cast, bulk alloy samples and it is uncertain if those results can be scaled effectively to smaller, microelectronic solder joints. Nishimura et al. for example, recommend a maximum Bi content of only 1.5 wt. % (Figure 7a) because of the uncertainly that the alloying effect can be sustained as the microstructure evolves in response to the thermal cycling in normal service [44]. Delhaise has shown that the Bi distribution and microstructure depend on solidification conditions and subsequent thermal exposure, which ultimately determine the relative contributions of Bi to solid solution and dispersion strengthening (Figure 7b). Furthermore, it is possible that adding enough Bi to take advantage of the Bi solubility limit at higher temperatures may have a negative effect because Bi does not necessarily precipitate homogeneously. Clustering of Bi is known to occur [77] and in the extreme case, stratification or segregation induces brittle behaviour [79, 80].

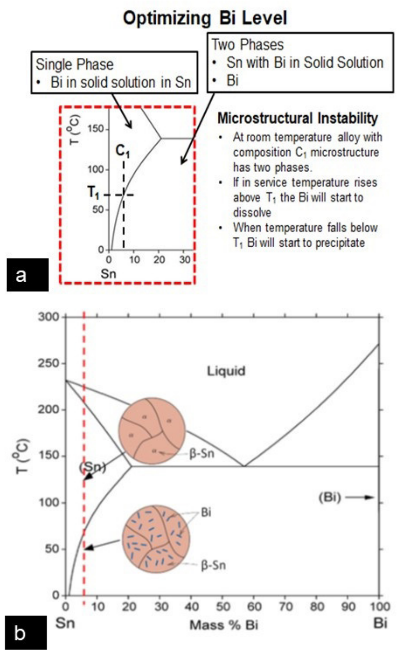


Figure 7: Emphasis on the Sn-rich regions of the Sn-Bi binary phase diagram showing: a) Factors to consider when for optimizing the Bi level, courtesy, K. Sweatman [78], and b) Microstructures shown schematically for solid solution (upper) and dispersion strengthening (lower) with the 6 wt. % Bi alloy (Violet), from Delhaise [77]. [Copyright SMTA]

EVOLUTION OF PB-FREE PERFORMANCE TESTING DATA

There have been countless tests conducted on Pb-free solder in the past 20 years. In the interest of brevity, this section will focus on some of the key industry tests conducted over the years, and how their results affected the direction of Pb-free research in high reliability, harsh environments. Each test has extensive reports of their own, but this paper will explain the scope of testing, show a sample of results, and the key general takeaways.

NCMS Pb-free 1998 [47]

The National Center for Manufacturing Sciences (NCMS) formed a consortium comprised of 11 industry OEMs, academic institutions and national laboratories in 1998 to conduct one of the first focused Pb-free solder alloy evaluations. The consortium focused on three primary operating temperature ranges:

- -55ºC to 100ºC representing consumer and telecom electronics
- -55ºC to +125ºC representing military electronics
- -55ºC to +180ºC representing aerospace and automotive electronics

The consortium conducted multiple screening tasks such as toxicology, economics/availability and manufacturability as a down-selection action prior to reliability testing. A total of 27 solder alloy systems were selected out of 79 initial solder alloy candidates being evaluated, with SnPb included for control and comparison purposes. The Pb-free solder alloy testing was comprised of both plated through hole (PTH) and surface mount technology (SMT) test vehicles. Figure 8 and Figure 9 illustrate the NCMS study PTH and SMT test vehicles.

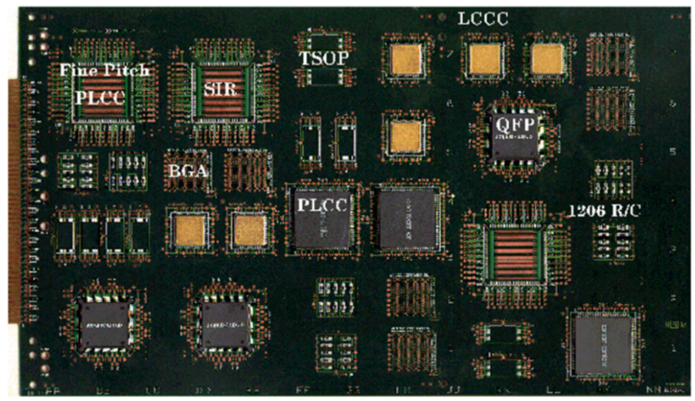


Figure 8: NCMS Surface Mount Test Vehicle [Copyright NCMS]

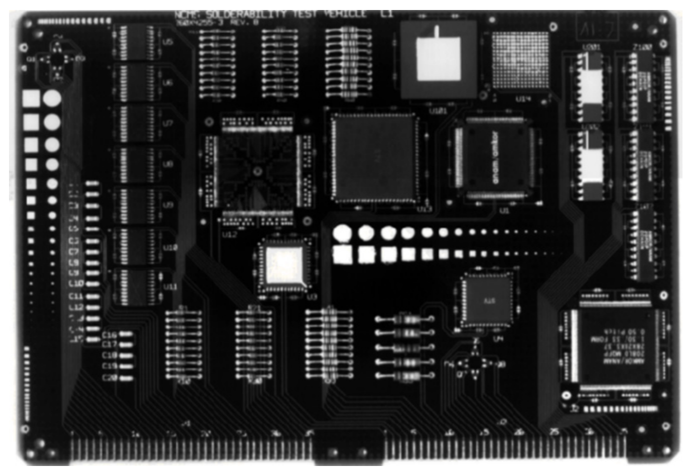


Figure 9: NCMS Through Hole Test Vehicle [Copyright NCMS]

The primary reliability test methodologies used in the study were thermal cycle and vibration. Thermal cycle testing was conducted in accordance with the IPC-SM-785 (precursor specification to the IPC-9701 specification). The vibration testing used the following conditions:

- Input frequency = 140 Hz for SMT and 70 Hz for PTH test vehicles
- Input g-levels = 6gs
- Duration = 120 minutes @ room temperature
- Stress reversals = one million for SMT and half million for PTH test vehicles

The key take-aways from the test results were:

- -55 ºC to 125 ºC Thermal Cycle Testing: for the SMT test vehicle, only the LCCC and 1206 chip resistor components exhibited failures. The other component types – PLCC, PQFP – did not register any failures after completing 5000 thermal cycles for any solder alloy. Note: BGA was not tested in this effort.
- -55 ºC to +125 ºC Thermal Cycle Testing: for the PTH test vehicle, the CPGA and CDIP components exhibited failures. The

other component types – PLCC and PDIP - did not register any failures after completing 2000 thermal cycles for any solder alloy.

• Vibration Testing: for both the SMT and PTH test vehicles, only the LCCC and PLCC components registered failures. The other component types –, PLCC, CPGA, 1206 resistors, etc. - did not register any failures after completing testing for any solder alloy. The PQFP components did record lead fractures but not solder joint fractures. Note, vibration part location dependent and this aspect should be considered. For this particular assembly, component location/position had a strong effect on time to first failure for PLCC-84 and LCCC-44 devices. This fact should be considered as part of the results from this study.

Figures 10-14 show a subset of the results from the NCMS study.

Table 2: Solder Alloy Composition Testing Legend

Legend	
A1	Sn63Pb37
A4	Sn95.5Ag3.5
A6	Bi52Sn48
E4	Sn95Ag3Bi2
F2	Sn96Ag2.6Cu0.8Sb0.5
F17	Sn91.8Ag3.4Bi4.8
F21	Sn77.2In20Ag2.8
F27	Sn95Ag3.5Zn1Cu0.5

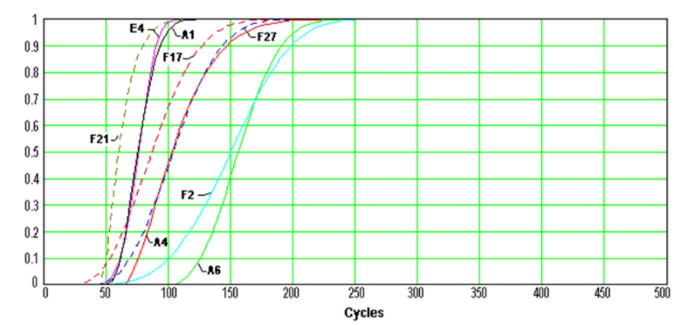


Figure 10: SMT Test Vehicle, Leadless Ceramic Chip Carrier (LCCC) Component, 3 Parameter Weibull Thermal Cycle Results (-55°C to +125°C) [Copyright NCMS]

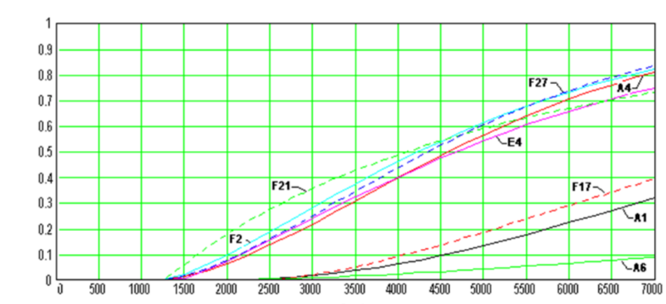


Figure 11: SMT Test Vehicle, 1206 Chip Resistor Component, 3 Parameter Weibull Thermal Cycle Results (-55°C to +125°C) [Copyright NCMS]

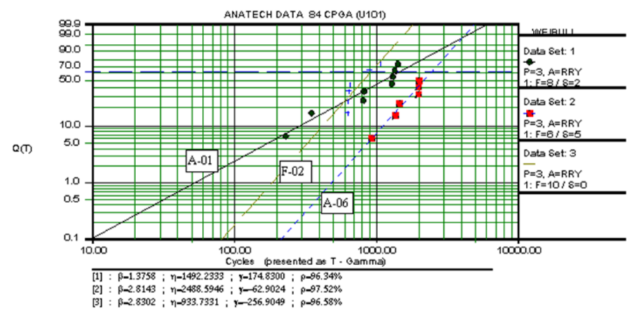


Figure 12: PTH Test Vehicle, Ceramic Pin Grid Array Package (CPGA) Component, 3 Parameter Weibull Thermal Cycle Results (-55°C to +125°C) [Copyright NCMS]

