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dissertation entitled

STUDIES ON LEAD-FREE SOLDERS REINFORCED WITH MECHANICALLY INCORPORATED Cu, Ag, and Ni PARTICLES

presented by

Fu Guo

has been accepted towards fulfillment of the requirements for

Ph.D. degree in <u>Materials</u> Science

and Engineering

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STUDIES ON LEAD-FREE SOLDERS REINFORCED WITH MECHANICALLY-INCORPORATED Cu, Ag, AND Ni PARTICLES

Bу

Fu Guo

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A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering and Materials Science

2002

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ABSTRACT

STUDIES ON LEAD-FREE SOLDERS **REINFORCED** WITH MECHAN**I**CALLY INCORPORATED Cu, **Ag**AND Ni **PARTICLES**

By

Fu Guo

Three types of composite solders were produced in the current investigation by mechanically adding nominally 15v% of ~ 6µm sized Cu, ~ 4µm sized Ag, or ~ 6µm sized Ni particles into the eutectic Sn-3.5Ag solder paste. The principal aim of this study is to investigate how the microstructure, isothermal aging, reflow as well as creep properties of the eutectic Sn-3.5Ag solder will be affected by the incorporation of these particles as reinforcements. Small realistic sized single shear lap solder joint design were used throughout the investigation to better mimic the condition for solders used in automobile and microelectronic industries. The initial microstructure of as-fabricated composite solder joints was examined and analyzed using optical and scanning electron microscopy (SEM) with Energy Dispersive X-ray (EDX). The effect of reflow and isothermal aging on the microstructure as well as the morphological changes in the interfacial intermetallic (IM) layers of the composite solder joints were extensively analyzed. Effect of solder reflow on the solderability and mechanical properties were studied. Nanoindentation testing (NIT) was used to obtain mechanical data from multiple reflowed composite solders. Creep tests were conducted on composite solder joints at 25°C. 65°C and 105°C representing homologous temperatures ranging from 0.61 to 0.78. Qualitative and quantitative evaluations of creep behavior were obtained from

the distortion of excimer laser induced surface ablation markings on the solder joint. Various creep parameters such as global and localized creep strain, variation of creep strain and strain-rate, activation energy for creep, and the onset of tertiary creep were determined. The resultant properties of the composite solders produced in this investigation were compared with those of non-composite solders and the composite solders produced by *in-situ* method.

Significant findings in this study revealed that both Cu and Ni composite solder joints significantly improved the creep resistance of eutectic Sn-3.5Ag solder joints. Although Ag composite solder joints exhibited comparable creep resistance to eutectic Sn-3.5Ag solder, very uniform deformation features were observed during creep. Excessive microstructural evolution in terms of IM growth was observed in Cu and Ni composite solder joints under isothermal aging at 150° C due to the profuse diffusion of Cu and/or Ni in Sn. In contrast, the microstructure in the Ag composite solder joint was very stable under isothermal aging and reflow conditions. The Ni composite solder joint exhibited a stable microstructure after multiple reflows whereas extensive IM growth was still observed in Cu composite solder joint under similar reflow conditions. Ag and Ni have comparable wetting characteristics to eutectic Sn-3.5Ag solder. Cu composite solder with 15v% of Cu reinforcements resulted in a high average contact angle due to the increase of effective volume fraction. Responsible mechanisms for the effects of reinforcement addition on microstructure, aging, reflow and creep behavior are discussed.

ACKNOWLEDGMENTS

I would like to express my sincere thanks to my advisor Professor James P. Lucas for all his excellent guidance, encouragement, friendly manner, and professional example throughout my doctoral studies at Michigan State University. Without his support and patience, this work would not have been possible. I would also like to sincerely thank Professor K.N. Subramanian and Professor Thomas R. Bieler for their kind help and instruction throughout the entire work. I also thank Professor P. Duxbury and Professor D. Liu for serving as my graduate committee and giving me valuable suggestions to both the thesis and experimental designs. The success of this work is also based on the help from all other members in our research group. Special thanks go to J. Lee, C. Brandon, H. Rhee, and S. Choi for specimen preparation, property testing and information exchange.

I sincerely appreciate the financial support provided by my advisors though the Research Excellent Fund administered through the Composite Materials and Structure Center at Michigan State University. The later part of this work was supported by the Visteon Electronic Technical Center, Dearborn, Michigan, and National Science Foundation under contract number NSF-DMR-0081796.

My deepest thanks are extended to my wife, my parents, and my friends whose love, continuous support and encouragement have supported me to achieve a Ph.D. degree from Michigan State University.

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CHAPTER I

INTRODUCTION

Lead-free solders have been the main focus of significant research activity for the Past decade due to the concerns of toxicity and health hazard of lead present in the commonly used lead-bearing solders. Under this global trend toward a lead-free environment, the acceptable lead-free solders should function as a complete alternative to traditional lead-bearing solders in terms of electrical interconnectability, structural integrity, and reliability. Although government legislation and regulations have been driving force to eliminate the use of leaded solders and there are lead-free solder ^{Can}didates already in the market [1,2], still no seemingly outstanding substitute has emerged to fully replace the eutectic and near eutectic Sn-Pb solders because of the stringent demands for excellent structural performance of these alternative solders for use in current industries for electronic packaging and assembly.

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Foremost among all the lead-free solder candidates, eutectic Sn-3.5Ag solder has received attention worldwide as a potential substitute because of its non-toxic nature as well as its comparable wetting and mechanical properties to eutectic Sn-37Pb solder [3-6]. Its higher melting point, 221°C, makes it more suitable for higher temperature applications [5]. Use of such lead-free solders in electronic industries is relatively new and the knowledge base of alternative solders is not well established due to the long-term dominance of leaded solders over centuries. An extensive property database is not yet available and some questions still remain concerning data that currently exist. Therefore, significant research activities have been involved in an effort to investigate the properties of eutectic Sn-3.5Ag solder and meanwhile to improve its comprehensive properties.

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Solders used in various applications, such as automobile under-the-hood, aerospace and defense, microelectronics, power generation and distribution etc., are subjected to severe service environments including multiple loading scenarios over a range of Operating temperatures [5]. Coefficient of thermal expansion (CTE) mismatch between substrate, solder and chip leads, environmental thermal fluctuation (as much as -40°C to 160°C), and the complex loading conditions (such as creep and mechanical fatigue) are the main contributing factors for solder joint failure, which is considered as the primary reason for the failure of electronic components [7,8]. These low melting point solder alloys are typically used at temperatures well above half of their absolute melting points, SO recrystallization, superplasticity, creep/relaxation, and creep-fatigue are operative under normal service conditions [9,10]. Solder materials functioning at such high homologous temperatures were also found to undergo extensive microstructural evolution, primarily including interfacial intermatallic layer growth and microconstituent phase coarsening, which will eventually degrade the solder joint [4, 11-14].

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Two major avenues are being pursued to mitigate the detrimental effects already alluded to. Several studies involve the addition of such alloying elements as copper, nickel, antimony, bismuth, etc. in order to reduce the melting points of eutectic Sn-3.5Ag solder as well as to improve its mechanical properties [15-21]. Another way to achieve improvement is to introduce a dispersion of second phase reinforcements into the solder matrix to stabilize the microstructure and thereby increase its mechanical strength [22-32]. This approach, the so-called composite approach, was designed for the purpose of improving the solder's intrinsic vulnerability to cyclic and creep deformation.

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In this investigation, composite solders are made primarily by incorporating micron-sized Cu, Ag or Ni particulate reinforcements into the eutectic Sn-3.5Ag solder matrix. The focus of this study is to characterize and investigate how different types of reinforcements would alter microstructure, aging, wetting, and reflow properties of the eutectic Sn-3.5Ag solder matrix. Quantitative understanding the preliminary creep behavior of these composite solders is another major part of this investigation. Global and localized creep deformation as well as the onset of tertiary creep of each composite solder material were quantified and analyzed using small realistic sized solder joint specimens typically used in microelectronics. In addition to the composite approach employed primarily in the study, the effects of alloying element additions $(and/or N^{ii})$ on the creep behavior of eutectic Sn-3.5Ag solder were investigated. - The second second

CHAPTER II LITERATURE REVIEW

2.1 Current Research Status on Lead-free Solders

2.1.1 Introduction

Several challenges are faced in the development of lead-free solders since they are not just drop-in substitutes for traditionally used leaded solders. These challenges may be related to the solder melt temperature, processing temperature, wettability, mechanical and thermo-mechanical fatigue behaviors etc. Knowledge base on leaded solders gained by experience over a long period time is not directly applicable to lead-free solders. As a result, a database for modeling for reliability predictions of lead-free solders is not for electronic currently available [33]. Most of the lead-free solder developments Sn-Ag alloy applications are aimed at arriving at suitable alloy compositions [3-6]. system, with or without small alloy additions such as Cu, is believed to have significant potential [3-6,15]. The binary Sn-Ag eutectic temperature is 221°C, and the ternary Sn-Ag-Cu eutectic temperature is 217°C, both being reasonably higher than the Sn-Pb bingre eutectic temperature of 183°C. Although the processing parameters have to be modified to accommodate this increase in eutectic temperature, use of such solders also provide higher service temperature capability to the solder joints. Results of several studies on such solders are recently reported in the published literature [3-6,15].

Although these approaches on high temperature lead-free solders tend to evaluate the alloy systems with a melting temperature of about 220°C, significant increase in the service temperature capability may not result as a consequence of the thermo-mechanical

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behavior of such systems. Current National Center for Manufacturing Systems (NCMS) project deals with lead-free solders for applications with a service temperature of 150°C [34]. For example in the automotive under-the-hood applications, there is significant interest from designers to mount the electronic circuit boards on the engine manifold. This will significantly decrease the amount of wiring, and minimize several complications in the electrical circuitry. Similar conditions also exist in aerospace and defense applications.

A more severe environment experienced by the solder joint is in a highcurrent/high temperature application such as in an automotive alternator or rectifier. At present there is no suitable and economical substitute for the high lead solders used for such applications. Solders based on Sn-Au alloys are cost prohibitive in large-scale automotive type manufacturing situations [35]. It is believed that this area will be the focus of significant number of investigations in the near future. Since regular electronic solders, such as in electronic components or computers, do not experience such severe environments, this aspect of lead-free solders has not been addressed so far.

Incorporation of dispersoids to improve the mechanical and the momechanical behavior of the solders, even in leaded-solder systems, has been an aven we that has been pursued to improve the service temperature capability without significantly alternating the processing parameters. Since there have been several studies dealing with dispersoids in leaded solders, a brief review illustrating the knowledge gained from them will be provided prior to addressing the lead-free solders.

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2.1.2 Service Requirements

Solders in general operate at high homologous temperature ranges. During turning on and off operations of the electrical circuitry when heat up or cool down, they also experience low cycle thermo-mechanical fatigue due to stresses that develop as a consequence of CTE mismatch between the solder/substrate/components. Mechanical vibration of other entities to which the electronic components are mechanically attached, such as automotive engines, can create higher frequency vibrational fatigue conditions. When an automobile/tank hits a pot-hole/major obstruction, or landing of an airplane can impose impact loading on the solder joint. Although fine-grained microstructure may be beneficial for mechanical fatigue considerations, it may not be ideal for creep resistance since creep deformation at the service temperature (high homologous temperature for the solder alloys) will be by grain boundary sliding. In addition to these opposing requirements, the highly in-homogenous as-joined solder joint microstructure coarsens during service. This aging process causes growth of solder/substrate interface intermetallic layer and coarsening of microstructural constituents within the solder joint. Such evolving microstructure continuously alters the mechanical properties of the solder joint resulting in significant hurdles in reliability prediction modeling. Presence of fine. stable, compatible dispersoids at the grain boundaries can retard coarsening, enhance mechanical fatigue behavior, decrease creep rate by decreasing grain boundary sliding tendency by ke ying the grain boundaries.

Although one would prefer a strong solder joint for creep resistance considerations, it may not be ideal in electronic applications. If the solder in the joint is not able to dissipate the stresses that develop, failure of the electronic components will result. One

Cau du would prefer a reasonably strong and pliable solder joint. Although these two requirements appear to be mutually exclusive, both of them can be satisfied by appropriate microstructural engineering of solders with suitable dispersoids.

The methodology that will be employed to enhance the service performance of the solder joint should not affect the well laid out current metallurgical processes in the electronic manufacturing. It is essential that the incorporation of dispersoids does not significantly alter the solderability, solder substrate wetting characteristics, melting temperature, etc. Solder development for high-current/high-temperature service environment is not currently being pursued vigorously. Electro-migration, which can cause significant decrease in solder reliability could probably be controlled by fine dispersoids in the grain boundaries. Fine dispersion of copper atoms in aluminum cause's significant decrease in electro-migration in computer circuitry [36, 37]. However, su aspects will not be addressed in this review due to a lack of available information relevant to Sn in the literature.

2.1.3 Prior Studies [38-40]

There have been significant worldwide active research activities of lead from soldering during the past decade. Examples of such research and devel spment projects can be listed in Table 2.1.

In US, a consortium of 11 industrial corporations in US carried **C I** the "lead-free solder project" led by National Center for Manufacturing Sciences (NC **N**S) in order to evaluate alternatives to eutectic Sn-Pb solder. Five alloys emerged **from** the downselection as vi = ble candidates to replace 80% of the currently used near eutectic Sn-Pb

solder. It was found during the NCMS project that Sn-58Bi eutectic, Sn-3.4Ag-4.8Bi and Sn-3.5Ag eutectic solders performed substantially better than the eutectic Sn-Pb solder in certain surface mount applications. The project also showed that Sn-58Bi and Sn-3.4Ag-4.8Bi had fatigue lives comparable to or better than eutectic Sn-Pb, possessing similar bulk properties at room temperature and very high tensile and yield strengths combined with moderate to high elongation. However, the NCMS concluded that a "drop-in" replacement for eutectic Sn-Pb solder was still not identified at the end of the "1992-1996" four-year project.

- word 2.1 Examples of Lease				
Country	Organization	Project NT and		
US	NCMS (AT&T/Lucent Technologies, Ford Motor Company, GM-Hughes Aircraft, NIST, etc.)	Lead-free Solder Project		
UK and Europe	DTI part funded project (GEC, BNR Europe, Multicore Solders and ITRI	Lead-free soldering		
Japan	JIPE Project (Senju Metals, Alpha Metals Japan, Nihon Handa, Ishikawa Metals, etc.)	Lead-free Soldering		

Table 2.1 Examples of Lead-free Solclering Project in the World

The DTI funded "lead-free soldering" project in UK was focused $free suitability for electronic assembly and supply potential during their lead-free allow selections. <math>Fi_{VA}$ solder alloys, mamely Bi-42Sn, Sn-9Zn, Sn-5Sb, Sn-3.5Ag, and Sn-0.7 free restand and Bi-42Sn, free restand restan

The JIPE project in Japan focused on the Sn-Ag-Bi (Bi 7-25%) alloy. It was found that any solder alloy containing more than 7% bismuth were very brittle and fillet lifting became a serious concern even though the melting temperature of the solder alloy is relatively low. The Sn-Ag-Cu alloys with or without a few percent of bismuth proved to be useful. It was also discovered that Sn-Zn and Sn-Cu alloys have a great potential for use as solder alloys. Studies dealing with these alloys are currently in progress.

As a result of recent research activities, a large number of lead-free Solders have been developed and number of patent applications have been filed for Various alloy compositions. Although not all these alloys are commercially available, there is still a wide range to choose from. The most convenient way to separate the available lead-free alloys is to consider their melting temperatures. Some typical examples of lead-free solders under research and development are listed in Table 2.2 along with their melting temperature ranges.

Development [50 to]				
Category	Alloy System	Composition (wt%)	Melting Range(°C)	
Low melting temp.	Sn-Bi	Sn-58Bi	138	
(<180°C)	Sn-In	Sn-52In	18	
Melting Term, (183-	Sn-Zn	Sn-9Zn	1 98.5	
200°C) equi valent to	Sn-Bi-Zn	Sn-8Zn-3Bi	189-199	
eutectic Sn-Pb solder	Sn-Bi-In	Sn-20Bi-10In	1-3-193	
Mid-range melting temp. (200-230°C)	Sn-Ag	Sn-3.5Ag	221	
	Sn-Cu	Sn-0.7Cu	227	
	Sn-Ag-Cu	Sn-3.8Ag-0.7Cu	217	
High meltine temp.	Sn-Sb	Sn-5Sb	232-240	
	Sn-Au	Sn-80Au	280	

 Table 2.2 Examples of Lead-free Solder Alloys Currently under Research and

 Development [38-40]

In summary, there are several lead-free alloys that are available, however there is no universal drop-in replacement for leaded solders identified so far. At the moment the

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most promising alloys for general electronic soldering appears to be those based on $Sn_3.5Ag$ and Sn_Ag -Cu. Other alloys with potential are $Sn_0.7Cu$ and Sn_Ag -Bi. The need for higher process temperatures is another important technological issue that has to be addressed when companies change over to lead-free soldering because higher process temperatures will impact existing soldering technology in such key areas as materials stability/reliability, equipment reliability and higher energy cost issues. No applicable lead-free solder alloys can be used at high service temperature except expensive Sn_0Au solder which will not be practical in large scale soldering operation. How to increase the service temperature of existing lead-free solders for such applications or arrive at new solder compositions is one of the serious problems that lead-free solder rese archers have yet to address.

2.2 Composite Solders

2.2.1 Composite Approach and Its Merit to Enhance the Behavior of Solders

2.2.1.1 Purpose of Composite Approach

Composite approach was developed mainly to improve the service performance including service temperature capability. In other words, the basic Durpose of this methodology is to engineer and stabilize a fine grained microstruction, homogenize solder joint de Formation, so as to improve the mechanical properties of the solder joint, especially creep and thermomechanical fatigue resistance. Also, the added reinforcements do not change the melting point of the solder matrix, but may effectively increase the service temperature of the base solder materials by improving the creep or thermomechanic al fatigue properties of the solder matrix.

2.2.1.2 Prior Studies of Composite Solders

Several efforts have been made to improve the comprehensive properties of le_{ad} bearing solders using composite approach [22-32]. Microstructural analysis as well as mechanical testing of such composite solders have been reported. Certain composite solders did show improved mechanical properties sought by electronic/automobile industries.

Marshall *et al.* have carried out studies in microcharacterization of composite solders [22-26]. Their composite solders were primarily prepared by mixing Cu_6Sn_5 (10, 20, 30wt%), Cu_3Sn (10,20, 30wt%), Cu (7.6wt%), Ag (4wt%), or Ni (4 wt%) particles with the eutectic Sn-37Pb solder paste. The microstructure features of these bulk composite solder specimens showed Cu-Sn, Ag-Sn, and Ni-Sn intermetallics were developed in the composite solders around Cu, Ag, and Ni particles respectively. Cu_6Sn_5 layer formed around Cu_3Sn particles in the Cu_3Sn reinforced composite solder, while no more new intermetallic formed in the Cu_6Sn_5 particle reinforced composite solder. The *m*icrostructural analysis showed good bonding of the particulate reinforcements to the **SC**Ider matrix suggesting that the resulting composite solders might exhibit enhanced **Strength**.

Intermetallic formation at the solder/copper interface was studied for the above **Composite** solder samples aged at 140°C for 0 to 16 days, as reported by Pinizzotto *et* **al.** [41]. Intermetallic formation near the Cu substrate was greatly affected by these **Particle** additions. Ag and Au retarded and Ni suppressed the formation of Cu₃Sn and **enh**anced the growth of Cu₆Sn₅ as compared to pure solder with the Cu substrate. **Add**ition of Cu containing particles to the solder results in a decrease of both the Cu₆Sn₅

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and Cu₃Sn interface intermetallic thickness relative to the pure solder. This effect w_{as} believed to be due to the particles acting as Sn sinks. Similar studies were carried out by Wu et al. with aging temperatures of 110°C to 160°C for 0 to 64 days [42]. The Cu containing reinforcements resulted in increased activation energies for Cu₆Sn₅ formation and decreased activation energies for Cu₃Sn formation as compared to pure solder. The activation energy for Cu₃Sn formation decreased relative to the eutectic solder for the Ag and Au composite solders even though less Cu₃Sn was formed at the substrate interface. Ni and Pd drastically reduced the Cu₃Sn thickness and increased the Cu₆Sn₅ thickness. Two mechanisms were proposed for the effects of Cu-containing particles and Ag particles on the kinetics of intermetallic formation. First, the particles act as Sn sinks which remove Sn from the solder and decrease the amount of Sn for reaction at the interface. Second, the particles reduce the solder cross-sectional area available for Sn diffusion, which also reduces the amount of Sn available at the interface for reaction.

Dispersion strengthened *in-situ* composite solders of Sn-Pb-Ni and Sn-Pb-Cu alloys containing 0.1-1.0 μ m dispersoids/reinforcements were produced by induction **melting** and inert gas atomization, reported by Sastry *et al.*[27]. It was found that, upon **reflow** of the solder specimens, the fine spherical dispersoids in rapidly-solidified Sn-Pb-Cu alloys coarsen to > 1 μ m platelets, however, the dispersoids in Sn-Pb-Ni alloys remain **Spherical** and remain stable with a size of < 1 μ m. The difference in stability of **dispersoids** in Cu- and Ni-containing solders was explained on the basis of the difference **in** solubilities and diffusivities of Cu and Ni in Sn-Pb matrix. These composite solders **showed** an increase of 25-180% in yield stress and 20-80% in the modulus values **Compared** to eutectic Sn-37Pb solder. Another type of dispersion strengthened composite solder was formulated b_y Betrabet *et al.* by adding 2.2wt% of Ni₃Sn₄ intermetallic particles into the Sn-40Pb solcler matrix [28]. Mechanical alloying, a solid-state high-energy milling process developed for superalloy manufacture, provided the means to process such dispersion strengthened solders. The presence of Ni₃Sn₄ dispersoids resulted in a smaller grain size in the as-cast microstructure and after aging at 100°C for 29 hours. Their subsequent study of Cu₉NiSn₃ intermetallic particles reinforced Sn-40Pb composite solder showed an increase of the strain to failure in shear by 40% while the ultimate shear strength essentially remained unchanged [29]. They claimed this as an indication of improved fatigue resistance because it was believed that fine, uniformly dispersed phases would stabilize microstructures by pinning grain boundary dislocations and by restricting grain boundary motion.

Mavoori and Jin prepared their composite solders by mixing 3v% of 10nm sized Al₂O₃ powders or 3v% of 5nm sized TiO₂ powders with 35µm sized eutectic Sn-37Pb *solder* powder [30]. Nanosized, non-reacting, non-coarsening oxide particles formed **uniform** coatings of solder after repeated plastic deformation for rearrangement of the **Particles**. Three orders decrease in the steady state creep rate was achieved by this **approach**. Such composite solder was found to be much more creep resistant than their **Cont**rol sample, the eutectic Sn-80Au solder. This has great significance in replacing the **Conventional** high melting point (278°C) Sn-80Au solder for its creep resistant **appl**ications such as optical or optoelectronic packaging.

Clough *et al.* (with G. Lucey) reported that, with properly controlled porosity, $Cu_{GSn_{5}}$ particle reinforced eutectic Sn-37Pb solders exhibited twice the yield strength

without significant ductility loss [31]. It was also shown in their study that the creep rate of the composite solder was nearly an order of magnitude less than that of unreinforced solders. The boundary layer fracture behavior was studied using single shear lap specimens using the same composite solder. The specimens failed as shear fracture ran in from opposite edges about 10 μ m inside of the interfaces. These boundary layer fractures were characterized and a fracture model was developed. Composite strengthening was shown to significantly improve the ductility, creep life and properties associated with improved reliability and creep-fatigue life [43].

The effects of phase additions on the microstructure, wettability and other mechanical properties of the composite solders have also been reported in other studies [44-45]. In general, composite solders tend to render improved properties. All the reported investigations were basically exploratory in nature, and the extent of improvement must be weighed against environmental and economic factors before widespread adoption can be realized. However, studies on lead-free Sn-Ag based *composite* solders have received attention only recently.

2-2.2 Important Considerations for the Selection of Reinforcements

Reinforcements added to the solder matrix should satisfy certain conditions for enhancing the solder performance [22]. Such conditions include: (1) the reinforcing Phases should bond to the solder matrix, and the bonding could be weak or strong depending on the need for specific considerations, (2) the reinforcements must have acceptable solubility in molten solder under normal reflow temperatures so as to maintain the stability of the reinforcements during reflow or aging process, (3) the density of the

reinforcements should be close to that of solder matrix, so that a uniform distribution of the reinforcing phase could be promoted, (4) the size of the reinforcing phases should be optimal in order to stabilize the microstructure (It has been found that reinforcement particles of ~1µm or smaller tend to stabilize the microstructure [46].), (5) the particles should not be prone to significant coarsening due to high interfacial energies of fine particles during service, (6) the reinforcement should not significantly alter the processing temperature, (7) the reinforcement should not alter the solderability by changing wetting characteristics with the substrate.

2.2.3 Methods for Introducing the Reinforcements — *in-situ*, Mechanical Mixing (Inert or Reactive Reinforcements)

Usually, reinforcement particles used in the composite solder can be grouped into two categories. One kind of reinforcement addition involves the intermetallic particles. These intermetallic reinforcements can be incorporated to the solder matrix either by adding preformed intermetallic particles (like Cu₆Sn₅, Cu₃Sn, or Ni₃Sn₄ [22-26,27-29,31]) or by converting from elemental particles (like Cu, Ni, or Ag [22-26]) by their reaction with Sn during fabrication or the subsequent aging and reflow process. Another kind of reinforcement addition involves those having a low solubility and diffusivity in Sn, or even non-reactive with Sn. Examples of such reinforcements could be Fe particles [32] or oxide particles like Al₂O₃ or TiO₂ [30]. Choices of such reinforcements serve several **Purposes**. Proper choice of foreign reinforcement additions could desirably introduce **uniform**ly distributed intermetallic hard particles or non-coarsening particles. Well**dispersed** reinforcements can serve as obstacles to grain growth, crack growth and dislocation motion so as to strengthen the solder against creep and fatigue deformation [28].

Two possible ways to introduce the desired reinforcements to the solder matrix are the *in-situ* method and the mechanical mixing method. *In-situ* method refers to the technique by which reinforcing phases, like Cu_6Sn_5 or Ni_3Sn_4 intermetallic particles, are readily formed upon processing the bulk solder. The mechanical mixing method is more related to extrinsically adding reinforcement particles into the solder matrix (usually solder paste, sometimes molten solder). In the latter, composite solder paste is usually prepared by mechanically blending the mixture for certain length of time to achieve uniform distribution of the reinforcements.

2.2.4 Microstructual/Interfacial Aspects of Lead-free Composite Solders

Subramanian *et al.* have reported the microstructural evolution in the Cu_6Sn_5 particle reinforced eutectic Sn-3.5Ag based composite solders made by *in-situ* method [47]. The effect of the intermetallic reinforcements on the growth of the intermetallic **interfacial** layer between the solder and substrate was studied by carrying out aging **studies** ranging from few hours to few thousand hours. In these studies the average **interface** thickness was measured after chosen aging times. The presence of the **intermetallic** reinforcements retards the growth of the interfacial intermetallic layer, even **after** several thousand hours. The presence of Cu_6Sn_5 reinforcements also decreases the **COarsening** kinetics of the Ag₃Sn phase that normally forms in the solder. Microstructural **studies** on the coarsening of Ag₃Sn and Cu₆Sn₅ indicate that during short-term aging of a **few** hundred hours Cu₆Sn₅ does not coarsen measurably. However, the Ag₃Sn particles

did coarsen during these aging studies. The composite solder showed a lower activation energy but a slower growth rate [13,48] when comparing the coarsening kinetics between the composite and the non-composite eutectic Sn-3.5Ag solder. The intentionally added Cu_6Sn_5 particles showed coarsening after several thousand hours long-term aging.

2.2.5 Resultant Properties of Lead-free Composite Solders

Certain composite solders have exhibited enhanced strength and other desired properties sought by the electronics industry. McCormack *et al.* have developed composite solders by adding 2.5wt% of ~2µm magnetic Fe powders into pure Sn and eutectic Sn-Bi solder [32]. The idea of adding Fe powders lies in the fact that Fe has low solubility and diffusivity in Sn-based solder and thus is impervious to coarsening. A fine, uniform dispersion of particles was obtained by imposing a magnetic field during the solidification process. The composite solder made by adding 2.5 wt% of Fe powders to pure Sn exhibited ~60-100% higher ultimate tensile strength than the dispersion-free *so*lder materials. More importantly, its creep resistance at 100°C showed an increase by **a** factor of 20. Fe particles reinforced eutectic Sn-Bi composite solder exhibited 10% **h i gher** tensile strength and 5 times improvement in creep resistance under the similar **COnditions**.

Subramanian *et al.* conducted creep tests with unaged and aged, non-composite and **Composite** solder joints with various loads at several temperatures [47]. The 20v% *in-situ* Cu_6Sn_5 particle reinforced composite solder has about two to three orders of magnitude **better** creep resistance as compared to non-composite solder at room temperature and **lower** strain-rates, representing conditions that will exist during cold hold time in a

thermomechanical cycle. Although aging reduces the creep resistance of these solders, the composite solder possesses better creep resistance as compared to the non-composite solder even under aged conditions. At higher temperatures and higher strain rates region, the composite solder approaches the non-composite solder in creep behavior. At higher temperatures, the ability of dislocations to climb over particles is apparently fast enough to render the particles as ineffective dislocation barriers. At lower temperatures, the time needed for a dislocation to climb around a particle (for a given stress) is much longer, so the creep resistance is significantly improved.

