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**AN INVESTIGATION OF AGING KINETICS AND
CREEP DEFORMATION IN COMPOSITE SOLDERS
WITH IN-SITU PARTICULATE REINFORCEMENTS**

By

Sunglak Choi

A THESIS

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ABSTRACT

AN INVESTIGATION OF AGING KINETICS AND CREEP DEFORMATION IN COMPOSITE SOLDERS WITH IN-SITU PARTICULATE REINFORCEMENTS

By

Sunglak Choi

The motivation for this study is to improve the reliability of lead-free solder joints in electrical systems while removing lead. Solder microstructures under service conditions at high homologous temperatures tend to be highly unstable, resulting in failure of solder joints. This is caused by enhanced microstructural coarsening resulting from thermally-induced or mechanical stress. To improve the reliability of solder joints as well as to eliminate lead, lead-free *in-situ* composite solders based on eutectic Sn/Ag (96.5Sn/3.5Ag), which is a potential candidate for replacing leaded solders, were developed. A similar composite approach also was used with the eutectic Sn/Pb matrix for comparison. The creep behavior of unaged and aged composite solder joints was improved by a factor of 100-1000 as a consequence of the composite phase. Although the creep resistance of aged joints were degraded, composite solders still exhibited better creep behavior as compared to the corresponding non-composite ones.

To My Parents and Wife

Eunsang Choi, Oksun Lee, and Junghee Sung

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CHAPTER 1

INTRODUCTION

Soldering is one of the oldest and most widely used metallurgical joining techniques. Soldering is technically defined as joining two base materials through the use of a third “filler” metal with a melting temperature below 425°C (800°F) [1, 2].

The earliest recorded evidence of soldering was found in Mesopotamia in 4000 B.C. when the gold-based hard solders were developed. Use of these solders was also found in Egypt (3600 B.C.), Ur (3400 B.C.), Greece (2600 B.C.), and other Mediterranean regions. The first mention of soldering is 3000 years ago in the Bible (Isaiah, 41:7) [3]. The first use of soft Sn/Pb solders historically appears to be about 1900 B.C.. It was the Celts and the Gauls in Northern and Central Europe that developed soft soldering. It was noted by the first Romans to enter the region that the Celtic pieces with high quality were constructed with tin-lead soft soldering. The Romans borrowed the expertise of the Celts on soft soldering technique and used tin/lead solders extensively in their construction of aqueducts. The soft soldering was continuously used since then as a joining method in fabrication of many crafts, plumbing, water container, and larger structures (e.g., automobile radiators). It was in the early 20th century that soldering technology entered the electronic industry. In those early applications, the soldering technology served a reliable means to provide electrical continuity between components. The electronic revolution has promoted further miniaturization and increased performance of devices

with the invention of silicon-chip technology. Soft soldering has been adapted to microchip packaging and higher level system assembly [2].

The most common solder materials are tin/lead solders. These solders have been used to join metals for at least a millennium, and they have been the most outstanding material for the interconnection and packaging of modern electronic components and devices during the past several decades. The prevalent use of tin/lead solders is due mainly to their low cost and unique combination of material properties [4].

Lead-bearing solders are categorized as either tin-based tin/lead solders or lead-based lead/tin solders. Tin-based tin/lead solders comprise the largest group of alloys used in electronic industry. The typical tin-based tin/lead solders are eutectic tin/lead (63Sn/37Pb) and near eutectic tin/lead (60Sn/40Pb) that are used most extensively in circuit-board assembly because their melting temperatures are low enough that processing can be compatible with printed wiring board materials and electronic devices. Lead-based lead/tin solders are not used in printed wiring board assembly because they show poor flow and their higher melting temperatures are incompatible with printed wiring board materials. Within that group, 95Pb/5Sn and 90Pb/10Sn are used in the controlled collapse chip component (C⁴) attachment of silicon chips to package boards [2].

However, in the light of environmental and health concerns, there have been increasing research efforts during the past few years to develop lead-free solders to replace the Sn/Pb alloys [5]. Lead and lead-bearing compounds are among the most toxic substances, and the environmental and health issues concerning the toxicity of Pb

threaten to ban the use of lead-bearing solders in electronic applications. These concerns have inspired a great deal of research efforts in the development of suitable Pb-free solder alloys.

The potential candidates of lead-free solders which have been investigated are eutectic Sn/Bi (42Sn/58Bi), eutectic Sn/Ag (96.5Sn/3.5Ag), eutectic Sn/Zn (91Sn/9Zn), and eutectic Sn/In (48.3Sn/51.7In). Even though some lead-free solders have been in use in special applications for several years (e.g., eutectic Sn/Bi (42Sn/58Bi) for step soldering which illustrates the use of progressively lower melting point solder alloys in subsequent assembly levels to preserve the integrity of the previously solidified joints [6], and eutectic Au/Sn (80Au/20Sn) for creep-resistant soldering in optical-fiber alignment and packaging [6]), there is no obvious substitute for lead/tin solder alloys at present.

Miniaturization in the microelectronics industry and the widespread use of surface mount technology (SMT) which was introduced in the 1960s have demanded higher performance on solders. Solders have to provide structural function by mechanically supporting the electronic devices in addition to playing a role of electronic contacts between printed circuit substrates and surface mount devices [7]. The mechanical properties of solders have become more important because of the small-size of solder joints in high density surface mount device (SMD) packages. Thus the development of alternative lead-free solder with superior mechanical properties to Sn/Pb solder to improve reliability of solder joint while removing lead in electronic packaging appears to be desirable. This thesis describes the development of *in-situ* composite solders and preliminary evaluation of improvements of properties.

CHAPTER 2

REVIEW OF RELATED LITERATURE

2.1 GENERAL CHARACTERISTICS OF SOLDERING

2.1.1 Soldering

Soldering is defined as “a joining process by which two substrates are joined using a filler metal (solder) which forms strong bonds with the flux on solidification [1]. The substrate materials remain solid during the joining process and the solder is distributed between the properly fitted surfaces of the joint by capillary action. The fundamental feature of the soldered joints is that a metallurgical bond is produced at the solder/substrate interface. The soldering temperatures in processing typically range from 30 to 50°C (55 to 90°F) above the liquidus temperature to ensure appropriate heating of the substrate and sufficient flow of the solder [8].

2.1.2 Solder

Solder is usually defined as fusible alloys with a liquidus temperature below 425°C (800°F) [9]. Solders are typically binary or ternary alloys. Most solder alloys are eutectic or near eutectic to take advantage of a low melting point.

The melting temperature of solders is a critical characteristic in practical joining processes because it determines the minimum processing temperature and the maximum operating temperature of the system. The mechanical and physical properties of solder such as strength, creep-fatigue resistance, thermal expansion coefficient or conductivity,

and corrosion are also of importance because the solder provides a means of fastening two components together. When a molten solder is used in processing, its surface tension is another important factor in determining its wettability with the substrates [10].

The solder can be typically applied in two different ways, (i) coating the surface, and (ii) an application of discrete amount. The common types of discrete solder placement are solder paste and preforms. The solder paste refers to a homogeneous mixture of prealloyed solder powder and flux in a composition that is a stable suspension and suitable for dispensing. The solder preform is defined as a shaped form of solder that has a determined amount of metal with or without a flux core of fixed size. These special forms of solder are used when proper amounts of the solder is necessary at individual joints to form a satisfactory joint [11].

2.1.3 Flux

Fluxing is used to produce a reliable bond between solder and substrate by improving the wetting properties of the solder/substrate system. Flux has significant influence on the wetting behavior of solder with substrates that determines the solderability of the solder, so the selection of flux and the development of new fluxes for a specific soldering application are important [12].

The major function of flux is to remove the thin tarnish layers on the surface of the substrates during the initial steps of the soldering process, allowing the molten solder to spread and react with the substrate. The additional roles of the flux are that it lowers the

surface tension of the solder, so that it more readily fills gaps and holes by capillary action and protects the metal surface from reoxidation during the heating stages.

The principal components of the flux are active chemical components such as halides for oxide removal, wetting agents to enhance surface spreading, and a vehicle to dilute and mix the cleaning compound and wetting agents together. The vehicles are usually water, isopropyl alcohol, glycerin, glycol (for liquid fluxes), and petroleum jelly (for flux pastes or cream).

Fluxes are categorized by their cleaning agent as following : rosin-base fluxes, organic-acid fluxes (also called intermediate or water-soluble fluxes), and inorganic-acid fluxes. The most common fluxes are rosin-based in the electronic applications. The rosin-based fluxes are divided into three classes according to their activity [13] :

- RA - rosin base, fully activated fluxes with a strong ionic activator such as halide,
- RMA - rosin base, mildly activated fluxes containing lower concentrations of halides or activated with organic acids (halide free), and
- R - rosin base fluxes without any activators, relying on the very weak organic acids in natural rosin for the fluxing action.

2.1.4 Substrate

Substrate is a base material on which electronic devices are soldered using a flux. The surface layer of a substrate consists of the so called solderable layer to which the molten solder metallurgically reacts and the additional coating or protective layer to preserve solderable layers from excessive oxidation on the solderable surface during atmospheric storage, prevent dissolution of the base metal, provide a good wettable surface for soldering [14].

The solderable surface can be either the substrate itself, usually copper, or coatings of elemental metals such as nickel or copper deposited by electroplating, electroless plating, evaporation, pretinning (solder dip coating), sputtering, chemical vapor deposition (CVD). The protective layer is an electroplated film that is entirely absorbed into the solder during soldering process. Protective layers are precious metals such as gold [15]. Less protective layers are electroplated tin and electroplated tin-lead solder.

Intermetallic compounds normally form at the interface between the solder and the substrate. Intermetallic reactions typically proceed much more slowly on Ni than on Cu substrates [16]. Sn/Pb solder system forms Cu/Sn intermetallic compounds (Cu_6Sn_5 and Cu_3Sn) on Cu substrate [17]. Other solder systems, such as Sn/Ag, Sn/Cu, and Sn/Bi, all form the same intermetallic compounds as Sn/Pb solder on both Cu [18, 19] and Ni substrates (Ni_3Sn_4 , Ni_3Sn_2 intermetallic compounds) [20]. Eutectic Sn/In solder is different from other Sn-based solder since ternary compounds are formed on Cu substrate, which are $\text{Cu}_2\text{In}_3\text{Sn}$ on the solder side and $\text{Cu}_2(\text{Sn}, \text{In})$ on the Cu side. On Ni

substrate a ternary In/Sn/Ni intermetallic forms whose stoichiometry has not been determined [16, 21].

The dissolution of the substrate into the solder when molten solder is in contact with substrate is another concern in electronic applications because the dissolved metal may adversely affect the solder microstructure and material properties [22]. Such dissolution of the substrate can (a) alter the alloy composition which may raise or lower its melting temperature, (b) alter the microstructure [16] and/or (c) cause dissolved metal to come out of solution in the form of undesired precipitates during the cooling process [15].

The dissolution of the substrate should be avoided to prevent degradation of solder joints. Foster [15] found that presence of gold in solder matrix forms gold/tin intermetallic compound which deteriorates the mechanical properties of solder alloy and recommended most of gold should be removed from the joint area. The removal of gold could be achieved by abrasion or by dissolving the gold in molten solder. Goldstein and Morris [16] reported that the Cu dissolution in the solder joint could be avoided by additional coating of nickel on Cu substrate since Ni diffuses much more slowly than Cu into the solder joint.

2.1.5 Solder Joint

Solder joints consist of three main components : the electronic device, solder, and the substrate. A variety of solder joints geometries in electronic applications have been developed. The selection of the connection type is determined by manufacturing, electronic and service considerations. Schematic examples of typical joint configuration

in electronic products are shown in Figure 1 [23, 24], and sample geometries that are used for the testing of solder joints are illustrated in Figure 2 [25, 26].

The two major classes of soldering technologies are through-hole technology and surface-mount technology. Through-hole technology refers to the soldering of the leaded device packages through a hole on substrate. The leads are inserted into the holes in the printed wire board (PWB) and are soldered in place. In the surface-mounted technology smaller components are soldered directly to the surface of the printed circuit board (PCB). Surface-mounted technology made it possible for components to be mounted on both sides of the board.

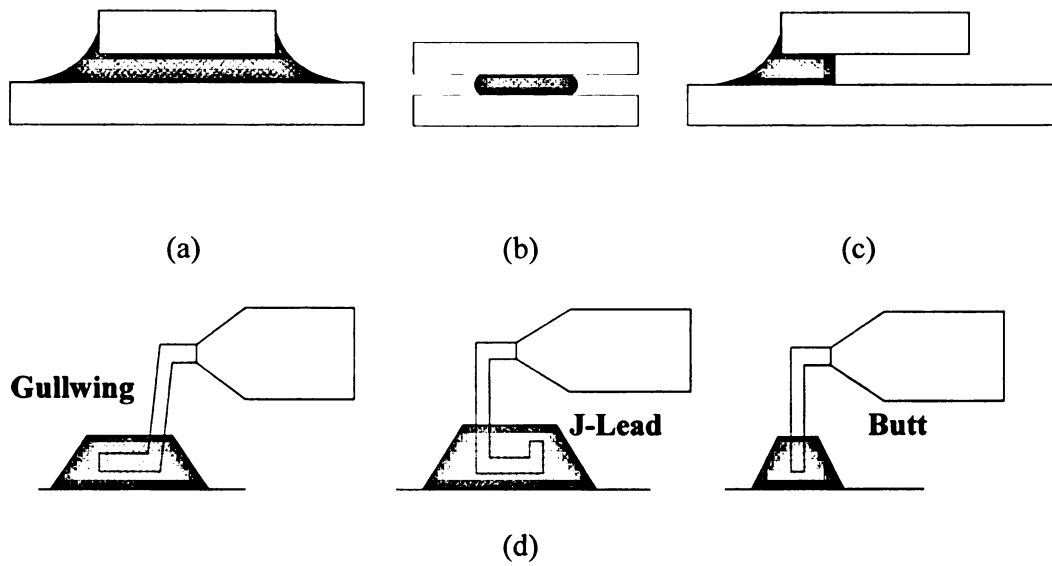


Figure 1 Schematic Diagram of Typical Joint Configuration

(a) Die or Substrate Bonding (b) Solder Bump

(c) Leadless Chip Carrier (LLCC) (d) Leaded Chip Carrier attachment

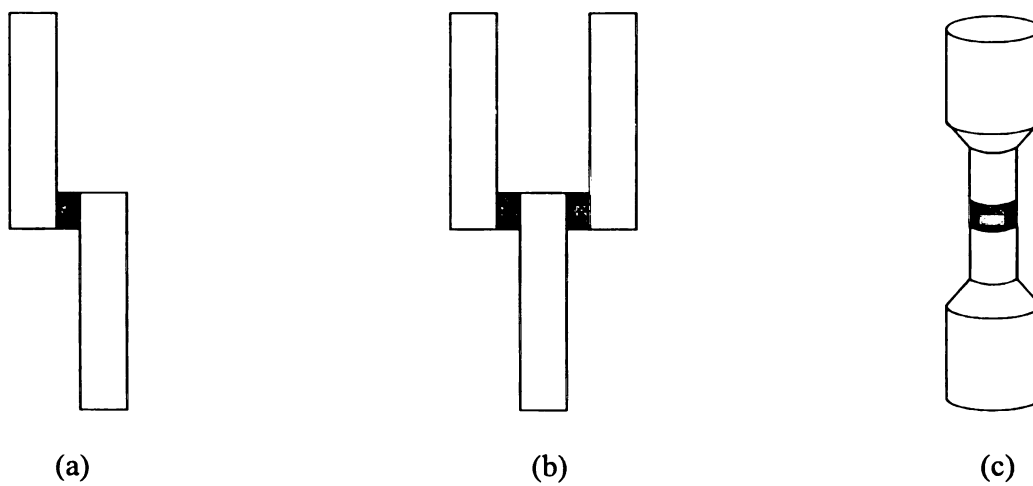


Figure 2 Sample Geometries for the Testing of Solder Joint

(a) Single Shear Lap Joint, (b) Double Shear Lap Joint, (c) Butt Joint

2.1.6 Service Conditions of Solder Joints

Soldering is by far the most economic and popular method to interconnect components to printed circuit boards or chips to substrate. With the advent of surface mounting technologies in 1960s, the miniaturization and functional integration of electronic modules have been pursued much more. As a consequence, solder joints became structural components by mechanically supporting the electronic devices [7], in addition to providing electrical connection between surface mounted devices and substrates. Consequently solder joints in electronic applications experience more severe conditions that critically affect the deformation behavior and reliability of solder joints.

The principal sources of deformation in service conditions are thermal fluctuations and mechanical vibrations. The thermal fluctuations stem from the heat generated within the devices themselves and temperature changes from the external operating circumstances [1]. When an electronic module is subject to thermal fluctuation in service, thermal strains which are cyclic in nature are induced in the joint due to the difference in the coefficients of thermal expansion produced by the various materials used. Since the solder is usually much softer than the other joint components, most of deformation generated is concentrated within the thin layer of solder joint.

The thermally-induced strain can be depicted using the schematic diagram in Figure 3 [24, 27]. Assumptions which should be applied in a simple model are that there are neither temperature gradients nor transients, and that the solder is fully pliant, or relaxes

fully. If the temperature changes from T_0 to T , this will then cause a thermal shear strain γ distributed uniformly through the solder joint.

$$\gamma = \frac{\left(\frac{L}{2} \cdot \Delta \alpha \cdot \Delta T \right)}{H}$$

γ is the thermally induced shear strain, $\Delta\alpha (= \alpha_1 - \alpha_2)$ is the difference in expansion coefficients between printed circuit board and component, ΔT is the amount of temperature change, L is the distance between the pinning points, and H is the height of the joint.

Solders have inherently low melting temperatures which are critical for solder processing and operation in electronic applications. These low melting temperatures of solders give a disadvantage in service conditions, or even at room temperature which corresponds to a high homologous temperature. The homologous temperature of a material refers to the ratio of a given temperature to the melting temperature in degrees K [28]. The conditions for solders are compared to high temperature structural alloys in Figure 4 [29]. These service conditions for solder consequently mean that time dependent effects such as creep, stress relaxation, surface and microstructural changes should be considered in the analysis of deformation behavior, in addition to cyclic phenomena.

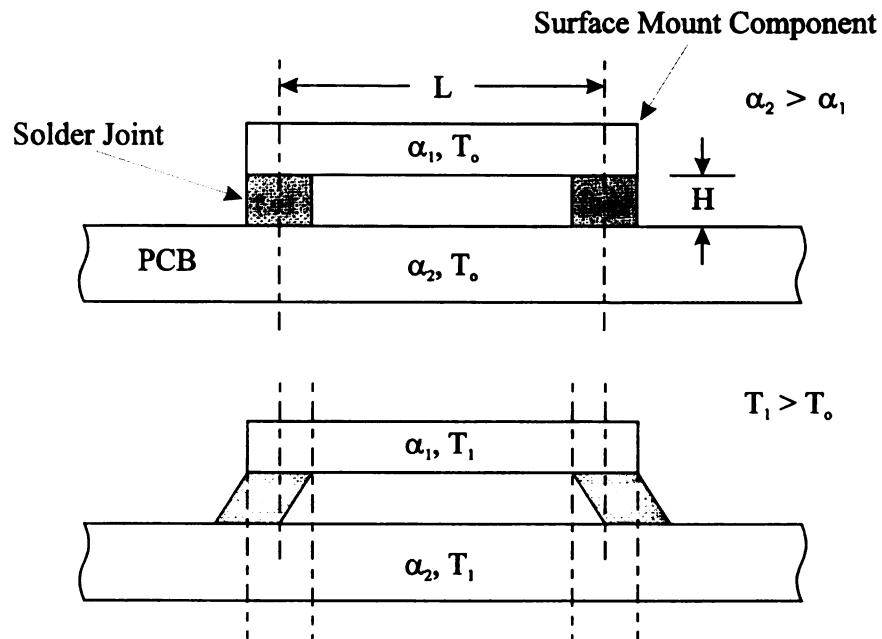


Figure 3 Schematic Diagram of Thermally Induced Strain in Solder Joint [24, 27]

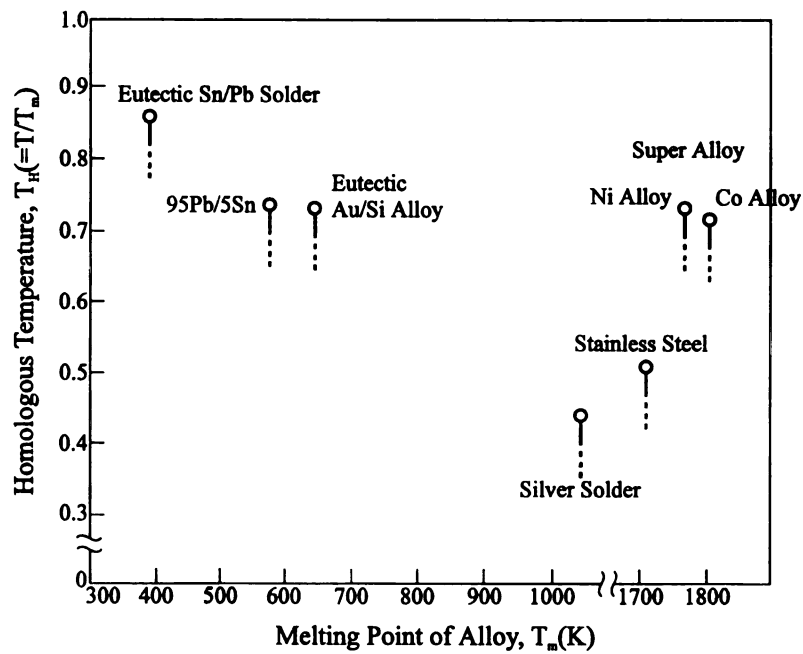


Figure 4 The Service Condition for Solders [29]

2.2 SOLDER MATERIALS

2.2.1 Tin/Lead Solder

Lead-bearing solders consist of the largest group of alloys used in electronic products. Within that group, the tin/lead eutectic (63Sn/37Pb) and near eutectic (60Sn/40Pb) solders are used most extensively in circuit-board assembly. The lead-rich lead/tin solders (5Sn/95Pb, 10Sn/90Pb) are commonly used at relatively high temperature applications (100°C to 250°C) such as for joining sections of automotive radiators. The Sn/Pb solders with high melting temperature are also used in controlled-collapse chip connection (C4) technology to attach integrated-circuit chips to packages for use in high speed computers [30].