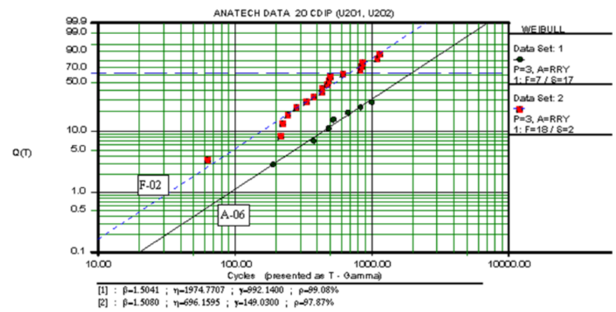


Figure 13: PTH Test Vehicle, Ceramic Dual Inline Package (CDIP) Component, 3 Parameter Weibull Thermal Cycle Results (-55°C to +125°C) [Copyright NCMS]

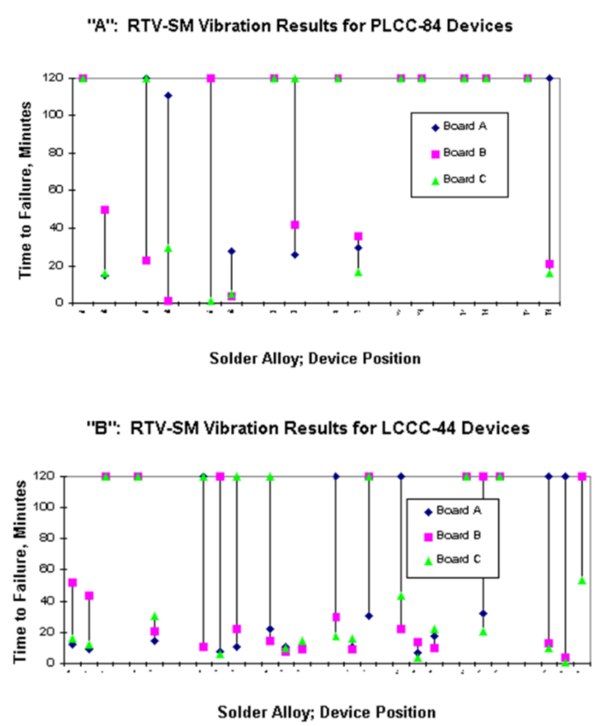


Figure 14: PLCC and LCCC Component, Vibration Results [Copyright NCMS]

JCAA/JGPP Testing [41]

In 2002-2006 the National Aeronautical Space Agency (NASA) and the Department of Defense (DoD) created a Pb-free solder alloy group due to concerns that the potential banning of lead compounds could reduce the supplier base and adversely affect the readiness of missions. The Joint Council on Aging Aircraft (JCAA)/ Joint Group on Pollution Prevention (JG-PP) Pb0free Solder Project, a partnership between DoD, NASA and OEMs, was created to examine the reliability of component solder joints using various Pb-free solders when exposed to harsh environments representative of NASA and DoD operational conditions. The solder alloys selected for the project were:

- Sn3.9Ag0.6Cu (SAC) for reflow and wave soldering
- Sn3.4Ag1.0Cu3.3Bi (SACB) for reflow soldering
- Sn0.7Cu0.05Ni (SNIC) for wave soldering
- Sn37Pb (SnPb) for reflow and wave soldering

The Pb-free solder alloy testing evaluated both plated through hole (PTH) and surface mount technology (SMT) using a specifically designed test vehicle (Figure 15).

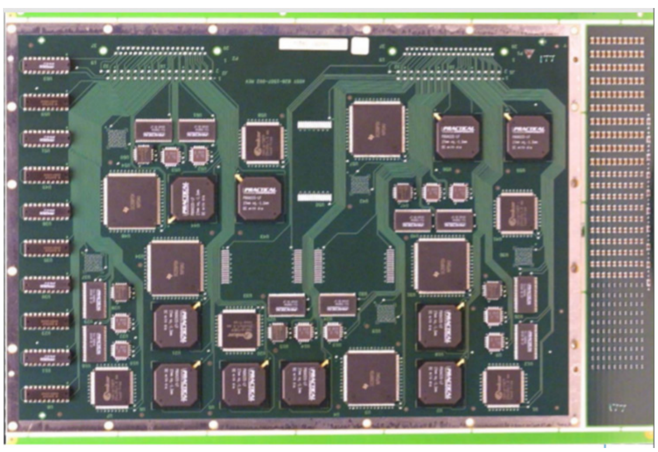


Figure 15: Test vehicle with both plated through hole (PTH) and surface mount technology (SMT) [Copyright SMTA]

The primary reliability test methodologies used were thermal cycle, vibration and combined environments. The following sections provide high level summaries of those test methodologies.

Thermal Cycle:

The thermal cycle testing used the following conditions:

- Testing conducted per IPC-9701 specification
- Temperature ranges of -55°C to +125°C and -20°C to +80°C
- Temperature dwells at maximum temperatures = 10 minutes minimum
- Ramp rate between temperature dwells = 5-10 °C/minute
- Test monitored using event detectors

The key take-aways from the test results were:

- The SnPb and Pb-free solder alloys performed equally well with most of the component technologies.
- Rework methodologies produced equal performance for the SnPb and Pb-free solder alloys with no major changes in equipment or techniques
- The introduction of SnPb finishes with Pb-free solder joints resulted in a significant loss of solder joint integrity for a wide number of component technologies
- The addition of bismuth in a Pb-free solder alloy provided significant improve in solder joint integrity for some component technologies
- When the bismuth containing Pb-free alloys were mixed with SnPb, a very low melting tertiary alloy can form and significanty reduced lifetime reliability in thermal cycle.

Figures 16-20 show a sample of the thermal cycling results from the JCAA/JGPP study.

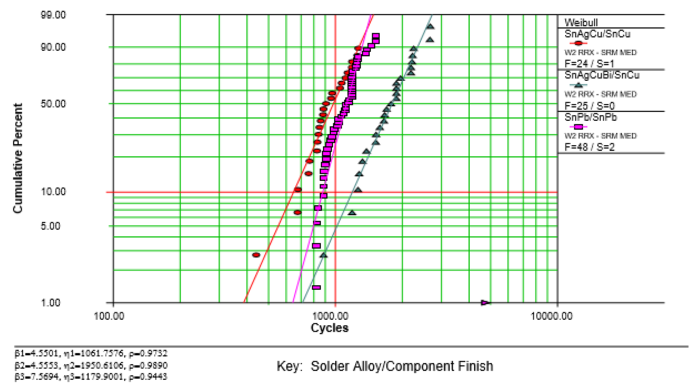


Figure 16: -55°C to +125°C for TSOP Component, 4743 cycles [Copyright SMTA]

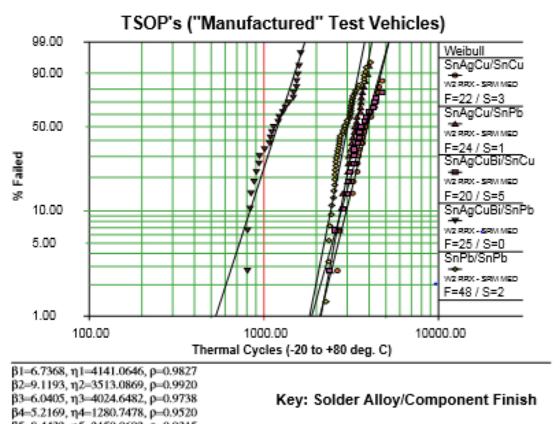


Figure 17: -20°C to +80°C for TSOP Component, 5700 cycles [Copyright SMTA]

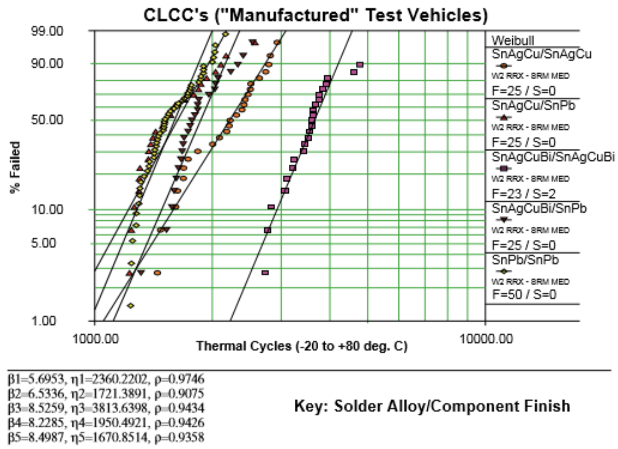


Figure 18: -20°C to +80°C for CLCC Component, 5700 cycles [Copyright SMTA]

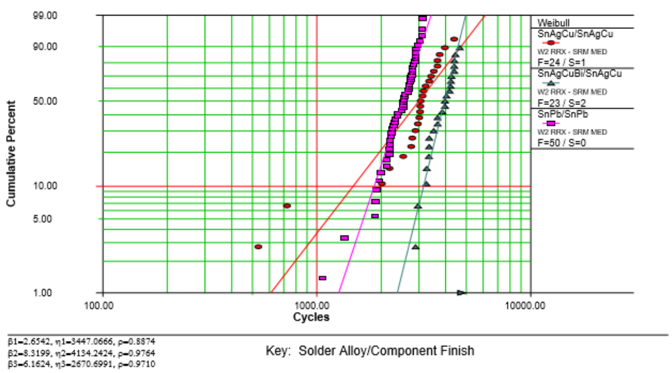


Figure 19: Rockwell Collins -55°C to +125°C for BGA Component, 4743 cycles [Copyright SMTA]