The isothermal mechanical fatigue fracture behavior of the composite solder containing 20% Cu₆Sn₅ was reported by Gibson *et al.* and compared with that of noncomposite solder [49]. The fracture surface of the composite eutectic Sn-3.5Ag solder containing 20% Cu₆Sn₅ exhibited cleavage of the Cu₆Sn₅ particulate reinforcement and ductile, Mode I fracture of the eutectic matrix with no single origin of initiation corresponding to homogeneous ductile fracture. Meanwhile, the fracture surface of noncomposite eutectic Sn-3.5Ag solder joints exhibited ductile, mixed mode (I and II)

Nanoindentation experiments by Lucas *et al.* have shown that the interfacial **strength** can be estimated from indenting particles that rotate about their initial position **[50]**. Weak interfaces between Cu_6Sn_5 reinforcement particles and eutectic Sn-3.5Ag **mat**rix were detected for the in-situ composite solder from the nanoindentation testing. It was shown that in-situ composite solder increases the ductility of the solder matrix **without** increasing the strength significantly. Similar results were also reported by **Betrabet** *et al.* for their Sn-Pb based composite solders [28, 29], as stated in 2.2.1.2. It is

believed that the Cu₆Sn₅ reinforcements create heterogeneities in the strain sites \mathbf{F}_{or} inhibiting deformation and thus to promote homogeneous deformation. Therefore, an increased ductility was achieved in the *in-situ* Cu₆Sn₅ reinforced composite solder.

2.2.6 Summary

Use of dispersoids is a viable means to improve the properties and service temperature capabilities of solders. Such an approach can provide these improvements without significantly affecting the currently used processing parameters to make the solder joints. These dispersoids need to be inert or compatible with the solder so that they will be relatively stable when solder joints are placed in service. They could be introduced in the solder by *in-situ* methods or by converting the mechanically mixed metallic particles into stable intermetallic compounds either by melting the solder prior to making the joint or during reflow. Presence of these dispersoids aid in stabilizing the solder joint microstructure by retarding the aging process. All dispersoids tend to improve the creep strength of the solder by several orders of magnitude. An ideal dispersoid should enhance the ductility without significantly strengthening it. Since **solder** joint is highly inhomogeneous the deformation within the joint is highly localized. With the presence of weakly bonded heterogenities due to dispersoids, deformation can begin at several locations within the joint and cause homogeneous deformation. The **latter** will aid in improving the ductility of the solder joint. Such features will make the solder more compliant and forgiving to accommodate the stress by relaxation while delaying the onset of tertiary creep. This will improve the thermomechanical fatigue

resistance of the solder joint. Reinforcements introduced by *in-situ* methods appear to be more suitable for achieving this goal.

2.3 Creep Deformation Behavior of Sn-Based Solders

2.3.1 Overview of Creep Deformation Theory [51-55]

2.3.1.1 Introduction to Creep

Creep is defined as a phenomenon of continuous deformation that materials undergo when subjected to a constant load at an elevated temperature (usually $T_{applied}/T_m > 0.5$). Accumulation of strain with respect of time is the basic information resulting from deformation under constant stress and temperature. The essential feature of the characteristic time behavior at constant load and temperature can be shown on the typical creep curve, as illustrated in Figure 2.1. Three regimes of the creep process: the primary creep, the secondary creep or steady state creep and the tertiary creep may usually be distinguished. At the primary creep, characterized by strain hardening, the strain rate decreases and at the secondary creep, characterized by the balance between strain hardening and recovery, the strain rate remains approximately constant. Finally, at the tertiary stage, the increase in strain rate is observed as a result of the change of the dimension of the cross-section and the materials deterioration preceding the creep rupture. Among these three stages, secondary creep rate is generally used for comparing the creep resistance of materials, while the onset of tertiary creep is one of the criteria used to predict the service life of the material.





Figure 2.1 The model shape of a typical creep curve [51-54, 56].

Creep data are often presented in the form of the empirical equation of power law creep. Solder materials also follow the same power-law relationship between applied stress and strain rate, as reported from many studies [57-65]. In evaluating the creep behavior of solder materials, a generally accepted theory is expressed as follows [51-55, 58, 64].

Steady-state creep is generally expressed by a relationship of the form [10, 54, 58]

$$\dot{\varepsilon}_{s} = \frac{CGb}{kT} \left(\frac{b}{d}\right)^{p} \left(\frac{\sigma}{G}\right)^{n} D_{0} \exp\left(\frac{-Q}{kT}\right), \qquad (2-1)$$

where $\dot{\mathcal{E}}_s$ is the steady-state strain rate, G is the shear modulus, b is the Burgers vector, k is the Boltzmann's constant, T is the absolute temperature, d is the grain size, σ is the applied stress, D_0 is a frequency factor, Q is the activation energy for the deformation process, n is the stress exponent, p is the grain size exponent, and C is a constant characteristic of the underlying micromechanism.

The stress exponent n is dependent on the rate controlling mechanism. Though there is considerable theoretical controversy as to the exact mechanism for creep deformation, there exists at least four different types of generally accepted creep deformation mechanisms. These include: (i) diffusional creep, characterized by n=1 and activation energy corresponding to self diffusion or grain boundary diffusion; (ii) grain boundary sliding, characterized by n=2 and activation energy corresponding to grain boundary diffusion; (iii) dislocation glide, characterized by n=3-4 and activation energy corresponding to solute atom diffusion; and (iv) dislocation climb, c haracterized by n=5-7 and activation energy corresponding to self diffusion and dislocation pipe diffusion [58, 66]. Both dislocation glide and dislocation climb belong to the dislocation creep process.

2.3.1.2 Diffusional Creep

Diffusional creep occurs under low stress, high temperature conditions, which describes viscous flow where n=1. Diffusional creep involves the flow of vacancies and interstitials through a crystal under the incluence of applied stress. All matter deforms by this mechanism if sufficiently slow times are taken. Diffusional creep occurs under stress levels around $\sigma/G < 10^{-4}$. Nabarro-Herring creep and Coble creep are included under this category.

When a polycrystalline metal creeps by the diffusion of atoms through the crystal lattice, the process is known as the Nabarro-Herring creep [67, 68]. Nabarro and Herring proposed that the creep process was controlled by stress-directed atomic diffusion. Stress

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changes the chemical potential of the atoms on the surfaces of the grains in a polycrystal in such a way that there is a flow of vacancies from grain boundaries experiencing tensile stresses to those which have compressive stresses. Simultaneously, there is a corresponding flow of atoms in the opposite direction, and this leads to elongation of the grain. The steady-state creep for Nabarro-Herring creep is

$$\dot{\varepsilon}_{NH} \approx \frac{14\sigma b^3 D_{\nu}}{kTd^2}, \qquad (2-2)$$

where d is the grain diameter and Dv is the lattice diffusion coefficient. We note that increasing the grain size reduces the creep rate.

Coble creep has the same idea, except it is based upon grain boundary diffusion for conditions where diffusion in the lattice is comparatively slower [69]. This kind of creep happened at lower temperatures than Nabarro-Herring creep. The steady-state creep rate can be expressed by

$$\dot{\varepsilon}_C \approx \frac{50\sigma b^4 D_{gb}}{kTd^3},$$
(2-3)

A schematic diagram showing Nabarro-Herring and Coble creep on an ideal grain is illustrated in Figure 2.2. Even though both forms of creep are favored by high temperature and low stress, it is expected that Coble creep will dominate the creep rate in very fine grained materials. In general case, the creep rate due to diffusional flow should be considered as a sum of $\dot{\mathcal{E}}_{NH}$ and $\dot{\mathcal{E}}_{C}$, since the mechanisms operate in tandem, i.e., they are parallel creep processes. bol ų ĥô Ŵ S

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2.3.1.3 Grain Boundary Sliding

To prevent the formation of internal voids or cracks during diffusional creep of a polycrystal, additional mass-transfer processes must occur at the grain boundaries. These results in grain boundary sliding and the diffusional creep rate must be balanced exactly by the grain boundary sliding creep rate if internal voids are not to be formed. Diffusional flow and grain boundary sliding, therefore, can be considered as sequential processes in which mass is first transported by Nabarro-Herring and/or Coble creep and a grain shape change and separation is resulted. This is followed by "crack healing" via grain boundary sliding. A schematic illustration of accommodating diffusional creep by grain boundary sliding is shown in Figure 2.3 [70]. Raj and Ashby [71] considered the role of grain boundary sliding and found that both Coble and Nabarro-Herring Creep tend to make a continuum. Given a boundary with ledges occurring periodically, under shear stress, vacancies move away from the compressed parts of boundary and move towards tensile parts. Beere [72], Speight [73] and Aigeltinger [74] also found the fact that diffusional creep can be considered as diffusion which is accommodated by grain boundary sliding, or grain boundary sliding which is accommodated by diffusion. Any consideration of mutually independent contributions of the grain boundary sliding and diffusion is meaningless [71]. Some actual data from Zn-22Al provided n=2 under this creep mechanism [75, 76]. It is important to note that the role of grain boundary sliding in diffusional creep differs from that in dislocation creep. In the former, grain boundary sliding is an indispensable prerequisite of diffusion, while in the latter, dislocation creep, grain boundary sliding need not occur at all if a sufficient number of glide and climb system operate for the Von Mises criterion to be met.



Figure 2.2 Schematic diagram of (a) Nabarro-Herring creep and (b) Coble creep on an ideal grain [67-69].



Figure 2.3 A schematic illustration of accommodating diffusional creep by grain boundary sliding. (a) Four garains in a hexagonal array before creep deformation. (b) After deforming by diffusional creep, one dimension of the grain is increased and the other is decreased, and voids are formed between the grains. (c)The voids are removed by grain-boundary sliding. The extent of sliding displacement is quantified by the distance Y'Y'', which is the offset along the boundary between grains 1 and 3 of the original vertical scribe line XYZ [55, 70]. د م ۲ ۲

2.3.1.4 Dislocation Creep

Dislocation creep involves the movement of dislocations, which overcome barriers by thermally assisted mechanisms involving the diffusion of vacancies or interstitials. It occurs at intermediate to high stress levels $(10^{-4} < \sigma/G < 10^{-2})$ under a temperature range between 0.4T_m and 0.7T_m, where the dominant mechanism of creep is the rate of dislocation motion by glide or climb. This regime is known as dislocation creep. The steady-state creep rate under such dislocation creep represents a balance between the competing factors of the strain hardening rate and the rate of thermal recovery by the rearrangement and annihilation of dislocations [51-55]. In other words, dislocation creep starts from the idea that creep can be conveniently viewed as a manifestation of competitive work hardening and recovery. The work hardening aspects of creep are related to factors involving dislocation glide. Recovery aspects are related to nonconservative dislocation motion, e.g., dislocation climb in which obstacles to dislocation motion are circumvented and/or by which dislocations are annihilated — i.e., removed from the structure.

(i) Dislocation Glide. This kind of creep occurs when dislocation motion is limited by solute atmosphere (in pure metals and alloys), which pin the dislocation due to the reduced strain energy associated with a dislocation core [75]. This mechanism occurs at relatively high stresses, $\sigma/G>10^{-2}$, as compared to other creep mechanisms. The creep rate is established by the ease with which dislocations are impeded by obstacles including precipitates, solute atoms, and other dislocations [51]. Weetman presented the first theory of creep controlled by viscous dislocation glide in solid solution alloys and assumed not a

specific type of interaction of solute atoms with dislocations [77]. Creep rate is described by the following equation,

$$\dot{\varepsilon} \approx \frac{\sigma^3 b^2}{GAB} = \frac{2\pi (1-\nu)G}{A} \left(\frac{\sigma}{G}\right)^3,$$
(2-4)

where A is a constant depending on temperature and the mechanism of interaction of solute atoms with dislocations, $B=Gb^2/2\pi(1-v)$. Thus the stress exponent is n=3. Other models, developed by Mott [78], Raymond [79], and Barrett [80], etc., involve the dislocation creep controlled by the glide of screw dislocation with jogs in pure metals where similar stress exponent values were found.

(ii) Dislocation Climb. The earliest models of dislocation creep were advanced by Weertman [81-84], which were based on a mechanism in which dislocation climb plays a major role. At elevated temperature, if a gliding dislocation is held up by an obstacle, a small amount of climb may permit it to surmount the obstacle, allowing it to glide to the next set of obstacles where the process is repeated. Almost all of the strain is produced by the glide step, however, the climb step controls the rate. Since diffusion of vacancies or interstitials is necessary for dislocation climb, the rate-limiting factor is atomic diffusion. This model again predicts an equation for creep rate in which stress is raised to the third power. However, creep experiments with a range of metals show that the stress exponent varies from \Im to 8, with a value of 5 most common. Thus, for intermediate to high stress levels at temperature above $0.4T_m$, the steady-state creep rate is described by a powerlaw relation

$$\dot{\varepsilon}_s = \frac{AD_v Gb}{kT} \left(\frac{\sigma}{G}\right)^n,\tag{2-5}$$

where A and n are materials constants. Since the diffusion coefficient D_v can be described by

$$D_v = D_0 \exp(-Q/kT),$$
 (2-6)

we can rearrange Equation (2-5) into

$$\dot{\varepsilon}_s = B\sigma^n \exp(-Q/kT), \qquad (2-7)$$

which results in a simplified form of Equation (2-1). The modification [85] to Equation (2-5) allows it to be used for both high temperature creep, where lattice diffusion predominates, and for low temperature creep, where diffusion along dislocation cores is the predominant mechanism.

2.3.1.5 Power-law Breakdown [10, 58, 85-88]

At $rac{d}{d}$ ven higher stress, $\sigma/G>10^{-3}$, the strain rate is an exponential function of stress. The intermediate-to-high stress power-law breakdown region can be described by a single expression

$$\dot{\varepsilon}_{s} = C_{1} \frac{G}{T} \left[\sinh\left(\alpha \frac{\sigma}{G}\right) \right]^{n} \exp\left(\frac{-Q}{kT}\right), \qquad (2-8)$$

where α prescribes the stress level at which the power law dependence breaks down, and C_l is a constant.

To Obtain the true activation energy, the temperature dependence of the shear modulus modulus to incorporated

$$G = G_0 - G_1 T', (2-9)$$

where G_0 is the modulus at 0°C, G_1 gives the temperature dependence, and \mathcal{T}' is the temperature in °C.

According to this theory, it was approved that all the creep data can be fitted on the same general form of constitutive equations [58], which provides a general criterion for the comparison of the creep properties of different solder materials. Deformation maps, developed by Ashby *et al.*[89], schematically shown in Figure 2.4, provided a practical way of illustrating and utilizing the constitutive equation for the various creep deformation mechanisms.



Figure 2.4 A schematic deformation mechanism map. The axes of the diagram are homologous temperature (T/T_m) and stress (in terms of the shear modulus). The stress-temperature combination determines the primary deformation mode. At the boundary lines, the deformation is due equally to two different mechanisms, and, at the intersection of the lines, to three different mechanisms [55, 89].



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2.3.2 Importance of Studying the Creep Behavior of Sn-based Solder Materials

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Sn-based solder alloys are widely used for interconnection and packaging of ^{Commercial} microelectronic assemblies. High reliability and good mechanical **performance** are required for solders, especially solder joints, because during normal service conditions, the low melting solder alloys are subjected to creep and fatigue deformation. Even at ambient temperature of operation, the homologous temperature for these alloys is high, around 0.6, while the interconnect temperatures can reach as high as ³⁵⁰ K due to local heating. In such environment, high temperature creep processes dominate the deformation. It is imperative for researchers that knowledge of high temperature creep behavior be gained in order to predict reliability and overall performance of solder materials.

There have been many reports about the creep deformation behavior of solder alloys, especially Sn-based solder alloys. The following review presents the set-up and results of creep tests performed on Sn-based solder alloys in some important studies. Creep **Properties** of the materials tested are presented and compared. Controlling mechanisms for creep are summarized. Due to the adoption of "green" manufacturing practices, there has been new interest in developing lead-free solders. The following review also focuses on the creep properties reported in the recent literature for lead-free solder alloys.

2.3.3 Materials Used in Creep Tests

Eutectic Sn-3.5Ag solder has been broadly targeted as the foremost candidate to replace lead-bearing solders. Creep deformation behavior of Eutectic Sn-3.5Ag solder
has been most frequently reported in the recent literature [57-62]. Other lead-free solders often used for creep study include Sn-5Sb [57], Sn-9Zn [59, 60], eutectic Sn-Bi [62], and Sn-4.0Ag-0.5Cu [63] solder alloys. Examples of lead-bearing solders used for creep study often include 60Sn-40Pb [58, 64], 62Sn-36Pb-2Ag [58], 97Pb-3Sn [58], 95Pb-5Sn [58], 62Sn-38Pb [64], etc. The creep properties for pure Sn were investigated for compari son in some cases [57]. Other solder alloy systems, like In-Ag solder alloys, were also tested for creep properties in an effort to explore suitable substitutes for the existing lead-bearing solders [65].

2.3.4 Set — ups for the Creep Tests

Somme creep tests are set up for testing bulk solder materials. As part of an investigat \mathbf{i} on of using eutectic Sn-3.5Ag solder for flip chip interconnection, reported by Yang *et al.*, constant load creep tests were performed at high homologous temperatures from 25° to 180°C (0.6Tm to 0.92Tm) using a dead load creep machine, and the displacement was monitored using a linear variable differential transformer (LVDT) with an accuracy of $\pm 5 \times 10^{-5}$ in [61]. Mavoori *et al.* also reported a constant load creep testing on bulk, Cast, dog-bone shaped specimens on a servo-hydraulic MTS machine [59]. Constant load and temperature were controlled by a 458.20 programmable microconsole.

Until recently, most of the creep tests were performed on bulk solder materials. Recent studies have pointed out that creep behavior of bulk solders does not truly represent the creep behavior of solder joints functioning in real engineering applications. Bulk solders do not behave in similar ways under creep conditions that thin solder joints with constraints do. As an initial consideration we know that the microstructure of bulk solders is significantly different than microstructure of routinely fabricated solder joints because solidification parameters and process variables are quite different, particularly cooling rates [90, 91]. Unlike the microstructure of bulk solder, the solder joint microstructure consists of an interfacial intermetallic layer that forms between the solder and the substrate and intermetallics particles found within the solder matrix consisting of constituent elements of all materials comprising the solder joint. The interfacial intermetallic layer inherent in solder joints can act as a constraint to plastic flow. Thus, the intermetallic layer can alter the stress state in the joint, which can be significantly different than that in bulk solders under creep conditions. So, creep data obtained using bulk solcer materials will not necessarily correlate well to creep data gathered using thin solder joints. Due to these reasons, recent studies are conducted with solder joints that are representative to real conditions for solders used in industrial practices. 11.11886 = 12 13 - + + ----

Single shear lap solder joint specimens were most frequently used in the creep tests. An example of using single shear lap solder joint for creep testing can be referred to the paper reported by Raeder *et al.* [62]. These specimens were prepared by joining two pieces of commercially pure copper with 0.25mm thick foil solder. Solder mask on the copper limited the spread of the solder during soldering process. Spacers, with the same thickness as the solder preform, were placed on either side of the solder to confine the joint thickness.

A double shear lap configuration used for creep testing was reported by Darveaux et al. [58] - Such a configuration minimizes the bending component during the tests. All these tests were conducted in a screw driven Instron 4501 with a load cell. LabVIEW data acquisition software was used to control the Instron and to record load and

2.3.5 Reported Creep Data and Related Mechanisms for Sn-based Solder Materials 2.3.5.1 Creep Deformation Behavior of Sn, Sn-3.5Ag and Sn-5Sb Solder Alloys [57]

Creep deformation mechanisms in pure Sn, Sn-3.5Ag and Sn-5Sb solder alloys (bulk) was studied by Mathew *et al.* in the temperature ranges of ambient to 473K [57]. **Power-law** relationships between strain rate and stress were generally observed. Stress **exponent** n=7.6 \pm 0.2, 5.0 \pm 0.2, 5.0 \pm 0.3 were obtained for Sn, Sn-3.5Ag and Sn-5Sb **respectively**. Activation energies for creep Q_c =60.3 \pm 3.8, 60.7 \pm 6.6, and 44.7 \pm 3.7 kJ/mole **for** Sn, Sn-3.5Ag, and Sn-5Sb respectively. From phenomenological analyses, activation energies for self-diffusion through the lattice and dislocation core for Sn were estimated as 65 and 46 kJ/mole respectively. Based on the experimentally determined stress **exponent** and activation energy values, it was suggested by the investigators that the creep **de**formation mechanisms are dislocation climb controlled by lattice diffusion in Pure Sn **and** Sn-3.5Ag alloy, and viscous glide controlled by pipe diffusion in Sn-5Sb alloys (**solid** solution alloy).

2.3.5.2 Comparison of Creep Behavior between Sn-3.5Ag, 60Sn-40Pb, and 62Sn-36Pb-2Ag [58]

The creep deformation behavior of Sn-3.5Ag solder was studied and compared with those of 60Sn-40Pb and 62Sn-36Pb-2Ag solder alloys, reported by Darveaux *et al.* [58]. From their plots of normalized strain rate versus normalized shear stress, they have proved there all of the creep data can be fitted to the same general form of constitutive relations; i.e., only the constants depend on the solder alloy type. Comparison shows that the Sn-3.5Ag has better high temperature creep resistance than 60Sn-40Pb or 62Sn-36Pb-2Ag solder alloys. It is evident that the power law break down regime is approximately 10^{-3} t/G for all alloys tested. The 60Sn-40Pb and 62Sn-36Pb-2Ag alloys showed a stress exponent of 3.0, indicating dislocation viscous glide controlled deformation. The Sn-3.5Ag alloy had a stress exponent of 5.5, indicating dislocation climb controlled deformation mechanism. A study of alloy ductility was conducted by plotting the onset of tertiary creep versus normalized shear stress [58]. They found that the Sn-3.5Ag and 97Pb-3SD alloys absorbed more strain before the onset of failure than the 60Sn-40Pb and 62Sn-36Pb-2Ag alloys. The 95Pb-5Sn alloy was the least ductile, but, as suggested by these investigators, this could be due to the constraining effect of the smaller joint size in their creep tests.

2.3.5.3 Careep Deformation Behavior of Eutectic Sn-3.5Ag and Sn-9Zn Solders [59]

Creep tests were performed to both eutectic Sn-3.5Ag and eutectic Sn-9Zn solders under load control with initial stresses ranging from 10 to 22 MPa at two different temperatures, 25 and 80°C, by Mavoori *et al.*[59]. The stress exponent for Sn-3.5Ag was found to be higher than that for the Sn-9Zn. It was observed that there is a crossover between the plots for eutectic Sn-3.5Ag and Sn-9Zn, which indicated that at lower stresses, creep rates for Sn-3.5Ag are found to be smaller than for Sn-9Zn; however, as the stress is increased, the creep rate of Sn-3.5Ag became faster than that of Sn-9Zn. The ²⁵ and 80°C creep data were compared with data derived from Dorn and Norton's equation at the stress ranges tested and a close agreement between theoretical and experimental results was found.

2.3.5.4 Creep Deformation Behavior of Eutectic Sn-3.5Ag and Sn-Bi Solder and Solder Joints [62]

The isothermal tensile steady state creep rates of cast Sn-Bi and Sn-Ag eutectic solders and their joints were reported by Raeder et al. at temperatures between 20°C and 160°C [62]. A stress exponent of n=8.4 for room temperatures and n=6.7 for high temperatures were reported for eutectic Sn-Ag solder. A stress exponent of n=3.1 was reported for eutectic Sn-Bi solder at all temperatures under intermediate strain rate. At room te perature, the creep rates for eutectic Sn-Ag solder joints were found to be higher the second higher the stress level was less than ~ 27 MPa. The tensil e behavior of bulk solder was compared with shear behavior of solder joints for each solder material. The shear lap joint specimens for eutectic Sn-Ag solder were found to be much stronger than the bulk specimens, while eutectic Sn-Bi solder did not show such a significant difference. The reason for such a behavior is attributed to the processin & variables; the Sn-Bi joints were reflowed for a shorter time period at 200°C and the Sn-Ag joints were reflowed at 250°C. At these temperatures copper dissolves more quickly in molten Sn-Ag solder than in Sn-Bi solder. Copper present in the form of intermetallics in the Sn-Ag joints may strengthen the joints. It was also suggested that quenchings the Sn-Ag joints might strengthen them in comparison to the slow cooled bulk solders.

2.3.5.5 Creep Deformation Behavior of Eutectic Sn-3.5Ag Solder and Its Solder Joints [61]

Yang et al. have reported constant-load creep test data on bulk Sn-3.5Ag solder alloy at high homologous temperatures from 25°C to 180°C [61]. At all testing temperatures, the strain rate increased with stress following a power-law relationship with a stress exponent n=10. This exponent is much higher than that usually noted for creep due to dislocation climb where generally the value varies from about 4 to 7. The activation energy they obtained was Q=12.1Kcal/mole (about 50kJ/mole). This value is about one half of the activation energy for self-diffusion in pure Sn and thus is identifiable with either grain boundary or dislocation-pipe diffusion. The relatively large value for the stress exponent (n=10) along with this observation points to lowtemperature climb of edge dislocation to be the rate-controlling mechanism [61].

Upcon comparing the creep data between bulk and joint specimens, it has been found that the joint specimens were more creep resistant than bulk specimens. Several possible reasons regarding the discrepancy in creep behavior between solder joints and bulk solder materials have been suggested [46]: (1) The substrate metal may dissolve into the molten solder during soldering process altering the chemical composition of the solder joint. (2) The substrate metal may also react with the solder to form intermetallics at the interface. Sometimes, the intermetallic layer(s) may break away from the interface and disperse into the bulk solder resulting the dispersion strengthening mechanism. (3) The grain size of the solder joint is process-dependent and may differ from that of a bulk solder specimen. (4) Geometry constraints (eg. thickness-to-aspect ratio) may also influence the creep behavior of the solder joints. (5) Microstructural difference in thin joint (usually a finer microstructure) due to substantial difference in cooling rates during fabrication could also be a possible factor to be accounted for.

2.3.5.6 Summary

It should be noted from the above review that there is no clear agreement in the experimental data, which resulted in the discrepancy for the operating creep mechanism. Such discrepancy may be due to the use of different type of specimens (bulk or joint), different processing conditions (cooling rate, aged or unaged), and/or different testing methods (tensile or compressive), etc. But it should be noted that eutectic Sn-3.5Ag solder generally exhibits superior creep resistance as compared to other solder materials discussed above.

2-4 Microstructural Issues in Solder Materials

Solders are known for their evolving microstructures especially when aged and **reflowed** at high temperatures and during thermal and isothermal mechanical fatigue **processes**. Microstructure evolution of solder materials has been known for a long time [13,49,92]. Even at room temperature, the microstructure of solder materials is prone to **coarsening**, as noted by Tien *et al.* from their microstructural observation of Sn-Pb **solders** [93]. Similar microstructure coarsening occurs also in lead-free solders, like in **Greating** Solders, as reported by Gibson et al. [13], and Yang et al. [14].

The microstructure of as-fabricated Sn-Ag solder joints usually consists of Ag₃Sn *precipitate* in the Sn matrix with Cu-Sn intermetallics in both the bulk solder in the form of **dend**rites and at the solder/copper substrate interface in the form of layers [13,14].

The Cu-Sn intermetallic phases in this layer are Cu₆Sn₅ (η -phase) and Cu₃Sn (ε -phase), where Cu₆Sn₅ is adjacent to solder and Cu₃Sn is adjacent to Cu [94, 95]. (In the cases of using Ni substrates, the intermetallic phases will primarily be Ni₃Sn₄, Ni₃Sn₂ and also a metastable phase, NiSn₃ [96-98].) These intermetallics are formed as a result of the diffusion and dissolution of Cu in molten solder during the soldering process [99-101]. Thus the microstructural evolution of Sn-Ag solder joints during aging and reflow usually consists of Ag₃Sn precipitate coarsening, Cu-Sn intermetallic dendrite coarsening in the bulk solder, and Cu-Sn intermetallic layer growth at the interface.

There have been a significant number of in-depth studies of the formation and growth of intermetallic layers during aging and reflow. It was reported that the growth rate of the intermetallic layer is initially much higher when the solder is molten and it is related to the rate at which the reactants can diffuse to and/or through the existing layer (frequently, the growth rate is proportional to $t^{1/2}$ or $t^{1/3}$, where t is time) [96]. The kinetics of intermetallic formation at the liquid solder/Cu interface appears to be similar for eutectic Sn-Pb, Sn-Ag and pure Sn, when comparing the work reported by London [102] and Warwick [97]. It was also reported that the intermetallic layer formation tended to proceed much faster on Cu substrate than on Ni substrate [103]. Choi et al. have found that the initial thickness of the Cu_6Sn_5 intermetallic layer was consistently smaller after solidification of the Sn-Pb composite solder joint, but subsequent growth With the interfacial thickness were similar with Sn-Pb non-composite solder [104]. sunwoo and Mei et al. have studied the growth of Cu-Sn intermetallics at a pre-tinned copper/solder interface and they constructed a multiphase diffusional model to analyze the ε - and n-phase at a plane Cu-Sn interface in a semi-infinite diffusion couple [105,

106]. Using their diffusion model, Mei *et.al.* were able to compute the position of the ε and η -phase with time by determining the interdiffusion coefficient in the ε and η -layers. An advantage of Mei's analytical model was that precise knowledge of the concentration profile at the growing interface was not required. Wu *et.al.* studied the formation and growth of intermetallics in the composite solders and suggested that tin was the predominant diffusing species that controlled formation and growth of the Cu-Sn intermetallic layer during aging and reflow [42]. The effect of Ag, Au, Ni, and Cu particle additions on the formation and growth of the intermetallic layer was discussed and compared to pure solder.