The tin/lead solder has been widely used in electronic applications because of the several advantages of the tin/lead solders. The eutectic tin/lead(63Sn/37Pb) and near eutectic (60Sn/40Pb) solders have sufficiently low melting temperature making them compatible with printed wired board materials and electronic devices during processing. Lead is relatively inexpensive and there are abundant resources of lead located in the United States [2]. Lead as an impurity in the tin/lead solders also prevents the white (β) tin to gray (α) tin allotropic transition when cooling through 13°C which is referred to as “tin pest” because of the loss of structural integrity by tin in cold service [31]. Lead also lowers the surface tension in tin-lead solders relative to pure tin [32, 33], thereby improving the solderability of circuit boards and devices by facilitating the wetting of the solder. The wettability of 60Sn/40Pb solder appears to be better than any other solder

alloys in terms of lower contact angle (θ_c), faster wetting rate, and shorter time required to form joints [34].

According to the phase diagram of tin/lead [35], the binary system of tin/lead shown in Figure 5 is a simple eutectic which has lead-rich α -Pb phase and tin-rich β -Sn phase. The tin-rich β -Sn phase has negligible equilibrium solubility for lead at room temperature. The lead-rich α -Pb phase can contain 1~2 wt.% tin at room temperature and the amount of Sn soluble in the lead-rich α -Pb phase increases considerably as temperatures are elevated. The solubility of Pb in β -Sn phase also increases appreciably with temperature.

Upon solidification, a two-phase microstructure is developed, the morphology of which is dependent upon the cooling rate. Slow cooling rate produces a lamellar microstructure of alternate layers of lead-rich and tin-rich phases. Volumes of lamellae of similar orientation are known as colonies (or grains). With increasing cooling rate, the colony size and interlamellar spacing decrease and with a high cooling rate, a fine spheroidal structure is obtained.

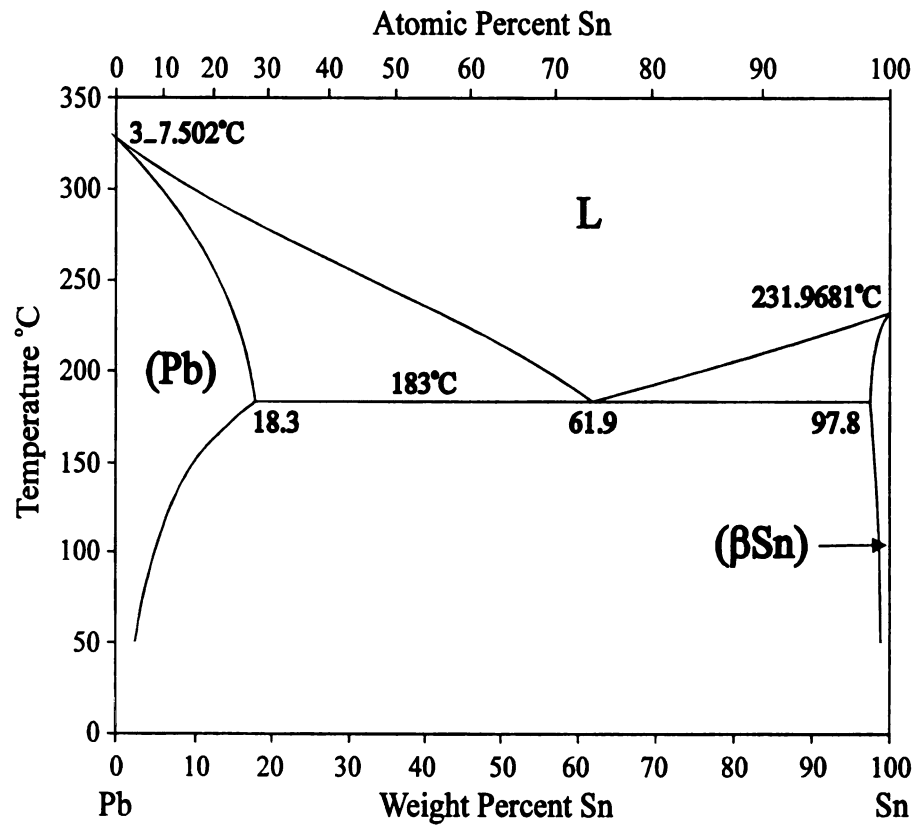


Figure 5 Sn/Pb Phase Diagram [35]

The microstructure of Pb/Sn alloys has great influence on deformation behavior and mechanical properties. The microstructure of Pb/Sn solder alloys formed by fast cooling rate exhibit superplastic behavior in creep tests as a consequence of the fine globular microstructure, grain boundary sliding at low stress and low strain rate and reduced strength, increased ductility, and a significantly increased the fatigue life by delaying crack initiation and growth [36, 37]. These desirable effects on mechanical behavior and properties result from fine and equiaxed microstructure and uniform distribution of eutectic phases which can be obtained from the fast cooling rate on solidification.

The microstructure of tin/lead alloys has the inherent microstructural instability which arises from high solid solubilities of the constituent elements within the two phases combined with service at high homologous temperature. Due to the high homologous temperature ($T/T_m = 0.64$ at 20°C) of tin-lead alloy even at the room temperatures, it is subjected to the precipitation of tin colonies within the lead-rich phase and overall coarsening of the lead-rich and tin-rich phases [38]. The microstructural changes due to precipitation and coarsening result in degradation of mechanical properties such as strength, ductility [39, 40], and microhardness [30].

The microstructural instability of eutectic and near eutectic Sn/Pb solder is also observed under thermal fatigue (thermal cycling), isothermal fatigue (mechanical cycling), and creep in shear at high temperature which occur in solder joints [41, 42]. The combination of shear strain and high temperature in these deformations creates regions of concentrated plastic deformation, which result in an inhomogeneously coarsened band similar to the recrystallization and grain growth, within the solder joints. This

heterogeneously coarsened band which is the weakest region becomes a source of crack initiation and propagation in solder joints.

Although the majority of the investigations have revealed that failures in the joints occur through the solder via a heterogeneous coarsening of the microstructure, some of the studies performed had failures occurred through the interface with intermetallic layers present in solder joints after exposure to high homologous temperature during deformation [43, 44]. It was also found that the joint strength was decreased as the thickness of the interfacial intermetallic layers increased [45]. Because the intermetallic layers tend to be brittle and the strain is induced in the joint due to the differing coefficients of thermal expansion between the solder and substrate, the reliability of a solder joint can be degraded by the presence of interfacial intermetallics.

For the Cu substrate with Sn/Pb solder, Sn reacts with Cu forming Cu_6Sn_5 η -phase which has a hexagonal crystal structure [46] adjacent to solder, and Cu_3Sn ϵ -phase which has a pseudo-hexagonal crystal structure [47] next to the Cu substrate as shown in Figure 6 [48]. Cu_6Sn_5 η -phase is formed during solidification but Cu_3Sn ϵ -phase is found to form during aging after solidification. The interfacial intermetallic layers grow faster when the solder is molten and will also continue to grow after the joint has solidified. The Cu_3Sn ϵ -phase was considered to grow at the expense of Cu_6Sn_5 η -phase [49, 50]. The mean total thickness of the interfacial intermetallic layers was observed to increase linearly with the square root of aging time and the growth was faster for higher annealing temperature, suggesting that the growth of interfacial intermetallic layers is controlled by the volume diffusion

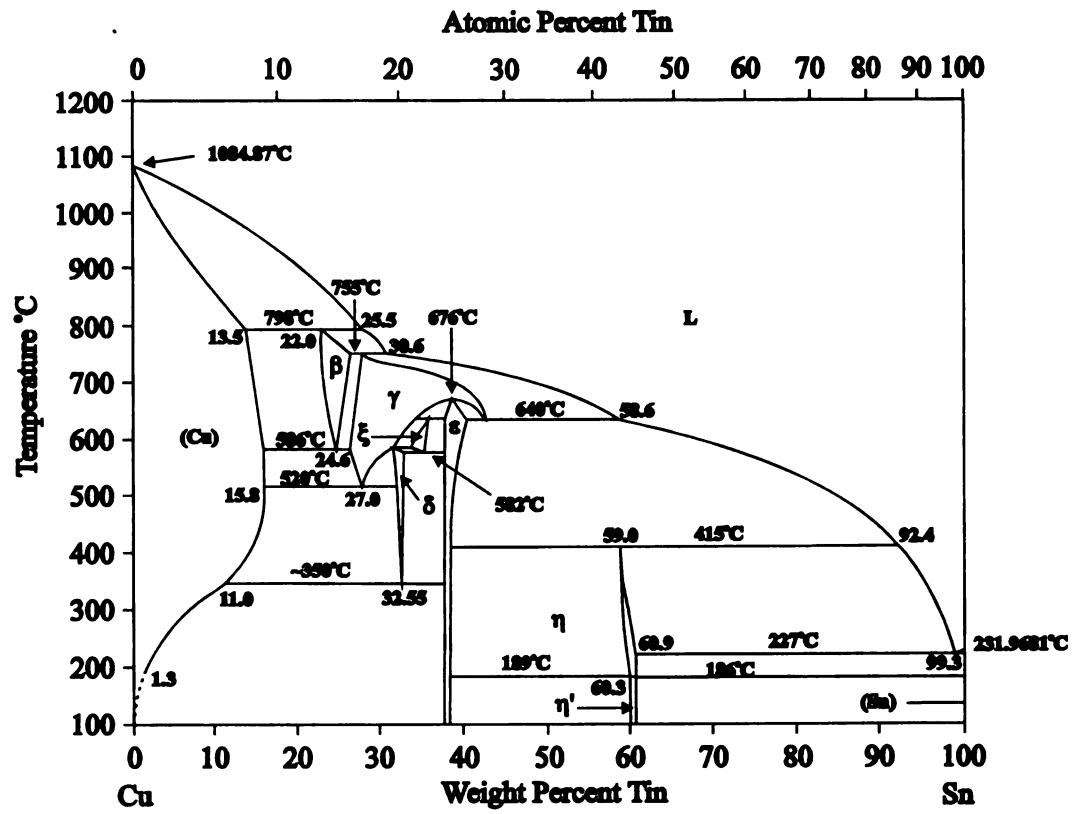


Figure 6 Cu/Sn Phase Diagram [48]

mechanism and the rate is controlled by the interdiffusion of active species, i.e. Cu and Sn [50].

The growth of the interfacial intermetallic layers appeared to alter the fracture behavior, wherein at as-soldered condition the joint failed through the solder but after aging, the joint showed brittle fracture through the interfacial intermetallic layers with increased thickness of the intermetallic layer. The failure behavior and strength of solder joint was very sensitive to the thickness of Cu_6Sn_5 interfacial layer [17, 51]. The growth of the interfacial intermetallic layers was observed to be suppressed in the presence of Ni in the Sn-Pb solder by increasing the activation energy for the solid state growth [50, 52].

The Cu-Sn intermetallic compound was also found in the Sn-Pb solder matrix in the joint [53]. Cu_6Sn_5 η -phase precipitates in rod or whisker form were observed in the Sn grains of solder joints. Cu diffused through the interfacial Cu_6Sn_5 η -phase layer and dissolved into the solder during reflow of the solder joint. The Cu_6Sn_5 η -phase precipitated from the supersaturated solid solder with Cu which was produced by further cooling because of the decreasing solubility of Cu in the solid solder with decrease in temperature. The bulk solder with Cu_6Sn_5 η -phase showed a smaller elongation at failure and higher work hardening rate than the pure solders [54].

2.2.2 Tin/Silver Solder

Tin/silver solder, especially eutectic tin/silver (96.5Sn/3.5Ag), is being considered as a potential lead-free candidate because tin/silver solder is basically free of toxic lead and it is better for high temperature applications due to its high melting temperature, and silver is available in sufficient quantities to be considered as minor alloying element [55, 56].

Like eutectic lead/tin solder (63Sn/37Pb), eutectic tin/silver solder (96.5Sn/3.5Ag) consists of two phases which are essentially pure tin-rich base-centered tetragonal (bct) β -phase with less than 0.04% Ag in volume fraction, and Ag_3Sn intermetallic orthorhombic short-range ordered ϵ -phase with less than 5% in volume fraction [56, 57]. The Sn-Ag phase diagram shown in Figure 7 [57] indicates virtually no solid solubility of Ag in Sn-rich phase even at temperatures near the melting point. Eventually all the Ag in the 96.5Sn/3.5Ag resides in the Ag_3Sn intermetallic compound.

The microstructure of 96.5Sn/3.5Ag might be altered depending on the soldering process, process parameters, thermal history after soldering, alloying elements, and deformation. In laser reflow soldering, the size and morphology of Ag_3Sn intermetallic compound was finer and the interfacial layer between solder and substrate was much thinner in as-solidified condition of the joint as a result of more rapid cooling rate (10^4C/sec). Ag_3Sn within the Sn-rich matrix, and Cu-Sn intermetallic compounds at interfacial layer were observed to coarsen with aging after soldering, becoming more

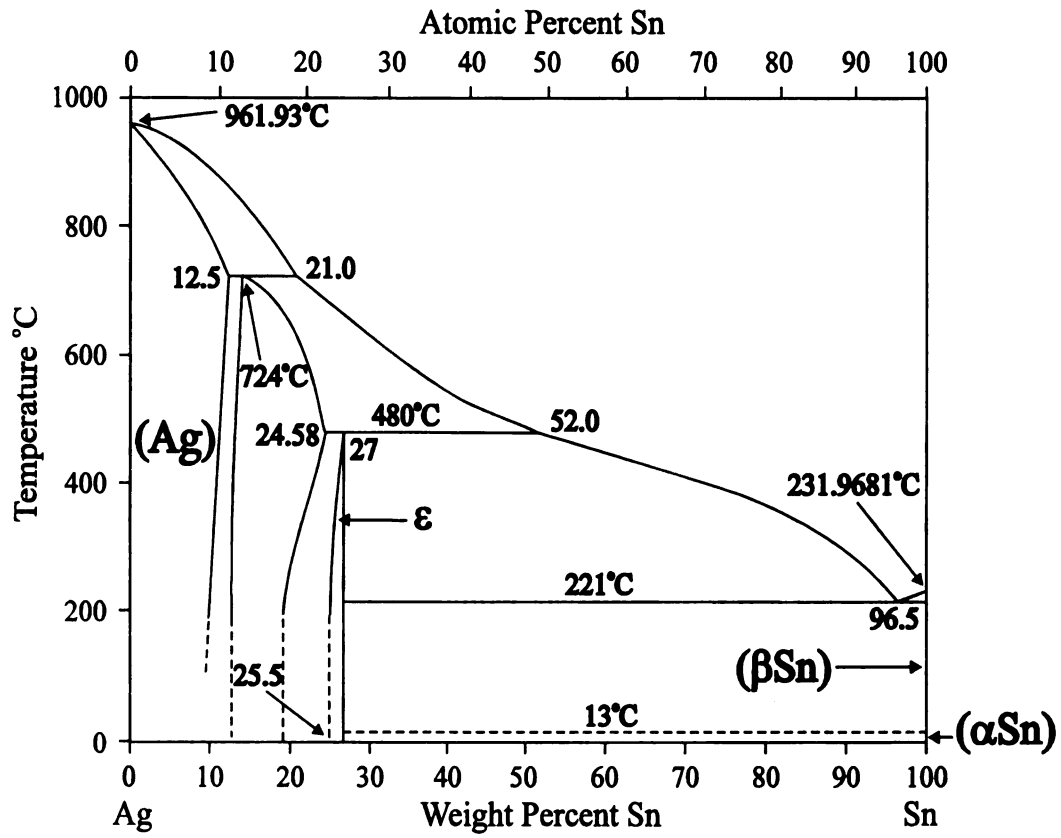


Figure 7 Sn/Ag Phase Diagram [57]

significant at higher temperature. Even though different microstructures are produced according to different soldering processes, they tend to be altered in high temperature environments [56].

The melting temperature (221°C) of 96.5Sn/3.5Ag is higher than that of 63Sn/37Pb (183°C) upon which current manufacturing technologies are based. 96.5Sn/3.5Ag might be suitable for more demanding high temperature service environments such as for under-the-hood service in automobiles and avionics systems. The most desirable Pb-free solder would possess almost the same melting characteristics as Sn/Pb solder. The incorporation of a solute addition into the matrix was considered to be the best way to depress the melting temperature of the 96.5Sn/3.5Ag without degrading the microstructure and mechanical properties. The solute additions should be such that the solute resides solely in solution with the matrix phase and not cause adverse microstructural segregation [4].

The depression of melting temperature of the 96.5Sn/3.5Ag was reported with improved microstructure and mechanical properties by addition of 1% Zn and 1% Zn/0.5% Cu to the 96.5Sn/3.5Ag. Addition of 1% Zn suppressed the melting temperature of the 96.5Sn/3.5Ag to 217°C and refined the microstructure, especially making rod shape of Ag_3Sn more spherical but the ductility decreased. 0.5% Cu addition helps to recover ductility by decreasing of the effective grain size [58].

96.5Sn/3.5Ag solder, like 63Sn/37Pb, forms the two intermetallic compounds (Cu_6Sn_5 , Cu_3Sn) with Cu substrate. Interfacial reactions in solder and substrate systems are of particular importance to the manufacturability and reliability of solder joints.

Excessive growth of interfacial intermetallic compounds during and after soldering can be detrimental to reliability of solder joints due to their consumption of protective or solderable finishes and the brittle nature of the intermetallic compounds. The growth of intermetallic compounds is substantially controlled by two processes which are diffusional process, the atomic transport of Sn and Cu through the intermetallic layer, and the reaction process at the solder/intermetallic and the intermetallic/Cu interfaces.

With molten Sn/Ag solder, the growth rate followed the relationship $x = kt^{1/3}$ for the total interfacial layer and $x = kt^{1/2}$ for Cu_3Sn layer in a previous study [59]. However, a different study showed a different result of parabolic relation ($x = kt^{1/2}$) for total interfacial layer [56, 60]. 'x' is the thickness of the alloy layer, 'k' is a temperature dependent reaction rate constant, and 't' is the time of exposure.

The interfacial layer growth may have a direct relationship with the fracture mechanism. During aging at high temperature, and tensile and shear loading, cracks were found within the interfacial layers or interface of the intermetallic layer and solder, and appeared to propagate leading to the failure of the entire joint after the growth of intermetallic compounds at the interfacial region [56, 59]. Ag was not observed in the interfacial layer, implying that Ag was not involved in the interfacial reaction [59, 61].

The gold coating on solderable layer of electronic parts is usually used to protect the solderable layer during the storage for a long time because gold is resistant to oxidation and shows good wettability. However, the dissolution of substrate into the molten solder

may affect the mechanical properties of solder by forming intermetallic compound within the solder matrix.