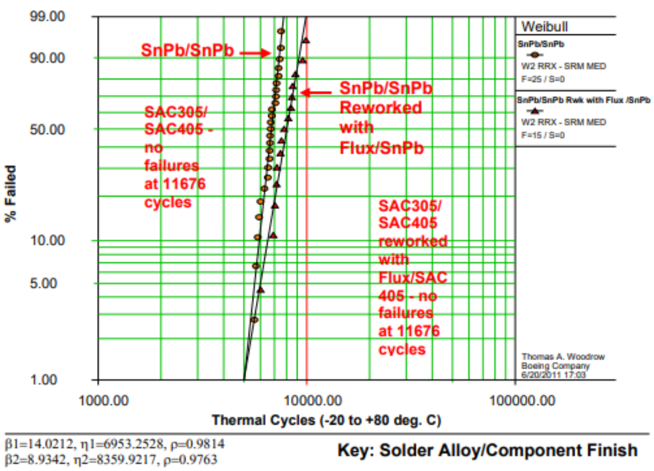


Figure 20: Boeing -20°C to +80°C for BGA Component, 11,676 cycles [Copyright SMTA]

Combined Environments (Vibration and Thermal Cycling):

The combine environments testing used the following conditions:

- Thermal Cycle:
    - o -55 to 125 °C temperature cycle
    - o 20 °C per minute ramp
    - o 15 minute soak
- Vibration
    - o Last 10 minutes of soak period
    - o 10 Grms, initial
    - o Increase 5 Grms after every 50 cycles
    - o 55 Grms, maximum
- Solder joint integrity monitored with event detectors

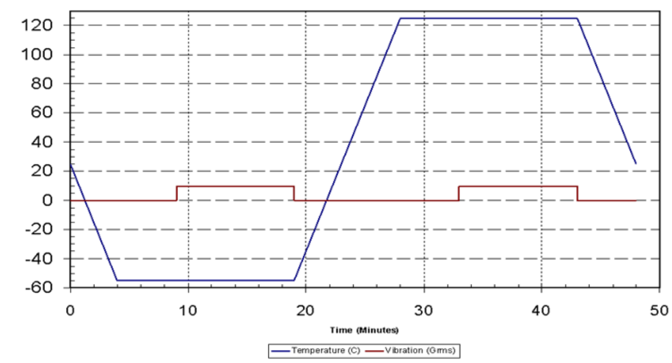


Figure 21: Combine Environments Profile [Copyright SMTA]

The key take-aways from the test results were:

- Component type had the greatest effect on solder joint integrity
- Solder joint alloy type had a major effect on solder joint integrity within the component influence variable
- The impact of SnPb component surface finishes had a significant impact of solder joint integrity

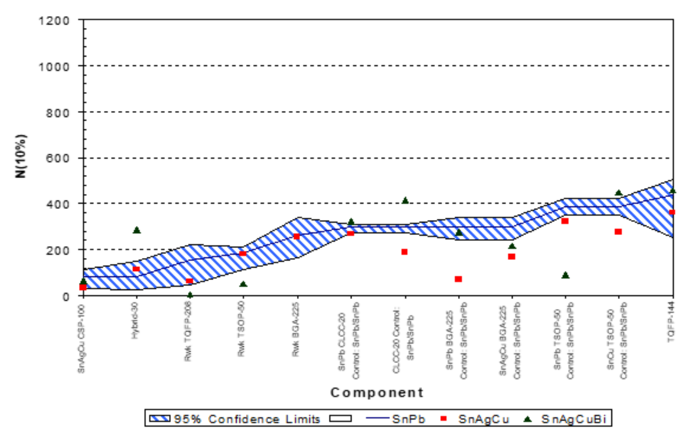


Figure 22: Performance by Component Type [Copyright SMTA]

Vibration:

The combine environments testing used the following conditions:

- Vibration
    - o MIL-STD-810
- Solder joint integrity monitored with event detectors

The vibration key take-aways from the test results were:

• Component type and location on the test vehicle had the greatest effect on solder joint integrity with solder alloy contributing as a secondary influence

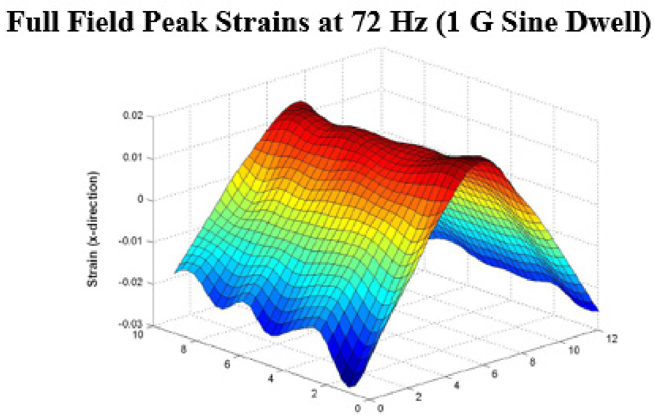


Figure 23: Vibration Test Vehicle Defection Data [Copyright SMTA]

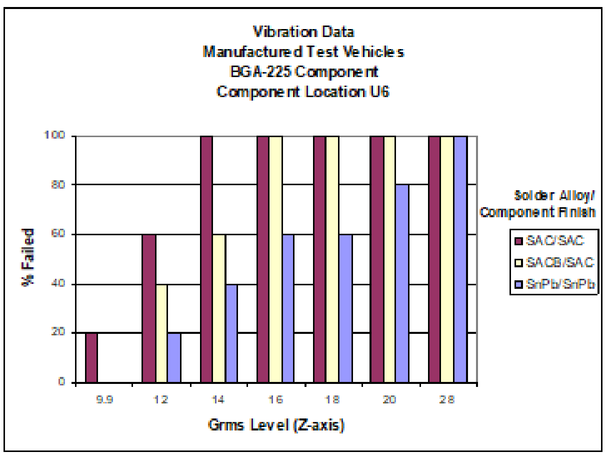


Figure 24: Vibration Results for BGA 225 Component [Copyright SMTA]

NASA DoD Phase II Testing [81]

In 2006 - 2010 the National Aeronautical Space Agency (NASA) and the Department of Defense (DoD) created a follow on project to the successful Joint Council on Aging Aircraft (JCAA)/ Joint Group on Pollution Prevention (JG-PP) Pb-free Solder Project completed in 2006. The solder alloys selected for the project were:

• Sn3.0Ag0.5Cu (SAC305) for reflow and wave soldering
• Sn0.7Cu0.05Ni (SNIC) for wave soldering
• Sn37Pb (SnPb) for reflow and wave soldering

The test vehicle was a slightly modified version of the JCAA/ JGPP test vehicle (Figure 25). The test vehicle construction, surface finish and laminate variables were intentionally selected to allow for minimally confounded test results comparisons to the JCAA/JGPP final results. The reworking of components was a primary variable in the project.

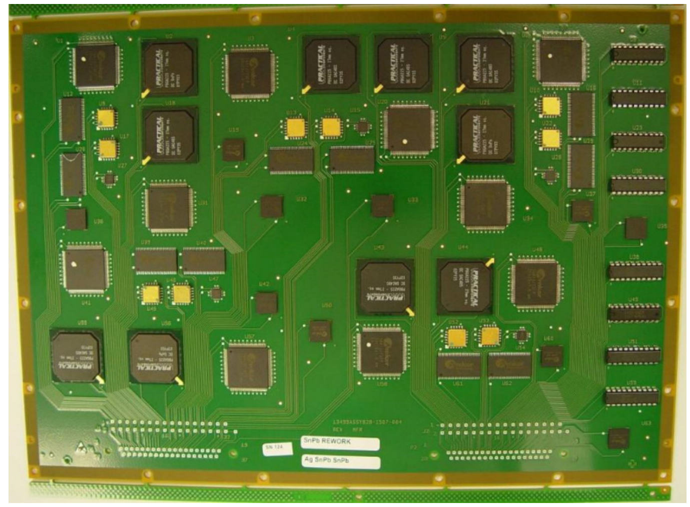


Figure 25: Test vehicle used in NASA DoD Phase II testing [Copyright SMTA]

The primary reliability test methodologies used were thermal cycle, drop shock and combined environments. The following sections provide high level summaries of those test methodologies. The acceptance criteria for all tests was to be better than or equal to the performance of the SnPb controls.

Table 3: Test Vehicle Performance Requirements

Test	Location	Reference	Electrical Test
Combined Environments Test	Raytheon McKinney, TX	MIL-STD-810F Method 520.2 Procedure I	Electrical continuity failure
Thermal Cycling	Rockwell Collins Cedar Rapids, IA	IPC-SM-785	Electrical continuity failure
Drop Testing	Celestica Toronto, Ontario	JEDEC Standard JESD22-B110A	Electrical continuity failure

Thermal Cycle:

The thermal cycle testing used the following conditions:

• Testing conducted per IPC-9701 specification
• Temperature ranges of -55°C to +125°C
• Temperature dwells at maximum temperatures = 10 minutes minimum
• Ramp rate between temperature dwells = 5-10 °C/minute
• Test monitored using event detectors
• 4068 cycles completed

The key take-aways from the test results were:

• There were no surprises in the PBGA-225 thermal cycle test results. The test results demonstrated that mixed metallurgy situations are non-optimal. An all SnPb or all Lead-free solder alloy/ component finish combination had a more consistent, predictable final solder joint integrity result compared to a mixed alloy solder joint configuration. The impact of mixed metallurgy solder joints and the influence of reflow profiles on producing uniform solder joint microstructures has been shown in other industry investigations [8].

• The rework portion of the DOE matrix was severely scrutinized prior to execution in an effort to minimize test result variation due to the rework processes/procedures. The "flux only" procedures which are widely used industry area array rework/repair procedures were problematic for the lead-free BGA and CSP DOE parameter segments. The poor performance of several of the rework/repair alloy/component finish combinations may be a maturity issue or a process refinement issue but it is clear that additional rework trials and process refinement are necessary in this area of Pb-free solder processes.

• The solder alloy had a secondary effect on the solder joint integrity test results. The SnPb solder alloy was generally more reliable than the Pb-free solder alloy but the results did not preclude their use in high performance electronics.

• The impact of Pb (lead) contamination on Pb-free solder alloys can have a significant detrimental effect depending on the component type, but especially in BGAs.

