

# Second Generation Lead-free Solder Alloys – A Challenge to Thermodynamics

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**Summary.** For environmental reasons, lead has to be removed from solder alloys used for interconnection purposes in electronics equipment. A new series of alloys, mainly based upon tin, and often containing copper and silver, has been evolved by empirical reasoning. A more theoretical approach is now being pursued, using thermodynamic principles, to produce the *second generation of solder alloys*.

The paper outlines the soldering process, the requirements of solder alloys, and the various mechanisms (such as overload, fatigue, creep, and thermomechanical fatigue) that are potential causes of failure in service. It also describes from the manufacturing and the performance perspectives, the physical and mechanical properties necessary for reliable solder joints. These include conductivity, melting point, strength, ductility, and thermal stability of microstructure. The challenging question is posed as to *how can thermodynamics contribute to prescribing and developing an improved series of alloys?*

**Keywords.** Alloy design; Lead-free solders; Mechanical behaviour; Service performance; Thermodynamics.

## Introduction

The world's largest industrial sector, Electronics, is facing two major challenges. The continuing miniaturisation of components places ever-increasing demands upon soldered joints to provide structural integrity and reliability. In addition, the content of the common solder alloys is under challenge from the environmental lobby. Most solders contain lead which causes groundwater pollution following landfill disposal of domestic electrical/electronic goods. Ingression of lead has been associated with several medical disorders, and in Europe, lead will be banned from solder alloys from June 2006. The first generation of replacement systems has been evolved on an empirical basis but there is now a concerted effort to develop improved alloys from fundamental principles based upon thermodynamics [1]. This *second generation* is the subject of the present paper.

A defence of ignorance is one of the weakest that can be invoked. Nevertheless, here I will use it as a shield to issue a challenge to the science of Thermodynamics and its practitioners. In essence, the question to be addressed is '*How*

is it possible to progress from the myriad of equations (exemplified for simplicity by  $G = H - TS$ ) that appear to the layperson to exist in thermodynamics, to the capability of identifying an improved alloy system for use as a solder in electronics equipment?" The intention of this presentation is not to point to any solutions but to articulate the question in more detail, so that the experts may have a clearer image of their goal.

## Background

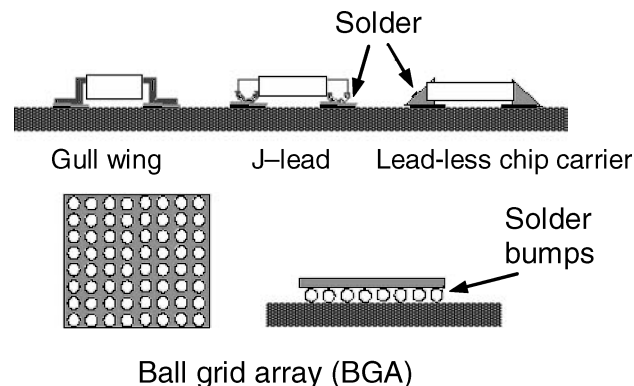
### *Basics of Soldering*

Soldering is a method used to produce permanent electrical and mechanical connections between two metallic materials, neither of which become molten in the joining process. There are four basic ingredients: base metals, solder, flux, and heat. The *base metal* reacts with the molten *solder* to form an *intermetallic compound (IMC)*, which establishes a bond between the two materials. The *heat* supplied must be sufficient to melt the solder (usually 30–40°C above the melting point is employed) but not enough to cause any melting of the metals being joined or damage to the board or components. A range of simple joints is illustrated schematically in Fig. 1.

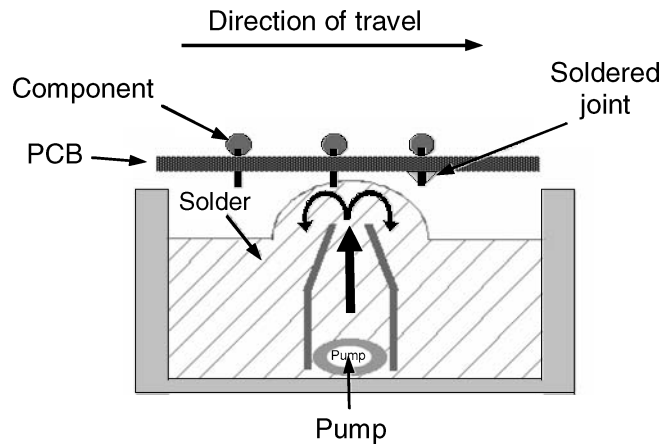
The thickness of an IMC layer increases with temperature and soldering time, and since these compounds are brittle, the joint may become embrittled and weak if the IMC layer is too thick. In electronics, the base metal is generally copper (or Alloy 42, a nickel–iron alloy), found on the printed circuit board (PCB) metallic circuitry, and component leads or pins. If oxidation products form on either the solder or base metals, the quality of the joint is impaired. Therefore, a *flux* is often applied to the surfaces of the base metals prior to soldering to prevent oxidation during heating and to remove any pre-existing oxide layers.