Solder joint failure has been found to occur during room temperature and high temperature aging. Lampe's aging study of nine Sn-Pb solder alloys showed dramatic decreases in shear strength within the first twenty days of room temperature aging and extensive microstructural coarsening [107]. Yang et al. observed the failure of eutectic Sn-Ag solder joints made by infrared reflow after three days of aging at 190°C [14]. Their joints made by laser soldering failed after seven days at the same temperature. The failure was due to crack initiation and growth cause by the stresses from thermal mismatch at local areas as well as void formation in the Cu₃Sn phase, as explained by these investigators.

CHAPTER III

MICROSTRUCTURE OF AS-FABRICATED Cu, Ag, AND Ni PARTICLE REINFORCED COMPOSITE SOLDER JOINTS

3.1 Preparation of Composite Solders

The composite solders were prepared by mechanically adding ~6 μm size Cu, ~4 μm size Ag, or ~6 μm size Ni particles to the Sn-3.5Ag eutectic solder paste for some studies. Copper, silver, and nickel powders used as the reinforcements were obtained from Atlantic Equipment Engineers, INC., Bergenfield, New Jersey. The purity of all materials was reached at 99.9%. The morphology and size of the as received Cu, Ag, or *Ni* particles were studied using scanning electron microscopy. Particle sizes were measured directly from scanning electron microscopy (SEM) micrographs using Adobe Photoshop 5.0[®], an imaging processing software package.

One way of making the composite solder material involved mechanically blending the reinforcing particles and solder paste in a ceramic crucible for at least 15 minutes to promote uniform reinforcement distribution. The composite solders used in this study nominally contained 15 volume percent Cu, Ag, or Ni reinforcements. In order to have a quick initial examination of the microstructure, after mechanical mixing, usually, a button-shaped composite solder specimen was prepared by melting and solidifying a small amount (~5 grams) of the composite solder paste on a copper substrate or in a ceramic crucible at 280°C. The composite solder was cooled from the molten state by placing the substrate or crucible on an aluminium plate. Solidified samples were cleaned, sectioned and polished for SEM and energy dispersive x-ray (EDX) examination. The composite solders were also examined using optical microscopy. Energy dispersive x-ray analysis was carried out to identify element phases within the solder matrix and IM layers.

Alternatively, composite solders were prepared by slowly adding the reinforcement particles into a molten Sn-3.5Ag solder at 280°C while stirring the mixture. The mixture was cooled from the molten state using the solidification procedure described above.

3.2 Solder Joint Fabrication

Single shear lap, dog-bone shaped solder joint specimens were used thoughout the study for microstructural examination or mechanical tests. The specimen consisted of Cu substrate arms which were fabricated by electro-spark discharge machining (EDM). The substrate dimensions are shown in Figure 3.1. The Cu substrates were chemically cleaned with a solution of 50% Nitric acid and 50% H₂O. Next, a solder masking compound was applied on the tip ends of the Cu substrate to limit solder joint size to an area of ~ 1 mm². Composite solder paste or several solder foil preforms ~ 30 µm thick by 1 mm² in area were then sandwiched between the two Cu substrates as shown in Figure 3.1 in order to fabricate solder joints that were typically 100 µm thick. In the cases when solder foil preforms were used, Alpha 200-L flux was applied to the solderable areas of the Cu substrate prior to applying the solder foils. The prepared joints were placed in a holding fixture and subsequently heated to a temperature of 280°C on a hot plate to achieve melting. The melted joints were then removed from the heat source

and quickly placed on an aluminum chill block which promoted cooling rates similar to or slightly faster than those in industrial practice of reflowed solder joints. The thermal history profile for solder joint fabrication is shown in Figure 3.2. The comparative dimensions of



Figure 3.1 Dimensions of shear-lap solder joint, copper substrate and aluminum fixture.



Figure 3.2 Temperature profile of single shear lap solder joint fabrication.

the solder joint are illustrated in Figure 3.3. The solder joint area is $\sim 1 mm^2$ and its thickness is nominally 100µm. The joint size is representative of solder joints used in microelectronics industrial applications. An essential step in our investigative procedures involves metallographical polishing one side of the solder joint for microstructural characterization and documentation prior to testing.



Fi Sure 3.3 Comparative dimension of a single shear lap solder joint used in the investigation.

3-3 Microstructure of As-fabricated Cu Particle Reinforced Composite Solder Joints

A typical microstructure in the as-fabricated Cu particle reinforced composite \mathfrak{G} ders joint is shown in Figure 3.4. The Cu-Sn IM layer that formed at the periphery of *cu* reinforcement particles is clearly shown in Figure 3.4(a) and (b). The IM layer *thickness* was approximately 1.5-2 µm thick. In fact, the IM layer that forms around the *Cu* reinforcement is an intermetallic co-layer consisting of a Cu₃Sn layer (ε-phase) that



Figure 3.4 Microstructure of as fabricated Cu particle reinforced solder joint. (a) Overall view of the microstructure in the joint, (b) Cu reinforcement particle and the IM layer formed around Cu, (c) IM layer formed at the Cu substrate/solder interface.

shares an interface with the Cu particle (Cu substrate) and of a Cu₆Sn₅ layer (η-phase) that shares an interface with Cu₃Sn and the solder. During the first reflow of the sample, the Cu₃Sn layer is fairly thin and virtually undetectable as noted by others [42, 51, 105]. The dark core region of the particulate reinforcement is pure Cu, and the light exterior layer surrounding the Cu particle is the Cu₆Sn₅/Cu₃Sn IM co-layer. The Sn-Ag solder matrix microstructure is characterized by eutectic Ag₃Sn phase residing between Sn spains. Energy dispersive x-ray analysis confirmed the chemical elements present in the *natrix* microstructure and in the IM layer. The IM layer at the Cu substrate/solder *interface* is also a Cu-Sn co-layer, as shown in Figure 3.4(c).

3.4 Microstructure of As-fabricated Ag Particle Reinforced Composite Solder Joints

The microstructure that is representative of the Ag Particle reinforced composite solders is shown in Figure 3.5 (a)-(b). The light contrast noted around the perimeter of the Ag particles was identified as a thin layer of Ag₃Sn. The darker core is non-reacted Ag. In the first reflow of the composite solders, the thickness of the Ag₃Sn IM layer that formed in the Ag particle reinforced composite solder was much smaller than the CuSn IM layer that formed in the Cu particle reinforced composite solder. An EDX scan across a number of Ag particles indicated that, except for a thin layer at the very edge, the Ag reinforcement was pure Ag. The Ag₃Sn IM layer that formed around the Ag reinforcements is only ~ 0.1-0.3 μ m thick. The solder matrix microstructure of the Ag composite shows the usual pure Sn cells with eutectic Ag₃Sn particles found at Sn cell boundaries. The IM layer at the Cu substrate/solder interface (Figure 3.5c) shows similar Cu-Sn IM co-layer as in Cu composite solder. No Ag was detected in the interfacial IM layer.

3.5 Microstructure of As-fabricated Ni Particle Reinforced Composite Solder Joints 3.5.1 Microstructure under Regular Heating and Cooling Condition

Microstructure that is representative of the as-fabricated Ni particle reinforced composite solder joint is shown in Figure 3.6(a). The eutectic Sn-3.5Ag solder matrix microstructure is characterized by eutectic Ag₃Sn phase residing between Sn grains. The dark core region of the particulate reinforcement is pure Ni, and the light exterior layer surrounding the Ni particle is the IM layer formed upon first reflow of the solder material. The IM layers developed around the Ni particles were approximately 1-2 μ m



Figure 3.5 Microstructure of as fabricated Ag particle reinforced solder joint. (a) Overall view of the microstructure in the joint, (b) Ag reinforcement particle and the IM layer formed around Ag, (c) IM layer formed at the Cu substrate solder interface.



thick and reinforc **त्र्हा** हो हो -Д. part Ener prese **r**einfor periphe compou Mlayer E of a Cu that sha substra phase under Cu su differe reinfo Sn, i thick and can be characterized by a "sunburst" pattern surrouncling the Ni particle reinforcements. The "sunburst" IMC patterning around the Ni particles may also be referred to as "sunflower". It is also clearly shown that there is a significant number of ~0.5 µm sized small IM particles scattered, mostly, along periphery of Ni reinforcement particles. A few of these small IM particles appear in the eutectic Sn-3.5Ag matrix. Energy dispersive X-ray (EDX) analysis was performed to verify chemical elements present in the particle and IM layer. The composition of IM layer surrounding the Ni reinforcement consisted of Cu-Ni-Sn. EDX analysis to identify small particles at the periphery of the IM layer revealed also that these particles were also a ternary IM compound of Cu, Ni and Sn. A higher magnified view the Ni particle and the surrounded IM layer is shown in Figure 3.6(b).

EDX analysis of Cu substrate interfacial IM layer revealed IM co-layer consisting of a Cu-Sn layer that shares an interface with Cu substrate and a Cu-Ni-Sn ternary layer that shares an interface with solder matrix. The Cu-Sn IM layer that is adjacent to the Cu substrate was mostly Cu₆Sn₅ (η -phase) in the as-fabricated solder joint. The Cu₃Sn (ε phase) is virtually undetectable in the first reflow but the ε -phase thickness increases under subsequent aging or reflow processes [42, 51, 105]. The interfacial IM layer at the Cu substrate is shown in Figure 3.6(c).

The diffusion results listed in Table 3.1 [13, 108] can be used to explain the difference in the extent of IM layer formation observed around the Cu, Ag and Ni particle reinforcements. In Table 3.1, which alludes to the extent of Cu, Ag, and Ni diffusion in Sn, it is evident that the diffusing distance for Cu in Sn perpendicular to its c-axis of the



Figure 3.6. Microstructure of as fabricated Ni particle reinforced solder joint. (a) Overall view of the microstructure in the joint. (b) Ni reinforcement particle and the IM layer formed around Ni, (c) IM layer formed at the Cu substrate sold interface.

unit cell is ~ 400 μ m after 100 hours at 25°C. In contrast, the diffus ing distance for Ag in Sn perpendicular to the c-axis is ~ 0.5 μ m under similar conditions. Cu diffuses nearly 10³ times faster in Sn perpendicular to its c-axis than does Ag. In similar calculations, Cu diffuses more than 10⁵ times faster in Sn parallel to its c-axis than Ag, which indicates that the diffusion couple of Sn-Cu is significantly more active than the diffusion couple of Sn-Ag. Ni and Cu are similar in chemical characteristics, such as atomic number, similar atomic radius, and electronegativity. Thus, their diffusion behavior in Sn is expected to be similar. Consequently, much thicker initial IM layers were observed around Cu and Ni particles as compared to the IM layers around the Ag reinforcement particles.

Table 3.1 Comparison of Diffusion Parameters for Ag, Cu, and Ni in Sn [13, 108] $(Dt)^{1/2}$ in μ m, **1** 00 hours D_0 0 150°C cm^2/s 75°C kJ/ mol 25°C **1**00°C Ag in $Sn\perp c^*$ 77 4.2 0.18 0.454 45 ---Ag in Sn //c** 55.1 7.5 37 0.0071 ---200 Cu in Sn⊥c* 0.0024 33.1 369 964 1414 2660 Cu in Sn // c** $D=2\times10^{-6} \text{ cm}^2/\text{s}^{***}$ 8485 ------Ni in Snlc* 54.2 0.0187 ---369 Ni in Sn // c** 21549 0.0192 18.1 36421 44915

indicates diffusion of species transverse to the c-axis of the unit cell of tin. / indicates diffusion of species parallel to the c-axis of the unit cell of tin. D_0 and Q values are not available in the references individually.

3.5.2 Microstructure under Different Heating and Cooling Conditions

3.5.2.1 Introduction

Intermetallic compound (IMC) formation around mechanically introduced metallic particles due to the joining operation is directly related to reflow temperature-time profile of the solder while it is in the liquid state [109, 110]. During reflow, reaction between the incorporated metal particles and the molten solder occurs, and IMC may nucleate and grow at the particle/solder interface. Two different IMC morphologies around the Ni reinforcement particles have been observed resulted from reflow operation. The effects of the reinforcement shape on the fracture behavior, ductility, residual stress, and particle cracking have been observed in metal matrix composites [111, 112]. However, such findings have not been reported for both lead-bearing and lead-free solders. In general, spherical shaped reinforcements would provide the composite material with superior mechanical properties as compared to angular shaped reinforcements. The objective of the study in this section is to investigate the thermal history dependence for the development of different IMC morphologies during reflow.

3.5.2.2 Experimental

To assess the effect of thermal history on the IMC formation and morphological development, several heating and cooling thermal profiles were used for reflowing Ni particles reinforced composite Sn-3.5Ag solder joints. Following are the types of experiments that were conducted.

(1) Cooling Rates Experiments

In order to evaluate the effects of cooling rate, four different cooling rates were attempted. This was achieved by reflowing all the specimens using a preheated hot plate as the heating source. The preferred cool down segments of the reflow profile were achieved by placing the assembly of specimens after the solder is molten either (1) in water, (2) on a chill alumium block, (3) on a firebrick, Or (4) on a wood block. It should be noted that the heat-up rates for these reflow profiles remained the same for all specimens used in this part of study; only the cooling rates differed to study role of different cooling rates. The corresponding temperature-time reflow profiles experienced in this series of experiments are given in Figure 3.7. Figure 3.8 compares temperaturetime profiles corresponding to fastest and slowest cooling rates, while maintaining fastest heating rate.

(2) Heating Rates Experiments

This series of experiments were carried out to evaluate the influence of heating fall. Three different heating rates were used. The desired heating rates were achieved by placing the specimen assembly (a) on the preheated hot plate with the highest power setting to provide the fastest heating rate, (b) on the preheated hot plate at the intermediate power setting to attain medium heating rate, and (c) by turning on the hot plate only after placing the assembly on it to provide the slowest heating rate. The temperature profiles corresponding to this series of experiments are given in Figures 3.9 and 3.10. Also to assess the effect of higher joining temperature, specimens were reflowed at the fastest heating rate but to a higher peak temperature (330°C). Normal peak temperature used during study was 280°C. In these heating rate experiments where



Figure 3.7 The temperature-time reflow profile with four different cooling rates (heat rates remained the same for all reflow conditions). (1) Cooling conditions in water, (2) on aluminum chill block, (3) on fire brick, (4) and on wood.





3 8 Temperature-time profiles of the fastest and the slowest cooling rate. Sunflower shape of IMC prevails around Ni particles after (a) the fasted cooling rate, and (b) the slowest cooling rate. The cooling rate apparently has no significant effect on IMC morphology.



Figure 3.9 The temperature-time profile with four different heating rates (cooling rates remained the same for all reflow conditions). A5, A6, and A7 indicate areas underneath the heating part of these profiles at temperatures above the melting point of the solder for heating rates 5, 6, and 7.



Figure 3.10 Temperature-time profiles associated with micrographs of Cu-Ni-Sn intermetallic are shown (a) Sunflower shape for heating profiles of 5 and 8, (b) mixed sunflower shape and single-crystal-faceted morphology occurred with the medium heating rate (6), and (c) single-crystal-faceted morphology accompanied with the slowest heating rate (7).

the heat-up rates were deliberately changed, the cooling rates were held the same by cooling all the specimens used in this part of the study on an aluminum chill block. The corresponding temperature profiles are given in Figure 3.9. Attention is called to the shaded features presented in Figure 3.9. The shaded areas of reflow profiles designated as A5, A6, and A7, are areas bounded by the heat-up curve between the melting and peak temperatures of the solder and a vertical line from the peak temperature to the melting temperature (T_m) line. The areas, A5, A6, and A7, define the amount of heat input involved in reflowing the solder joint. It should be noted that a fast heating rate to the peak reflow temperature gives the smallest area, A5, hence, a low heat input, while areas A6 and A7 represent medium and high heat input, respectively. There appears to be a direct correlation between the extent of the so-called "heat input" as defined above and the IMC morphology observed around the Ni reinforcements in the composite solder. Whether "sunflower" or "blocky" IMC morphologies prevails seems to depend on the "cumulative" heat input as defined by the area of the heat up portion of the thermal reflow profile.

(3) Multiple Reflow Experiments

Studies dealing with multiple-reflow thermal profiles were carried out using the fastest heating rate to the peak temperature of 280°C. The heat input designated by A5 was maintained for each reflow as shown in Figures 3.11 and 3.12. These multiple-reflow studies were helpful to compare the IMC morphological changes due to differences in amount of heat input.

Another set of multiple-reflow experiment was conducted by manipulating the peak temperature vs. heating rate so that the heat input of each reflow equals the same



Figure 3.11 Effect of reflow at 280°C with fastest heating rate on the growth of IMC layers around Ni particles in Ni composite solder joint. (a) first reflow, (b) second reflow, (c) third reflow, and (d) fourth reflow. A5 is the heat input area above melting temperature to peak temperature. 4A5 and A7 were measured. The arrows indicate the microstructure associated with each reflow.



Figure 3.12 Heat input area comparison of A5 and A6 ($A6 \le 3A5$).

amount of heat input represented by area A5. This reflow temperature profile, A9, was carefully designed and successfully achieved by heating the solder joint to peak temperature of 250°C under the slowest heating rate, as shown in Figure 3.13.

Fast cooling rate was employed for both these multiple-reflow experiments by cooling the solder joints on an aluminum chill block after each reflow.



Figure 3. 13 Effect of reflow at a peak temperature of 250°C with the slowest heating rate on the growth of IMC layers around Ni particles. The heat input of one reflow is equivalent to heat input with the reflow that undergone fast heating rate (A5=A9). The heat input for the four reflows in temperature region above the melting point is almost the same as that of the slowest heating rate (A7=AA9). Arrows indicate IMC morphology observed.

(4) Heat to Routine Peak Temperature with Long Hold Time Experiments

To evaluate the effect of long hold time in the molten state, the reflow profile which is equivalent to heat input area as three times A5 (3A5) was achieved by keeping the molten solser for 15 more seconds at 280°C with the fastest heating rate as shown in Figure 3.14. Again, the cooling rate was maintained by cooling on the aluminum chill block.



Figure 3.14 Heat input approximately equivalent to 3A5 obtained with a hold of 15 seconds at peak temperature-time profile and the resultant single-crystal-faceted morphology.

(5) Heat to Low Peak Temperature with Long Hold Time Experiments

To study the influence of long hold time at just above melting temperature, experiments were carried out at a peak temperature of 230°C for 126 seconds and 225°C for 258 seconds using the slowest heating rate as shown in Figure 3.15. The amount of heat input of both thermal reflow profiles was about 2 times of A5 (2A5). Again both reflows used the same fast cooling rate.

Temperature profiles of all reflows were obtained with a thermocouple attached to the specimen fixture at a region very close to the solder joint.

Metallographic polishing was carried out after reflow at side surface of the solder joints. The polished sides of solder joints were **Observed** with a scanning electron microscope (SEM) to reveal the intermetallic formation around Ni particles after each set of reflow experiments.

3.5.2.3 Results and Discussion

It has been reported that the morphology of IMC layer is strongly influenced by heating and cooling rates [109]. Thus, in order to evaluate the relative influence of heating and cooling rates on the IMC morphology around Ni particles in the composite solder, several different thermal reflow profiles were investigated as described in the experimental procedures. The resultant IMC morphologies obtained due to various reflow **pr**ofiles are discussed as follows.



Figure 3. 15 Effect of low peak temperature and long hold times at this temperature on the IMC morphology. These two temperature profiles represent heat input approximately equivalent to two reflows with peak temperature of 250° ($2A9 \approx A10 \approx A11$). Sunflower IMC morphology was observed after both these conditions.

(1) Effect of Cooling Rates on IMC Morphology

Examination of the IMC layer using the reflow profiles shown in Figure 3.7 revealed that regardless of the cooling rate, the resultant IMC morphology observed was the "sunflower" shape. Figure 3.8, indeed, shows sunflower morphology was obtained for fastest as well as slowest of cooling rates employed. The inset micrographs clearly illustrate that cooling rate has virtually no effect on the resultant IMC morphology. Therefore, it can be deduced that the cooling segment of the thermal reflow profile does not significantly affect the morphological development of the IMC layer around the Ni particles in the composite solder. Since the cooling segment of the reflow profile did not have an apparent influence on the IMC morphology, more attention was focused on the investigation of heating segment in the reflow profiles to ascertain the possible effects it may have on the IMC morphology.

(2) Effect of Heating Rates on IMC Morphology

In contrast to the above findings that the cooling rate does not affect the IMC morphology, two different morphologies of the IMC were observed around Ni particles depending on the nature of the heating rate segment of the reflow curve, as shown in Figure 3.10. A sunflower shape IMC morphology shown in Figure 3.10a was observed with the fastest heating rate (reflow profile # 5 in Figure 3.9), and fastest heating rate with higher peak temperature (reflow profile # 8 in Figure 3.9). Figure 3.10b illustrates a **moi** xture of both sunflower and single-crystal-faceted (blocky) morphology of IMC with medium heating rate (reflow profile # 6 in Figure 3.9). Pure single-crystal-faceted **morphology** is shown in Figure 3.10c and was observed under the slowest heating rate (**reflow** profile # 7 in Figure 3.9). Since the cooling segment of the reflow profiles in



Figure 3.9 and Figure 3.10 are the same, it is reasonable to suggest that it is the "heating segment" of these reflow profiles that influences the IMC morphology observed. When the heat input, as defined earlier by the area related to the heating segment, is sufficiently large, the preferred IMC morphology is "blocky" single-crystal-faceted in shape. When the heat input is smaller, as is the case with a fast heating rate, the appearance of the IMC morphology is sunflower. There must exist a critical heat input where the transitions of the IMC morphology from sunflower shape to a blocky shape will occur.

(3) Comparison of IMC Morphology Obtained after Multiple-Reflows with Those from Different Heating Rates

In an attempt to ascertain whether just temperature or amount of heat input (represented by area under the heating segment of reflow profile curve above melting temperature) is influencing the IMC morphology, multiple reflow studies were carried out using the fastest heating rate to 280°C peak temperature followed by cooling on the aluminum chill block (reflow profile # 5 in Figure 3.9). Although the initial morphology is the sunflower shaped as shown in Figure 3.11a and b, the single-crystal-faceted "blocky" morphology develops after about the third reflow.

The area underneath the heating segment curve can represent the heat input received by solder during each reflow from the melting point (221°C) to peak temperature (280°C). Figure 3.11 illustrates that a small heat input which normally gives sumflower morphology will give a blocky IMC morphology if the cumulative heat input as result of multiple reflows is at least equal to the critical transition heat input required for blocky morphology. 3A5 in Figure 3.12 represents the critical heat input required to achieve "blocky" IMC morphology. It is shown that the heat input of three such reflows
provides critical heat input required to change the IMC morphology from sunflower to single-crystal-faceted blocky shape.

To validate the 3A5 criterion for causing the change in IMC morphology, the amount of heat input with medium heating (A6) was compared to that of three reflows (3-A5, three fastest heating rate reflows), as shown in Figure 3.12. It was found that A6 which is less than 3A5 (but close to it) did not provide enough heat input to completely change the sunflower shaped IMC morphology into the blocky single-crystal-faceted morphology. However, the sunflower morphology tends to change into blocky single-crystal-faceted morphology due to this heat input of A6. Since A6 is slightly smaller than 3A5, the transition is not complete as shown in Figure 3.10b. The cumulative heat input represented by four reflows (4-A5 areas) was approximately equivalent to the heat input of A7 in Figure 3.11 that results in the single-crystal-faceted IMC morphology.

These findings established that a critical amount of heat input is required for IMC morphological change. It is also clear that path by which critical heat input is achieved is immaterial as long as this critical value is reached cumulatively. In Figure 3.13, a reflow profile to a peak temperature of 250°C was used. Again, when the cumulative areas of A9 are greater than the critical heat input, single-crystal-faceted IMC morphology was observed.

(4) Routine Peak Temperature with Hold Time

The reflow profile shown in Figure 3.14 again confirms that as long as the area under the heating segment is equivalent to the critical heat input, the IMC morphology will be altered. Temperature-time profile and micrographs for this routine peak temperature (280°C) with long hold time, equivalent to 3-reflows, is shown in Figure 3.14.

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Since again the single-crystal-faceted shape was found to occur, and it corresponded well with 3A5 criterion in this study.

(5) Low Peak Temperature with Long Hold Time

In order to evaluate the effect of low temperature with longer hold time, the heat input profiles corresponding to heating to 225°C for 258 seconds, and to 230°C for 126 seconds, were imposed as illustrated in Figure 3.15. The heat input of both reflows was approximately the same heat input provided by the sum of 2A5 areas (i.e., $2A5 \approx A10 \approx$ A11). Both reflow profiles gave the sunflower IMC morphology as shown in Figure 3.15. Such observations once again confirming that there exists a critical heat input to facilitate the development of blocky single-crystal-faceted morphology.

Presently, it is unclear as to the precise nature and mechanisms that influence the morphological change and patterning of the IMC formed around the Ni particles reinforcements in the composite solder. However, it is well understood from this study that the heat input of the heating segment of the reflow profile must reach some critical value before the IMC morphology changes from "sunflower" to "blocky" single-crystal-faceted shape.

Albeit speculative, a final comment related to the formation and growth of IMC is offered. From results of this study, it can be observed that a scallop shaped IMC was possibly formed initially and then grew to the sunflower morphology. Under the slowest heating rate, the channel between each "sunflower petal" would provide an easy path for the interdiffusion between Sn, Ni and Cu species, which resulted in a morphology change to single-crystal-faceted shape in a gradual manner with sufficient heat input. Longer Soldering time and high temperature holds in the molten state also causes generally



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thickened IMC and a gradual morphological change from the initial shape by a similar mechanism.

The salient findings of this investigation are given in Table 3.2. The results presented in this table strongly suggested that amount of heat input in the heating part of the reflow at temperatures above the melting point of the solder has significant influence in the development of the IMC morphology.

Area of heat input used in this study	Sunflower shaped IMC	Single-crystal-faceted shaped IMC
A5 and A9	\checkmark	
2A5 and 2A9	\checkmark	
3A5 and 3A9		\checkmark
4A5 and 4A9		V
A6 (Medium heating)	√	\checkmark
A9 (Slowest heating)		V
3A5 (Fastest heating rate with 15 sec hold time)		√
A10 (Heat at 230°C for 126 sec)	V	
A11 (Heat at 225°C for 258 sec)	V	

 Table 3.2 Results Based on the Study on IMC Morphology

3.6 Summary

 Extensive formation of scallop-shaped Cu-Sn IM layers around the Cu reinforcements was observed, whereas the formation of Ag-Sn around the Ag reinforcement was minimal in the as-fabricated composite solder joints. The IM layers developed around the Ni particles were also significant and can be characterized by a "sunburst" pattern surrounding the Ni particle reinforcements. A significant number of ~0.5 μ m sized small IM particles were observed scattering, mostly, along periphery of Ni reinforcement particles.

- 2. The morphology of IM layer around Ni particles was affected due to different heating rate, but not cooling rate. Sufficient heat input to cause a "blocky" singlecrystal-faceted shape IMC morphology can be achieved by multiple reflows of the solder provided the cumulative heat input reaches the critical value.
- 3. The IM layer around the Cu reinforcement was a co-layer consisting of a Cu₃Sn layer close to Cu particles and a Cu₆Sn₅ layer close to the solder. The IM layer formed around Ag particles was thin Ag₃Sn layer. The IM layers surrounding the Ni reinforcements were detected as a Cu-Ni-Sn ternary IM layer.
- 4. The IM layers formed at the Cu substrate/solder interface were found to be Cu-Sn IM layer in both the Cu and the Ag particle reinforced composite solder joints. This Cu-Sn IM layer is also a co-layer consisting of a Cu₃Sn layer close to Cu substrate and a Cu₆Sn₅ layer close to the solder. However, the IM layers formed at the Cu substrate/solder interface in the Ni composite solder joints was determined as a co-layer consisting of a Cu-Sn IM layer close to Cu substrate and a ternary Cu-Ni-Sn IM layer close to Ni composite solder.
- 5. The thick IM layer formed around the Cu or Ni particles is due to the fast diffusion behavior of Cu or Ni atoms in Sn, whereas the diffusion of Ag in Sn is much slower which results in a significantly thinner Ag-Sn intermetallics around Ag particles.



CHAPTER IV

MICROSTRUCTURAL EVOLUTION IN Cu, Ag, AND Ni PARTICLE REINFORCED COMPOSITE SOLDER JOINTS UNDER ISOTHERMAL AGING AT 150⁰C

4.1 Introduction [95]

When two metals parts are joined by solder, a metallic continuity is established as the result of two interfaces that form where the solder is bonded to both metal parts [113]. This metallic continuity, or joining interface, is referred to as the intermetallic (IM) layer. Intermetallic compounds grow at the interface of the solder and the substrate during long term storage at ambient temperatures and more rapidly at high temperatures [114, 115].