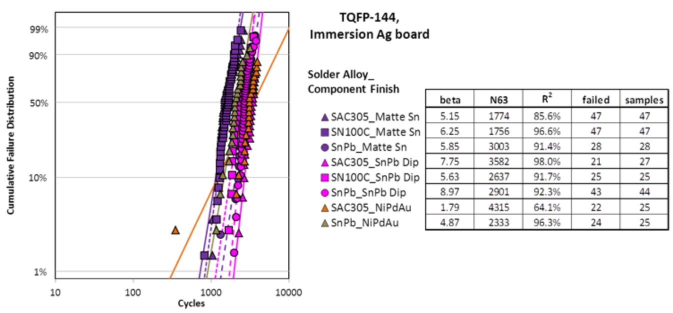


Figure 26: TQFP-144 Weibull Plot for Immersion Silver PWB Finish [Copyright SMTA]

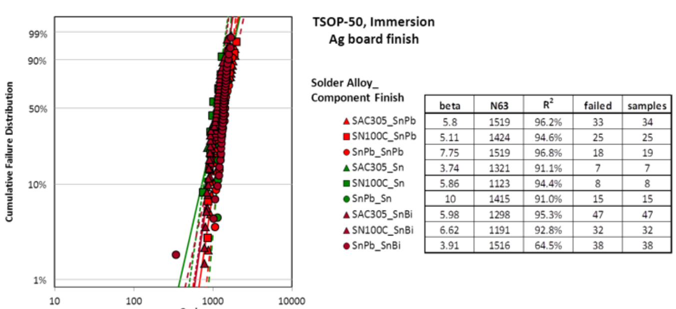


Figure 27: TSOP-50 Weibull Plot for Immersion Silver PWB Finish [Copyright SMTA]

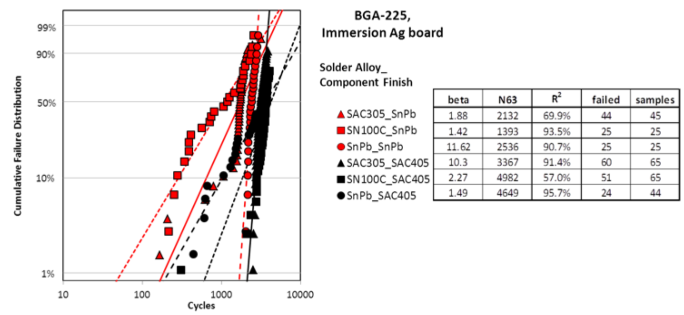


Figure 28: PBGA-225 Weibull Plot for Immersion Silver PWB Finish [Copyright SMTA]

Combine Environments:

The combine environments testing used the following conditions:

• -55°C to +125°C
• Number of cycles ≥ 500
• 20°C/minute ramp
• 15 minute soak
• Vibration for duration of thermal cycle
• 10 Grms, initial
• Increase 5 Grms after every 50 cycles
• 55 Grms, maximum
• Solder joint integrity monitored by event detectors

The key take-aways from the test results were:

• The component type was the dominate variable in the solder joint integrity test results.

• The solder alloy had a secondary effect on the solder joint integrity test results. The SnPb solder alloy was generally more reliable than the Pb-free solder alloy but the results did not preclude their use in high performance electronics.

• Reworked components, in general, had lower solder joint reliability than non-reworked components.

• The impact of Pb (lead) contamination on Pb-free solder alloys can have a significant detrimental effect depending on the component type, but especially in BGAs.

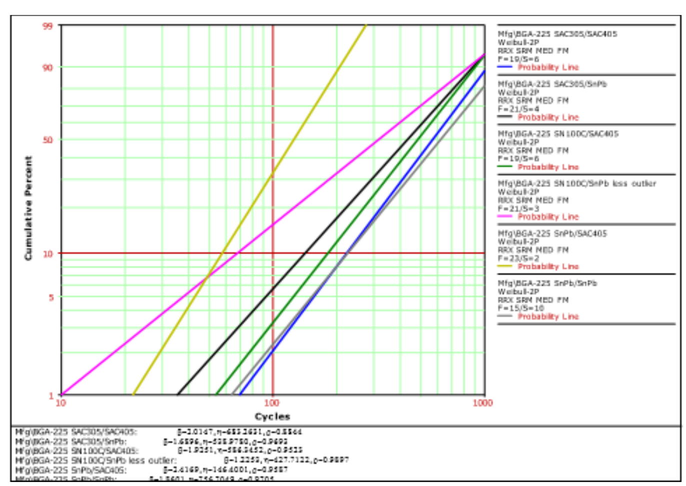


Figure 29: Weibull Plots of BGA-225 on Manufactured Test Vehicles [Copyright SMTA]

Table 4: Comparison of Manufactured Test Vehicle Test Results to 2005 JCAA/JG-PP Lead-Free Solder Project Results

Component	Alloy	Finish	2009 Nf (10%)	2005 Nf (10%)
BGA-225	SAC305	SAC405	224	166[1]
BGA-225	SAC305	SnPb	142	66[1]
BGA-225	SnPb	SnPb	226	297
CLCC-20	SAC305	SAC305	267	186[2]
CLCC-20	SAC305	SnPb	237	268[1]
CLCC-20	SnPb	SnPb	373	296
CSP-100	SAC305	SAC105	536[3]	34[2]
CSP-100	SnPb	SnPb	539[3]	84
TQFP-144	SAC305	Matte Sn	535	360[1]
TQFP-144	SnPb	Matte Sn	488	438
TSOP-50	SAC305	SnPb	312	321
TSOP-50	SnPb	SnPb	318	387

Drop Shock:

The vibration testing used the following conditions:

- Shock testing will be conducted in the -Z direction
- 500Gpk input, 2ms pulse duration
- Test vehicles will be dropped until all monitored components fail or 10 drops have been completed

The key take-aways from the test results were:

- Only the BGA components registered a significant number of electrical failures
- The drop shock test did not provide results allowing for differentiation between the solder alloys

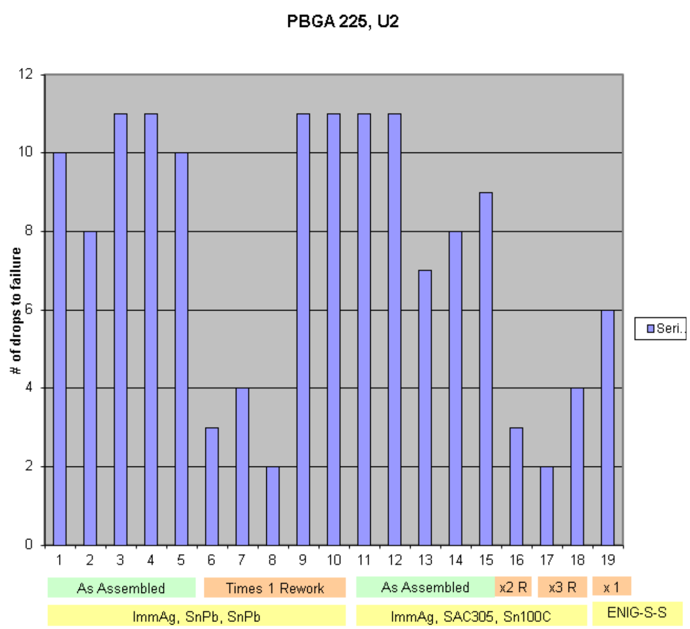


Figure 30: Number of drops to failure for the BGA-225 [Copyright SMTA]

REMAP Pb-free Testing Program [82]

In 2014 - 2019 the Refined Manufacturing Acceleration Process (REMAP) consortium initiated an extensive Pb-free solder reliability program investigating the influence of bismuth as a SAC solder alloy family constituent element addition. The REMAP consortium investigated topics such as solder joint microstructure evolution, solder joint aging, bismuth solid solution strengthening and precipitation hardening behaviors, tin whisker initiation/growth behavior and solder joint reliability. The solder alloys included in the research are listed in Table 5 with the bismuth content ranging from 3 wt.% - 7 wt.%.

Table 5: Solder alloys and composition used in the study

Alloy	Composition	Comment
SAC305	Sn 3%Ag 0.5%Cu	▪ Baseline
SnPb	Sn 37%Pb	▪ Baseline
Senju M42	Sn 2%Ag 0.75%Cu 3%Bi	▪ Commercially Available ▪ Low Bi content
Violet	Sn2.25%Ag 0.5%Cu 6%Bi	▪ Top Performer in Vibration
Sunflower	Sn 0.7%Cu 7%Bi	▪ No Ag

The REMAP test vehicle was 7.25 inches by 14 inches and 0.100 inches thick and it was fabricated from high Tg FR4 laminate. The component population consisted of daisy chained 1156 I/O BGAs, 240 I/O QFPs, PLCC84s, SSOP48s and SOL20s.

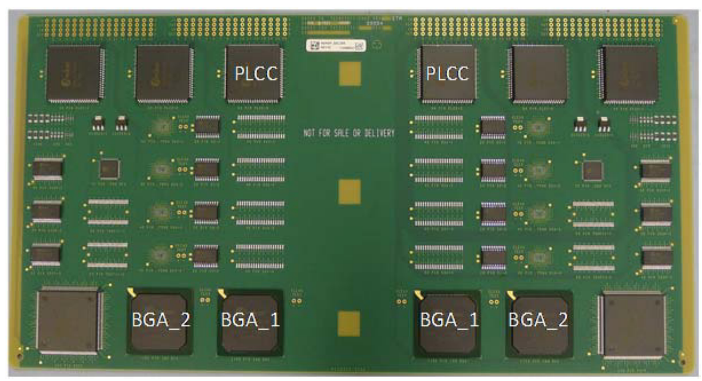


Figure 31: Remap test vehicle [Copyright REMAP]

The primary reliability test methodologies used were thermal cycling per the IPC-9701 specification, vibration and combined environment (1M vibration cycles plus 1000 thermal cycles) testing. Testing was conducted at different temperatures (i.e. 25C, 75C, 125C) to allow for data modeling. The results of the combined environments testing is shown in Tables 6, 7, and 8. The primary contribution of the REMAP consortium was to providing a full understanding of how bismuth constituent additions to a SAC solder alloy influence solder joint reliability.