### *Soldering Methods*

The commonest methods of soldering large batches of electronic components are *wave* soldering and *reflow* soldering.



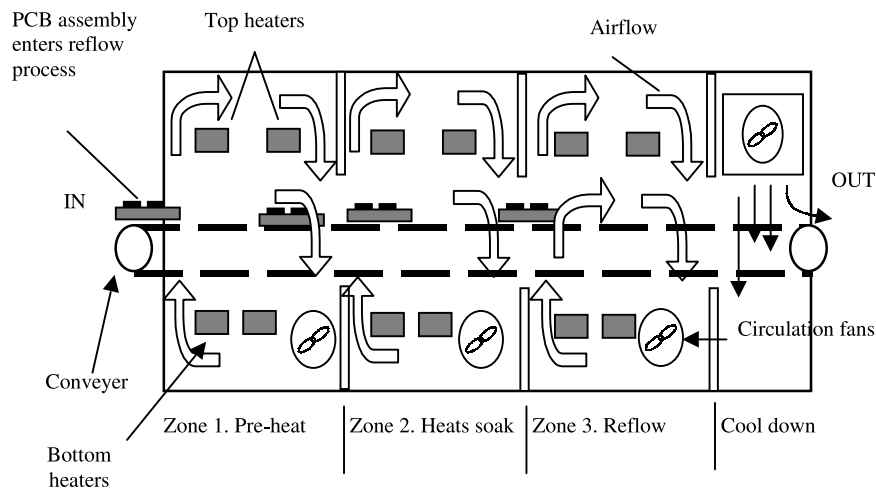
**Fig. 1.** A selection of typical solder joints (schematic)



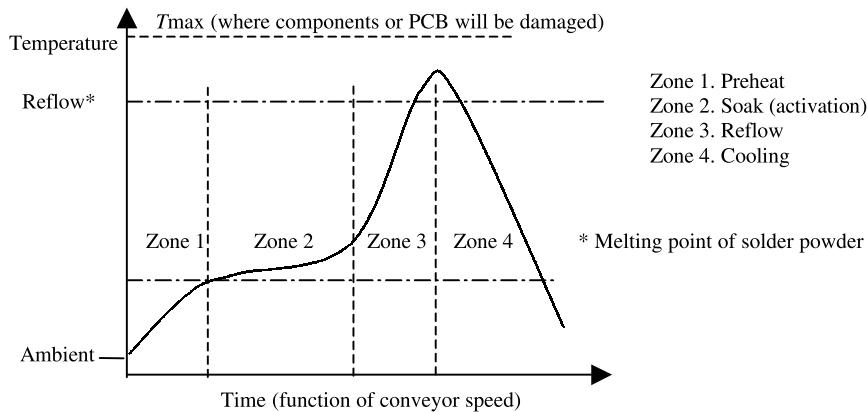
**Fig. 2.** The wave soldering process

Wave soldering involves liquid solder being pumped up through a nozzle against the underside of a PCB carrying electronic components and allowing it to fall back into the bath, and is generally used for the attachment of through-hole components. The solder rises by capillary action up the leads of the plated through-hole components forming the joints (Fig. 2).

In reflow soldering, *solder paste* has the dual function of a source of the solder for the joint and an adhesive for accurate location. The paste is generally printed onto the copper ‘*component lands*’ on the PCB using a screen printer; components are then placed on top of the solder paste (Fig. 3). The board and attached components are passed by a conveyor through a multi-zoned oven to preheat the assembly, activate the flux, and melt (or reflow) the solder paste. The entire soldering procedure lasts for approximately three minutes. During the reflow phase, the temperature is maintained at 30–40°C above the melting temperature of the alloy for between 30–90 seconds depending upon the



**Fig. 3.** Reflow soldering



**Fig. 4.** Thermal profile during reflow soldering

population density of components and the mass of the PCB. A typical thermal profile is shown in Fig. 4, and further details of these processes may be found in Ref. [2].