The 96.5Sn/3.5Ag was more tolerant for dissolved gold than 63Sn/37Pb. The tensile fracture elongation was found to be less sensitive for the 96.5Sn/3.5Ag with dissolved gold than 63Sn/37Pb. The tensile fracture of 96.5Sn/3.5Ag still exhibited ductile fracture with 5 mass% gold. These results were attributed to much smaller size of the AuSn_4 gold intermetallics formed in the 96.5Sn/3.5Ag solder joints compared to the 63Sn/37Pb joints [62]. The Cu dissolution forming Cu_6Sn_5 intermetallic compound into the 96.5Sn/3.5Ag solder matrix of the joint was observed in the laser reflow soldering in which the 96.5Sn/3.5Ag was superheated typically from 400°C to 600°C followed by the rapid cooling (10^4°C/sec). Cu dissolution was much more dependent on the temperature reached than the time at temperature. Such Cu dissolution is expected to increase strength of the joints [56].

Adequate solderability is essential for any practical soldering application, even if the melting temperatures are satisfactory. Solderability is controlled by the wettability of the solder which is another significant property of solders in determining a reliable solder joint and is defined as the ability for a liquid solder alloy to spread on a solid surface. Wettability can be influenced by several factors such as solder composition, flux, temperature, surrounding atmosphere, etc. The kinetics of the wetting behavior are dominated by the physical and chemical processes at the solder-substrate, solder-flux, and flux-substrate interfaces.

The wettability of molten 96.5Sn/3.5Ag appeared to be poorer than molten 63Sn/37Pb but still acceptable for practical soldering applications. It was attributed to the high values of γ_{LF} , which describes the surface tension between solder and flux, caused by higher surface tension of silver itself. The wettability of the 96.5Sn/3.5Ag can be improved by using flux which decreases its surface tension [34, 63]. In reflow experiments, the 96.5Sn/3.5Ag exhibited better wetting characteristics than the 63Sn/37Pb, displaying less sensitivity to the change of reflow atmosphere between nitrogen and air [64]. The minor addition of alloying elements which are Sb, Bi, Cu, and In did not produce substantial improvement on wettability [65].

2.2.3 Composite Solder

With the advent of surface mount technology and the pursuit of miniaturization in the electronic industry, the solder was demanded to be an electrical connection between electronic devices and printed circuit substrates, as well as a mechanical support the devices as a structural means. As a result, the reliability of solder joints has grown in importance in electronic packaging technology.

The service temperature for solders are generally high relative to their absolute melting point and solder microstructures tend to be highly unstable under typical operating conditions. Solder materials also are readily subject to thermal stresses induced due to the thermal expansion mismatch between components and substrates during thermal cycling. Consequently, alternative solder materials possessing stable

microstructure and improved mechanical strength to ensure reliability of solder joint in electronic applications need to be developed.

Approaches to strengthen the conventional solder materials by introducing fine second phase particles to solder to create a composite have been under investigation [66, 67, 47, 70 - 74]. Such particles may be introduced either by precipitation from supersaturated solid or liquid solution or by external addition of foreign particles as dispersoids. The precipitation strengthening may not be suitable method because the precipitates are generally prone to coarsening unless one or more of the constituent elements in the precipitate phase are chosen to have low solubility and diffusivity in the solder matrix. On the other hand, foreign dispersoid particles introduced within solder alloys would not coarsen easily since the elements or compound involved can be chosen to have low solubilities and diffusivities or no reactivity with the matrix solder alloy [68].

Several approaches has been adapted using Sn/Pb solder to develop advanced alternative solders, called composite solder. Among them, three principal approaches have been pursued.

1. Blending conventional solder paste and powdered metals or intermetallics, and subsequently reflowing the mixture [66, 69, 70, 71]
2. Mechanical alloying of conventional solder particles and high strength intermetallic powders [67, 72]

3. Incorporation of fine dispersoids by rapid solidification processing of induction melting and gas atomization using solder alloy with small addition of third element [47, 73, 74]

The first approach has a limitation with the size of second phase reinforcements in the solder matrix, which is determined by the size of the reinforcement powders that are typically more than 10 μm . The approach of mechanical alloying produces significant oxygen contamination and may not be a suitable process [47, 73].

Several types of particles were used to produce composite solder with stable microstructure and improved mechanical properties. The representative particles used are the powder of intermetallic compound (Cu_6Sn_5 , Cu_3Sn), elemental metals such as Cu, Ni, Ag, Au to introduce intermetallic compound with Sn in the solder matrix, aluminium oxide [75], and carbon fiber.

The second phase dispersoids should be small enough (typically less than 500nm) and closely spaced (generally $< 1\mu\text{m}$) to yield significant strengthening without considerable loss in ductility. Incorporation of dispersoids by rapid solidification processing produced *in-situ* composite solders with large volume fraction of small, incoherent dispersoids in solder matrix and improved strength, increased fatigue lives and creep resistance [47, 73, 74]. Fine dispersoids in the solder matrix was believed to stabilize dislocation substructures and microstructures by pinning dislocations and grain boundaries, and act as effective deformation barriers at elevated temperatures [74].

It is also important to uniformly distribute small dispersoid particles in sufficient quantity and maintain this dispersion after the alloy is melted and reflowed to affect mechanical properties of the solid solder. A magnetic field was applied to molten solders containing fine Fe particles to overcome the gravity-induced particles segregation problem and to achieve a microstructure with a uniformly distributed three-dimensional network of the dispersoid particles [68].

The dispersoids should be well wetted by the solder or should possess a similar specific density to solder, otherwise they will tend to sink or float during the composite preparation or during soldering processes. When carbon fiber was used as a dispersoid to composite solder, carbon fiber was coated with copper to improve wetting with solder matrix. Composite solder containing carbon fiber coated with copper exhibited better mechanical properties than that containing uncoated carbon fiber [76].

The Cu_6Sn_5 intermetallic compound has been adapted in the previous studies as a second phase that provides several benefits to the composite solder. The Cu_6Sn_5 intermetallic compound is readily wet by solders with the use of flux [77]. The solubility of Cu_6Sn_5 is very low in Sn/Pb solder at typical reflow temperatures as well as practically zero in solid Sn/Pb. The density of Cu_6Sn_5 which is 8.23 g/cm^3 at room temperature is quite close to that of liquid eutectic Sn/Pb which is 8.2 g/cm^3 at the eutectic temperature. These similar densities are expected to promote a uniform distribution of particles [69].

The dispersoids could make composite solder more resistant to creep fatigue deformations by acting as heterogeneous nucleation sites to produce a very fine, initial

microstructure of solder matrix upon reflow, and by serving as obstacles to grain growth, crack growth, and microstructural coarsening to retain the stable microstructure of solder even after thermal exposure [67 69, 77].

There is a need for a solder with a low coefficient of thermal expansion, since the stresses are thermally induced in solder joints due to the difference in thermal expansion coefficient between substrate and solder. Carbon fiber with nearly zero thermal expansion coefficient as a dispersoid was attempted to adjust thermal expansion coefficient of a solder. Composite solder with the amount of carbon fiber which makes thermal expansion coefficient of solder to be similar to that of substrate exhibited prolonged fatigue lives [76].

The dispersoids added to the Sn/Pb solder strongly affected the growth of the intermetallic layers at the solder/Cu substrate interface. Cu containing particles such as Cu_6Sn_5 , Cu_3Sn , and elemental Cu increased the thickness of the Cu-rich interfacial layer (Cu_3Sn) by reducing the amount of Sn available for interfacial reaction. The dispersoids acted as a sink for Sn in the solder matrix. The dispersoids without copper, such as Ag, Au, Ni enhanced the formation of Sn-rich interfacial layer (Cu_6Sn_5). One possibility was that these elements diffuse to the intermetallic/substrate and act as a diffusion barrier impeding the diffusion of Cu out of the substrate. This reduced the amount of Cu available to form Cu_3Sn layer with Sn and the Cu_6Sn_5 increased at the expense of the Cu_3Sn [71].

The strengthening effect of the second phase in composite solders could be offset because of the formation of microvoids in solder [65, 70]. The strength of composite solder appeared not to correlate with the volume fraction of dispersoids but to correlate with the concentration of voids in the microstructure of the composite solder. These voids acted as stress concentration centers and decreased the strength of the composite solder. The formation of microvoids appeared to be very sensitive to processing method of composite solder. The origin of voids is not known. The conceivable causes are flux or gas bubbles trapped by the higher viscosity of the composite solder melt during solidification.

A discussion about microvoids formation was given by Clough *et. al* [70]. The upward velocity, 'v', of a flux bubble in the melt can be described by the Stoke's Law given below

$$v = \frac{g (\Delta \rho) d^2}{18 \eta}$$

where $g = 9.80 \text{ m/s}^2$ is the acceleration due to gravity, $\Delta\rho = \rho_s - \rho_b$ is the difference between the density of the solder (ρ_s) and the bubble (ρ_b), 'd' is the bubble diameter, and η is the dynamic viscosity of the melt. It was found experimentally that the viscosity of the solder melt increases with the additions of increasing amounts of particles to the melt. As a result, the velocity of flux bubbles decreases as the additions of the particles increase. Thus the presence of large amounts of reinforcements tends to cause large volume fractions of residual porosity to be trapped in the solder [68].

2.3 CREEP BEHAVIOR OF SOLDERS

2.3.1 The Description of Creep Deformation

Creep is a time-dependent deformation of a material when it is subjected to a constant load at constant temperature. Creep is important at temperatures greater than $0.5T_m$ where T_m is the melting point of a material in degrees absolute. Creep strain is measured as a function of time and the slope of the creep strain-time curve is referred as a creep strain-rate. Creep deformation is categorized into three stages : (I) primary or transient, (II) secondary, constant rate, or quasi-viscous, and (III) tertiary. When a constant load is applied to a specimen, the creep-rate decreases with time after an initial rapid elongation of the specimen, then reaches a steady-state in which the creep-rate does not change with time, and finally the creep-rate increases rapidly with time until fracture occurs. The creep-rate in steady-state deformation is known as the minimum creep-rate.

The creep resistance of a material is often explained using the minimum creep-rate in steady-state in creep deformation. The creep deformation in secondary or steady-state stage is commonly described using a generalized, dimensionless rate equation called the Mukherjee-Bird-Dorn equation,

$$\frac{\dot{\epsilon}_s k T}{D E b} = A \left(\frac{\sigma}{E} \right)^n \left(\frac{b}{d} \right)^p$$

where $\dot{\epsilon}_s$ is the steady state strain rate, k is Boltzmann's constant, T is the absolute temperature, σ is the applied stress, E is the elastic modulus of the material, b is the magnitude of Burgers vector, d is the grain size of the material, A is a material constant, n

is stress exponent dependent on deformation mechanism, and p is a constant related to grain size. The secondary stage of creep is a period of nearly constant creep-rate which results from a balance between the competing processes of strain hardening and recovery. the recovery mechanisms that are most important at high temperatures involve diffusion of atoms through the crystals or along the grain boundary. In the above equation D is the diffusion coefficient for the diffusion mechanism that controls the recovery rate and is expressed such as

$$D = D_0 \exp\left(-\frac{Q}{kT}\right)$$

where D_0 is the pre-exponential constant and Q is the activation energy for the rate-limiting diffusion process. The temperature influence on the creep-rate is dominated by the exponential temperature dependence of the diffusivity, so as an approximation, the Mukherjee-Bird-Dorn equation is often used

$$\dot{\epsilon}_s = A' \sigma^n \exp\left(-\frac{Q}{kT}\right)$$

where A' is a material-specific constant.

2.3.2 Creep Mechanisms

Creep deformation in high homologous temperature can occur by various mechanisms and each mechanism may have its own unique effect on the microstructure and may cause its own distinctive form of damage. Thus, it is important to be able to predict what mechanism(s) will be prevalent under a given set of stress, temperature, and microstructure conditions. Deformation mechanisms map is a graphical description of creep mechanisms in the stress versus temperature space that provide a convenient way to predict what mechanism(s) will be predominant under a given set of deformation conditions.

The deformation mechanisms for creep can be divided into three groups, diffusional creep, dislocation creep, and grain boundary sliding. The dominant creep mechanism at low stresses and high temperatures is diffusion of vacancies in response to the applied stress. There are two types of diffusional creep. Nabarro-Herring creep represents the deformation by diffusion of vacancies through the lattice and Coble creep describes the diffusion of vacancies along grain boundaries which is a rapid path at lower temperatures. The stress exponent, n , is one for both mechanisms and the activation energy is higher for lattice diffusion than that for boundary diffusion. Coble creep is more favored for finer grain sizes compared to Nabarro-Herring creep.

Dislocation climb is a rate-controlling process of creep at moderate to high stress. Climb is a process in which the dislocation can change the glide plane by emission or absorption of vacancies. This diffusion controlled process limits the strain-rate by

allowing dislocations to bypass or penetrate obstacles such as dislocation tangles, cell walls, precipitates, and dispersoids only as fast as climb occurs. There are a variety of stress exponents ranging from 4 to 9 at higher stresses which imply many deformation and recovery processes involving climb.

In solid solution alloys, dislocation glide in response to shear stress can also be retarded. At moderate to high stress, the glide of dislocations can be the rate-limiting mechanism because the dislocation velocity is limited by the solute atom atmospheres that must move with the dislocation. Dislocation processes become more important with increasing grain size, increasing stress, and/or decreasing temperature. For this mechanism, the stress exponent, n , is about three.

At very high stress, the strain-rate increases dramatically with a small increase of stress. This behavior is often referred to as power law breakdown, where the influence of diffusion based processes become less important.

Grain boundary sliding (GBS) is also known as a fundamental mechanism for creep deformation of superplastic materials. Superplastic deformation accompanies very large strains before fracture and exhibits a stress exponent, n , between one and three and an activation energy close to the value for grain boundary diffusion. GBS has a strong dependence on the grain or phase size. Superplastic deformation occurs in a material with stable, fine, and equiaxed grains. The distinctive characteristic of superplastic materials is high strain-rate sensitivity, m ($m = 1/n$), which is about 0.3 to 0.9. The grain boundary sliding in superplastic deformation requires some accommodation mechanisms such as

diffusion, boundary migration, or intragranular slip to maintain material continuity during the GBS process.

All creep processes exhibit tertiary creep after the minimum creep rate is reached, and this is related to crack initiation and propagation. Grain boundary sliding without accommodation process required to maintain material continuity during the sliding process is known to be responsible for this stage by nucleating intergranular cavity on grain boundaries or interphase boundaries.

2.3.3 Deformation behavior of Solder Joint

Solder joints in electronic modules undergo temperature cycling which is caused by power on/off cycles, daily temperature variations, and seasonal changes. Solder joints are subject to a cyclic loading condition imposed by thermal stresses induced by the difference between the thermal expansions of electronic components. Since the thermal cycling ordinarily exhibits the slow strain-rate, solder joints basically undergo low frequency thermal fatigue. The service temperatures of solder joints corresponding to high homologous ($T \geq 0.5T_m$) temperature and relatively long hold times are often encountered during service conditions. Thus time-dependent, thermally-activated deformation or creep becomes significant at high homologous temperature greater than 0.5. Consequently, damages or failures of solder joints are caused by creep-fatigue interaction which typically describes the cyclic application of a load at temperatures where time dependent, thermally-activated processes are significant.

The creep-fatigue damage in solder joints has been identified in the analysis of fracture surface of solder joints which were thermally cycled, where fatigue striations were observed side by side with creep voids and extensive intergranular cracking [78]. The eutectic Sn/Pb solder subjected to isothermal cyclic loading at room temperature showed that deformation occurred primarily by creep process and was very sensitive to hold time or frequency resulting in increasing creep rate and decreasing cycles to failure with increasing hold time [79, 80]. Creep was also observed to be the predominant mode of deformation for isothermal fatigue in which good correlation was found between the isothermal fatigue life of solder joints and the amount of creep strain per cycle [81].

2.3.4 Creep Deformation of Sn/Pb Solder

The creep behavior of mechanically worked and recrystallized eutectic Sn/Pb solder which has various grain sizes ranging from a few micron to several microns is known to exhibit sigmoidal relationship between strain-rate and stress. This relationship divides the variation of the steady-state strain-rate with stress into three distinct regions: region I at low stresses in which stress exponent, n , is equal to three, region II at intermediate stresses where it is close to two, and region III at high stresses where it is equal to or larger than six.

In region III with highest strain-rate, dislocation climb controlled creep was found to be dominant deformation mode. Region III exhibited a stress exponent larger than six and activation energy similar to that of lattice diffusion in pure lead or tin. There was no

dependence on the phase size in region III, so the exponent on grain size, p , was equal to zero [82].

Region II at intermediate strain-rate ($\sim 10^{-5}$ - 10^{-2} sec⁻¹) was found to be dependent on superplastic deformation according to the results of many researchers. Eutectic lead/tin solder showed exceptional ductility up to 4000% when pulled in tension at a strain rate in this region [83]. Region II was revealed to have a stress exponent close to two and activation energy similar to that for grain boundary diffusion and to be sensitive to grain size. Two different activation energies were observed depending on temperature which are 44.7 ± 1.1 kJ/mol below $0.89 T_m$ and 81.1 ± 3.9 kcal/mol above $0.89 T_m$. Since the effective diffusivities were dominated by the grain boundary diffusivities even at a homologous temperature of 0.97, this change in activation energy with temperature seemed to suggest a change in creep mechanism, not a change in diffusion path from grain boundaries to the lattice [84]. The other study indicated that dominant deformation mode in region II was grain boundary sliding with accommodation process of diffusional creep to maintain grain coherency [85].

The existence of region I in creep behavior of eutectic Sn/Pb is controversial. Region I at very low strain-rates ($\leq 10^{-5}$ sec⁻¹) showed the stress exponent is equal to three, the grain size exponent is 2.3, and the activation energy of ~ 84 kJ/mol which is similar to that for lattice self diffusion [86]. Region I was speculated to result from diffusional creep but it is incompatible with experimental results because diffusional creep requires a stress exponent of unity at low stresses. It was concluded that Region I may result from a distinct deformation processes operating in sequence with region II. However, region I

was not observed in the experiments by Murty [87] and Lam *et. al.* [88]. The stress exponent was observed to remain constant down to the lowest strain-rate ($\sim 10^{-7} \text{ sec}^{-1}$), indicating that the superplastic deformation is still operative with $n \cong 2$ and with a activation energy equal to that for grain boundary diffusion.

Some attempts have been made to construct a deformation mechanism map in the space of normalized grain size versus normalized shear stress [89] and normalized strain-rate versus normalized stress [90] for the eutectic Sn/Pb alloy. A significant feature of the experimental results for creep behavior of eutectic Sn/Pb is that a higher activation energy occurs in region I than in region II. It was anticipated that two additional processes, Nabarro-Herring and Coble diffusional creep, may also contribute to the deformation of these materials under some conditions [89].

Sn/Pb solder in an as-solidified joint condition was also shown to exhibit superplastic deformation in creep testing. Mei *et. al.* identified two regions in creep testing of as-solidified Sn/Pb solder joints [37]. At low stress and strain-rate a stress exponent value close to two and activation energy for grain boundary diffusion was measured, implying superplastic deformation whose mechanism is grain boundary sliding. At higher stresses and strain-rates a stress exponent of seven and activation energy for self-diffusion indicated that dislocation climbing was the operating mechanism.

The superplastic behavior of the as-solidified Sn/Pb solder joint was attributed to the initial microstructure of the joint which is fine and equiaxed [36, 91]. When eutectic Sn/Pb is solidified in lamellar eutectic microstructure which results from the slow cooling

rate, the dominant mechanism of creep at normal strain-rate is a bulk mechanism which has a stress exponent in the range of four to seven and activation energy close to that for bulk diffusion. The quenched joint with initially more globular, fine-grained microstructure showed the transition from region III (dislocation climb process) to region II (superplastic deformation process) which was accompanied by a change in activation energy, while slow-cooled joints showed no transition to a superplastic deformation process [92]. The steady-state creep-rate was microstructure sensitive at low stress and strain rate in the grain boundary creep region, while at high stress and strain-rate the creep-rate was microstructure insensitive in the matrix creep region.

A different creep behavior was revealed for lead-rich Sn/Pb solder alloy. Lead-rich Sn/Pb bulk solder alloy with 3 to 9% Sn and grain size ranging from 0.01 to 2.5mm was tested under creep conditions at high temperatures. Four distinct regions in normalized stress versus strain-rate creep curve were observed [93, 94].

Region I in the lowest stress regime showed viscous creep with the strain exponent of 1.05 ± 0.15 . Diffusional creep deformations such as Nabarro-Herring and Coble creep were considered to be responsible for this region. However, since an activation energy close to that of lattice self-diffusion in pure lead and the grain size of the materials is too large, Coble creep was not regarded as dominant deformation mode for region I. On the other hand, the material constant, i.e. prefactor A , in region I which is 9.97×10^{-10} was 4000 times greater than the predicted value for Nabarro-Herring creep and the grain size was still too large to expect Nabarro-Herring creep to be operative. Thus the grain size independent viscous creep which was known to be the dislocation based Harper-Dorn

creep was considered to be responsible at these large grain size, but the underlying mechanism is still speculative.