Table 6: Experimental runs at 125°C for BGA and PLCC failure times in 1000 time cycles (Note: cycles in thousands)

Paste type	SAC305	Violet	SnPb	SAC305
Temp (C)	125	125	125	125
Strain (ue)	375	375	300	300
Avg Input G Level	1.6	1.8	0.9	0.9
Surface Finish	ENIG	ENIG	ENIG	ENIG
Serial #	37	60	15	39
TOTAL CYCLES	1,080 K	925 K	1,620	1,400 K
U1 BGA	392	118	1130	340
U201 BGA	608			
U7 PLCC			> 1130	
U8 PLCC	854		> 1130	
U9 PLCC	238	356	> 1130	343
U101 BGA	677	739	855	
U200 BGA				
U107 PLCC	207		910	
U108 PLCC				
U109 PLCC	595		393	393

Table 7: Experimental runs at 75°C for BGA and PLCC failure times in 1000 times cycles. (Note: cycles in thousands)

Paste type	SAC305	SnPb	Violet	SAC305	SnPb	Violet
Temp (C)	75	75	75	75	75	75
Strain (ue)	375	375	375	300	300	300
Avg Input G Level	2.0	1.6	1.5	1.1	1.3	1.2
Surface Finish	ENIG	ENIG	ENIG	ENIG	ENIG	ENIG
Serial #	48	17	65	44	18	61
TOTAL CYCLES	893 K	1,572 K	5,680 K	4,988 K	5,040 K	10,000 K
U1 BGA	841	161	1,005		695	
U201 BGA						
U7 PLCC		201				
U8 PLCC						
U9 PLCC	523	201	3,253	1,922	> 3,850	
U101 BGA	601	510			3,850	
U200 BGA						
U107 PLCC		1,130			1,800	~ 7,230
U108 PLCC						~ 7,230
U109 PLCC	412			2,364	2,660	~ 7,230

Table 8: Experimental runs at 75°C for BGA and PLCC failure times in 1000 times cycles. (Note: cycles in thousands)

Paste type	SAC305	SAC305	SnPb	SnPb	Violet	SAC305
Temp (C)	25	25	25	25	25	25
Strain (ue)	450	375	375	375	375	300
Avg Input G Level	2.5	2.1	1.9	1.5	1.8	1.0
Surface Finish	ENIG	ENIG	ENIG	ENIG	ENIG	ENIG
Serial #	38	52	14	23	68 (P)	47
TOTAL CYCLES	1,231 K	1,256 K	2,210 K	1,592 K	2,972 K	5,161 K
U1 BGA	578	1,222	162	534		
U201 BGA			782			
U7 PLCC						
U8 PLCC			393			
U9 PLCC	388	1,170	606	1,289		
U101 BGA	1,090	754		590		
U200 BGA						
U107 PLCC			1,010			
U108 PLCC						
U109 PLCC	383	431		1,229		

The key takeaways from the test results were:

• Just bismuth as an additive do not make up for the removal of silver.

• Increasing bismuth content in SAC based alloys improves performance generally.

• The different temperatures provided a significant portion of data for the modelling community to improve Pb-free models.

iNEMI Pb-free Testing Program [11]

In 2008 – 2019, the International Electronics Manufacturing Initiative (iNEMI), a not-for-profit, R&D consortium of approximately 90 leading electronics manufacturers, suppliers, associations, government agencies and universities initiated an extensive - solder reliability program. The overall tenants of the program were to: (1) help manage the supply chain complexity created by alloy choices, (2) address reliability concerns and, (3) highlight the opportunities created by the new Pb-free alloy alternatives. Specific goals in the early years of the program included:

• Assess existing knowledge and identify critical gaps related to new Pb-free alloys. Provide technical information to the industry that will make selection and management of alloys easier.

• Raise awareness of this information through publication and presentation of findings.

• Propose a methodology and set of test requirements for assessing new alloys.

• Work with industry standards bodies to address standards that require updating to account for new alloys.

The solder alloys investigated in the program were initially the SAC solder alloy family include SAC405, SAC396, SAC387 and SAC305 systems. Further work progressed into the SAC205, SAC105 and other commercial solder alloy systems that contained lower silver constituent additions. Topics such as isothermal preconditioning, solder joint microstructure evolution, Pb-free solder alloy mixed alloy reliability and the impact of extended dwell time were investigated. The iNEMI consortium followed industry solder alloy evolution with continued investigation of Pb-free solder alloys that utilized a variety of element constituent additions such as manganese, bismuth, antimony and indium. The following section highlights some of the critical results produced in the iNEMI Pb-free solder reliability program.

The use of a standardized test vehicle by the iNEMI Pb-free solder reliability program allowed for continuous learning, comparison and validation of test results over the course of time. The test vehicle was 2.36 mm (93 mils) thick, with a 6 layer construction with 16 sites for a large daisy chained 192 I/O chip array BGA (192CABGA), and another 16 sites for a smaller daisy chained 84 I/O thin core chip array (84CTBGA) (Figure 32). The attributes of the components and PCB are provided in Table 9. The test vehicles were fabricated with a variety of different high temperature PCB laminate materials such as Panasonic R-1755V and Hitachi MCL-E-679FG, and different surface finishes such as Entek HT organic solderability preservative (OSP) and electroless Ni/immersion Au (ENIG).

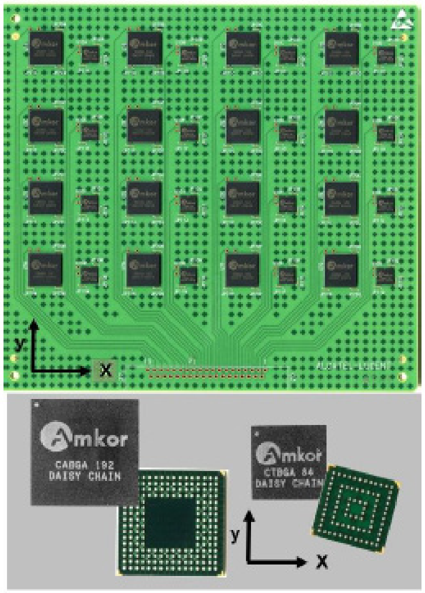


Figure 32: iNEMI test vehicle and components [Copyright iNEMI]

Table 9: Attributes of the components and PCB

BGA Package Attributes		
Designation	192CABGA	84CTBGA
Die Size	12x12 mm	5x5 mm
Package Size	14x14 mm	7x7 mm
Ball Array	16x16	12x12
Ball Pitch	0.8 mm	0.5 mm
Ball Diameter	0.46 mm	0.3 mm
Pad Diameter	0.381 mm	0.3 mm
Pad Finish	Electrolytic Ni/Au	Electrolytic Ni/Au
Au thickness	0.6 μm	0.6 μm
PCB Attributes		
Dimensions	165 x 178 x 2.36 mm	
Laminate	Panasonic R-1755V or Hitachi MCL-E-679FG	
Surface Finish	Entek HT OSP or ENIG	
No. Cu Layers	6	
Pad Diameter	0.356 mm	0.254 mm
Solder Mask Dia.	0.483 mm	0.381 mm
Laminate	Panasonic R-1755V	Hitachi MCL-E-679FG
Glass Transition Temperature, T_g	165 °C	165 °C
Decomposition Temperature, T_d	350 °C	340 °C
Room Temperature Storage Modulus	11.6 Gpa	18GPa

The primary reliability test methodologies used was thermal cycling per the IPC-9701 specification because of the large number of solder alloy systems/combinations being evaluated. An understanding of the impact of silver as a constituent addition was published demonstrating the coarsening rate temperature dependence of Ag_3Sn intermetallic phase was an output of the early investigations. Figure 33 and 34 illustrates the impact of the different temperature cycle regimes on both high and low silver content of Pb-free solder alloy systems.

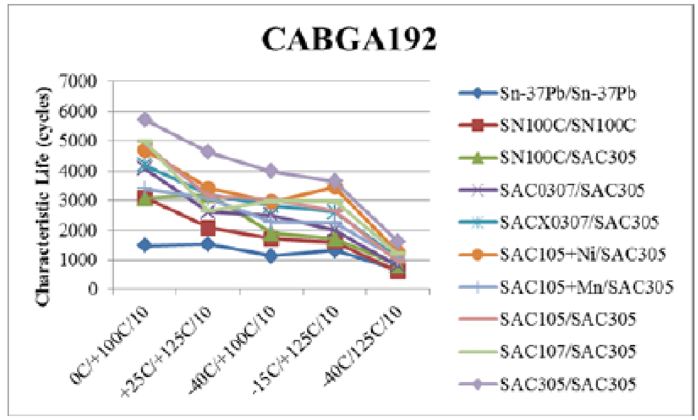


Figure 33: Characteristic life as a function of thermal cycling regime with 10 minute dwells [Copyright iNEMI]

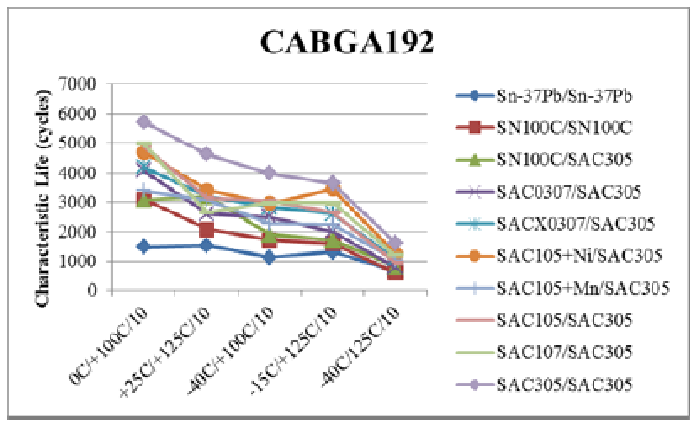


Figure 34: Characteristic life as a function of thermal cycling regime with 10 minute dwells [Copyright iNEMI]

The introduction/evolution of the SAC solder alloy family with new elemental constituent additions such as manganese, bismuth, antimony and indium by solder alloy suppliers was evaluated as an understanding of what metallurgical considerations such as solid solution strengthening and precipitation hardening could provide in terms of alloy creep resistance was realized. Table 10 illustrates the wide range of solder alloys/compositions comprised the investigations. Figure 35-38 lists the 192CABGA thermal cycle data illustrating how the various elemental constituent additions interacted with the various thermal cycle regimes. The iNEMI consortium testing revealed that different solder alloys could be matched with different environment conditions – the belief that one solder alloy would suffice for all product use environments was no longer valid and that custom solder alloy application could be a valid consideration for product design teams emerged.