#### *Requirements of Solder Alloys*

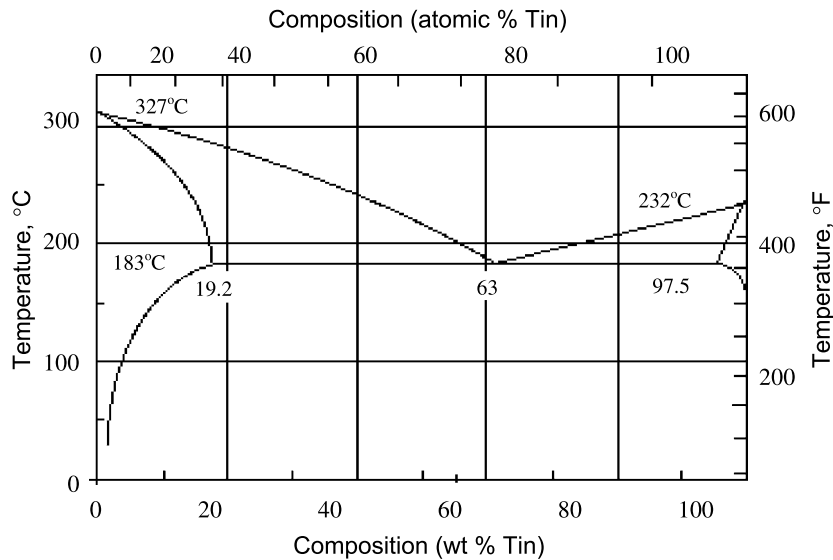
Continuing miniaturisation of electronic equipment and the advent of surface mount technology (SMT) have put a greater focus on the role of a solder joint, especially with regard to its performance in service. However, it should be recognised that processability (or manufacturability) is a paramount consideration from the commercial perspective.

A suitable replacement solder should possess the following attributes:

- be a good conductor of heat and electricity to limit overheating and to ensure functionality;
- possess a low melting point to conserve energy in production and avoid thermal damage to the board material or to the components;
- the liquid solder should quickly solidify to allow rapid production and prevent components moving during the soldering process;
- the alloy constituents should have a lower toxicity than lead, and be readily available and economically priced.

Examination of metallic elements with low melting points indicates that cadmium, mercury, thallium, and lead may be excluded due to their toxicity. Gallium, bismuth and indium are quite scarce elements, unlikely to be available in sufficient quantities. The most promising alloys are based upon tin, which has excellent wetting and spreading properties, is non-toxic, and readily available. Alloying tin with a second or third element improves the mechanical properties and lowers the melting point.

Alloy systems which are suitable for solders are those that contain a *eutectic* reaction in the phase diagram. The melting point is a minimum for the system; solidification is rapid rather than prolonged with a 'mushy' stage, and the resulting microstructure is fine, conveying good mechanical properties. Hence, eutectic



**Fig. 5.** The tin–lead phase diagram

compositions are associated with the lowest costs for heating, minimum thermal damage, and the smallest risk of component displacement during the soldering process. The traditional solder alloy, favoured by the electronics industry, is the eutectic tin-37 weight percent lead (Sn-37Pb) which melts at 183°C (Fig. 5). Slow, equilibrium cooling of molten solder does not occur in practice, and a range of microstructures and properties may result, according to the specific cooling rates that individual joints experience. The other advantages of using lead are its relatively low cost, good wettability/solderability, low production of intermetallics, significant solid solubility in tin which confers strength, and the wealth of information and experience that has been accumulated on this alloy. In specifying replacement alloys, manufacturers would prefer the melting point to be as close as possible to that of Sn-37Pb.

In service, the conditions under which electronic assemblies are required to operate vary dramatically with application. Temperature is frequently the biggest variant and can range from  $-55$  to  $180^{\circ}\text{C}$ . Typical examples include, Consumer electronics and telecommunications equipment:  $-20$  to  $100^{\circ}\text{C}$ ; military applications:  $-55$  to  $125^{\circ}\text{C}$ ; aerospace and automotive applications:  $-55$  to  $180^{\circ}\text{C}$ . The trend is for the degree of severity to increase. *Reliability* may be defined as the probability that a component or structure will perform its intended function for a specified period of time, under a given operating condition, without failure. Again, acceptable values for reliability are application dependent.