Regions II and III were observed to operate with n values of 4.6 and 3.2 respectively. As stress increases to region II, stress exponent increased to 4.6 and the climb of the edge dislocations (climb I) appeared to be rate-controlling step for this region. Region III with the stress exponent close to 3 appeared with further increasing stress and indicated creep due to viscous glide of edge dislocations controlled by the locking of the gliding dislocations by solute atoms with the activation energy to be identified with that for the diffusion of the solute atoms in the lead matrix.

As stress increases to the other extreme, region IV, stress exponent increased to 4.74 and dislocation climb (climb II) became the dominant deformation mechanism again where the dislocations were able to get free from the solute atmosphere locking. The experimental data at the highest applied stress exhibited a higher strain-rate than that predicted from the power law with $n = 4.7$, which is indicative of power law break-down.

The characteristics of creep behavior were influenced by the intentionally added second phase. The Ag_3Sn particles which were introduced by adding Ag element in eutectic Sn/Pb, which do not normally cavitate during superplastic deformation, caused cavitation at many of the interfaces between Ag_3Sn and matrix [95]. Addition of elemental gold appeared to suppress the grain boundary sliding mechanism of creep in fine-grained eutectic Sn/Pb [96]. No transition from bulk creep to grain boundary sliding creep was observed in Au-containing solder joints and the stress exponent between 4 and

6 remained down to the lowest strain-rates of 10^{-7}sec^{-1} . The integrity of the materials during creep deformation requires that the grain boundary sliding should be accompanied by some bulk deformation so that the grains do not separate from one another. It was suggested that Au may inhibit the bulk deformation processes that must accompany grain boundary sliding.

2.3.5 Creep Deformation of Sn/Ag Solder

Eutectic Sn/Ag solder exhibited different creep behavior from Sn/Pb solder. Primary creep was found to be significant, contributing to large portion of the total creep deformation [97]. For eutectic Sn/Ag solder tested at 298 K to 453 K ($0.6T_m$ to $0.92T_m$) with stresses varying from about 1 MPa to 30 MPa, the primary creep followed a stress-dependent relationship.

Steady-state creep for most of eutectic Sn/Ag bulk solder and joint was observed to increase with temperature and stress. The steady-state region showed a stress exponent of $n \approx 10$ and an activation energy of 50.2 kJ/mol for bulk and joint [97], ≈ 6.7 to 8.4 and 62.7 kJ/mol for bulk solder [98], and ≈ 5.5 and 38 kJ/mol for a ball grid array configuration [99]. Eutectic Sn/Ag solder was identified to be controlled by dislocation climb.

The exponent of 10 is a much larger value than that generally noted in creep due to dislocation climb where usually the n value varies from about 4 to 7. The data might be analyzed in terms of an exponential stress dependence in tertiary creep but such dependence is expected to occur at high stresses rather than low stresses used in tests [97]. Thus the

power-law creep was expected to be applicable. The activation energy of 12 kcal/mol was about one half of that for self diffusion and was identifiable with either grain boundary or dislocation-pipe diffusion. In a relation with activation energy, which is 46 kJ/mol for pure tin at low temperature, a relatively large value for the stress exponent along with the observed activation energy indicated the low-temperature climb of edge dislocations to be the rate-controlling mechanism.

In stress-rupture tests, eutectic Sn/Ag solder exhibited temperature dependence on stress to give the same life time [100, 101]. The stress-rupture properties of the eutectic Sn/Ag soldered ring-and-plug joint decreased with increasing temperature in the range of 100-150°C resulting in a lower stress for a given life time at high temperature. The stress-rupture properties were superior to those of the eutectic Sn/Pb solder.

2.4 FATIGUE BEHAVIOR OF SOLDERS

2.4.1 Fatigue Deformation of Sn/Pb Solder

Isothermal Fatigue (Mechanical Cycling)

In low cycle fatigue, the number of cycles to failure (N_f) is usually less than 10^4 , as described by Coffin-Manson relation [102],

$$N_f^\beta \Delta\gamma_p = C$$

where N_f is the number of cycles to failure, $\Delta\gamma_p$ is the cyclic plastic strain range, β is the Coffin-Manson exponent, and C is a constant. This relation is plotted on $\Delta\gamma_p$ versus N_f as a single straight line on log-log scales with a slope of $-\beta$. Increasing the strain range during cycling leads to a decrease in the number of cycles to failure.

60Sn/40Pb solder joint followed the Coffin-Manson relation when it was tested in shear in the 1% to 10% high plastic strain range at 35 and 150°C at a frequency of 0.3 Hz [103]. Eutectic Sn/Pb solder also followed the Coffin-Manson relation above 0.6 % total strain range (total plastic + total elastic) at 25°C [104]. However, low tin lead-based solder (96.5Pb/3.5Sn) tested in tension-tension at low plastic strain range below 0.6% and at temperatures from 5 to 100°C fit much better to two straight lines with a breakpoint at about 0.3% plastic strain rather than a single straight line in the plot on $\Delta\gamma_p$ versus N_f . The two lines were shown to have high value of slope (β) at low strain ranges below 0.3% and low value of slope (β) at high strain ranges above 0.3%. The break in the lines in the plot of the Coffin-Manson relation was attributed to the change in the fracture

mode from intergranular at low strain ranges to mixed transgranular-intergranular at high strain ranges [105].

The influence of frequency on isothermal fatigue life is significant. The number of cycles to failure for 60Sn/40Pb solder tested in shear at 35 and 150°C was reduced substantially when the cycling frequency was decreased below approximately 3×10^{-4} Hz at 35°C and 3×10^{-3} Hz at 150°C [103]. At frequencies above the 3×10^{-4} Hz at 35°C and 3×10^{-3} Hz at 150°C, the decrease in the number of cycles to failure with increasing frequency was less significant. For 96.5Pb/3.5Sn solder [105], practically no change in the number of cycles to failure was observed on varying frequency in the comparatively high frequency region. A reduction in the number of cycles to failure with decreasing frequency below 10^{-2} Hz was found at 25, 50, 80°C. The frequency effect on the fatigue life of 96.5Pb/3.5Sn solder appeared to be a function of the strain range : the higher the strain range, the larger the effect of frequency on fatigue life.

Hold time at maximum strain exhibited a dramatic effect on the number of cycles to failure of 96.5Pb/3.5Sn and eutectic Sn/Pb solder [104, 105]. Hold time of a few minutes at maximum strain reduced the number of cycles to failure by almost an order of magnitude. Further increase in hold time eventually led to a constant value of the number of cycles to failure. On the other hand, the fatigue life of 60Sn/40Pb solder in tests employing equal hold time at positive and negative shear strains was observed to be unaffected by such combination of hold times [106]. However, for 96.5Pb/3.5Sn solder, equal hold time at both tensile and compressive strains was found to be damaging by

reducing the number of cycles to failure as compared to tensile or compressive hold times separately [105].

Thermal Fatigue (Thermal Cycling)

In thermal cycling, solder joints undergo thermomechanical strains which eventually lead to joint failure. This strain is produced by the combination of temperature fluctuations experienced by the package and the differing thermal expansion coefficients between materials used in the package. The source of temperature fluctuations that result in thermal fatigue can be either environmental or due to on-off power cycling.

The failure of near eutectic Sn/Pb (60Sn/40Pb) solder joint under thermal cycling was preceded by the formation of a locally coarsened region along the direction of maximum shear within the joint. The coarsened region was the weakest point of the joint and failure occurred exclusively through this coarsened microstructure [41].

The localized coarsening was due to high local shear strain imposed during thermal cycling on the solder joint by the thermal expansion differences between joined materials at high temperature. The combination of shear strain and high temperature created regions of concentrated plastic deformation within the solder joint. The accumulated deformation along with the elevated temperature caused local microstructural changes. The localized coarsening was a thermally-assisted stress-driven phenomenon and it appeared that recrystallization and subsequent grain growth are the causes of the observed coarsened band [42].

An increase in the amount of shear strain imposed on 60Sn/40Pb solder joint during thermal cycling was significant, resulting in more rapid localized coarsening and more rapid failures. In contrast to isothermal fatigue behavior, decreasing the strain-rates drastically increased the number of cycles to failure. This was attributed to the delay or elimination of the formation of coarsened region in isothermal tests, which resulted from dynamic recovery during thermal cycling. At the high temperature part of the thermal cycle, and the slower strain-rate, the dislocation substructure recovered faster than it work hardened which tended to minimize the subsequent recrystallization and growth of the solder microstructure [107].

It was observed that extensive stress relaxation occurred during the elevated temperature hold time, and very little stress remained after one minute at that temperature. The stress at low temperature portion had little or no relaxation over a period of hours. A drop in load with increasing number of thermal cycles was a complicated function of microstructural coarsening and the formation of cracks that decrease the area carrying the load [107].

2.4.2 Fatigue Deformation of Sn/Ag Solder

Isothermal Fatigue (Mechanical Cycling)

In the isothermal fatigue conducted at room temperature under constant total shear strain control of $\Delta\gamma_t = 0.04$ to 0.79 , the near eutectic Sn/Ag solder (96Sn/4Ag in wt %) joint showed far superior fatigue resistance compared to eutectic Sn/Pb solder joint at the high strain regime ($\Delta\gamma_t \geq 0.2$), but was far inferior to eutectic Sn/Pb solder joint at the lower strain range ($\Delta\gamma_t < 0.2$) [108]. It was suggested that the superior resistance of eutectic Sn/Ag solder joint at the high strain regime must be due to a higher resistance to crack initiation rather than to crack propagation, since this solder was observed to have higher crack growth rate.

Previous studies [100, 101] by other investigators under cyclic tension/compression with a mean stress of zero and a 0.2 mm/min strain rate using ring in plug joint have shown that the isothermal fatigue resistance of eutectic Sn/Ag solder was better than Sn/Pb solder at 20 and 100°C.

Thermal Fatigue (Thermal Cycling)

Near eutectic Sn/Ag solder (95Sn/5Ag in wt %) joint showed a longer fatigue life than Sn/Pb solder in the thermal cycling from -30 to $+100^\circ\text{C}$ and 10 cycles/day. 95Sn/5Ag solder joint exhibited fatigue failure through the intermetallic layer between the solder and Cu substrate that coarsened during thermal cycling. It was believed that the fatigue failure for 95Sn/5Ag solder joint was postponed because the microstructural coarsening that led to earlier failure in Sn/Pb solder did not occur in the 95Sn/5Ag solder

[109]. Another study on thermal fatigue of Sn/Ag solder also revealed that eutectic Sn/Ag and 95Sn/5Ag solder joints were more fatigue resistant than eutectic Sn/Pb solder joint in the thermal cycling from -54 to $+75^{\circ}\text{C}$ [10].

2.5 STRATEGY FOR DEVELOPING AN *IN-SITU* COMPOSITE SOLDER

The reliability concerns of solder joints in addition to the environmental concerns for toxic materials place more demands for high performance of solder joints in electronic applications. With these concerns for solder joints in electronic packaging, lead-free composite solders incorporating particulate reinforcement have been considered.

This study will aim at the development of lead-free, *in-situ* composite solders to improve reliability of solder joints in electrical systems while removing lead. The lead-free, *in-situ* composite solder will be based on eutectic Sn/Ag (96.5Sn/3.5Ag) solder and developed by incorporating fine Cu_6Sn_5 intermetallic particles as a composite phase to make composite solder. A similar approach is applied to eutectic Sn/Pb (63Sn/37Pb) for comparison.

Eutectic Sn/Ag (96.5Sn/3.5Ag) solder has been considered as a potential candidate for replacing leaded solders because it is free of toxic lead, better for high temperature applications due to its high melting temperature, and silver is available in sufficient quantities to be considered as minor alloying element. Cu_6Sn_5 intermetallic compound is known to wet readily by solders with the use of flux. It is therefore expected that the particulate will be well bonded to the matrix of the resulting composite solders. Phase diagrams show no intermediate phases between Cu_6Sn_5 and Sn, or between Cu and Ag.

Based on the literature review, the presence of the composite phase will affect microstructural evolution which causes continuous change in mechanical properties. Aging of composite solder joints will be performed to evaluate microstructural evolution.

The service temperatures for solder joints corresponding to high homologous temperature ($T > 0.5 T_m$) and relatively long hold times are often encountered during service conditions, indicating that time-dependent, thermally-activated deformation or creep becomes important. Creep deformation has been observed to occur in isothermal cyclic loading, and the amount of creep was very sensitive to hold time or frequency. The effect of particulate reinforcements on the creep behavior of the *in-situ* composite solder will be evaluated.

The mechanical properties of solder joints are known to be sensitive to the microstructure of solder materials as reviewed in literature survey. Thus it is considered that the microstructural evolution due to aging will affect the creep properties of solder materials. The creep testing of unaged and aged composite solder joints will be done to investigate the effect of microstructural evolution on creep properties.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 MATERIALS

3.1.1 Solder Material

The solder materials used in this study are eutectic Sn/Ag composite solder and eutectic Sn/Pb composite solder. Composite solders were prepared by induction melting of constituent materials. The base or matrix material of the composite solder was eutectic Sn/Ag solder (96.5Sn/3.5Ag) and eutectic Sn/Pb solder (63Sn/37Pb) which were provided as ingots with dimensions of 2 x 36.5 x 1.5 cm³ by Ford Scientific Laboratory. Cu₆Sn₅ intermetallic η -phase was introduced into eutectic Sn/Ag and Sn/Pb solders as second phase to make composite solders by adding the determined amount of pure Cu and Sn elements to produce 20 vol % Cu₆Sn₅ intermetallic η -phase while retaining the eutectic composition of the matrix.

The fabrication of the composite solder was performed in an Induction or Radio Frequency (RF) furnace shown schematically in Figure 8. The inside of the quartz tube had an inert atmosphere of argon(Ar) and helium (He) gases to prevent the oxidation during the melting of the component materials. Eutectic Sn/Ag solder or eutectic Sn/Pb solder with additional Cu and Sn elements were placed in the graphite cup inside the quartz tube and the temperature was raised by induction heating to a temperature above the melting temperature of pure Cu, which has the highest melting point, 1085°C, among

the constituent materials. The temperature of the melt was measured using an optical pyrometer.

After maintaining the temperature above the melting point of pure Cu for about 20 minutes to ensure complete melting of all constituent materials, induction furnace power was turned off to solidify the melt. It was observed by visual observation to take about 10 min for the melt to solidify into a disk-shaped solid, and it took almost 2 hours to reach room temperature. The composite solder ingot was cut using a diamond saw, polished, and etched by a 3.3% nital (a mixture of HNO_3 and methanol) to analyze the microstructure with an optical microscope.

3.1.2 Substrate Material

The substrate material used to make solder joints using composite solder was pure copper. Cu dogbone halves which had the dimensions shown in Figure 9 were machined using EDM, to obtain a reduced width of 1 mm from a copper sheet, to simulate the actual solder joint geometry in the electronic applications.

3.1.3 Flux

The flux used in this study was a liquid flux called 200-L Flux, provided by Ford Scientific Laboratory. The 200-L flux contained 25 ~ 35 wt % zinc chloride, 2 ~ 7 wt % ammonium chloride, 1 ~ 5 wt % hydrochloric acid, and water as a balance. This flux was used to ensure reliable bonding of solder joints.

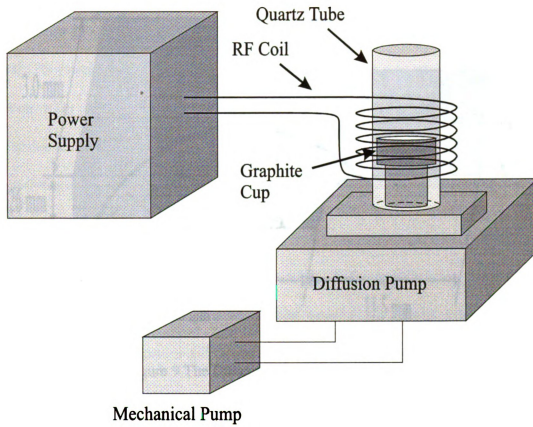


Figure 8 Schematic Diagram of Induction or Radio Frequency (RF) Furnace

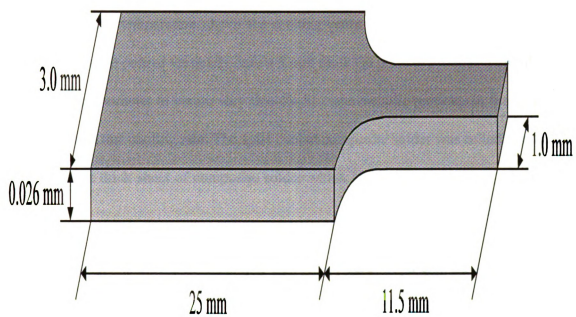


Figure 9 The Dimensions of The Cu Substrate

3.2 THE PREPARATION OF SOLDER JOINTS

3.2.1 The Pre-Treatment for Manufacturing a Solder Joint

The composite solders of about 20 grams produced by induction melting were remelted using a small ceramic crucible with a size of 2.7 cm diameter and 3.0 cm height in a furnace at a temperature above the melting point of Cu_3Sn intermetallic ϵ -phase, 676°C . They were poured vertically onto a 5 mm thick Cu plate to produce a circular splat of about 5 cm diameter to obtain very fine Cu_6Sn_5 intermetallic particles in the composite solder due to a fast cooling rate. The splat cooled composite solder was rolled resulting in about 100 μm thick sheet of composite solder which was cut into preforms of about 1.0 mm^2 .

Copper dogbone halves were painted with solder mask to prevent the spread of solder beyond the 1 mm^2 soldered area at the end of each half. The area soldered was pre-cleaned with a 50 % aqueous HNO_3 just prior to soldering to remove the thin tarnish layers.

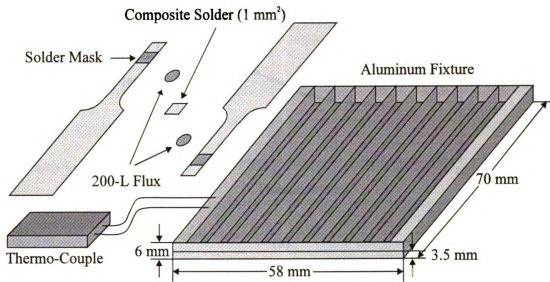
3.2.2 Soldering Process

Copper dogbone halves were placed in an aluminum fixture designed to hold the Cu dogbones in their proper alignment. Copper dogbone halves were fluxed with 200-L liquid acid flux to remove a thin tarnish layer on Cu dogbone halves and to improve wettability between solder preforms and copper dogbone halves. Eutectic Sn/Ag composite solder and eutectic Sn/Pb composite solder preforms, 1.0 $\text{mm}^2 \times 100 \mu\text{m}$ thick,

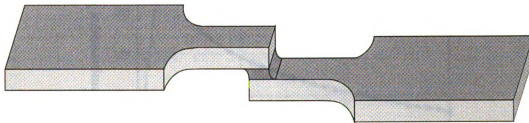
were sandwiched between the two Cu dogbone halves. The assembly is shown in Figure 10.

The entire aluminum fixture was placed on a preheated (about 500°C) hot plate and allowed to reach a temperature of 270°C for the eutectic Sn/Ag composite solder, and 250°C for the eutectic Sn/Pb composite solder before being removed to the non-metallic laboratory bench to cool. The Cu_6Sn_5 intermetallic η -phase remained in the solid state and only the eutectic Sn/Ag and eutectic Sn/Pb matrix were reflowed and solidified during soldering process. Ten solder joints were manufactured in the aluminum fixture at a time following the heating/cooling history shown in Figure 11.

One side of the single shear lap joint was polished using 2000 grit sand paper and 0.05 μm SiO_2 colloidal suspension. The surface of eutectic Sn/Ag composite solder joint was etched with a solution of 50 ml H_2O , 50ml acetic acid, and 1 drop of H_2O_2 for approximately 4 seconds, the specimen was washed with methanol prior to observing the microstructure in Hitachi S2500 scanning electron microscope. It was not necessary to etch the eutectic Sn/Pb composite solder joints because each phase in eutectic Sn/Pb composite solder was clearly observed in the scanning electron microscope due to the large difference of atomic numbers between Sn and Pb.