The effect of IM growth within solder joints is not clearly understood. While the presence of IM compounds are an indication that a good metallurgical bond has formed, the fact that these compounds are brittle may also make them deleterious to a joint's mechanical integrity. When these compounds form as continuous layers at the solder/substrate interface, the intermetallics can interrupt electrical currents with their high resistivity, effectively isolating the metals that were to be electrically joined [116]. In addition, if these IM compounds become too thick, the reliability of the joint can be jeopardized due to cracking. This will be a problem especially if the joint is exposed to any mechanical forces, such as expansion or contraction of the printed wiring board (PWB) laminate caused by variations in temperature [115]. Exposure of these IM compounds to the atmosphere via microtunnels formed through the solder during the tinning or aging process has also been recently postulated as allowing for the



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[117]. The interdiffusion processes, which produce the intermetallic layers, can also produce Kirkendall voids which can also degrade the mechanical properties of the connection [94].

The intermetallic is more brittle than the bulk solder, and one might predict that failure therefore would occur at the IM layer. However, the intermetallic does not play a role in the failure of a solder joint. This point has been proved by many researchers. For example, Morris *et al.* [118] has shown that low-cycle thermomechanical fatigue and ultimate failure of a properly soldered solder joint occurs though the bulk of the solder. However, if the solder joint is subjected to extended periods of high temperature or long term aging even at ambient temperature, the IM layer formed in the solder joint will grow excessively which will degrade the solder joint due to its brittle nature and the voids formed in the joint. In the composite solder joint with mechanically incorporated . reinforcements, the IM layers are formed not only at the solder/substrate interface, but also around the reinforcement particles. Therefore, it is very important to study the formation and growth of these IM layers in order to predict the lifetime of the solder joint under service conditions.

The objective of the aging study in this chapter is to investigate whether mechanically added Cu, Ag, or Ni particles would alter the microstructure as well as the aging characteristics of eutectic Sn-3.5Ag solder, especially in small solder joints that are more representative of solder joints used in microelectronics. This work is focused on the microstructural characterization of mechanically-introduced Cu, Ag, and Ni particle reinforced composite solders. The effects of isothermal aging on (i) substrate/solder and (ii) particle/solder IM interfaces and on the overall microstructure are also examined. Possible mechanisms are proposed for IM layer growth due to solid-state isothermal aging of solder joints at 150°C.

4.2 Experimental Procedures

Aging experiments were performed by placing the solder joints on an aluminium plate maintained at a constant temperature for up to 1000 hours. The aging temperature used in the experiments were room temperature (25°C), 50°C, 100°C, and 150°C for the Ni composite solder joints, and 150°C only for the Cu and Ag composite solder joints. The polished solder joints were slightly repolished to remove the oxide layer at aging times of 100, 500, and 1000 hours to reveal the change in microstructure. SEM micrographs were taken before and at set aging time intervals during the experiment. Particular attention was given to the investigation of the formation and growth of IM layers around the reinforcement particles and at the copper substrate-solder interface. Each of these studies was carried out by monitoring the same targeted area of the solder joint to provide a reliable measurement of the changes that took place during the aging process.

4.3 Microstructural Evolution in Cu Particle Reinforced Composite Solder Joints

4.3.1 Intermetallic Layer around Cu Particles

The effect of isothermal aging at 150°C on the IM layer growth around the Cu Particles in the Cu composite solder joint is illustrated in Figure 4.1. Note that the icrograph series of Figure 4.1 represents the same field of view imaged at different Reing times. Both Cu₆Sn₅ and Cu₃Sn intermetallics grew rapidly with isothermal aging.











(c)

(d)

i gure 4.1 Effect of isothermal aging at 150°C on the growth of Cu-Sn intermetallic layer around Cu particles in Cu reinforced composite solder joint: (a) as-fabricated, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours. After aging for 100 hours, the layer had grown to nearly twice its initial thickness. Growth of ε and η intermetallics is quite apparent, where the volume of the Cu-Sn IM layer formed is ~ 1.4 times the initial volume of the Cu particle before aging (cf., Figures. 4.1a and 4.1b). With continued aging (Figure 4.1d), the Cu particles were completely consumed and converted to ε and η intermetallics within 1000 hours. A thin layer of Cu₃Sn adjacent to the Cu substrate (Cu particle) is shown in Figure 4.1(c) after aging for 500 h at 150°C. The contrast of the ε phase appears darker than the η phase in SEM secondary electron and backscattered electron images. Also, with aging, the extent of porosity increases between the Cu₃Sn IM layer and the Cu particles.

Aging effects on the evolution of Cu-Sn intermetallics around Cu particles and Cu particle consumption during aging are depicted graphically in Figure 4.2. There was an initial rapid growth rate of Cu-Sn IM and expeditious consumption of Cu particles during the first 100 h of aging. With subsequent aging, the growth rate of Cu-Sn intermetallics and the consumption rate of Cu particles were slower. IM layer growth around the Cu particle fitted a parabolic equation, i.e., the layer growth exponent was 0.5, suggesting that the IM layer growth is diffusion controlled [119].

4.3.2 Intermetallic Layer at the Cu Substrate/Solder Interface

The influence of isothermal aging at 150°C on the IM layer growth at the Cu substrate/solder interface in the Cu composite joints is presented in Figure 4.3. The initial layer thickness of 1.8 μ m grew to 7.8 μ m after 1000 hours (Figures 4.3a-4.3d). The coarsening of matrix Ag₃Sn intermetallics was dramatic and is clearly shown when comparing Figure 4.3(a) and (d).



Figure 4.2 Effect of isothermal aging on the growth of Cu-Sn intermetallic layer around the Cu particles and Cu particle consumption.





(a)

(b)



(c)



(d)

Figure 4.3 Effect of isothermal aging at 150°C on the growth of Cu-Sn intermetallic layer at Cu substrate-solder interface in Cu reinforced composite solder joint: (a) asfabricated, layer thickness=1.81 μm, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours, layer thickness =7.76μm. The development of Kirkendall voids is clearly evident between the Cu substrate/IM layer after long aging times in (c) and (d).

4.3.3 Mechanism for IM Layer Growth During Solid-state Isothermal Aging

Formation of IM compound layers is inherent to soldering. It is of great importance to understand how such IM layers evolve in solder joints, particularly since the IM layer is considered to be a potential source of joint failure due to its brittleness and the tendency to grow excessively during high-temperature aging.

We describe a phenomenological model for Cu-Sn IM layer growth inspired by experimental results obtained during careful monitoring of the IM layer growth around several Cu particles in a composite solder joint isothermally-aged at 150°C for up to 1000 h. From earlier work by Wu *et al.* [42], it is suggested that tin is the predominant diffusing species that controlled formation and growth of the Cu-Sn IM layer. During reflow Sn is perhaps the dominant diffusing species contributing to IM layer growth. However, during solid-state aging, it is apparent that interdiffusion of both Sn and Cu through pre-existing IM layers is responsible for growth. Initial soldering produces layers of both Cu₀Sn₅ and Cu₃Sn, although the Cu₃Sn layer may be barely detectable. The η phase forms adjacent to the solder and the ε -phase forms adjacent to the copper substrate.

The Cu-Sn co-layers thicken by the movement of the various interfaces in both directions normal to the layer surfaces. Interfacial motion occurs both by inward movement towards the Cu substrate and by outward movement towards the SnAg solder matrix. It is proposed that Sn and Cu interdiffuse through η and ε phases and the following reactions occur to promote growth of the IM co-layers upon aging (cf., Figure 4.4):

1. Formation of Cu_6Sn_5 occurs by the reaction of Sn with Cu_3Sn at the ϵ/η interface as a consequence of Sn diffusing through the η -phase.

$$3Sn + 2Cu_3Sn => Cu_6Sn_5$$
 (4-1)

This reaction results in growth of the η -phase by movement of the ϵ/η interface towards the Cu substrate. Consequently, diminution of Cu₃Sn (ϵ) occurs.

2. Formation of more Cu₃Sn results due to the reaction of Sn with Cu at the Cu/ ϵ interface as Sn diffuses through the η -phase.

$$Sn + 3Cu \implies Cu_3Sn \tag{4-2}$$

As a result of this reaction, growth of the ε -phase occurs and dissolution of the Cu substrate is observed. The Cu/ ε interface moves into the Cu substrate.

3. Further thickening of the η -phase (Cu₆Sn₅) takes place as Cu atoms diffuse through both ε and η phases to react with Sn at the η /Sn interface.

$$6Cu + 5Sn \implies Cu_6Sn_5 \tag{4-3}$$

The reaction produces growth of the η -phase into the SnAg solder matrix, with consequent movement of the η /Sn interface to the right.

Another observation is that without variance Kirkendall voids occur at the Cu/ ϵ interface. Kirkendall voids were seen after prolonged isothermal aging at 150°C. The voids were readily observed after 100 h of aging (see Figures. 4.1, 4.3, and 4.4b). Such findings suggest that net mass flow of Cu through the ϵ - and η -phase is greater than mass flow of Sn in the opposite direction. Kirkendall porosity was however never observed at the η /Sn interface.



Proposed Reaction:

- $\begin{array}{ll} \mbox{(a) } 3Sn + 2Cu_3Sn \Rightarrow Cu_6Sn_5 \\ \mbox{(reaction at the ϵ/η interface conversion of Cu_3Sn to Cu_6Sn_5)} \end{array}$
- (b) $Sn + 3Cu \Rightarrow Cu_3Sn$ (reaction at the Cu/ ϵ interface – conversion of to Cu₃Sn)
- (c) $6Cu + 5Sn \Rightarrow Cu_6Sn_5$ (reaction at the η/Sn interface - formation of Cu_6Sn_5)
- Figure 4.4 Proposed mechanism for Cu-Sn intermetallic layer growth during aging for a Cu/Sn solder diffusion couple.

4.4 Microstructural Evolution in Ag Particle Reinforced Composite Solder Joints

The effect of isothermal aging at 150°C on the IM layer growth around the Ag particles in the Ag composite solder joint is shown in Figure 4.5. In sharp contrast to the Cu reinforced composite solder joint, Ag particles were only "partially" converted to Ag₃Sn intermetallics after 1000 hours aging. The thickness of Ag₃Sn IM layer around the Ag particles did not increase significantly with aging in comparison with Cu₆Sn₅/Cu₃Sn IM layer around the Cu particles. This phenomenon indicates that during solid-state isothermal aging at 150°C, interdiffusion of Ag and Sn through the AgSn IM layer.

The influence of isothermal aging at 150° C on the IM layer growth at the Cu substrate/solder interface in the Ag composite solder joints is presented in Figure 4.6. As stated in 4.3.2, in Cu reinforced composite solder joints (Figures 4.3a-4.3d), the initial layer thickness of 1.8 µm grew to 7.8 µm after 1000 hours, while in the Ag reinforced composite solder joint (Figures 4.6a-4.6d) the initial layer thickness of 1.6 µm grew up to 7 µm after 1000 hours. The growth rates are quite similar for the two composite solder joints, with both exhibiting a final Cu-substrate/solder interfacial IM layer ~ 4.3 times the initial layer thickness after aging for 1000 hours. A comparison of the aging effect on interfacial layer growth between Cu and Ag particle reinforced composite solder joints is shown in Figure 4.7. As illustrated in previous micrographs, the overall thickness of the interfacial IM layer that evolves in Cu composite solder joints is greater than in Ag composite solder joint after aging for 1000 hours. However, the growth rates of interfacial layers in both Cu and Ag composite solders are comparable.







(b)



(c)



(d)

Figure 4.5 Effect of isothermal aging at 150°C on the growth of Ag₃Sn intermetallic layer around Ag particles in Ag reinforced composite solder joint: (a) as-fabricated, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours.



(a)



(b)



(c)



(d)

Figure 4.6 Effect of isothermal aging at 150°C on the growth of Cu-Sn intermetallic layer at Cu substrate-solder interface in Ag reinforced composite solder joint: (a) as-fabricated, layer thickness= 1.59 μm, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours, layer thickness = 6.95 μm.



Figure 4.7 Effect of isothermal aging on the intermetallic layer growth at the copper substrate/solder interface.

4.5 Microstructural Evolution in Ni Particle Reinforced Composite Solder Joints

Isothermal aging studies were performed using single shear lap solder joint specimens at different aging temperatures (25, 50, 100, and 150°C) for up to 1000 hours. In this aging study, it was revealed that significant microstructural changes only occurred in Ni reinforced composite solder joints aged at temperatures above 100°C. Therefore, detail discussions will be presented only for isothermal aging at 150°C where profuse microstructural changes were observed. However, SEM micrographs showing the microstructure of joints aged at 25, 50, 100°C are presented in Figure 4.8(a)-(d), Figure 4.9(a)-(d), and Figure 4.10(a)-(d), respectively. Figures 4.8, 4.9, and 4.10 of targeted areas of the solder joint are shown mainly to illustrate that the microstructure was extremely stable under isothermal aging conditions below 100°C for 1000 hours. The most noticeable change in the microstructure during isothermal aging below 100°C was coarsening of Ag₃Sn particles.

4.5.1 IM Layer around the Ni Particle Reinforcements

The effect of isothermal aging at 150°C on the IM layer growth around the Ni particles in the Ni composite solder joint is illustrated in Figure 4.11. This series of micrographs represent the same field of view (targeted area) imaged at different aging times. The Cu-Ni-Sn intermetallics around the Ni particle reinforcements grew very rapidly with isothermal aging at 150°C. After aging for 100 hours (Figure 4.11b), the IM layer had grown to nearly four times its initial thickness. Some smaller Ni particles were completely converted to Cu-Ni-Sn intermetallics. The IM layer continued to grow significantly and even the larger Ni particles were completely consumed and converted to



(c)



Figure 4.8. Effect of isothermal aging at room temperature(25°C) on the growth of Cu-Ni-Sn intermetallic layer around Ni particles in Ni reinforced composite solder joint. (a) as fabricated, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours. Note: No growth of the IM layer with aging time at 25°C.





(a)



(c)

(b)



(d)

Figure 4.9 Effect of isothermal aging at 50°C on the growth of Cu-Ni-Sn intermetallic layer around Ni particles in Ni reinforced composite solder joint. (a) as fabricated, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours. Note: No growth of the IM layer with aging time at 50°C.



(c)

(d)

Figure 4.10 Effect of isothermal aging at 100°C on the growth of Cu-Ni-Sn intermetallic layer around Ni particles in Ni reinforced composite solder joint. (a) as fabricated, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours. Note: Insignificant growth of the IM layer with aging time at 100°C.



NI Gir-Ni Sn IM Laver 30µm

(a)





(c)



(d)

Figure 4.11 Effect of isothermal aging at 150°C on the growth of Cu-Ni-Sn intermetallic layer around Ni particles in Ni reinforced composite solder joint. (a) as fabricated, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours. Note: Profuse growth of the IM layer with aging time at 150°C. Cu-Ni-Sn ternary intermetallics after aging for 500 hours, as shown in Figure 4.11(c). IM layer that formed around Ni particles grew and developed a faceted morphology after 500 hours. After 500 hours, the volume fraction of the intermetallics represented ~ 60% of the total volume of the solder joint material. No significant growth of the intermetallics was observed between the aging time of 500 to 1000 hours. Slight growth and some rearrangement of the intermetallics were noted in the solder matrix, as shown in Figure 4.11(d). Coarsening of eutectic Ag₃Sn particles and an increase in the amount of porosity in the solder matrix are evident with aging when comparing Figure 4.11(a) and 4.11(d). IM layer growth and Ni particle consumption are clearly illustrated in Figure 4.12(a)-(d) where the targeted area followed throughout the aging process was an individual Ni reinforcement particle.

Effect of aging at 150°C on the evolution of Cu-Ni-Sn IM layer around Ni particles is illustrated graphically in Figure 4.13(a) and compared with previously reported Cu particle reinforced composite solder. It is evident that the growth rate and thus the net thickness of the IM layers around Ni particle reinforcements are much higher than those in Cu composite solder joint. The IM layer formed around the Ni particles was ~13 times thicker than its initial layer thickness after aging for 1000 hours, while the IM layer formed around the Cu particles was only 5 times thicker than its initial layer thickness under the same aging condition. It is also shown that the IM layer around the Ni particles did not show any significant growth when aged at temperatures lower than 100°C. The lack of IM growth suggests that Ni reinforced composite solder joints would be desirable in industrial applications where the temperature environment is below 100°C. The





(b)



Figure 4.12 Effect of isothermal aging at 150°C on the growth of Cu-Ni-Sn intermetallic layer around one Ni particle. (a) as fabricated, (b) after 100 hours, (c) after 500 hours, (d) after 1000 hours. Note: profuse IM layer growth and consumption of Ni reinforcement particle.



Figure 4.13 Effect of isothermal aging at 150°C on the growth of IM layers around the Ni particles and Ni particle consumption. Data for Cu composite solder and Ni composite solder aged at 100°C, 50°C, and room temperature are plotted for comparison. (a) IM layer evolution around the particle reinforcement, (b) reinforcement particle consumption.

Figure 4.13(b). Much more expeditious dissolution rate of Ni particles was noted than of Cu particles during the first 100 hours aging. With subsequent aging, the dissolution rate for both Ni particles and Cu particles were similar, resulting in complete or near complete conversion of the reinforcement particles into intermetallics.

4.5.2 IM Layer at the Cu Substrate/Solder Interface

The influence of isothermal aging at 150°C on the IM layer growth at the Cu substrate /solder interface in the Ni composite joint is presented in Figure 4.14. The initial layer thickness of $\sim 4 \ \mu m$ grew to 56 μm after 1000 hours, over an order of magnitude greater than the initial IM layer thickness. Note that the micrographs in Figure 4.14 were still chosen from the same targeted area of the solder joint interface, but, in order to fit the breath of the IM layer into one micrograph, the magnification was lowered in Figure 4.14(c) and (d). The relative interfacial IM layer growth is presented in Figure 4.15(a). The growth rate of the interfacial IM layer in Ni composite solder joint is much faster than that in Cu and Ag particle reinforced composite solder where the final interfacial IM layer thickness was only about 4 times the initial IM layer thickness. It is also shown in the figure that isothermal aging at 100°C, or at lower temperatures, did not cause significant modifications in the microstructure at the Cu substrate/solder interface in terms of IM layer thickness. As stated previously, the interfacial IM layer is a co-layer of Cu-Ni-Sn layer adjacent to solder and Cu-Sn layer adjacent to Cu substrate, which is composed of a Cu₆Sn₅ and a Cu₃Sn IM layer. Significant growth of Cu₃Sn layer was observed during aging, as seen in Figure 4.14(a)~(d). The thickness of the Cu_3Sn layer increased from 0.5µm in the as-fabricated condition to 12 µm after aging for 1000 hours,







Figure 4.15 Effect of isothermal aging at 150°C on the growth of IM layers at the Cu substrate/ solder interface in the Ni composite solder joint. (a) Comparison of interfacial IM layer growth in Ni, Cu and Ag composite solder joint under aging at 150°C. Interfacial IM layer growth in the Ni composite solder joint aged at 100°C and less is plotted as well for comparison. (b) Comparison of Cu₃Sn IM layer growth at the Cu substrsate/ solder interface in Ni and Cu composite solder joint under aging at 150°C.

as depicted in Figure 4.15(b). The growth rate for Cu₃Sn layers was also much faster in Ni composite solder joint than that in Cu composite solder joint under similar aging conditions. As is illustrated in Figure 4.15(b), only an ~ 4 μ m thick Cu₃Sn layer was developed after 1000 hours aging at 150°C in Cu composite solder joint which had a similar initial layer thickness as the Ni composite solder joint.

4.5.3 Possible Mechanism for IM layer Growth during Solid-State Isothermal Aging

In the previous studies on Cu and Ag particle reinforced composite solders, the formation and growth of IM layers both around the reinforcements and at the Cu substrate/solder interface exhibited diffusion controlled behavior under isothermal aging conditions. However, diffusion data for these metallic particles in solder matrix (primarily Sn) are not readily available at all temperature ranges. Table 3.1 [13, 108] gives a comparison of diffusion behavior between Ni in Sn and Cu in Sn. The diffusing distance for Ni in Sn parallel to its c-axis of the unit cell is ~21550 µm after 100 hours at 25°C. In contrast, the diffusing distance for Cu in Sn parallel to its c-axis of the unit cell is ~8500 µm under similar conditions. Ni diffuses 2.5 times faster in Sn parallel to its caxis than Cu at room temperature. Although we can expect that Ni diffuses much faster than Cu in Sn parallel to its c-axis at 150°C, there are data showing that Cu diffuses 7 times faster than Ni in Sn perpendicular to its c-axis at 150°C. Ni and Cu are similar in chemical characteristics, such as atomic number, similar atomic radius, and electronegativity. Thus, their diffusion behavior in Sn is expected to be similar. The data in Table 3.1 show that both Ni and Cu diffuse rapidly in Sn in the solid state. The simultaneous presence of Ni and Cu in Sn-3.5Ag solder apparently accelerates the growth

of Cu-Ni-Sn intermetallics. Wu *et al.* [42] suggested that the presence of Ni in Sn-Pb solder tended to suppress the ε -phase (Cu₃Sn) by raising the activation energy for layer growth, whereas, the presence of Ni, alternatively, enhanced the growth of the η -phase (Cu₆Sn₅) IM layer by lowering the activation energy for growth of the η -phase. The presence of Ni and Cu in Sn seems to alter the thermodynamics of the Ni composite solder such that profuse IM layer occurs, particularly, under solid state aging condition at 150°C and above. The Cu-Ni-Sn intermetallics in Ni composite solder is about 60%, as compared to about 45% Cu-Sn intermetallics in Cu composite solder, after aging for 1000 hours at 150°C. This is probably due to the presence of Cu, in combination with Ni, in the Ci-Ni-Sn intermetallics formed in the Ni composite solder.

4.6 Summary

- Isothermal aging studies showed that more intermetallics formed in Cu composite solder joints (both around the reinforcements and at the substrate/solder interface) than in Ag composite solder joints after aging for 1000 hours.
- 2. Cu reinforcements were totally converted to Cu₆Sn₅ intermetallic with sufficient aging, whereas Ag particles were only partially converted to Ag₃Sn intermetallic.
- 3. A proposed phenomenological model shows that the growth of IM layers around the Cu particle reinforcements and at the substrate/solder interface is produced by interdiffusion of both Sn and Cu atoms through the ε and η IM layers.
- 4. Solid state isothermal aging studies at 25, 50, and 100°C for ~1000 hours induced only slight modifications in the microstructure of Ni composite solder joint. However, aging at 150°C revealed that the microstructure was unstable with profuse growth of

the IM layer and coarsening of the Ni reinforcement as a result of Cu-Ni-Sn intermetallics formation and growth.

5. The large volume fraction of intermetallics formed in the Ni composite solder joint after aging at 150°C for 1000 hours is probably due to the presence of Cu, in addition to Ni and Sn, in the intermetallics formed in the Ni composite solder.
CHAPTER V

EFFECT OF REFLOW ON THE SOLDERABILITY, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Cu, Ag, AND Ni PARTICLE REINFORCED COMPOSITE SOLDERS

5.1 Introduction

Typically, the electronics industry involves multiple-pass solder operations in which the solder is reflowed. In such operations, wettability of the solder materials is of extreme importance. Investigations dealing with wettability issues of Pb-free solders have been conducted [120-124] and ongoing research is moving at a rapid pace. Vianco and others [120,121] have found the wetting characteristics of Sn-Ag based lead-free solder to be comparable to leaded solder on copper substrate. The wettability of gold substrate with eutectic Sn-Ag solder has been shown to be commensurate to that of Pb-Sn solder alloys [6]. The wetting characteristics of any particular solder alloy are strongly influenced by the flux used [122,124]. In particular, the wetting parameters, such as interfacial tension and wetting rate, of eutectic Sn-Ag solder can be highly variable depending on the choice of flux [122].

In this chapter, the effects of solder reflow on wettability characteristics, microstructure and mechanical properties were investigated. Multiple-reflow experiments were conducted using eutectic Sn-3.5Ag non-composite and eutectic Sn-3.5Ag based composites with mechanically-added Cu, Ag, and Ni particles on a copper substrate. The motivation to conduct this investigation on reflow characteristics of composite solders was due to limited amount of published literatureon this subject and

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this type of solder material. It is also believed that the composite approach to engineered solder properties should be advanced [47].

5.2 Experimental Procedures

5.2.1 Materials

The composite solders used in this study nominally contained 15 volume percent Cu, Ag, or Ni reinforcements. In order to study the effect of different volume fraction of the reinforcing phase on the wettability of composite solders, Cu particle reinforced composite solders with 6 and 12 volume percent Cu particles were also prepared and used in the present study. Eutectic Sn-3.5Ag solder paste was used as a baseline for comparison.

5.2.2 Wetting Experiments

The copper substrates with dimension of 2 cm×2 cm were chemically cleaned with a solution of 50% nitric acid and 50% H₂O before each experiment. Reflow specimens were made first by preparing disc-shaped solder paste preform. This was accomplished by flowing the solder paste through an orifice of 5 mm in diameter and then cut to size using a razor blade. With this method, consistent size discs weighting approximately 0.3 grams were achieved for the subsequent melting and reflow process.

All the disc-shaped solder preforms were placed on copper substrates for melting on a hot plate. Reflow experiments were carried out by remelting solder materials on the same copper substrate for at least 3 times without refluxing to better mimic industrial prictice. The thermal history profile for initial melting and subsequent reflow experiments is shown in Figure 5.1. Specimens were heated to a maximum temperature

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of 280°C and then placed on a chill aluminum block to cool to room temperature. Upon solidification, all specimens exhibited a spherical-cap shape. As-melted and reflowed samples were cleaned, sectioned, polished and examined using optical and scanning



Figure 5.1 Temperature profile of solder/copper wettability experiment.

electron microscopy to determine the wetting angles. Image processing software was used to measure the wetting angles from the SEM micrographs. This technique for determining contact angles provided consistent results similar to those previously published [47].

5.2.3 Reflow Experiments on Solder Joints

Effects of reflow on the microstructure of Ni composite solder were studied using solder joint specimens considering that the microstructure of bulk solder is significantly different from the routinely-fabricated solder joint. Also, reflow of solder joints is a common manufacturing process. Such reflow experiment will enable the assessment in performance of composite solders. Reflow analysis was carried out by remelting the solder joints in aluminum fixture on a hot plate for at least 3 reflows at 280°C. The thermal history profile for the reflow experiment on the solder joints is exactly the same as the profile for solder joint fabrication, as shown in Figure 3.2. The reflowed solder joints were metallographically polished and microstructural features were examined using SEM. In the SEM analysis of all these joint samples, particular interest was focused on the formation and growth of IM layers around Cu and Ag particle reinforcements in the composite solder and at the copper substrate/solder interface.

5.3 Effect of Reflow on Solderability of Cu, Ag, and Ni Particle Reinforced Composite Solders

Results of wetting angles measured as a function of reflow conditions are shown in Table 5.1.

Results in Table 5.1 indicate that eutectic Sn-3.5Ag solder paste has the best wettability of all non-reflow solders with an average contact angle of about 10.5°. The wetting angle determined in this study using solder paste preform was compared to that determined using solid solder preform of a previous study [47]. The results of this study indicate that the wetting angle of eutectic Sn-3.5Ag solder paste is ~8° smaller than the eutectic Sn-3.5Ag solid solder preform, where the nominal wetting angle was typically around 18°. The wetting angle for first reflowed composite solder with 15 v% Cu particles was significantly higher, approximately 47°. However, composite solder with comparable volume fraction of Ag reinforcements exhibited a wetting angle of about 21°. Ni particle reinforced composite solder exhibited a wetting angle of 13° under the same experimental conditions.

As indicated in Table 5.1, there is no statistically meaningful difference in the wetting angles between first reflowed (as-melted) and multiple reflowed solder materials.

Materials	Conditions	Angle 1	Angle 2	Angle 3	Angle 4	Aver. 1*	Aver. 2**
Eutectic Sn-3.5Ag (paste)	Reflow 1	13.6	8.1	9.5	10.6	10.45	10.5±2
	Reflow 2	11.4	7.9	6.1	10.9	9.08	
	Reflow 3	21.3		9.9	15	15.40	12.1±3.9
	Reflow 4	14.4	8.6	14.7	9.8	11.88	
Cu composite solder	reflow 1	43.3	51.1	52.6	42.2	47.30	47.3±5.3
	reflow 2	57.1	48.7	55.8	28.1	47.43	
	reflow 3	38.2	37.9	37	44.6	39.43	44.1±10
	reflow 4	33.4	49.1	65	34.8	45.58	
Ag composite solder	reflow 1	25.7	17.3	22.3	19.2	21.13	21.1±3.2
	reflow 2	19.4	22.6	12.1	11.4	16.38	
	reflow 3	23.5	21.0	19.3	9.7	18.38	18.5±4.6
	reflow 4	21.4	23.1	14.7	23.9	20.78	
Ni composite solder	reflow 1	12.5	14.8	12.2	12.3	12.95	13.0±1.2
	reflow 2	12.5	9.1	10.4	10.9	10.73	
	reflow 3	12.0	11.5	15.4	15.8	13.67	12.1±1.5
	reflow 4	12.3	12.8	13	10.0	12.03	
Eutectic Sn-3.5Ag (preform)	reflow 1	18.2	17.8	19.2	16.8	18.00	18.0±0.9
	reflow 2	22.5	18.9	20.7	20.7	20.70	
	reflow 3	25.3	23.7	19.7	21.3	22.50	19.6±3.4
	reflow 4	16.4	15.7	15.3	14.6	15.50	

 Table 5.1. Wetting Angles as a Function of Reflow Conditions (Angles Measured in Degrees)

* Aver. 1 is the average of all the angle measurement under each different condition.

