

**Mechanical Behavior and Microstructural Evolution of SAC and SAC+Bi Solder
Alloys in Harsh Environment Applications**

by

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Abstract

The microstructure and mechanical properties of lead free solder joints in electronic assemblies are constantly evolving when exposed to isothermal aging. These changes lead to dramatic reductions in reliability of lead free electronic assemblies subjected to aging. The root cause of the changes in solder joint mechanical behavior is the evolution of the SAC solder microstructure that occurs during aging. The most well-known and widely observed changes are coarsening of the Ag_3Sn and Cu_6Sn_5 intermetallic compounds (IMCs) present in the eutectic regions between beta-Sn dendrites. In the most prior studies, it has been impossible to measure the changes that occur in IMC size and spacing since observations for different aging conditions (e.g., different aging times) were made using different solder joints. Thus, the comparisons made were necessarily qualitative in nature since the two microstructures were from different samples, and thus could not be directly compared in a quantitative manner. This dissertation demonstrates new procedures that removed the limitations of prior studies on the effects of aging on lead free solder microstructure and addresses those changes in the properties of lead free solders by conducting four different projects.

In the first and second part of this work, Scanning Electron Microscopy (SEM) has been utilized to examine aging induced microstructural changes occurring within lead free solders. Unlike many prior studies, fixed regions in the solder cross-sections were monitored throughout the aging process, rather than examining different samples and/or different regions after the various aging exposures. Nanoindentation marks were added to the cross-sections at certain locations to facilitate locating the fixed regions of interest in subsequent microscopy observations. After preparation, the samples were aged at $T = 100$

and 125°C, and the microstructures were observed and recorded in the selected regions after various aging exposures using SEM. With this approach, time-lapse imagery of the microstructure evolution in a particular region of a solder joint has been recorded as a function of the aging time. When placed together sequentially, these images can be used as frames to create experimentally recorded movies of the microstructural evolution in SAC solders exposed to aging. This approach has allowed the visualization of phenomena such as the coalescence and migration of intermetallic compounds (IMCs) and the coarsening of beta-Sn dendrites. The aging induced changes in number of IMCs, total area of all IMCs, average particle area, and average particle diameter have been quantified for several fixed regions in the solder samples.

In the third project, it was found that adding Bismuth (Bi) to the SAC composition to form SAC+Bi alloys has been effective in reducing both intermetallic coarsening and the degradations in material properties. These studies have been performed with the well-known SAC_Q alloy that modifies SAC405 to include 3.0% Bi. There have been no prior studies to examine the performance of SAC+Bi alloys with other concentrations of Bi. In this investigation, the mechanical behavior, microstructural evolution, and reliability of several different SAC+Bi alloys with various levels of Bismuth (1.0%, 2.0%, and 3.0%) have been chemically analyzed and then mechanically tested. To examine base mechanical behavior, stress-strain tests were performed for SAC_Q and SAC305 alloy.

The effects of aging were studied for the SAC305 and SAC_Q alloys using both mechanical testing and microstructure observations. For the solder mechanical response, the fabricated uniaxial specimens were aged (preconditioned) at $T = 125\text{ }^{\circ}\text{C}$ for several durations of aging including 0, 2, 6, 12, and 24 hours. Stress-strain tests on the aged

specimens were then performed at a single strain rate of 0.001 (sec^{-1}), at temperatures of 125 °C. In particular, aging induced coarsening of the IMCs was studied for each alloy using Scanning Electron Microscopy (SEM), and correlated to the corresponding material property evolution findings. The results have shown that all of the SAC+Bi alloys demonstrate superior resistance to aging effects relative to SAC305. During aging, the bismuth was observed to go into solution within the beta-Sn dendrites and in the intermetallic rich regions between dendrites. It was observed that the coarsening of the intermetallic compounds was greatly mitigated in the SAC+Bi alloys relative to that observed in SAC305. The resistance to aging and increases in mechanical properties were found to be directly proportional to the amount of Bi present in the SAC+X alloy.

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CHAPTER 1

INTRODUCTION

1.1 Lead Free Solders in Microelectronics

Solders have been used as the interconnecting material in electronic assemblies to provide both electrical and mechanical connections between components. The conventional eutectic or near eutectic Sn-Pb solder has been extensively used in the electronics industry due to its outstanding solderability and reliability [1]. However, the lead solders have been prohibited in many countries despite their advantages, this is because lead is a toxic element and it is detrimental to both the environment and the human body [2-8]. Therefore, efforts have been made to eliminate lead in electronics and search for the lead free solder alloys. Lee [3] outlined some features that the lead free solder candidates should have: similar melting temperature to the standard lead solders, good wetting ability, good electrical and mechanical properties, nontoxicity, and low cost. Sn–Ag, Sn–Ag–Cu, and other alloys containing elements like Sn, Ag, Cu, Bi, In, and Zn have been identified as the promising lead free solders for replacing the conventional eutectic lead solder [1]. Among these candidates, Sn-Ag-Cu (SAC) lead free solder series are the most widely used lead free solders in the industry at present [9].

Compared with the 96.5Sn-3.5Ag binary eutectic alloy, near eutectic SAC solder alloys have relatively low melting temperatures, and they have better mechanical and manufacturability properties than other lead free solders. The addition of Cu in the SAC alloys contributes to lowering melting temperature and improving the wettability [10]. The composition and melting temperature of the ternary eutectic SAC solder have been investigated by many researchers. Initially, it was reported that the eutectic composition of the SAC solder system was Sn-3.6Ag1.5Cu [11] or Sn-4.7Ag-1.7Cu [12]. Recent studies tend to agree that the eutectic point of SAC solder is close to Sn-3.5Ag-0.9Cu (3.5 wt. % Ag, 0.9 wt. % Cu and the balance 95.6 wt. % Sn), and its melting point is around 217.2 °C [13-15]. There are a variety of other SAC alloys being used, including the SACN05 series (SAC105, SAC205, SAC305 and SAC405), near eutectic SAC alloys (SAC387, SAC396, and SAC357), and some other alloys (SAC3810, SAC3595, SAC0307, and SAC107) that used in special applications such as elevated temperature application, drop and shock optimization, etc. [16].

Figure 1.1 shows the ternary phase diagram for the SAC lead free solder series [17]. The near eutectic SAC solidifies into three phases, i.e., β -Sn (primary phase), Ag_3Sn and Cu_6Sn_5 . Figure 1.2 shows a typical microstructure of SAC lead free solders. It consists of β -Sn dendrites surrounded by interdendritic eutectic regions incorporating a fine dispersion of Ag_3Sn and Cu_6Sn_5 intermetallic particles in β -Sn. The volume fraction of Ag_3Sn IMCs is much higher than that of Cu_6Sn_5 IMCs in SAC solder microstructures. It has been reported that the IMC particles have higher strength than the bulk material [18, 19], and the dendrite structure can effectively pin and block movement of dislocations and therefore improve solder mechanical behavior [20, 21].

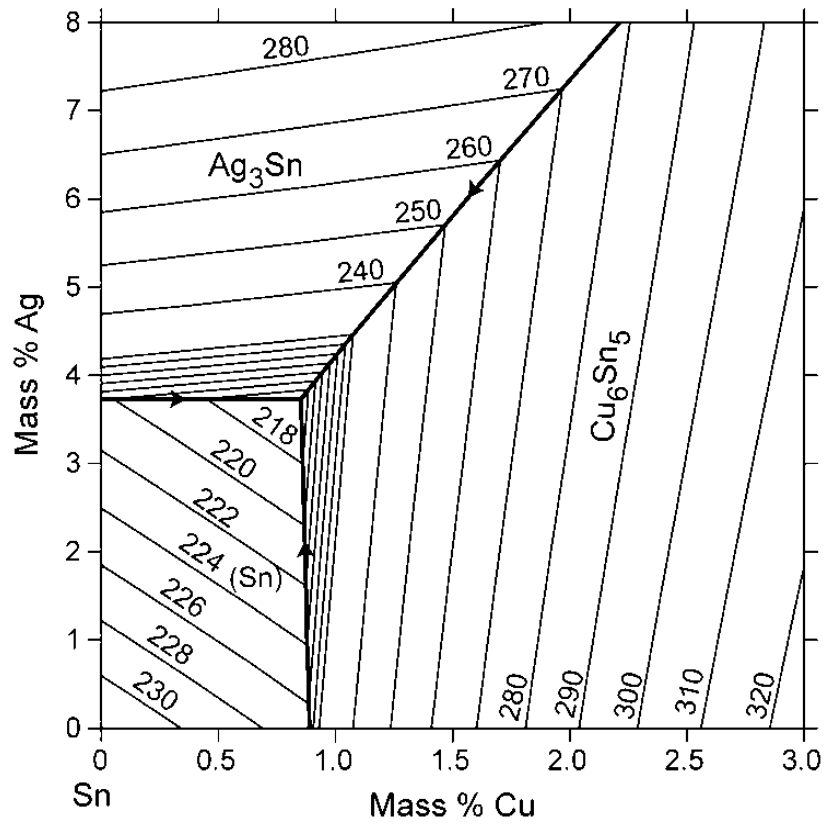


Figure 1.1 Ternary Phase Diagram for Sn-Ag-Cu System [17]

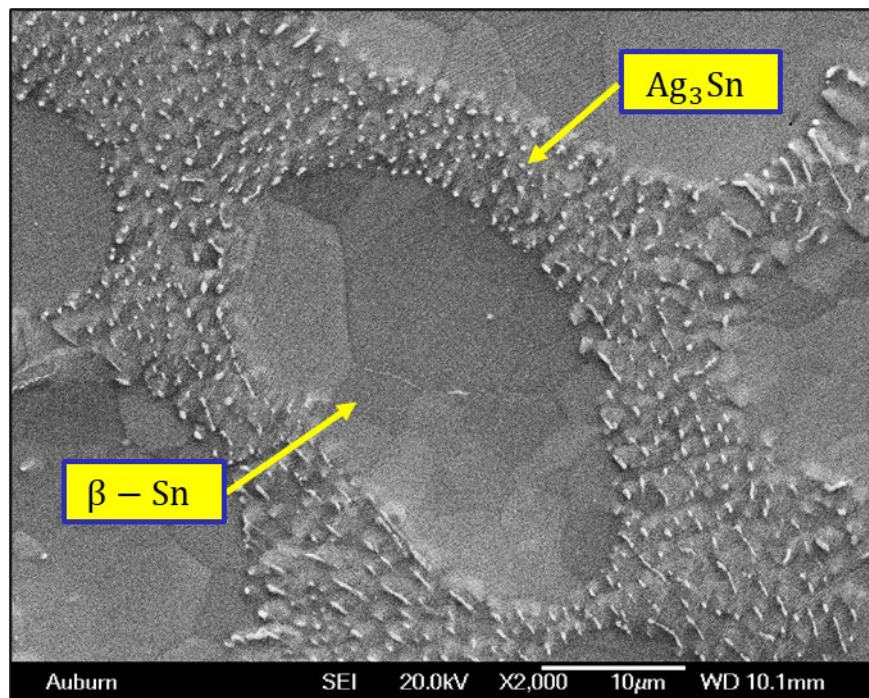


Figure 1.2 Typical Microstructure of SAC Lead Free Solders

For the SAC lead free solders, the properties of Sn dominate their behavior as Sn has a very high weight percentage. Sn has a Body-Center Tetragonal (BCT) crystal structure with lattice parameters $a = b = 5.83 \text{ \AA}$ and $c = 3.18 \text{ \AA}$. Therefore, it is highly anisotropic in mechanical properties such as elastic modulus and hardness. In other words, the mechanical properties of Sn are highly dependent on the grain orientation. As shown in Figure 1.3, the elastic modulus of Sn is 67.6 GPa in the (001) direction, while it is only 23.6 GPa in the (100) direction [22]. Also, Sn is highly thermally anisotropic: the coefficients of thermal expansion (CTE) in the principal directions at 30 °C are $\alpha[100] = \alpha[010] = 16.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ and $\alpha[001] = 32.4 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [23].

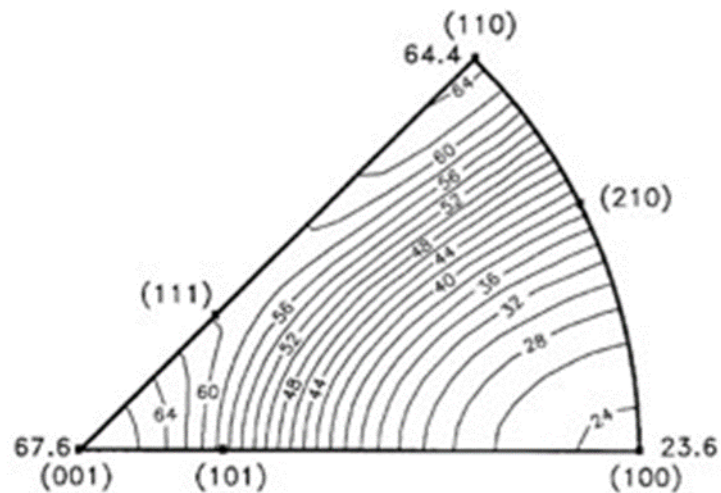


Figure 1.3 Variation of Elastic Modulus of β -Sn with Grain Orientation [22]

1.2 Candidates for Alternative Lead Free Solders

About 70 different alloys were proposed as an alternative to the Sn-Pb solder. Most of these are Sn based solder where Sn is the main constituent along with one, two or even three other minor elements. These minor elements are added mainly to 1) decrease the melting temperature and 2) improve wetting and reliability of the solder [2]. The properties

of Sn and the effects of different alloying elements on the Sn based solder alloys are described below:

1.2.1 Tin

The melting temperature of elemental Sn is 231 °C. One of the main reasons of choosing Sn as the principle component in the lead free solder for electronic applications is its ability to spread and wet a number of various different substrates. In the solid state, tin can have two different phases or crystal structures 1) white or β -Sn with tetragonal crystal structure and 2) gray or α -Sn with diamond cubic crystal structure. At the room temperature the thermodynamically stable phase is β -Sn. Upon cooling, when the temperature goes below 13 °C (allotropic transformation temperature), α -Sn becomes the thermodynamically stable phase. The allotropic transformation of β -Sn to α -Sn, results a significant volume change (around 27%) causing blistering of the tin surface, cracking or disintegration. This phenomenon is mainly a surface event and often referred as ‘tin pest’. The low ductility of α -Sn is another reason of causing blistering and cracking of the tin after the transformation [2, 24, 25]. Although the equilibrium temperature for β -Sn to α -Sn is 13 °C, the transformation occurs only after a significant undercooling and an extensive incubation period as long as several years. For example, no ‘tin pest’ was found on a SAC387 bulk sample after storing at -40 °C for 5 years [25]. Presence of heterogeneous nuclei, also known as seeding, can considerably accelerate the kinetics of the transformation. The possibility of $\beta \rightarrow \alpha$ transformation in a actual solder joint is even limited due to the constraints (component and substrate) on the both side of the joint [24, 25].

Addition of other elements, as an impurity, can affect the allotropic transformation. For example, the presence of Pb, Bi, Sb, Cu, Ge and Si inhibit $\beta \rightarrow \alpha$ transformation while the presence of As, Zn, Al and Mg promote the transformation [24, 25].

Sn has a body centered tetragonal crystal structure (β -Sn), at room temperature, which is anisotropic. Hence, tin shows an anisotropic thermal (e.g. CTE) and mechanical (e.g. elastic modulus) properties as shown in Figure 1.4. As a result, during thermal cycling experiment, cracking occurs along the grain boundaries [2].

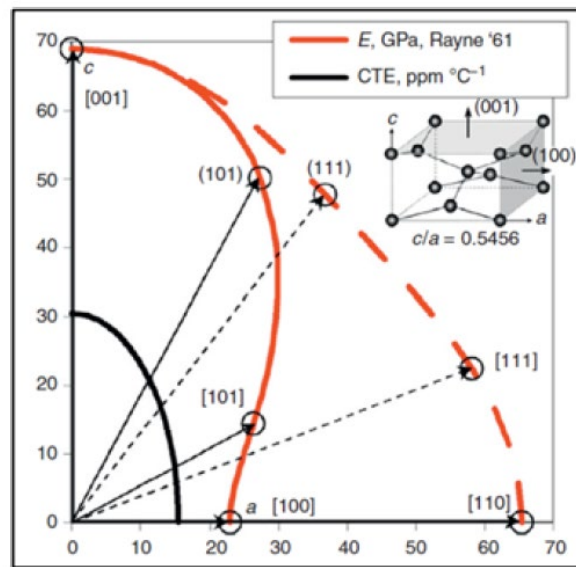


Figure 1.4 Elastic Modulus and Coefficient of Thermal Expansion (CTE) of Tin as a Function of Crystal Orientation [2]

1.2.2 Chromium (Cr)

Cr helps to improve shear ductility after long term aging. Besides, it also suppress kirkendall void formation in the solder joints [26].

1.2.3 Nickel (Ni)

Among all the micro-alloy additives, Ni is one of the most common element. Addition of Ni improves fluidity of SAC solders. Ni also improves the high strain rate properties of solder joints. For example, the drop strength of SAC alloys can be significantly improved by Ni addition. Although Ni does not have any significant influence on the creep properties of the solder, it inhibits Cu diffusion and thus reduce the thickness of Cu_3Sn intermetallic compound (IMC). The Ni addition greater than 0.01 wt% could suppress the growth of Cu_3Sn IMC even after long term (2000 hours) aging. Since Cu_3Sn IMC is very brittle, the growth of Cu_3Sn layer is very critical for the brittle failure of the solder joints. Addition of Ni on SAC solder causes to form more stable $(\text{Cu}, \text{Ni})_6\text{Sn}_5$ IMC which act as a barrier layer and suppress the growth of Cu_3Sn layer. Therefore, by reducing the thickness of brittle Cu_3Sn layer, Ni helps to improve strength of the solder joints. Ni also helps to improve strength by refining solder microstructure [27].

1.2.4 Zinc (Zn)

While Ni reduces only the formation Cu_3Sn , Zn doping can retard both Cu_3Sn and Cu_6Sn_5 IMC's in SAC solders. Zn also helps to improve the interface quality after multiple reflow and high temperature aging. Addition of 1.5% Zn in SAC207 solder could refine Ag_3Sn and Cu_6Sn_5 IMC's and hence increase strength by dispersion strengthening [26].

1.2.5 Cobalt (Co)

Co helps to reduce the growth of Cu_3Sn layer during high temperature aging. Addition of small amount of Co (<0.1 wt%) can improve the properties of SAC solders.

Co increases the number of nucleation sites and hence significantly refine the grains of SAC305 solder. Thus it helps to improve shear strength of the solder joints [26].

1.2.6 Bismuth (Bi)

If added in small amount, Bi can improve the wetting ability and reduce melting temperature of lead free solder alloys. It also increases strength of the bulk solder and inhibit the large Ag_3Sn formation in the bulk solder. It is recommended to avoid Pb contamination in the solder before using Bi as an additive. Because Bi can react with Pb to form a brittle IMC at the grain boundary and reduce strength significantly. If present in excess amount, Bi can cause solidification crack due to the increase in the gap between solidus and liquidus temperature [26].

1.2.7 Antimony (Sb)

Sb improves mechanical properties of lead free solders but it is toxic in nature. A small percentage (0.5 wt%) of Sb can improve drop test reliability of SAC solder joints [27]. Besides, Sb also helps to enhance strength of the solder by solid solution strengthening [28].

1.2.8 Germanium (Ge)

Ge doped solders shows low Cu dissolution from the Cu pad and hence suitable for the wave soldering process. Ge significantly improve wetting properties of the lead free solders and refine the solder microstructure. As a result, Ge addition improves the strength and ductility of the lead free solder [27].

1.2.9 Sn-Ag-Cu System

As shown in Figure 1.1, Sn-Ag-Cu (SAC) has been the most popular, widely used lead free solder in today's market. Although they are still not identified as the "drop in" replacement for all applications, a variety of SAC alloys with different chemical compositions have been proposed by various user groups and industry experts. These include: SAC105 (98.5Sn-1.0Ag-0.5Cu), SAC205 (97.5Sn-2.0Ag-0.5Cu), SAC305 (96.5Sn-3.0Ag-0.5Cu), and SAC405 (95.5Sn-4.0Ag-0.5Cu), known as the SACN05 series; SAC387 (95.5Sn-3.8Ag-0.7Cu), SAC396 (95.5Sn-3.9Ag-0.6Cu), and SAC357 (95.2Sn-3.5Ag-0.7Cu), identified as near eutectic SAC choices; SAC3810 (95.2Sn-3.8Ag-1.0Cu), SAC3595 (95.55Sn-3.5Ag-0.95Cu), SAC0307 (9Sn-0.3Ag-0.7Cu), and SAC107 (98.3Sn-1.0Ag-0.7Cu), designed for special needs such as high temperature application, drop and shock optimization, etc. The main benefits of the various SAC alloy systems are their relatively low melting temperatures compared with the 96.5Sn-3.5Ag binary eutectic alloy, as well as their superior mechanical and manufacturability properties when compared to other lead free solders [29].

Figure 1.3 shows a typical 3-D ternary phase diagram. The contours on the top surfaces of the figure represent the isothermal lines. Each of the 3 sectors represents the binary phase diagram of two of the three elements. The center of the diagram, where the isothermal lines reach the common, lowest point, is the eutectic point of the ternary system. Figure 1.4 is the top view (2-D) of the ternary phase diagram of Sn-Ag-Cu.

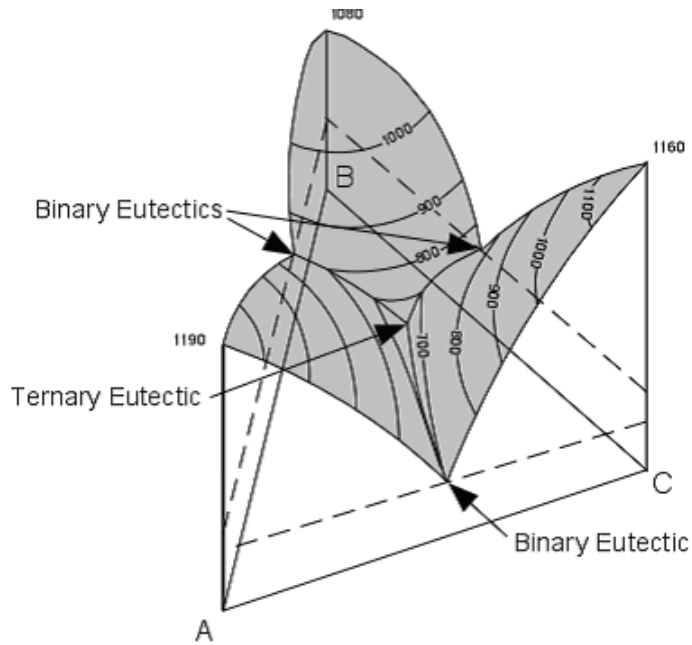


Figure 1.5 Typical 3-D Ternary Phase Diagram

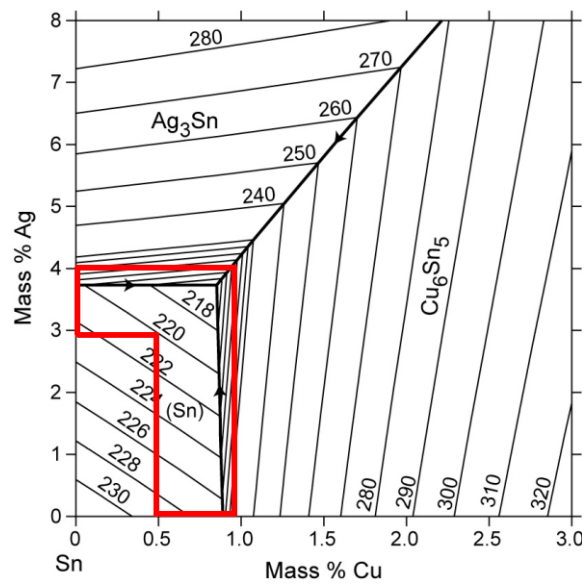


Figure 1.6 Sn-Ag-Cu Ternary Phase Diagram

The area indicated in the red box is the near eutectic region. Most of the SAC alloy compositions currently on the market are within this region. The eutectic and near eutectic

melting temperature has been determined to be 217 °C, although the precise eutectic point is not known [30].

In SAC alloys, the formation of intermetallic compounds between the primary elements Sn and Ag, and Cu affect all the properties of the alloys. There are three possible intermetallic compounds that may be formed: Ag_3Sn forms due to the reaction between Sn and Ag (Figure 1.5) and Cu_6Sn_5 forms due to the Sn and Cu reaction. The compound Cu_3Sn will not form at the eutectic point unless the Cu content is high enough for the formation of Cu_3Sn at higher temperatures, so in bulk specimens Cu_3Sn is not presented. There is no reaction between Ag and Cu to form any kind of intermetallic compounds. The particles of intermetallic compounds possess much higher strength than the bulk material. Fine intermetallic particles in the Sn matrix can therefore strengthen the alloys. The intermetallic compounds can also improve the fatigue life of the solders, as SAC alloys are reported to be 3-4 times better fatigue properties than the Sn-Pb eutectic solders. The higher fatigue resistance is believed to be contributed by the interspersed Ag_3Sn and Cu_6Sn_5 particles, which pin and block the movement of dislocations. The many patents that have been granted for SAC systems have limited their use and hindered research on several of the SAC alloys. However, many familiar alloy such as SAC305 and SAC405 are not patented to avoid excessive licensing and fees [29].

Despite the benefits mentioned above, SAC family solders sometimes are still questionable as complete substitutes for eutectic Sn-Pb because of costs, some patent issues (particularly outside Europe), aesthetic consideration (dross problem of SAC solders), and relatively high melting temperature (217 °C vs. 183 °C).

1.2.10 Sn-Ag-Cu + X System

Sn-Ag-Cu alloys have shown potential to be successful substitutes for eutectic Sn-Pb, however, the industry is still looking for a “perfect” solution. According to the results of many recent studies, performance characteristics of solder alloys are able to be optimized by doping, that is, by adding a small amount of other alloying elements into the SAC solder alloys.

The proposed doping element candidates include Bi, Ni, Co, Ge, Zn, La, Mg, Mn, Ce, Ti, Fe, In, B, etc. For example, adding 0.05% (wt.) Ni can successfully stabilize the microstructure, inhibit the excessive consumption of metal base and thus increase the reliability of the solder joints [31-33]. In addition, doping rare earth (RE) elements can significantly enhance wettability, refine microstructure and improve ductility of SAC alloys [34-37].

Even though dopants can greatly alter the mechanical, electrical and physical behavior of SAC solders, the effect on melting temperature, however, is found to be negligible. This is another advantage for doped solder alloys because manufacturers can still use the same processing conditions as conventional SAC alloys.

Meanwhile, the known issues for SAC-X solders are also apparent. For instance, the material properties and interfacial behavior of solder alloys have been demonstrated to be very sensitive to the quantity of the X-additive. As a result, it takes much more time and cost to figure out the optimal composition levels for the dopants.

1.3 Mechanical Properties of Lead Free Solders

As the electronic industries transition to lead free soldering by the motivation of environmental concerns, legislative mandates, and market differentiation, great efforts have been undertaken to develop desirable lead free solders and establish a corresponding database of material properties. Many researchers have attempted to measure the key mechanical properties of lead free solders. However, large discrepancies have been found in the published data from various groups. There are several reasons for these discrepancies. Firstly, the differences in specimen preparation methods among the researchers cause different microstructures in the specimens that directly affect the experimental results significantly. Secondly, the testing methods and the test conditions may also be different which will again affect the results. Thirdly, mechanical properties obtained from the bulk solders might be different from the measured properties of solder joints. Finally, the lack of standardization in the data acquisition and processing of mechanical properties makes it difficult to obtain good laboratory-to-laboratory comparisons. Hence, mechanical properties of solder joints are critically important to ensure reliability of the electronic products. Among all the mechanical properties, tensile, fatigue, and creep performance of the solder are critically important. Thus an accurate measurement of mechanical properties and development of constitutive equations for solder materials are required in mechanical design, process optimization and reliability assessment.

Under the action of an increasing stress, metals usually exhibit elasticity, plasticity, and a maximum in stress is followed by necking and fracture. The slope of the linear elastic portion of the stress vs. strain plot is the modulus, and the stress at termination of elastic

behavior is the yield stress. The extent of deformation prior to fracture is known as ductility. Ceramics display only elastic behavior until fracture, which is associated with cracking and very limited deformation (brittleness). Polymers may exhibit both characteristics above according to the temperature. Above the glass transition temperature, T_g , extensive deformation due to mechanisms quite unlike those in metals may follow a small degree of elasticity. Below this temperature, polymers exhibit ceramic-like behavior. In all material categories, the maximum stress attained is the tensile/compressive/shear strength according to the mode of stressing employed. Composites are physical mixtures and exhibit the average properties of their components, taking into account the proportions of each. These characteristic features of monotonic behavior are summarized in Figure 1.5. The fracture strains of brittle materials and the yield strains of metals are generally less than 1% (the yield strain of solders is around 0.1–0.2%). The amount of deformation prior to the attainment of maximum strength is between about 3% and 7% for common solder alloys.

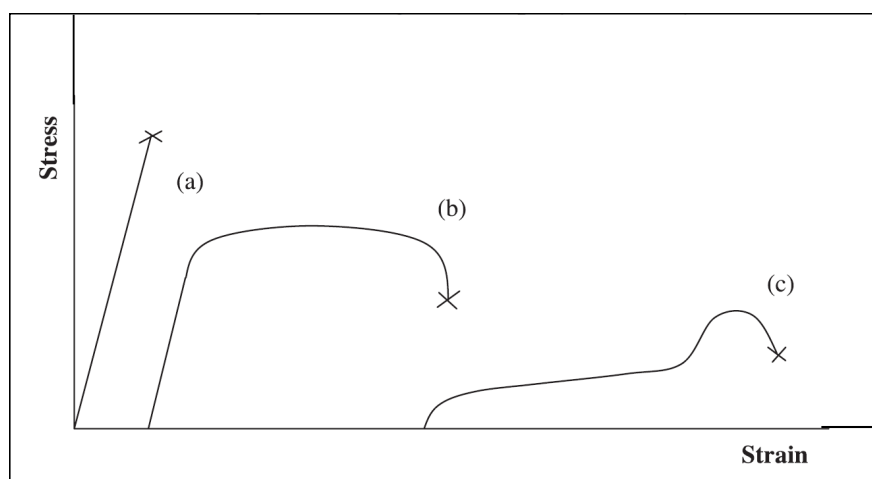


Figure 1.7 Schematic Overview of Mechanical Behavior of a) Ceramics, Polymers below their Glass Transition Temperature (T_g) and Non Ductile Material b) Ductile Materials c) Polymers above T_g

Tensile properties indicate how the material will react to forces being applied in tension. Although solder joints are rarely under pure tensile/compressive loading, tensile properties are still crucial indicators for design purposes. Through tensile tests, several material properties can be determined, such as effective modulus, yield stress (YS), ultimate tensile strength (UTS), elongation, etc. In most of the cases that engineering stress-strain curves are employed by neglecting the change in cross sectional area.