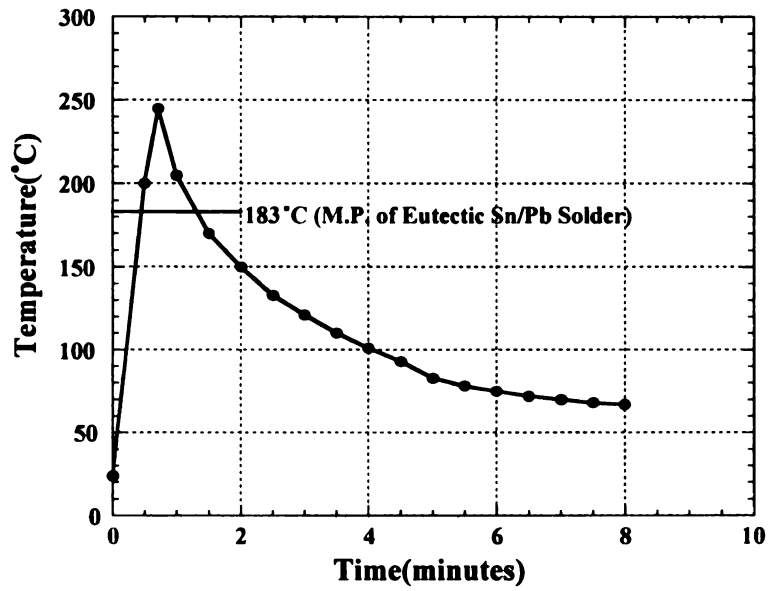


(a)

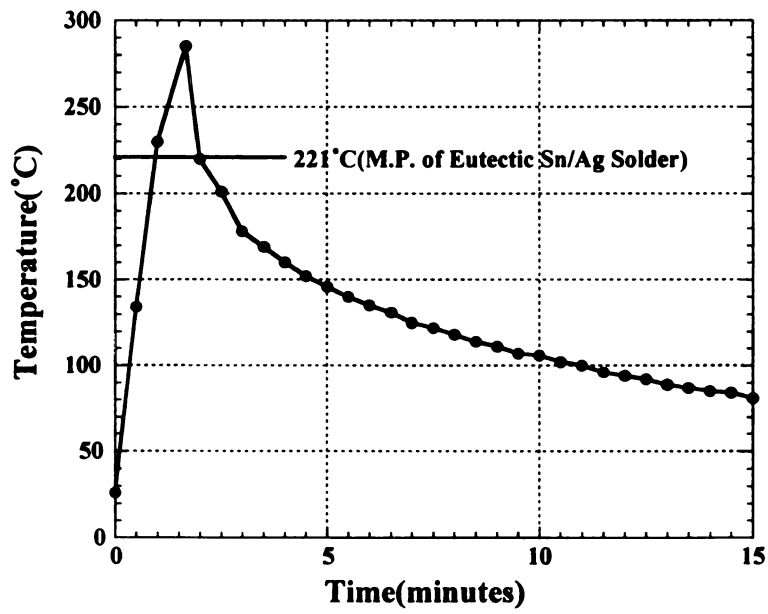


(b)

Figure 10 Schematic Diagram of
(a) The Solder Joint Fixture Assembly and
(b) A Fabricated Single Shear Lap Joint



(a)



(b)

Figure 11 The Temperature versus Time Profile for Manufacturing of
 (a) Eutectic Sn/Pb Composite Solder Joints and
 (b) Eutectic Sn/Ag Composite Solder Joints

3.3 AGING OF THE SOLDER JOINTS

Aging of solder joints was conducted by placing the solder joints on a piece of aluminum which was on a hot plate, that had a known and steady temperature at particular locations.

The eutectic Sn/Pb composite solder joints were statically aged for 100 hours at four different temperatures (120, 100, 80, 50°C), and cyclically aged at three different temperatures (120, 100, 60°C). The eutectic Sn/Ag composite solder joints were aged for 100 hours at four different temperatures (150, 120, 100, 60°C), and cyclically aged at three different temperature (150, 120, 100°C). Aging by thermal cycling between the three predetermined aging temperatures and room temperature was performed by turning on and off hot plate 40 times. The time at the aging temperature and room temperature was one hour respectively, resulting in two hours per cycle as shown in Figure 12. The thermal cycling provided 20 hours at elevated temperature in a thermal cycling process. There was an overnight hold time at room temperature for three times during the experiment of thermal cycling.

For eutectic Sn/Pb composite solder joints, aging by thermal cycling was performed again to inspect the repeatability of the result from first aging by thermal cycling. Aging by thermal cycling was accomplished using an appliance timer that turned the hot plate on and off every hours.

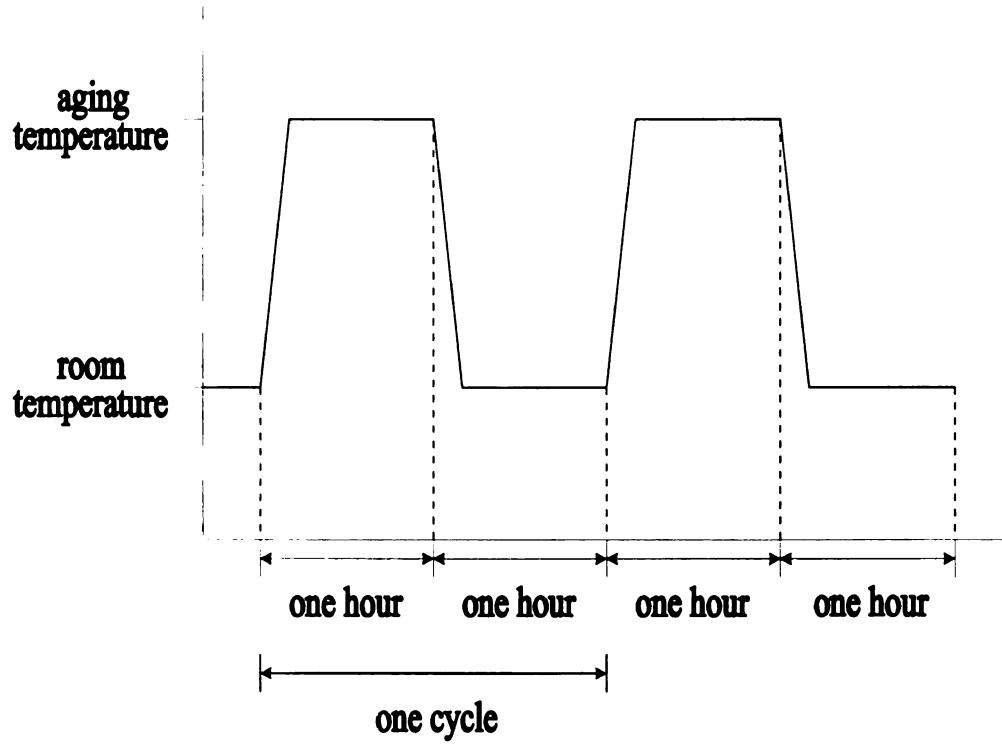


Figure 12 The Schematic Diagram of the Temperature-Time History in Thermal Cycling

After aging, the eutectic Sn/Ag composite solder joints were repolished slightly and re-etched. Such a procedure was essential to eliminate original etching grooves and to remove the influence of surface conditions such as oxidation, so that a direct comparison of the microstructural changes due to aging could be made. It was not necessary to re-etch the eutectic Sn/Pb composite solder joints because each phase was clearly observed in the scanning electron microscope. Secondary electron images of the microstructure of the solder joints were recorded using an Hitachi S2500 scanning electron microscope prior to and after aging.

Micrographs of eutectic Sn/Ag composite solder joints were scanned with an AGFA model scanner. The scanned images were then analyzed using LECO image analysis software to determine Ag_3Sn particle size and growth as a result of aging. The software measured the area of each Ag_3Sn particle assuming that the Ag_3Sn particles to be circular. An average particle area was calculated from which an average particle radius was determined. By using the average particle size before and after aging, and by knowing aging time and temperature, the aging kinetics were determined using a simple kinetic model.

For eutectic Sn/Pb composite solder joints, a number of lines were drawn in different directions on a micrograph of an eutectic Sn/Pb composite solder joint. The number of intercepts between the line and interface boundary were counted. The length of the line was divided by the number of intercepts to obtain a length/intercept. Several length/intercepts were obtained for each micrograph from which an average length/intercept was calculated. The length/intercept was used to determine coarsening

effects as a result of aging, with and without including the intercept length of the Cu_6Sn_5 phase.

3.4 CREEP TESTING OF COMPOSITE SOLDER JOINTS

Creep tests were performed with the eutectic Sn/Ag and eutectic Sn/Pb composite solder joints. Both unaged and aged specimens were deformed with dead loading at room temperature as illustrated in Figure 13. Scratches were made by grinding solder joint on a rough cloth across the polished side of the solder joints and the amount of creep deformation was measured using the location and shape of scratches present across the joints. The specimens were removed periodically from the creep fixture shown in Figure 13 to photograph the scratches with optical microscope and then reloaded in the creep fixture.

The geometry of the solder joints was such that the deformation was in simple shear mode at constant load, which also corresponded to a constant shear stress. In creep tests for eutectic Sn/Ag composite solder joints, a constant load was used for each unaged specimen. For aged specimens a constant load of 2.25 lbs (10 N) for eutectic Sn/Pb composite solder joints and 3.5 lbs (15.6 N) for eutectic Sn/Ag composite solder joints was applied first. After the strain-rate reached a steady-state value, the load was increased to 2.5 lbs (11.1 N) for eutectic Sn/Pb composite solder joints and 4 lbs (17.8 N) for eutectic Sn/Ag composite solder joints. Since the mechanical properties of solder and solder joint are microstructurally sensitive as reviewed in the previous chapter, this method was used to reduce the number of test joints and to facilitate the evaluation of the

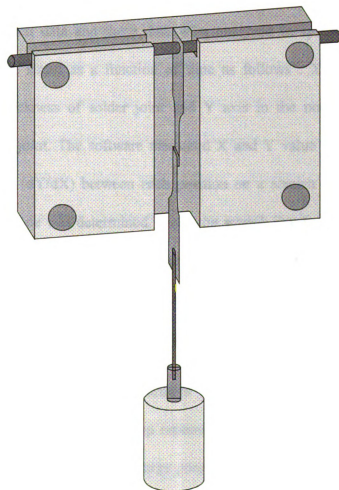


Figure 13 The Creep Fixture

stress dependence of strain-rate of solder joints with same microstructure by retaining nearly the same microstructure during creep testing.

All micrographs containing scratches were scanned with an AGFA model scanner and the scanned images were converted to PICT files after adjusting the contrast to provide optimal clarity of the scratch, using Adobe Photo software. Datathief software was used to digitize the scratch data and these data were analyzed in spreadsheet programs to determine the shear strain as a function of time as follows : X axis was put in the direction of the thickness of solder joint and Y axis in the normal direction of the thickness of solder joint. The software measured X and Y value for 15 positions on a scratch. The slopes (dY/dX) between each position on a scratch were calculated from which an average slope was determined. Since the scratch line before creep testing was oblique with respect to the direction of solder joint thickness, an average slope of scratch before creep testing was subtracted by an average slope of the deformed scratch after a given time to obtain a shear strain value at a given time.

The examination of the fracture surfaces was performed using a Hitachi S2500 scanning electron microscope after creep rupture of the solder joint. These micrographs indicated that there were a number of large pores in the solder joints, and these regions could not carry the load. The area of pores larger than 50 μm in diameter were subtracted from the soldered area to obtain the load carrying area used to determine the average stress operating in the solder joint. The solder joints were found to have a porosity up to 20 % of the solder joint area.

CHAPTER 4

RESULTS

4.1 MICROSTRUCTURAL OBSERVATION OF BULK MATERIALS

4.1.1 Eutectic Sn/Pb (63Sn/37Pb) and Sn/Ag (96.5Sn/3.5Ag) Solders

The microstructure of eutectic Sn/Pb solder shown in Figure 14 consisted of two phases of lead-rich α -Pb phase and tin-rich β -Sn phase which are the same microstructure identified in the literature review. The dark regions represents the lead-rich α -Pb phase and the bright regions represents the tin-rich β -Sn phase. This microstructure appeared intermediate one between globule and lamellae microstructure since the colony boundaries which define regions having similar orientation are not clear in all areas.

The microstructure of cast eutectic Sn/Ag (96.5Sn/3.5Ag) solder shown in Figure 15 were characterized by a colonized eutectic microstructure consisting of tin-rich primary dendrites (appearing white in optical micrography) which are surrounded by regions of a true eutectic phase of tin-rich β -phase with dispersed rod-shpaed Ag_3Sn intermetallic ϵ -phase.

The existence of tin-rich dendrites in the microstructure of the eutectic Sn/Ag solder was also observed in another study [58] where these dendrites appeared to be quite stable and were present after months of room temperature aging. The presence of this tin rich dendrites in cast eutectic Sn/Ag solder is indicative of the nonuniform cooling rate during

solidification [58]. Another study [98] observed only the true eutectic phase for slow-cooled eutectic Sn/Ag cast bulk where the tin-rich β -phase dendrites were not observed.

In the true eutectic phase Ag_3Sn intermetallic ϵ -phase appeared to have an acicular shape and areas having similar orientation of Ag_3Sn Intermetallic ϵ -phase are visible. In eutectic Sn/Ag alloy, the volume fraction of Ag_3Sn intermetallic ϵ -phase is very small (i.e., less than 5 % in volume) [56].

To evaluate the effect of cooling rate on microstructure, eutectic Sn/Ag and Sn/Pb solder droplets were splat-cooled on copper and microstructurally examined as shown in figure 16 and 17. The left sides of the micrographs shown in Figure 16 and 17 exhibits a globule microstructure for eutectic Sn/Pb solder and a finer grained microstructure for eutectic Sn/Ag solder caused by fast cooling rate when the solder was in contact with the copper plate resulting in rapid heat withdrawal and solidification. The microstructure of eutectic Sn/Ag solder on this side is characterized by the eutectic phase being evenly distributed. In contrast, the right sides of the micrographs shown in Figure 16 and 17 showed a slower cooling rate near the air-cooled side than the left sides of the micrographs. Eutectic Sn/Pb solder shows the lamellar eutectic microstructure on this side. The microstructure of eutectic Sn/Ag solder in this region is characterized by a colonized eutectic consisting of Sn-rich primary dendrites ranging in size from 5 to 25 μm which are surrounded by the true eutectic phase.

As shown in the Figure 16 and 17, it was evident that the microstructures of eutectic Sn/Pb and Sn/Ag solders were dependent upon the cooling rate. The variation in cooling

rate in the thickness of the splat from severe to moderate from the Cu surface to the outer surface of the solder caused the inhomogeneous phase distribution.

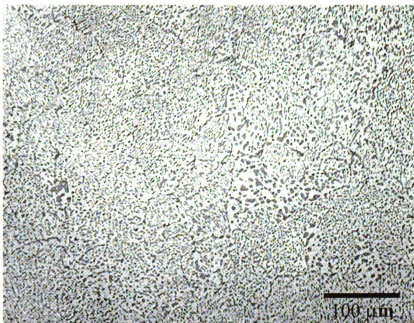


Figure 14 Optical Microstructure of Eutectic Sn/Pb Solder Ingot

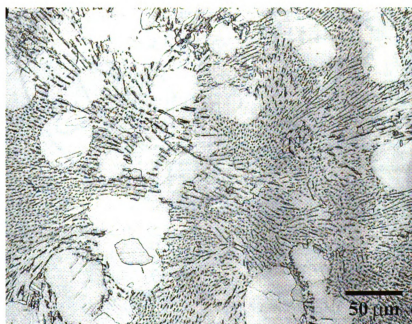


Figure 15 Optical Microstructure of Eutectic Sn/Ag Solder Ingot

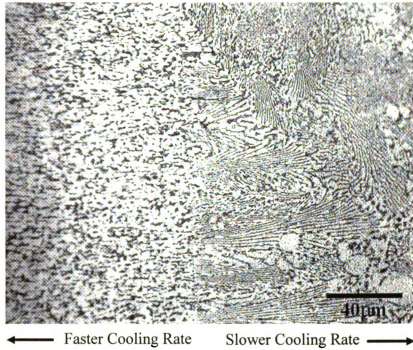


Figure 16 Microstructural Variation of Eutectic Sn/Pb Solder
Due to Variation of Cooling Rate During Splat Cooling

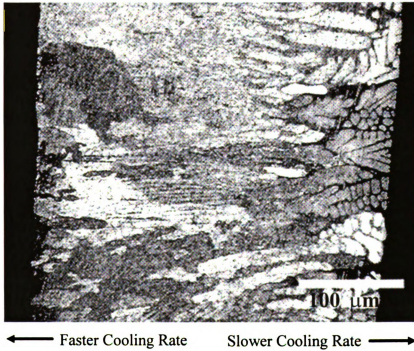


Figure 17 Microstructural Variation of Eutectic Sn/Ag Solder
Due to Variation of Cooling Rate during Splat Cooling

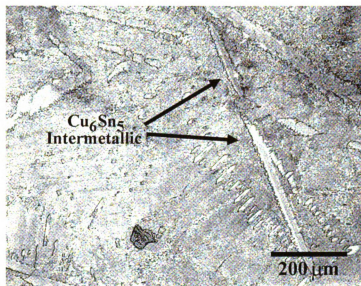
4.1.2 Slow Cooled Eutectic Sn/Pb and Sn/Ag Composite Solders

Eutectic Sn/Pb composite solder produced by induction melting and slow cooling is shown in Figure 18. Eutectic Sn/Pb composite solder contained Cu_6Sn_5 intermetallic η -phase of long, rod-like shape in the eutectic Sn/Pb matrix. The eutectic Sn/Pb matrix clearly showed lamellar microstructure resulting from the slow cooling rate during solidification where colonies having similar orientation are easily visible.

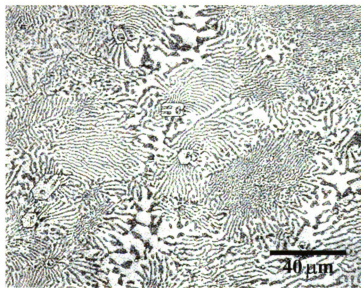
Eutectic Sn/Ag composite solder shown in Figure 19 exhibited Cu_6Sn_5 intermetallic η -phase surrounded by colonized eutectic Sn/Ag microstructure. Cu_6Sn_5 intermetallic η -phase had a rod shape shorter than that in the eutectic Sn/Pb composite solder. Eutectic Sn/Ag matrix in composite solder retained nearly the same microstructure as eutectic Sn/Ag solder. Eutectic Sn/Ag matrix showed the tin-rich β -phase dendrites and the true eutectic phase of tin-rich β -phase with dispersed Ag_3Sn intermetallic ϵ -phase. In the eutectic Sn/Ag matrix the primary and secondary dendrites of tin-rich β -phase without Ag_3Sn intermetallic ϵ -phase are easily visible and the true eutectic phase comprised of Ag_3Sn intermetallic ϵ -phase of acicular shape and tin-rich β -phase.

The addition of Cu and Sn elements to introduce 20 vol% Cu_6Sn_5 intermetallic η -phase exhibited no effects on the microstructure of eutectic Sn/Pb and Sn/Ag matrix, since the microstructure of eutectic Sn/Pb and Sn/Ag matrix of composite solders was the same as that without composite phase. A previous study showed that adding 1% Zn to eutectic Sn/Ag suppressed the formation of the tin-rich β -phase dendrites and introduced a finer and more uniform eutectic microstructure throughout the alloy [4]. In this study

Cu and Sn elements added to eutectic Sn/Ag and Sn/Pb solders appeared to be consumed to form 20 vol% Cu_6Sn_5 intermetallic η -phase without affecting the microstructure of eutectic Sn/Pb and Sn/Ag microstructure.