** Aver. 2 basically averages the angles in the multiple reflow experiment to compare with the first reflow conditions.

The wettability ranking of these materials is shown in the last column of Table 5.1 and schematically illustrated in Figure 5.2. The first reflowed and multiple reflowed solder all produced spherical caps of the solder on the substrate.

It is contended that the eutectic Sn-3.5Ag solder paste has the best wettability due in part to the way in which the solder paste is manufactured. The self-fluxed paste would



Figure 5.2 Schematic drawing of wetting properties of different solder materials observed in the reflow experiment.

tend to prevent formation of metal oxides that can be detrimental to wettability. A rough estimation of the amount of flux which encompasses the particles of the solder paste was approximately 12 wt%. Apparently, fluidity is therefore enhanced giving a significant lower contact angle.

As noted previously, the Cu composite solder showed the highest contact angle and hence the least wettable. To ascertain the variation in contact angle with reinforcement content, we conducted a collateral experiment where the volume fraction of mechanically added Cu particle reinforcements ranged from 6 to 18 v%. For first reflowed Cu composite solder, as shown in Figure 5.3, the wetting angle increased with the increase of the volume fraction of Cu reinforcements. At the lowest volume fraction of 6 v%, the wetting angle was 18° whereas at $18 \sqrt{6}$ the wetting angle increased to 47° . The propensity for the Cu reinforcement to form Cu_6Sn_5 intermetallics apparently affects the flow properties of this composite solder. From out microstructural analysis, we find that ~ 6 micron size Cu particle reinforcements will be converted to Cu_6Sn_5 intermetallics after 3 - 4 reflows. Due to the prolific growth of the Cu-Sn intermetallic layer around the Cu reinforcements, the effective volume fraction is enhanced even for the as-melted composite solder. For example, after four reflows, the effective volume fraction becomes approximately twice that of the as-mixed reinforcement volume fraction of the solder paste. One might envisage that the Cu reinforcements could act to increase the interfacial surface tension with the molten solder (chemically constrained) thus reducing flow on the substrate. Also, there can be a geometric effect where the Cu particles prevent contact of the molten solder with the Cu substrate and/or inhibit flow of the leading edge of the spreading spherical cap which can lead to decrease in the wettability. Also, Cu particles

modified by the growth of Cu-Sn intermetallic layer will tend to constrain the advancing edge of the molten solder cap.



Figure 5.3 Changes of wetting angles with the volume fraction of the copper particles in the Cu particle reinforced composite solders.

It is also significant that Ag particle reinforced composite solder at 15 v% did not show high wetting angle as observed in Cu particle reinforced composite solder. In contrast to Cu reinforcements that form a thick Cu-Sn IM layer, Ag reinforcements form only a thin Ag₃Sn IM layer. Moreover, there is no significant increase in the effective volume fraction due to the reflow process. Apparently, wettability of composite solder is not significantly affected when the effective reinforcement volume fraction is approximately 20 v% or less. Similar wetting angles of around $18^{\circ}-20^{\circ}$ were observed in a composite solder containing 20 v% non-coarsening *in situ* Cu₆Sn₅ reinforcements fabricated in our laboratory [47].

Also, it was found that reflow had no noticeable influence on contact angle of the Cu and Ag composite solders. However, it is worthy noting that upon reflow the substrate being rewetted is the Cu_6Sn_5 IM layer.

Results in Table 5.1 indicate that the wettability of the nominally 15v% of Ni composite solder (θ =12.5°) is comparable with the wettability of eutectic Sn-3.5Ag solder paste (θ =10.5°). The average wetting angle was smaller than that of Ag (θ =21.1°) or Cu composite solder (θ =47.3°). The wettability of Ni composite solder paste ranked the first among three composite solders investigated. There was also no significant meaningful difference in the wetting angles between first reflowed and multiple reflowed Ni composite solder. This is primarily due to the fact that the extent of intermetallics formed both around the Ni particles and at the Cu substrate/solder interface was sparse during subsequent multiple reflow conditions. The micrographs proving this fact will be introduced in the later part of this chapter. Thus, the total effective volume fraction of the reinforcements remained nearly unchanged during the reflow process. As stated above, the wettability of composite solder was not significantly affected when the effective reinforcement volume fraction is approximately 20% or less. Therefore, the wettability was not affected by the reflow of the 15v% of Ni particles in the Ni composite solder. Evaluating the effective volume fraction is very important because the reinforcement and its concomitant IM layers around them could act to increase the interfacial surface tension with the molten solder, and thus, affects the wettability of the solder.

5.4 Effect of Reflow on Microstructure of Cu, Ag, and Ni Particle Reinforced Composite Solder Joints

5.4.1 Intermetallic Layer around the Particulate Reinforcements

The effect of multiple reflow on the growth of Cu-Sn intermetallics formed around Cu particle reinforcements is shown in Figure 5.4. The IM layer around the Cu particles grew dramatically with each reflow condition at the expense of the Cu particles. After the fourth reflow, the Cu reinforcement particles were almost completely converted to Cu-Sn intermetallics. Also, significant voiding was observed due to Kirkendall effects. Figure 5.5 shows the effect of multiple reflow on the growth of Ag-Sn intermetallics around Ag particulate reinforcements. In stark contrast to extensive Cu-Sn IM layer formation around the Cu particles, significant Ag-Sn IM layer formation was not observed after four reflows around the Ag reinforcement. However, there were slight changes in Ag particle morphology after the fourth reflow, as shown in Figure 5.5d.

We have used the diffusion results listed in Table 3.1 earlier to explain the difference in the extent of IM layer formation observed around the Cu and Ag reinforcement particles. At reflow temperatures, diffusion kinetics are extremely rapid as the reflow process represents diffusion between transport species due to melting of the solder materials. Consequently, the difference in the initial IM layer thickness around particulate reinforcements and the extent of IM layer growth is greater around Cu particles of Cu composite solders after multiple reflows.

Figure 5.6 summarises the effect of multiple reflow on the growth of the Cu-Sn IM layer around the Cu particle, and concurrently, consumption of the Cu particle. It is also evident that after four reflows full conversion of the Cu particles to Cu-Sn intermetallics has been achieved. Micrographs illustrating formation of Cu-Sn intermetallics and

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(a)

(b)





(d)

Figure 5.4 Effect of reflow on the growth of Cu-Sn intermetallics around Cu particle reinforcements: (a) first reflow, (b) second reflow, (c) third reflow, (d) fourth reflow.





(a)

(b)



(c)

(d)

Figure 5.5 Effect of reflow on the growth of Ag₃Sn intermetallics around Ag particle reinforcements: (a) first reflow, (b) second reflow, (c) third reflow, (d) fourth reflow.



Figure 5.6 Effect of reflow on the Cu-Sn intermetallic layer growth around Cu particles and Cu particle consumption.

hickness or Average Diameter (micron)

growth around Cu particle along with the concurrent depletion the Cu particle are shown in Figure 5.4.

The effect of multiple reflow on the microstructure of the Ni particle reinforced composite solder joint is shown in Figure 5.7. The Cu-Ni-Sn ternary "sunburst"-shaped IM layer circumscribes the dark core region representing unconverted Ni particles in the as-fabricated solder joint in Figure 5.7(a). It is observed that even with four reflows of the Ni composite solder joint, the Ni particles were not completely converted into intermetallics. As a result of multiple reflow, the most significant microstructural changes in the joint were a slight increase in the growth of IM layer around the Ni reinforcement and a significant increase in the size of matrix Ag₃Sn precipitates.





(a)





(c)



(d)

Figure 5.7. Effect of reflow on the growth of Cu-Ni-Sn IM layers around the Ni particles in the Ni composite solder joint. (a) first reflow, (b) second reflow, (c) third reflow, (d) fourth reflow.

5.4.2 Interfacial Intermetallic Layer in the Composite Solder Joints

The influence of multiple reflow on the growth of the Cu-Sn IM layer at the copper substrate-solder interface in the Cu reinforced composite solder is shown in Figure 5.8 where significant interfacial layer growth was noted. The initial IM layer thickness due to the first reflow of the specimen was 1.9 μ m. However, after only four reflows the layer thickness increased up to 5 μ m, that is about 2.7 times its initial thickness. For the Ag reinforced composite solders shown in Figure 5.9, the initial layer thickness was 1.2 μ m. After four reflows, the layer thickness increased to 2.8 μ m, that is about 2.3 times its initial thickness. The final interfacial layer thickness for the Ag composite solder was about 1/2 the interfacial layer thickness of the Cu composite solder after four reflows. Nevertheless, the ratio of the final IM interfacial layer thickness and the initial IM layer thickness for the Ag and Cu composite solders, are comparable (Figure 5.10) indicating that the growth kinetics are controlled by similar diffusion mechanisms. Figure 5.10 graphically depicts the interfacial layer growth in both Cu and Ag composite solder as a function of the number of reflows.

As mentioned above, a thicker IM layer tends to form in the Cu composite solder than in Ag composite solders. Why this is so, can be rationalised by incorporating the findings of Wu *et.al.* [42]. While investigating eutectic Pb-Sn solder reinforced with various types of particle reinforcements, they found that the addition of Ag particle reinforcement increased the activation energy for formation of the Cu₆Sn₅ (η -phase) layer. This increase in the activation energy of the η -phase makes nucleation more difficult, and as such, formation of Cu₆Sn₅ is suppressed. Consequently, the initial IM layer thickness of Ag reinforced composite solder tends to be smaller than that of Cu reinforced





(b)



Figure 5.8 Influence of reflow on the growth of Cu-Sn IM layer at Cu substrate/solder interface in Cu reinforced composite solder: (a) first reflow, layer thickness= $1.85 \ \mu m$, (b) second reflow, (c) third reflow, (d) fourth reflow, layer thickness = $4.95 \ \mu m$.







(b)



(c)



(d)

Figure 5.9 Influence of reflow on the growth of Cu-Sn IM layer at Cu substrate/solder interface in Ag reinforced composite solder: (a) first reflow, layer thickness= $1.23 \ \mu m$, (b) second reflow, (c) third reflow, (d) fourth reflow, layer thickness = $2.78 \mu m$.



Figure 5.10 Comparison of the effect of reflow on the IM layer growth at Cu substrate/solder interface in Cu and Ag composite solders. The layer thickness was divided by its initial thickness for comparison.

composite solder (Figure 5.9). The activation energy of η-phase formation was also slightly higher for the Cu particle reinforced composite solder than that in un-reinforced eutectic Pb-Sn solder and correspondingly the initial IM layer thickness was nominally lower. A thinner initial IM layer should promote joint integrity and reliability by mitigating extensive brittle IM layer formation.

In Ni composite solder, similar to the IM layers around the Ni particles, multiple reflow of the solder joint did not result in a significant increase in the growth of the interfacial IM layer, as shown in Figure 5.11. The scanty growth of IM layer during multiple reflow is assumed to be due to the inability of Ni to diffuse through the IM layer





(a)





within the short time period the specimen is held (5 seconds) at the reflow temperature of 280°C. The fact that the microstructure remains stable under reflow conditions is beneficial for manufacturing operations where reflow of solder joints is a required process.

5.4.3 Effect of Reflow on the Microstructure of Eutectic Sn-3.5Ag Solder Joints

The microstructure of eutectic Sn-3.5Ag solder joints as a function of reflow is shown in Figure 5.12. The microstructure in Figure 5.12(a) for first reflowed solder is characterized by Sn cells separated by wide bands of eutectic Ag₃Sn. With multiple reflows, the Ag₃Sn bands separating the Sn cells became narrower and simultaneously the size of the Sn cells increased, as exhibited in Figure 5.12(b)-(d).

The effect of reflow on the interfacial intermetallic layer in the eutectic Sn-3.5Ag solder joint is illustrated in Figure 5.13. The interfacial layer grew with reflow from the initial layer thickness of 1.7 μ m to a final layer thickness of 4.3 μ m. The interfacial layer grew by a factor of 2.5 after reflow. This is very similar to the interfacial intermetallic layer growth behavior that occurred during reflow in the Cu particle reinforced composite solder joints as shown in Figure 5.14. Figure 5.14 compares the growth of interfacial layers at the copper substrate in all the solder joint materials studied.

5.5 Effect of Reflow on Mechanical Properties of Eutectic Sn-3.5Ag Solders

Reflowing of the solder materials, particularly solder joints on circuit boards, is required in manufacturing processes. Two or three reflows are considered normal for a typical wave soldering process. To assess whether multiple-reflow of solder materials



(a)





(c)

(d)

Figure 5.12 Effect of reflow on the microstructure of eutectic Sn-3.5Ag non-composite solder joint: (a) first reflow, (b) second reflow, (c) third reflow, (d) fourth reflow.



(a)

(b)



(c)

(d)

Figure 5.13 Effect of reflow on the growth of Cu-Sn intermetallic layer at Cu substratesolder interface in eutectic Sn-3.5Ag non-composite solder joint: (a) nonreflow, layer thickness = 1.74 μm, (b) first reflow, (c) second reflow, (d) third reflow, layer thickness = 4.27 μm.



Figure 5.14 Comparison of interfacial intermetallic layer growth due to reflow between Cu composite solder, Ag composite solder, Ni composite solder and eutectic Sn-3.5Ag non-composite solder joint.

will affect the resultant mechanical properties, nanoindentation testing (NIT) was performed on eutectic Sn-3.5Ag solder. NIT was conducted on eutectic Sn-3.5Ag solders reflowed up to 4 times using the Nano Indenter[®] XP mechanical properties microprobe (MPM) from MTS Corporation. With the MPM, simultaneous measurement of indenter penetration depth and load makes it possible to determine certain mechanical properties. Mechanical properties assessed were hardness, modulus and creep properties. The most significant finding with regards to mechanical properties change turned out to be the difference in hardness as a function of reflow as shown in Figure 5.15. With reflow of the solder, the hardness decreased. Also, the yield strength can be estimated according to Tabor [125] from hardness data. In Figure 5.16, the relative change in yield strength is



Figure 5.15 Change in hardness of eutectic Sn-3.5Ag solder as a function of reflow.



Figure 5.16 Change in yield strength of eutectic Sn-3.5Ag solder as a function of reflow. Yield strength decreases with multiple reflows.

shown as a function of reflow. On average, the yield strength of eutectic Sn-3.5Ag solder is reduced by ~ 30 %. The reduction in hardness/yield strength motivated by the change in solder chemistry and microstructure due to the reflow process. It is suggested that the composition of the solder change from the eutectic composition (96.5Sn-3.5Ag) to an offeutectic composition containing less Sn due to reflow. The reduction in the amount of Sn is due to its consumption in the formation of the intermetallic layer consisting of Cu₆Sn₅ and Cu₃Sn compounds [126]. Change in solder microstructure is expected for offeutectic stoichiometry. Proeutectic Ag₃Sn will precipitate out of the liquid first followed by solidification at the eutectic composition. As indicated in Figure 5.12, the Sn cells became larger and the necklace of eutectic Ag₃Sn became narrower subsequent to multiple reflows. The microstructure of the first reflowed and 4-reflowed solder around indent is shown in Figure 5.17. In Figure 5.17(a) for first reflowed solder, smaller Sn cells and wider Ag₃Sn bands were evident. Whereas, Figure 5.17(b) showed larger Sn cells and thinner Ag₃Sn bands after four reflows. The lower hardness and yield strength observed is consistent with materials having a larger grain size.

Nanoindentation creep tests were conducted. Assuming steady-state behavior, $\dot{\varepsilon} = A \cdot \sigma^n$, the stress exponent for indentation creep was determined for multiple reflowed specimens. The stress exponent for eutectic Sn-3.5Ag solder materials after four reflows was n=8, whereas the first reflowed solder exhibited a value of n=7.1. The stress exponent data are shown in Figure 5.18. The difference in *n*-values suggests that creep deformation in the solder is influenced by reflow history. From *n* values obtained, the steady-state creep rate of reflowed solder materials is higher due to reflow-induced microstructure and composition changes.







(b)

Figure 5.17 Microstructure of eutectic Sn-3.5Ag solder around indent: (a) non-reflow solder; (b) three reflowed solder. The size of the Sn cells is larger for reflowed materials, correspondingly, the yield strength is lower.



Figure 5.18 The effect of reflow on steady-state creep strain rate of eutectic Sn-3.5Ag solder. The stress exponent is slightly higher for multiple reflowed solder.

5.6 Summary

 Eutectic Sn-3.5Ag solder paste showed the best wettability on Cu substrate among all the solder materials studied. The 15 v% Ni composite solder showed comparable wettability to eutectic Sn-3.5Ag solder paste. The wettability of 15 v% Agreinforced composite solder was significantly better than 17 v% Cu-reinforced composite solder. Because of a profuse intermetallic layer growth around Cu reinforcements, the effective volume fraction doubled. Wettability can be improved by lowering the volume fraction of the reinforcing phase.

- 2. No significant changes in contact angles were observed with multiple reflow of all the solder materials studied.
- 3. The formation of Cu-Sn intermetallics around the Cu reinforcements was considerable, whereas the Ag₃Sn IM layer thickness around the Ag reinforcements was minimal. Growth of the IM layer around the Cu particle reinforcements was excessive leading to total consumption of the Cu particles after 3-4 reflows. No significant coarsening of the Ag reinforcements was evident after multiple reflows. Multiple reflow does not significantly change the microstructure in Ni composite solder joints. The IM layer growth was minimal, although coarsening of Ag₃Sn particles was observed.
- 4. Reflow studies showed that the IM layer at the Cu substrate/solder interface also grew much faster in Cu composite solder joints than in Ag composite solder joints. However, multiple reflow did not cause significant growth of interfacial IM layers in Ni composite solder joints.
- 5. The microstructure of first reflowed eutectic Sn-3.5Ag solder can generally be characterized by small Sn cells surrounded by wide-banded eutectic Ag₃Sn phase. In comparison, the microstructure of multiple reflowed solder is characterized by large Sn cells circumvented by a thin necklace of eutectic Ag₃Sn precipitates.
- 6. The hardness and yield strength of multiple reflowed eutectic Sn-3.5Ag solder were reduced by 30% after three reflows. This finding is commensurate with the

increasing size of Sn cells produced by multiple reflow as a larger grain/cell size gives a lower yield strength.

7. The stress exponent, *n*, determined using indentation creep testing was 7 for first reflowed solders and 8 for multiple reflowed solders. From the stress exponents observed, the steady-state creep rate for the multiple reflowed solder will be higher compared to first reflowed solder.

CHAPTER VI

CREEP DEFORMATION BEHAVIOR OF EUTECTIC Sn-3.5Ag SOLDER JOINTS WITH OR WITHOUT SMALL ALLOYING ELEMENT ADDITIONS, OR Cu, Ag, Ni REINFORCEMENT PARTICLES

6.1 Introduction

Eutectic Sn-3.5Ag solder has received attention worldwide as a potential substitute due to its non-toxic nature as well as its comparable wetting and mechanical properties to eutectic Sn-37Pb solder [1-6]. In order to be an acceptable substitute for lead-bearing solders it has to satisfy both the process requirements and the reliability requirements that commonly used Sn-Pb solder possesses. In terms of process requirements, the most important factor is the melting point. The melting temperature of eutectic Sn-3.5Ag solder (221°C) is ~ 40°C higher than eutectic Sn-Pb solder (183°C), which causes manufacturing difficulties and cost increase compared to processing methods used for Pb-bearing solders, although the advantage of this higher melting point has proven to be more suitable for higher temperature applications [5]. In terms of reliability issues, recent growth of surface mount technology, and especially the miniaturization in microelectronics industry have made the structural role of solder joints as mechanical support to components become ever more critical compared to their traditional function of just providing electrical contact. Solder alloys are typically subjected to harsh environments and are used at temperatures well above half of their melting points in degrees absolute. So microstructural evolution, recrystallization, superplasticity, creep, and creep-fatigue are operative under normal service conditions, among which creep is the most common and important micromechnical deformation phenomena [4, 7-14].

Since eutectic Sn-3.5Ag solder is considered as a leading candidate of Pb-bearing solders, several approaches have been used to improve its comprehensive properties such as creep resistance, thermomechanical fatigue resistance, mechanical strength, and solder joint reliability [13, 20, 47-50, 91, 104, 127]. Among these approaches, composite approach was designed mainly to improve its service performance including service temperature capability. Composite solders, whether tested as bulk or as joint specimens, generally showed improved properties [13, 22-32, 47-50, 91, 104, 127]. However, systematic studies of the creep deformation behavior of composite solders, especially lead-free composite solders, have been rarely reported [127]. Addition of alloying elements to eutectic Sn-3.5Ag solder is another major avenue attempting to combat the above stated issues [15-21]. Such additions usually include copper, nickel, antimony, silver, or bismuth, etc. This methodology was initially designed to achieve a suitable melting temperature range primarily for processing purposes. The improvement of mechanical properties is closely related to the amount and type of the alloying elements, so some alloying additions may not improve the properties to a desirable extent, and sometimes even deteriorate them [20, 21]. Although significant effects of alloying element additions on the mechanical properties of binary systems are expected, these alloying effects have not been systematically investigated, i.e., no fundamental work on these areas is found for lead-free solders in published literature.

In this chapter, creep studies were carried out to solder materials based on the two major approaches discussed above. The first research effort was aimed at a systematic parallel study to characterize the creep deformation behavior of lead-free eutectic Sn-3.5Ag based composite solders produced by mechanically adding Cu, Ag, or Ni particles.

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Various creep parameters are quantified and compared with the non-composite eutectic Sn-3.5Ag and Sn-4Ag-0.5Cu solder alloys. Possible mechanisms for creep are suggested for these composite solders. As a second research effort, we report on near-eutectic Sn-Ag based ternary alloys, two ternary alloys (Sn-4Ag-0.5Cu and Sn-Ag-0.5Ni) and a quaternary alloy (Sn-2Ag-1Cu-1Ni) which were developed in an attempt to depress the melting temperature, improve the creep properties, and reduce the cost of the eutectic Sn-3.5Ag solder. Choices of Cu and/or Ni as alloving elements are primarily due to formation of additional intermetallic phases that could improve mechanical properties of the solder. Also, small additions of Cu were found to decrease the melting temperature and improve wetting of the eutectic Sn-3.5Ag solder [15-21]. These solder alloys represent some of the leading lead-free solder candidates that are being considered for use in the automotive industries in the near future. Preliminary evaluations of such solders using reliability test vehicles in accelerated thermal cycling tests indicated significantly improved performance as compared to eutectic Sn-3.5Ag solder. Motivated by these findings, room and high temperature creep studies were carried out on the solder joints made of these solder alloys to investigate the effects of Cu and/or Ni additions on the creep deformation behaviors of eutectic Sn-3.5Ag solder joints.

6.2 Experimental Procedures

To facilitate creep strain measurement, a straight-line laser ablation pattern was intentionally formed on the surface of the solder joint spanning the thickness and length of the solder joint. This geometric pattern was created by near-surface ablation using an inert gas Kr-F excimer laser from Lamda Physik[®] with a wavelength of 248 nm and a maximum pulse power of 1,500 mJ. The pulse duration is 25 ns. By exposing the masked solder joint to a single excimer laser pulse a distinctive pattern dictated by the mask geometry is imprinted on the surface of the solder joint due to highly localized surface melting and ablation. The pulse energy was 300 mJ and the energy density for a spot size of 0.5 cm x 1.1 cm was 0.55 J/cm^2 . An excimer laser ablation mapping pattern imprint on the solder joint is shown in Figure 6.1. Figure 6.1(b) illustrates how these line patterns change their shape due to creep deformation. SEM images of the whole joint were taken before and after creep testing to assess the extent of creep deformation in 2-D.

Creep testing was carried out primarily on the micro-sized solder joints using dead weight loading on a miniature creep testing frame equipped with an electrical resistance furnace, as shown in Figure 6.2. The creep tests were conducted at 25°C, 65°C and 105°C to the solder joints made from the particulate (Cu, Ag, or Ni) reinforced composite solder materials, representing homologous temperatures of 0.6, 0.68, and 0.78, respectively. Alternatively, creep tests were conducted at 25°C and 85°C only for Sn-Ag based solder alloys with different Cu and Ni alloying element additions. For elevated temperature tests, the solder joints were heated by conduction. The testing temperature was measured by a thermocouple kept in contact with the solder joint. The temperature fluctuation observed in the joint area was maintained at \pm 1°C for the duration of the creep test.

During creep testing, the deformation of the laser-ablation line pattern was tracked by capturing digital images at regular time intervals with a LECO[®] image analyzer. The loads used in the creep tests ranged from 1 to 5 pounds (0.45-2.3 Kg) and solder joints were typically loaded until tertiary creep stage started.

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Figure 6.1. Laser ablation patterns imprinted on solder joints used in creep testing. (a) before creep; and (b) after creep.



Figure 6.2 Traditional dead load creep testing frame with an electrical resistance furnace.

Creep data were obtained by mapping the time-sequence images of the distorted laser-ablation line patterns on the solder joint, as shown in Figure 6.1(b). By this laserablation mapping and data extraction technique developed previously [56, 127], a variety of creep-related parameters such as (i) unnormalized and normalized displacement of the solder joint vs. time, (ii) global and localized strain vs. time, (iii) secondary creep strain rate, (iv) variation of local strain rate with time and joint thickness, and (v) strain for the onset of tertiary creep, etc. were obtained.

A new setup for creep testing was recently developed. Creep tests on Ni composite solder joints were mostly preformed using this setup. Under this new creep setting, creep tests were carried out on the small, excimer-laser-marked solder joints still using dead weight loading on a new miniature creep testing frame fixed on an optical microscope, as shown in Figure 6.3. The deformation of the polished side of the solder joint was monitored using a Kodak[®] CCD camera connected to a microscope with a computer. Time-sequence images of the distorted laser-ablation patterns were captured automatically by the camera at set time intervals. This creep testing setup has many advantages over the previously introduced setup. The present design effectively eliminated vibration of the solder joint during creep testing. Also, through-lens lighting in the microscope and the auto-balance function of the imaging software significantly improved the image quality. Such improvement facilitated the subsequent image analysis as well as promoted accuracy in data acquisition. Finally, the auto-snap function of the software made it possible to automatically acquire time-sequenced images and data during creep testing.


Figure 6.3 New design of the dead weight loading miniature creep testing frame.

Microscopy on undeformed specimens was examined after the joint was mounted in a fixture to polish one side using conventional metallographic techniques. Scanning electron microscopy was conducted on a Hitachi S-2500C SEM with a Link SIS Energy Dispersive Spectroscopy analysis system. The prior polished side of specimens was observed after deformation to observe heterogeneous strain effects.

6.3 Creep Deformation Behavior of Cu, Ag, Ni Particle Reinforced Solder Joints as Compared to Eutectic Sn-3.5Ag and Sn-4Ag-0.5Cu Solder Joints

6.3.1 Typical Creep Data

6.3.1.1 Creep of Non-composite — Eutectic Sn-3.5Ag Solder Joints

Variation of the localized and global creep strain with time for a non-composite eutectic Sn-3.5Ag solder joint is illustrated in Figure 6.4(a). The solder joint was loaded at 13 MPa at 25°C for about 6 hours. The global shear strain is indicated with a solid heavy line, which exhibits classical creep behavior with typical regions of primary, secondary and tertiary creep. Other lines represent the shear strain at different positions throughout the solder joint thickness, where one side of the solder joint is defined as position 0 while the other side of the joint is defined as position 1.0. The localized shear strain at each position followed the same trend as the global strain. It is shown that the highest localized shear strain occurred at position 0 and position 1.0, which indicates that intensive creep deformation was primarily along the substrate-solder interface region in this specimen. In the middle region of the solder joint, position 0.5, the localized creep strain was found to be the lowest. The secondary creep rate measured from the global strain curve was 2.0×10^{-5} s⁻¹.



Figure 6.4.(a) Localized and global creep strain vs. time for the non-composite eutectic Sn-3.5Ag solder joint. (b) 3-D plot of the creep strain rate vs. time and position across the solder joint.

The variation of creep strain rate with respect to time and position is plotted in a 3-D format in Figure 6.4(b). The plot indicates that the creep rates are highest at the opposing interfaces of the solder joint throughout the duration of the experiment. The mid-thickness position has the lowest creep rate at all times. It is also evident that the creep rate reached the highest value at the start of the creep test and near the end of the creep test representative of primary and tertiary creep deformation respectively. The lowest creep rate was reached at about 1×10^4 seconds (2.8 h) after creep test started, which corresponds to the steady-state indicated by the global creep strain curve.

6.3.1.2 Creep of Non-composite —Sn-4.0Ag-0.5Cu Solder Joints

The localized and global creep strain for a non-composite Sn-4.0Ag-0.5Cu solder joint is plotted as a function of time in Figure 6.5(a). The solder joint was loaded at a stress of 16.2 Mpa at 25°C for about 5 hours. The localized and global shear strain were comparable to the eutectic Sn-3.5Ag solder joints except the strains were slightly lower in some locations. The localized shear strain at each position still followed a trend similar to the global shear strain with slight variation. The highest localized creep strain (damage accumulation) was observed on one side of the specimen near the interface at position 0, whereas the lowest localized creep strain was found at position 1. Creep deformation was inhomogeneous and the deformation was dominant on one side of the solder joint (Figure 6.5a). The global strain curve was quite similar to the localized creep strain at positions 0.4 and 0.5, which is near the mid-thickness region of the solder joint. The secondary creep rate was measured to be 2.06×10^{-5} s⁻¹. Notably, the secondary creep strain rate was lower in Sn-4.0Ag-0.5Cu solder compared to Sn-3.5Ag solder despite the



Non-Composite 95.5Sn-4.0Ag-0.5Cu Solder Joint at 25°C, 16.2MPa

(b)

Figure 6.5 (a) Localized and global creep strain vs. time for the non-composite Sn-4.0Ag-0.5Cu solder joint. (b) 3D plot of creep strain rate vs. time and position across the solder joint.

applied stress being 25% greater during creep testing. The 3-D plot of the variation of creep strain rate with time and position is shown in Figure 6.5(b).