Tensile properties are generally described by stress-strain curves. Figure 1.6 shows a typical engineering stress strain curve. A typical engineering stress-strain curve for solder alloys consists of an elastic region and a plastic region. In the elastic region, when the stress is reduced, the material will return to its original shape. In this linear region, the material obeys the relationship defined by Hooke's Law. However, since the effective modulus includes small inelastic deformations or time-dependent deformations such as creep, it is usually smaller than the dynamic modulus measured by the acoustic or ultrasonic wave method, which largely eliminates the inelastic deformation due to rapid wave propagation [38-40]. Also, Ralls, et al. showed that the elastic modulus of metal will decrease with increasing temperature [42]. The underlying reason for this is because the distance between adjacent atoms increases at higher temperatures which in turns decrease the elastic modulus.

When the load is high enough to exceed the elastic limits the material will experience plastic deformation, which is permanent. At this stage the material is undergoing a rearrangement of its internal molecular or microscopic structure, in which atoms are being moved to new equilibrium positions. Specimens subject to plastic deformation will simultaneously elongate and decrease in diameter. The Yield Stress (YS)

is defined as just enough stress to cause the onset of plastic deformation. However, YS is difficult to determine. In engineering practice, a specified small amount of plastic deformation is used, with 0.2% being the widely accepted value [42]. This is determined by a parallel line drawn at 0.2% of the strain to the elastic slope (Figure 1.6). When the load is removed at a point above the yield stress, the stress-strain curve will be approximately parallel to the initial modulus.

The ultimate tensile strength (UTS) is the maximum engineering stress level reached in a stress-strain test. In ductile materials similar to solders, the UTS are usually well outside of the elastic portion and the elastic strain is very small comparing to the plastic strain. When necking occurs, the engineering stress decreases and the specimen eventually fail.

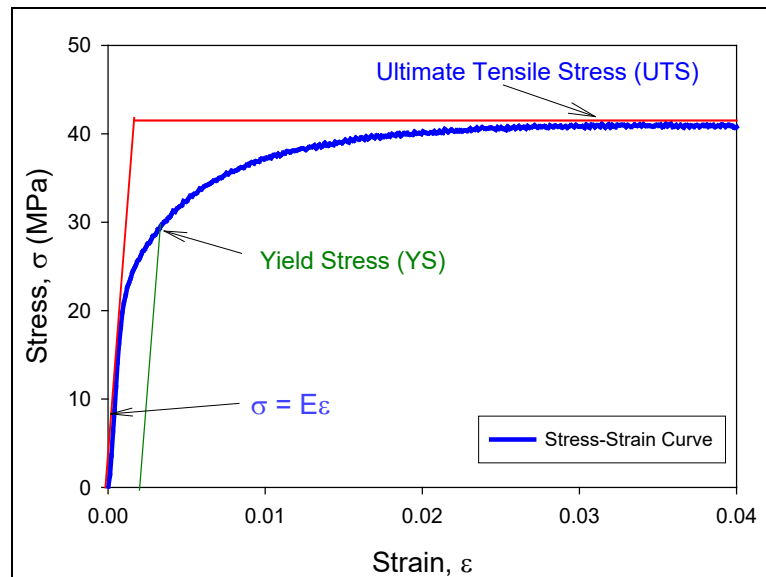


Figure 1.8 Typical Stress-Strain Curve.

1.4 Nanoindentation

Indentation testing is a technique where a hard tip, with known mechanical properties, is pressed into the surface of a test sample to extract the test sample's properties. The load applied on the indenter tip caused it to penetrate into the test sample surface. When the applied load reaches to the user specified value, it can be held for a certain period of time (for creep properties) or remove instantaneously (for hardness and elastic modulus). Removal of the applied load leaves an impression or indent on the sample surface.

Nanoindentation (NI) is a kind of indentation testing where the penetration length is measured in nanometer. The development of the NI technique has been motivated by the miniaturization of the engineering materials as well as the development of the nanostructured materials. Since the area of the indenter tip is well defined (known geometry), the indent area can be easily determined from the tip penetration depth from the sample surface. Elastic modulus, hardness and creep properties of a material can be obtained from indentation load displacement data [43].

Because of having very high hardness and elastic modulus, diamond is typically used to make indenter tip. Indenter tips are available in different shape and the choice of indenter tip shape depends on the type of required information from a NI test. Berkovich tip is used in this study (Figure 1.9).

This is the most common indenter tip and used to measure mechanical properties using a NI technique. The shape of a Berkovich tip is similar to a three sided pyramid where the faces meet at a single point (Figure 1.5). The tip can maintain its self-similar geometry to a significantly small scale. The center to face angle of the tip is 65.3° .

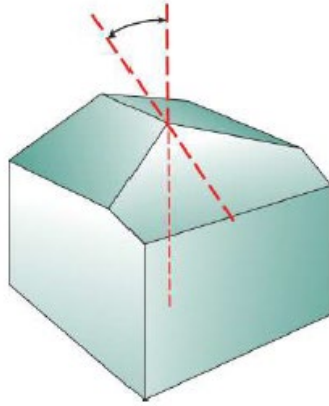


Figure 1.9 Berkovich Tip.

1.5 Scanning electron microscope (SEM) and Focused Ion Beam (FIB)

By using combined imaging and analytical performance of a high resolution field emission scanning electron microscope (FE-SEM) with the processing ability of a focused ion beam (FIB), 2D surface sensitive images or when performing 3D tomography can be obtained. By scanning the sample with a focused beam of electrons, SEM can be used to produce images with high resolving power and high depth of focus. There are various signals that result from the interactions of the electron beam with the sample atoms, including secondary electrons (SE), back-scattered electrons (BSE), photons of characteristic X-rays, etc[44,45]. Figure 2.16 shows the various depths of the produced signals within the sample. SE and BSE have been used to form images in this study. The inelastic collision of electronic beam and the sample results in secondary electrons, and SE images provide information about morphology and surface topography. The back-scattered electrons emit backwards elastically during the collision of electron beam and the sample, and they are sensitive to atomic mass of the nuclei they scatter from. The brightness of a heavier element is greater than that of a lighter element in BSE imaging [46].

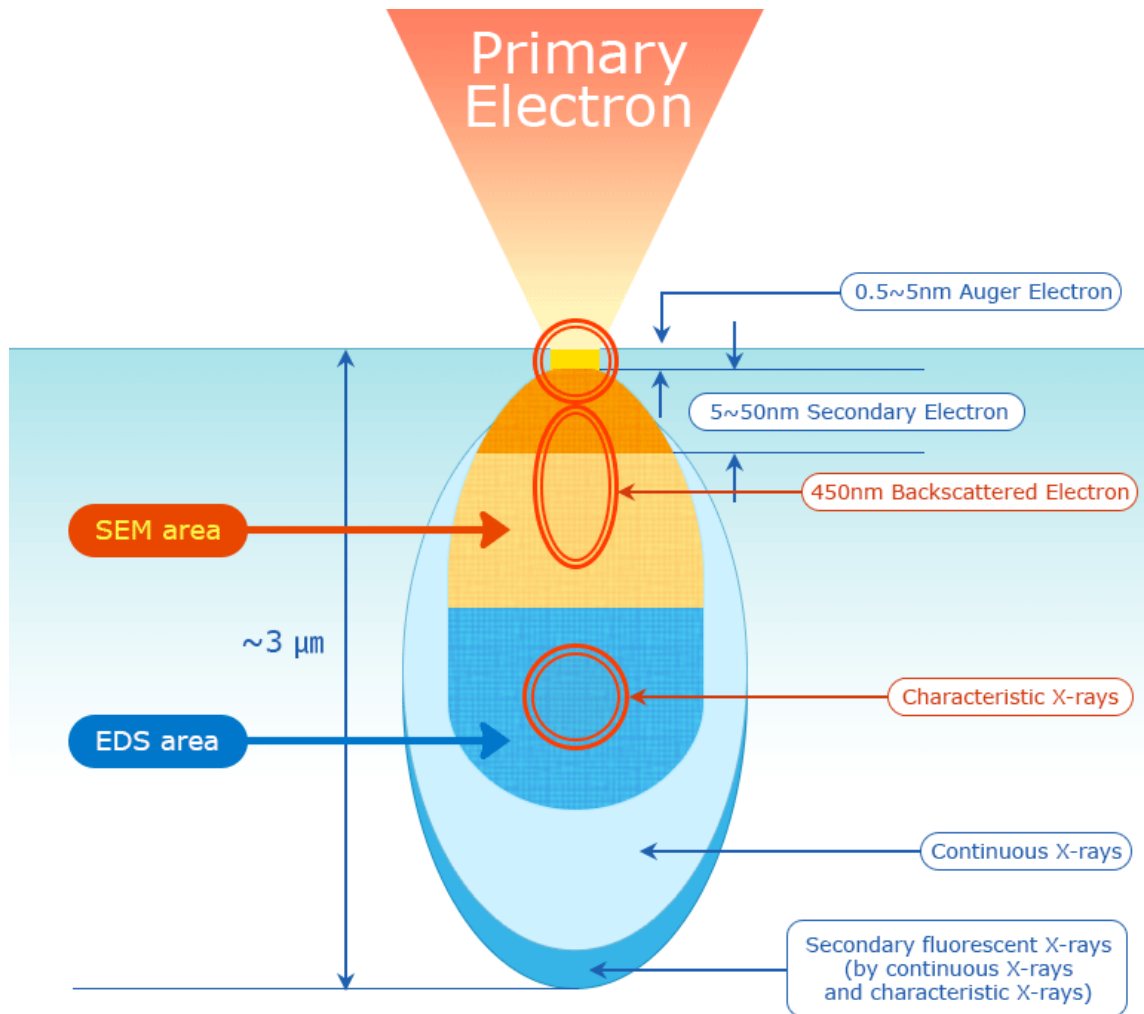


Figure 1.10 Various Signals at Different Depths Within the Sample

1.6 Objectives of This Research

The motivation of this research is to explore the high temperature mechanical behavior and microstructural evolution of lead free solder alloys for harsh environment applications, and to develop new constitutive equations and reliability models that include aging effects to predict solder joint reliability in microelectronic packaging. The Primary objectives of this research involve:

- (1) Investigate the uniaxial tensile properties of SAC305 and doped SAC solders at high temperatures.
- (2) Compare the tensile properties of the solder alloys to examine the effect of the dopants.
- (3) Study the effects of extreme high temperature aging on the mechanical behavior (tensile and creep) of lead free solders.
- (4) Investigate the effects of different aging temperature and aging time on the microstructure of lead free solders using Scanning Electron Microscopy system.
- (5) Investigate the chemical composition and typical microstructure of different SAC+Bi alloys by using EDS and SEM.
- (6) Perform quantitative analysis of the microstructural evolution of SAC and SAC+Bi alloys subjected to extreme high temperature aging.
- (7) Compare the aging induced degradation of SAC305 and different SAC+Bi alloys and explain the effect of Bi in SAC solder.
- (8) Obtain the microstructure of the cross-section after FIB cut to explore the diffusion inside the alloys.

1.7 Organization of the Dissertation

This dissertation mainly focuses on investigating the aging dependent Mechanical behavior and microstructural evolution of lead-free Solder alloys and is presented in the following chapters:

Chapter 1: Introduction to lead free solders alloys and mechanical properties of solder materials.

Chapter 2: Literature review on isothermal aging effects, mechanical properties, nanoindentation on SAC and SAC+Bi solder joints, microstructural evolution during aging of SAC alloys, life prediction and reliability models of electronic packages that consist of lead free solder materials based on coarsening of IMC particles.

Chapter 3: Description of experimental procedure, sample preparation, uniaxial tensile, data processing and quantitative analysis.

Chapter 4: Investigation of aging induced evolution of the microstructure of SAC305 lead free solder.

Chapter 5: Quantitative analysis of the aging induced evolution of IMC particles in fixed regions.

Chapter 6: Investigation and comparison of aging effects in SAC+Bi solders exposed to high temperatures.

Chapter 7: Effects of high temperature aging on the mechanical behavior of SAC305 and SAC_Q solder alloys.

Chapter 8: Summary and conclusions of the dissertation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

When an electronic assembly is subjected to temperature changes, the solder joints in the assembly remain under mechanical stress due to the mismatch in the coefficient of thermal expansion (CTE) of the printed circuit board (PCB) and the component. Hence mechanical properties of the solder material are critical to ensure reliability of the package. Historically, 63/37 Sn-Pb solder is most commonly used material for solder joint. In recent days, the electronic packaging industry has widely transitioned to Pb-free solders due to environmental concerns. Among the diversity of Pb-free solders, the Sn-Ag-Cu (SAC) alloys have become the most popular and are often considered to be the standard lead-free alloys. NEMI (National Electronics Manufacturing Initiative) recommended to replace SnPb solders by eutectic Sn-Ag-Cu solder in reflow processing and eutectic Sn-Cu solder in wave soldering [19]. Depending on the percentage of silver (Ag), there are several types of SAC alloys available in the market. Solder joint fatigue life under thermal cycling has been shown to increase with increasing Ag content in the SAC solders joints, due to improved mechanical properties and increased fatigue resistance [20]. However, the drop performance of electronic assemblies with SAC Pb-free solder joints is often reduced when increasing the Ag content in the SAC solder [21]. Low silver content solders are increasingly used in electronic assembly for handheld electronic products to improve the

drop performance of the solder joints and to lower costs. Hence, there are trade-offs based on the silver content, and no one SAC alloy is typically suitable for all applications.

Solder joint fatigue that occurs during thermal or mechanical cycling is often the predominant failure mode exhibited by lead free electronic assemblies. Thus, engineers must have accurate constitutive equations and failure criteria for lead free solder materials for use in mechanical design and reliability assessment.

The microstructure of a lead free solder, which depends on solidification profile and thermal aging after solidification, strongly controls its mechanical properties. Thermal aging causes changes in the microstructure and hence the mechanical response of lead free solders. Changes in mechanical response include reductions in the initial effective elastic modulus, yield stress, and ultimate strength, as well as increased creep rates.

In real applications, solder joints are continuously exposed to aging/thermal cycling during service. It has been well documented that the microstructure, mechanical response, and failure behavior of solder materials are constantly evolving under such circumstances [49-84]. It has also been demonstrated that aging effects are universally detrimental to reliability and cause reductions in stiffness, yield stress, ultimate strength, and strain to failure, as well as highly accelerated creep. Solder joints with highly degraded microstructure and material properties are so vulnerable that the service life of the package is often severely shortened.

2.2 Effects of Aging on Solder Mechanical Properties

Aging has a strong effect on mechanical properties of lead free solders, as they have high homologous temperatures in most product applications. Due to the low melting

temperatures of solder materials, their homologous temperatures are high even in room temperature environments. Take SAC solders for example, their homologous temperatures are 0.61 at room temperature, and it is greater than 0.5 at which creep is considered critical [16]. Ma, et al. [1] reviewed the mechanical properties of lead free solders and found large data discrepancies in the literature. For instance, at room temperature, the elastic modulus of SAC lead free solders ranges from 30 to 54 GPa, while the ultimate tensile strength and yield stress are in the range of 30 - 60 MPa and 20 - 47 MPa, respectively. They believe aging plays a significant role in the data discrepancies in the literature.

The effects of aging were first investigated on lead solders by Medvedev, et al. [24] and Lampe, et al. [25], and they reported significant degradations of mechanical properties caused by room temperature aging. As the world transitions to lead free soldering, more and more studies have been focusing on the effects of aging on lead free solders. Miyazawa and Ariga [26, 27] reported that Sn-Pb, Sn-Ag and Sn-Zn eutectic solder materials experienced significant hardness degradation and microstructural coarsening after being aged at room temperature for 1000 hours. Ding and coworkers [28] observed a quick softening effect on Sn-3.5Ag solder samples after exposing the samples at 180 °C for 120 hours. Xiao, et al. [29] studied the effects of both room temperature aging and elevated temperature aging (180 °C) on SAC396 solder, and found the tensile strength loss was 25% for 35-day room temperature aging and 33% for 9-day elevated temperature aging. Similarly, aging induced degradations in tensile properties [30-35] and creep properties [36-38] of lead free solders have been reported by many researchers.

The cyclic stress-strain behavior of solder materials has been studied extensively in the past [39-57]. For example, several researchers [39-46] have developed fatigue life

prediction models for solder alloys under thermal cycling or thermomechanical fatigue loading. Hall [47, 48] measured deformations and stress-strain hysteresis experimentally during the thermal cycling of a leadless ceramic chip carrier (LCC) mounted to an organic PCB. For lead free solders, Raeder and co-workers [53] have explored thermomechanical deformation behavior of Sn-Bi eutectic solder under fatigue loading, and the findings were quantified using the plastic strain energy density. In addition, Dusek, et al. [54] have investigated the cyclic stress-strain behavior and hysteresis loop evolution for SAC lead free solders during isothermal fatigue at several different temperatures ($T = 24, 30, 60,$ and $125\text{ }^{\circ}\text{C}$). They reported that the number of cycles to failure increases with higher temperatures for the same stress level, and attributed this to the use of slow cycling, where creep and stress relaxation play dominant roles. Kanchanomai, et al. [55] have performed uniaxial fatigue tests on Sn-Ag solder, while Pang and coworkers [56] have performed uniaxial fatigue tests on SAC387 lead free solder. Andersson, et al. [57] compared the fatigue properties of bulk lead-free solder specimens to those found for solder joints. While aging effects have been studied in some detail on the solder constitutive behavior such as stress-strain and creep, there have been few prior studies on the effects of aging on solder cyclic stress-strain or fatigue behavior [58-60].

Our research center (Center for Advanced Vehicle and Extreme Environment Electronics, CAVE3) has been studying the effects of aging on various mechanical properties of lead free solders and has found that aging is universally detrimental to solder constitutive and failure behaviors. In particular, large degradations have been observed in creep behavior [61-65], thermal cycling reliability [66-70], Anand model parameters [69-70], nanoindentation joint modulus and hardness [71-73], high strain rate mechanical

properties [74], uniaxial cyclic stress-strain curves and fatigue life [75, 76], and shear cyclic stress-strain curves and fatigue life [77, 78]. For example, it has been found that elevated temperature aging (100 °C) led to dramatic changes of the stress-strain curve of SAC305 solder, especially during the first few days of aging, as shown in Figure 2.1 [64]. Mustafa [79] systematically studied the effects of aging on the fatigue life of lead free solders and proposed modified fatigue models that includes aging effects. Flat uniaxial test specimens (3 mm × 0.5 mm × 30 mm) were used to determine the uniaxial fatigue life of SAC solders in his study. Figure 2.2 shows the effects of aging on uniaxial fatigue life of SAC105 solder, and it is clear that aging decreases solder fatigue life. However, it has been found that the failure of flat specimens was often due to buckling, and the determined uniaxial fatigue life is much shorter than that from other researchers [55, 57, 80-84]. Therefore, micro-cylinder shaped specimens have been introduced in this study to solve the problem of buckling, and more details will be discussed in later chapters.

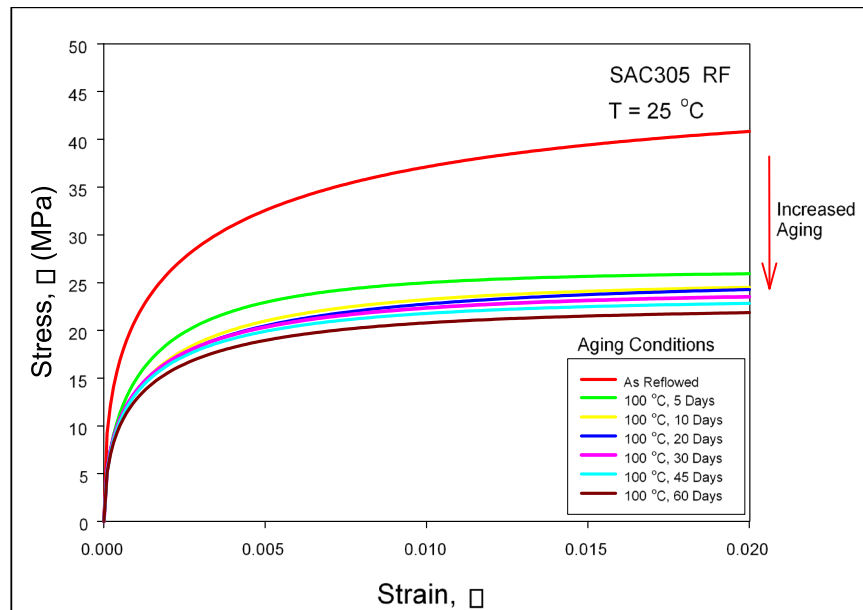


Figure 2.1 Drop of Stress-Strain Curve of SAC305 Solder with Increased Aging

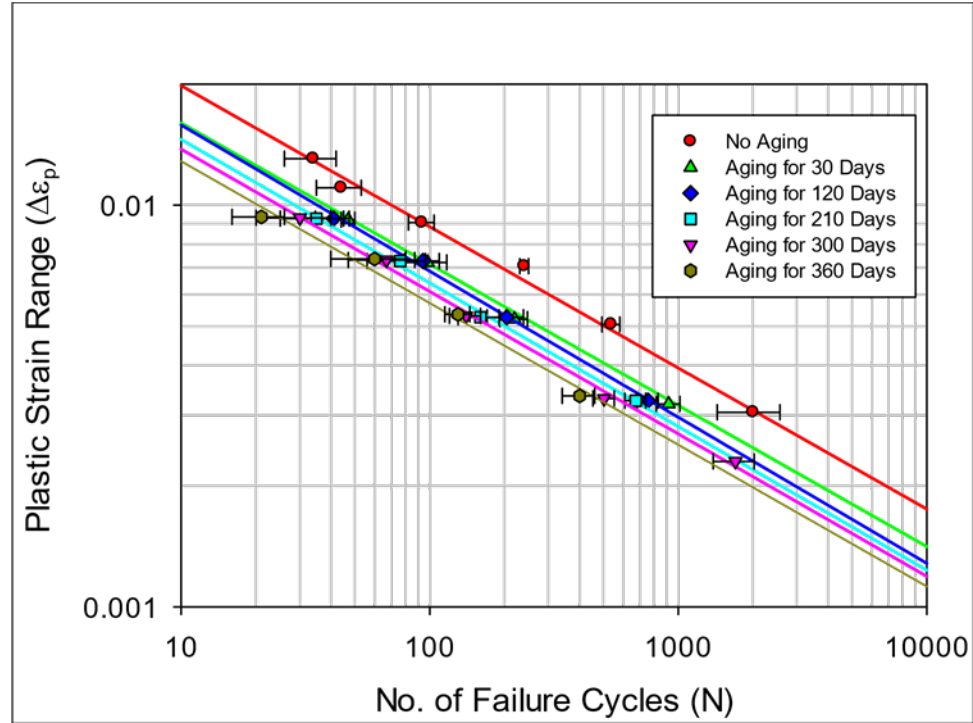


Figure 2.2 Effects of Aging on the Uniaxial Fatigue Life of SAC105 Solder

2.3 Effects of Aging on Solder Microstructure

The microstructure, mechanical response, property, and failure mechanisms of Sn-based solder joints are constantly changing due to the effects of isothermal aging. The observed variation in material behavior during thermal aging is universally detrimental to reliability and includes reductions in stiffness, yield stress, ultimate strength, and strain to failure, as well as highly accelerated creep. Many researchers have studied effects of aging on the evolution of solder microstructure, and several examples are listed in references [29, 85-104].

As the solidification microstructure is metastable, thermal activation will lead to microstructural evolution into structures with less interfacial energy and possibly changes in crystal structure of the IMCs. The most well-known and widely observed changes are

coarsening of the Ag_3Sn and Cu_6Sn_5 IMCs present in the eutectic regions between β -Sn dendrites. Several researchers [89, 92, 94, 95, 99-104] have also used empirical models to describe the growth of IMC particles or layers as a function of aging temperature and aging time. For example, Dutta, et al. [89, 94, 99] studied the microstructural coarsening of Sn-Ag based solders during thermal-mechanical cycling (TMC) and reported that TMC results in both static and strain-enhanced coarsening. Thus, they proposed a model to describe the growth of Ag_3Sn IMC particles during TMC, and the static coarsening part (solely isothermal aging) is given by

$$d_p^3 - d_{p_0}^3 \approx (8K \frac{C_{eq}}{T} D_{sol})t \quad (2.1)$$

where d_p is the diameter of Ag_3Sn particles at any instant during aging and d_{p_0} is the initial particle diameter. K is the static coarsening constant, and C_{eq} and D_{sol} are the equilibrium solubility and diffusivity of the solute Ag in Sn. T is the aging temperature and t is the aging time. In many studies on the effects of aging on solder microstructure, observations were made on two different solder joints (one non-aged and one aged). For example, Xiao, et al. [29] investigated the effects of aging on the microstructure of Sn-3.9Ag-0.6Cu lead free solder, and found that the microstructure changed remarkably after aging at room temperature for 35 days by comparing two different samples, as shown in Figure 2.3. However, the comparisons made were often qualitative in nature since the two microstructures were from different samples and could not be directly compared.

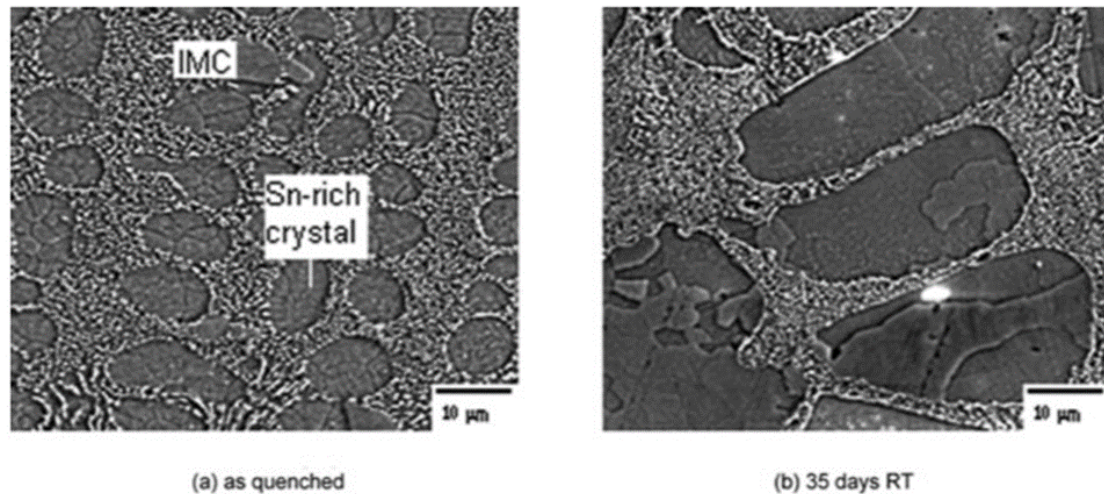


Figure 2.3 Effects of Room Temperature (RT) Aging on the Microstructure of Sn-3.9Ag-0.6Cu Lead Free Solder (Comparing Two Different Samples)

There are limited investigations that have involved the monitoring of evolving microstructure in a fixed region in a single solder sample [85, 90, 93, 100, 102]. For example, Choi and Lee [85] made photographs of growing intermetallic layers at the boundary between a Sn-Ag solder joint and the copper bonding pad. Ubachs, et al. [90] made experimental observations of aging-induced Sn-Pb solder microstructure evolution, and compared their results to predictions made with two-dimensional diffusion simulations. Telang and coworkers [93] made before and after grain boundary maps in fixed regions in pure-Sn and Sn-Ag samples subjected to high temperature aging at 150 °C. Similarly, Kumar, et al. [100] and Sahaym, et al. [102] observed changes to the IMC particles occurring within fixed regions in SAC105 and SAC305 solder joints exposed to aging at 150 °C for 100 - 300 hours. To obtain quantitative data and develop models, observations of a large set of IMC particles were made before and after aging, and average particle size and subgrain size were measured and plotted, as shown in Figure 2.4 [102].

Figure 2.5 illustrates the microstructural changes of SAC105 bulk solder that occurred in a fixed region during isothermal aging at 150 °C, and the coarsening of IMC particles is obvious [103].

Other changes in the SAC solder microstructure have also been observed to occur during aging, but they are not well characterized and their effects on mechanical behavior and reliability are not well understood. These include changes in size/shape of the β -Sn dendrites, growth of pure Sn subgrains within the β -Sn dendrites, migration of IMC particles to subgrain boundaries, changes in Sn grain orientation, etc.