Table 10: Solder alloy and compositions involved in the iNEMI testing

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 277	89.0	3.8	0.7	0.5	3.5	2.5		214-223
Indalloy 279	89.3	3.8	0.9		5.5	0.5		221-228
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

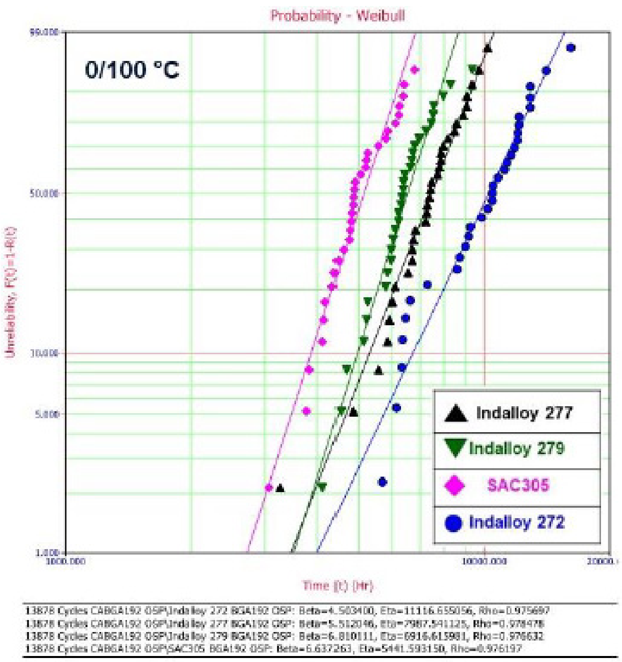


Figure 35: Weibull distribution plots for the 192CABGA package and SAC 305, Indalloy 272, Indalloy 277 , and Indalloy 279 tested with the 0/100 °C thermal cycling profile. [Copyright SMTA]

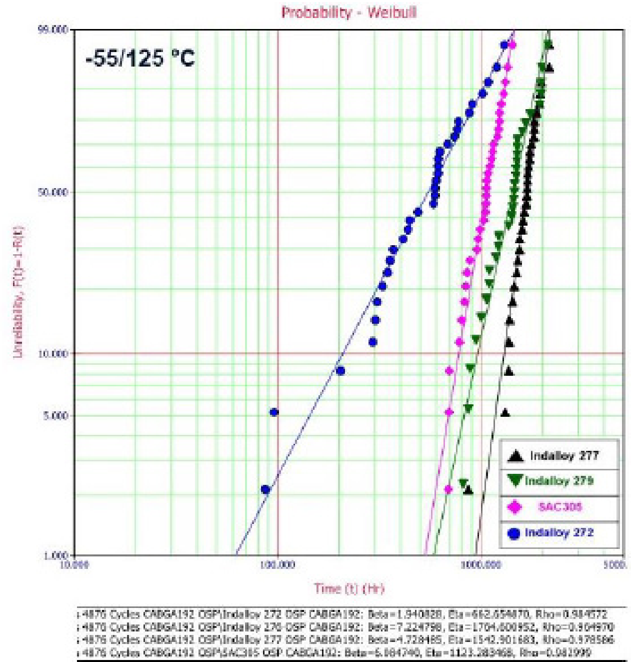


Figure 36: Weibull distribution plots for the 192CABGA package and SAC 305, Indalloy 272, Indalloy 277 , and Indalloy 279 tested with the -55°C/125°C thermal cycling profile. [Copyright SMTA]

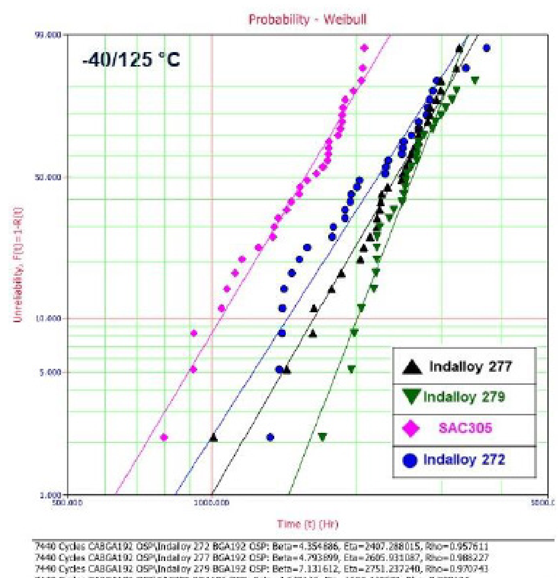


Figure 37: Weibull distribution plots for the 192CABGA package and SAC 305, Indalloy 272, Indalloy 277 , and Indalloy 279 tested with the -40/125 °C thermal cycling profile. [Copyright SMTA]

192CABGA Thermal Cycling Data				
a Alloy	Temperature Cycle	Characteristic Lifetime η	Slope β	Correlation Coefficient ρ
SAC305 (Sn3Ag0.5Cu)	0/100 °C	5542	6.6	0.98
	-40/125 °C	1692	3.6	0.99
	-55/125 °C	1123	6.1	0.98
Violet (Sn2.25Ag0.5Cu6Bi)	0/100 °C	5607	5.0	0.95
	-40/125 °C	1557	5.4	0.99
	-55/125 °C	834	2.8	0.99
SB6NX (Sn3.5Ag0.8Cu0.5Bi6In)	0/100 °C	6183	6.0	0.98
	-40/125 °C	2042	3.6	0.96
	-55/125 °C	1290	2.9	0.96
Indalloy 272 (Sn3.8Ag1.2Cu3.5Sb1.5Bi)	0/100 °C	11117	4.5	0.98
	-40/125 °C	2407	4.4	0.96
	-55/125 °C	663	1.9	0.98
Indalloy 277 (Sn3.8Ag0.7Cu3.5Sb0.5Bi2.5In)	0/100 °C	7988	5.5	0.98
	-40/125 °C	2606	4.8	0.99
	-55/125 °C	1543	4.7	0.99
Indalloy 279 (Sn3.8Ag0.9Cu5.5Sb0.5In)	0/100 °C	6917	6.8	0.98
	-40/125 °C	2751	7.1	0.96
	-55/125 °C	1765	7.2	0.96

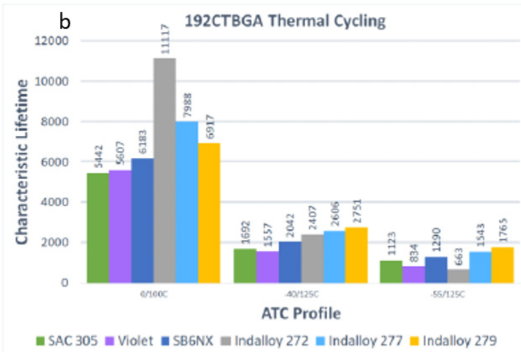


Figure 38: a) Summary of accelerated temperature cycling failure statistics for the 192CABGA with SAC305 and the five Pb-free high reliability solder alloys. b) Bar charts comparing the characteristic lifetimes (N63) for the 192CABGA with SAC305 and the 5 high reliability solder alloys tested using 0/100°C, -40/125°C, and -55/125°C thermal cycling profiles [Copyright SMTA]

Academic Research Centers Pb-free Testing

This paper would be orders of magnitude larger if every industry and individual company program contributions to the understanding/evolution of Pb-free solder alloys were detailed. However, three university affiliated research centers: Center for Advanced Life Cycle Engineering (CALCE), in conjunction with the University of Maryland, the Center for Advanced Vehicle and Extreme Environment Electronics (CAVE3) in conjunction with Auburn University and Advanced Research in Electronics Assembly (AREA) in conjunction with Binghamton University have contributed hundreds of detailed investigations on the topic of Pb-free solder [96-98]. The investigation results assisted significantly in the understanding/evolution of Pb-free solder alloys.

RELATIONSHIP OF HIGH PERFORMANCE SOLDERS TO A & D REQUIREMENTS

The term acronym “A & D” refers to Aerospace, Defense, and High-Performance products and represents the sphere of operation for aerospace and defense products.

A & D products are expected to work in harsh conditions, specifics of these being dependent on the associated industry. Given that there are multiple A & D industries (e.g. telecom, commercial aerospace, automotive, defense), this section will discuss the defense service conditions and environments. (Note that a similar approach can be used for the other A & D groupings). Before evaluating the possibility of high-performance solders operating in defense products, it would be beneficial to discuss the challenges that Pb-free solders may present.

Challenges of Pb-free in High Performance Products/Systems

The challenges of using Pb-free materials in defense products has been well documented [83, 84]. In general, the concerns are: performance and long-term reliability of Pb-free interconnections (i.e. solder joints) and deleterious effects of tin whiskers. (Figures 39 and 40 illustrate the concerns.) For more than fifty-years, A & D utilized eutectic (63Sn37Pb) and near-eutectic (60Sn40Pb) solders in interconnections and plating/finishes. With an established benchmark for performance, the concern with new materials is justified.