6.3.1.3 Creep of Cu Particle Reinforced Composite Solder Joints

The creep history of a Cu particle reinforced composite solder joint subjected to creep deformation under a stress of 17 MPa at 25°C for about 8 hours is presented in Figure 6.6(a). The localized and global strain was significantly lower in this specimen in comparison to the non-composite solder joints presented above. The localized strain varies dramatically at different position throughout the solder joint thickness. Similar to the non-composite solder joints, the creep deformation occurred mostly along one side of the specimen. The joint reached the highest localized strain near one Cu substrate/solder interface at position zero, while the lowest localized creep strain was shown at position 1, the opposite side of the solder joint. Figure 6.6(a) shows that the localized creep strain was nil at position 1, indicating intensive deformation at only one interface of the joint. In the center region of the specimen, position 0.4~0.5, the localized strain curve was found to be very similar to the global strain curve. From the global strain curve, the secondary creep rate was determined for this sample to be 4.08×10^{-6} s⁻¹, which is 5 times lower than that of the non-composite eutectic Sn-3.5Ag solder and Sn-4.0Ag-0.5Cu solder joints in spite of higher applied stress levels imposed on the composite solder. The 3-D plot, Figure 6.6(b), shows the variation of creep strain rate with time and position for a Cu particle reinforced composite solder joint.



Cu Particle Reinforced Composite Solder Joint at 25°C, 17Mpa

Figure 6.6 (a) Localized and global creep strain vs. time for the Cu particle reinforced composite solder joint. (b) 3-D plot of strain rate vs. time and position across the solder joint.

6.3.1.4 Creep of Ag Particle Reinforced Composite Solder Joints

The variation of localized creep strain with time for the Ag particle reinforced composite solder joints, shown in Figure 6.7(a), is quite different from the non-composite and Cu particle reinforced composite solder joints. This specimen was stressed with 10.6 MPa at 25°C for 3.6 hours. It is evident that the localized creep strain was closely following the same path as the global strain curve. The localized creep strain at every location through the solder joint thickness was virtually the same as the global strain, which indicates a uniform deformation in this solder joint throughout the creep testing process. Unlike the prior specimens, significant variations in the local creep strain were not found at any location of the joint region. Moreover, extremely uniform deformation was exhibited throughout the solder joint. The secondary creep rate was $1.20 \times 10^{-5} \text{ s}^{-1}$, approximately the same as non-composite eutectic Sn-3.5Ag and Sn-4.0Ag-0.5Cu solder joints. Compared to the Cu particle reinforced composite solder joint, the secondary creep strain was higher for the Ag particle reinforced composite solder joint.

The 3-D plot, Figure 6.7(b), shows the variation of creep strain with respect to time and position through the joint thickness. The creep strain rate correlated well with the creep stain behavior shown in Figure 6.7(a). The plot indicates that the creep rate is quite uniform over the solder joint thickness for the duration of the test. Figure 6.7(b) shows that the creep rate reached the highest value at the start of the creep test and near the end of the creep test. The lowest creep rate was reached at about 0.7×10^4 seconds (1.9 hours) after creep test started, which corresponds to the steady state in the global creep strain curve.



Ag Particle Reinforced Composite Solder Joint at 25°C, 10.6 Mpa

(b)

Figure 6.7 (a) Localized and global creep strain vs. time for the Ag particle reinforced composite solder joint. (b) 3-D plot of creep strain rate vs. time and position across the solder joint.

6.3.2 Secondary Creep Rate for Different Solder Joints at Different Temperatures

Secondary creep rate was determined using linear regression from the global creep strain curve. Steady-state creep rates under a nominal stress at 17 MPa are plotted as a function of temperature in Figure 6.8. The secondary creep rates were much higher for all solder joint materials at 105°C (0.78 T_m) due to diffusion mechanisms and grain boundary sliding. Among these, Ni composite solder joints exhibited the lowest steadystate creep rate. Cu composite solder joints exhibited much lower secondary creep rate than the Ag composite solder and both non-composite solders. At room temperature, Ni composite solder joints was 5 times more creep resistant than Cu composite solder joints and ~30 times better than Ag composite and non-composite solder joints. Even at 105°C, the Ni composite solder joints were ~3 times more creep resistant than Cu composite solder joints and more creep resistant than Ag composite and non-composite solder joints by a factor of 12. The creep performance of Sn-4.0Ag-0.5Cu solder joints was only slightly better than eutectic Sn-3.5Ag solder joints. Comparing the secondary creep rates of Cu and Ag reinforced composite solder joints, Cu particle reinforced composite solder joints exhibit a lower steady state creep rate than Ag particle reinforced composite solder joints. Despite extremely uniform deformation of Ag reinforced composite solder joints, no significant improvement in creep resistance was found in comparison to noncomposite solder joints. The creep property of Sn-4.0Ag-0.5Cu solder alloy is slightly better than the eutectic Sn-3.5Ag solder alloy at all test temperatures.

Cu particle reinforcement was successful in improving the creep resistance. The inprovement is primarily due to an increase in the *effective* volume fraction of the reinforcement with reflow. The effective volume fraction of reinforcement intrinsically

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Figure 6.8 The secondary creep rate for composite and non-composite solder joints as a function test temperatures. The Ni particle reinforced composite solder joint exhibited the best creep resistance at all test temperatures.

increases due to profuse formation of a Cu_6Sn_5/Cu_3Sn intermetallic (IM) layer around the Cu particle reinforcement. Essentially, the volume of hard (Cu + Cu-Sn IM) reinforcement phase increases at the expense of the much softer solder matrix. It is believed that the IM-modified Cu particle reinforcements act to restrain plastic flow on the solder matrix due to elastic constraints, thus, enhancing creep resistance. IM layer formation (Ag₃Sn) around Ag particles in Ag composite solder joints was minimal compared to Cu composite solder joints. Since the IM layers formed around the Ag reinforcements were very thin, the volume fraction of the reinforcing phase remained

essentially the same. The Ag₃Sn IM layer around the Ag particles did not grow significantly during creep testing. The introduction of 15 v% of ~4 μ m Ag particles into the solder matrix tended to homogenize the strain and promote uniform deformation in the joint. However, the steady state creep resistance was not significantly affected by the addition of the Ag particle reinforcements.

The reason that the Ni composite solder joint exhibited the best steady-state creep resistance may be also due to the increase in volume fraction of fine Cu-Ni-Sn intermetallic particles formed in the joint, which act as additional reinforcement. These individual Cu-Ni-Sn particles in the solder matrix can constrain plastic flow during creep deformation, thus, enhancing creep resistance. Provided the deformation mechanism for creep in this material is by dislocation climb/glide, the Ni reinforcement and the fine Cu-Ni-Sn IM particles can act as obstacles to the motion of dislocations resulting in improved steady-state creep behavior.

6.3.3 Strain at the Onset of Tertiary Creep

Strain for the onset of tertiary creep (OTC) is plotted versus secondary creep rate in Figure 6.9. Figure 6.9 contains data obtained for joints made with solder materials of the current investigation and the OTC data for Cu_6Sn_5 reinforced composite solder produced by *in-situ* method (@ 25°C) for comparison. Generally, the OTC occurred at a significantly higher shear strain level for non-composite solder alloys in comparison to the composite solders. This was the finding except for the *in-situ* Cu_6Sn_5 particle reinforced composite solder joint. A shear strain level of ~0.5 observed for the OTC of *in-situ* Cu_6Sn_5 reinforced composite solder solder joints was similar to non-composite solder.



Figure 6.9 Onset of tertiary creep for different solder joint materials as a function of secondary creep rate. Composite solders made by mechanical mixing method generally showed a lower strain for the onset of tertiary creep than non-composite solders and composite solder made by *in-situ* method.

joints. In contrast, the OTC occurred at strain levels between 0.1 and 0.15 for Cu and Ag particle reinforced composite solder joints in which the reinforcements were mechanically added. The average strain for OTC in the Ni composite solder joint was 0.11, which is comparable to the strain for the OTC in the Cu and Ag composite solder joints. Strain at the OTC can be considered as a failure criterion to predict the service life and thus the reliability of the solder joint. As an example, the *in-situ* Cu₆Sn₅ reinforced composite solder joint starts tertiary creep at a much higher strain level (~0.4) as compared to the Ni composite solder joint (~0.18). The strain for the OTC as a criterion would tend to suggest that *in-situ* Cu₆Sn₅ reinforced composite solder joints would

perhaps be more reliable in comparison to Cu, Ag, or Ni reinforced solder joints. The higher strain value for the OTC of *in-situ* Cu₆Sn₅ reinforced composite solder joints, as compared to the other composite solder joints with mechanically-incorporated Cu, Ag and Ni particle reinforcements, could be due to the difference in interfacial bonding strength between the reinforcements incorporated *in-situ* (intrinsically) and by mechanically mixing (extrinsically). Nanoindentation tests by Lucas et. al. have shown that interfacial shear strength of Cu_6Sn_5 reinforcements added *in-situ* is much weaker [50] than the interfacial shear strength of Cu, Ag, or Ni reinforcements added mechanically. The deformation features in an in-situ Cu₆Sn₅ reinforced composite solder joint are shown in Figure 6.10(a)-(b). It is assumed that the weak interfacial bonding of homogeneously distributed Cu₆Sn₅ particles provides multiple nucleation sites for deformation throughout the entire solder joint. A multitude of deformation sites would promote homogenization of the deformation over the joint while simultaneously reducing the propensity for intense deformation at a single site which would result in the OTC occurring at significantly lower strain levels. Admittedly, other factor may affect the strain levels at which OTC occurs, but their contributions are believed to be minimal in comparison to effect associated with interfacial bonding strength of the reinforcement types in the composite solder.

6.3.4 Activation Energy for Creep

The secondary creep strain is described quite well by the constitutive equation proposed by Dorn [54]:



Figure 6.10 Micrographs showing creep deformation of an *in-situ* Cu₆Sn₅ reinforced composite solder joint. (a) solder joint before creep, where there is no damage (interfacial debonding, voids, cracks, etc.), (b) solder joint after creep, showing multiple damage sites (particle rotation, particle/matrix interfacial debonding, voids formation, etc.) across the thickness of the solder joints, as indicated by arrows. A multitude of deformation sites would tend to promote homogenization of the deformation over the joint, as shown in (b).

$$\dot{\gamma} = A \left(\frac{\sigma}{G}\right)^n \exp\left(\frac{-Q}{kT}\right),\tag{6-1}$$

where $\dot{\gamma}$ is the steady-state creep rate, σ is the shear stress, G is the shear modulus, Q is the activation energy, k is the Boltzmann's constant, and A and n are constants. The activation energies for creep for the four solder joint materials were obtained by plotting the variation of log strain rate vs. I/T as shown in Figure 6.11. The activation energy for these non-composite and Cu or Ag composite solder joint materials were in the range of 0.52 eV and 0.56 eV. The Cu and Ag reinforced composite solders revealed slightly higher activation energies than the non-composite solders. The activation energies obtained in this study are somewhat less than the activation energy (0.62 eV) obtained by Raeder *et al.* [62] for Sn-3.5Ag solder using single shear lap solder joint specimen. However, the activation energy for creep in Sn-3.5Ag obtained by Yang *et al.* [61] was similar to those obtained in the present study, Q = ~ 0.54 eV. The activation energy for Ni composite solder was 0.64 eV, which was higher than that for all the other solder materials (0.52 eV-0.56 eV) tested. The higher activation energy for creep for the Ni composite solder corresponds well with its better creep resistance. The extrinsically-incorporated particle-reinforced composite solders all revealed somewhat higher activation energy barrier for creep in the composite solders is raised and dislocation motion is hindered by the reinforcements and by microstructural modifications induced by reinforcement additions.

As reported by Renolds *et al.* [65], a typical eutectic material that is sufficiently fine-grained shows a low-stress creep mechanism, which is dominated by grain boundary sliding. The grain boundary sliding mechanism is frequently seen in fine-grained eutectic Pb-Sn and other fine-grained solder joints, and is responsible for superplastic creep in fine-grained materials [65]. This creep mechanism is characterized by an activation energy for grain boundary diffusion, which is about half of the activation energy for bulk diffusion: $Q_{GB}=0.5Q_{BULK}$. The activation energies obtained for the solders studied suggest that grain boundary or dislocation pipe diffusion is likely the controlling

mechanism governing their creep behavior. At lower temperature and with a high stress exponent dislocation climb can also be a contributing factor for creep in these solders.



Figure 6.11 Plot of log strain-rate vs. inverse absolute temperature. The activation energy for creep is listed in the legend. The activation energy for creep for Ni particle reinforced composite solder is higher than all other solders listed.

6.3.5 Deformation Profiles in Composite and Non-composite Solder Joints

Typical creep deformation profiles of non-composite and Cu particle reinforced composite solder joints are shown in Figure 6.12(a)-(d) before and after creep deformation. The SEM micrographs reveal clearly the distortion of the laser-ablation line patterns due to creep deformation. Significantly more deformation occurred on one side



(c)

(d)

Figure 6.12 The deformation profile for (a) non-composite solder joint before creep; (b) non-composite solder joint after creep; (c) Cu particle reinforced composite solder joint before creep; and (d) Cu particle reinforced composite solder joint after creep. (the left side in the figure) of the solder joint than the other side (the right side in the figure). The distortion of the laser ablation patterns tends to show that intense deformation is localized to a particular side of the specimen, but there is no significant evidence to suggest fracture of the Cu substrate/solder interface. Actually fracture occurred in the solder near the Cu-Sn interfacial IM layer. Such a deformation behavior was common in solder alloys and also in Cu reinforced composite solder joints.

Figure 6.13 shows the typical deformation profile of the Ag reinforced composite



Figure 6.13 Example of uniform creep deformation in Ag particle reinforced composite solder joint: (a) before creep; (b) after creep.

solder joints. In contrast to non-uniform deformation noted in solder alloys and Cu composite solder, very uniform deformation was most often exhibited by the Ag reinforced composite solders. Moreover, uniform creep deformation occurred throughout the thickness of the joint. The line patterns deformed linearly across solder joint thickness. The straight-line creep deformation pattern was maintained during the secondary creep stage for the Ag reinforced composite solder joint. Such highly uniform shear deformation suggests the strain in Ag reinforced composite is homogeneous [47]. We contend that Ag particle stimulate plastic deformation at numerous sites, and therefore mitigate localized intense strains in just one or two regions of the solder joint that eventually develop into deformation bands.

A close examination of the creep-fractured Ni composite solder joint revealed that most joints deformed heterogeneously during creep. While deformation occurred in the solder close to one of the copper substrates, still intense deformation and fracture always occurred in the solder and is not accommodated by fracture in the Cu substrate/solder interface. Typical creep deformation features in the Ni composite solder are illustrated in Figure 6.14(a)-(d). Generally, as is seen in Figure 6.14(d), very little lifting of Sn grains was revealed in the deformation and fracture of Ni composite solder joints, though this type of deformation features were often observed in the Sn-Ag based solder alloys [7]. Grain boundary sliding as a mechanism for creep was not as prevalent in Ni composite solder joint. Others [57, 58, 61] reported that dislocation climb is the likely controlling mechanism for creep of eutectic Sn-3.5Ag solder/joint based on experimentally





(a)





(c)



(d)

Figure 6.14 SEM micrographs showing non-uniform deformation in the crept Ni composite solder joint as exhibited by the distortion of the laser ablation patterns. (a) whole joint, before creep, (b) whole joint, fracture due to creep, (c) one part of the joint, before creep, (d) one part of the joint, after creep. determined values of the stress exponent and the activation energy. Judging from the activation energy obtained, we contend that dislocation climb/glide is the mostly likely controlling mechanism for creep in the Ni composite solder joint.

6.3.6 Summary

- 1. The creep resistance was improved significantly for Cu particle reinforced composite solder joints at all test temperatures.
- The creep resistance of Ag particle reinforced composite solder joints was comparable to the steady state creep rate observed for eutectic Sn-3.5Ag and Sn-4.0Ag-0.5Cu solder joints. Addition of 0.5Cu to eutectic Sn-Ag solder did not significantly improve the creep properties.
- 3. The creep resistance was significantly improved for Ni particle reinforced composite solder joints at all test temperatures. Ni composite solder joint had the best steadystate creep resistance of the particle reinforced composite solder joints. Similarly, the steady-state creep performance of the Ni composite solder joints was better than eutectic Sn-3.5Ag and Sn-4Ag-0.5Cu non-composite solder joints.
- 4. The onset of tertiary creep for Ni composite solder joints was reached at a similar strain level as Cu and Ag particle reinforced composite solder joints. Generally, the onset of the tertiary creep stage occurred at a lower strain level for composite solders with mechanically added reinforcement than the non-composite solders and the *insitu* Cu₆Sn₅ reinforced composite solder.
- 5. The activation energy for creep for Ni composite solder was 0.64 eV, which was higher than the activation energy values obtained for Cu, Ag composite solders and

the eutectic Sn-3.5Ag, Sn-4.0Ag-0.5Cu non-composite solders (0.52eV-0.56eV). The activation energies for Cu, Ag composite solders and the eutectic Sn-3.5Ag, Sn-4.0Ag-0.5Cu non-composite solders were very similar which suggests that the controlling mechanism for creep for these materials is grain boundary or dislocation pipe diffusion.

6. Deformation in Ag particle reinforced composite solder joints was very uniform throughout the joint thickness, whereas, the deformation patterns for other types of solder joints were localized mostly along one side near the Cu substrate/solder interface. Deformation in Ni particle reinforced composite solder joints was not uniform throughout the joint thickness. The deformation also occurred close to one side of the solder joint in the solder. Grain boundary sliding deformation was not as prevalent in creep of Ni composite solder joints based on microstructural analysis. Dislocation climb/glide is the mostly likely controlling mechanism for creep in the Ni composite solder joint.

6.4 Evaluation of Creep Behavior of Near Eutectic Sn-3.5Ag Solders Containing Small Amount of Alloy Additions

The solder materials used to make the solder joints for the present study are: (1) Eutectic Sn-3.5Ag solder alloy, (2) Sn-4Ag-0.5Cu and (3) Sn-3.5Ag-0.5Ni ternary solder alloys, and (4) Sn-2Ag-1Cu-1Ni quaternary solder alloy. The Sn-3.5Ag-0.5Ni solder alloy was prepared by *in-situ* methods in our laboratory, and other solder materials were provided as solder paste by Visteon Technical Center, Dearborn, MI.

6.4.1 Microstructure

The microstructures of the solder joints made with these solder alloys are shown in Figure 6.15. The microstructure of the eutectic and the two ternary alloys are similar. The background microstructure of all three can be characterized by Sn cells separated by wide bands having about 15 vol% Ag₃Sn precipitates, as shown in Figure 6.15(a)-(c). For the 0.5 Cu ternary alloy in Figure 6.15(b), small amounts of globular Cu-Sn intermetallics were observed that were slightly larger than the Ag₃Sn precipitates. In the 0.5Ni ternary alloy shown in Figure 6.15(c), Cu-Sn intermetallics were somewhat larger, more rod-like, and more evenly distributed than in the 0.5 Cu alloy. In addition, some larger blocky Ni₃Sn₄ intermetallics were observed having a layer of a Cu-Ni-Sn intermetallic at the interface with Sn (Figure 6.15(c) inset), indicating that Cu partially invaded the Ni₃Sn₄ intermetallic. The microstructure of the Sn-2Ag-1Cu-1Ni solder joint shown in Figure 6.15(d) shows multiple Cu-Ni-Sn intermetallic strengthening phases. Since there is less Ag in this alloy, the Ag₃Sn bands were much narrower than the other alloys.

6.4.2 Comparison of Secondary Creep Strain Rate under Different Applied Stresses

Secondary creep strain rates were determined for these four solder joint alloys under different applied stresses, as shown in Figure 6.16. In this figure (as well as following ones), eutectic Sn-3.5Ag is represented by circles and bold lines, Sn-4Ag-0.5Cu by triangles and dashed bold lines, Sn-3.5Ag-0.5Ni by diamonds and narrow lines, and Sn-2Ag-1Cu-1Ni by squares and narrow dashed lines. The solid symbols represent



(a)

(b)



(c)



Figure 6.15 Microstructures of solder joint materials: (a) Eutectic Sn-3.5Ag solder alloy, (b) Sn-4Ag-0.5Cu solder alloy, (c) Sn-3.5Ag-0.5Ni solder alloy (inset indicating Cu-Ni-Sn intermetallics), and (d) Sn-2Ag-1Cu-1Ni solder alloy.



Figure 6.16 Comparison of steady-state creep rates of the four solder alloys. (a) room temperature data, (b) 85°C data.

room temperature creep experiments and the open symbols represent the 85°C creep experiments.

Figure 6.16(a) compares the secondary creep rates of room temperature experiments for all four alloys. In contrast to the eutectic and quarternary 1Ni-1Cu alloy that exhibit a single stress exponent, the ternary alloys with 0.5 Cu *or* 0.5 Ni show a higher (and similar) stress exponent at lower stresses and a lower stress exponent at higher stresses. Such transitions in the stress exponent suggest the operation of a threshold stress. The ternary alloy with 0.5 Ni is the most creep resistant alloy (at stresses below about 15 MPa). Both of these ternary alloys have a crossover point in common with the eutectic alloy near 13 MPa, where the creep resistance is similar. The 1Cu-1Ni quaternary alloy and the eutectic alloy have similar stress exponents, but the quaternary alloy has secondary strain rates about 10 times higher than the eutectic over the tested range of stresses. Due to the crossover behavior, the relative creep resistance of the alloys changes from low stress to high stress is summarized in Table 6.1 (using ex trapolation of some data).

Figure 6.16(b) shows the 85°C creep data, which show similar strain rates for stresses that are about half of the room temperature values. Similar trends are observed as at room temperature, except the 1Cu-1Ni quaternary alloy is the least creep resistant because it is about 100 times less creep resistant than the eutectic alloy. Due to cross over effects, creep resistance is similar for the eutectic and the ternary alloys at a stress near 8 MPa.

In Figure 6.16, both eutectic data sets, and the 85°C 1Cu-1Ni set have apparent outlier datum points that are stronger than the rest of the specimens. From related work,

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this variability is not due to experimental errors, but is usually correlated with more homogeneous strain across the joint than is commonly observed, where a preferential shear band develops that is often near one of the two interfaces.

Table 6.1	Ranking of Creep	Resistance of Solder	Alloys Based	Upon I	Best Fit	Power
		Law Creep				

Room Temperature	~10 MPa low stress rank	~20 MPa high stress rank	
Least	Sn-2Ag-1Cu-1Ni	Sn-4Ag-0.5Cu	
Creep resistance	eutectic Sn-3.5Ag	Sn-3.5Ag-0.5Ni	
	Sn-4Ag-0.5Cu	Sn-2Ag-1Cu-1Ni	
Most	Sn-3.5Ag-0.5Ni	Eutectic Sn-3.5Ag	
85°C	~6 MPa low stress rank	~12 MPa high stress rank	
Least	Sn-2Ag-1Cu-1Ni	Sn-2Ag-1Cu-1Ni	
Creep resistance	Sn-4Ag-0.5Cu	Sn-3.5Ag-0.5Ni	
	eutectic Sn-3.5Ag	Sn-4Ag-0.5Cu	
Most	Sn-3.5Ag-0.5Ni	eutectic Sn-3.5Ag	

Sn-3.5Ag-0.5Ni solder joints thus exhibited best creep resistance among all the joints tested. The reason for the difference in creep resistance among these solder alloys may be explained from the microstructural point of view. Both the intermetallic reinforcing phase formed in the matrix as well as the small matrix Ag₃Sn particles play important roles in the improvement of the creep behavior of these solder alloys. There is not much microstructural difference between eutectic Sn-3.5Ag and Sn-4Ag-0.5Cu solder. But the small amount of Cu-Sn intermetallics present in the Sn-4Ag-0.5Cu improved the creep resistance of this alloy to a little extent. That's why comparable but slightly higher creep resistance was observed in this alloy compared to eutectic Sn-3.5Ag solder. The presence of Ni in the Sn-3.5Ag-0.5Ni solder seems to stimulate the formation of Cu-Sn intermetallic phases in the matrix though the Cu comes only from the substrate

during soldering process. On the contrary, much less number of Cu-Sn intermetallic particles were observed in the Sn-4Ag-0.5Cu solder alloy though Cu is already contained in the solder prior to joint fabrication. It is reasonable to relate more intermetallic reinforcements to the improved creep resistance, as exhibited by Sn-3.5Ag-0.5Ni. In addition to the increased number of the reinforcement in the Sn-3.5Ag-0.5Ni alloy, they are also larger and more rod-like than in the 0.5 Cu ternary alloy. The larger size and rod shape may constrain plastic flow during creep deformation because the height of the climb barrier is larger [128], which hinders dislocation climb and improves secondary creep behavior. However, the shape of the intermetallics tends to become more globular with an increase of Cu, as is shown in Figure 6.15(d) for the Sn-2Ag-1Cu-1Ni solder alloy. This quaternary alloy also has lower silver content, which implies that fewer Ag₃Sn particles exist, and this may also account for the poorer creep resistance. Therefore it may be possible to improve creep resistance of the Sn-Ag solder alloy by increasing the Ni content carefully.

6.4.3 Comparison of Creep Behavior of Alloys in Normalized Strain Rate vs. Normalized Stresses Plot

Normalized secondary creep strain rates are plotted versus normalized stresses for these solder joint materials in Figure 6.17 along with Darveaux's data for aged eutectic Sn-3.5Ag solder joints [58]. Darveaux' data show the effect of power law breakdown at high creep stress in the shape of the curve that is often modeled using $\dot{\gamma} = \sinh(\alpha\sigma)^n \exp(-Q/RT)$. Thus, creep data are expected to have slight upward curvature in the stress and strain rate space examined in this paper. It is evident that the eutectic and the 1Cu-1Ni quaternary alloy creep data obey the power law relation, but the



Figure 6.17 Normalized steady-state creep strain rates versus normalized stresses for eutectic Sn-3.5Ag, Sn-4Ag-0.5Cu, Sn-2Ag-1Cu-1Ni, and Sn-3.5Ag-0.5Ni solder joints along with Darveaux's data for aged eutectic Sn-3.5Ag solder joints [58].

ternary alloys exhibit high stress exponents at lower stress due to the operation of a temperature dependent threshold stress, above which a particular deformation mechanism is able to operate [129-131]. Temperature dependent threshold stresses are known to operate in alloys with solute atom strengthening or incoherent particle strengthening. The higher threshold stresses in the nickel ternary alloy account for the higher creep resistance observed at lower stress. Over the range of stresses examined in the eutectic and 1Cu-1Ni quaternary alloy, there is no apparent threshold stress phenomena.

Also, the eutectic data is generally more creep resistant than the Darveaux's data. The creep resistance in Darveaux's specimens may have been reduced by the aging treatment, in contrast to the present data, where all the solder joints were deformed in the as-fabricated condition within a week after they were fabricated. Compared to the other alloys, the eutectic data are rather noisy. We have observed that compared to the other alloys, the eutectic alloy is most likely to develop a shear band close to one or the other interface, and this tendency to develop a plastic instability may account for the range of scatter. Figure 6.17 also illustrates that Sn-2Ag-1Cu-1Ni solder joints are the least creep resistant among all the tested solder joints. This alloy had significantly less Ag than the others, so this may account for the weakness of creep resistance of this alloy.

6.4.4 Strain and Time at the Onset of Tertiary Creep

The strain at which the tertiary creep stage starts may be useful for modeling and predicting the service life of solder joints. A comparison of the strain for the onset of tertiary creep for these solder alloys is shown in Figure 6.18(a) and (b) for room temperature and 85°C, respectively. At room temperature, the onset of tertiary creep stage is delayed to strains near 0.6 for the ternary 0.5Cu solder joints, whereas, it is ~0.3 for eutectic, the 0.5Ni ternary, and the 1Cu-1Ni quaternary solder joints.

At 85°C, the shear strain at the onset of tertiary creep is lower, and tends to show the reverse phenomena as at room temperature. Tertiary creep is delayed the most for the quaternary 1Ni-1Cu (~0.5) solder joints, compared to eutectic Sn-3.5Ag (~0.3), and near ~0.2 for the ternary 0.5Cu and 0.5Ni solder joints. Thus the quaternary 1Cu-1Ni alloy may provide beneficial compliance for some applications. This enhancement of shear strain for the onset of tertiary creep can be attributed to the ability of the material to resist heterogeneous deformation, analogous to necking in tensile tests. Alloys with a high stress exponent (low strain rate sensitivity) are intrinsically less able to resist localized deformation [132]. Also, spherical intermetallics would be less likely to stimulate







(b)



Figure 6.18 (a) Average strains for the onset of tertiary creep at room temperature, (b) average strains for the onset of tertiary creep at 85°C, (c) time for the onset of tertiary creep at room temperature, (b) time for the onset of tertiary creep at 85°C.

localized deformation gradients than rod-shaped reinforcements. The 0.5Ni ternary alloy having more rod-shaped reinforcements has the lowest strains to tertiary creep of the alloys tested. The relative merits of these alloys in the strain to the onset of tertiary creep is summarized by rank in Table 6.2, and compared with secondary creep resistance.