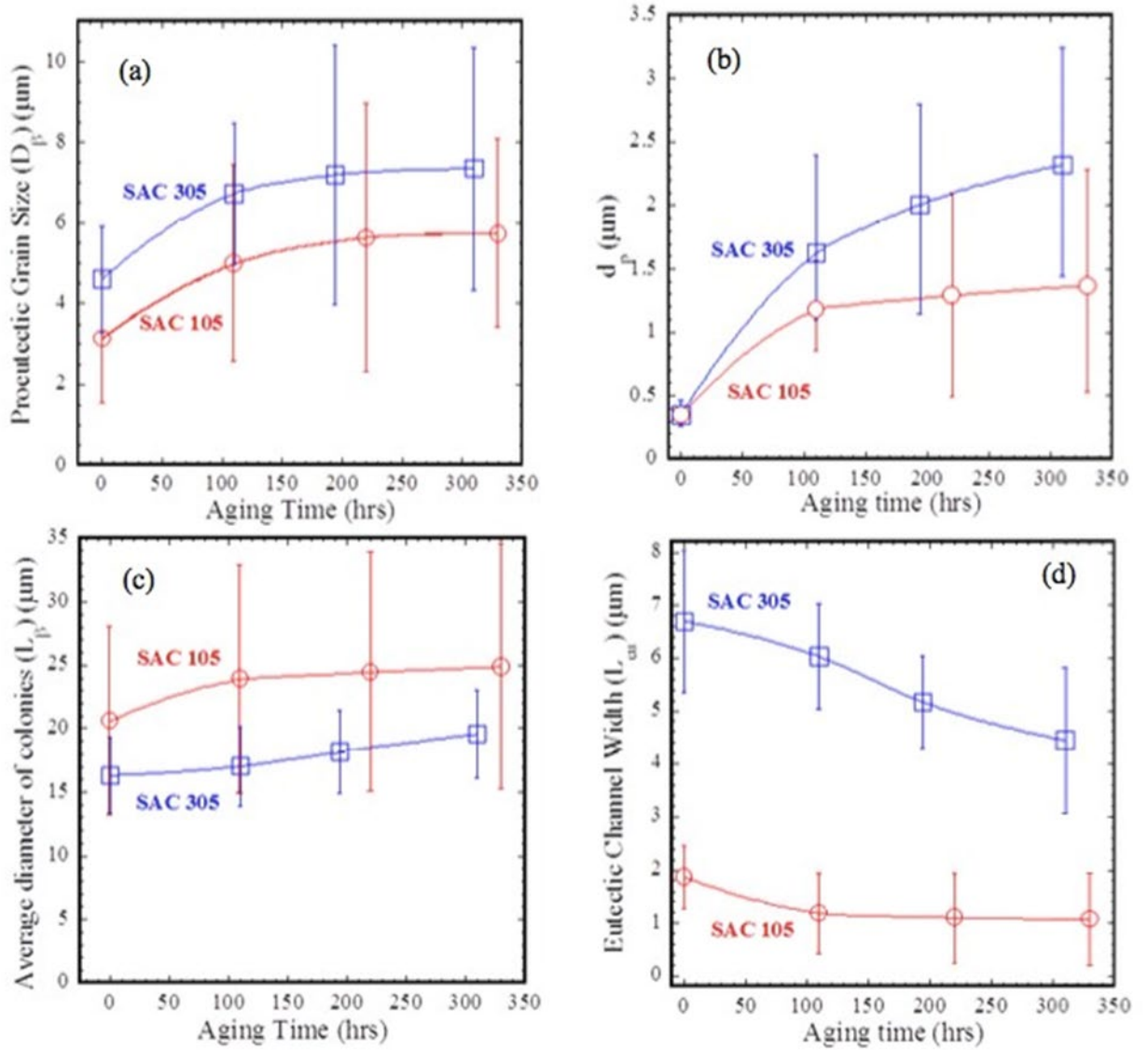


Figure 2.4 (a) Proeutectic Grain Size, (b) Ag₃Sn Particle Size, (c) Proeutectic Colony Size, and (d) Eutectic Channel Width as a Function of Aging Time During Isothermal Aging at 150 °C

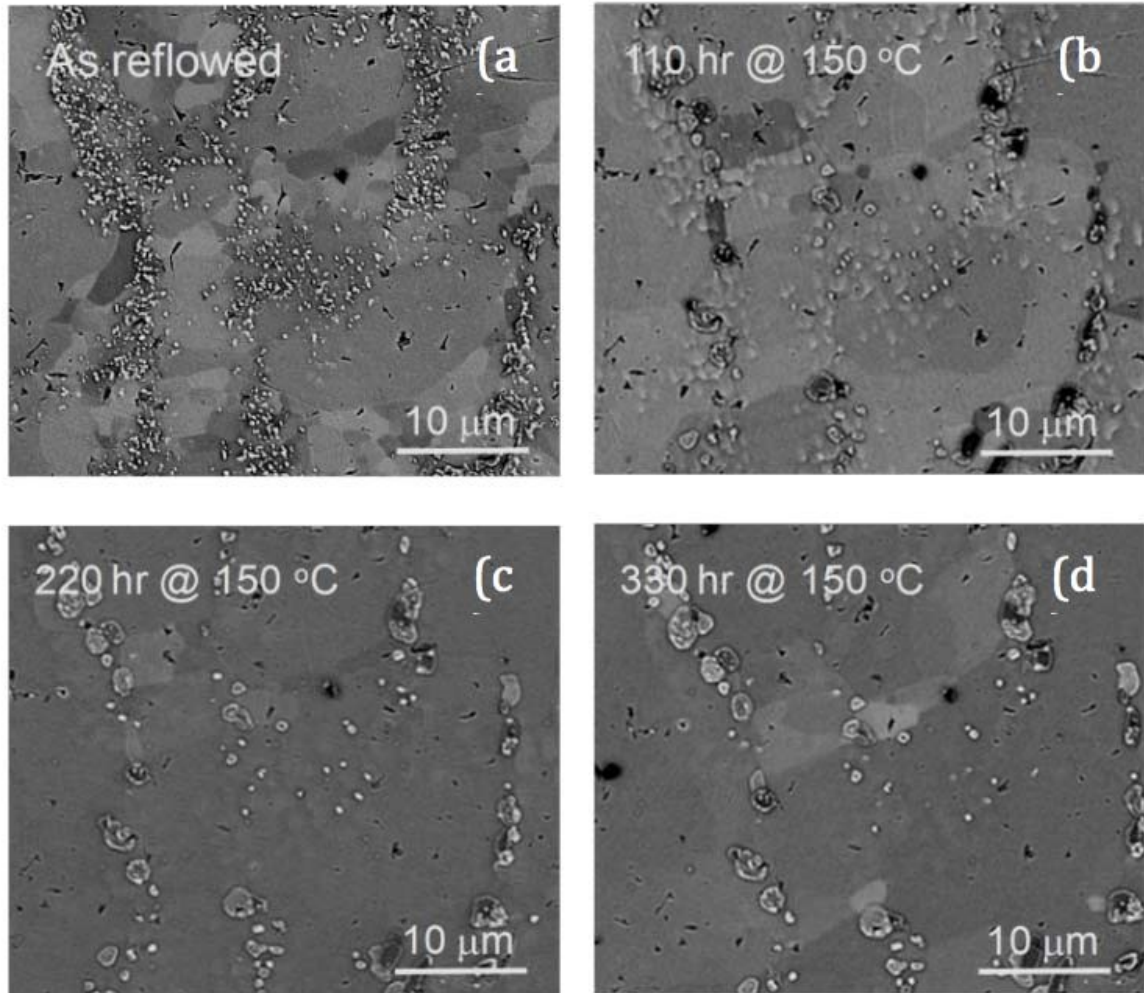


Figure 2.5 Effects of Aging on the Microstructure of SAC105 Bulk Solder at 150 oC, (Studying on a Fixed Region)

2.4 Various Influential Factors on Solder Mechanical Behavior

Apart from aging, there are many other parameters such as cooling rate, strain rate (frequency) and testing temperature that can influence the mechanical behavior of solder materials, and a better understanding of the effects of aging and those parameters on solder mechanical behavior is critical to resolving the large discrepancies in solder mechanical testing data found in the literature.

Different solidification profiles (cooling rates) result in different initial microstructures of a solder test specimen, which will dramatically influence the results of any mechanical test performed on that material. Typically, fast cooling rates lead to a finer initial lead free solder microstructure and then enhance its mechanical properties [105-110]. Kim, et al. [105] studied the effects of cooling rate on the microstructure and tensile properties of SAC lead free solders. They found that slow cooling rate led to additional large primary Ag_3Sn platelets in the $\text{Sn}_{3.5}\text{Ag}-0.7\text{Cu}$ and $\text{Sn}_{3.9}\text{Ag}-0.6\text{Cu}$ microstructures, which resulted in a decrease in tensile strength and elongation. Liang, et al. [108] compared the macro/micro-structure and mechanical properties of SAC387 solder samples that were solidified at different rates, and they reported that fast cooling rate results in the decrease of Sn dendrite arm spacing and the enhancement of solder creep resistance. Similarly, Basit, et al. [109, 110] compared the effects of two solidification profiles (reflow and water quenching) on the tensile properties of SAC lead free solders, and found that fast cooling (water quenching) results in finer solder microstructure and better mechanical properties.

As solder materials are viscoplastic, their mechanical properties are highly rate and temperature dependent. For materials that exhibit viscoplastic behavior, Anand [111] proposed a unified plastic/creep constitutive model that establishes a relationship between flow stress and plastic strain, with strain rate and ambient temperature as parameters. In finite element simulations, this model has been widely used to represent material behavior of lead free solders. Typically, when tested at lower temperatures or higher strain rates, solder test specimens exhibit better mechanical properties [45, 55, 57, 80, 81, 112-119]. For instance, Figure 2.6 shows the effects of testing temperature on fatigue life of 96.5Sn-3.5Ag lead free solder [55], while Figure 1.10 illustrates the effects of frequency (strain

rate) on fatigue life of 99.3Sn-0.7Cu solder [115]. The fatigue life data in Figure 2.6 and Figure 2.7 are represented using Coffin-Manson model and Morrow model, respectively. In addition, some researchers proposed modified fatigue models to include the effects of test frequency or strain rate [45, 55, 80, 112, 113, 115, 117, 119].

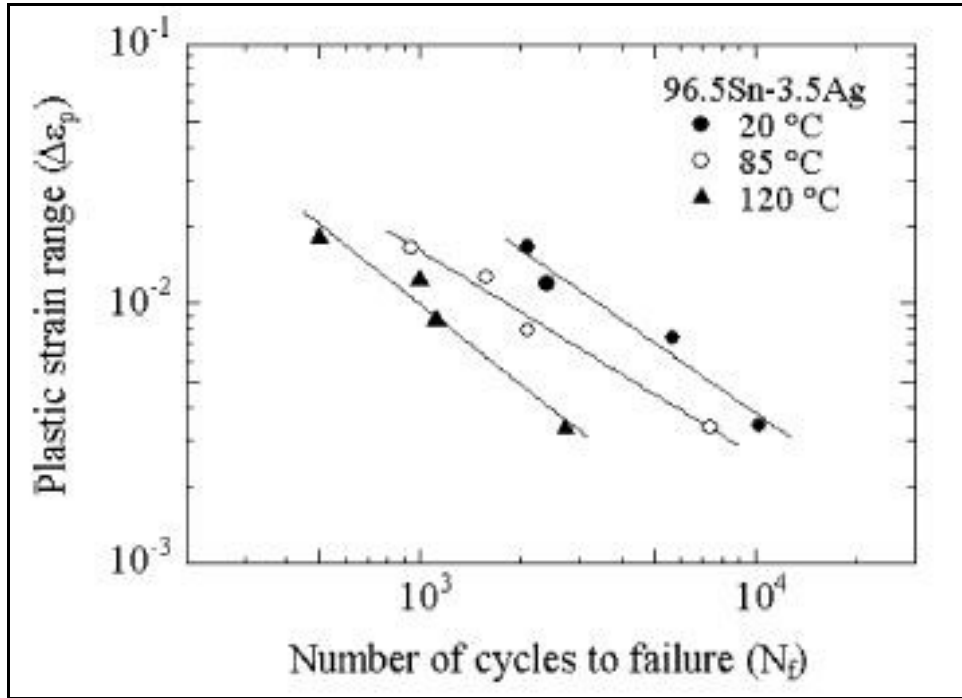


Figure 2.6 Effects of Testing Temperature on Fatigue Life of 96.5Sn-3.5Ag

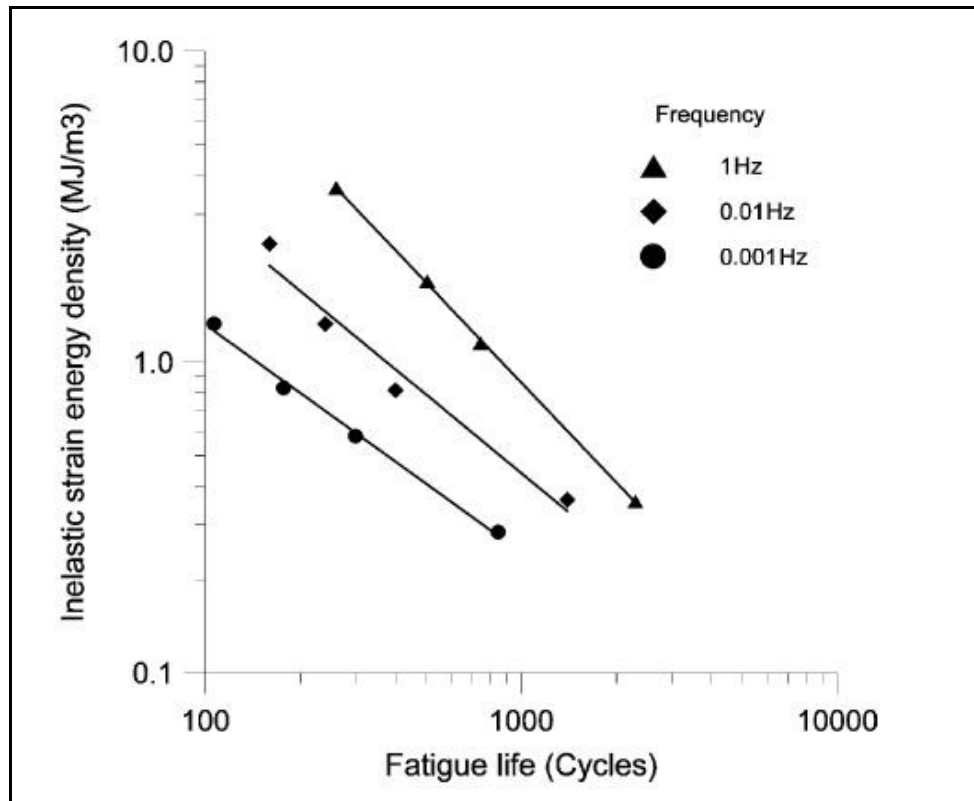


Figure 2.7 Effects of Frequency on Fatigue Life of 99.3Sn-0.7Cu

2.5 Constitutive Modeling for Stress-Strain Tests

The linear elastic region in a uniaxial stress-strain curve can be modeled by Hooke's law where stress and strain are related by an elastic modulus (E). The plastic strain hardening region can be modeled by a time-independent non-linear stress-strain relationship based on either isotropic or kinematic strain hardening. Isotropic hardening assumes that the origin of the von Mises yield surface remains stationary in the stress space and the size of its yield surface expands resulting from strain hardening. In kinematic hardening, the von Mises yield surface does not change in size, but the origin of the yield surface is allowed to translate in the stress space to model strain hardening effects of increasing plastic flow stress. For solder materials, the tensile stress and strain curves are

dependent on the test temperature and strain rate. The elastic modulus (E), yield stress (YS) and the tensile strength (UTS) properties vary with temperature and strain rate.

For a typical thermal cycling temperature range from -40 to 125 °C, these mechanical properties reduce with the increase in temperature. The solder material has a homologous temperature from 0.5 to 0.8 for this temperature range. Also, the creep deformation in a solder material is highly dependent on the stress and temperature state. Thus, a time-dependent elastic-plastic-creep constitutive model, or viscoplastic constitutive model, is needed to facilitate finite element modeling for simulation of solder joint reliability during thermal cycling tests. High temperatures induce transitions in macroscopic fracture, and these transitions parallel the changes in the strength and ductility of materials [104]. Materials lose strength at higher temperatures. Hertzberg stated that the material strength increases with the testing strain rate, following a form similar to Holloman's Equation [104], where stress is related to strain rate through some strain hardening exponent.

Solder alloys possess very high homologous temperatures. The properties of solder alloys are strongly dependent on both the temperature and strain rate. Jones, et al. [105, 106] have observed an approximately linear relationship between the strength and temperature. Pang, Shi and co-workers [107] have observed similar experimental results, with a near linear relationship with temperature and a power law relation with the strain rate. Several other studies have also observed similar material behavior for both Sn-Pb eutectic and lead-free solder alloys [108-111].

The Ramberg-Osgood model describes the elastic-plastic behavior of materials, and can be used to describe the stress-strain curve of solder materials [112]. In prior

work, the Ramberg-Osgood model hardening exponent n and the stress coefficient σ_0 were modified to be temperature and strain rate dependent. The temperature and strain-rate dependent modified Ramberg-Osgood model was also applied by Pang, et al. [112].

2.6 Reduction of Aging Effect by Dopant

Addition of 4th element in the SAC solder is known as doped SAC alloy. Dopants play an important role to control microstructure and mechanical properties of the alloy. Dopants have been found to strongly influence the properties and behaviors of lead free solders. For example, addition of Bismuth (Bi) as a dopant has been demonstrated to have several beneficial effects. Bi helps to reduce solidification temperature, increases strength by means of precipitation hardening, and also helps to reduce IMC (Intermetallic Compound) layer thickness in lead free solder materials [123]. The Effect of Bi on the mechanical properties of a SAC (Sn3.5Ag0.9Cu) alloy was investigated by Matahir and coworkers [124]. They reported that the shear strength increased with increasing Bi addition up to 2 wt%. Beyond that point, the shear strength decreased with increasing Bi%. Improved shear strength might attribute to the role of Bi on the morphology of microstructure and distribution of dominant IMC (Ag_3Sn). Reduction of strength at higher Bi content was due to the evolution of Bi rich phase and fragmentation of the IMC. Pandher, et al. [125] also reported that addition of 2% Bi in SAC alloys improves wetting and alloy spreading.

Zhao, et al. [126] found that addition of 0.02% Ni to SAC105 increased the formation of NiCuSn IMC and reduced the localized grain size at solder/NiAu pad interface. In addition, the effects using various doped elements (i.e. Co, Fe, In, Ni, Zn and Cu) in

SAC305 BGA solder joints on Cu pads were studied by Sousa, et al. [127]. They concluded that addition of low levels of Zn had a significant beneficial effect on the interfacial IMC. Lee and coworkers [128] found that micro-alloying SAC alloys with Ni and Bi improved thermal fatigue life and drop impact resistance. Yeung, et al. [129] studied a novel lead-free solder SAC_Q. Based on drop test, thermal cycling, and finite element simulation, they conclude that the doped alloy has improved board level reliability when compared to SAC105. Additional literature publications on the effects of dopants have been reviewed in reference [51].

Sun et. al. [130] reviewed the effects of different alloying elements (Mn, Fe, Bi, Ni, In, Zn, Ga, Sb, Mg), Rear Earth (RE) Elements (Ce, La, Y, Er, Pr, Nd, Yb), and nanoparticles (Al_2O_3 , Al, TiO_2 , ZnO, ZrO_2 , CNT, Graphene, CeO_2 , TiB_2 , Ni-Coated CNT, Mo, SiC, SrTiO_3 , Co) on melting temperature, wettability, mechanical properties, microstructure, interfacial reaction and Sn whiskers.

For SAC305 solder, average width of eutectic region was found as $6.8 \pm 2.8 \mu\text{m}$ and grain size of $\beta\text{-Sn}$ was $24.8 \pm 5.9 \mu\text{m}$. Indium (In), helps to refine IMC and Sn-rich phase as well as makes the microstructure more uniform. Titanium (Ti) can significantly reduce Sn grain size and width of eutectic region by heterogeneous nucleation of IMC's. Iron (Fe) forms large FeSn_2 IMC which has a weak interface with $\beta\text{-Sn}$ matrix. Magnesium (Mg) helps to coarsen eutectic region. Addition of Al in SAC105 refines $\beta\text{-Sn}$ dendrites and enlarge eutectic regions. Besides, it also prevent Ag_3Sn and Cu_6Sn_5 and forms two new IMC Ag_3Al and Al_2Cu . Zn also helps to refine $\beta\text{-Sn}$ dendrites significantly. Ni was found to reduce the size of Sn-rich phase and refine the microstructure. Since Antimony (Sb) has

higher affinity towards Sn, presence of Sb reduces the driving force to form Cu-Sn IMC's resulting a narrow IMC layer in the solder joint. Sb also helps to refine IMC grain size.

RE elements can significantly refine the microstructure of SAC solders. Er can reduce the particle size of Ag_3Sn and Cu_6Sn_5 whereas Pr and Nd refine β -Sn dendrites and IMC particle size by forming uniformly dispersed fine RESn_3 . These fine particles act as heterogeneous nucleation sites during solidification. However, excessive amount of RE elements will cause to form bulk RESn_3 phase which has a negative effect on mechanical properties. La, Ce, and Y also have a similar effect on solder microstructure.

Al and Ni nanoparticle was found to reduce IMC particle size, spacing and IMC layer thickness by forming very fine and uniformly dispersed Sn-Ni-Cu and Sn-Sg-Al IMCs. Addition of small amount of Fe nanoparticles refine the microstructure and forms FeSn_2 phase. Al_2O_3 nanoparticles increase the size of eutectic region and reduce Ag_3Sn particle size. TiO_2 and SiC nanoparticle reduces the size and spacing between Ag_3Sn particles. SrTiO_3 nanoparticle reduces the size of Ag_3Sn and Cu_6Sn_5 particles by promoting the rate of nucleation during solidification. ZnO suppresses Ag_3Sn and Cu_6Sn_5 IMC formation and reduces β -Sn grain size by 22%.

The Effect of dopants on the aging induced changes in microstructure was also studied by a number of scientists. Sadiq et al. [131] worked with different Lanthanum (La) doped SAC305 alloys and recorded the changes in microstructure and mechanical properties during isothermal aging at 150 °C for 6 different aging conditions (i.e. 0, 10, 25, 50, 100 and 200 hours). They reported that La drastically reduces the IMC particle size and also significantly inhibit the growth of IMC particles during isothermal aging. Based on polarized light image they found that in as cast condition, grain size of SAC305 was ~8

mm and was significantly reduced (~ 1 mm) after La addition. From the graph presented in that paper, it is also clear that aging doesn't have any significant influence in average grain size.

In another study, Lee et al. [132] studied the effect of Lanthanum (La) addition and high temperature storage on the microstructure and microhardness of Sn-3.5Ag solder joints. Their experimental results confirms that addition of La refine the solder microstructure. They explained that during solidification of the solder, LaSn_3 compounds form at the beginning and provide extra nucleation sites for Ag_3Sn IMC to grow resulting a refine microstructure. Addition of La was also found to reduce the thickness of IMC layer after soldering as well as isothermal aging. They also reported that La addition helps to improve microhardness and thermal resistance of solder joints.

Hao et al. [133] studied the effects rare earth element Er addition on the evolution of microstructure of lead free eutectic SAC (Sn-3.8Ag-0.7Cu) solder joints during isothermal aging. Aging was conducted at 170°C for 4 different holding periods (i.e. 0, 200, 500 and 1000 hours). The authors measured the thickness of IMC layer of Sn-3.8Ag-0.7Cu and Sn-3.8Ag-0.7Cu-0.15Er alloy after different aging duration. They found that Er addition reduces the thickness of IMC layer in as reflowed condition and also significantly reduces the growth during aging. They argued that Er combines with Sn to form ErSn_3 IMC and reduces the activity of Sn which subsequently suppress the formation of Cu_6Sn_5 IMC layer. They also observed that ErSn_3 IMCs formed during solidification of solder act as a heterogeneous nucleation site for Ag_3Sn and Cu_6Sn_5 precipitates. The increase in nucleation sites results a refinement of Ag_3Sn and Cu_6Sn_5 particles. Addition of Er also

found to make the microstructure more uniform and reduce the coarsening rate of the IMCs during isothermal aging.

Witkin [134] and Delhaise et al. [135] studied the effect of aging of Bi doped SAC alloys. In both study, the authors reported an elimination or at least reduction of aging induced degradation in SAC-Bi alloys.

2.7 Nanoindentation on SAC Solder Joints

Most prior work on solder mechanical behavior and aging effects has involved tension, compression, and shear testing of miniature bulk solder specimens. Sample geometries have included traditional uniaxial tensile specimens, small cylinders in compression, lap shear specimens, and Iosipescu shear specimens. A more limited number of researchers have examined aging effects by mechanical loading of solder joints [57, 64, 65, 92]. These studies have involved shearing of custom fabricated solder ball arrays [64, 65, 92], as well as impression creep experiments [57].

Nanoindentation techniques [40] have recently become popular for measuring mechanical properties and creep deformation behavior of extremely small material samples, and several investigators [75, 136-148] have applied them to lead free solders. Early solder nanoindentation studies included room temperature measurements of the elastic modulus E and hardness H of β -Sn dendrites, eutectic phases, and individual Ag_3Sn and Cu_6Sn_5 intermetallic compounds [136, 137, 146, 148]. Hasnine et al. [75, 140-142], have examined aging effects in SAC solder joints extracted from PBGA assemblies using nanoindentation. Their results showed that the aging induced degradations of the room temperature mechanical properties (modulus, hardness) of single grain SAC joints were of

similar magnitudes to those seen previously by testing of larger “bulk” solder specimens with hundreds of grains. However, the degradation of the creep response, while still significant (15-100X increase), was less in the solder joints relative to larger uniaxial tensile specimens (200-7500X increase). This was due to the single grain nature of the joints considered, and the lack of the grain boundary sliding creep mechanism. They also tested very small tensile specimens (10 mm long) with 10-20 grains, and the creep degradation results were similar to the single joint specimens.

Knowledge of elevated temperature behavior, especially creep behavior, is critical to understanding solder joint reliability in thermal cycling and accelerated life testing. Elevated temperature nanoindentation measurements of modulus and hardness of bulk SAC305 and SAC357 solder samples were performed by Gao, et al. [138], and Han and coworkers [139]. In addition, the latter authors also examined the sensitivity of the creep response of lead free solder to temperature. Sadiq, et al. [147] have investigated the nanoindentation elastic modulus and hardness of β -Sn and eutectic phases within a SAC305 solder joint at temperatures ranging from 45-85 °C. Another solder nanoindentation study over a larger temperature range (25-150 °C) was performed by Lotfian, et al. [143], where they reported the mechanical properties of the constituent phases of SAC397 solder joints. Marques, et al. [144, 145] used nanoindentation to study mechanical properties and creep behavior of SAC305 solder joints over a wide temperature range (25-175 °C). Based on finite element simulations, they also developed a method to correlate nanoindentation creep results with uniaxial creep data.

Nanoindentation pile-up, defined by an uplift of material near the edges of an indent, is often observed in testing of solders [136, 137, 143, 147, 148]. Pile-up depends significantly

on the work hardening ability of the material [149]. For a material that easily work hardens, the top surface near the indent will be hardened during the deformation and thus will prevent pile up by resisting upward flow of the material. Prior researchers have used different techniques to include the pile-up area in their measurement. Kese, et al. [150] proposed a semi ellipse method for pile up correction, which was based on the assumption that the pile-up contact area had a semi-elliptical shape. While some researchers [147, 148, 151] have used the Kese, et al. method, others [137] have used FEA simulations to guide pile-up corrections.

2.8 Summary

In this chapter, the existing literature on the effects of aging on the mechanical properties and the microstructure of lead free solder was extensively discussed. The mechanical properties of a solder are strongly influenced by its microstructure, which is controlled by its thermal history including its solidification rate and thermal exposures after solidification. Aging of lead free solders leads to degradations in their constitutive and failure behaviors. For example, research in the literature has shown that aging leads to large reductions in solder material properties including shear strength, elastic modulus, nanoindentation joint modulus and hardness, high strain rate mechanical behavior, creep response, and Anand model parameters. Other studies have shown that aging causes severe degradations in uniaxial cyclic stress-strain curves and fatigue life, shear cyclic stress-strain curves and fatigue life, fracture behavior, drop reliability, and thermal cycling reliability.

Dopants have been found to strongly influence the properties and behaviors of lead free solders. For Example, Bi helps to reduce solidification temperature, increases strength by means of precipitation hardening, helps to reduce IMC (Intermetallic Compound) layer thickness, and also reduce aging induced degradation of mechanical properties in lead free solder materials. Ni helps to improve thermal fatigue life and drop test performance by refining Sn grain size and reducing the IMC layer formation near the Cu pad. The effects of rear earth (RE) elements and nanoparticle addition on the properties of lead free solder was also discussed in this chapter.

The changes in solder mechanical behavior are a result of the evolution of the SAC solder microstructure that occurs during aging. The most well-known and widely observed changes are coarsening of the Ag_3Sn and Cu_6Sn_5 intermetallic compounds (IMCs) present in the eutectic regions between beta-Sn dendrites. Several researchers have proposed empirical models to describe the growth of these secondary phase particles as a function of aging temperature and aging time and related this growth to mechanical property changes.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Introduction

The specimen preparation and testing techniques are presented in this chapter. Micro-scale uniaxial tensile specimens were prepared in a rectangular shaped hollow glass tube using a vacuum suction method. The test specimens were then cooled either by a water quenched profile or an industry standard reflow profile. Typical dimension of the uniaxial tensile specimens was 80 (length) $\times$ 3 (width) $\times$ 0.5 (height) mm. The mechanical testing was performed using a tension thermo-mechanical test system. For the microstructural analysis, the solder cross-sectional specimens were polished and then the microstructures were examined using the SEM.

3.2 Uniaxial Tensile Test Sample Preparation

The solder is first melted in a quartz crucible using a pair of circular heating elements (see Figure 3.1). A thermocouple is attached on the crucible and a temperature control module is used to direct the melting process. One end of the glass tube is inserted into the molten solder, and suction is applied to the other end via a rubber tube connected to the house vacuum system. The suction forces are controlled through a regulator on the vacuum line so that only a desired amount of solder is drawn into the tube. The specimens

are then cooled to room temperature using a user-selected cooling profile (can be the same as actual solder joints). Both water quenched (WQ) and reflowed (RF) lead free solder specimens were studied in this work. Typical temperature versus time plots for water quenching and reflow profile cooling of the test samples are shown in Figure 3.2 and Figure 3.3, respectively. The water quenching profile represents an extreme condition that yields an extremely fine microstructure due to the fast-cooling rate, which results in the upper limits of the various mechanical properties. For the reflow profile cooling, the glass tube assemblies are first cooled to room temperature by water quenching, and then subjected to the temperature profile shown in Figure 3.3 using a reflow oven (9 zone Heller 1800EXL, see Figure 3.4). The reflow profile yields microstructures similar to those found in actual solder joints used in the industry.

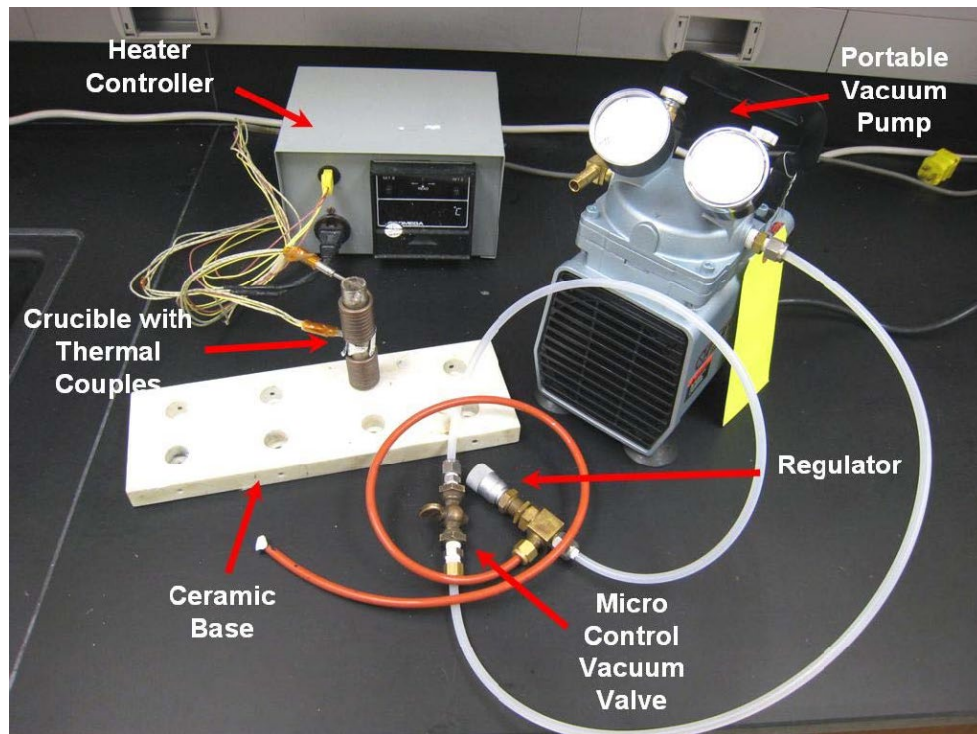


Figure 3.1 Equipment used for Specimen Preparation

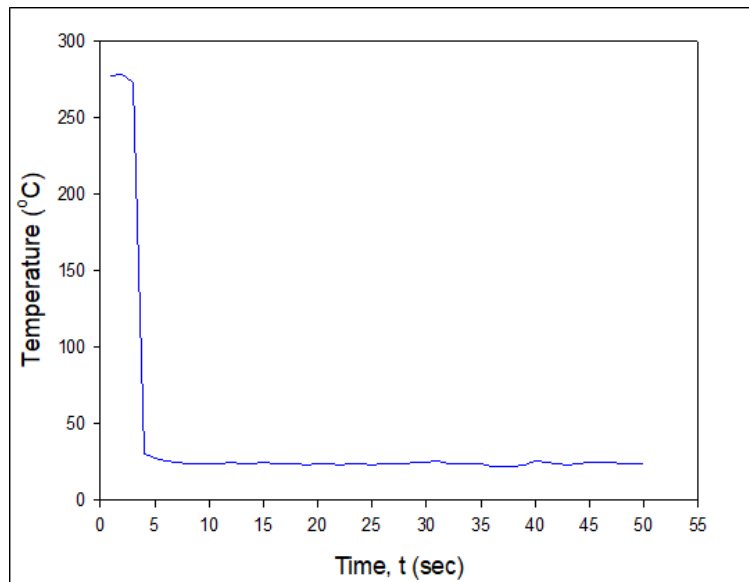


Figure 3.2 Water Quenched (WQ) Cooling Profile



Figure 3.3 Heller 1800EXL Reflow Oven

Inside the oven, solder samples were re-melted and experienced to a pre-set temperature profile which is very similar to that used for the actual solder joints. The reflow temperature profile used in this study is presented in Figure 3.4.