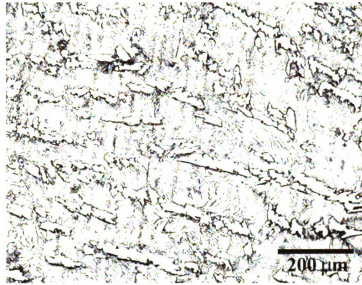


(a)

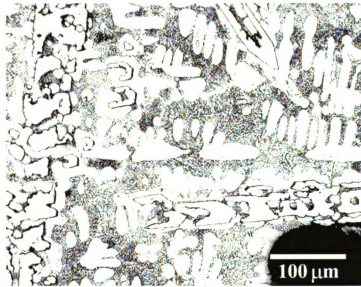


(b)

Figure 18 Microstructure of Slow Cooled Eutectic Sn/Pb Composite Solder
(a) Cu_6Sn_5 Intermetallic η -phase Morphology (b) Eutectic Sn/Pb Matrix



(a)



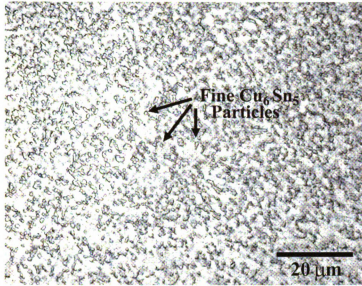
(b)

Figure 19 Microstructure of Slow Cooled Eutectic Sn/Ag Composite Solder
(a) Cu_6Sn_5 Intermetallic η -Phase Morphology (b) Eutectic Sn/Ag Matrix

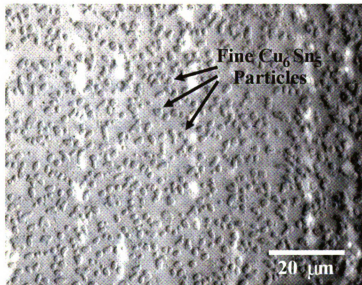
4.1.3 Remelted Composite Solders

The eutectic Sn/Pb and Sn/Ag composite solders were remelted in a furnace and splat cooled on a Cu plate. Figure 20 shows the morphology of Cu_6Sn_5 intermetallic η -phase in eutectic Sn/Pb and eutectic Sn/Ag composite solders as a result of fast cooling rate by quenching on a Cu plate. The Cu_6Sn_5 intermetallic η -phase was changed by such a treatment to a very fine particle shape with the size less than 2 μm distributed homogeneously throughout the eutectic Sn/Pb and eutectic Sn/Ag matrix. It should be noted that the size of Cu-rich Cu-Sn dispersoids was about 0.1~1.0 μm [47] and 0.2~0.5 μm [74] in *in-situ* Sn/Pb composite solder produced by rapidly solidifying Sn/Pb/Cu ternary alloys containing 2.5, 5, and 7.5 wt % Cu by induction melting/gas atomization (IMGA).

The solder joints were fabricated with preforms of the remelted eutectic Sn/Pb and Sn/Ag composite solder cut out of rolled sheet at the reflow temperature below the melting temperature of Cu_6Sn_5 intermetallic η -phase, retaining this morphology of Cu_6Sn_5 intermetallic η -phase.



(a)



(b)

Figure 20 The Modified Morphology of Cu_6Sn_5 Intermetallic η -Phase due to Splat Cooling in (a) Eutectic Sn/Pb composite solder and (b) Eutectic Sn/Ag Composite Solder

4.2 MICROSTRUCTURES OF COMPOSITE SOLDER JOINTS

In order to obtain solder joints of the scale of those found in actual electronic solder joints with representative, air-cooled microstructures, small single shear lap joints were manufactured using the copper dogbones halves and the heating history described in the experimental procedure.

Figure 21 illustrates the typical, as-formed microstructure of eutectic Sn/Pb composite solder joint. The microstructure is characterized by Cu_6Sn_5 intermetallic particles evenly distributed in the eutectic Sn/Pb matrix without agglomeration of the particles. The Sn/Pb matrix surrounding Cu_6Sn_5 intermetallic particles showed a typical globular eutectic microstructure which consisted of lead-rich α -phase of bright areas and tin-rich β -phase of dark areas.

The eutectic Sn/Ag composite solder joint shown in Figure 22 exhibits typical, colonized microstructure of eutectic Sn/Ag matrix containing Cu_6Sn_5 Intermetallic particles. The eutectic Sn/Ag matrix in the joint revealed nearly same microstructure like bulk eutectic Sn/Ag solder which consisted of tin-rich dendrites and regions of a true eutectic phase comprised of tin-rich β -phase and Ag_3Sn ϵ -phase. Ag_3Sn ϵ -phase showed equiaxed shape rather than acicular shape in bulk solder.

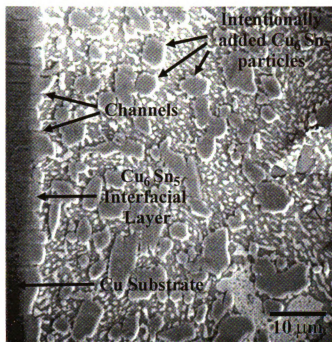


Figure 21 SEM Microstructure of Eutectic Sn/Pb Composite Solder Joint Containing Cu₆Sn₅ Intermetallic η -Phase Particles

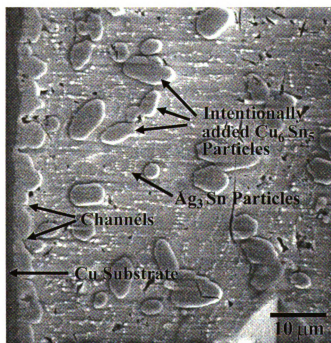


Figure 22 SEM Microstructure of Eutectic Sn/Ag Composite Solder Joint Containing Cu₆Sn₅ Intermetallic η -Phase Particles

The Cu_6Sn_5 intermetallic particles had undergone a change of size from less than 2 μm to 3-8 μm upon reflow of eutectic Sn/Pb and Sn/Ag composite solders but retained nearly the same particle shape. Cu_6Sn_5 intermetallic compound was also found as an interfacial layer between the Cu substrate and the eutectic Sn/Pb and Sn/Ag composite solders. Cu_6Sn_5 interfacial layer formed between the eutectic Sn/Pb and Sn/Ag composite solder and Cu substrate appeared to be a continuous interfacial layer. However, closer observation reveals channels in the Cu_6Sn_5 interfacial layer. These channels have been proposed to provide an open diffusion path for Cu during solidification [110].

The density of Cu_6Sn_5 intermetallic compound, 8.23g/cm^3 , at room temperature is reasonably close to that of liquid eutectic Sn/Pb solder, 8.2 g/cm^3 , at the eutectic temperature [69]. These similar densities of Cu_6Sn_5 intermetallic compound and liquid Sn/Pb solder indicates that the buoyancy of Cu_6Sn_5 intermetallic particles during reflow should be small, and this will promote a uniform distribution of particles without floating of Cu_6Sn_5 intermetallic particles in eutectic Sn/Pb matrix during reflow.

The coarsening of the Cu_6Sn_5 intermetallic particles from less than 2 μm to 3 ~ 8 μm upon reflow of eutectic Sn/Pb composite solder could be expected during reflow and solidification due to the fast rate of diffusion of Cu in Sn shown in Table 3. The previous studies [47] revealed that Cu-Sn intermetallic particles experienced drastic changes in morphology from particle shape to plate shape as well as in size from 0.2-1 μm to greater than 1 μm upon reflow of *in-situ* Sn/Pb bulk composite solder. In the composite solders produced by reflowing mixtures of Cu_6Sn_5 particles and eutectic Sn/Pb solder paste, most

of Cu_6Sn_5 intermetallic particles appeared to be in the form of sintered clusters of small particles ranging from about twenty to sixty microns [69].

A previous study [111] showed that during reflow of dispersion-strengthened Sn/Pb solder joint, the dispersion-strengthened solder revealed finer microstructure than that of the conventional solder upon solidification suggesting that the dispersoids acted as heterogeneous nucleation sites resulting in fine microstructure. It is unclear in this study if the Cu_6Sn_5 intermetallic particles similarly provided heterogeneous sites for nucleation of Sn/Pb matrix, since the microstructure of eutectic Sn/Pb matrix is also subject to change depending on the cooling rate upon solidification.

However, it appeared that the Cu_6Sn_5 intermetallic particles affected the growth of colony in Sn/Pb matrix which is volumes of lamellae of similar orientation. The size of colony was checked by counting the number of intercept of colony boundary and a linear line. The size of colony in Sn/Pb composite solder joint was smaller than Sn/Pb solder joint without composite phase. There was areas with no specific orientation like globular microstructure in Sn/Pb composite solder joint, indicating that the Cu_6Sn_5 intermetallic particles caused the matrix not to form the colony by limiting the growth of colony.

A previous study [56] on the eutectic Sn/Ag solder joint produced by laser soldering showed that Cu_6Sn_5 intermetallic η -phase was formed in the form of dendrites by dissolution of Cu substrate during reflow and dispersed throughout the eutectic Sn/Ag matrix. Laser soldering superheated eutectic Sn/Ag solder to high temperatures, typically from 400°C to 600°C, and this superheating was considered to result in more rapid

dissolution of Cu from substrate and great amounts of Cu_6Sn_5 intermetallic in the bulk solder. However, Cu_6Sn_5 intermetallic η -phase was not formed in infrared (IR) soldering which heats the solder to only 240 to 260°C. It was concluded that Cu dissolution is much more dependent on the temperature reached than the time at the temperature.

In this study the temperature reached during soldering is similar to that in infrared(IR) soldering. It could be thought that all of the Cu_6Sn_5 intermetallic η -phase resulted from preformed Cu_6Sn_5 intermetallic η -phase by intentionally adding Cu and Sn elements, not Cu dissolution from substrate upon reflow and solidification.

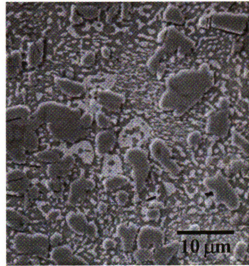
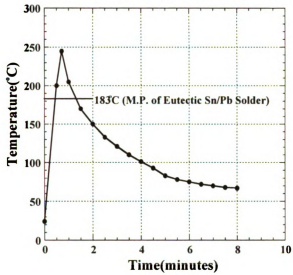
The previous study [56] also found that in laser soldering the Ag_3Sn intermetallic ϵ -phase was much finer and appeared only at magnifications over 4000X. The small size of this phase was attributed to the rapid cooling rate, typically 10^4°C/sec , and such rapid cooling promoted nucleation but severely limited the growth. In this study, the cooling rate was about 1°C/sec as shown in Figure 11, which appeared to be fast enough to result in Ag_3Sn intermetallic ϵ -phase of fine particle shape with size less than $0.5\text{ }\mu\text{m}$. However, this result is controversial because the rod-like Ag_3Sn intermetallic ϵ -phase was formed in infrared (IR) soldering in which the cooling rate is 10°C/sec .

4.3 AGING OF COMPOSITE SOLDER JOINTS

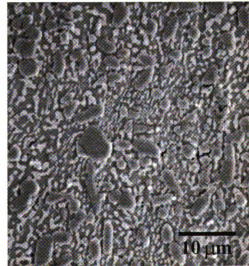
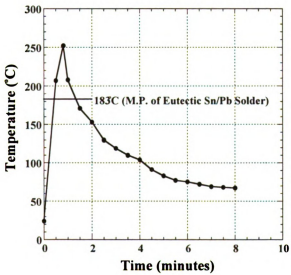
Figure 23 shows the monitored heating/cooling history when the eutectic Sn/Pb composite solder joints used in first and second aging were manufactured. These two heating/cooling histories show that the eutectic Sn/Pb solder joints used in first and second aging were fabricated in a similar condition resulting in similar microstructure shown in Figure 23.

The microstructure of eutectic Sn/Pb composite solder joints after static aging are shown in Figure 24. By comparison with Figure 23, the eutectic Sn/Pb composite solder joints revealed dramatic coarsening in size and shape of tin-rich α -phase and lead-rich β -phase when aged at 50, 80, 100, and 120°C for 100 hours. All of the globular microstructure observed in the as-solidified microstructure disappeared for all of the aged joints. It was apparent that increasing the aging temperature caused more coarsening in both phases.

Figure 25 shows the microstructure of eutectic Sn/Pb composite solder joints after 20 cyclic aging between room temperature and aging temperature (20 hours at aging temperature). By comparison with Figure 24, the 100 hours static aged solder joints showed more coarsening in both phases than after 20 hours during cyclic aging between room temperature and aging temperature. The time at aging temperature for static aging was 5 times longer, accounting for the greater amount of coarsening.



(a)



(b)

Figure 23 The Temperature versus Time Profile for Manufacturing and Corresponding Microstructure of Eutectic Sn/Pb Composite Solder Joints Used in (a) First Aging and (b) Second Aging

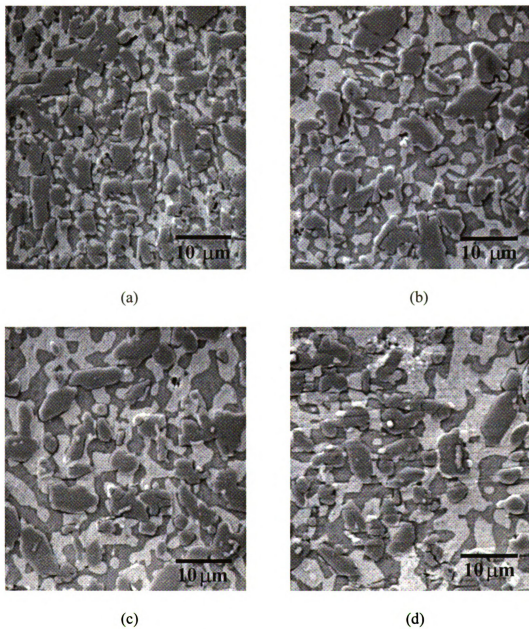


Figure 24 The Microstructure of Eutectic Sn/Pb Composite Solders after Static Aging at (a) 50, (b) 80, (c) 100, (d) 120°C for 100 hours

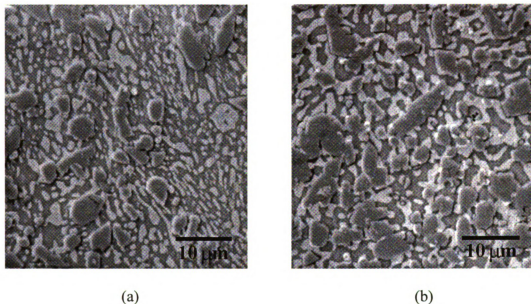


Figure 25 The Microstructure of Eutectic Sn/Pb Composite Solder Joints after 20 Aging Cycles (20 Hours at Aging Temperature)
(a) 20 Aging Cycles **between** RT and 60°C (20 Hours at 60°C)
(b) 20 Aging Cycles **between** RT and 120°C (20 Hours at 120°C)

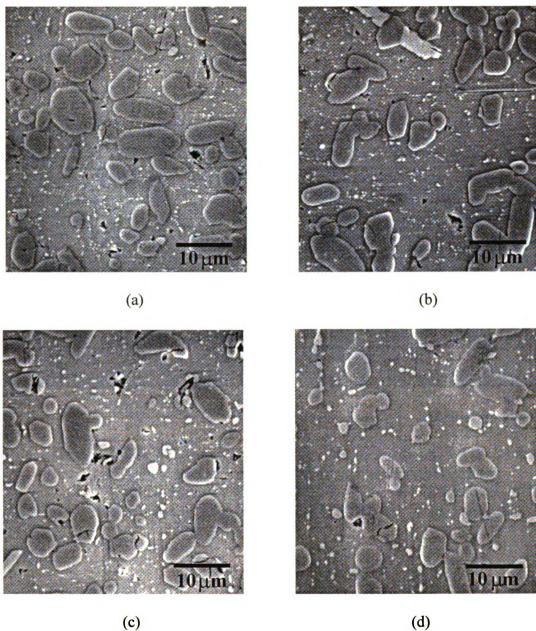


Figure 26 The Microstructural Change of Eutectic Sn/Ag Composite Solders after Static Aging at (a) 60, (b) 100, (c) 120, (d) 150°C for 100 hours

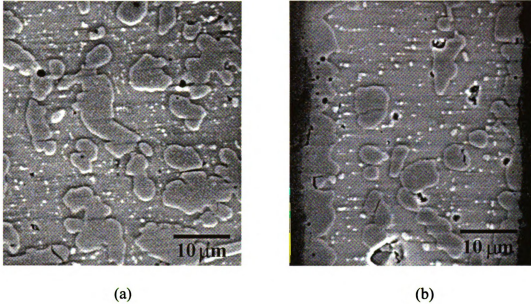


Figure 27 The Microstructure of Eutectic Sn/Ag Composite Solder Joints after 20 Aging Cycles (20 Hours at Aging Temperature)
(a) 20 Aging Cycles between RT and 100°C (20 Hours at 100°C)
(b) 20 Aging Cycles between RT and 150°C (20 Hours at 150°C)

The microstructures of eutectic Sn/Ag composite solder joints obtained after static aging are shown in Figure 26. The eutectic Sn/Ag composite solder joints exhibited significant coarsening in the Ag_3Sn ϵ -phase particle size when aged at 60, 100, 120, and 150°C for 100 hours. Similar results were observed in a previous study on the coarsening of Ag_3Sn ϵ -phase particle [56]. Large acicular Ag_3Sn ϵ -phase were sometimes observed as shown in Figure 26 (b) and (c).

It was evident that increasing the aging temperature had a dramatic effect on Ag_3Sn ϵ -phase particle size. By comparison with Figure 22, the joint aged at 60°C retained most of the colonied characteristics observed in the as-solidified microstructure. The tin-rich dendrites were apparent in matrix, but the surrounding Ag_3Sn ϵ -phase particles coarsened. The specimen aged at 100°C retained few colonied characteristics of as-solidified microstructure. After aging at 120 and 150°C, all of the colonied characteristics observed in the as-solidified microstructure have disappeared as a result of extensive Ag_3Sn ϵ -phase particle coarsening.

Figure 27 shows the microstructure of eutectic Sn/Ag composite solder joints after 20 cyclic aging between room temperature and aging temperature (20 hours at aging temperature). By comparison with Figure 26, cyclic aged solder joints for 20 hours showed similar coarsening of Ag_3Sn particle to static aged solder joints for 100 hours. Since the 20 hours aging time for cyclic aging was shorter than 100 hours for static aging, a similar coarsening in static and cyclic aging indicated that the rate of coarsening is faster in cyclic aging than in static aging.

In contrast, Cu_6Sn_5 intermetallic particles for eutectic Sn/Pb and Sn/Ag composite solder joints showed no obvious coarsening during the times and temperatures used in this study. The Cu_6Sn_5 intermetallic particles were stable at elevated temperature up to 150°C for 100 hours.

4.4 CREEP DEFORMATION OF COMPOSITE SOLDER JOINTS

4.4.1 Scratch Technique for Shear Strain Measurement

Scratches made across the joint area were used to determine the strain distribution and average shear strain across the eutectic Sn/Ag and Sn/Pb composite solder joint. Figure 28 shows scratches used to determine the average shear strain and strain distribution of an eutectic Sn/Ag composite solder joint before loading and after creep deformation at 21.7MPa for 374 ksec. The scratch line was nearly linear in the as-made condition before loading and after some time the scratch deviated from its original configuration.

The deviation of the scratch line from the original position was not homogeneous across the joint, indicating that the strain distribution was inhomogeneous across the joint as shown in Figure 28 (c). Since the deviation of scratch from its original position was dominated by deformation in the eutectic Sn/Ag matrix, the Cu_6Sn_5 intermetallic particles in which a less deviation of the scratch was observed caused this inhomogeneity in shear strain across the joint. This effect is most apparent in the drop in strain on the right of the upper scratch. In addition, the deviation of scratch from its original position was not observed in Cu substrate and Cu_6Sn_5 η -phase interfacial layer between eutectic Sn/Ag composite solder and Cu substrate. The shear strain was computed by measuring the

displacement of the scratch, Δy , using $\gamma = \Delta y / \Delta x$, where Δx refers to the distance from the interface where the displacement was measured. The average shear strain was calculated from the inhomogeneous shear strain distribution and was used to make plots of shear strain versus time.

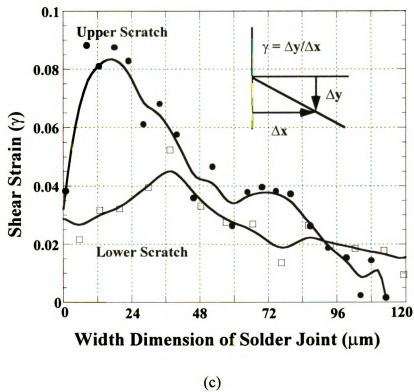
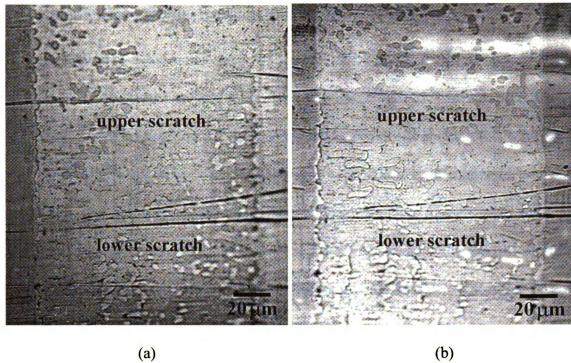


Figure 28 Two Scratches Across The Eutectic Sn/Ag Composite Solder Joint
 (a) before loading (b) after creep deformation at 21.7 MPa for 374 ksec
 (c) shear strain distribution across the solder joint

4.4.2 Eutectic Sn/Ag Composite Solder Joints

Figure 29 shows the creep curve of average shear strain versus time for unaged eutectic Sn/Ag composite solder joints which were crept with 21.7 MPa and 25.8 MPa. Immediately after loading, the unaged eutectic Sn/Ag composite solder joints exhibited a brief period of primary creep in which the strain-rate decreased to its minimum, or steady state value. The strain-rate of the steady state region was higher in high stress condition than low stress condition. The rupture time differed significantly for the two different stress conditions, but the strain at which the rupture process started was near 0.2 for both conditions.