Figures 6.18(c) and (d) illustrate the time to tertiary creep instead of strain to tertiary creep. It is clearly shown that the ternary Sn-4Ag-0.5Cu and Sn-3.5Ag-0.5Ni alloys exhibit longer deformation time before the onset of tertiary creep than the eutectic Sn-3.5Ag alloy and the 1Cu1Ni alloy at a similar stress level at both room temperature and 85°C at lower stress levels. This proves the improved creep resistance for the ternary Sn-4Ag-0.5Ni and Sn-3.5Ag-0.5Cu alloys because it takes longer time for these alloys to reach the final creep stage where fracture usually occurs as soon as tertiary stage started.

 Table 6.2 Comparison of Creep Properties of Solder Joints Made with Eutectic Sn-3.5Ag, Sn-4Ag-0.5Cu, Sn-2Ag-1Cu-1Ni, and Sn-Ag-0.5Ni Solders

Creep	Property	Steady-state	Onset of
Solder Material		Creep Rate	Tertiary Creep
Sn 3 5 A q	Room Temp.	++++	++
311-3.JAg	85°C	+++	+++
Sp 4Aq 0.5Cu	Room Temp.	++++	++++
511-4Ag-0.JCu	85°C	+++	++
Sp 2Ag 1Cu 1Ni	Room Temp.	+++	+++
SII-ZAg-ICu-IINI	85°C	+	++++
Sp. Ag 0 5Ni	Room Temp.	++++	++
SII-Ag-0.5INI	85°C	+++	++

Note:

+ + + + +: Excellent; + + + +: Very good; + + +: Good; + +: Marginal; +: Poor.

6.4.5 Microstructural Examination of Deformed Solder Joints

Representative micrographs that illustrate deformation on previously polished surfaces in the crept solder joints are presented in Figure 6.19(a)-(e) for the four alloys. Preferential deformation on one side was observed for all the solder joint materials. The





(c)





(e)

Figure 6.19 Creep deformation in the solder joints: (a) Eutectic Sn-3.5Ag solder, (b) Sn-4Ag-0.5Cu solder, (c) Sn-Ag-0.5Ni solder, (d) Sn-2Ag-1Cu-1Ni solder, and (e) a magnified view of the deformation in a Sn-Ag-0.5Ni solder joint.

surface features of all the tested solder joints are similar, as shown in Figure 6.19 The most important microstructural characteristic is the decohesion at Sn-Sn grain boundaries that leads to ultimate failure of the solder joint. This feature was often observed along the side that had intense deformation. The grain boundary decohesion is apparently due to the grain boundary sliding effect on particular boundaries which makes the Sn grain (or cluster of grains) to either slide up or sink down with respect to neighboring grains within the solder. A magnified view of grain boundary decohesion is illustrated in Figure
6.19(e). These micrographs suggest that the deformation mechanism that leads to failure in creep of these solder joints is grain boundary sliding. The fact that the stress exponents are high and variable (and not close to 2, which is typical for superplasticity), implies that this deformation mechanism does not operate uniformly throughout the joint, nor is it the rate limiting process of deformation.

6.4.6 Summary

Creep tests were conducted on solder joints made with eutectic Sn-3.5Ag, two ternary alloys, Sn-4Ag-0.5Cu, Sn-3.5Ag-0.5Ni, and a quaternary Sn-2Ag-1Cu-1Ni solder alloy. The relative performance of these alloys using secondary creep rate and strain to tertiary creep is summarized in Table 6.2.

- 1. The ternary alloys showed improved creep resistance at low stresses due to threshold stress phenomena, but similar deformation behavior as the eutectic solder at higher stresses.
- 2. The ternary alloys with 0.5 Ni showed substantially better creep resistance at lower stresses. The quaternary alloy with about half the silver as the other alloys had uniformly poorer creep resistance.
- 3. The average strain for the "onset of tertiary creep" at room temperature in Sn-4Ag-0.5Cu solder joints was higher than solder joints made with the other three alloys, but it was low at elevated temperature, where the quaternary alloy had the largest strain before tertiary creep.

- 4. Sn-4Ag-0.5Cu and Sn-3.5Ag-0.5Ni alloys exhibit longer deformation time before the onset of tertiary creep than the eutectic Sn-3.5Ag alloy and the 1Cu1Ni alloy at a similar stress level at both room temperature and 85°C.
- 5. Microstructural examination showed significant creep deformation along particular Sn-Sn grain boundaries, and fracture nucleation probably developed from boundaries that were sliding excessively.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In the current investigation, composite solders were prepared by mechanically incorporating metallic Cu, Ag, or Ni particle reinforcements to the eutectic Sn-3.5Ag solder paste. Microstructural characterization of composite solder joints before and after solid-state isothermal long term aging and multiple reflow were carried out. Effects of solder reflow on wettability and mechanical properties of these solder materials were studied. Creep tests were performed to study the creep deformation behavior of the composite solder joints as well as solder joints made with near eutectic Sn-Ag solders with small alloying element addition.

The major results of this investigation are concluded as follows.

1. In the as fabricated composite solder joints, extensive formation of Cu-Sn IM layers around the Cu reinforcements was observed, whereas the formation of Ag-Sn around the Ag reinforcement was minimal. The IM layers developed around the Ni particles were also significant and can be characterized by a "sunburst" pattern surrounding the Ni particle reinforcements. There is a significant number of ~0.5 µm sized small IM particles scattered, mostly, along periphery of Ni reinforcement particles. A few of these small IM particles appear in the eutectic Sn-3.5Ag matrix. The morphology of IM layer around Ni particles was affected due to different heating rate, but not cooling rate. With the heat input equivalent to three reflows, the sunburst shaped IM layer around Ni particles can be completely transformed into a single-crystal-faceted shape. The IM layer around the Cu reinforcement was a co-layer consisting of a

Cu₃Sn layer close to Cu particles and a Cu₆Sn₅ layer close to the solder. The IM layer formed around Ag particles was thin Ag₃Sn layer. The IM layers surrounding the Ni reinforcements were detected as a Cu-Ni-Sn ternary IM layer. The IM layers formed at the Cu substrate/solder interface were found to be Cu-Sn IM layer in both the Cu and the Ag particle reinforced composite solder joints. This Cu-Sn IM layer is also a co-layer consisting of a Cu₃Sn layer close to Cu substrate and a Cu₆Sn₅ layer close to the solder. However, the IM layers formed at the Cu substrate/solder interface in the Ni composite solder joints was determined as a co-layer consisting of a Cu-Sn IM layer close to Cu substrate and a ternary Cu-Ni-Sn IM layer close to Ni composite solder. The thick IM layer formed around the Cu or Ni particles is due to the fast diffusion behavior of Cu or Ni atoms in Sn, whereas the diffusion of Ag in Sn is much slower which results in a significantly thinner Ag-Sn intermetallics around Ag particles.

2. Isothermal aging studies showed that more intermetallics formed in Cu composite solder joints (both around the reinforcements and at the substrate/solder interface) than in Ag composite solder joints after aging for 1000 hours. Cu reinforcements were totally converted to Cu₆Sn₅ intermetallic with sufficient aging, whereas Ag particles were only partially converted to Ag₃Sn intermetallic. A proposed phenomenological model shows that the growth of IM layers around the Cu particle reinforcements and at the substrate/solder interface is produced by interdiffusion of both Sn and Cu atoms through the ε and η IM layers. Solid state isothermal aging studies at 25, 50, and 100°C for ~1000 hours induced only slight modifications in the microstructure of Ni composite solder joint. However, aging at 150°C revealed that

the microstructure was unstable with profuse growth of the IM layer and coarsening of the Ni reinforcement as a result of Cu-Ni-Sn intermetallics formation and growth. The large volume fraction of intermetallics formed in the Ni composite solder joint after aging at 150°C for 1000 hours is probably due to the presence of Cu, in addition to Ni and Sn, in the intermetallics formed in the Ni composite solder.

- 3. Wettability studies showed that eutectic Sn-3.5Ag solder paste has the best wetting characteristics on Cu substrate among all the solder materials studied. The 15 v% Ni composite solder showed comparable wettability to eutectic Sn-3.5Ag solder paste. The wettability of 15 v% Ag reinforced composite solder was significantly better than 17 v% Cu reinforced composite solder. The poor wettability of Cu composite solder is primarily due to the increase in the effective volume fraction due to reflow. Such increase in volume fraction was not observed in the Ag and Ni composite solder after multiple reflow. Wettability can be improved by lowering the volume fraction of the reinforcing phase. No significant changes in contact angles were observed with multiple reflow for all the solder materials studied.
- 4. The effects of multiple reflow on the microstructure of the composite solder joints were investigated and compared with eutectic Sn-3.5Ag solder. The most significant microstructural changes were observed in the Cu composite solder joints. Growth of the IM layer around the Cu particle reinforcements was excessive leading to total consumption of the Cu particles after 3-4 reflows. No significant coarsening of the Ag reinforcements was evident after multiple reflows. Multiple reflow did not significantly change the microstructure in Ni composite solder joints. The IM layer growth was minimal, although coarsening of Ag₃Sn particles was observed. Reflow

studies also showed that the IM layer at the Cu substrate/solder interface also grew much faster in Cu composite solder joints than in Ag composite solder joints. However, multiple reflow did not cause significant growth of interfacial IM layers in Ni composite solder joints. Therefore, both Ag and Ni composite solders exhibited much more stable microstructure in their joints under the same reflow conditions than Cu composite solder. The microstructure of first reflowed eutectic Sn-3.5Ag solder can generally be characterized by small Sn cells surrounded by wide-banded eutectic Ag₃Sn phase. In comparison, the microstructure of multiple reflowed solder is characterized by large Sn cells circumvented by a thin necklace of eutectic Ag₃Sn precipitates.

- 5. The effects of reflow on the mechanical properties of eutectic Sn-3.5Ag solder were evaluated from the data of hardness, yield strength, steady-state creep rate, and stress exponent for creep using nanoindentation testing. The hardness and yield strength of multiple reflowed eutectic Sn-3.5Ag solder were reduced by 30% after three reflows. This finding is commensurate with the increasing size of Sn cells produced by multiple reflow as a larger grain/cell size gives a lower yield strength. The stress exponent, n, determined using indentation creep testing was 7 for first reflowed solders and 8 for multiple reflowed solders. From the stress exponents observed, the steady-state creep rate for the multiple reflowed solder will be higher compared to first reflowed solder.
- 6. In terms of creep properties of the composite solder joints, it was found that the creep resistance was significantly improved for Ni particle reinforced composite solder joints at all test temperatures. Ni composite solder joint had the best steady-state

creep resistance of the particle reinforced composite solder joints. Similarly, the steady-state creep performance of the Ni composite solder joints was better than eutectic Sn-3.5Ag and Sn-4Ag-0.5Cu non-composite solder joints. The creep resistance was also improved significantly for Cu particle reinforced composite solder joints at all test temperatures. However, the creep resistance of Ag particle reinforced composite solder joints was comparable to the steady state creep rate observed for eutectic Sn-3.5Ag and Sn-4.0Ag-0.5Cu solder joints. Addition of 0.5Cu to eutectic Sn-Ag solder did not significantly improve the creep properties.

- 7. The onset of tertiary creep for Ni composite solder joints was reached at a similar strain level as Cu and Ag particle reinforced composite solder joints. Generally, the onset of the tertiary creep stage occurred at a lower strain level for composite solders with mechanically added reinforcement than the non-composite solders and the *insitu* Cu₆Sn₅ reinforced composite solder.
- 8. The activation energy for creep for Ni composite solder was 0.64 eV, which was higher than the activation energy values obtained for Cu, Ag composite solders and the eutectic Sn-3.5Ag, Sn-4.0Ag-0.5Cu non-composite solders (0.52eV-0.56eV). This data corresponds well with the improved creep resistance of Ni composite solder joints. The activation energies for Cu, Ag composite solders and the eutectic Sn-3.5Ag, Sn-4.0Ag-0.5Cu non-composite solders were very similar and close to the activation energy for grain boundary diffusion, which suggests that the controlling mechanism for creep for these materials is grain boundary or dislocation pipe diffusion.

- 9. Although the improvement of creep resistance for Ag composite solder joint was insignificant, deformation in Ag particle reinforced composite solder joints was very uniform throughout the joint thickness, whereas, the deformation patterns for other types of solder joints were localized mostly along one side near the Cu substrate/solder interface. The deformation in Ni composite solder joints also occurred close to one side of the solder joint in the solder. Grain boundary sliding deformation was not as prevalent in creep of Ni composite solder joints based on microstructural analysis. Dislocation climb/glide is the mostly likely controlling mechanism for creep in the Ni composite solder joint.
- 10. Creep tests were conducted on solder joints made with eutectic Sn-3.5Ag, two ternary alloys, Sn-4Ag-0.5Cu, Sn-3.5Ag-0.5Ni, and a quaternary Sn-2Ag-1Cu-1Ni solder alloy to study the effects of alloying element addition on the creep behavior of eutectic Sn-3.5Ag solder. The ternary alloys showed improved creep resistance at low stresses due to threshold stress phenomena, but similar deformation behavior as the eutectic solder at higher stresses. The ternary alloys with 0.5 Ni showed substantially better creep resistance at lower stresses. The quaternary alloy with about half the silver as the other alloys had uniformly poorer creep resistance. The average strain for the "onset of tertiary creep" at room temperature in Sn-4Ag-0.5Cu solder joints was higher than solder joints made with the other three alloys, but it was low at elevated temperature, where the quaternary alloy had the largest strain before tertiary creep. Sn-4Ag-0.5Cu and Sn-3.5Ag-0.5Ni alloys exhibit longer deformation time before the onset of tertiary creep than the eutectic Sn-3.5Ag alloy and the 1Cu1Ni alloy at a similar stress level at both room temperature and 85°C.

Microstructural examination showed significant creep deformation along particular Sn-Sn grain boundaries, and fracture nucleation probably developed from boundaries that were sliding excessively.

7.2 Closing Thought / Recommendations

There has been a lot of research effort involved in the present investigation for composite solders with mechanically incorporated Cu, Ag, and Ni particle reinforcements. Many tests, such as aging, reflow, nanoindentation and creep etc., have been performed to evaluate these composite solders. Since this batch of the experiment was just the starting exploration of composite solders made with extrinsical incorporation method, there were several places that the author feels need to have more input and further investigation due to lack of experience or experimental conditions. Some key knowledge or specific mechanism is still unclear and more effort should be pursued to make the current investigation more complete and comprehensive.

1. The volume fraction of the composite solders was 15% used in the current investigation. This cause a problem that the effective volume fraction of Cu or Ni composite solders will be much more than 15 v% under aging or reflow conditions at elevated temperatures, which leads to poor wettability and brittle solder joint. In the future investigation, much lower initial volume fraction should be used in order to control the ultimate volume fraction of the reinforcement to be around 20%. An initial 5 v% of reinforcement addition may be a good starting point. The effect of different volume fraction on aging, reflow, and creep characteristics of the composite solder can be pursued if possible.

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- 2. The creep testing on these composite solder joints was focused primarily on the deformation analysis of the solder joints where microstructural features due to creep, global and localized strain distribution, strain for the onset of tertiary creep etc., were evaluated. In the future investigation, a systematic study on the creep deformation mechanism of these composite solder joints can be pursued using a wide range of applied stresses at four different temperatures. The effect of the particles added to the eutectic Sn-3.5Ag solder on the responsible creep mechanisms can be discussed based on a series of systematic creep tests. Since Cu and Ni composite solder joints showed improved creep resistance in terms of steady-state creep rates, it would be meaningful to start with these two solder materials. Also, creep tests can be carried out on one solder joint with fixed stress level while the testing temperature being varied. This is a possible means to have a quick evaluation of activation energy for creep for the materials tested.
- 3. As for the activation energy for creep, our data showed that the activation energies for these composite solders are about half of the self-diffusion of Sn, which are typical grain boundary diffusion activation energies for grain boundary sliding type of deformation mechanism. Our surface damage due to creep also showed significant grain relief effect. If grain boundary sliding is the controlling mechanism, does adding reinforcements still contribute to the improved creep resistance? Which is the most contributing factor need to have further thought. However, there is no clear agreement in the experimental data that clearly defines the operating creep mechanisms in the literature just for the eutectic Sn-3.5Ag solder. This aspect needs to be further clarified, with possible repeated experiments, by extensively studying

stress exponent, activation energy as well as microstructural features of creep deformation.

- 4. It is also advisable to study the residual mechanical properties (eg. creep, simple shear properties) of these composite solder joints after aging and reflow when significant microstructural evolution has taken place. Alternatively, changes of mechanical properties with aging or reflow can also be pursued.
- 5. From out laser pattern and established creep data extraction technique, both global and localized creep parameters can be evaluated. We always use global secondary creep rate and global strain for the onset of tertiary creep as parameters to compare creep resistance and service life. Are the global parameters the controlling factors or the localized ones? This aspect needs to be further pursued possibly by using one parameter/variable to represent comprehensive effects on the creep behavior caused by both the global and local parameters.
- 6. The reflow temperature profile can be modified in the future investigation where different heating/cooling rate and even different dwell time at peak temperature can be pursued. The current profile has very short time above melting point where sometimes it may not cause discernible changes in the microstructure even due to 4 reflows, as reported for Ni composite solder. Alternatively, increasing the number of reflows under current temperature profile for Ni composite solder may be helpful.
- 7. The premise to clarify the above observed disagreements is to consistently have good quality solder joints ready for the tests. Solder joints with different thickness or fillet shape/size have to be rejected. Therefore, methods need to be further developed and completed to improve the integrity of the solder joint though we are making great

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progress towards that. For example, the formation of voids should be avoided or lowered to the minimum extent by choosing proper flux or improving our current processing method in the lab environment. Proper references from industries may be taken and adopted.

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APPENDICES

APPENDIX A

PROCEDURES FOR THE CALCULATION OF GLOBAL AND LOCALIZED CREEP PARAMETERS

1 Image Processing

1.1 Image Selection

A series of images were captured during creep testing at certain time intervals. Usually more than 20 or 30 images were captured for each individual creep testing using the old creep testing technique. More than 100 images were obtained with the newly developed creep testing fixture with an CCD camera that can automatically capture at set time intervals. To assure that reasonably correct creep parameters to be obtained in the subsequent date extraction steps, usually, 12-15 images were needed, as shown in Figure A1. In Figure A1, totally 15 out of 38 images were selected from a creep testing on *insitu* Cu₆Sn₅ particle-reinforced eutectic Sn-3.5Ag solder joints. We will use this creep test as an example for the following image process, data extraction/analysis illustration. The selection of these 15 images should represent all the three creep stages with ~4-5 images in each stage. Sometimes, more images are needed at the transition point from steady-state creep to tertiary creep stage in order to assess the strain or time at the onset of tertiary creep.

1.2 Image Processing Using Adobe PhotoShop[®]

The purpose of image processing is to provide a series of images with consistent size and quality for the subsequent data extraction in DataThief[®]. The following steps are needed to accomplish the image processing.





- Figure A1 Example of selection of creep images. Totally 15 out of 38 images were selected from a creep testing on *in-situ* Cu₆Sn₅ particle-reinforced eutectic Sn-3.5Ag solder joints. These 15 images represent creep deformation in the solder joint at different time intervals.
- (1) Start Adobe PhotoShop[®].
- (2) Open all the 15 images ready to process. This can be done by going to "File" menu, choosing "Open", going to the proper directory, then selecting first image and clicking the last image while holding the "shift" key. By this way, 15 images are selected simultaneously, as shown in Figure A2. Click "open" after selection. All 15 images with TIF format thus are opened in Adobe PhotoShop[®].



Figure A2 Open the selected images in PhotoShop®.

- (3) The last image is the first one to process because last image represents largest deformation throughout creep testing. Make the last image (in this example, the last image is #15) as your current opened file by selecting the corresponding file name from WINDOW menu, as shown in Figure A3.
- (4) The first step to process these pictures is to rotate the canvas so that the Cu substrate/solder interfaces of the solder joint are exactly perpendicular.
- (5) There are many excimer laser marks on the solder joint. Pick a line that is clear throughout the creep testing, for example, the line as shown in Figure A4. The deformation of this line will be traced in every picture.



Figure A3 The last image is the first one to edit.



Figure A4 Pick a line that is clear throughout to trace.

(6) Inverse image of the original image is often used because the line is clearer than the original image. Invert the image by using Ctrl+I. as seen in Figure A5.



Figure A5 Invert the original image to edit.

- (7) Select a rectangular region that contains the line you want to edit, using the rectangle selection tool. Make sure that rectangle box is small as long as it contains the line. This step is illustrated in Figure A6.
- (8) Crop the image so that it only contains the selected rectangular area, as seen in Figure A7.
- (9) Carefully trace the line from the left side of the solder joint to the right side, using the line tool with black foreground color. It is better to zoom the area to 200% to promote accuracy when drawing the line. See Figure A8 for an example of the line traced.



Figure A6 Select the line to trace.



Figure A7 The image is cropped to the line region.



Figure A8 Carefully trace the line. Use 200% magnification when tracing the line.

(10) Now, we have had images with different sizes due to the amount of deformation at different stages. It is necessary to make all the images have the same size so that it is under the same magnification when opened by DataThiet[®] in the next step. (Otherwise, DataThiet[®] will end up blowing a small sized image the same size as a big image.) This can be accomplished by setting the same canvas size to all the images. So, the canvas size should be determined from the biggest image, i.e., the last image. The canvas size change can be done by selecting "Canvas Size" from the "Image" menu. Usually, the canvas size for the last image could be just a little bigger than the image size itself. When you change the canvas size for other images later. This step is illustrated in Figure A9.



Figure A9 Canvas size change. (a) select "canvas size" in "image" menu. (b) Change the width and height in the box. (c) A white margin was formed due to canvas size change.

(11) Image analysis can be finalized by saving the image files as ".pct" files for use in DataThief[®] Macintosh version, or alternatively, ".gif" files for use in DataThief[®] PC version, as shown in Figure A10.



Figure A10 Save the edited image to ".gif" file type for use in DataThief® PC version.

(12) Repeat steps (4)-(11) for prcessing other images.

2 Data Extraction Using DataThief®

DataThief[®] is a program to reverse engineer a set of data from a given plot in a magazine or journal. This program gives you the opportunity to incorporate somebody else's data points in your plots. This comes in very handy when f.i. you would like to compare your data with the data in a published article for which you don't have the data in table format.

The purpose of using DataThiet[®] is to extract a group of data points across the solder joint thickness (localized places) along the prescribed deformation lines at designed time intervals under the same coordinate system.

The following steps are needed to accomplish the data extraction.

(1) Set up a coordinate system. This can be done by using a transparency on which a square grid pattern is printed. More grid points will facilitate the accuracy of the data. Stick the transparency firmly on the corner of the computer screen with scotch tape so that it won't fall or change position during the data extraction process. Set up the positive x and y direction on the transparency. This step is shown in Figure A11.



Figure A11 A transparency with grid is taped on the computer screen. A coordinate system is set up on the transparency.

(2) Launch the DataThief[®] software. Don't maximize the DataThief[®] window. Make its window have a medium size so that it can be freely dragged and moved on the computer screen, as can be seen in Figure A12.



Figure A12 Launch the DataThief[®] software. Don't maximize the DataThief[®] window.

- (3) Open the last image first (#15) in DataThief[®]. Make a mark on the transparency at the point which was chosen as a reference point. This point has to be on one side of the solder joint preferably at the Cu substrate/solder interface, as shown in Figure A13.
- (4) Set up the coordinate system in DataThief[®], which exactly matches the coordinate system previously set on the transparency, as shown in Figure A14. Enter the minimum/maximum x and y values in DataThief[®].
- (5) Choose the data extraction mode to "scattered data mode". Carefully Click along the black line from one side of the solder joint to another to extract data, as shown in

Figure A14. The distance of each clicked data point along x direction is designed such that 15-17 data points are collected in total. Once this distance (between each data point along x direction) has decided, use exactly the same distance consistently for all other images.



Figure A13 Choose the reference point from the image and mark on the transparency.



Figure A14 Set up the coordinate system in DataThief[®].

(6) Save the collected data by selecting "Save" from the "File" menu, as shown in Figure A15. The data can be saved as text file format (*.txt) for the time being. In each data file, there will be two columns of x-y data pairs.



Figure A15 Illustration of data extraction. (a) Scattered data is collected. (b) Data is saved in ".txt" format.

- (7) Open the next image (#14) in DataThief[®]. Move the DataThief[®] window so that the same reference point on this image matches exactly the mark on the transparency in step (3), as illustrated in Figure A16. Repeat steps (4)-(6) for the data extraction.
 - move this window with your mouse
- (8) Repeat steps (4)-(7) for the data extraction from other images.

Figure A16 Each image should match the reference point on the transparency.

3 Data Analysis — Creep Parameters

By now we have text files containing the extracted data from all the selected images. The purpose of data analysis is to calculate various creep parameters from the collected data points. These parameters usually include the global and localized creep strain and strain rate, localized displacement vs. solder joint thickness, the strain and time at the onset of tertiary creep, as well as the three dimensional plot of creep strain/strain rate vs. time and solder joint thickness, etc. Microsoft Excel[®], KaleidaGraph[®], and DeltaGraph[®] are used in this part of the analysis. The following steps are needed to accomplish the data analysis.

3.1 Displacement vs. Unnormalized Position Though Joint Thickness

(1) Import the extracted data from the text files to a Microsoft Excel[®] spreadsheet in the format as shown in Figure A17. The first column is the coordinate position of each data point along x direction. The next 15 columns are the coordinate position of each corresponding data point along y direction at different time intervals during the creep deformation process.

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Figure A17 Import the extracted data from DataThief® to Microsoft Excel®.

(2) Normalize all the y position with respect to the initial y position in image 1. This step can be shown in Figure A18 by looking at cell B27 in the spreadsheet. B27=B3-\$B3. Once B27 is obtained, all the y data in rows 27-45 can be copied from B27. Column 1 is kept unchanged at this step.

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4.50€+00	0.00E+00	-4.57E-01	-8.90E-01	-1.21E+00	-1.53E+00	-1.78E+00	-2.05€+00	-2.10E+00	-2.16E+00	-2.258+00	-2.348+00	-2
5 00 00	0.00E+00	-4.84E-01	-9.38E-01	-1.29E+00	-1 68E+00	-1 92E+00	-2.20E+00	-2.25E+00	-2.34E+00	-2.42E+00	-2.44E+00	-2
5 500 +00	0.000 +000	-4.846-01	-9.868-01	-1.352+00	-1.73E+00	-1.96E+00	-2.25E+00	-2.38E+00	-2.46E +00	-2.53E+00	-2.72E+00	-2
6 00f +00	0.005+00	-4.836-01	-9 90E-01	-1 362+00	-1 798 +00	-1.905+00	-2.34E+00	-2 42E+00	-2 51E +00	-2.52E+00	-2 82E+00	-3
5 50E +00	0 00E+00	-4.96E-01	-1 05E +00	-1 385 +00	-1 832 +00	-2.01€+00	-2.416+00	-2 51E-00	-2 65E +00	-2.73E+00	-2.868 +00	-3
7 00E +00	0.00E+00	-4.92E-01	-1.08E =00	-1.42E+00	-1.83E+00	-2.10E+00	-2.495+00	-2.588-00	-2.68E <00	-2.79E +00	-2.968 +00	-3
7 50€ +00	0.00€+00	-4 96E-01	-1 10E+00	-1.47E+00	-1.84E+00	-2.16E+00	-2.58E+00	-2.67E+00	-2.78E =00	-2.90E+00	-3.00E+00	-3
8 006+00	0.006+00	-4.70E-01	-1.096-00	-1 47E+00	-1.86E+00	-2.18E+00	-2.61E+00	-2.69E+00	-2.81E+00	-2.93E <00	-3.05E+00	-3.
8 505 +00	0.00E+00	-4 500-01	-1.146 +00	-1.430+00	-1 09E+00	-2.29E+00	-2.72€+00	-2.80E+00	-2.91E=00	-3.01E+00	-3.14E+00	-3.
9 000 +00	0.002+00	-4716-01	-1 158 +00	-1.438+00	-1 37E+00	-2 298 +00	-2 728 +00	-2 89E+00	3 026 400	-3 10E +00	-3 198 +00	-3
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Figure A18 Normalized the y position with respect to the initial y position before creep.

(3) Displacement vs. (unnormalized) position across solder joint thickness can be plotted using data in row 27-row 45, column A-column P, as shown in Figure A19. A sample displacement-position curve plotted in KaleidaGraph[®] is given in Figure A20.

3.2 Global Creep Strain & Steady-State Creep Rate

(4) Global creep strain can be calculated using the data at the end points where x=0 and

x=9 in this example. The global creep strain is defined as
$$\gamma = \frac{\Delta y}{\Delta x}$$
, assuming change

in angle θ is very small. The manipulation of data in Excel spreadsheet is given in Figure A21 in cell B49, where B49=(B45-B27)/(\$A45-\$A27). B49 is the global creep strain before deformation, while data in C49 to P49 are the global creep strains at different time intervals during creep.

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1000 400	0.000 +00								1006-00			
2 OFF HOL	0.000-000								1.1.185-00	1111111	1115-00	
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1506-00	0.005 +00							-1546 800			1205.000	
4 000 -00	0.000 +00			-1.16E+00	1446-00		-1958-00	-1.96E+00	-2036+00		-2.27E+00	
	0.000 +00											
	0 000E =00			-129E+00	-1635-00		-2206-00	-2.2KE+00	2345+00		2445+00	
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Figure A19 Data used to generate displacement vs. unnormalized position curve.