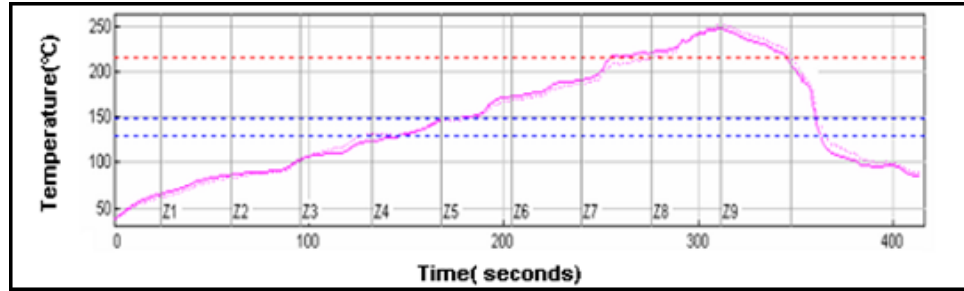


Figure 3.4 Reflow (RF) Cooling Profiles

A typical glass tubes filled with solder and final solder samples after extraction from the glass tubes are shown in Figure 3.5. Glass has lower coefficient of thermal expansion (CTE) compared to solder. As a result, for some solder alloy and cooling rate combinations, solidified solder samples were easily pulled out from the glass tube due to the difference is the CTE of glass and solder. Another way followed to extract the solder sample from the glass tube is by carefully breaking the glass. The tubes in this work had a length of 120 mm, and a cross-sectional area of 3.0 x 0.5 mm. Sample cross-sectioning has shown that the microstructure of any given sample was consistent throughout the volume of the sample, and the repeatable sample microstructures were obtained from sample to sample for a given solidification temperature profile. With proper experimental techniques, samples with no flaws and voids were generated.



(a) Within Glass Tubes



(b) After Extraction

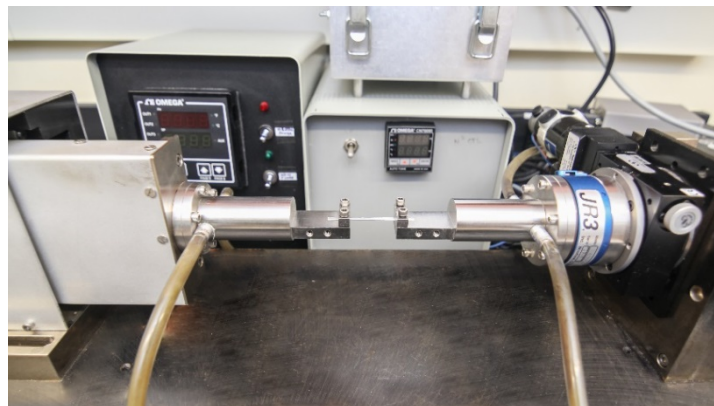


(c) Cross-Section

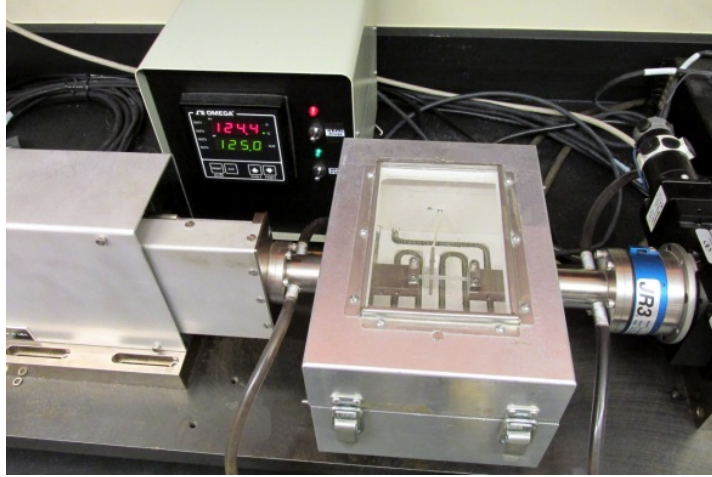
Figure 3.5 Solder Uniaxial Test Specimens

3.3 Uniaxial Tensile Testing System

The MT-210 tension/torsion thermo-mechanical test system from Wisdom Technology, Inc., shown in Figure 3.6 was used to perform the tensile stress-strain testing in this work. This instrument is optimized for loading small specimens such as thin films, solder joints, gold wire, fibers, etc. The system provides an axial displacement resolution of 0.1 micron, and universal 6-axis load cell was utilized to simultaneously monitor three forces and three moments during sample mounting and testing. Use of the pictured heating chamber allowed samples to be tested up to +200 °C. However, the high temperature system has been calibrated to accurately control the specimen temperature.



(a)



(b)

Figure 3.6 Mechanical Test System with Uniaxial Sample

3.4 Tensile Testing Data Analysis

3.4.1 Test Data

The axial stress and axial strain during testing were calculated from the measured applied force and crosshead displacement using

$$\sigma = \frac{F}{A} \quad \varepsilon = \frac{\Delta L}{L} = \frac{\delta}{L} \quad (3.1)$$

where σ is the uniaxial stress, ε is the uniaxial strain, F is the measured uniaxial force, A is the original cross-sectional area, δ is the measured crosshead displacement, and L is the chosen specimen gage length (initial length between the grips). The gage length of the specimen was kept as 60 mm (thus the length to width ratio was 20 to 1).

A typical SAC solder tensile stress strain curve is illustrated in Figure 3.7. The standard material properties are labelled on the graph including the effective elastic modulus E (initial slope of the stress-strain curve). This effective modulus is rate dependent since solder behavior is viscoplastic. The value of the effective modulus will become the true elastic modulus as the testing speed is increased to the limit of infinite

strain rate. The yield stress σ_Y (YS) is defined using the typical definition of the stress level that results in a permanent strain of $\varepsilon = .002 = 0.2\%$ upon unloading. The maximum (saturation) stress on the stress-strain curve is the ultimate tensile strength σ_u (UTS). As shown the figure, the stress-strain curve for the solder material has an elastic region at the beginning, a small transition region followed by a plastic region. As the strain becomes significantly high, localized deformation takes place which is also known as necking. Necking causes a visible reduction in cross-sectional area and a drop in the applied load, near the end of the stress strain curve, leading towards a rupture.

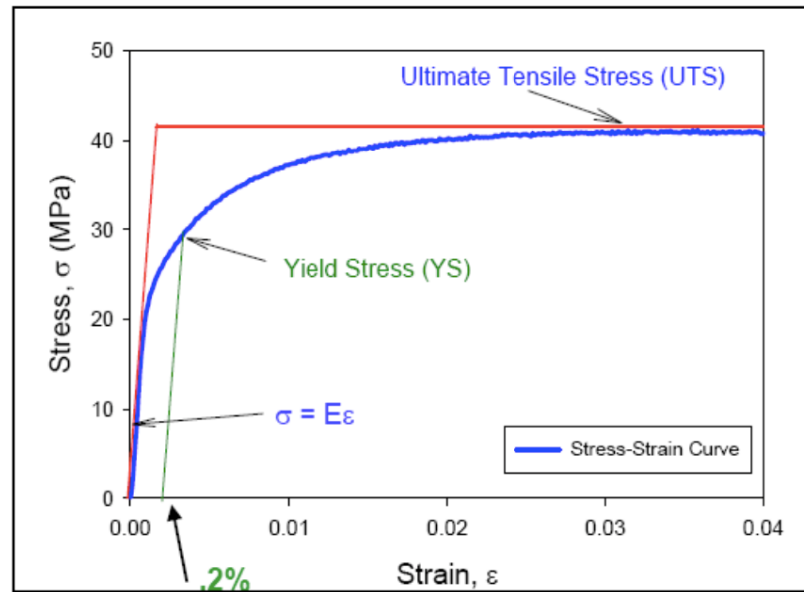


Figure 3.7 SAC Stress-Strain Curve and Material Properties

3.4.2 Empirical Model

Figure 3.8 illustrates a typical set of 5 solder stress strain curves measured for the same alloy under similar environmental and aging conditions. For tensile testing, Mustafa,

et al. [75] proposed a four-parameter hyperbolic tangent model (Eq. (3.2)) to represent the experimental stress-strain data.

$$\sigma = C_1 \tanh(C_2 \varepsilon) + C_3 \tanh(C_4 \varepsilon) \quad (3.2)$$

where C_1 , C_2 , C_3 , C_4 are material constants to be determined through regression fitting of the model to experimental data. The effective elastic modulus E at zero strain is calculated from the model constants using

$$E = \sigma'(0) = C_1 C_2 + C_3 C_4 \quad (3.3)$$

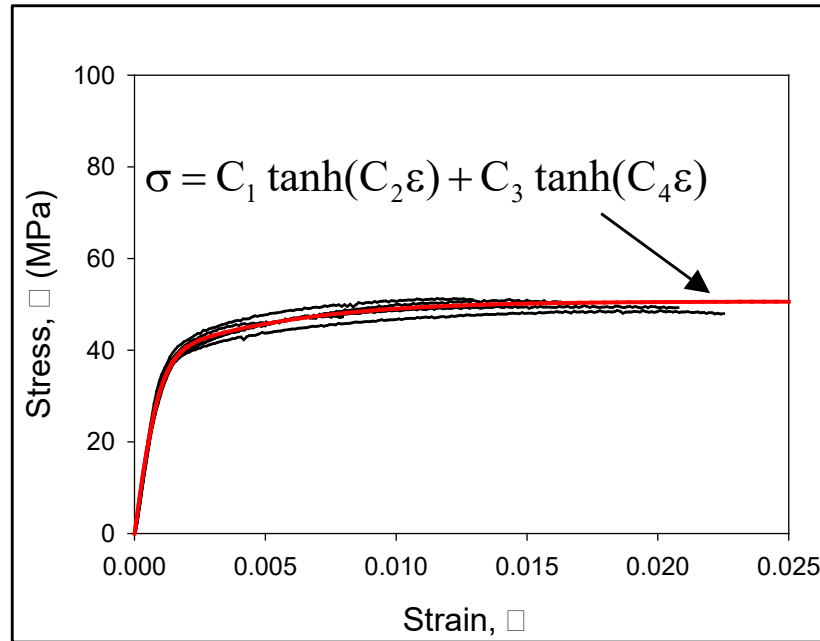


Figure 3.8 Empirical Model Fit to Solder Stress-Strain Curves

3.5 Microstructure Study

For microstructure analysis, lead free solder joint samples were prepared using a nine-zone reflow oven. A typical solder joint temperature profile was utilized. Solder cross-sectional specimens were first encapsulated in epoxy mold and then polished using

standard procedures. Details of the preparation process included mechanical grinding with several SiC papers (#320 to #400, #600, #800 and #1200) in a rotating metallographic disc as shown in Figure 3.9. The final polishing was conducted with 0.02 μm colloidal silica suspensions (BUEHLER MasterMet 2) and BUEHLER ChemoMet polishing cloth. A standard polishing method by using Struers TegraPol-15 Auto-polisher (shown in Figure 3.10) is generated and shown in Appendix A.1. Both procedures resulted in mirror finish samples suitable for optical microscopy, Scanning Electron Microscopy (SEM), as well as nanoindentation and FIB.

Microstructure analysis of the solder alloys was performed on the mounted and polished testing coupons by using an OLYMPUS BX60 Optical Microscope (Figure 3.11) and JEOL JSM 7000F Field Emission SEM (Figure 3.12). Regions of interest with typical Sn-Ag-Cu (SAC) microstructures were identified to monitor within the polished samples. As shown in Figure 3.13, the pyramidal indents were formed using a nanoindentation system and were placed near the corners of the regions of interest. For the example shown in Figure 3.13, the region of interest was approximately 60 x 40 μm , while the center-to-center spacing between the indentation marks was approximately 90 μm . The indentation marks were positioned so that the region of interest was centered within the marks, and were also placed suitably away from the region to minimize any influence on the microstructure evolution. The polished solder samples with indentation marks were aged at high temperature for various durations. After each aging increment, the microstructures of the regions of interest in the samples were captured using SEM microscopy. In addition, EDS (Energy-Dispersive X-ray Spectroscopy) was employed to explore the chemical composition of different phases in the microstructure.

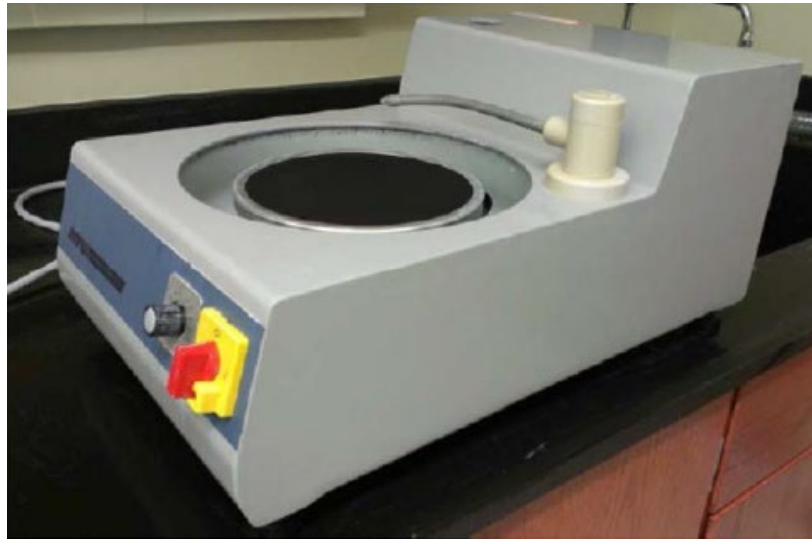


Figure 3.9 Grinding and Polishing Machine



Figure 3.10 Struers TegraPol-15 Auto-polisher with Tegraforce-1



Figure 3.11 OLYMPUS BX60 Optical Microscope

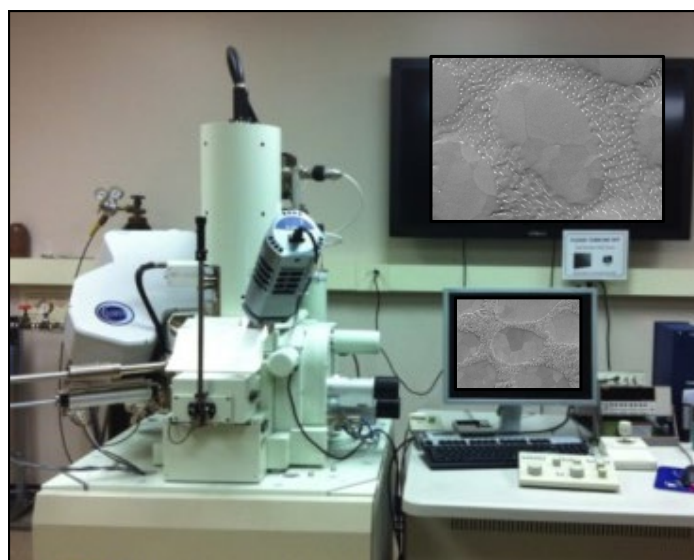


Figure 3.12 JEOL JSM-7000F Field Emission SEM

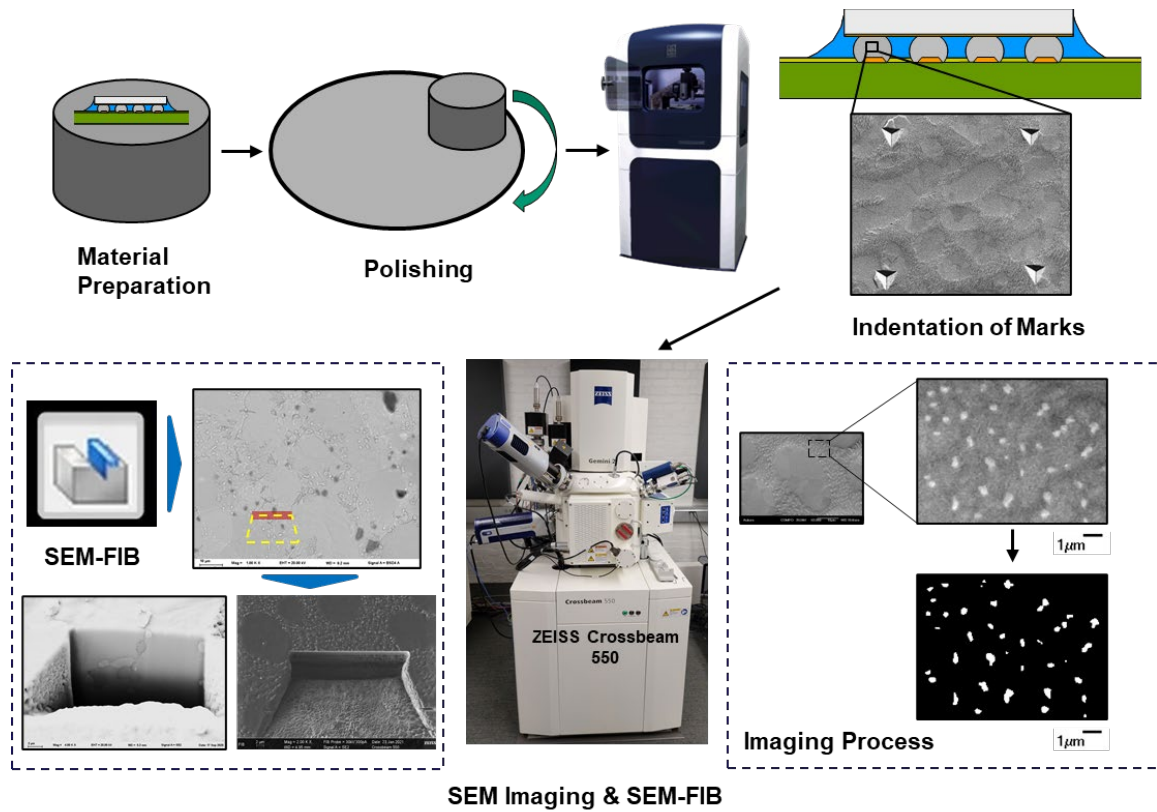


Figure 3.13 Flow Chart of Sample Preparation and Experimental Procedure
(Including SEM and Nanoindentation System)

3.6 Sample Preparation for Nanoindentation

SAC305 (96.5Sn-3.0Ag-0.5Cu) lead free solder joints were extracted from PBGA assemblies (Amkor CABGA, 14 x 14 mm, 192 balls, 0.8 mm ball pitch, 0.46 mm ball diameter) that were assembled for the iNEMI Characterization of Pb-Free Alloy Alternatives Project (Figure 3.15). Prior to cross sectioning, the PBGA test assemblies were stored in a freezer at $T = -10\text{ }^{\circ}\text{C}$ to minimize any aging effects after board assembly. The assembled PBGA components were cut out from the test boards and then cross sectioned using BUEHLER IsoMet 1000 Precision Cutter (Figure 3.16). Cross-sectioned sample was potted in epoxy and polished in the same way to prepare microscopic samples

as described in this section. After polishing, the epoxy encapsulated sample was mounted rigidly on a 12 mm diameter steel SPM sample puck to reduce system compliance. Initially, the steel puck was cleaned with acetone to remove any oily substance from the surface. After cleaning, a small amount of cyanoacrylate-based adhesive (super glue) was applied on the surface. Sample was placed on the adhesive and a firm pressure was applied on the sample for around 20 second to ensure curing and proper bonding with the steel puck. Since the stage within the nanoindentation system has several magnets, the steel puck will allow the magnetic attraction of one of the magnets to hold the sample firmly on the stage.

The nanoindentation tests in this work were performed using an instrumented Hysitron TI 950 nanoindentation system (Figure 3.17) and a Berkovich indenter tip. The heating stage and scanning probe microscopy (SPM) facility within a nanoindentation system were utilized to achieve the in-situ aging study. The sample was kept within the nanoindentation system and exposed to a high temperature aging using the heating stage present in the instrument.

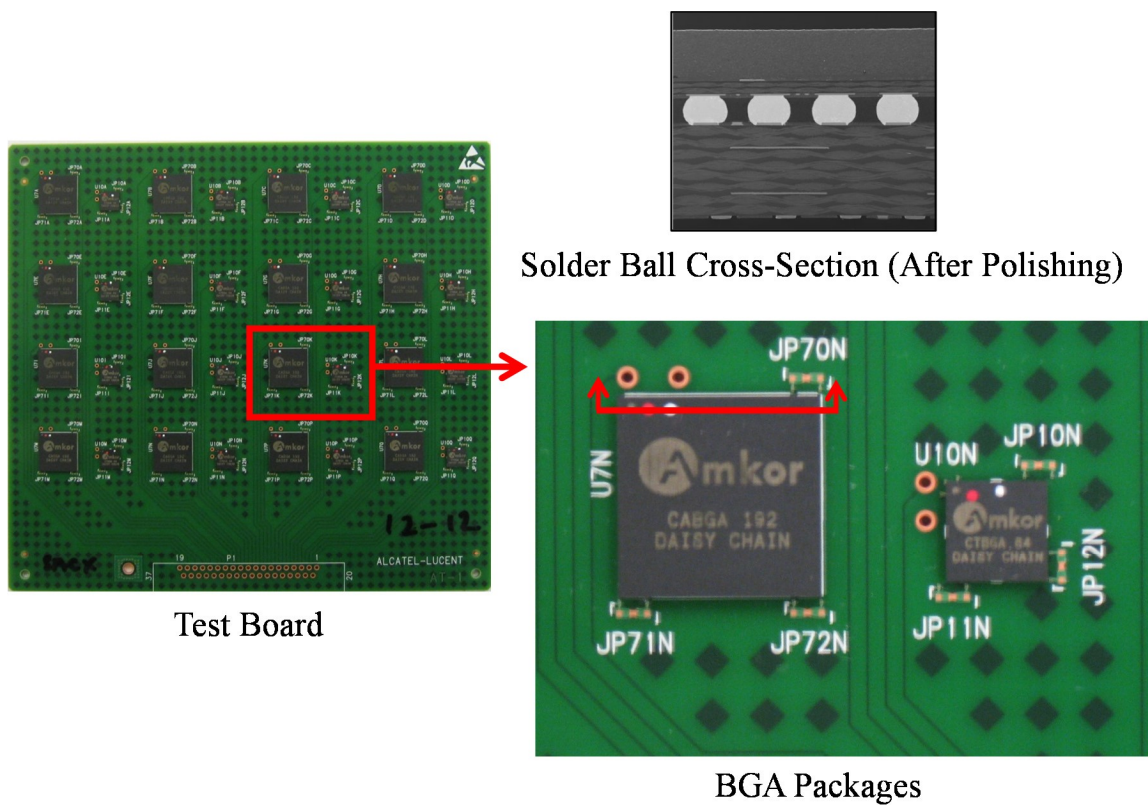


Figure 3.14 iNEMI Test Board and BGA Package



Figure 3.15 IsoMet 1000 Precision Cutter



Figure 3.16 Hysitron TI950 TriboIndenter

3.7 Summary and Discussion

All the experimental procedures and the data processing steps were presented in this chapter. Micro-scale uniaxial tensile specimens were prepared in a rectangular shaped hollow glass tube using a vacuum suction method. The mechanical testing was performed using a tension/torsion thermo-mechanical test system. After testing, empirical models were utilized to represent the stress-strain experimental data.

To study the solder microstructural changes during aging, lead free solder samples were formed with RF and WQ cooling profiles and resulting initial microstructures, and then microscopy cross-sections were prepared. After polishing, small indentation marks were added to the cross-sections to facilitate locating the identical regions of interest. Then the microstructural changes in the fixed regions during aging were examined using SEM.

CHAPTER 4

INVESTIGATION OF AGING INDUCED EVOLUTION OF THE MICROSTRUCTURE OF SAC305 LEAD FREE SOLDER

4.1 Introduction

Due to their low melting temperatures, lead free solders are exposed to high homologous temperatures in most product applications. Thus, there is a continuous state of active diffusion processes in the solder alloys, and their microstructures are inherently unstable and will continually evolve during normal operating temperature conditions of electronic packaging assemblies. Typical microstructure evolution in lead free solders includes coarsening of intermetallic phases and subgrains, breakdown of dendrite structures, as well as potential recrystallization of Sn grains. Such changes in solder microstructure are accompanied by dramatic changes in mechanical response and failure behavior, and these multifaceted evolutions occurring in the material are typically referred to as solder aging phenomena.

In this chapter, Scanning Electron Microscopy (SEM) has been utilized to examine the aging induced microstructural changes occurring within lead free solders. Unlike many prior studies, fixed regions in the solder joint cross-sections were monitored throughout the aging process, rather than examining different samples and/or different regions after the various aging exposures. SAC305 lead free solder joint samples were formed with reflowed (RF) and water quenched (WQ) cooling profiles and resulting initial

microstructures, and then polished microscopy cross-sections were prepared. Nanoindentation marks were added to the cross sections at certain locations to facilitate locating the fixed regions of interest in subsequent microscopy observations. The joints were then aged at $T = 125\text{ }^{\circ}\text{C}$, and the microstructures were observed and recorded in the selected regions after various aging exposures using SEM. With this approach, time-lapse imagery of the microstructure evolution in a particular region of a solder joint has been recorded.

4.2 Disadvantages of the Conventional Procedure

The conventional procedure to study the effects of aging on solder microstructure is comparing two different solder joint samples subjected to different aging conditions. However, this method is not accurate and sometimes can be misleading as two different samples cannot be directly compared even, they have the same composition. Figure 5.1 shows the solder microstructures of RF SAC305 in three different regions at the same magnification. In all the three regions, there are many subgrains within the dendrite and the subgrain boundaries can be discerned. However, the size and shape of the subgrains, IMCs or dendrites vary from region to region. Therefore, the results of microstructural changes may not be reliable by comparing two different samples or regions, especially when it comes to the quantitative analysis such as determination of the growth of IMC particles or subgrains with aging. This kind of comparison can lead to either right conclusion or wrong one. For example, Figures 5.2 and 5.3 illustrate the comparisons of non-aged microstructures (left-hand side) with aged microstructures (right-hand side) of RF SAC305 in different regions. Figure 5.2 shows the coarsening of IMC particles with

aging, which is the known/expected trend. However, by choosing two other regions, the result can be opposite, that is, aging led to finer IMC particles (Figure 5.3). In this chapter, the microstructure of an identical region has been examined before and after aging for various durations at 125 °C.

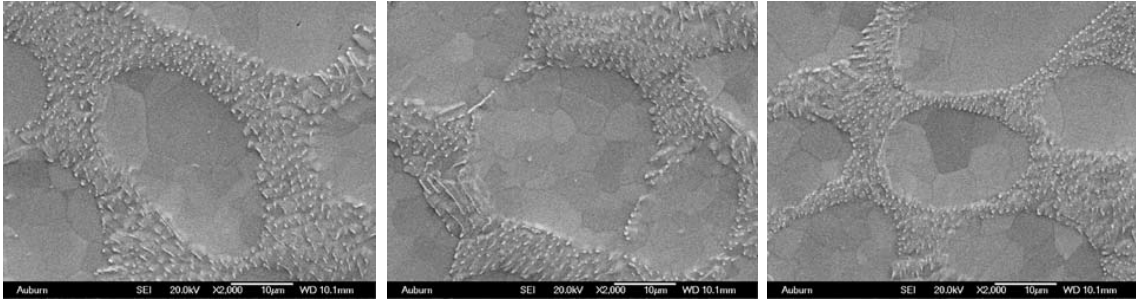


Figure 5.1 Comparison of RF SAC305 Microstructures in Three Different Regions

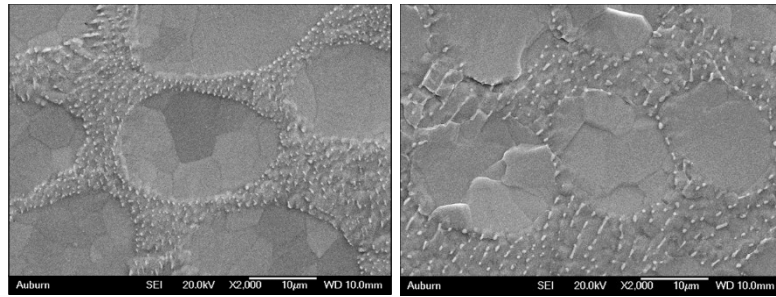


Figure 5.2 Aging Led to Coarser IMC Particles (Left: No Aging; Right: 6-Hour Aging)

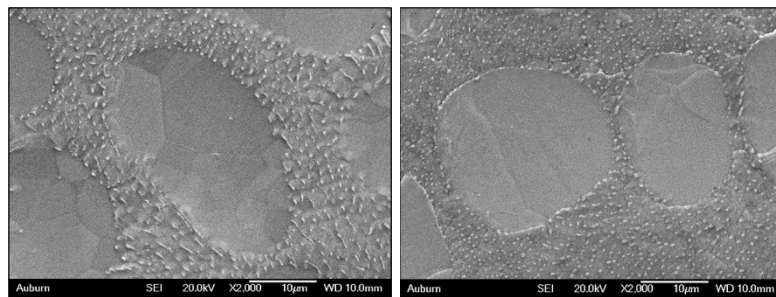
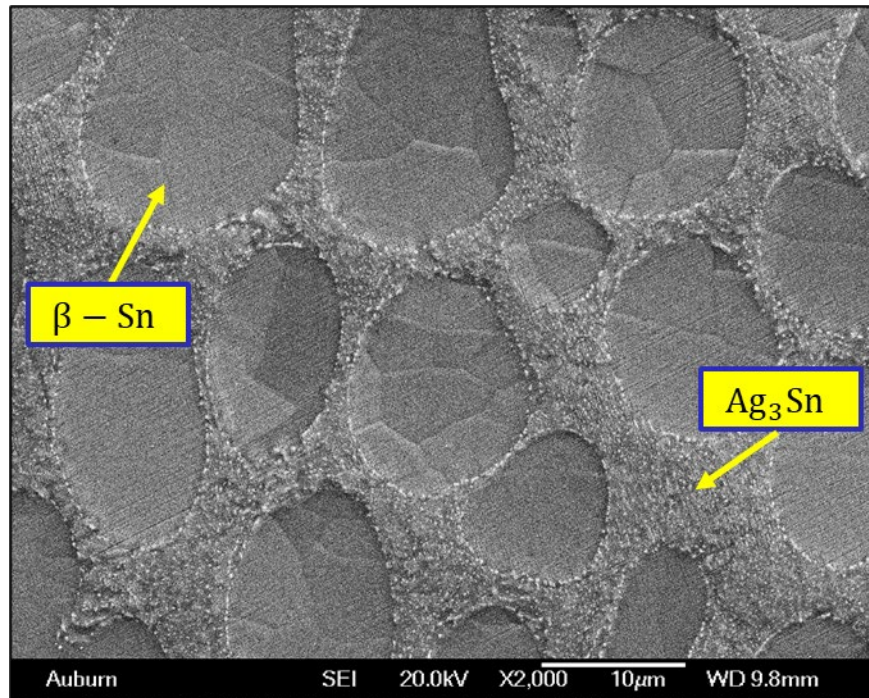


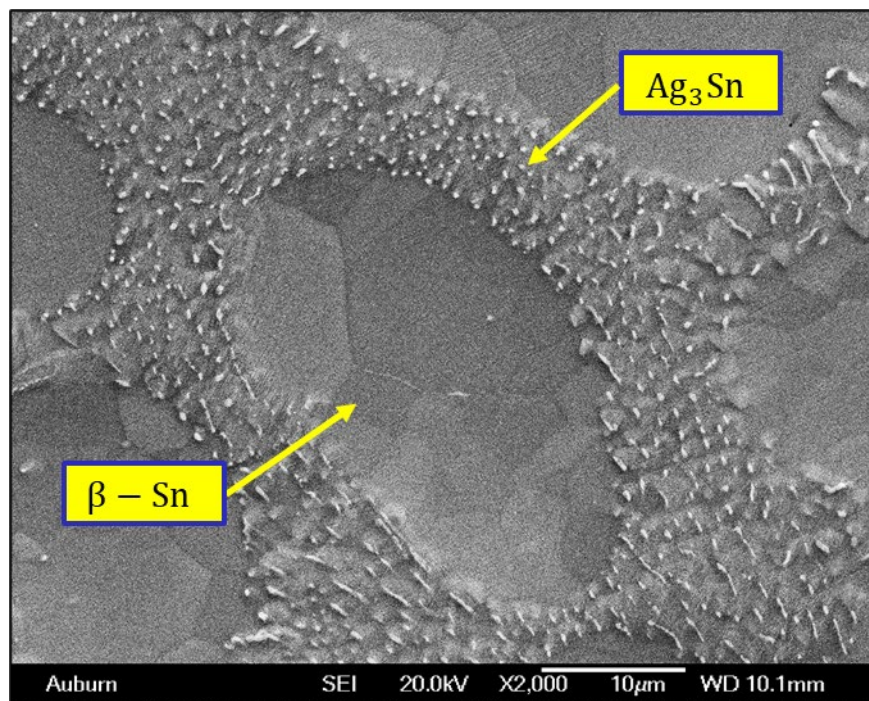
Figure 5.3 Aging Led to Finer IMC Particles (Left: No Aging; Right: 7-Hour Aging)

4.3 Aging Induced Solder Microstructural Evolution

Sn-Ag-Cu (SAC) lead free solder microstructures typically consist of β -Sn dendrites surrounded by interdendritic eutectic regions incorporating a fine dispersion of Ag_3Sn and Cu_6Sn_5 intermetallic particles in β -Sn. For example, Figure 5.8 shows typical WQ and RF microstructures for the non-aged solder joint samples in this work. Since the same length scale has been used in each image, it is clear that the microstructure of WQ SAC305 is much finer than that of RF SAC305. This was expected due to the much faster cooling rate of WQ temperature profile. Relative to the RF solder sample, the WQ sample features smaller IMC particles and dendrites, as well as smaller β -Sn subgrains within the dendrites and interdendritic eutectic regions. For instance, there is just one complete dendrite in the field of view of the RF SAC305 sample (Figure 5.4(a)), while there are approximately twelve dendrites in the region of same size for WQ SAC305 sample (Figure 5.4(b)). In addition, the IMC particles are clearly much finer in the WQ microstructure relative to the RF microstructure, which has been verified quantitatively by image analysis as discussed later in this chapter. The IMC particles and dendrite structures can pin and block the movement of dislocations. Thus, the WQ specimens have superior mechanical properties and reduced creep relative to the RF specimens. However, the WQ microstructure is inherently more unstable and suffers larger changes when exposed to isothermal aging. The coarsening of Ag_3Sn particles has greater influence on solder mechanical properties than the coarsening of Cu_6Sn_5 does, as the volume fraction of Ag_3Sn is much higher in SAC alloys [99, 145].