#### *Failure in Service*

There are numerous ways in which electronics equipment may fail by mechanical means during service:

*Overload* failures may be ductile or brittle according to the materials involved. Copper, aluminum, and solder elements may be stressed above their yield point

during attachment or by misuse, producing potentially deleterious distortions and residual stresses. In contrast, ceramics, glasses, or polymers below their glass transition temperature may exhibit brittle failures, if their fracture toughness is exceeded. An added complication is the *interface* between the solder and the components being joined. This intermetallic compound (IMC), such as  $\text{Cu}_3\text{Sn}$ , may be generally weaker than the adjacent materials and prone to fracture. Such vulnerability is exacerbated if the interface layer is defective, when delamination may occur.

*Fatigue* failure may occur due to either high frequency vibrational stresses of small magnitude, as in automobile or aerospace electronics, or to occasional high stress applications, as, for example, in keypad pressing. PCB flexing or twisting can transmit stress to the components and joints.

The high homologous temperatures at which solders generally operate ( $T_h \geq 0.6$ ) are likely to produce *creep* deformation. This may be global deformation when there is no physical constraint, or internal redistribution may result in *stress relaxation* under strain-limited conditions. In either case, microstructural damage such as grain boundary voids and cracks may result.

The most common cause of failure of electronics equipment during service is *thermomechanical fatigue* (TMF) of the soldered interconnection. This arises due to the wide disparity in the coefficients of thermal expansion that exists between the material components of a joint. Thermal fluctuations, arising from either power-on/off switching or from changes in the external environment, generate strains which eventually lead to crack initiation, growth, and final failure. The cracks may be contained within the solder or interact with interface between the materials being joined. Because it is the softest material, solder accommodates most of the cyclic damage. Temperature profiles in service introduce dwells at various locations in the cycle and establish low cycle fatigue-creep conditions.

The classic example of thermomechanical fatigue of a soldered interconnection on a PCB is illustrated in Fig. 6. A single temperature excursion is unlikely to produce permanent damage unless it is sizeable and rapidly applied, as in thermal

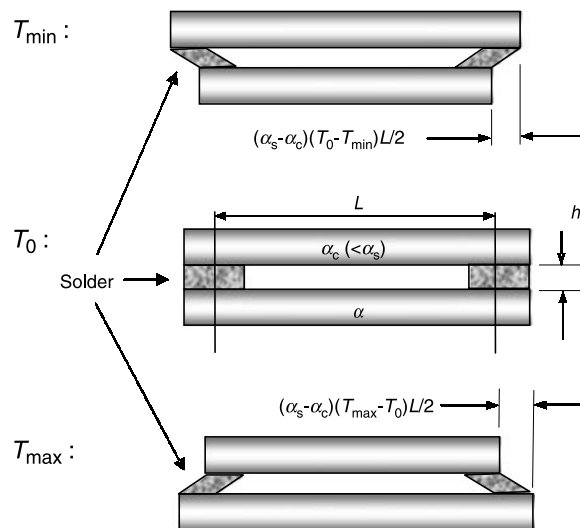


Fig. 6. Thermomechanical fatigue in a model joint system

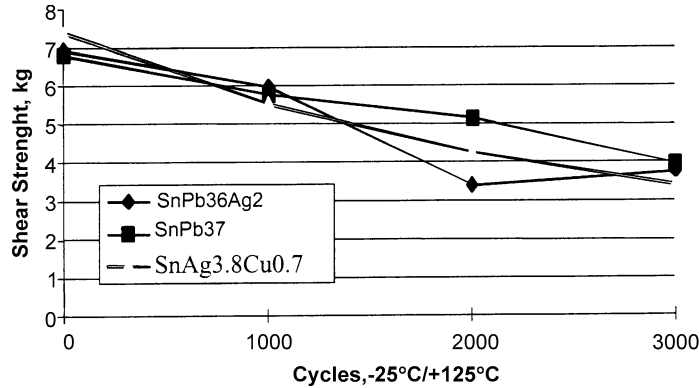


Fig. 7. Loss of joint strength after thermal cycling [3]

shock. The major problem arises during temperature cycling when incomplete reversibility of deformation leads to a gradual accumulation of damage, crack initiation, growth and failure. During thermal cycling, the joint strength diminishes at a rate influenced by the cyclic temperature range, the rates of heating and cooling, and the number of cycles experienced (Fig. 7) [3]. The key question is whether the strength or integrity is retained for the duration of the design life.