Figure A20 A sample displacement-position curve plotted in KaleidaGraph®.

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005.00	0.005+00	-1 10E-01	2995.01	1007-01	4 145-01	4 558.01	4 575.01	4 645.01	4 915-01	5 445.01	4 556.01	1.2
50F =00	0.00F+00	-1 87E-01	3945.01	A 195.01	7 205-01	7 307.01	8 475.01	.9 795.01	1.000.400	1.000.000	-1.000+00	1.57
00F+00	0.005+00	2645-01	A 16F 01	A 745-01	8025-01	896.01	-1.04E+00	11167+00	1105+00	1 215 400	-1 715+00	1.1.1
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005+00	0.005+00	4 196-01	7.53E-01	en		OFF-m	-1.40F=00	1.455+00	151E+00	1.635-00	-166E+00	1.0
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000 +000	0.002 +00	-4.70E-01	-8 79E-01	-1 162 +00	-1.440+00	-1710+00	1965-00	1995+00	2006+00	211E-00	2 27E+00	1.5
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mF+m	0.005+00	4 B4E-01	A 195-01	1205-00	-1.665 +00	-1 100 +00	-2 205 -00	2 258 +00	-2 345 400	-2428+00	-7 AAE #00	.26
50E+00	0.00F+00	4 BME-01	A REF 01	1 96.00	177 +00	-1 96F +00	2255.00	-2 395 =00	2.00	-2.535 +00	-2 726 -00	.28
00F+00	0.00F+00	4.805-01	-9 90E-01	1365-00	179F+00	-1 98F+00	-2 MF+00	2425+00	-251E+00	-2 62F+00	-2 ROF #00	30
50F+00	0.005+00	-4.968-01	-1 057-00	1.395+00	-1 835 +00	-201E+00	2 41F+00	2.515+00	2665+00	-2 73E =00	2 165 -00	30
00+100	0.000 +000	-4 908-01	-1 085 -00	-1 428 -00	-1 835 +00	-2 10F+00	2 (95+00)	2 555+00	2685+00	2 79F+00	296F +m	31
505+00	0.005+00	4965-01	-1.105+00	1475.00	-1 IME +00	-2 166 +00	2 505 -00	2675+00	-2 700 +00	2905+00	1005-00	3.2
m+ m	0.002+00	4705-01	-1.095-00	1477.400	1.002 +00	-2 105 +00	-2.618+00	-2.695+00	2815+00	-2 935 +00	-1055-00	1.12
50F+00	0.00F+00	4 595-01	114F+00	DO	1895-00	2285.00	2725+00	2805+00	-2 91E M	3.015+00	-1 WE-00	1.55
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	9000	-O XOWARE		9000	0.30366666							
	10800	-0 3193333		10000	0 31933333							

Figure A21 Example showing how global strain data were obtained.

- (5) Copy the data from B49 to P49, and transpositively paste only the value (not the equation) to a column in the spreadsheet, for example in the column from C52. The detailed operation can be expressed as the following: select the data from B49 to P49, copy, click on C52, go to "Edit" menu, choose "paste special", then select "Value" and "Transpose". Type in the time, from the lab notebook, for each corresponding image in the column left to the global strain column. Note if the global strain values are negative, they can be converted to positive numbers to make the plot looking better without affecting anything. This step is illustrated in Figure A22.
- (6) The "time" and "creep strain" columns thus can be used to generate the global creep strain curve for this material in either Excel[®] or KaleidaGraph[®]. A plot of global strain curve is shown in Figure A23.

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Figure A22 Illustration of how to prepare data for global strain-time plot.



Global Strain vs Time

Figure A23 A sample plot of global creep strain vs. time using the data from Figure A22.

(7) The steady-state creep rate can be obtained using linear regression with the data in the secondary stage, as shown in Figure A24.



Strain Rate Determined from Secondary Stage (Linear regression)

Figure A24 Steady-state creep rate obtained using linear regression with the data from the secondary stage in the global creep strain-time plot.

3.3 Normalized Displacement vs. Normalized Position Through Joint Thickness

The next a few steps are needed to generate normalized displacement vs. normalized position curves. This curve is important for the calculation of localized creep parameters. The final normalized displacement vs. normalized position curve should have all the data points above 0 in y (y>0) and the x values of which are between 0 and 1 ($x \in [0,1]$.)

(8) Start a new spreadsheet. Copy the raw data and paste it to row 1-row 20 as shown in Figure A25.

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- Figure A25 Copy the raw data and paste it to row 1-row 20 in a new spreadsheet for normalized displacement-normalized position plot.
- (9) Normalize x values by using A23=(A2-0)/(9-0). 0 and 9 are the unnormalized

extreme values in x. Thus A24 to A41 can be copied from A23. See Figure A26.

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0 944444	0 0158682	-0 000005	-0 14222	-0174	0 22544	-0 27044	-0.31767	-0 32633	-0 X3544	-0 34978	-0.36411	-0.305.78	-0.459	-0 47378	-0.
1	0 0100006	-0.06789	-014344	-0.174	-0.234	0 27044	-0.31767	-0.33887	-0 35067	40.36	40.30'022	-0 39244	-0.40633	-0.40967	-0.
0	0	0.00065	0 00011	0 00067	40 002	40 00167	0 00144	40 00178	40 00111	0 00039	0.00033	0	0.00064	0.001/8	
0.0666666	0	4 00666	001644	0.01756	0,0000	0.029	0 03144	003456	00,6	0.04256	40.04511	0.09030	0.05509	006144	- 2
		4001222	003,96	0.04022	-0.046	0.00056	0.090/8	0.0274	0.06456	0.06044	006411	4006367	0.08211	0.00362	-9
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0.222222		0 02400	-0.09944	0.07544	0.00911	-0.009944	40 11509	01,200	013133	40.134	-0145/0	015467	-0.17470	0 1/909	- 2
201110		403633	00/511	0.00522	0 10256	0 11950	-013011	-0.141/0	0 15,50	40 16150	-010922	0 10033	0.21544	0 21000	12
1000		-0.04000	-0.08367	-0.096	-0 12356	40 13000	40 15067	40.16178	-0.16/78	0 10000	40 163/2	-0 70/6/	40 237 33	0.25144	1.00
		0.062222	0.09752	0.17009	0 16044	0.12	0.24511	0 22022	0.17922	0 23367	0 21001	0 23/ 33	0 2000	0 31167	
0.6		0.06222	0.09000	011473	0.2000	0 19772	0 22280	0 22033	0 24178	0 20011	0.25	0 20067	0 21211	0 13678	1
0.5		40 060 18	0.09666	0 13433	0 17033	0.19/22	9.20.69	0.23511	0.24178	0 2011	~ ~	0 2000	031311	0.32678	12

Figure A26 Illustration of normalizing x values.

- (10) Find the first data in the last y column (cell P2=5.706 in this example) and normalize it to 0 w.r.t. x in cell P23 by using P23=(P2-5.706)/(9-0). Copy this cell and paste it to every cell between row 23 and row 41, as shown in Figure A27.
- (11) Normalize all the y position with respect to the initial y position in the first y column. This step can be seen in Figure A28 by looking at cell B43 in the spreadsheet. B43=B23-\$B23. Once B43 is obtained, all the y data in rows 43-61 can be copied from B43.
- (12) Now find the last data in the last y column (cell P61=-0.5421 in this example) and normalize it to 0 w.r.t. x in cell P83 by using P83=(P61+0.5421)/(1-0). Copy this cell and paste it to every cell between row 65 and row 83, as shown in Figure A29. Now all the data between row 65 and row 83 satisfy the condition that (y ≻ 0∩ x ∈ [0,1]).
- (13) The normalized displacement vs. normalized position through joint thickness curve can be plotted with the data obtained from (12). An example is shown in Figure A30.

3.4 Localized Creep Parameters

- (14) Open the "normalized displacement vs. normalized position through joint thickness" curve in KaleidaGraph[®] and curve fit all the displacement lines with 3rd order polynomial. The relationship between y and x thus can be expressed as $y = M_0 + M_1 x + M_2 x^2 + M_3 x^3$, as shown in Figure A31.
- (15) Record the coefficients M_1 , M_2 , and M_3 for all the displacement curves (M_0 is not needed) and fill in a new spreadsheet as formatted in Figure A32.
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| 6 336 -00 | 6.14 | 6.776 | 6.7.0 | 1.0 | 6 730 | 6.147 | 10000 | 6 734 | 14400 | 6,000 | 19000 | 19800 | 21000 | 23400 | |
| 5732-00 | 6.074 | 1.00 | 1.00 | 11 | 1.00 | 374 | 4.772 | 6.700 | 2/8 | 6.777 | 6.70 | 6.10 | | 5/06 | |
| 5 600 -000 | 0.04 | 4 101 | 4 177 | | 4 770 | 4 777 | 4.7 | 4 1000 | 2.1 | 6.174 | - 101 | | - | 0.00 | |
| 6.000-000 | 6 497 | 6.79 | 6.146 | 1. | 4 1000 | 4 10107 | 4 100 | 1.00 | 100 | 4.072 | 1.0 | | 1.004 | 4.781 | |
| 6 875-00 | 6.000 | 6 112 | 4 9923 | 10 | 4 777 | 4.070 | 4613 | 1.45 | 4 400 | 4.70 | 4.70 | 4 000 | 4.000 | 3.021 | |
| 6.676-00 | 6 164 | 4 007 | 4 906 | 12 | 4 600 | 4 457 | 4 307 | 43 | 4 718 | 10 | 105 | 2734 | 9 000 | 2,622 | |
| 6 665-400 | 6 779 | 4 005 | 4 790 | 100 | 4 4 15 | 4 347 | 4 192 | 41700 | 4000 | 3 999 | 3 729 | 3613 | 3 365 | 3 166 | |
| 1000 | 6.70 | 1 000 | 1041 | 7.2 | 1 1 1 1 | 4.000 | 3,000 | 3.000 | 3.010 | 2,202 | 3.000 | 2012 | 3.305 | 2,000 | |
| 1.000.00 | 6.100 | 4 787 | 4.600 | 70 | 3.647 | 3 7.1 | 1000 | 3,630 | 2012 | 3 390 | 3 707 | 2042 | 2007 | 2010 | - |
| 6 616 -00 | 6 16.4 | 4 711 | 4 472 | 100 | 3.000 | 3.00 | 3613 | 3.634 | 3,000 | 3 771 | 3.000 | 2 702 | 2.000 | 2,010 | |
| 5.635-00 | 6 1.41 | 4 007 | 4.34 | 3.96 | 3 310 | 2.00 | 3 373 | 3,707 | 3,700 | 3.004 | 3.003 | 2.660 | 3.33 | 2.400 | |
| 6416-00 | 6 1 30 | 160.0 | 1 1 1 1 1 | Tom | Sar | 107 | 2 | 3.16 | 3 (100 | 2.000 | 3.000 | 2.000 | 2000 | 1.000 | - |
| 6 615-00 | 6 13 | 100 | l u a i | 1011 | 101 | 5.4. | 3 192 | 21 | 2 992 | 3 234 | 1 600 | 2 192 | 1962 | 1600 | |
| 6 645 .00 | 6.110 | 1000 | 4 7 7 7 7 | 3 382 | 3.000 | 3,704 | 3 100 | 2.00 | 3 000 | 2.24 | 2.004 | 3.000 | 1 0004 | 1.75 | |
| 6.000-00 | 8.110 | 100 | 4 104 | 3 7 70 | 3 600 | 1.00 | 3 000 | 2.00 | 2,000 | 200 | 2,004 | 20.50 | 1.021 | 1.00 | |
| 6 608-00 | 6.100 | | 4.1.00 | 3 104 | 3.000 | 3 010 | 30.00 | 2.02 | 2 800 | 2.04 | 2.00 | 1000 | 1.000 | 100 | |
| 5 605 -00 | 6 004 | 1.00 | 4 (1990) | 3 201 | 3 307 | 2.007 | 2072 | 2.00 | 1000 | 7.610 | 2.30 | 1.00 | 1.410 | 0.0001 | |
| 6 676-00 | 6 1/17 | 110 | 4.14 | 3 677 | 3 222 | 1047 | 1 100 | 344 | 3649 | 2.000 | 3.754 | 1.474 | 1.000 | 0.83 | |
| 5 57E+00 | 5.095 | 4 415 | 4.14 | 36 | 3 272 | 2.847 | 2676 | 2.56 | 2.466 | 2.374 | 2.174 | 1 509 | 1.299 | 0.6871 | |
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| 0.0031111 | 0 00378 | 6 00022 | 0.00244 | 0.00111 | 0.00144 | 0.00455 | 0.00133 | 0.002 | 0.00344 | 0.00344 | 0.00011 | 0.00378 | 0.00489 | 0 | |
| 0.0025666 | -0.00911 | -0.019 | -0.02011 | -0.03122 | 40.00166 | 40.034 | -0.03711 | -0.03756 | -0.D4511 | -0.04767 | -0.05209 | -0.00344 | -0.064 | 0.07.200059 | |
| 0 0024444 | -0.01467 | -0.035 | -0.04267 | 004844 | 0.053 | -0.05322 | -0.05622 | 40.057 | -0.06289 | -0.06458 | -0.06611 | -0.06456 | 0.000 V | -0.108 | |
| 0 0024444 | -0.02302 | 40.04622 | 0.06233 | 0 08244 | 0.08311 | 40,09656 | -0.11122 | -0.114 | -0.11622 | -0.11969 | -0 13344 | -0.13944 | -0.13 | -0 19833333 | |
| 0 0037778 | 0.03011 | 0.06322 | 0.0/922 | -0.09205 | -0.10322 | 0.11967 | 6.13256 | 013611 | -0.13778 | -0.14956 | 0.15844 | 4117866 | 9.1667 | 40 797 22222 | |
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| 0.00004444 | -0.05289 | -0.097 | -0 11833 | 0 15267 | -0.17633 | -0.16056 | -0.193/6 | 0.20567 | -0.29011 | -0.21711 | -0.243/ | 43 | A 20344 | -0.30344444 | |
| -0.00496699 | -0.05/11 | 40 10256 | -01332/8 | 40 19630 | 40 194899 | 40.221 | 40 22522 | -0.23044 | -0.299 | -0.25667 | -0 27767 | -0.31344 | -0.31656 | -0.34333339 | |
| 0 0105666 | -0.06133 | 40.10944 | 0 14489 | -0 19089 | 6 2778 | 0 23644 | 40 24 967 | 0 25233 | 40 29067 | -0.27066 | -0.29722 | 0.32367 | 40.339733 | -0.36722222 | |
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| 000000000000000000000000000000000000000 | -0.06411 | -0.11767 | -0.16 | 40.202 | 43.22778 | -0.20044 | -0.275 | 42.284 | -0.29111 | -0.312 | -0.33 | 0.37156 | | 0 4004444 | |
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Figure A27 Make the first data in the last y column zeroed.

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05	0	0 05078	-0 096699	-0.13433	-0 17033	-0.19722	-0.22789	-0.23311	0 24178	0 25011	-0.26	-0.29667	4 31311	-0 32678	-0.3
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Figure A28 Normalize all the y position with respect to the initial y position in the first y column.

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0 5421	0.60677	0.482299	0.45689	0.43954	0.42254	0.40039	0.40032	0 33964	0 38054	0 37200	0.36177	O TAXES	0 32254	0 304302222
0 5421	049664	0.45843	0.4471	0.41654	0.40521	0.39643	0.38032	0.37432	0.36154	0 35000	0 33443	0.30477	0 29066	0.200433333
0 5421	0.49566	0.45154	0.43021	0.39688	0.37221	0.36299	0.35477	0.34288	0 33843	0 33143	0.30477	0.27143	0.2651	0,2451
0.5421	0.49999	0 44443	0.41321	0.38195	0.3521	0.30599	0.30177	0.31654	0.30799	0 29032	0 20832	0.23954	0 23043	0 203665666
0 5421	0 49132	0.44321	0 40777	0.37177	0.34408	0 31421	0.30899	0 30032	0.29199	0.2821	0 25543	0.22899	0.21532	0.185433333
0 5421	0 49632	0 43788	0 399332	0 35539	0.32099	0.2981	0.29177	0 28177	0.27299	0 27088	0 25077	0 20132	0 17599	0.152211111
0.5421	0.40832	0.43477	0.39243	0.35043	0.32466	0.29199	0.27743	0,20043	0.26132	0.24343	0 22263	0.10000	0.1491	0.10520300
3 5421	0.49843	0.4321	0.39132	0.34343	0.32177	0.281.77	0.2731	0.26268	0.25099	0.22888	0.2071	0.16199	0 13643	O DESERTOR
15421	0.43699	0.4251	0.38866	0.3391	0.31868	0.27432	0.2631	0.24721	0.23921	0 22368	0 20321	0.14443	0.12066	0.068322222
0.5421	0.48743	0.42232	0.36454	0.33921	0.30999	0 26632	0.25721	0.2441	0.23173	9-25299	0.19221	0.12543	0.10499	0.052302222
0 5421	0.49689	0.41966	0.3791	0 33788	0.30177	0.2551	0.24508	0.23299	0.220	Not-	0.1841	0.1051	0.09366	0.040766667
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0 5421	0.49121	0.41554	0.38377	0 33232	0.26732	0.2401	0.23143	0.21932	0.20799	0.19365	0.17120	010027	0.07799	O DISCHARGE
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Figure A29 Illustration of how to make all the data greater than 0.



Figure A30 A sample plot of normalized displacement vs. normalized position through joint thickness curve.



Figure A31 Curve fit all the displacement lines with 3rd order polynomial.

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	0.01952	-0.06634	0.11112	-0.1530	40.18037	0.238*5	40.23637	0.24766	0 25425	-0.27116	-0.27333	0 25446	-0.38796	-0.4
	0 00137	-0.04943	-0.06917	0.10536	0.13403	0.18292	-0.10619	0.19715	40 20215	4,20839	0.20618	-0.29974	-0.30768	43
	0.01216	-0.04307	-0.02019	0.05218	-0.09319	-0 12967	-0 1453	-0.15316	40 15678	40 14881	-0 14559	-0.22906	-0 22782	0.3
	0.02207	-0.04624	0.01183	-0.01475	-0.05784	-0 02/09/0	-0.1107	-0.11569	-0.11016	-0.09242	-0.09190	-0.17629	-0 14036	07
	0 00936	-0.05896	0.05088	0.02792	-0.02799	0 03027	-0.08139	-0.06475	-0 00620	-0.03924	-0.04413	-0.12968	-0.06901	0.14
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Figure A32 Record the coefficients M₁, M₂, and M₃ form Figure A31 for all the displacement curves (M₀ is not needed) and fill in a new spreadsheet.

(16) Localized creep strain can be calculated using the equation

$$\gamma = \frac{dy}{dx} = M_1 + 2M_2x + 3M_3x^2$$
 for whatever x values desired. Usually, x values

are taken from 0 to 1 with 0.1 as the interval representing different positions through the joint thickness. So localized strain at these positions can be calculated using the above equation. See cell B7 in Figure A33 for the calculation example, where B7=B\$3+2*(B\$4*\$A7)+3*(B\$5*\$A7^2). All the cells between row 7 and row 17 can be copied from B7.

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	-0.0013	-0.04943	0.06917	-0 10536	-0.13403	-0.16292	-0.10019	-0.19715	-0 20215	-0.20839	-0.20618	-0.28874	-0.30768	43
	0.0121	-0.04307	40 00919	40,05918	4 09319	-0.12987	-0.1463	-0.15316	-0 15678	-0.14881	-0.14559	-0.22935	-0 22782	43
	0.02203	0.04624	0.01163	0.01475	4.05784	-0.07898	40.1102	-0.11569	-0 11816	4.09242	-0.09158	-0.17629	-0.14836	4.2
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Figure A33 Illustration of how to obtain localized creep strain.

(17) The localized creep strain data can be copied and transpositively pasted in the format as shown in Figure A34 between row 49 and row 62 with positive values. An example of variation localized strain with time at different location through the solder joint thickness is shown in Figure A35. Localized creep strain can also be plotted with global creep strain as shown in Figure A36.

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Figure A34 Manipulation of data prepared for plotting localized creep strain with time.



Figure A35 Variation of localized creep strain with time.



Figure A36 Plot of localized and global strain with time.

- (18) In order to calculate localized creep strain rate, the localized creep strain curves have to be differentiated. Open the "localized creep strain vs. time" curve in KaleidaGraph[®] and curve fit all the localized strain lines with 3rd order polynomial. The relationship between γ and t thus can be expressed as $\gamma = M_0 + M_1 t + M_2 t^2 + M_3 t^3$, as shown in Figure A37.
- (19) Record the coefficients M₁, M₂, and M₃ for all the localized strain curves (M₀ is not needed) and fill in the spreadsheet as formatted from row 64 to row 68 in Figure A38.
- (20) Fill in A71 to A84 again with time as shown in Figure A39. Localized creep strain rate can be calculated using the equation $\dot{\gamma} = \frac{d\gamma}{dt} = M_1 + 2M_2t + 3M_3t^2$ for whatever t values desired. An example of such calculation can be seen in cell B71, where

B71=B $66+2*(B67*A71)+3*(B68*A71^2)$. All the cells between row 71 and

row 84 can be copied from B71.



Figure A37 Curve fit the "localized creep strain vs. time" curves in KaleidaGraph[®] with 3rd order polynomial.

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3600	4,962-05	4.672-05	4 368-05	4.028-05	3.646-65	3 226 06	2.77E-05	2.288-05	1768-06	1.206-05	6.00E-06			
5400	4.008-05	3748-05	3 396-06	3.04E-05	2.69E-45	2346-05	1.995-05	1.846-05	1296-06	9.338-06	5.80E-06			
7200	3.376-05	2 98E-05	2.61E-06	2.27E-05	1.96E-05	1.66E-05	1.39E-05	1.15E-05	9 30E-06	7.36E-06	5 65E-06			
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23400	304E-05	3.81E-05	4 368-05	4.658-05	4.798-05	4 678-05	4 328-05	3.75E-05	2 968-06	1.948-05	6 968-06			
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Figure A38 Record the coefficients M₁, M₂, and M₃ for all the localized strain curves (M₀ is not needed) and fill in the spreadsheet.

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m2	-3.33E-09	-3.77E-09	-4.05E-09	-4. 6E-09	4.096-09	3.655-09	-3.45E-09	-2.876-09	-2.11E-09	-1.195-09	-871E-11			
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Figure A39 Illustration of how to obtain localized creep strain rates.

(21) Localized creep strain rate can be plotted with time using the data from row 71 to row 84 in Figure A40, as shown in Figure A41, or alternatively, with normalized position through joint thickness using the data from row 87 to row 97 in Figure A40, as shown in Figure A42.

3.5 Three Dimensional Plots

(22) The variation of localized creep strain rate can be plotted with time and normalized position through solder joint thickness using DeltaGraph[®] in a three dimensional format. Before inputting data in DeltaGraph[®], the time, position, and the localized creep strain/strain rate data should be reorganized in a format as shown in Figure A43. The three columns of data can be directly pasted to DeltaGraph[®], as shown in Figure A44.

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Figure A40 Manipulation of data prepared for localized strain rate vs. time/position plot.



Figure A41 A sample plot of localized creep strain rate vs. time.





Figure A42 A sample plot of localized creep strain rate vs. position through solder joint thickness.

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Figure A43 Reorganization of the data in Excel[®] prepared for use in DeltaGraph[®].



Figure A44 Illustration of data directly copied from Microsoft Excel®.

- (23) A three dimensional plot of localized creep strain rate with time and normalized position through solder joint thickness thus can be generated with DeltaGraph[®] by selecting the 3-D surface fill chart in the "chart gallery" menu, as can be seen in Figure A45. An example of the 3-D plot is shown in Figure A46.
- (24) Similarly, the variation of localized creep strain can also be plotted with time and normalized position through solder joint thickness using DeltaGraph[®] in a three dimensional format. The data organization format is also shown in Figure A43 at columns G, H, I from row 101. Follow steps (22) and (23) to obtain this 3-D plot. A sample plot is shown in Figure A47.



Figure A45 Illustration of how to generate three-dimensional graph in DeltaGraph®.



Figure A46 Variation of localized strain rate with normalized position and time.



Figure A47 Variation of localized creep strain with normalized position and time.

APPENDIX B

PROCEDURES FOR OPERATING HITACHI-2500C SCANNING ELECTRON MICROSCOPE

1. HITACHI-2500C SEM Start Up

- (1) Check the three green lights. Those should be on.
- (2) Check x, y, z knobs, those should be at 17, 20 and EX-EX position, respectively.
- (3) Open outer chamber (EVAC-AIR), put the sample on the sample stage using carbon tape. Then EVAC
- (4) Wait until the green light is on for the outer chamber, then open the door of specimen exchange chamber, slide the specimen to the sample stage, unscrew it, pull the long rod back, close the door.
- (5) Wait until all the green lights are on.
- (6) Turn on the electron beam by rotating the black knob clockwise 90 degrees, slowly pull it out, then lock it by rotating back 90 degrees(counterclockwise).
- (7) Turn on the display switch. Never turn off the vacuum switch next to it!
- (8) Wait until the green "ready" light stops blinking in the main panel.
- (9) On screen, check the accelerating voltage and working distance. We usually use 25KV and 15mm. When everything is ok in the menu, hit "enter" to get out of the menu screen.
- (10) Turn on the accelerating voltage by pressing ON in ACC VOLTAGE.
- (11) Turn the filament current up too $100\mu A$ with the speed of $\frac{1}{2}$ division every 30 seconds.
- (12) Press rapid scanning mode.
- (13) Turn up contrast and brightness. Use focus knob to acquire a focused image.

2. HITACHI-2500C SEM Shut Down

- (1) Turn data display off.
- (2) Turn down the brightness and contrast completely.
- (3) Magnification set to: 1.00K.
- (4) Turn down the filament current at a speed of 1 division every 30 seconds.
- (5) Turn off the accelerating voltage by pressing OFF in ACC VOLTAGE.
- (6) Display switch off. Never turn off the vacuum switch next to it!
- (7) Turn off the electron beam by rotating the black handle 90 degrees clockwise, push in, then 90 degrees counterclockwise.
- (8) Set the x, y, z knobs to 17, 20 and EX-EX positions.
- (9) Wait until all the green lights are on.
- (10) Open the specimen exchange chamber, slide the long rod in, take the specimen out of the stage, pull all the way out, hold the rod with your right hand, close the door with your left hand.
- (11) Hold the rod, wait until all the green lights are on
- (12) Open the outer chamber by pressing EVAC-AIR, unscrew the whole stage from the rod, take the sample off, then screw back the stage to the rod,
- (13) Close the outer chamber, then AIR-EVAC, pressing it for a little while.
- (14) Sign in the SEM log book.
- (15) Wait until you see all the three green lights are on before you leave.

APPENDIX C

LIST OF PERSONAL PUBLICATIONS & PRESENTATIONS DIRECTLY RELATED TO THE INVESTIGATION IN THIS THESIS

PUBLICATIONS:

- 1. J.P. Lucas, F. Guo, J. McDougall, T.R. Bieler, and K.N. Subramanian, "Creep Deformation Behavior in Eutectic Sn-Ag Solder Joints Using Novel Mapping Techniques", J. Electronic Materials, 28(11), 1268 (1999)
- F. Guo, S. Choi, J.P. Lucas, and K.N. Subramanian, "Effects of Solder Reflow on Wettability, Microstructure and Mechanical Properties", J. Electronic Materials, 29(10), 1241 (2000)
- F. Guo, S. Choi, J.P. Lucas, and K.N. Subramanian, "Microstructural Characterization of Reflowed and Isothermally-Aged Cu and Ag Particulate Reinforced Sn-3.5Ag Composite Solders", Soldering and Surface Mount Technology, 13(1), 7 (2001)
- 4. F. Guo, J.P. Lucas, and K.N. Subramanian, "Creep Behavior in Cu and Ag Particle-Reinforced Composite and Eutectic Sn-3.5Ag and Sn-4.0Ag-0.5Cu Non-Composite Solder Joints", J. Materials Science: Materials in Electronics, 12, 27(2001)
- 5. F. Guo, J. Lee, S. Choi, J.P. Lucas, T.R. Bieler and K.N. Subramanian, "Processing and Aging Characteristics of Eutectic Sn-3.5Ag Solder Reinforced with Mechanically Incorporated Ni Particles", J. Electronic Materials, 30(9), 1073 (2001).
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PRESENTATIONS:

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- "Microstructural Characterization of Reflowed and Isothermally-Aged Cu and Ag Particulate Reinforced Sn-3.5Ag Composite Solders", F. Guo, S. Choi, J.P. Lucas, and K.N. Subramanian, Pb Free and Pb Bearing Solders, TMS Fall Meeting, Oct. 31-Nov. 4, 1999, Cincinnati, OH, presented by F. Guo.
- "Creep Behavior in Cu and Ag Particle-Reinforced Composite and Eutectic Sn-3.5Ag and Sn-4.0Ag-0.5Cu Non-Composite Solder Joints", F. Guo, J.P. Lucas, and K.N. Subramanian, Pb Free and Pb Bearing Solders, TMS Fall Meeting, Oct. 31-Nov. 4, 1999, Cincinnati, OH, presented by F. Guo.
- "Effects of Solder Reflow on Wettability, Microstructure and Mechanical Properties", F. Guo, S. Choi, J.P. Lucas, and K.N. Subramanian, Packaging and Soldering Technologies for Electronic Interconnects, TMS Annual Meeting, Mar. 12-16, 2000, Nashville, TN, presented by J.P. Lucas.
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