(a) Water Quenched (WQ)

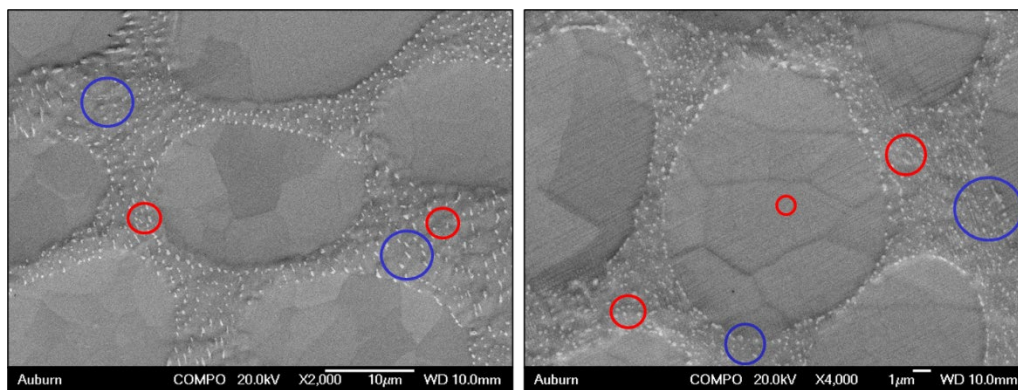


(b) Reflowed (RF)

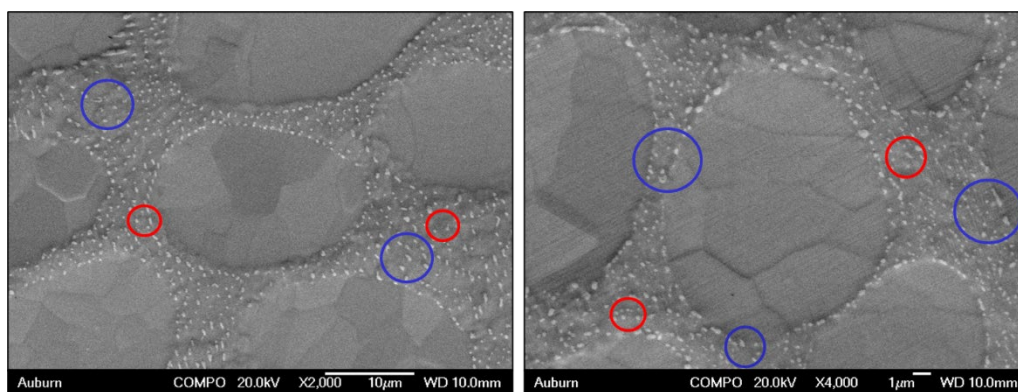
Figure 5.4 SAC305 Microstructures as Reflowed

Figure 5.5 shows the observed microstructural evolution in the selected region of the WQ SAC305 sample with isothermal aging at 125 °C for up to 270 hours. Even though the sample was only aged for few hours, the WQ microstructure changed significantly. As expected, the most obvious changes were the coarsening of IMC particles. In particular, the number of IMC particles decreased, while the average size of the particles and average particle separation distance increased significantly with aging. As shown in Figure 5.5, the microstructure of RF SAC305 also evolved with aging, but to a lesser degree than the WQ microstructure. For example, blue circles in Figure 5.5 show typical positions where particles were growing, while red circles illustrate positions where the particles disappeared, and the number of particles decreased. Additionally, it was observed that needle-shaped IMCs broke into several small, rounded sphere-like particles with aging. Note that the scale of WQ microstructure images is twice as big as the scale of RF microstructure images in Figure 5.5.

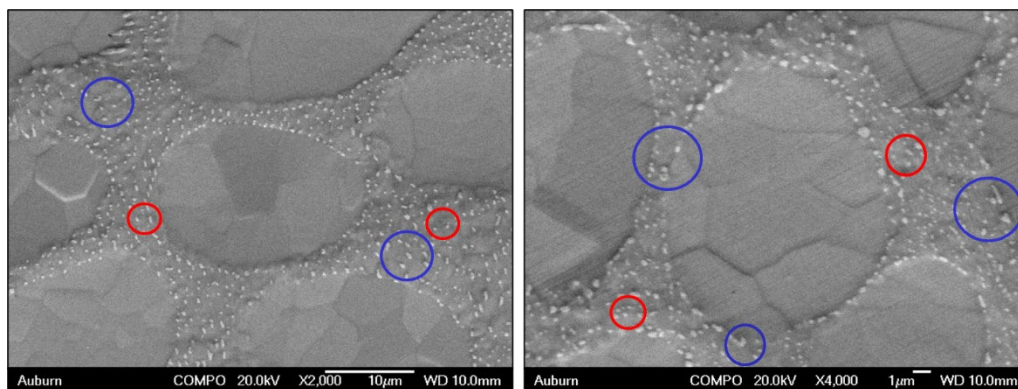
In addition, it is noticeable that some Sn grains experienced the issue of “pop-up” during aging, and this is mainly due to the free surface created by cross-sectioning. During aging, the thermal anisotropy of Sn results in the force to elevate some subgrains, and there are no constraints in the Z direction (perpendicular to the field of view) as it is free surface. As a result, the “pop-up” of those subgrains is more and more obvious as the aging progresses, which can be observed in the microstructural evolution of several regions of interest.



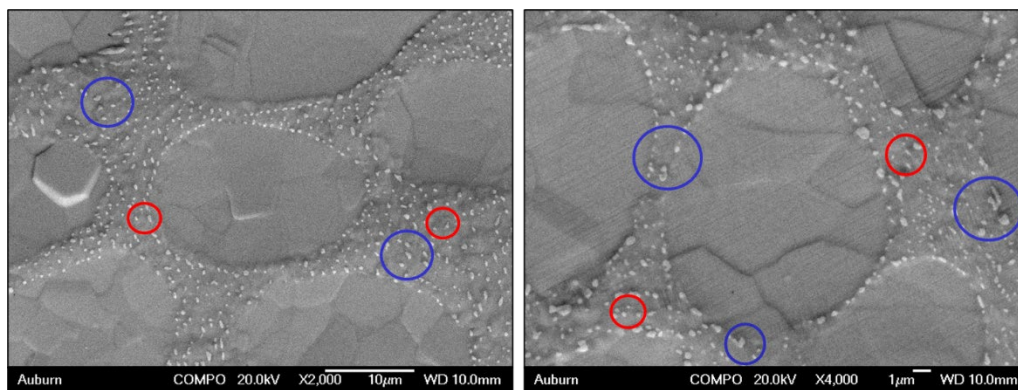
(a) No Aging (Left: RF SAC305; Right: WQ SAC305)



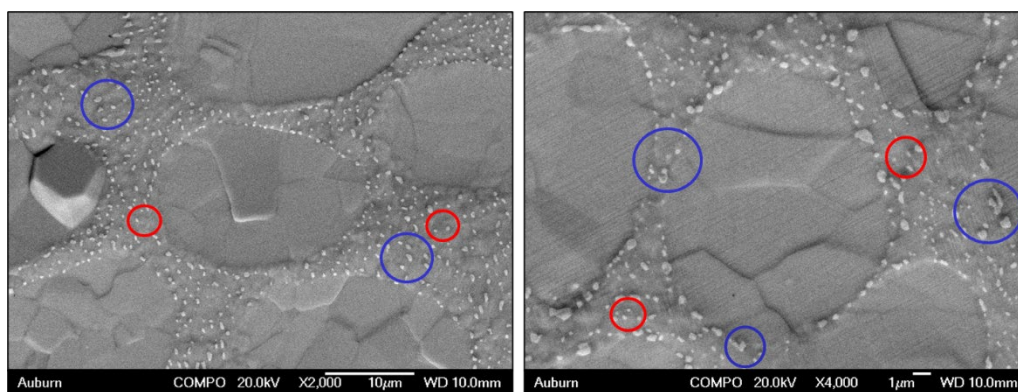
(b) 1 Hour of Aging (Left: RF SAC305; Right: WQ SAC305)



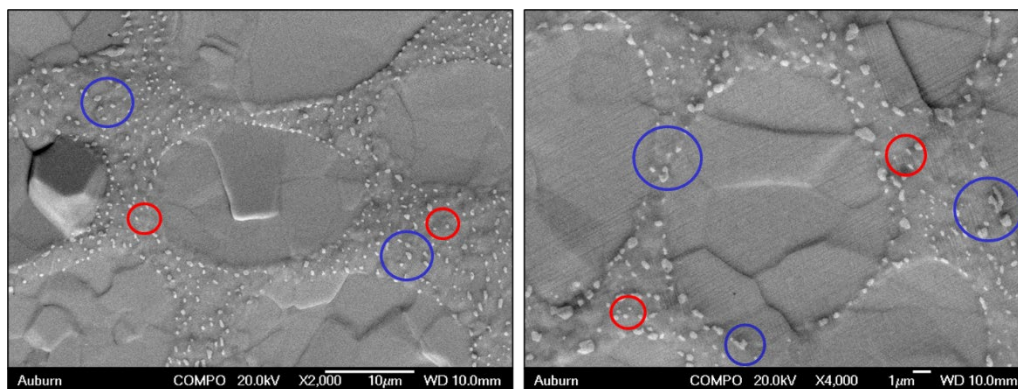
(c) 2 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



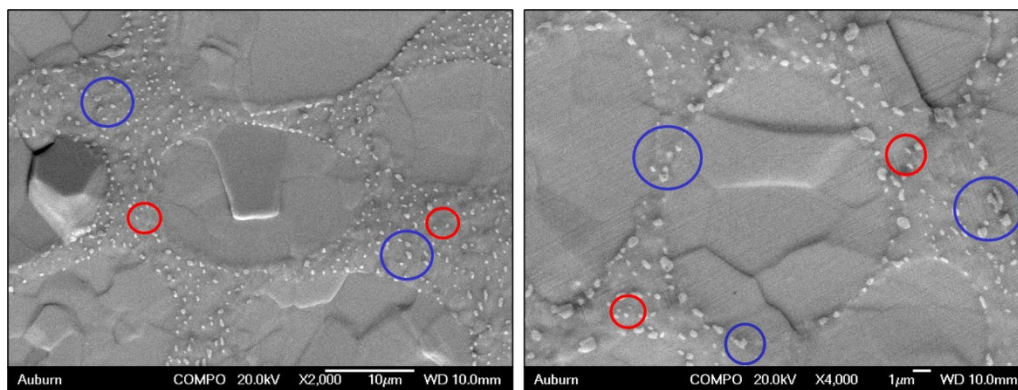
(d) 4 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



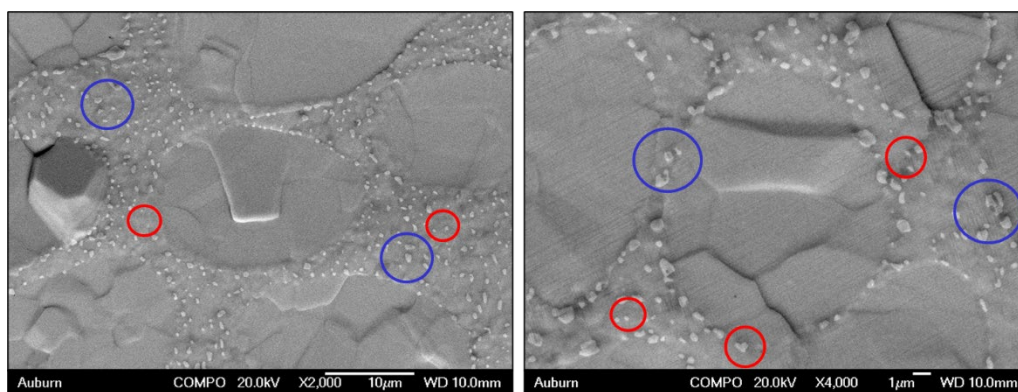
(e) 6 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



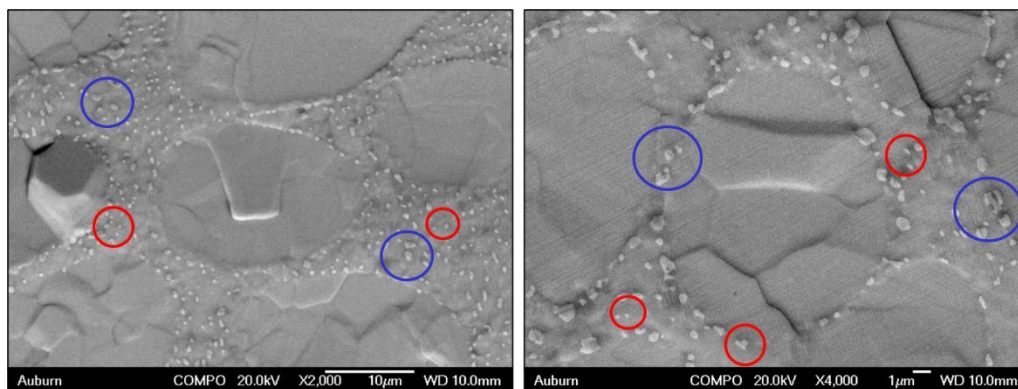
(f) 8 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



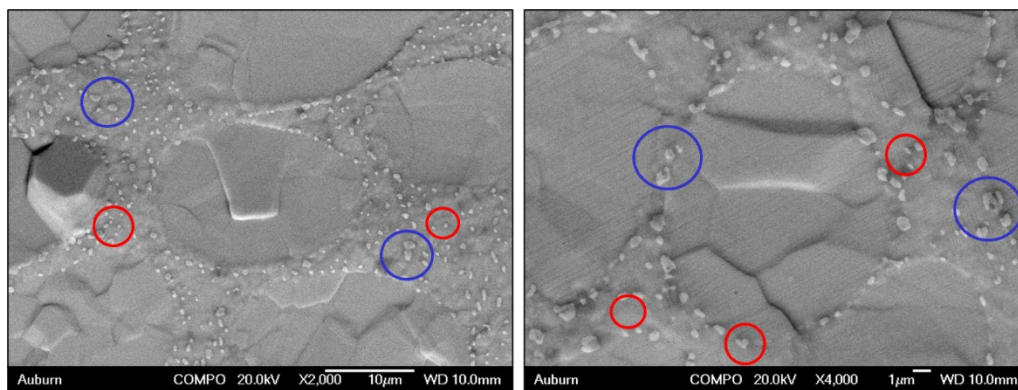
(g) 10 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



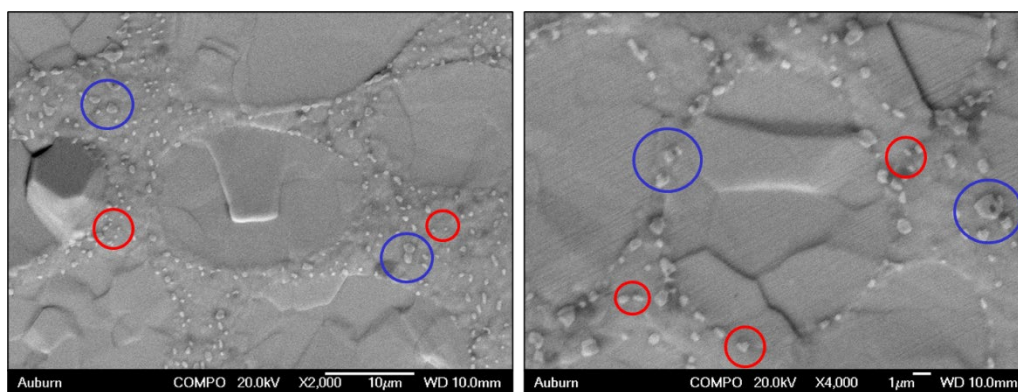
(h) 20 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



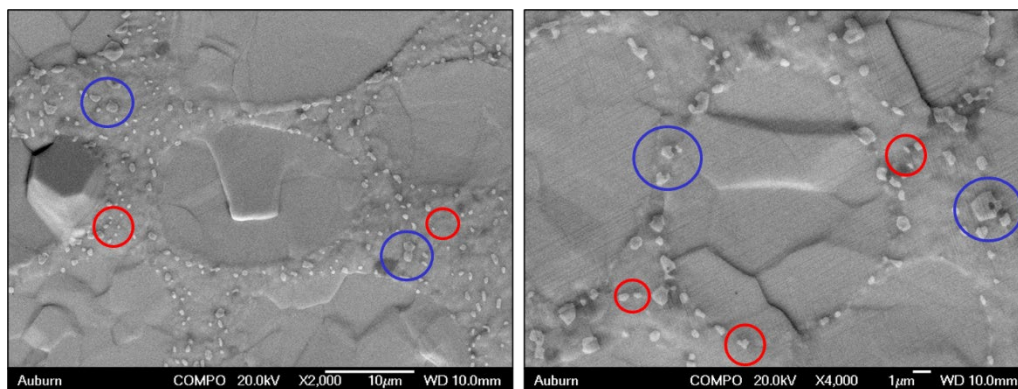
(i) 30 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



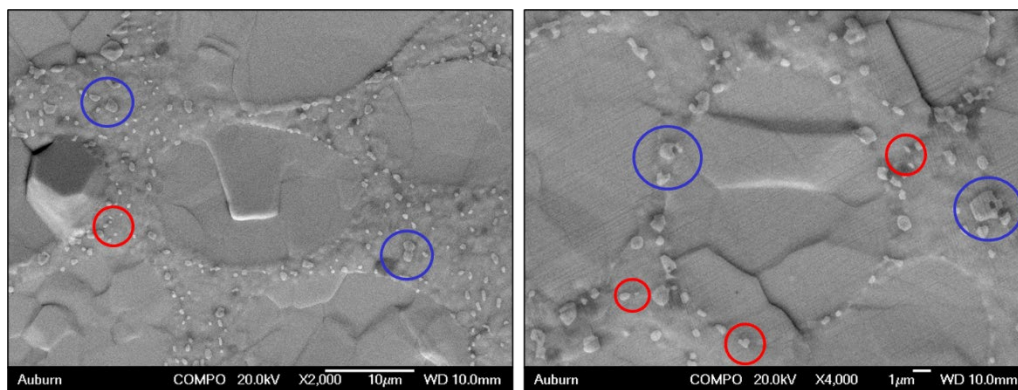
(j) 40 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



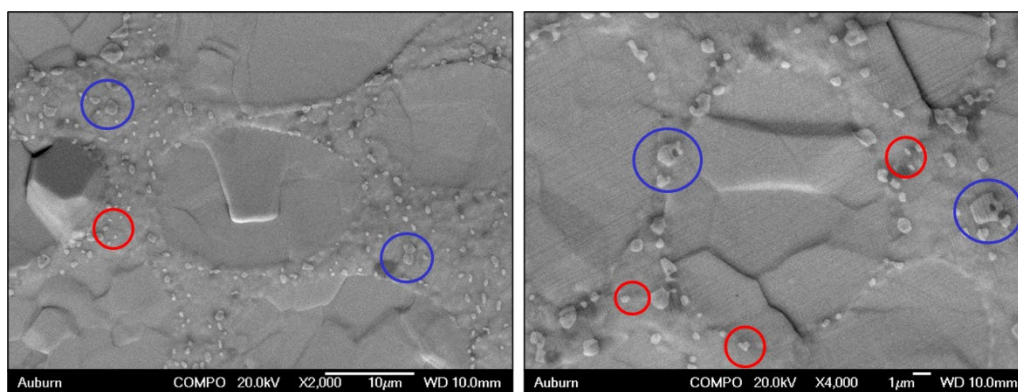
(k) 60 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



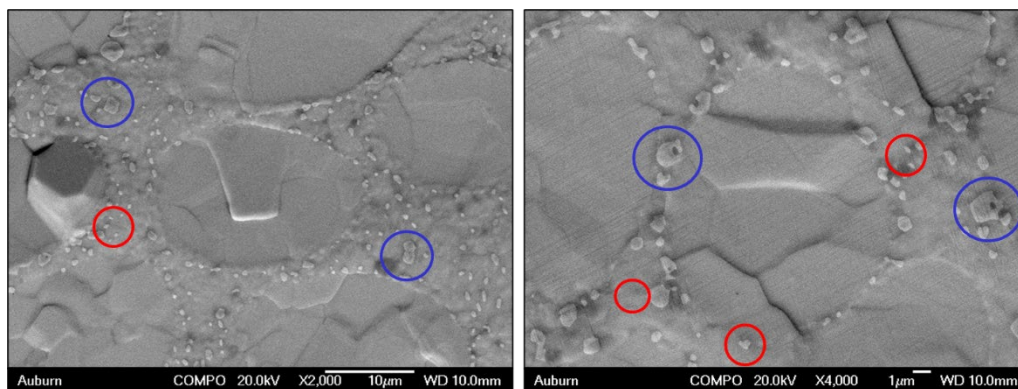
(l) 80 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



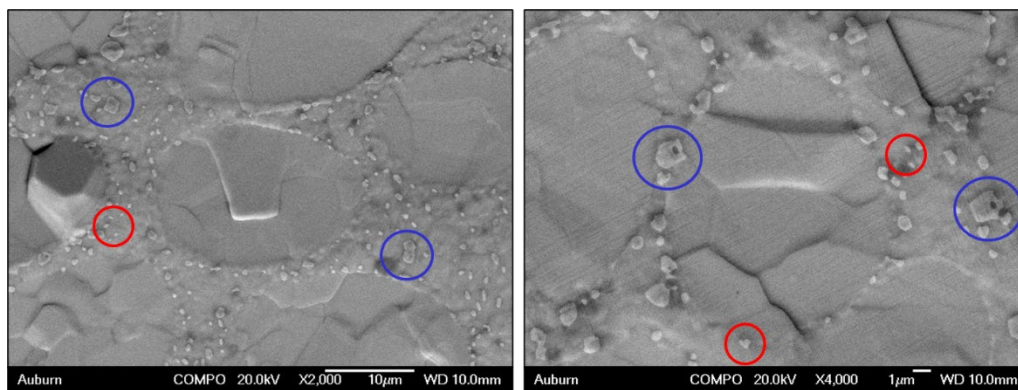
(m) 100 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



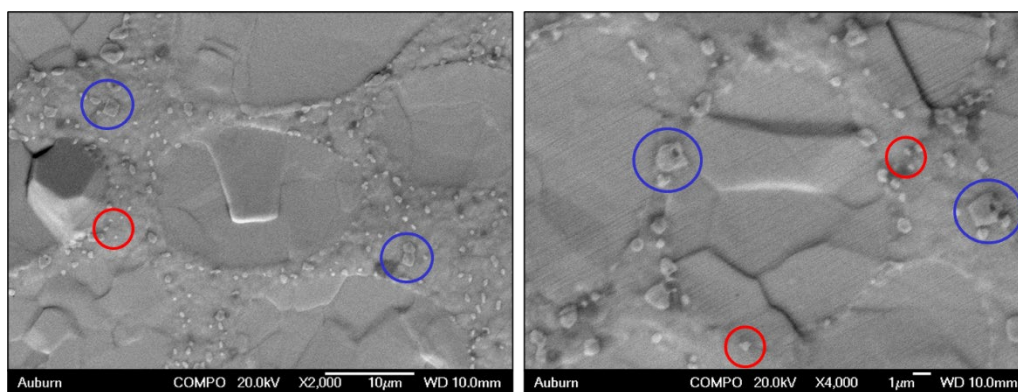
(n) 120 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



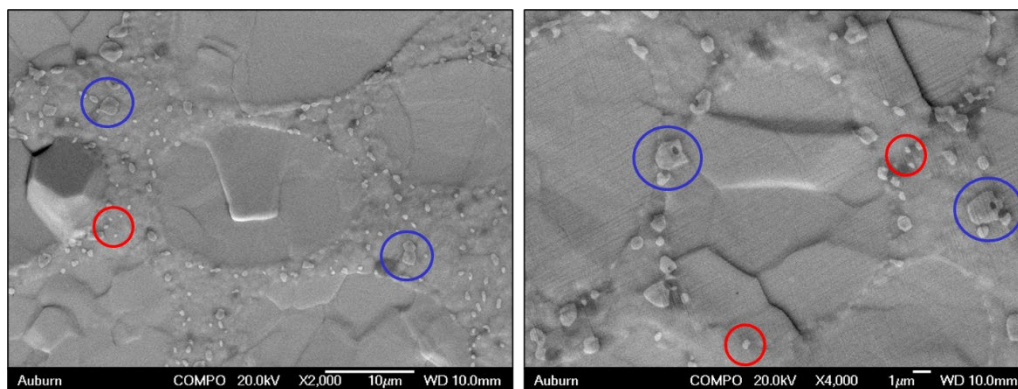
(o) 140 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



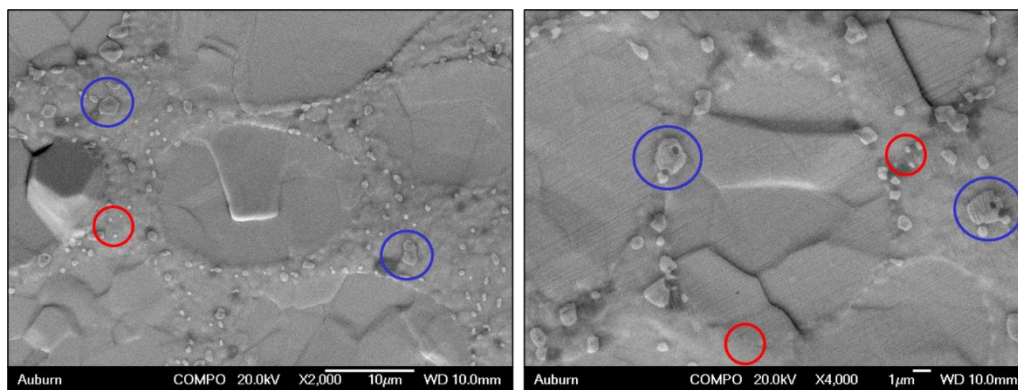
(p) 160 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



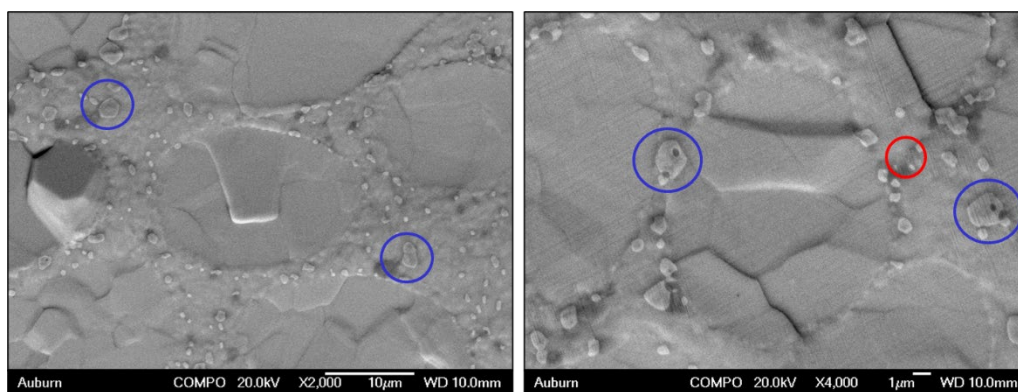
(q) 180 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



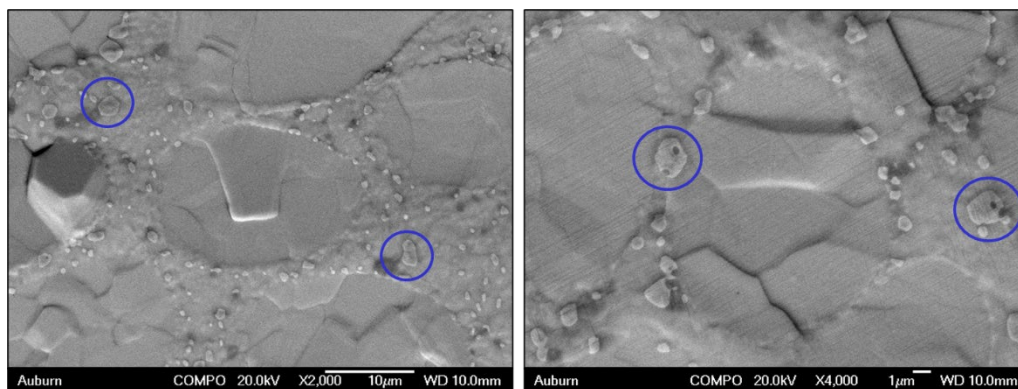
(r) 200 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



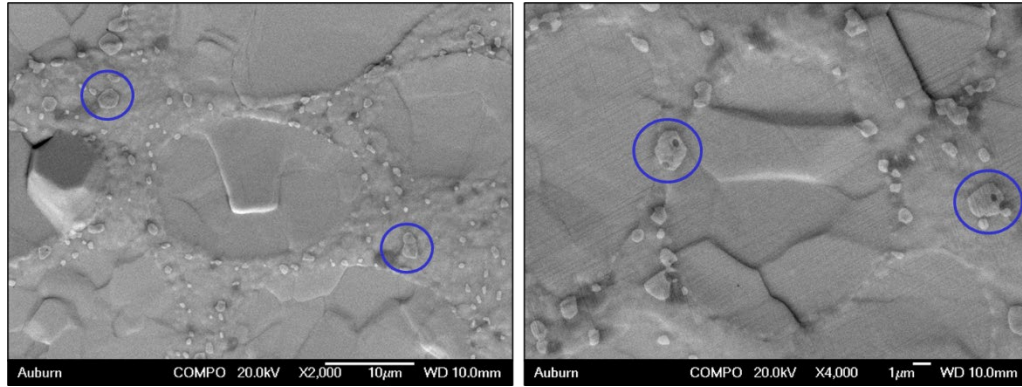
(s) 220 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



(t) 240 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



(u) 260 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)



(v) 270 Hours of Aging (Left: RF SAC305; Right: WQ SAC305)

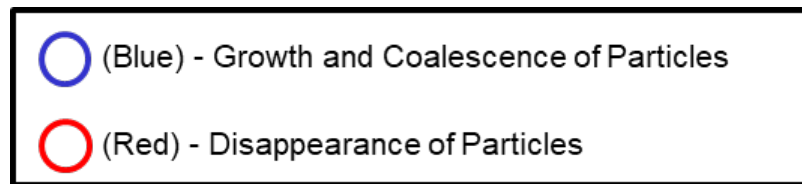


Figure 5.5 Aging Induced Microstructural Evolution of RF and WQ SAC305 by SEM

(Aging at $T = 125\text{ }^{\circ}\text{C}$, up to 270 Hours)

4.4 Discussions on the Coarsening of IMCs with Aging

Similar microstructural changes have been found on the samples that were aged at $125\text{ }^{\circ}\text{C}$ for a longer time. Compared with RF SAC305, WQ SAC305 had much finer initial IMC particles but they coarsened to a greater degree during isothermal aging. The coarsening of IMCs was more obvious for longer durations of aging, which was expected. Typically, IMC particles tend to become rounder (spherical) with aging. Atoms on the surface of a particle have higher energy than the atoms inside a particle due to unsatisfied bonds in the surface atoms. A cylindrical or elongated particle has a higher fraction of surface atoms (or higher surface to volume ratio) compared to a spherical (round) particle with the same volume. As a result, the free energy per atom of an elongated particle is

higher than that of a round particle. This free energy difference is the driving force that causes the transition of IMC particles from needle-shaped to a more rounded shape.