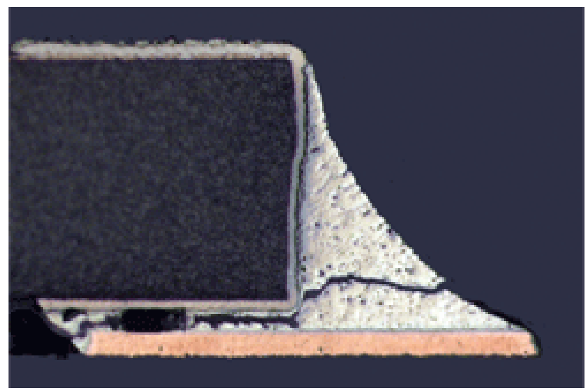
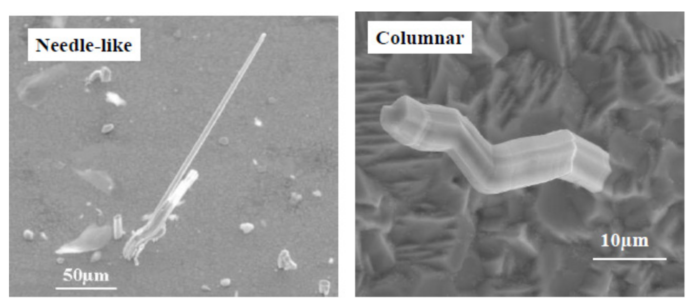


Figure 39: A Pb-free solder joint can fail earlier than a SnPb solder joint when subjected to mechanical vibration or shock in the field (courtesy of Dr. Craig Hillman, DfR Solutions.)



(a) (b)

Figure 40: Examples of whiskers observed in CALCE (University of Maryland) experiments. a). Needle-like whisker structure, b). Columnar-like whisker structure. (Courtesy of Center for Advanced Life Cycle Engineering [CALCE])

Focusing on the first concern, the challenge is finding Pb-free solder materials that can withstand four major service/environmental conditions: thermal cycling (-55C to +125C), thermal shock (-55C to +125C), vibration (e.g. MIL-STD-810F, Method 514.5), and mechanical shock (e.g. MIL-STD-810F, Method 516.5 and/or MIL-S-901). The tin-silver-copper alloy SAC 305 has been comparable to eutectic SnPb for thermal cycling although there are still some concerns with SAC 305 behavior at the temperature extremes of -55C and +125C. Figures 41a and 41b present two interpretations of this concern. Another concern is the undesirable mechanical properties and the potential occurrence of solder joint surface cracks and other production-related defects and issues (e.g., head-on-pillow, pad-cratering) [85].

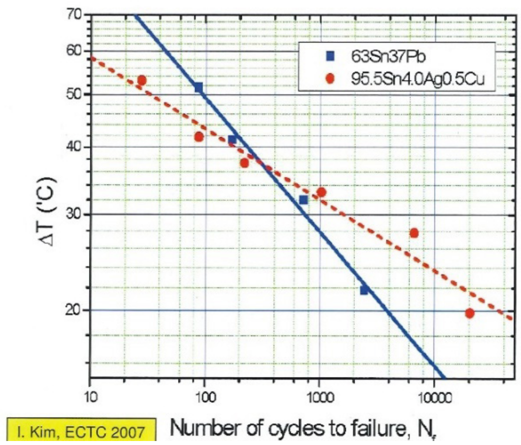


Figure 41a: Larger delta T (indicative of thermal cycling) favors SnPb solder (courtesy of C. Hillman, DfR Solutions)

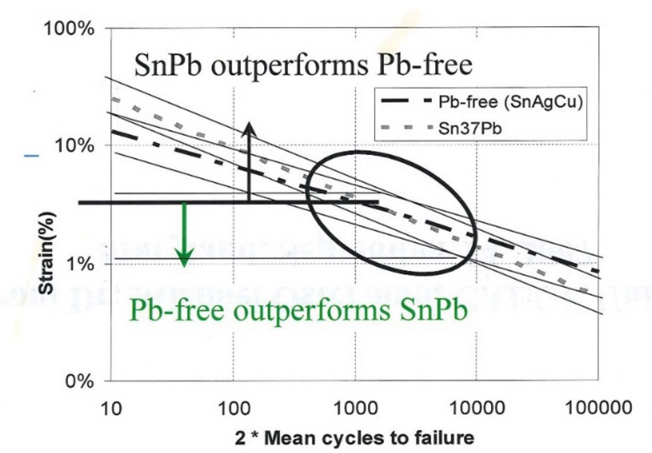


Figure 41b: Presenting the thermal cycling comparison from a percentage strain aspect (courtesy of M. Osterman, University of Maryland Center for Advanced Life Cycle Engineering)

Regarding vibration and shock, use of SAC105 alloys has shown improvement compared to SAC305 but still not comparable to eutectic tin-lead. Tin-bismuth alloys have currently been objects of numerous openly published studies but the inherent brittle nature of bismuth is challenge to overall industry acceptance [86].

Sources of the Challenges: The DoD "World"

The U.S. Department of Defense (DoD), National Institute of Standards and Technology (via Federal Standards), and several industry organizations (AIA, IPC, SAE, etc.) have been the source of most standards and specifications governing use of products and equipment in harsh environments. DoD programs have historically relied on military and federal standards/specifications to provide necessary diligence and guidance in the development and evaluation of products and systems required to function under severe, battlefield conditions. The implementation of these standards /specifications into the design/manufacture of defense products has been coined as "mil-spec". The "mil-spec" designation usually refers to a product's ability to withstand and combination of 1 thermal cycling, thermal shock, mechanical vibration, and mechanical shock conditions (although additional harsh conditions such as sand, dust, fungus, etc. can also be grouped here). Sourcing the origins of these requirements and their limits has been an interesting exercise in "mil-spec" archeology. Some of these standards/specifications are (but not limited to) MIL-STD-202, MIL-STD-2036, MIL-STD-810, MIL-STD-883, and MIL-DTL-901.

Table 11 provides a summary (but not all inclusive) of the origination of the "infamous mil-spec" requirements typically used to qualify defense equipment.

Table 11: Harsh Condition Requirements for Military Applications (some A & D as well)

Requirement Name	Requirement	Source	Purpose
Thermal Cycle	- 55C to +125C (Test Condition B)	Method 1010.9 of MIL-STD-883-1	Life Test
Thermal Shock	55C to +125C (Test Condition B)	Comes from Method 1011.9 of MIL-STD-883-1	Service Condition
Mechanical Shock (component level)	Peak g-level ranges from 500 (Pulse duration 1.0 ms) to 30000 (Pulse duration of 0.12 ms)	MIL-STD-883-2, Method 2005.5	Service Condition
Mechanical Shock (high impact, shipboard systems)	Pre-defined pass/ fail criteria when subjected to one of several class shock loads with further categorizations based on combat capability, dependency of mountings, and test item hierarchy.	MIL-DTL-901E (formerly MIL-S-901E)	Service Condition
Vibration	Fatigue and Variable Frequency peak ranges from acceleration levels of 20 g's to 70 g's	MIL-STD-883-2, Method 2005.2 for fatigue vibration; MIL-STD-883-2, Method 2007.3 for variable frequency	Service Condition

As Pb-free materials have presented their own set of challenges, the defense industry has turned to industrial resources to aid in the evaluation/qualification of these materials. Table 12 presents a summary (but not all-inclusive) of these standards/specifications.

Table 12: Harsh Condition Standards/Specifications From Industry (i.e. Non-Military Sources)

Requirement Name	Requirement	Source	Purpose
Thermal Cycle	Can range from -55C to +150C dependent upon test condition	JESD22-A104E Temperature Cycling	To determine the ability of components and solder interconnects to withstand mechanical stresses induced by alternating high- and low-temperature extremes
Thermal Cycle	Can range from -65C to +125C	IPC-TM-650 2.6.6 Temperature Cycling PWBs	Conducted for purpose of determining resistance of material such as a laminate or multilayer circuit board, to the shock of repeated exposures to extremes of high and low temperatures for comparatively short periods of time.
Thermal Cycle	0C to +100C -25C to +100C -40C to +125C -55C to +125C -55C to +100C	IPC-9701 Performance Test Methods	Establishes specific test methods to evaluate performance and reliability of surface mount solder attachments of electronic assemblies with inclusion of performance/reliability levels to rigid, flexible, and rigid-flex assemblies. Relates results to reliability in environmental and use conditions as well.
Vibration	G-levels can vary from 6.27 down to 0.06 (dependent on service conditions)	JESD22-B103B.01 Vibration, Variable Frequency	Intended to evaluate component(s) for use in electrical equipment
Drop Shock[1]	Shock levels of at least 150 G's	IPC-TM-650 Test No. 2.6.5 Drop Shock	This method is to determine the electrical performance of multilayer printed wiring boards by following the shock with an electrical continuity test as specified.
Drop Shock[1]	Peak shock level 1500 G's	JESD22-B111A Board Level Drop Test Method of Components for Handheld Electronic Products	Evaluation/comparison of drop performance of surface mount electronic components for handheld electronic product applications in an accelerated test environment, where excessive flexure of a circuit board causes product failure

[1] While not considered a military or aerospace test, its prominence in Pb-free testing and evaluation may warrant drop shock as an alternative and cost-effective method to assess low-level shock performance as a "first-start" in qualifying Pb-free solders.

Presenting Tables 11 and 12 has several purposes. First, these tables simply answer the question "Why are we testing to these parameters" and "Where did these requirements come from". For many years whenever mentioning thermal cycle and/or thermal shock, inevitably the phrase "-55C to 125C" is included in the conversation, we now know the source of these requirements. Second, Tables 11 and 12 provide resources for supporting adequate designs and implementation plans to meet these requirements. Third, the data in these tables can help customers and contractors work together to analyze system requirements and assess realistic expectations.

The Impact of COTS and Low-Cost Solutions

Traditionally, acquisition of defense products and systems were expensive due in part to a combination of the following factors: 1) requirement to operate in severely harsh service and environmental conditions and, 2) strict procedures & processes warranting government oversight. These factors directly affected a constantly increasing DoD budget each year resulting in push-back from Congress and reflecting the frustrations of its constituents. Recognizing the need to reform skyrocketing costs, in June 1994 the U.S. Secretary of Defense, Dr. William Perry, issued his "Mandate for Change" memorandum [87]. The memo directed the armed forces to purchase Commercial-Off-The-Shelf (COTS) products "to the extent possible" rather than from traditional defense suppliers thereby instituting a philosophical change from purchasing "mil-spec" grade components and parts. It was estimated that over 30,000 military specifications and standards were the cause of inflating the cost of military items. To this day, the spirit of the mandate continues, and electronic components comprise a large portion of the COTS items acquired by A&D companies. Subsequently, COTS items are subject to market trends (e.g. new materials, increased technology updates, no requirement for change notices, etc.) and consequently, A&D OEMs must address such challenges in their designs to meet performance requirements.