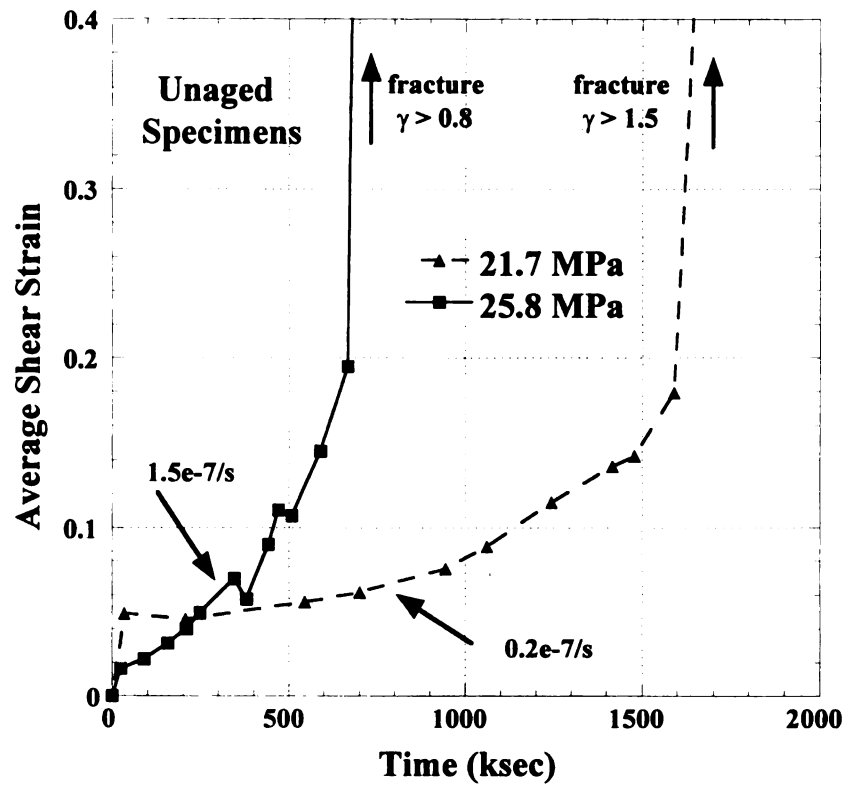


Figure 29 Creep Curve of Average Shear Strain versus Time for Unaged Eutectic Sn/Ag Composite Solder Joints

Figure 30 shows the creep curve of average shear strain versus time for eutectic Sn/Ag composite solder joints which were aged at 150, 120, 100, 60°C for 100 hours. The creep experiments were performed under dead loading condition of 3.5 lb (about 19 MPa for solder joint aged at 120, 100, and 60°C, and 16.3 MPa for solder joints aged at 150°C) and 4 lb (about 18.6, 21.1, 22 MPa for solder joints aged at 150°C, 100°C, 60°C) as shown in Table 1. The same loading condition produced slightly different stress conditions for each solder joint due to slightly different load carrying areas as determined from the fracture surface.

At the first stress condition of about 19 MPa, the solder joints aged at 100 and 60°C showed similar strain-rate ($1.8\text{e-}7/\text{s}$) at steady-state condition, while the solder joint aged at 120°C exhibited faster strain-rate ($7.2\text{e-}7/\text{s}$). At the second stress condition of about 21 MPa for the joint aged at 100°C and about 22 MPa for the joint aged at 60°C, the solder joint aged at 100°C revealed faster strain-rate ($16\text{e-}7/\text{s}$) than that aged at 60°C ($2.9\text{e-}7/\text{s}$). It was evident that the solder joints aged at higher temperature showed higher steady-state strain-rate. The solder joint aged at 150°C showed much lower strain and strain-rate ($0.2\text{e-}7/\text{s}$ for the first stress condition and $2.5\text{e-}7/\text{s}$ for second stress condition) compared to the other solder joint aged at lower temperatures because it had a lower applied stress than the other solder joints.

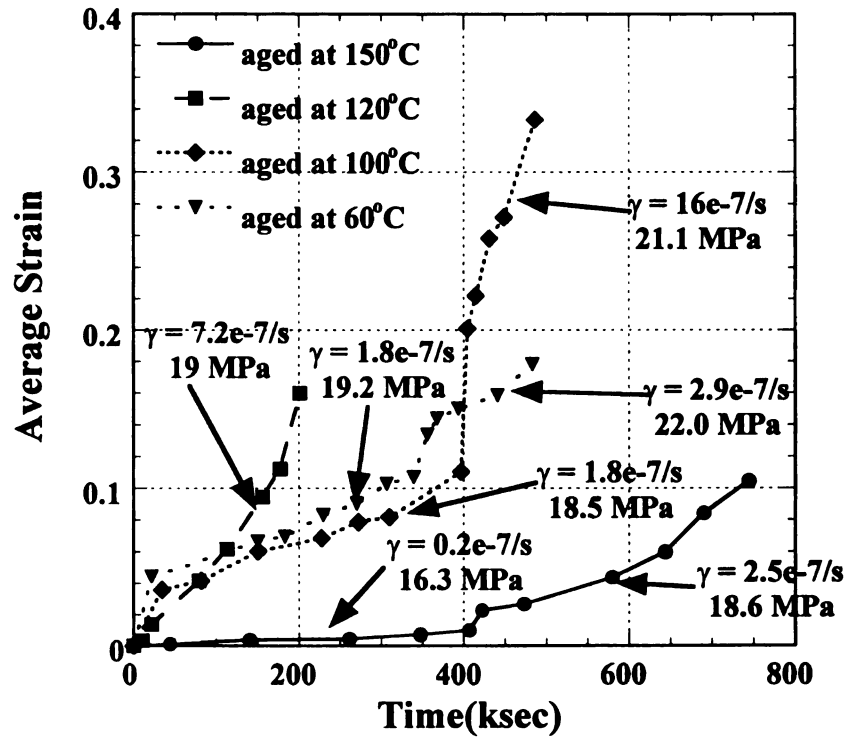


Figure 30 Creep Curve of Average Shear Strain versus Time for Aged Eutectic Sn/Ag Composite Solder Joints

Table 1 Creep Deformation Parameters for Eutectic Sn/Ag Composite Solder Joints

	Unaged Eutectic Sn/Ag Composite Solder Joints		Aged Eutectic Sn/Ag Composite Solder Joints							
			150°C		120°C		100°C		60°C	
Thickness of Joints (μm)	120	57	70		100		80		67	
Soldered Area (10 ⁵ μm ²)	8.2	9.3	10.1		8.4		9.0		10.4	
Pore Area (10 ⁵ μm ²)	1.0	0.67	0.53		0.16		0.5		2.3	
Porosity (%)	12.5	7.2	5.2		2.0		5.6		22.3	
Applied Loads (lbs)	3.5	5	3.5	4	3.5	3.5	4	3.5	4	
Applied Stress (MPa)	21.7	25.8	16.3	18.6	19	18.5	21.1	19.2	22	

4.4.3 Eutectic Sn/Pb Composite Solder Joints

The average shear strain versus time for eutectic Sn/Pb composite solder joints which were aged at 120, 100, 80, 50°C for 100 hours is shown in Figure 31. The creep experiment of the eutectic Sn/Pb composite solder joints were performed under dead loading condition of 2.25 lb (about 8.9, 10.2, 10.5, 8.8 MPa for solder joint aged at 120, 100, 80, and 60°C) and 2.5 lb (about 11.7, 9.8 MPa for solder joints aged at 80°C, 50°C) as shown in Table 2. The same loading condition produced slightly different stress condition for each solder joint due to variations in the soldered area and pore area present in solder joints.

As with eutectic Sn/Ag composite solder joints, a higher aging temperature in caused a higher steady-state strain-rate in creep deformation, even though the applied stress for each solder joint was different due to the porosity. The solder joints aged at 80°C and 60°C also showed a similar trend at the second stress condition. It was evident that aging at the higher temperature produced higher steady-state strain-rates. The solder joint aged at 50°C exhibited a large soldered area and no apparent porosity, resulting in a low applied stress.

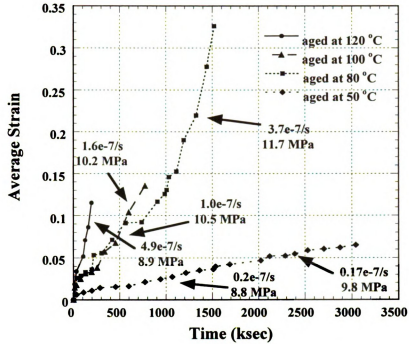


Figure 31 Creep Curve of Average Shear Strain versus Time for Aged Eutectic Sn/Pb Composite Solder Joints

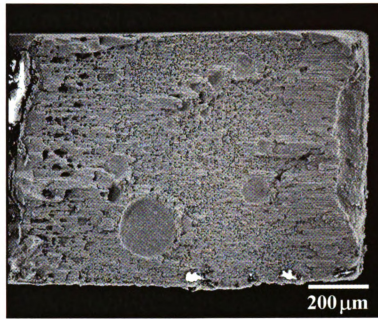
Table 2 Creep Deformation Parameters for Eutectic Sn/Pb Composite Solder Joints

	Aged Eutectic Sn/Pb Composite Solder Joints					
	120°C	100°C	80°C		50°C	
Thickness of Joints (μm)	98	76	117		77	
Soldered Area ($10^3 \mu\text{m}^2$)	13.3	10.3	10		11.4	
Pore Area ($10^3 \mu\text{m}^2$)	2	0.5	0.47		0	
Porosity (%)	14.6	4.6	4.7		0	
Applied Loads (lbs)	2.25	2.25	2.25	2.5	2.25	2.5
Applied Stress (MPa)	8.9	10.2	10.5	11.7	8.8	9.8

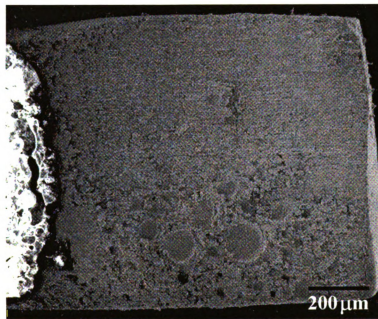
4.4.4 The Fracture Surfaces of Composite Solder Joints

Representative fracture surfaces of crept eutectic Sn/Ag and Sn/Pb composite solder joints are shown in Figure 32. The fracture surface showed that the solder joints contained big and small pores up to 20 % of the soldered area which did not carry the load during the creep deformation. The porosity present in each solder joint was subtracted from the soldered area to calculate the applied stress to solder joints. The soldered area and porosity were different for each solder joint, as shown in Tables 1 and 2.

The fracture process consisted of smearing and tearing actions. The eutectic Sn/Ag and Sn/Pb matrix were identified to be smeared through the whole fracture surface during fracture process. Figure 33 (a) shows a smeared area on the fracture surface of an eutectic Sn/Ag composite solder joints showing a high peak intensity of Sn-rich β -phase as identified by EDAX. There is a small Ag peak to the left of the Sn peak. The small Ag_3Sn particles which could not be visually identified in the fracture surface due to their small size were considered to be distributed over the whole area of fracture surface. Cu_6Sn_5 intermetallic η -phase particles were pulled out of their original position, and distributed over the fracture surface by smearing action of two faces of fractured joint. They were identified as Cu containing particles as shown in the EDAX profile in Figure 33 (b).



(a)

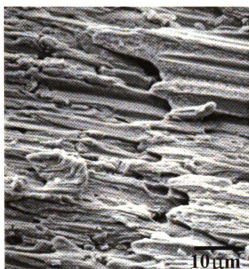


(b)

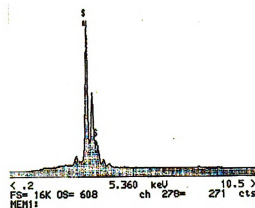
Figure 32 The Fracture Surface Showing Pores in

(a) Eutectic Sn/Ag Composite Solder Joints Aged at 100°C

(b) Eutectic Sn/Pb Composite Solder Joints Aged at 100°C



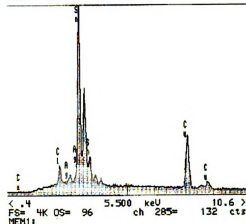
X-RAY: 0 - 20 keV
 Live: 100s Preset: 100s Remaining: 0s
 Real: 163s 39% Dead



(a)



X-RAY: 0 - 20 keV
 Live: 100s Preset: 100s Remaining: 0s
 Real: 127s 21% Dead



(b)

Figure 33 SEM Micrograph showing
 (a) The Smeared Matrix in Eutectic Sn/Ag
 Composite Solder Joint and EDAX Result
 (b) The Cu_6Sn_5 Intermetallic Particles
 in Fracture Surface and EDAX Result

The composite solder joints showed two kinds of fracture paths. Most fractures showed the fracture through bulk composite solder and sometimes fracture near the interface between composite solder and interfacial layer was identified in the side view of fractured solder joints such as the joint in Figure 34.

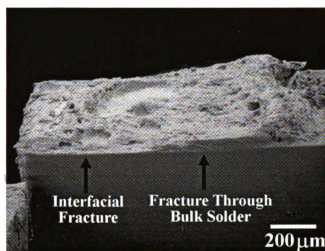


Figure 34 SEM Micrograph Showing Side View of Fracture Surface of Eutectic Sn/Ag Composite Solder Joint Aged at 60°C For 100 Hours

CHAPTER 5

ANALYSIS AND DISCUSSION

5.1 AGING OF COMPOSITE SOLDER JOINTS

The analysis of aging effects was performed using length/intercept measurement between Pb-Sn interfaces for eutectic Sn/Pb composite solder joints, and measurement of the particle size of the Ag₃Sn ε-phase for eutectic Sn/Ag composite solder joint.

The aging kinetics (activation energy for diffusion) was determined from the known aging time and temperature, using the equation [112]

$$r^3 - r_0^3 = kt \exp(-Q / RT)$$

where r_0 is the length/intercept for eutectic Sn/Pb and the Ag₃Sn particle radius for eutectic Sn/Ag before aging, r is the length/intercept for eutectic Sn/Pb and the Ag₃Sn particle radius for eutectic Sn/Ag after aging, t is the aging time (100 hours for static aging and 20 hours for cyclic aging), k is a proportionality constant, Q is the activation energy for the aging process, T is the temperature in degrees Kelvin, and R is the gas constant (8.314 J/mol °K).

The above equation was modified as follows

$$\log \left\{ \frac{(r^3 - r_0^3)}{t} \right\} = - \frac{Q}{2.303 RT} + \log k$$

and the activation energy for the aging process was determined from the slope, $(-Q/2.303R)$, of the $\log\left\{(r^3 - r_0^3)/t\right\}$ versus $1/T$ plot.

Figure 35 shows the Arrhenius plot of the change of size with inverse temperature for Sn/Pb composite solder joints. The slope provides an activation energy of 60 kJ/mol for cyclic aging, and 60 kJ/mol at high temperatures and 21 kJ/mol at low temperatures for static aging. A similar activation energy at high temperatures was found for static and cyclic aging conditions, indicating that the same mechanism was active for both aging conditions. However, a change in mechanism is apparent at lower temperatures for static aging, where the rate of coarsening appears to become faster than observations in cyclic aging, with an activation energy of 21 kJ/mol.

An activation energy of 60 kJ/mol for static aging at high temperatures and cyclic aging corresponds to the approximately half of activation energy for lattice diffusion of Sn and Pb shown in Table 3. Previous studies [113] showed that diffusion in the lattice as well as in the grain boundaries has been found to be appreciable at the temperatures which the solders may experience during operation. It also implies that an effective diffusion coefficient involving lattice and grain boundary diffusion should be used for explanation of diffusion process. Since the activation energy for grain boundary diffusion has been observed to be approximately the half of activation energy for lattice diffusion, the observed activation energy of 60 kJ/mol implies that grain boundary or interfacial diffusion was dominant in the aging process.

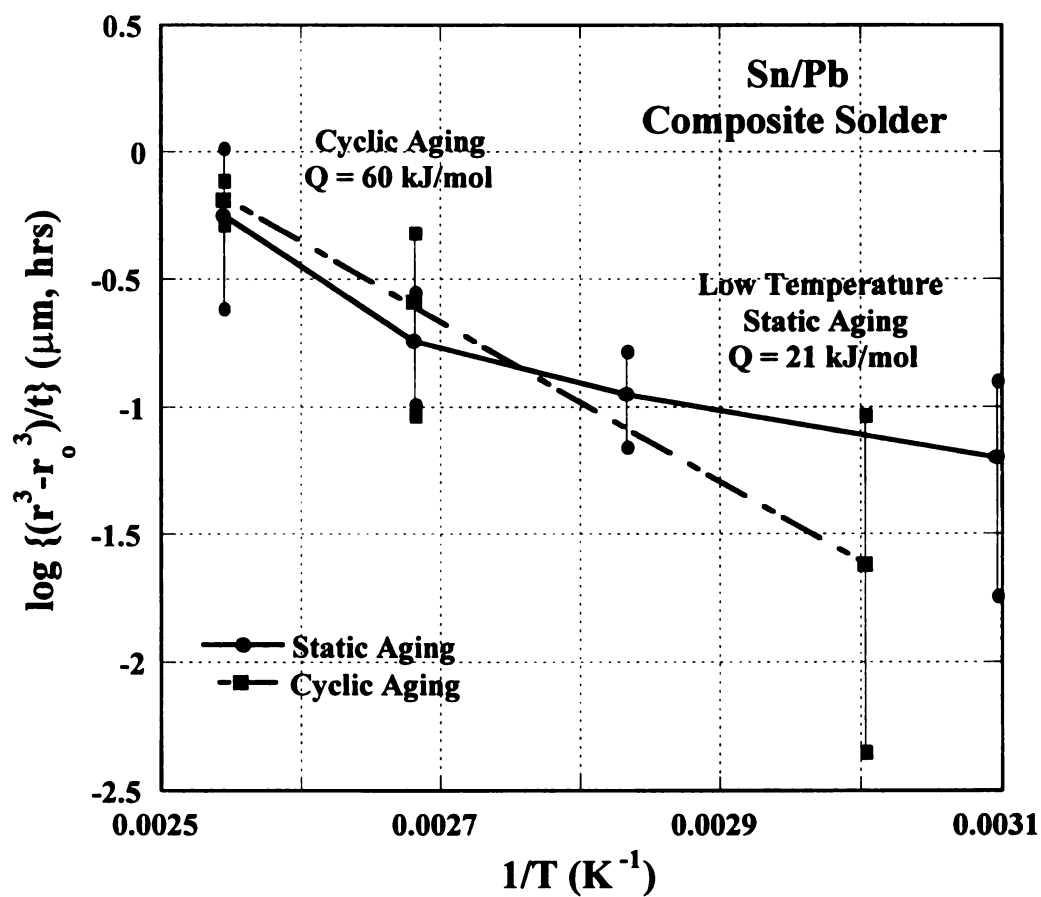


Figure 35 Arrhenius Plot for Aging of Eutectic Sn/Pb Composite Solder
 (The error bars were determined from the average value of r_0 and standard deviation of r values evaluated from 7 measurements of the length/intercept for each aging condition)

Table 3 Relative Diffusivities of elements in Solders [114]

	Diffusivity D_0 (cm ² /sec)	Activation Q (kJ/mol)	(Dt) ^{1/2} μm for 100 hours		
			25°C	75°C	150°C
Pb in Pb	0.995	107.4	0.002	0.052	1.399
Pb in Sn	4.0	99.6	0.012	0.201	8.58.5
Sn in Sn ⊥ c axis	10.7	105.1	0.012	0.254	6.364
Sn in Sn c axis	7.7	107.2	0.007	0.150	4.005
Ag in Sn ⊥ c axis	0.18	77	0.454	4.24	44.8
Ag in Sn c axis	0.0071	55.1	7.5	37.0	200.3
Cu in Sn ⊥ c axis	0.0024	33.1	369	964	2658
Cu in Sn c axis	2 x 10 ⁻⁶ at 25°C		848528		

However, an activation energy of 21 kJ/mol at lower temperatures for static aging and this transition to lower activation energy was not understood at this time. Thus to evaluate the repeatability of this result, aging by thermal cycling was performed again using an appliance timer that turned the hot plate on or off each hour without an overnight hold time.

Figure 36 describes observed aging kinetics from the second aging experiment. A similar activation energy of 25.5 kJ/mol for static and 20.3 kJ/mol for the cyclic aging condition was also observed. However, a transition to higher activation energy was not observed at higher temperatures.