Another common observation is that larger particles are produced at the expense of smaller particles. This IMC coarsening phenomenon is also known as Ostwald Ripening. According to the Gibbs-Thompson effect [146-148], an increase in particle size is accompanied by a decrease of the solute concentration in the matrix surrounding the particle. This leads to a concentration gradient, and solute atoms near smaller particles will diffuse towards the larger particles where the reduction in solute concentration has occurred. In addition, atoms from the smaller particles will go back into solution. The overall effects are shrinkage of smaller particles, and growth of larger particles. Since Ostwald Ripening is a diffusion-based process, use of higher aging temperatures will increase the rate of coarsening significantly.

The coarsening and coalescing of IMC particles during aging is known to play a critical role in the degradations of solder mechanical properties. IMC particles will pin and block the movement of dislocations. However, aging leads to both a smaller number of larger IMC particles and increased spacing between the IMC particles. Orowan proposed a mechanism that when a dislocation crosses incoherent precipitate particle (like the IMC particles in present case), it will bow and leave a loop of stress field around the particle [149]. The yield stress and strength of a material depends on the shear stress (also known as the Orowan stress) that is required for a dislocation to pass through the particles. This shear stress will decrease as the inter-particle spacing increases during aging. Therefore, the yield stress and strength of a material will decrease with the coarsening and coalescing of IMC particles.

CHAPTER 5

QUANTITATIVE ANALYSIS OF THE AGING INDUCED EVOLUTION OF IMC PARTICLES IN FIXED REGIONS

5.1 Introduction

The microstructure and mechanical properties of Sn-Ag-Cu (SAC) solder joints in electronic assemblies are constantly evolving when exposed to isothermal aging. Such exposures lead to evolution of the solder microstructure, which results in changes in the mechanical properties and creep behavior of the solder joints. These changes often lead to dramatic reductions in reliability of lead free electronic assemblies subjected to aging. The root cause of the changes in solder joint mechanical behavior is the evolution of the SAC solder microstructure that occurs during aging. This includes coarsening of the Ag_3Sn intermetallic compounds (IMCs) present in the eutectic regions between β -Sn dendrites. The coalescence and migration of Ag_3Sn IMCs and the coarsening of β -Sn dendrites have been observed as a function of aging time, and quantitative analysis of the variations in IMC particle size during aging has been performed. Different increments and two solidification profiles (RF and WQ) have been examined. Several SAC305 lead free solder samples were prepared and well-polished for this purpose. After each aging duration, the microstructures of the regions of interest in the samples were captured using SEM microscopy.

Multiple regions were observed in several different RF and WQ solder joint samples. At last, the coarsening of IMC particles in fixed regions during aging has been recorded as a function of the aging time. Particularly, the aging induced evolutions of number of IMCs, total area of all IMCs, average particle area, and average particle diameter have been quantified. Some researchers have proposed empirical models to describe the growth of these secondary phase particles as a function of aging temperature and aging time and related this growth to mechanical property changes. In most of the prior investigations, microstructural changes during aging have been observed by comparing two different solder joints subjected to different aging conditions. Thus, the comparisons made were qualitative in nature (e.g., average IMC particle size) since the two microstructures were from different samples and could not be directly compared.

5.2 Measurement of Area and Number of IMCs

To quantitatively analyze the coarsening of IMC particles during aging, several subregions have been selected and Figure 5.1 and Figure 5.2 show the examples interdendritic eutectic sub-region present in the SEM micrograph of RF SAC305 sample. Image analysis methods were used to perform the quantitative analysis. The gray-scale images were first converted to binary images (shown in Figure 5.3), and then the areas of IMC particles (white objects) were calculated using image analysis code written in MATLAB. The microstructure of this sub-region was studied every 1 hour of aging, and Figure 5.4 shows SEM images that illustrate aging induced evolution of IMC particles up to 270 hours in this sub-region for WQ SAC305. From these images, it is easy to see that aging causes: (1) the number of IMC particles to decrease, (2) the average size of the

intermetallic particles to increase, and (3) the average spacing between intermetallic particles to increase. Figure 5.5 shows the evolution of IMCs with aging up to 270 hours for RF SAC305. Similar changes have also been found in other studied sub-regions of RF and WQ SAC305 samples that were subjected to longer durations of aging (see Figures 5.6-5.7). It is clear that WQ microstructures suffered more changes during aging relative to RF microstructures. For the samples that were aged at an increment of 10 days, relative larger sub-regions were chosen to perform the analysis as they experienced more significant microstructural changes.

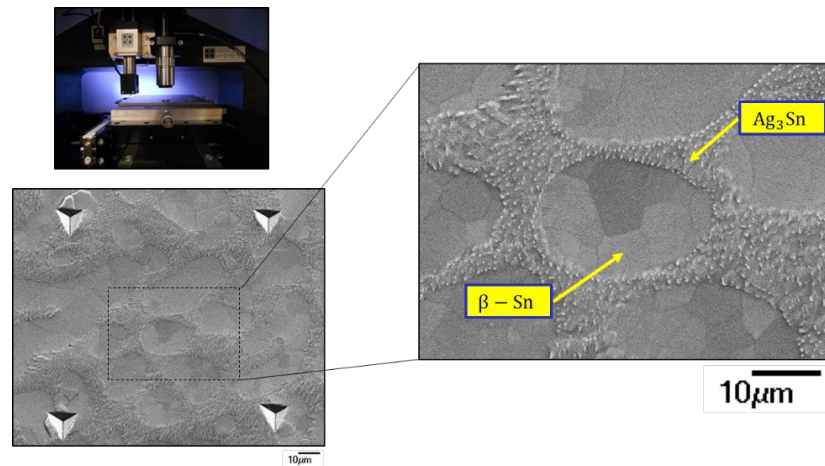


Figure 5.1 Example Region of Nanoindentation Locating Markers with Region of Interest

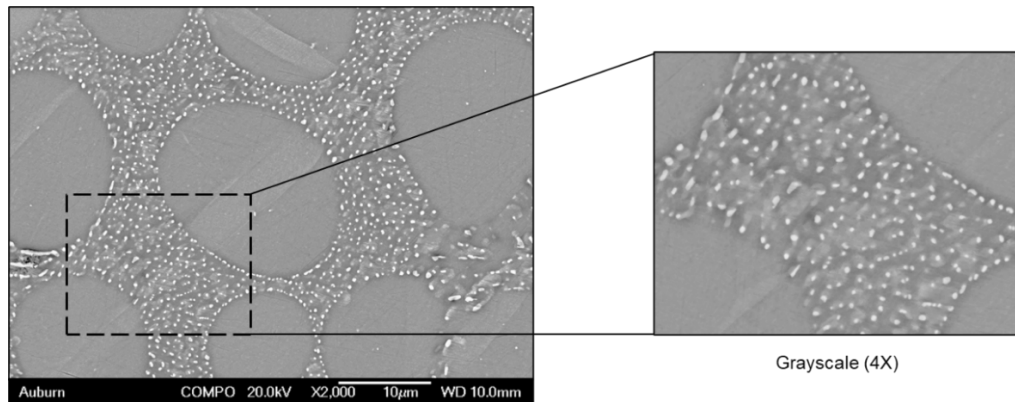


Figure 5.2 Sub-Region for Quantitative Analysis of Aging Effects on IMCs

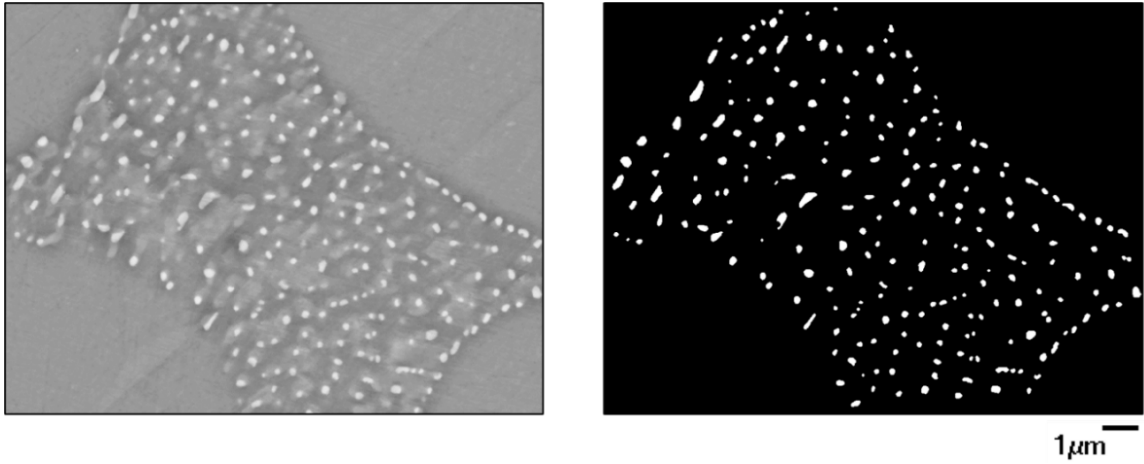


Figure 5.3 The Conversion from a Gray-Scale Image to a Binary Image

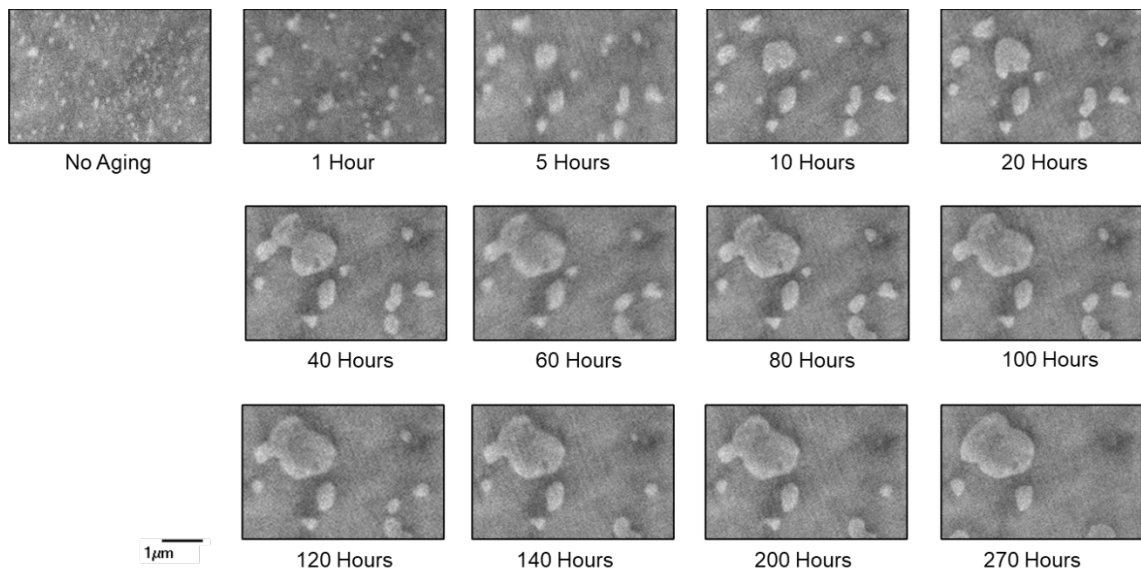


Figure 5.4 Aging Induced Evolution of IMCs at 125 °C
(Aging Increment: 1 Hour; WQ SAC305)

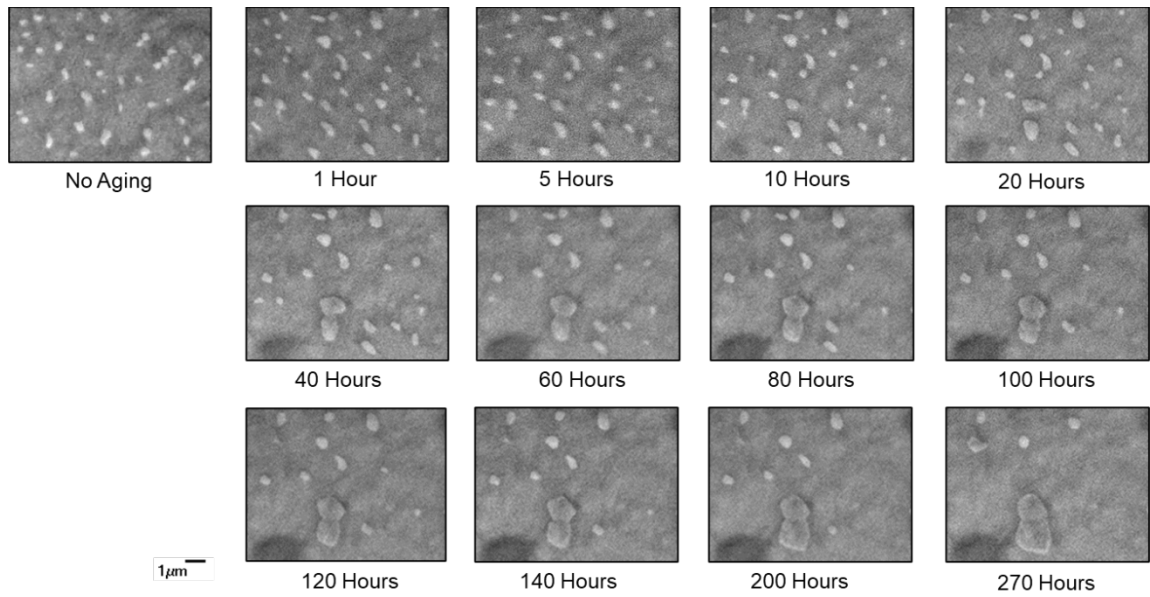


Figure 5.5 Aging Induced Evolution of IMCs at 125 °C
(Aging Increment: 1 Hour; RF SAC305)

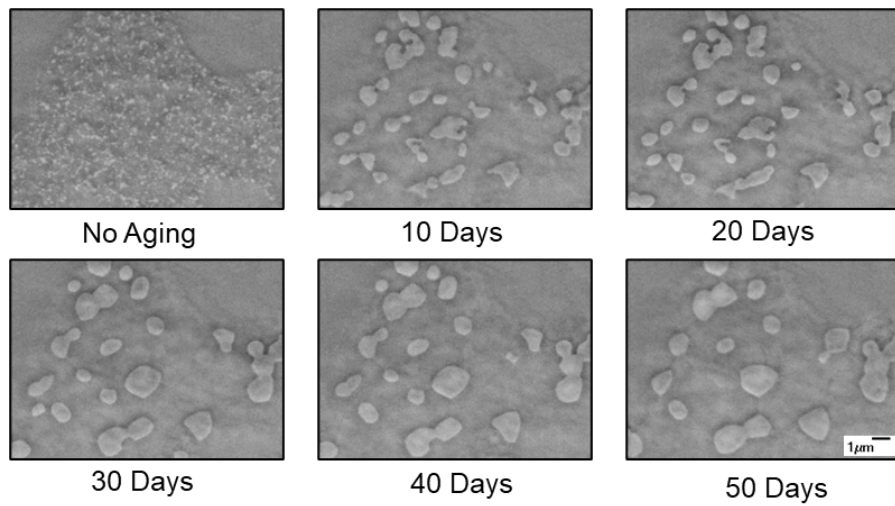


Figure 5.6 Aging Induced Evolution of IMCs at 125 °C
(Aging Increment: 1 Hour; WQ SAC305)

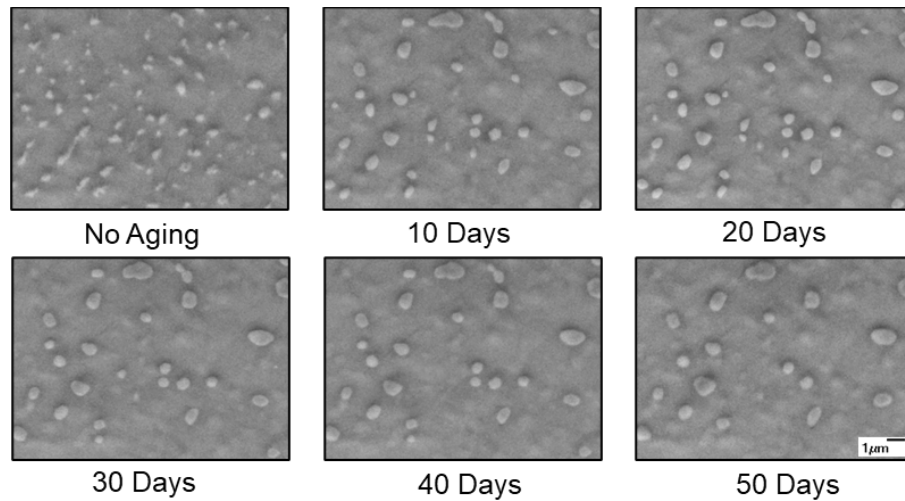


Figure 5.7 Aging Induced Evolution of IMCs at 125 °C

(Aging Increment: 1 Hour; RF SAC305)

5.3 Measurement of Particle Diameter

As shown for an ideal spherical IMC particle in Figure. 5.8, the amount of the particle that is visible on the polished cross-sectional surface is actually unknown. Here, the black portion of the particle represents the portion on IMC exposed on the polished surface, while the gray shaded portion is the portion of the IMC below the surface. As indicated in Figures. 5.8 and 5.9, the observed particle diameter (apparent diameter) for a particle is actually less than or equal to the actual particle diameter. Thus, the measured (apparent) average particle diameter must be adjusted to calculate the actual average particle diameter.

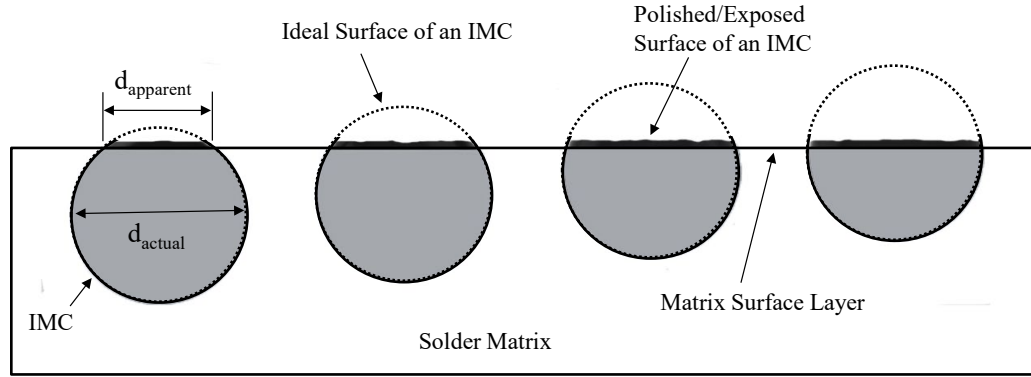


Figure 5.8 A Schematic Representation of an IMC with Several Possible Exposed Area above the Surface Layer.

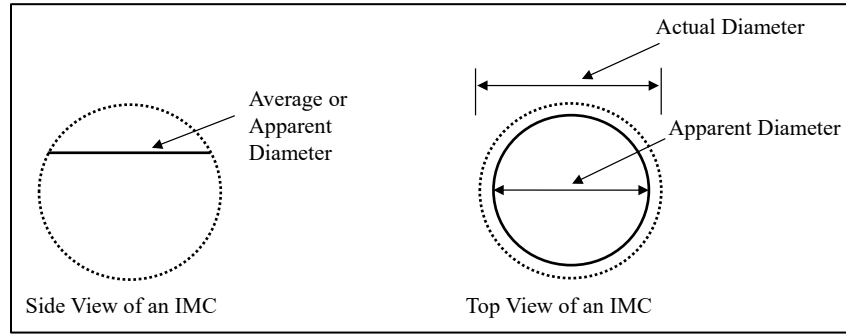


Figure 5.9 Side and Top View of an Ideal Spherical IMC Particle Showing Actual and Apparent Diameters.

For a fixed particle with diameter d , the apparent/measured particle diameter d_{apparent} can be several different values based on the vertical position of the particle (Figure 5.8). The average value of d_{apparent} can be found mathematically by averaging all possible values obtained from all possible vertical positions for the particle:

$$(d_{\text{apparent}})_{\text{ave}} = 2 \times (R_{\text{apparent}})_{\text{ave}} = \frac{2}{R} \int_0^R \sqrt{(R^2 - x^2)} dx \quad (5.1)$$

$$(d_{\text{apparent}})_{\text{ave}} = \frac{2}{R} \times \frac{\pi R^2}{4} = \frac{\pi}{4} d_{\text{actual}} \quad (5.2)$$

$$d_{\text{actual}} = \frac{4}{\pi} (d_{\text{apparent}})_{\text{ave}} \quad (5.3)$$

Equation 5.3 was used to estimate the actual diameter of each particle by adjusting the measured (apparent) diameter.

If the particles are spherical, the apparent diameter of the exposed surface of each particle can be calculated by assuming a circular relation between particle surface area and apparent diameter:

$$A_{\text{apparent}} = \pi R^2 = \frac{\pi}{4} (d_{\text{apparent}})^2 \quad (5.4)$$

$$d_{\text{apparent}} = \frac{2}{\sqrt{\pi}} \sqrt{A_{\text{apparent}}} \quad (5.5)$$

Combining of Equations (5.3, 5.5) yields the relation for the particle diameter in terms of the measured/particle surface area:

$$d_{\text{actual}} = \frac{4}{\pi} (d_{\text{apparent}})_{\text{ave}} = \frac{8}{\pi^{3/2}} \sqrt{(A_{\text{apparent}})_{\text{ave}}} \quad (5.6)$$

In addition to the averaging assumptions made above, this analysis also assumes that the particle does not move vertically during the aging process.

5.4 Aging Induced Microstructural Evolution in RF SAC305

Figure 5.10 shows the observed time lapse imagery of the microstructural evolution in one example region of a SAC305 sample for isothermal aging at 125°C for up to 270 hours. As expected, coalescing and coarsening of the intermetallics has occurred. In

particular, diffusion of Ag has taken place leading to a decrease in the number of Ag_3Sn IMC particles, and an increase in the average particle size and average particle separation distance. The most dramatic changes occurred in the first 24 hours with slower but steady diffusion following. As shown in Figure 5.10, needle-shaped IMC particles (black circles in Figure 5.10) transition to more rounded (spherical) shapes. During this transition, larger particles (blue circles in Figure 5.10) are produced at the expense of smaller particles (red circles in Figure 5.10) through an Ostwald Ripening diffusion process. Similar results were observed for different temperatures and different alloys. The images in Figure 5.10 and from two similar regions have been processed to extract the evolution of the average particle diameter. Figure 5.11 illustrates the extracted data for short-term aging of SAC305 up to 270 hours at 125°C . The red curve in this plot is an empirical model (two term exponential) fit to the three data sets.

Similar observations of microstructural changes have been made for additional SAC305 samples subjected to long term isothermal aging of up to 7000 hours at 125°C . Figure 5.12 shows example results from one of the interdendritic eutectic regions. Analogous to prior results, there was significant coarsening of the IMC particles during the first 250 hours of aging. Subsequently, the diffusion-based coarsening occurred at a much slower but steady (linear) rate as illustrated by the particle diameter vs. aging time graph in Figure 5.13. The averaged data from Figure 5.11 and Figure 5.13 are plotted together in a single graph in Figure 5.14. This plot includes both short term and long term aging data, and the particle diameter has been normalized using the initial diameter values for each data set. The results obtained from short and long term aging studies appear to be consistent with one another.

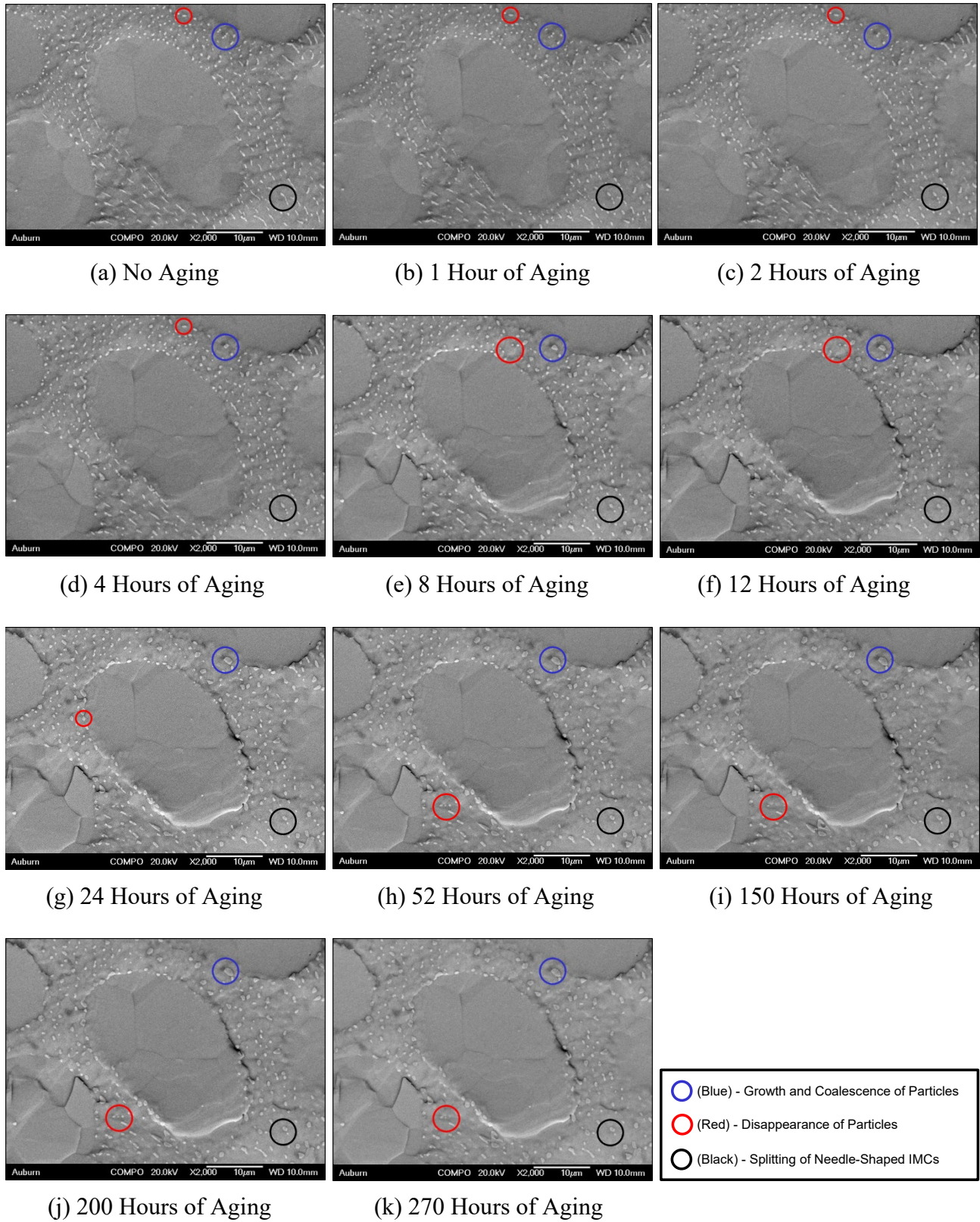


Figure 5.10 Microstructural Evolution for Short Term Aging of SAC305 (up to 270 Hours of Aging at $T = 125^{\circ}\text{C}$)

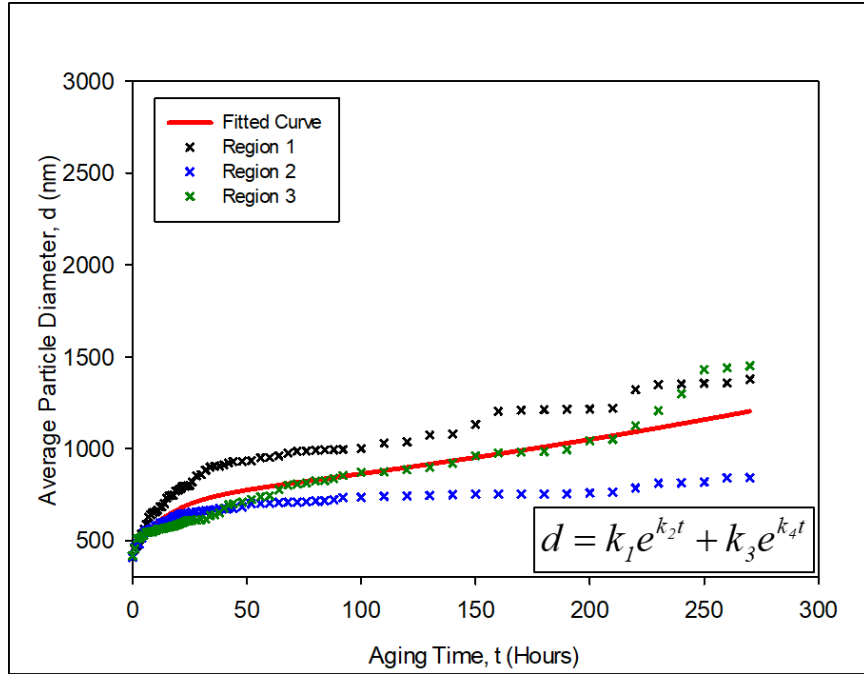


Figure 5.11 Variation of IMC Particle Diameter with Aging Time
(SAC305; Aging Increment: 1 Hour; Aging at 125 °C)