Despite these challenges, COTS still provide a more affordable solution to lower cost A&D systems. While the initial reaction to industrial/commercial standards and best manufacturing practices may be dismissed by many, one cannot help but think that COTS items, in general, must be of high quality as the worldwide consumer community has a greater influence over company success than all the aerospace/defense organizations combined.

Adapting A & D Requirements to COTS and Pb-free Integration

Presently, there are no validated high-performance reliability models for Pb-free electronics [99, 100]. However, it is possible to execute some conservative approaches to design/implementation and testing to meet performance requirements.

From a design and implementation perspective, IPC-PERM-2901 "Pb-free Design & Assembly Implementation Guide" provides resources for designers forced to use Pb-free solders and finishes in their products [88]. Mitigating the concerns with Pb-free performance under severe service and environmental conditions are presented in three high-level strategies: The first approach focuses on ruggedization which for a COTS assembly might include a) component underfills, b) shock hardening a chassis or card guide, c) any other mechanical/physical attribute to ward off harsh effects. Note that this approach will result in a modified COTS item, or MOTS as known in the industry. A second strategy is the concept of "aggressive" preventative maintenance in which additional spares of COTS items would be purchased as part of an acquisition plan such that in-service units would be "swapped out" after a pre-determined period and replaced with spares. The swapped-out units could then be analyzed for various reliability attributes, e.g. remaining life, impending failure, etc. The data could be used to bolster eventual reliability modeling for that COTS item or family of items. This scheme could be expanded to develop some prognostic & health maintenance (PH&M) tools for monitoring Pb-free products during operation. The final strategy, implementation, is the simple concept of use limitation which is the concept earlier mentioned on realistic expectations. Design data (drawings, specifications, etc.) of a sub-system or system (assuming either one includes COTS) would include restrictions on use conditions and storage environments of the system. Examples of these restrictions would include a) use of item only in a shock hardened enclosure/shelter and b) no storage in an uncontrolled environment (temperature, humidity, sunlight, etc. or combination thereof).

Utilizing test as a means to validate performance and reliability of Pb-free products is considered to be in its "infancy" stages primarily due to immaturity of reliability models. The immaturity component refers to the lack of plentiful data to validate such models. Using traditional reliability approaches for Pb-free is risky due to the inherent differences between Pb-free and eutectic/near-eutectic SnPb solders. Material differences can include mechanical creep, aging effects, homogeneity, etc. which would affect acceleration factors as well as other key modeling parameters. Given the many families of Pb-free solders, the magnitude of differing properties becomes a large challenge. A work-around is to test COTS products at the "macro" level to assess specifically desired results. In other words, the first step would be to decide on what kind of data/parameters are desired, then design a test based on those outcomes, and finally execute the test. A simple example of this approach would be as follows: If a COTS assembly is required to withstand mechanical shock or vibration, then a production version of that item should be subjected to that specific test. If the COTS item is required to function over a relatively long period of time, then a production version of the item should be subjected to an operational test over some pre-determined fraction of the life using conservative acceleration factors based on general scientific principles. Engineering may be required to determine if additional conservancy is needed based on application. GEIA-STD-0005-3 is an effective resource to use for testing Pb-free products and systems [89].

In summary, making COTS/Pb-free-built products compliant to A & D requirements will require the following:

- Review and understanding of published resources addressing Pb-free and Pb-free risk mitigation such as the suite of standards and documents as listed in Table 13
- Use all resources that address and support general hardware reliability testing while using sound engineering judgment to decide on key parameters such as activation energies, constants, models, etc. Note that lack of a Pb-free reliability strategy should not prevent good engineering of a specific reliability test or, better yet, life test.
- The availability of assets to test (testing is preferred over modeling as there is little confidence in the latter at this time)

Therefore at this time, incorporating A & D requirements to COTS/Pb-free requires sound engineering assessment and action before implementation.

SUMMARY AND CONCLUSIONS

This paper has provided a chronological narrative of a) the onset of Pb-free electronic materials in the supply chain, b) A & D industry's struggles to respond to the challenges, and c) the lengthy but deliberate efforts to develop mitigations and solutions.

The onset included the early warnings circa 1995 of impending global regulations [90, 91] of hazardous substances (element Pb not withstanding) and A & D reliance on the exclusions from 2006 to the present. However, despite exclusions, the global supply chain aligned with the European Union resulting in a shift from readily available SnPb solder to SAC, SnC100, and a plethora of other Pb-free materials becoming the commercially available choice. Now, with the threat of elemental Pb becoming a RoHS Authorized substance, continuous acquisition and use of SnPb would become a customized purchase. The lesson learned here: never underestimate the influence of global trends on the supply chain no matter how critical the product end use.

Fortunately, the A & D struggles with response to challenges overcame the initial stages of denial [92-95] and in 2004, the DoD, along with several industry and academia groups, formed the Lead-Free Electronics in Aerospace Project (LEAP) which transformed into today's IPC PERM (Pb-free Electronics Risk Mitigation) Council. The PERM has, and continues to, provided awareness and resources to help A & D work with Pb-free materials providing a forum for the open exchange of ideas and tools to help comply with customer requirements.

Efforts to develop mitigations and solutions have included:

- The work of the IPC PERM Council in generating a set of document tools (Table 16)
- Several stages of the Lead-Free Manhattan Project which is an industry collaborative funded by the US DoD to baseline the state of Pb-free knowledge and develop a roadmap to close gaps
- Pockets of independent research by consortia and academia attempting to close some of the gaps
- The DoD-funded Defense Electronics Consortium Pb-free pilot program which will accelerate adoption of new solders, reduce supply chain risk, and modernize defense electronics

Table 13: IPC Developed Suite of Tools for Pb-free Risk Identification and Mitigation

- GEIA-STD-0005-1 "Standard for Managing the Risks of Pb-free Solders and Finishes in ADHP Electronic Systems"
- GEIA-STD-0005-2 "Standard for Mitigating the Effects of Tin in Aerospace and High Performance Electronic Systems"
- GEIA-STD-0005-3 "Performance Testing for Aerospace and High Performance Electronics Containing Pb-free Solder and Finishes"
- GEIA-HB-0005-1 "Program Management / Systems Engineering Guidelines for Managing the Transition to Pb-free Electronics"
- GEIA-HB-0005-2 "Technical Guidelines for Aerospace and High Performance Electronic Systems Containing Pb-free Solder"
- GEIA-HB-0005-3 "Rework and Repair Handbook To Address the Implications of Pb-free Electronics and Mixed Assemblies in Aerospace and High Performance Electronic Systems"
- IPC/PERM 2901 'Pb-free Design & Assembly Implementation Guide"

A thorough discussion on the evolution of solder alloys and the methodology has been provided in this paper so that future alloy developments can be likewise categorized, characterized, and assessed for specific applications. A solid summary of performance data for these solder families has been provided for use in not only direct design applications but to guide in assessing new families of Pb-free solders to address mission needs. Finally, some insight into the use and call-outs of military standards and specifications has been presented to help understand the nature and origins of A&D performance requirements encouraging the use new paradigms [84] in meeting those requirements.

In conclusion, Pb-free materials are here to stay. Despite trepidations in the 1990's, dedicated and deliberate efforts have vastly improved the ability to adopt these alloys and finishes in many applications. There are still several instances (space, missiles, i.e. very high reliability conditions) which will still require SnPb for the foreseeable future. However, an increasing resource and database is available that will allow the "engineering" of products and systems to meet performance requirements for a variety of application areas. Those unknown application areas are well on the way in acquiring the data and resources to engineer the solution.

This document does not contain technology or technical data controlled under either the U.S. International Traffic in Arms Regulations or the U.S. Export Administration Regulations.

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David D. Hillman retired as a Metallurgical Engineer in the Advanced Operations Engineering Department of Collins Aerospace. Mr. Hillman graduated from Iowa State University with a B.S. (1984) and M.S. (2001) in Material Science & Engineering. In his present assignment he serves as a consultant to manufacturing on material and processing problems. He served as a Subject Matter Expert (SME) for the Lead-free Manhattan Project in 2009. He has published 200+ technical papers. Mr. Hillman was named a Rockwell Collins Fellow in 2016. He was named an IPC Raymond E. Prichard Hall of Fame award recipient in 2018. He serves as the Chairman of the IPC JSTD-002 Solderability committee. Mr. Hillman served as a Metallurgical Engineer at the Convair Division of General Dynamics with responsibility in material testing and failure analysis prior to joining Rockwell. He is a member of ASM, TMS, SMTA and IPC.

Richard Coyle is a Consulting Member of the Technical Staff in the Reliability Engineering Organization of Nokia Bell Labs in Murray Hill, NJ. He is involved in the reliability and quality of electronic assemblies. He utilizes his expertise in materials characterization and metallurgy to perform root cause and failure analyses of interconnects and product reliability risk assessments. In recent years, he has been focused on Pb-free manufacturing, particularly the evaluation and implementation of 3rd generation Pb-free solder alloys for high reliability and low temperature soldering applications. He received his Ph.D. in Metallurgical Engineering and Materials Science from the University of Notre Dame. He is a member of TMS, ASM, the EPS of IEEE, AWS, the Board of Directors of iNEMI, and the Board of Directors of SMTA where he served as VP of Technical Programs.

Charmaine Johnson is a Materials Engineer at Collins Aerospace and previously worked as a Member of the Technical Staff at Nokia Bell Labs in the Reliability Physics department. She received her B.S. in Materials Engineering from Iowa State University. Charmaine works in failure analysis specializing in microscopy and metallurgy.

Tim Pearson is a Materials and Process Engineer in the Advanced Operations Engineering department of Collins Aerospace in Cedar Rapids, Iowa. Mr. Pearson graduated from Iowa State University with a BS in Materials Science and Engineering. Tim began his career as a Thin Films Engineer at Texas Instruments in a 300mm wafer fab. Tim has been working for Collins Aerospace (formerly Rockwell Collins) since 2015. In his current role, he helps develop new manufacturing processes, troubleshoots production issues, and does root cause analysis of failures related to soldering. He is a member of SMTA and IPC.