#### *The First Generation of Lead-free Solder Alloys*

These have been evolved largely on an empirical basis from various studies worldwide. There is no obvious drop-in replacement for eutectic tin-lead, and the majority of possible alternative alloys fall into one of the following groups: Tin-silver, tin-copper, tin-silver-copper, tin-silver-bismuth, and tin-zinc-bismuth (Table 1).

The first generation of lead-free alloys differ from Sn-37Pb in that the solute content in the tin matrix is substantially (up to 70×) smaller. As a consequence, whereas the latter possesses a conventional two-phase microstructure, the new systems fall into the particle-reinforced or solid solution categories. This can have a profound affect on microstructure (Fig. 8) and mechanical response, especially creep behaviour [5]. The high homologous temperature each group normally experiences results in microstructural instability, which is enhanced by the presence of strain or cyclic strain. In practical terms, a freshly formed solder joint is unstable. Equating solder alloys at room temperature to nickel-base superalloys

Table 1. Solder compositions and melting points [(e) denotes the eutectic composition] [4]

Alloy system	Composition (wt%)	Melting range (°C)
Sn-Bi	Sn-58Bi	138 (e)
Sn-Bi-Zn	Sn-8Zn-3Bi	189-199
Sn-Ag	Sn-3.5Ag	221 (e)
Sn-Cu	Sn-0.7Cu	227 (e)
Sn-Ag-Bi	Sn-3.5Ag-3Bi	206-213
Sn-Ag-Cu	Sn-3.8Ag-0.7Cu	217
Sn-Ag-Cu-Sb	Sn-2Ag-0.8Cu-0.5Sb	216-222

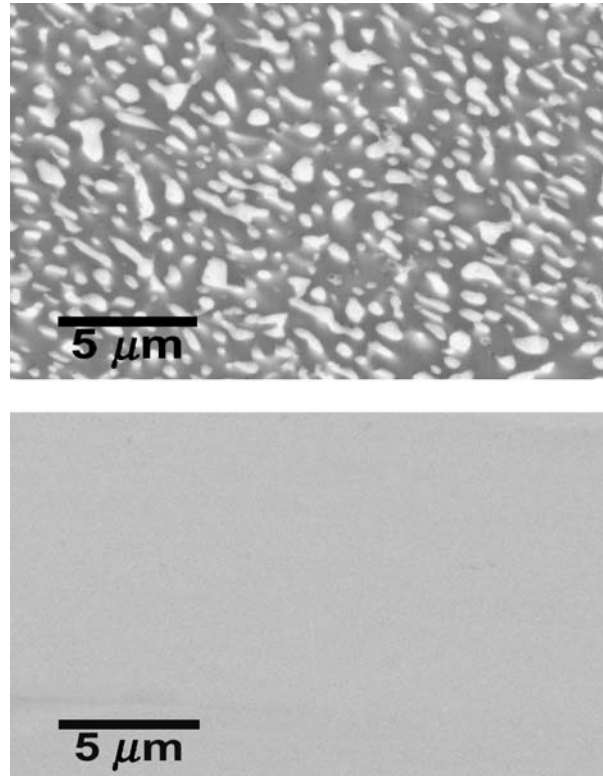


Fig. 8. Microstructures of Sn-37Pb and Sn-0.5Cu after rapid cooling

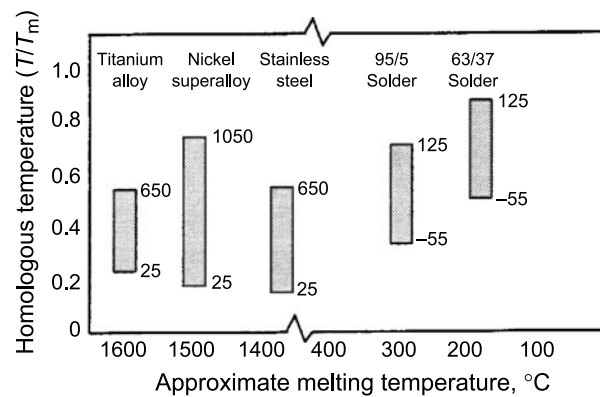


Fig. 9. Homologous temperatures of operation of some engineering alloys [6]

operating at temperatures in excess of 1000°C is a challenge to perception but Fig. 9 demonstrates that this is the case [6].