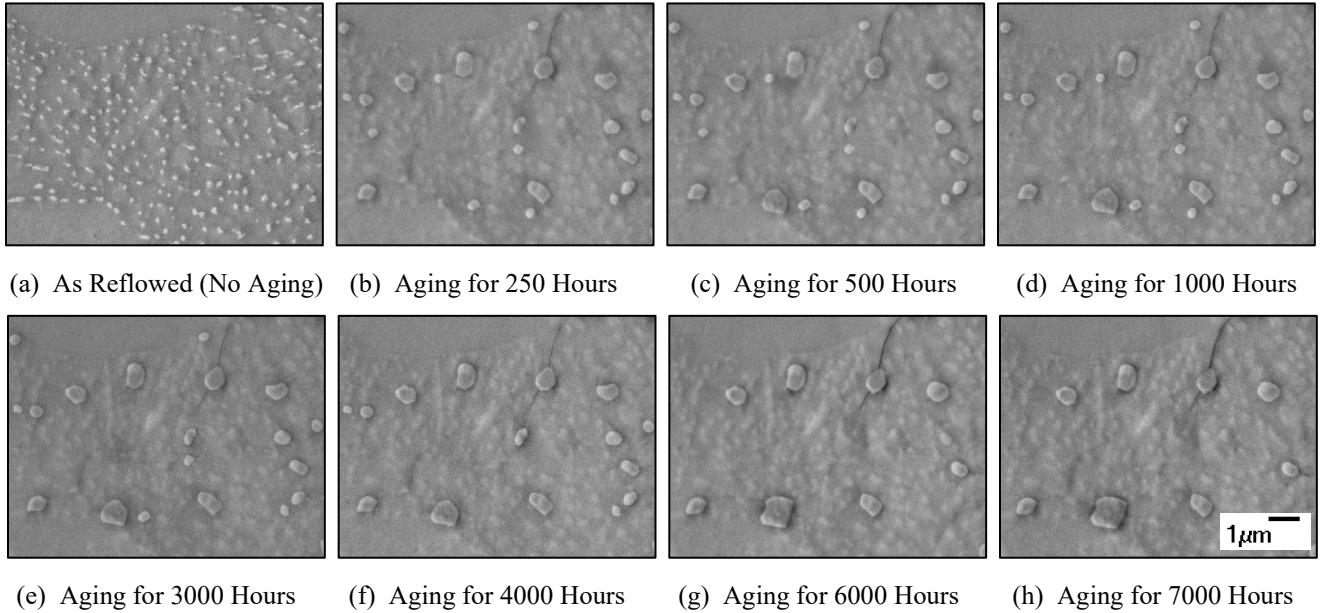


Figure 5.12 Example Microstructural Changes in SAC305 Subjected to Long Term
Aging for 7000 Hours at $T = 125\text{ }^{\circ}\text{C}$

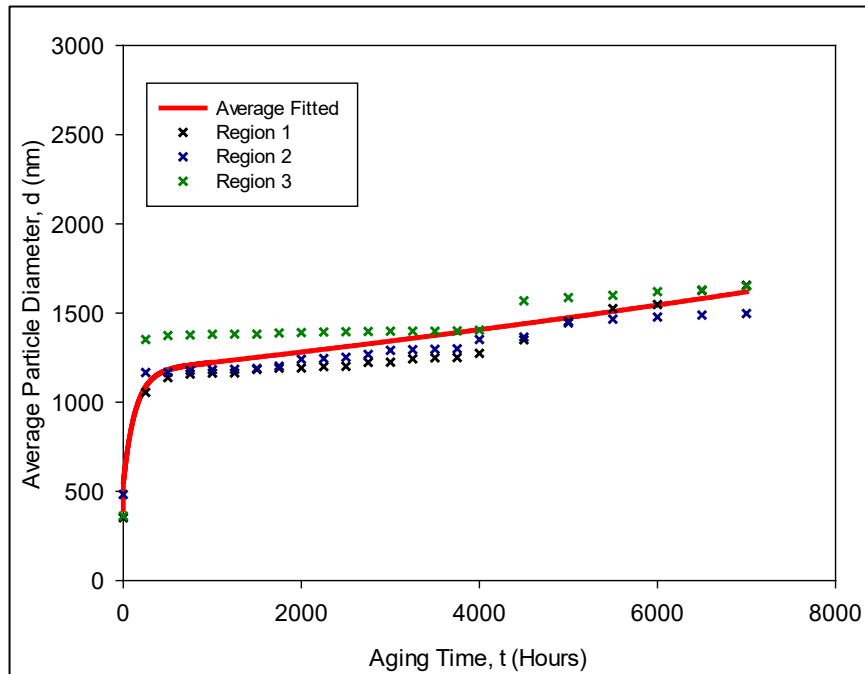


Figure 5.13 Variation of IMC Particle Diameter with Aging Time
(SAC305; Aging Increment: 250 Hours; Aging at 125 °C)

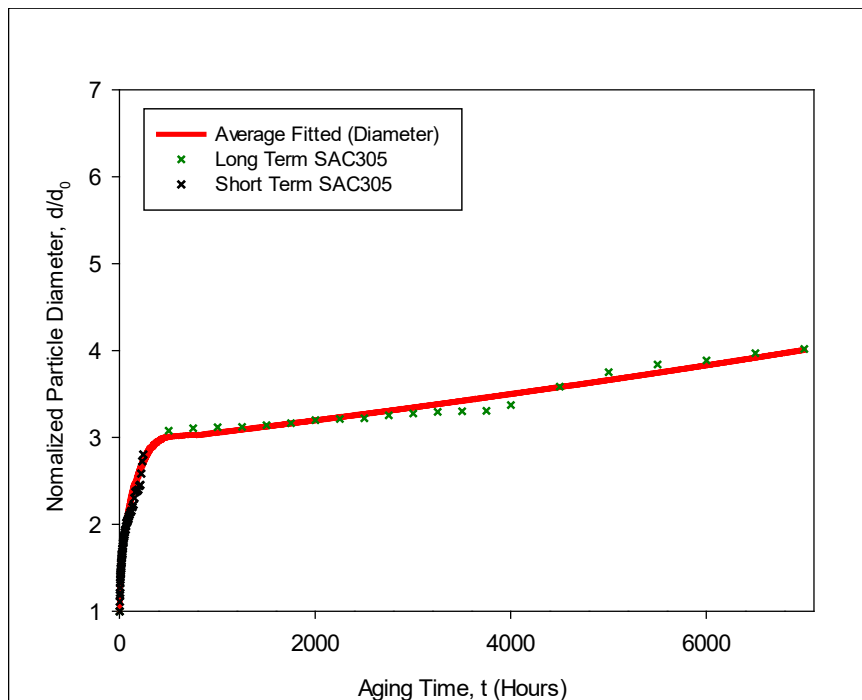


Figure 5.14 Variation of Normalized Particle Diameter with Aging Time
(SAC305; Short Term and Long Term Aging)

5.5 Comparison of Ag₃Sn IMC Particle Size between WQ and RF SAC305

The evolutions of the number of IMC particles and average IMC particle diameter with aging are shown graphically in Figure 5.15. Similar analysis was performed for WQ SAC305 and those parameters were quantified for each aging duration, as shown in Figure 5.16. It has been found that the IMCs of WQ SAC305 are much finer than those of RF SAC305 at no aging condition, as their initial average particle diameters are 121 and 327 nm, respectively. However, the WQ microstructure suffered more changes due to aging. As shown in Figure 5.15, the number of IMC particles in the analyzed region decreased by over 50% from 40 to 19 during the 11 hours of aging for RF SAC305, while it decreased by over 80% from 81 to 14 for WQ SAC305 (Figure 5.16). The most dramatic changes of particle number occurred during the first few hours of aging for both microstructures, and then the changes became smaller. From Figure 5.15 and Figure 5.16, it has also been found that the average IMC particle diameter increased by approximately 62% (327 to 530 nm) for RF SAC305 and about 230% (121 to 400 nm) for WQ SAC305 during the 12 hours of aging. For each microstructure, there was an increase in the total area of all IMC particles with aging, suggesting that IMC atoms from other regions had diffused into the region under consideration.

Similar quantitative analyses have also been performed for RF and WQ SAC305 that were aged at an increment of 10 days, and the results are shown in Figure 5.17 and Figure 5.18. Again, aging led to significant drop of number of IMCs and increase of average particle diameter, as graphically illustrated in Figures 5.15-5.18. For example, after aging for 50 days at 125 °C, the number of IMC particles dropped about 80% (93 to 19) and 97% (495 to 15) for RF SAC305 and WQ SAC305, respectively. Moreover, the

average diameter of IMC particles increased by around 157% (307 to 789 nm) for RF SAC305 and 781% (167 to 1472 nm) for WQ SAC305 during the 50 days of aging.

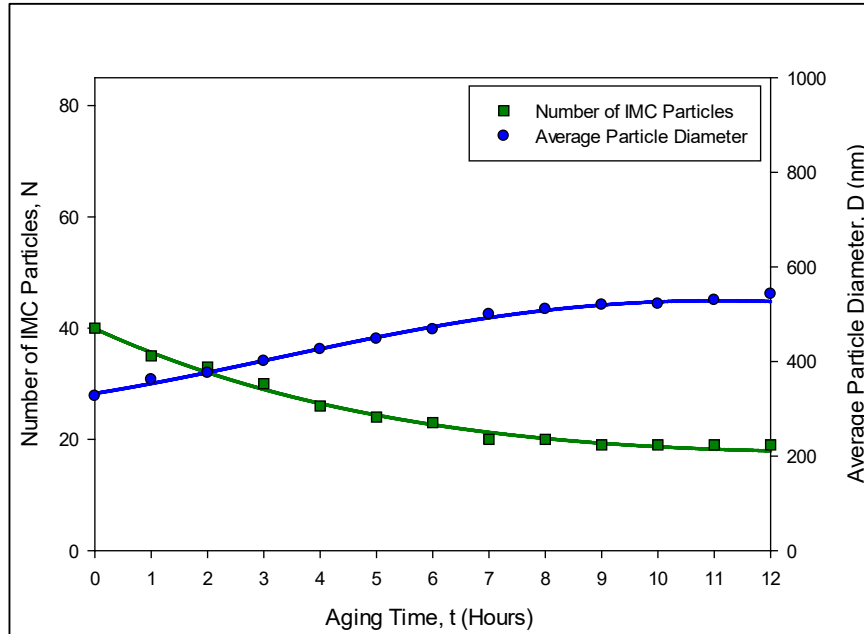


Figure 5.15 Variation of Number and Average Diameter of IMC Particles with Aging Time at 125 °C (Aging Increment: 1 Hour, RF SAC305)

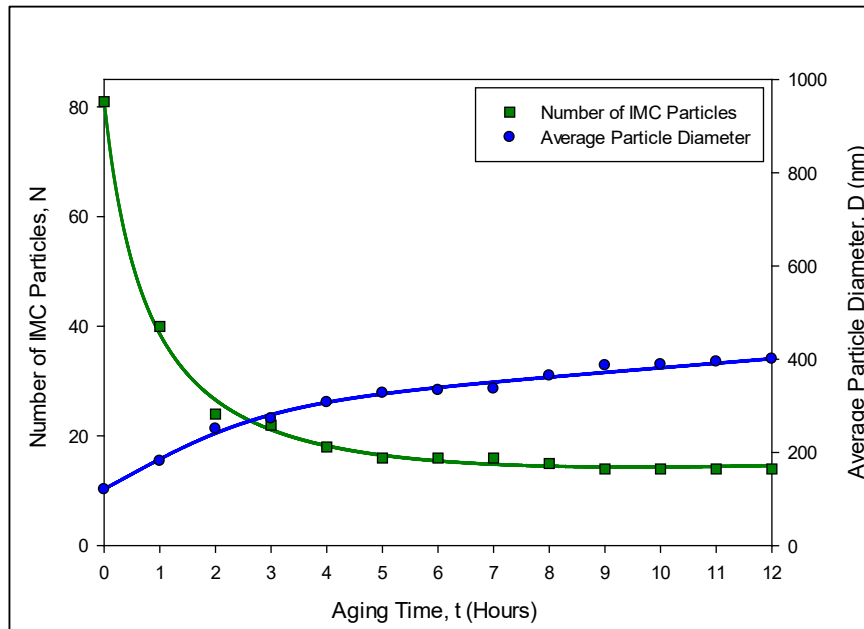


Figure 5.16 Variation of Number and Average Diameter of IMC Particles with Aging Time at 125 °C (Aging Increment: 1 Hour, WQ SAC305)

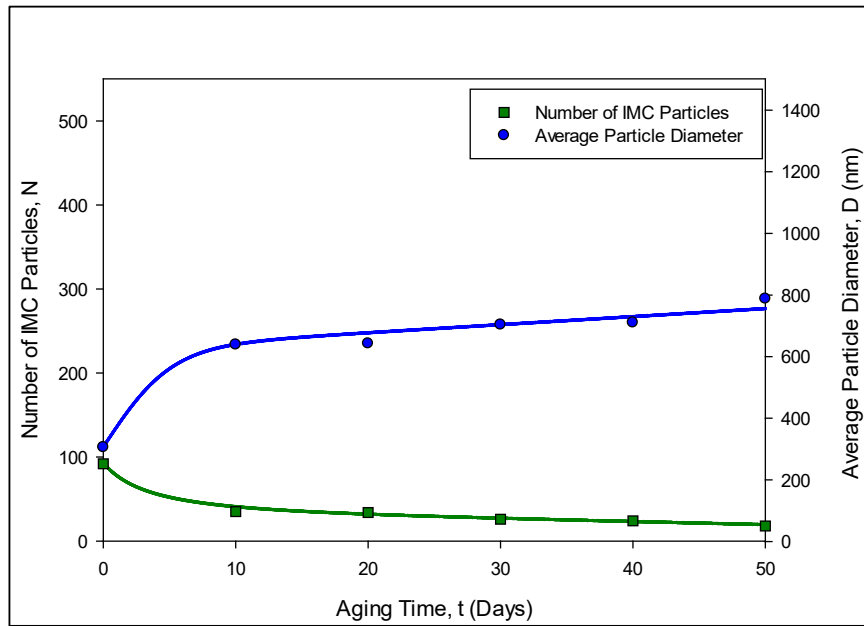


Figure 5.17 Variation of Number and Average Diameter of IMC Particles with Aging Time at 125 °C (Aging Increment: 10 Days, RF SAC305)

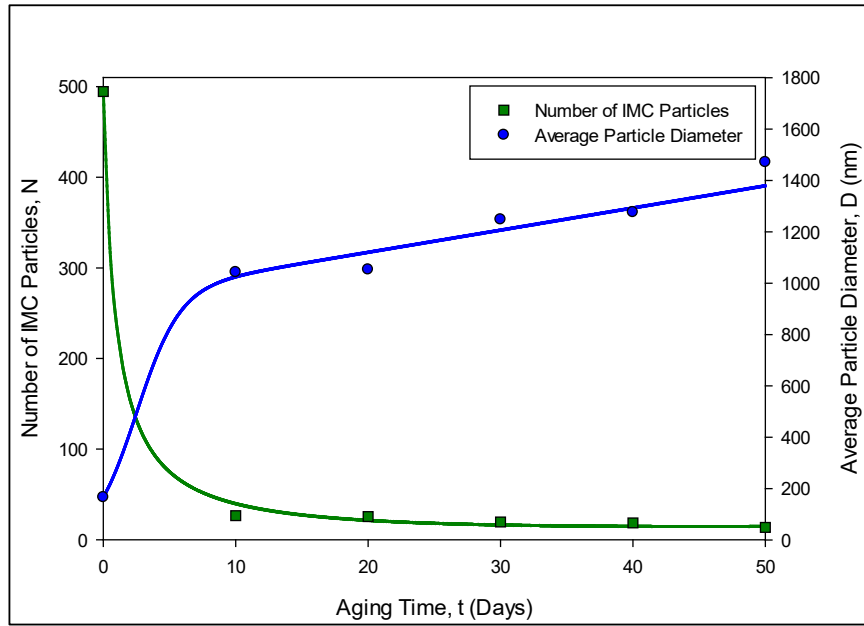


Figure 5.18 Variation of Number and Average Diameter of IMC Particles with Aging Time at 125 °C (Aging Increment: 10 Days, WQ SAC305)

5.6 SPM Image of SAC305 Solder

In this part, example results for a typical RF SAC305 sample were presented. Typical SPM topography data are shown in Figure 5.19 for a single β -Sn dendrite in one of the regions studied. In this case, the region encompassing the dendrite is 30 x 30 μm in size. The microstructural evolution was characterized in the smaller 10 x 10 μm subregion in the interdendritic eutectic area identified by the dashed line square.

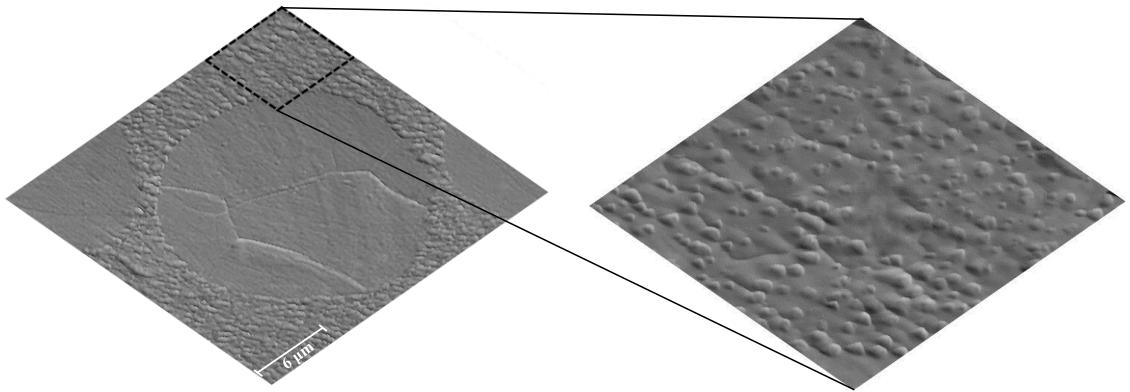
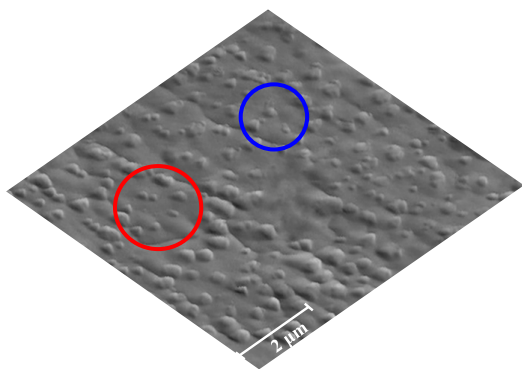
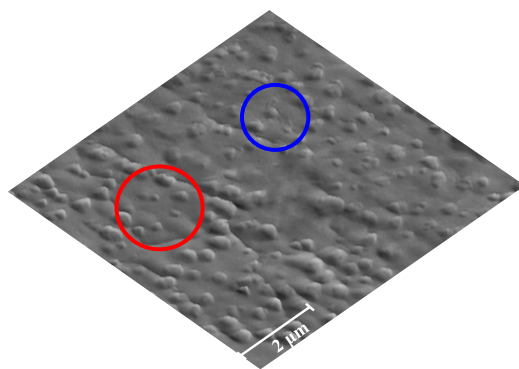


Figure 5.19 SPM topography image of RF SAC305 sample showing beta-Sn dendrite, subgrain boundaries, and eutectic region (no aging)

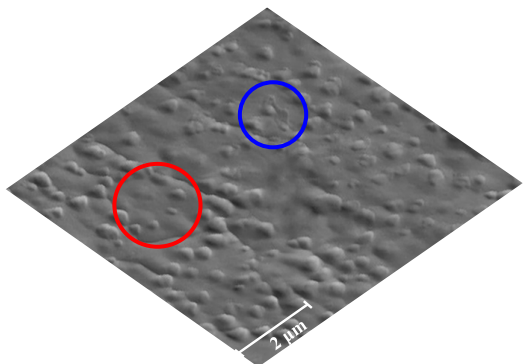
SPM images obtained after each hour of aging are presented in Figure 5.20 (a-k). It is clearly evident that some IMC particles were decaying whereas others were growing in size as the aging progressed. To help visualize this, red circles have been used to identify examples of decaying particles, while blue circles have been used to identify examples of growing particles.



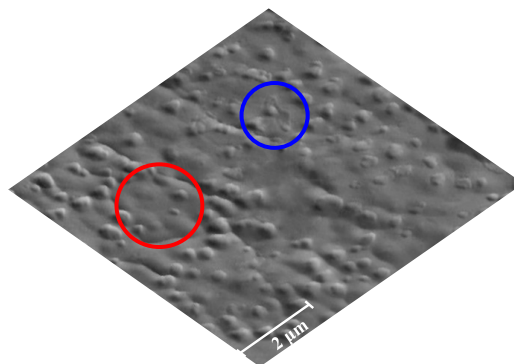
(a) No aging



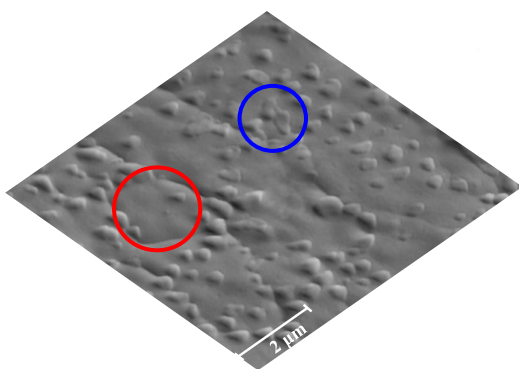
(b) 1 hour of aging



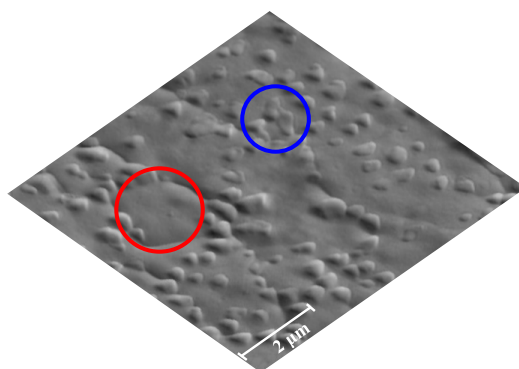
(c) 2 hours of aging



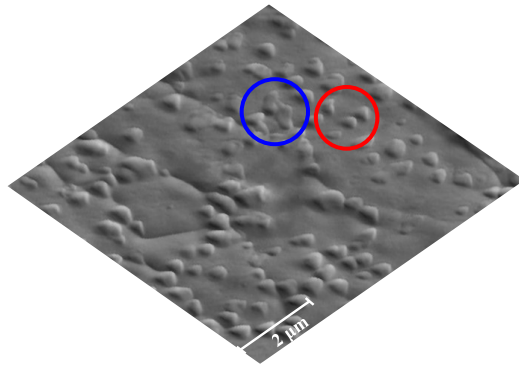
(d) 3 hours of aging



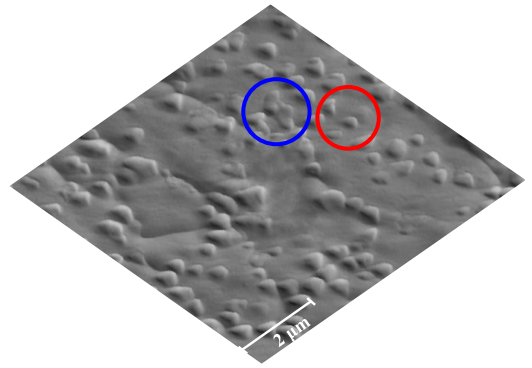
(e) 4 hours of aging



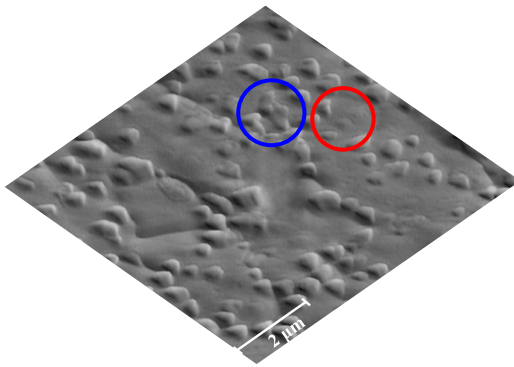
(f) 6 hours of aging



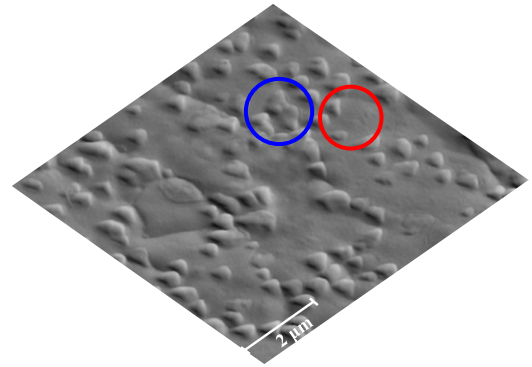
(g) 8 hours of aging



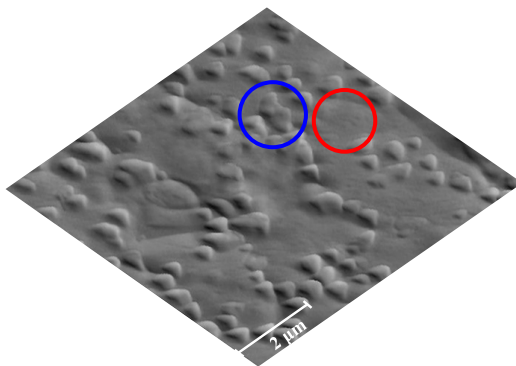
(h) 12 hours of aging



(i) 16 hours of aging



(j) 20 hours of aging



(k) 26 hours of aging

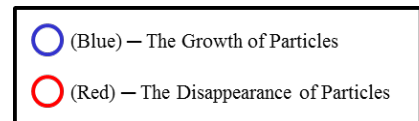


Figure 5.20 Short term aging induced microstructural evolution of SAC305 by SPM imaging (Aging at $T = 125\text{ }^{\circ}\text{C}$)

5.7 Distribution of IMC Particles

The quantitative analysis results reported in this work are based on coarsening phenomenon observed at the solder surface. The surface diffusion rates in the plane of the sample surface can be different than those in the sample bulk. And the IMC particles observed during SEM imaging were similar to the ice burgs, where a tiny portion of an ice burg is exposed above the water layer and the rest of it is underneath the water. To make sure that the particle size above the surface is similar as the particle underneath the surface, Focused Ion Beam (FIB) was used to observe the IMC particles underneath the exposed surface. Microstructure of SAC305 solder and the location of the eutectic region where FIB analysis was performed is shown in Figure 5.19(a) and Figure 5.20(a). The images obtained during the FIB analysis are presented in Figure 5.19(b) and Figure 5.20(b). EDS is also used to verify the elements shows in the cross-section (shown in Figure 5.21). It is clear from the FIB images that the IMC particle size measured from the surface are similar to the IMC particle size underneath the surface for both aging and no aging condition.