Several issues that could affect coarsening kinetics were investigated. Coarsening effects as a result of aging was evaluated without including the intercept length resulting from the area of the Cu_6Sn_5 composite phase, and similar activation energies were obtained. Since the Cu_6Sn_5 composite phases in each solder joint occupied almost equal intercept lengths correlated with the 20 % volume fraction, it was concluded that the Cu_6Sn_5 composite phase had the same effect for all solder joints. Also, use of $r^2 - r_o^2$ was considered instead of $r^3 - r_o^3$, and this resulted in only a small increase in activation energy.

The differences in the initial microstructures used in first and second aging experiments due to differences in the heating/cooling history were compared. The time span between the beginning of wetting and the beginning of solidification for these two heating/cooling history shown in Figure 23 was also similar resulting in similar microstructure. The initial lengths/intercept, r_o , shown in Table 4 for the eutectic Sn/Pb

solder joints used in first and second aging were also similar. Consequently the aging result was not affected by the initial microstructure of eutectic Sn/Pb solder joints used in the first and second aging experiments.

The effect of specimen geometry was considered such as thickness of the solder joint. The thickness of solder joints was also checked because the thickness of solder joints affects to the thermally induced shear strain between substrate and solder due to the difference of thermal expansion coefficient which can influence the aging effect. However, in this study the thickness of eutectic Sn/Pb solder joints used in first and second aging cannot be correlated to higher or lower values in the aging kinetic plots.

In the several regards discussed above, the repeatability of the results from aging experiments is doubtful and low activation energies are not understood at this moment.

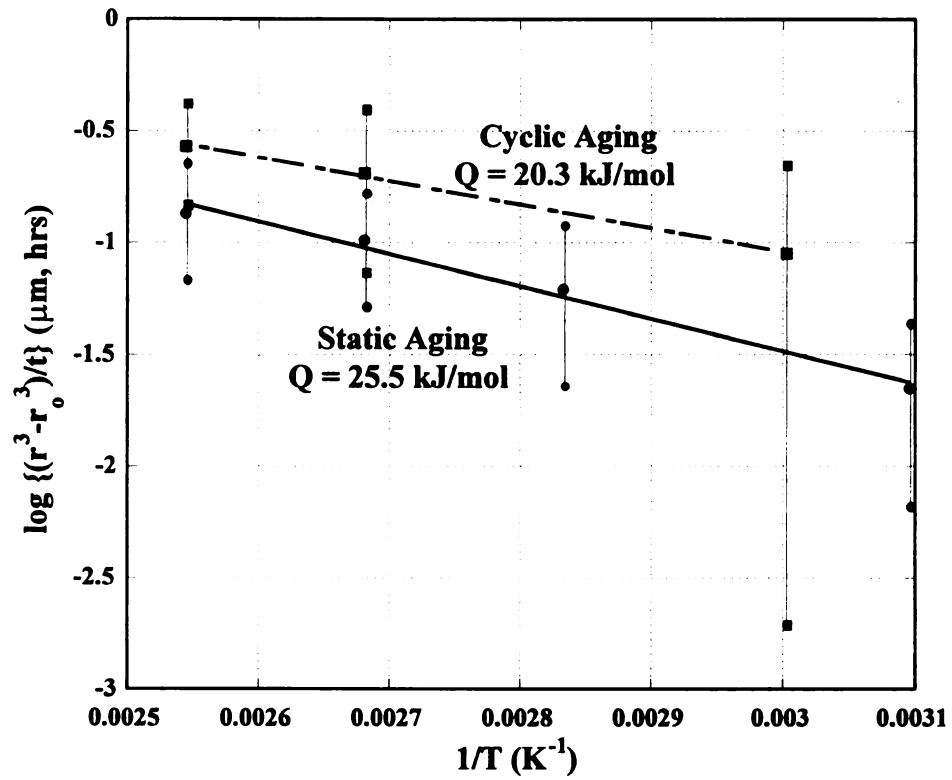


Figure 36 Arrhenius Plot for Aging of Eutectic Sn/Pb Composite Solder
(The error bars were determined from the average value of r_0 and standard deviation of r values evaluated from 7 measurements of the length/intercept for each aging condition)

Table 4 Aging Parameters For Eutectic Sn/Pb Composite Solder Joints
 Used in First and Second Aging
 (r_0 is the initial length/intercept, r is the length/intercept,
 and t is the thickness of solder joints)

		Static Aging (100 hours)				Cyclic Aging (20hours)		
		120°C	100°C	80°C	50°C	120°C	100°C	60°C
First Aging Experiment	r_0 (μm)	1.26	1.17	1.12	1.43	1.19	1.25	1.15
	r (μm)	3.87	2.70	2.33	2.09	2.44	1.91	1.26
	Standard Deviation of r_0	0.26	0.16	0.27	0.13	0.13	0.18	0.16
	Standard Deviation of r	0.89	0.41	0.29	0.41	0.14	0.34	0.24
	t (μm)	116	70	103	70	116	121	80
Second Aging Experiment	r_0 (μm)	1.07	1.23	1.2	1.13	1.07	0.99	1.13
	r (μm)	2.44	2.28	1.99	1.54	1.87	1.71	1.47
	Standard Deviation of r_0	0.24	0.28	0.25	0.25	0.09	0.28	0.21
	Standard Deviation of r	0.44	0.36	0.40	0.26	0.26	0.36	0.33
	t (μm)	98	76	117	77	98	105	92

Figure 37 shows the Arrhenius plot of the size change with inverse temperature for the Sn/Ag composite solder. A similar activation energy of about 37 kJ/mol was found for static and cyclic aging conditions for all temperatures used in this study. The rate of coarsening was faster in cyclic aging as compared to static condition.

The activation energy of about 37 kJ/mol corresponds to about a half of activation energy 77 kJ/mol $\perp$ c axis (55 kJ/mol $\parallel$ c axis) for Ag in Sn as shown in Table 3. This suggests that grain boundary or interfacial diffusion was prevalent in aging process. Since the diffusion distances for Ag in Sn shown in Table 3 are quite large, even at ambient temperatures, they are consistent with extensive Ag_3Sn coarsening. A previous study [115] on coarsening effects of eutectic Sn/Ag solder joints without composite phase revealed an activation energy of 48 kJ/mol, which corresponds favorably to the activation energy 55 kJ/mol $\parallel$ c axis for Ag in Sn. The rate of coarsening in the non-composite Sn/Ag solder joints was much lower, by a factor of about 5 to 100. The activation energy of 37 kJ/mol for Sn/Ag composite solder joints was lower than observed for non-composite Sn/Ag solder joints.

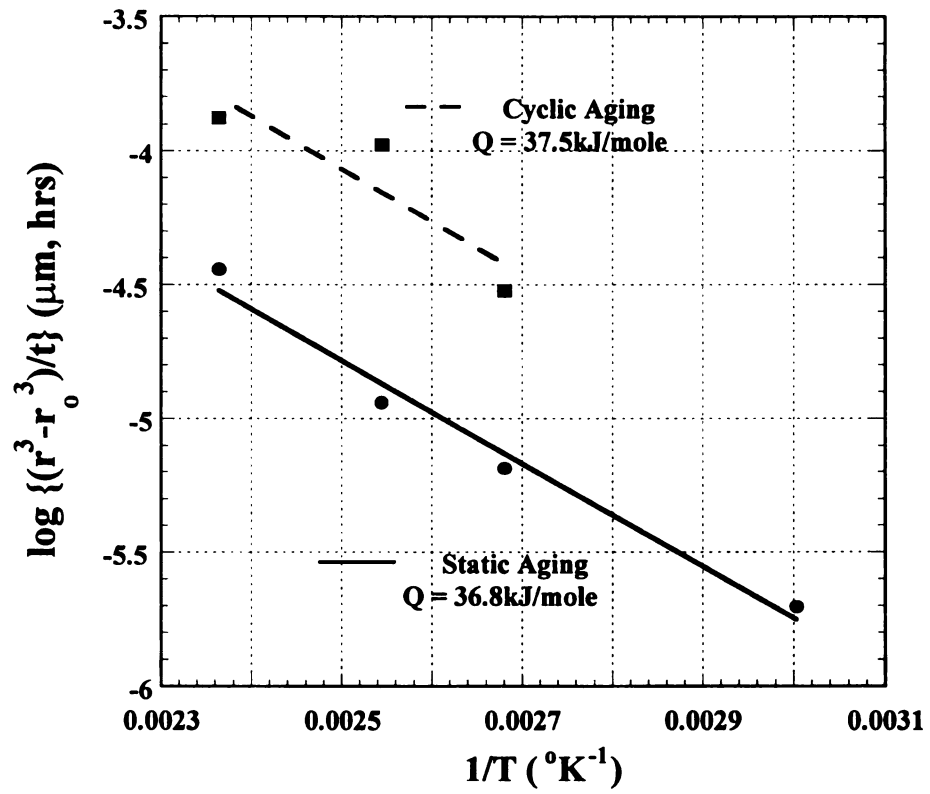


Figure 37 Arrhenius Plot for Eutectic Sn/Ag Composite Solder

5.2 CREEP DEFORMATION OF COMPOSITE SOLDER JOINTS

5.2.1 Eutectic Sn/Ag and Sn/Pb Composite Solder Joints

The unaged eutectic Sn/Ag composite solder joints revealed that 20 % shear strain could be accommodated in the composite solder joint before tertiary creep commences as shown in Figure 29. This is similar to the amount of creep strain that non-composite Sn/Pb solders can sustain, but lower than eutectic Sn/Ag solder can sustain in double shear lap chip carrier configuration [99]. The single shear lap joint used in this study appeared to cause more severe damage during creep deformation than double shear lap joint.

The eutectic Sn/Ag solder joint aged at 150°C showed much lower strain and strain-rate compared to the other solder joint aged at lower temperatures. The fracture surface of the solder joint aged at 150°C revealed that this solder joint had larger soldered area and less pore area than other solder joints. Consequently the solder joint aged at 150°C had larger load-carrying area which is estimated by subtracting the pore area from the soldered area and lower actual applied stress (16.3 MPa for 3.5 lb and 18.6 MPa for 4 lb) than the other solder joints. The low applied stress due to larger soldered area and lower porosity resulted in a low strain and strain rate.

The creep resistance of a material is often explained using the minimum creep-rate in steady-state in creep deformation. The minimum creep-rates in steady-state of eutectic Sn/Ag and Sn/Pb composite solder joints shown in Figure 29, 30, and 31 are compared with eutectic Sn/Ag and Sn/Pb solder joints without the composite phase in Figure 38 and

39 in which the normalized strain-rate was plotted versus normalized shear stress. The normalization parameters were the same as used by R. Darveaux and K. Banerji [99]. The solid line curves [99] are for eutectic Sn/Ag and Sn/Pb solder joints without composite phase, which was obtained by incorporating the temperature dependent shear modulus.

It is apparent in Figure 38 that all of the aged eutectic Sn/Ag solder joints showed higher strain-rates than the unaged eutectic Sn/Ag solder joints indicating that the solder joints in the unaged condition are more creep resistant. The eutectic Sn/Ag composite solder joints showed approximately two to three orders of magnitudes lower strain-rates than non-composite eutectic Sn/Ag solder joints. The eutectic Sn/Pb composite solder joints exhibited approximately one to two orders of magnitudes lower strain-rates than non-composite eutectic Sn/Pb solder joints. The degree by which the strain-rates were decreased depended on the amount of aging and indicated that eutectic Sn/Ag and Sn/Pb composite solder joints containing Cu_6Sn_5 intermetallic particles had higher creep resistance.

All of the aged eutectic Sn/Ag composite solder joints exhibited a higher strain-rate than the unaged eutectic Sn/Ag composite solder joints. The aging of the solder joints resulted in coarsening of small Ag_3Sn ϵ -phase particles present in the matrix of the solder. The size of Ag_3Sn ϵ -phase particles increased and the number of Ag_3Sn ϵ -phase particles decreased due to coarsening. A previous study [97] regarded eutectic Sn/Ag solder as a dispersion-hardened alloy because in eutectic Sn/Ag solder, most of the Ag resides in Ag_3Sn intermetallics particles that are finely distributed in the β -Sn matrix. It was also considered that the finely distributed Ag_3Sn intermetallics particles act like dispersed

particles that can block dislocation glide and climb. In this study the effects of aging appeared to be consistent with softening resulting from overaging in precipitate strengthened alloys. The higher strain-rates in aged solder joints indicate that coarsened Ag_3Sn ϵ -phase particles in the aged condition were less effective in blocking dislocation motion than in the unaged condition.

Since all of the aged data appear to fall on a similar line nominally parallel to the unaged data, it appears that a small amount of aging results in enough coarsening to make the contribution of Ag_3Sn particles to the strength, and the Cu_6Sn_5 particles then dominate the creep resistance.

The eutectic Sn/Ag and Sn/Pb composite solder joints showed much higher creep resistance than the eutectic Sn/Ag and Sn/Pb solder joints without composite phase. This result indicated that creep resistance without sacrificing ductility is possible in composite solders. The increase in creep resistance by the incorporation of hard particles was observed in previous studies [70] in which eutectic Sn/Pb solder exhibited an increasing trend in the creep resistance with increasing volume fraction of Cu_6Sn_5 intermetallic particles.

The exact mechanism by which the creep strength of eutectic Sn/Ag and Sn/Pb composite solder joints was increased is uncertain at this time. However, it was apparent that the Cu_6Sn_5 intermetallic particles impeded plastic flow of the eutectic Sn/Ag and Sn/Pb matrix. During the creep deformation the scratches present in Cu_6Sn_5 intermetallic particles showed no deviation from its original position and such deviation was observed

only in eutectic Sn/Ag and Sn/Pb matrix. The Cu_6Sn_5 intermetallic particles appeared to be a effective barrier to plastic flow of eutectic Sn/Ag and Sn/Pb matrix during creep deformation resulting in lower strain-rates in eutectic Sn/Ag and Sn/Pb composite joints than eutectic Sn/Ag and Sn/Pb solder joints without composite phase.

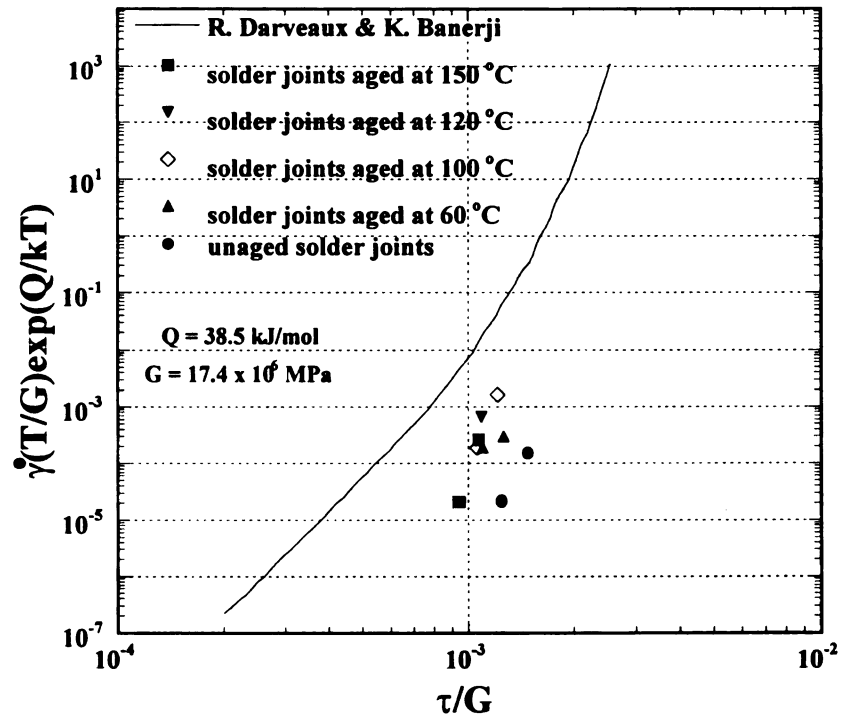


Figure 38 The Normalized Steady-State Behavior of Eutectic Sn/Ag Composite Solder joints

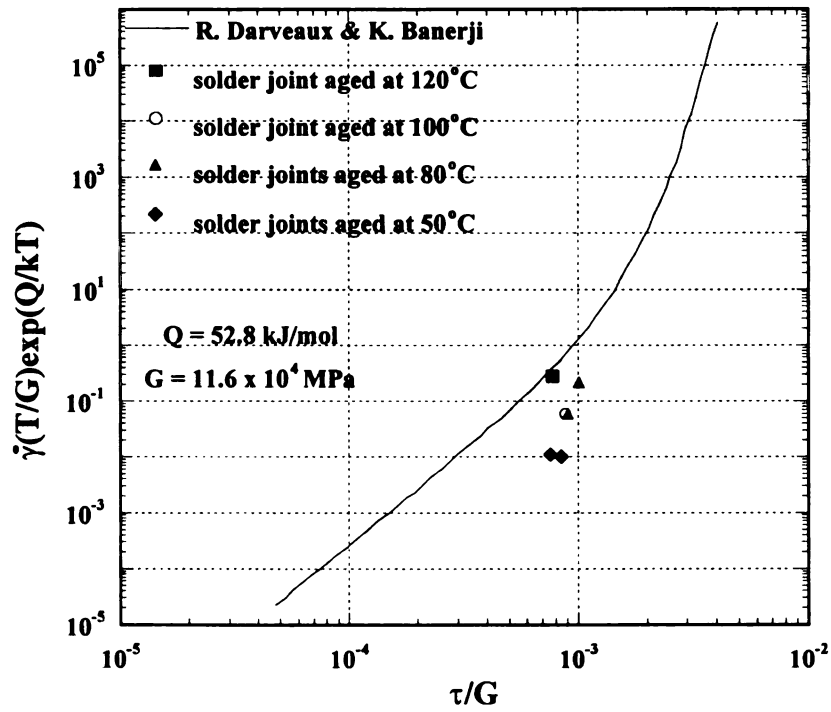


Figure 39 The Normalized Steady-State Behavior of Eutectic Sn/Pb Composite Solder joints

5.2.2 The Fracture Surfaces of Composite Solder Joints

The formation of pores in eutectic Sn/Pb solder joints containing Cu_6Sn_5 intermetallic particles and Au element was reported in the previous studies [70, 96] in which the amount of porosity tended to increase with the volume fraction of Cu_6Sn_5 and Au. It was observed [70] that for Sn/Pb composite solder the inverse relationship appeared to exist between vol % porosity and strength, i.e., lower volume fractions of porosity correspond to higher amounts of strengthening, and vice versa. Large volume fractions of porosity in the matrix can inhibit or prevent composite strengthening by reducing effective joint cross sectional area. Pores within the bulk of the joint can act as crack nucleation sites, just as the external surface does. However, in this study composite solder joints did not show any significant relation between porosity and creep strength.

Previous studies [70, 96] discussed a possible origin for the pores present in the joints is through flux or gas bubbles trapped by the viscosity of the melt. It was also considered that porosity will increase with increasing amounts of reinforcement because the viscosity of the melt increases with increasing amounts of reinforcement, resulting in the decrease of the velocity of flux or gas bubbles motion and large volume fractions of residual porosity. The origin of porosity present in composite solder joints and the effect of viscosity on porosity remain as an open question to evaluate.

CHAPTER 7

CONCLUSIONS

1. The lead-free Sn/Pb and Sn/Ag composite solders containing very fine Cu_6Sn_5 intermetallic particles of about less than $2\text{ }\mu\text{m}$ in size were successfully developed by a splat quenching method. The small single shear lap joints of the scale of those found in actual electronic solder joints with lead-free composite solder were manufactured using the copper dogbone halves.

2. The aging of composite solder joints caused microstructural coarsening of the Sn/Pb and Sn/Ag matrix. However, The Cu_6Sn_5 intermetallic particles were resistant to microstructural coarsening and stable within the regime of time and temperature used in this study. Aging kinetics for eutectic Sn/Ag composite solder joints were faster in cyclic aging conditions, and the activation energy of the coarsening process is comparable with grain boundary diffusion of Ag atoms. The measurement of aging kinetics for eutectic Sn/Pb composite solder joints did not provide any conclusive result.

3. The composite solder joints exhibited a lower creep strain-rate than solder joints without the composite phase, indicating that the composite solder is more creep resistant. The Cu_6Sn_5 intermetallic particles appeared to cause a lower creep strain-rate in the composite solder.

4. The fracture surface of composite solder joints showed that composite solder joints contained porosity up to 20 % which can inhibit or prevent composite strengthening by

reducing effective joint cross section. The composite solder joints showed two kinds of fracture paths which are through bulk composite solder and near the interface between composite solder and interfacial layer.

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