### Current Design

Strategies are usually based upon accelerated testing that involves an enlarged temperature range and an abbreviated cycle in which dwell periods are severely



curtailed, and heating and cooling rates increased. The acceleration factor is simply the ratio of the service lifetime to the duration of the accelerated test, and its value is usually in the 'hundreds'. The temperature range is equated with a strain range, and this is employed in an equation for life. The most common example is the *Coffin-Manson* expression, [7, 8] or a modified form of it, *i.e.*,  $\Delta\varepsilon_p N_f^\alpha = C$  where  $\Delta\varepsilon_p$  is the plastic strain range per cycle,  $N_f$  is the number of cycles to failure, and  $C$  and  $\alpha$  are constants.

Standards exist for accelerated testing and for life estimation [9, 10]. Considerable empiricism is involved, and where high reliability is required, the validation programme for statistical analysis may be prohibitively long [11]. This problem is accentuated with continuing miniaturisation and more severe demands in service.

Some investigators mechanically apply the estimated thermal strain range, and this can accelerate testing dramatically [12] because it eliminates time-dependent behaviour. However, the critical, and sometimes ignored, assumption is that the dominant failure mechanism remains unchanged in both service and the accelerated test. For example, failure by thermomechanical fatigue may involve any of several mechanisms: time-independent high strain fatigue, time-dependent creep or stress relaxation which may be either matrix or grain boundary processes, or a mechanistic interaction between fatigue and creep in which a growing fatigue crack is accentuated by prior creep damage. Their relative importance depends on the conditions encountered in service. Since each mechanism may be described by a distinctive equation, the need to identify the controlling process is obvious.

### Requirements of New Alloys

Performance of an interconnection is strongly influenced by the geometry and distribution of the components and the joints, the materials, and their thermal history. From the solder perspective, it should retain its mechanical integrity when subjected to TMF. To achieve this, it should be resistant to thermal deterioration associated with the substantial homologous temperatures *and* the mechanical degradation resulting from strain and cyclic strain. Processes such as coarsening and slip band intensification may be accentuated by such mechanical factors [13].

So, the challenge to thermodynamiscists is to prescribe an alloy of the optimum composition and the optimum microstructure. In this context, several questions arise:

- Is it possible to achieve intrinsically stable precipitates – *e.g.*, by manipulating the coherency of interfaces of particles and phases?
- Is thermodynamic equilibrium a realistic condition?
- Assuming that the effect of temperature can be accommodated in particle/phase coarsening, is it possible to include the additional effects of strain and cyclic strain?
- If stability cannot be achieved, can these parameters be incorporated in mapping microstructural change – and hence change in mechanical properties?

While several possible mechanisms of failure in service have been described, probably the most important and challenging is thermomechanical fatigue. This is

now considered in a context of ‘thermodynamics’ approach to the prescription of improved alloys. Assuming that the requirements relating to toxicity, processability, and melting point ( $\leq 230^{\circ}\text{C}$ ) have been satisfied, the ability of an alloy system to resist thermomechanical fatigue is governed by:

- The service operating temperatures – more strictly the homologous temperatures encountered. As the temperature increases, precipitate, phase, and grain coarsening occur to reduce overall energy. This may be associated with a fall off in strength although the effects on ductility may vary [14].
- The range of temperature experienced – this can be equated with the cyclic strain range and has a profound influence on the number of thermal cycles to cause fatigue failure.
- Mean temperatures may be associated with mean stress or strains but these are usually eliminated by the cyclic plasticity developed during the temperature excursions, as high mean stresses and cyclic plasticity are incompatible [15].
- Heating and cooling rates may be influential if they are dissimilar when time-dependent damage in one direction is not balanced or cancelled by that in the reverse direction.
- The presence of isothermal dwells allows time-dependent damage, particularly in grain boundaries which may be additive to the purely cyclic damage. As for heating/cooling rates, accumulation of damage may occur when the dwells are not balanced. This is likely to be the case in TMF since the hold periods will be at different temperatures and dwells of equal duration will be associated with quite different amounts of damage.

## Conclusions

The second generation of lead-free alloys for use as interconnections in electronics has to satisfy the demands of production/manufacture (melting point, toxicity, cost, availability). With regard to performance, and in particular thermomechanical fatigue, successful alloys should be stable, and retain their properties (strength, ductility, creep, and fatigue resistance) in the face of prolonged exposure to high homologous temperatures, cyclic temperatures, and mechanical strain. The nature of precipitates, phase boundaries, and other interfaces has an important role to play.

Prescription of optimum, or near optimum, compositions and microstructures presents a major challenge. Thermodynamics has the ball – Good Luck!

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