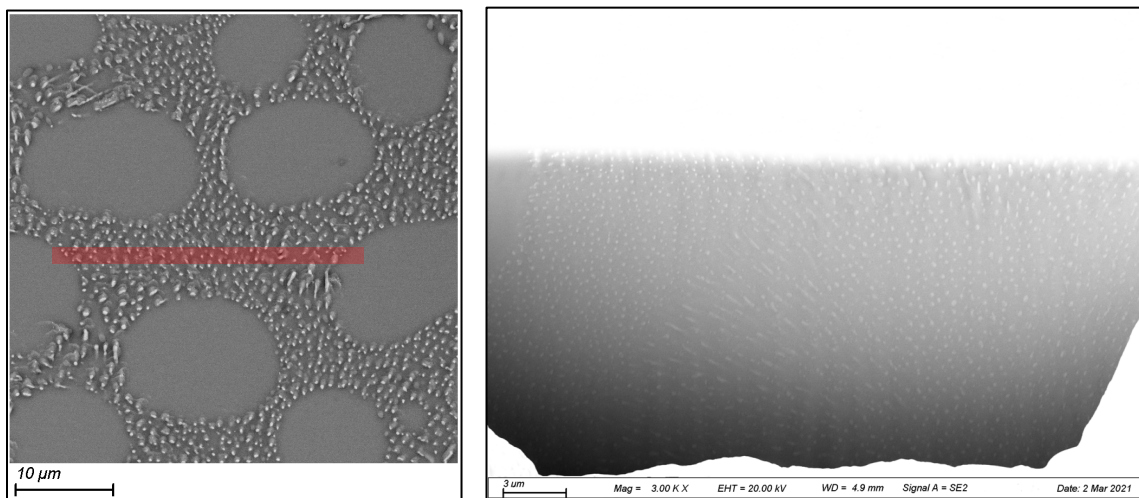


Figure 5.21 SAC305 Microstructure as Reflowed
(a) Exposed Surface (b) Cross-section after FIB

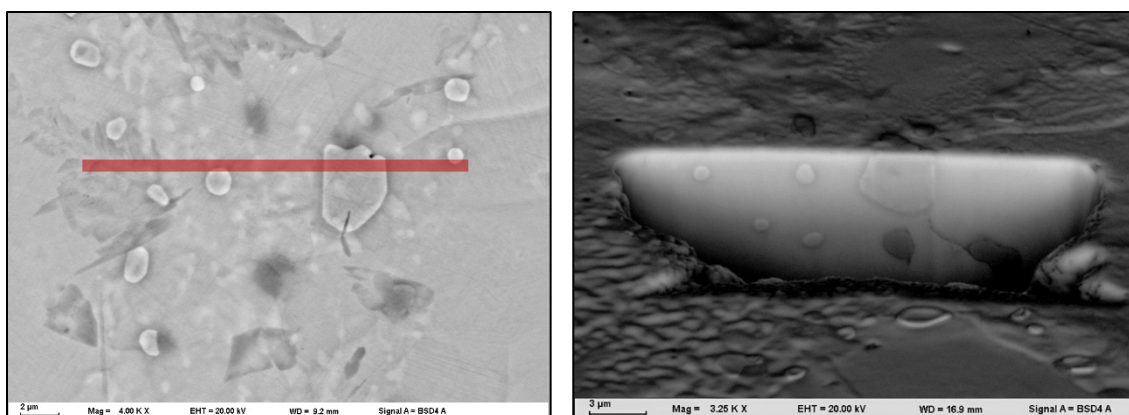
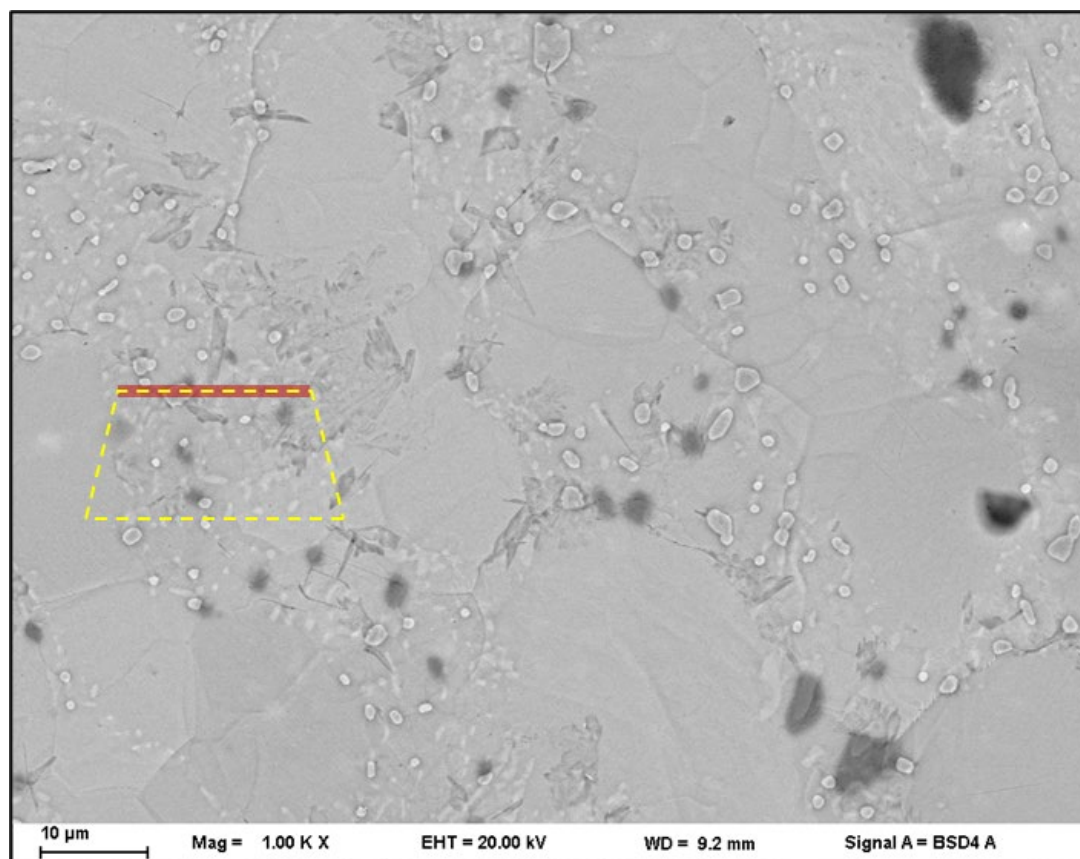
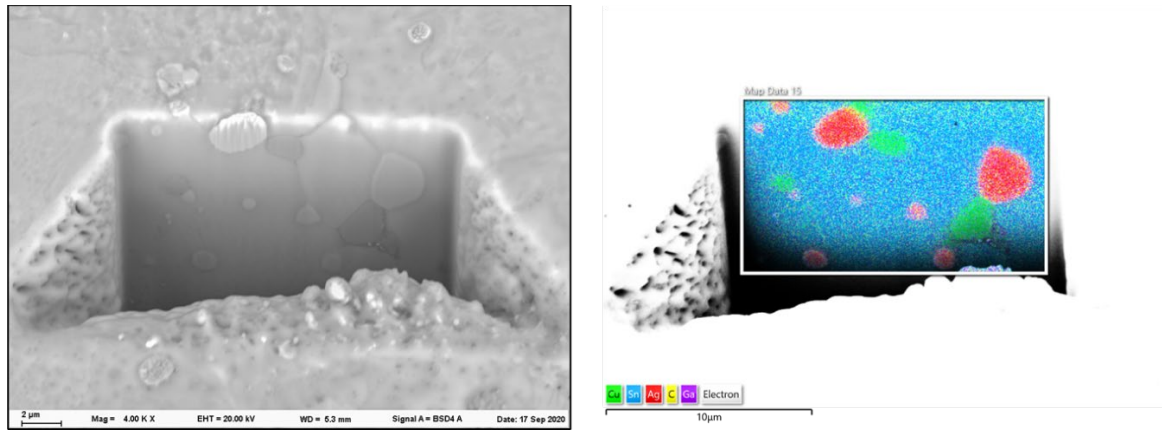


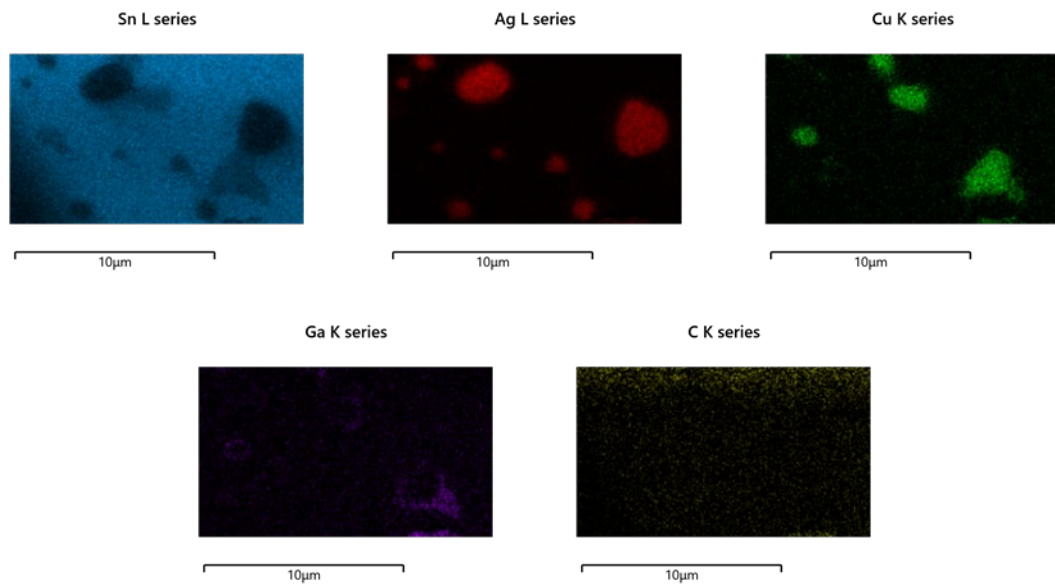
Figure 5.22 SAC305 Microstructure after 7000 Hours of Aging at 125 °C
(a) Exposed Surface (b) Cross-section after FIB



(a) Location of the Exposed Surface



(b) Cross-section after FIB with EDS Mapping



(c) EDS Mapping of Different Elements

Figure 5.23 SAC305 Microstructure after 7000 Hours of Aging at 125 °C

5.8 Summary and Discussion

In this investigation, Scanning Electron Microscopy (SEM) has been utilized to examine aging induced microstructural changes occurring within lead free solders. Unlike many prior studies, fixed regions in the solder joint cross-sections were monitored

throughout the aging process, rather than examining different samples and/or different regions after the various aging exposures. Nanoindentation marks were added to the cross-sections at certain locations to facilitate locating the fixed regions of interest. Three aging increments (1 hour and 10 days) and two solidification profiles (RF and WQ) have been examined. After preparation of suitable cross-sectional samples, the samples were then aged at $T = 125\text{ }^{\circ}\text{C}$, and the microstructures were observed and recorded in the selected regions after various aging exposures using SEM. With this approach, time-lapse imagery of the microstructure evolution in a particular region of a solder joint has been recorded as a function of the aging time.

Using the recorded images, migration, coalescence, and coarsening of intermetallic compounds were visualized. It has been found that the number of IMC particles decreased, while the average size of the particles and average particle separation distance increased significantly with aging. The early aging period features the most rapid and dramatic changes in microstructure. Compared with RF SAC305, WQ SAC305 had much finer initial IMC particles but they coarsened to a greater degree during isothermal aging. For small aging times up to 270 hours at $T = 125\text{ }^{\circ}\text{C}$, experimentally recorded movies of microstructural evolution during aging have been made to visualize those aging phenomena.

Additionally, the coarsening of IMC particles in fixed regions during aging has been quantitatively analyzed. Particularly, the aging induced evolutions of number of IMCs, total area of all IMCs, average particle area, and average particle diameter have been quantified. For instance, during the first 12 hours of aging at $125\text{ }^{\circ}\text{C}$, the average IMC particle diameter increased by approximately 62% for RF SAC305 and 230% for WQ

SAC305. After 50 days of aging, the average diameter increased by around 157% and 781% for RF SAC305 and WQ SAC305, respectively. The FIB results show that the IMC particle size underneath the surface and above the exposed surface are quite similar.

CHAPTER 6

INVESTIGATION AND COMPARISON OF AGING EFFECTS IN SAC+Bi SOLDERS EXPOSED TO HIGH TEMPERATURES

6.1 Introduction

In recent investigations, it has been found that adding Bismuth (Bi) to the SAC composition to form SAC+Bi alloys has been effective in reducing both intermetallic coarsening and the degradations in material properties. These studies have been performed with the well-known SAC_Q alloy that modifies SAC405 to include 3.0% Bi. There have been no prior studies to examine the performance of SAC+Bi alloys with other concentrations of Bi.

In present work, three SAC+Bi lead free solder materials recommended for high reliability applications have been chemically analyzed and then observed after aging. The alloys are referred to as SAC_Q (3.0% Bi), SAC+2.0% Bi, and SAC+1.0% Bi. Solder joints have been extracted from SAC+Bi assemblies and subjected to aging exposures up to 2000 hours at high temperatures ($T = 100$ and 125 °C). After each aging time, we were able to quantitatively analyze the evolution of Ag_3Sn and other IMCs with aging. Specifically, the aging induced changes in number of IMCs, total area of all IMCs, average area of particles, average diameter of particles and the normalized diameter were quantified in the fixed regions. In addition, the Energy Dispersive Spectroscopy (EDS) mapping was used to visualize the diffusion of Bi in SAC+Bi alloys after aging.

6.2 Microstructure and Chemical Composition of SAC+Bi Solder

In the current work, the chemical compositions of the SAC+Bi alloys in this study were verified using Oxford EDS Analysis. The experimental procedure is shown in Figure 6.1. Several samples were prepared, and the average result shown in Table 6.1 was determined which matched with the vendor claimed alloy composition (shown in Table 6.2).

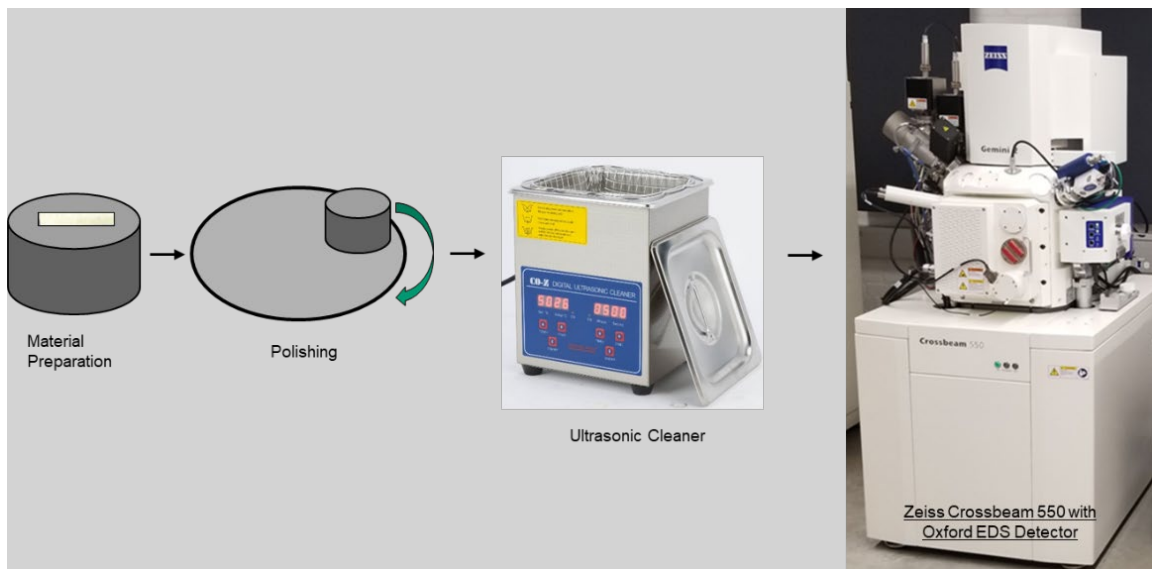


Figure 6.1 Flow Chart of Experimental Procedure

Table 6.1 Specimen Composition from EDS Analysis(wt%)

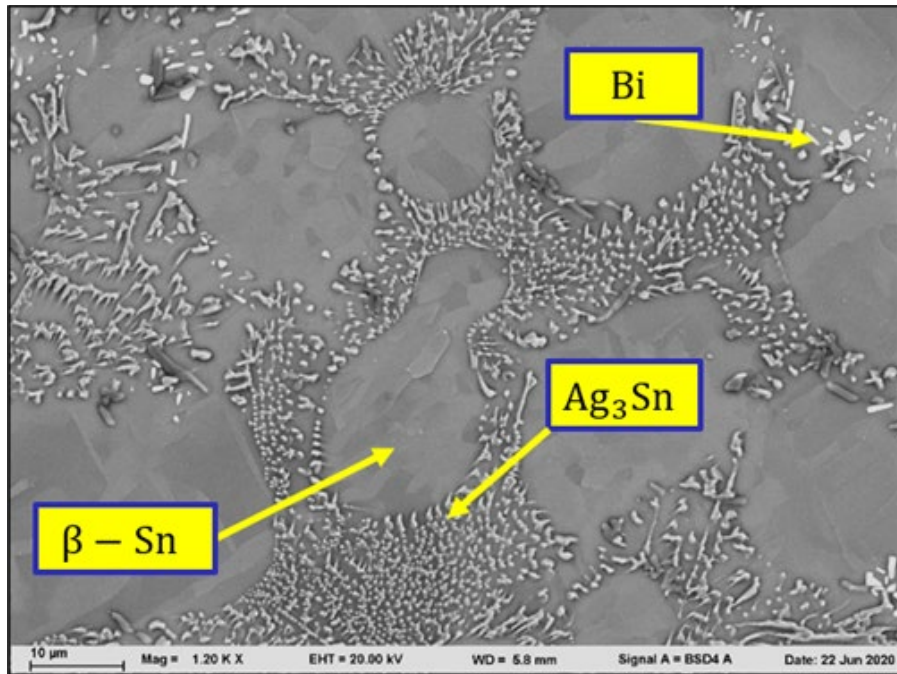
Alloy	Sn	Ag	Cu	Bi	Ni
SAC_Q	92.2	4.3	0.5	3.0	0.02
QSAC+2.0% Bi	93.2	4.2	0.5	2.1	0.03
QSAC+1.0% Bi	94.2	4.2	0.6	1.0	0.00

Table 6.2 Vendor Claimed Alloy Composition

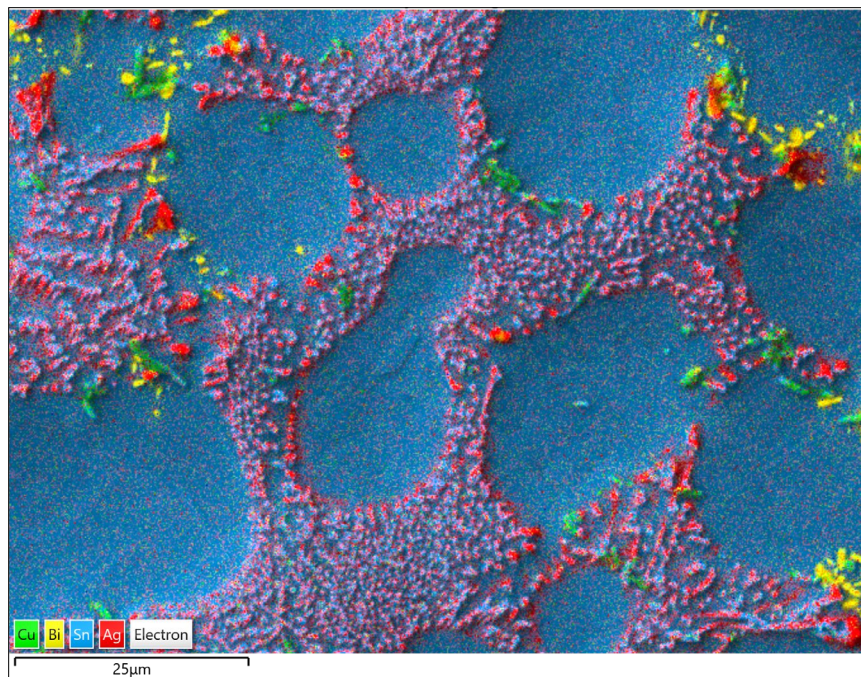
Alloy	Composition (Alleged/Rumored)
SAC_Q	Sn-4.0Ag-0.5Cu-3.0Bi-0.05Ni-0.007Ge
QSAC+2.0% Bi	Sn-4.0Ag-0.5Cu-2.0Bi
QSAC+1.0% Bi	Sn-4.0Ag-0.5Cu-1.0Bi

Typical microstructure for SAC_Q solder joints after reflow solidification is shown in Figure 6.2(a). To verify each element, the EDS mapping is done on the region shown in Figure 6.2(a). The microstructure typically consists of β -Sn dendrites surrounded by interdendritic eutectic regions incorporating a fine dispersion of Ag_3Sn and Cu_6Sn_5 intermetallic particles in β -Sn. The IMC particles provide pinning points that help mitigate and block dislocation movements. The inclusion of Bi in SAC+Bi led to a dispersion of Bi rich phases, which appear as white regions in the SEM micrograph in Figure 6.2(a) (using back scattered electrons) and as yellow regions in EDS mapping in Figure 6.2(b) and Figure 6.2(c).

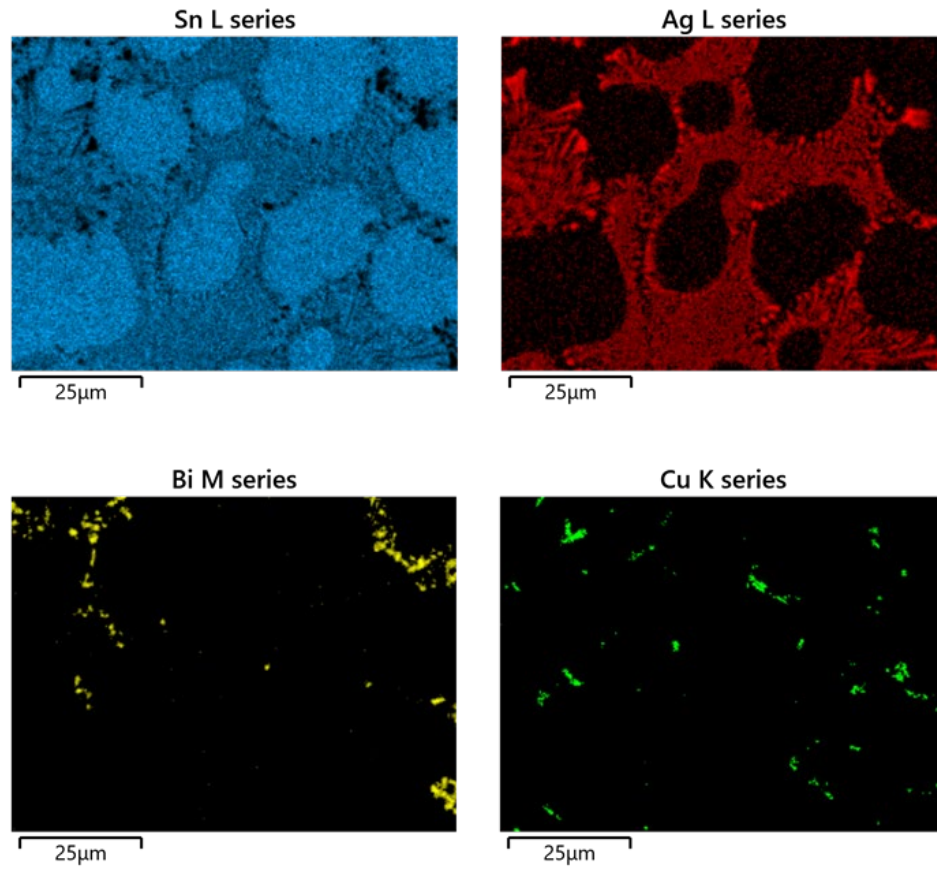
As shown in the phase diagram in Figure 6.3, bismuth has a high solid solubility (about 1.7% at 25 °C) in tin, which leads to an improved strength of the Sn matrix by the solid solution strengthening (SSS) mechanism. Figure 6.4 shows several example regions of different SAC+Bi alloys. For SAC+1.0% Bi alloys (Figure 6.4(c)), all the Bi dissolved into the Sn solution, so the SEM image is more like SAC only alloys. As the percentages of Bi increased from 1.0% to 3.0%, more separate Bi rich phases can be captured in SAC_Q. Compared with high Bi percentage alloys, SAC+1.0% Bi alloy shows more even dispersion of Ag_3Sn IMC particles.



(a) SEM Image of SAC_Q



(b) Combined EDS Mapping of SAC_Q



(c) EDS Mappings of Different Elements
Figure 6.2 EDS Mapping of SAC_Q Alloy

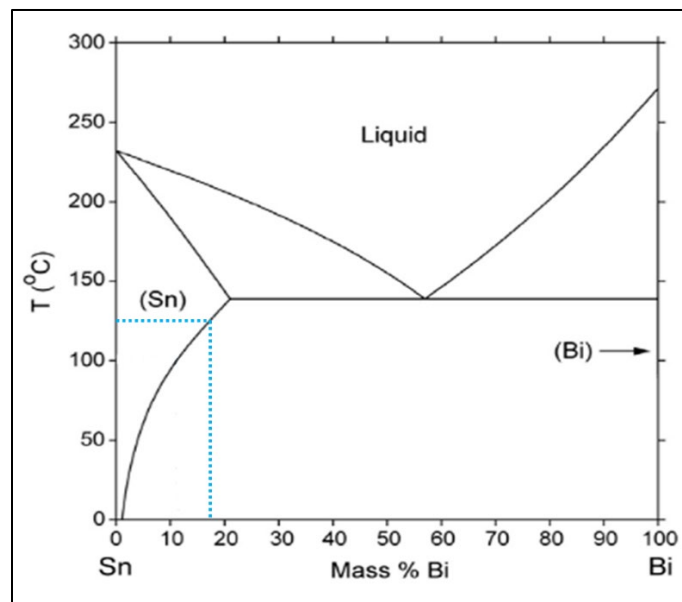
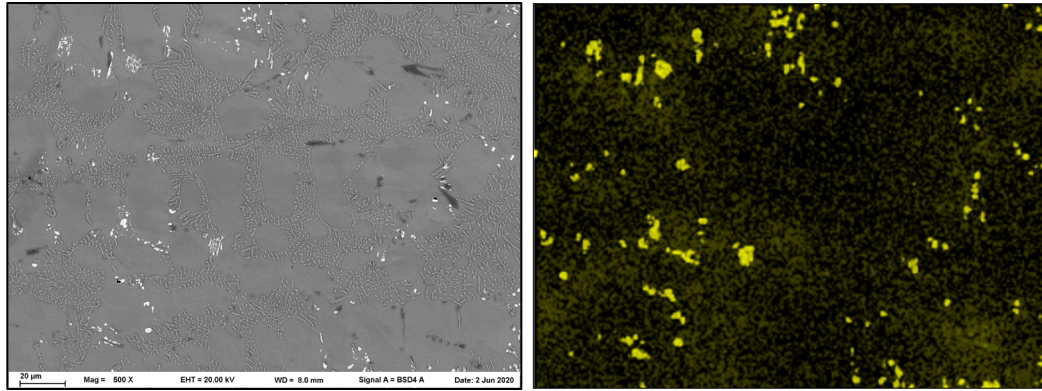
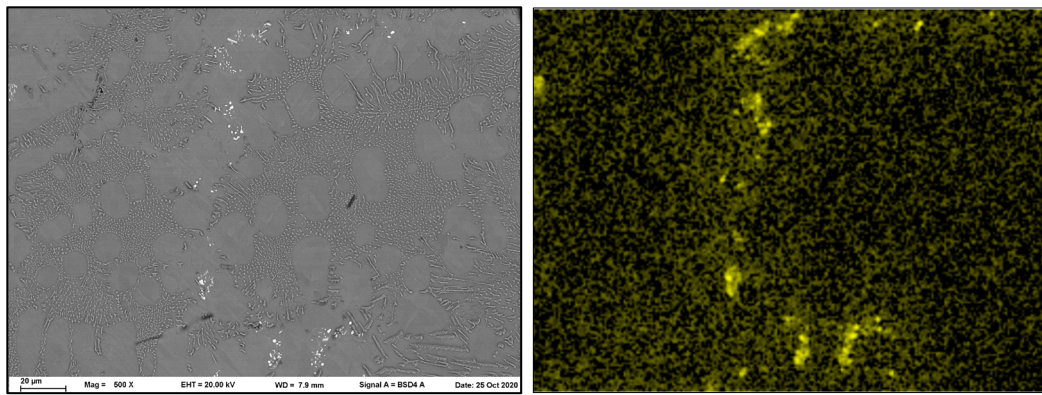


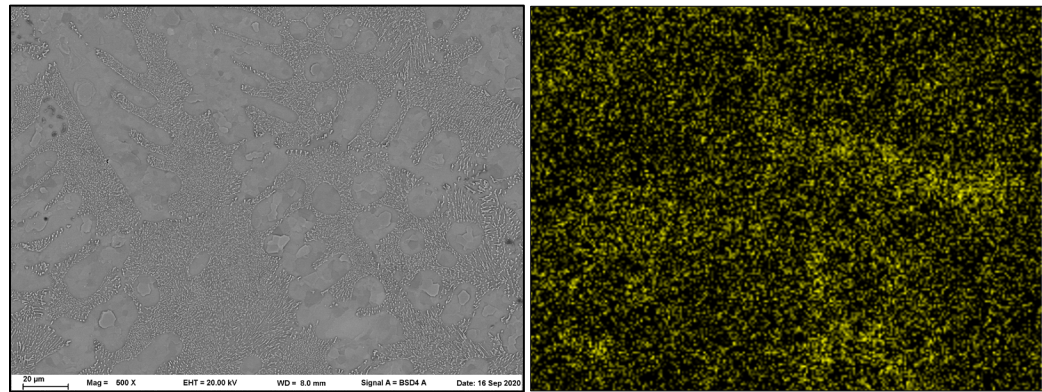
Figure 6.3 Sn-Bi Phase Diagram [<http://www.metallurgy.nist.gov/>]



(a) SAC_Q (SAC+3.0% Bi)



(b) SAC+ 2.0% Bi

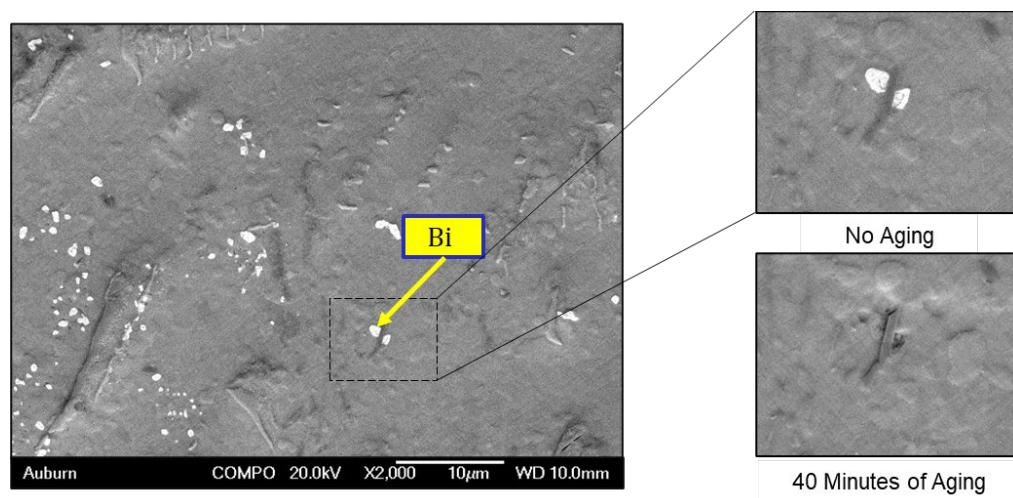


(c) SAC+1.0% Bi

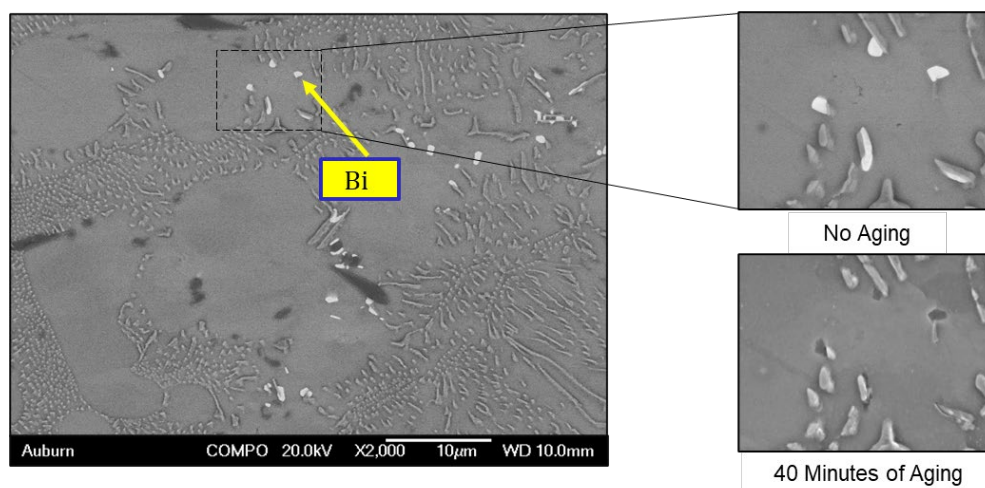
Figure 6.4 SEM Images of SAC+Bi Alloys (As Reflowed) with Bi Phases EDS Mapping

6.3 Observations and EDS Mapping of Diffusion of Bismuth

The solubility limit of Bi in Sn is approximately 11% for $T = 100\text{ }^{\circ}\text{C}$ and 17% for $T = 125\text{ }^{\circ}\text{C}$, which are the temperatures used for aging in this work. Figure 6.5 - 6.7 contain sets of images illustrating example microstructural evolutions of the bismuth rich phases in SAC_Q joints subjected to isothermal aging at $125\text{ }^{\circ}\text{C}$. Figure 6.6 contains sets of images illustrating the EDS mapping of SAC_Q after reflow solidification and after aging at 100°C . The images in Figure 6.8(a) were taken immediately after reflowed and exhibit a distribution of white Bi-rich phases throughout the lead free microstructure. EDS analysis of these white particles (shown in Table 6.3) has confirmed that they are Bi rich phases with more than 80% Bi. During aging, the bismuth was observed to dissolve into solution within the beta-Sn dendrites and in the intermetallic rich regions between dendrites. After a short time of aging (less than one hour) the Bi dissolved into the solution and dispersed evenly in the Sn solution. As discussed previously, this leads to strengthening of the solder during aging by the mechanism of solid solution strengthening.

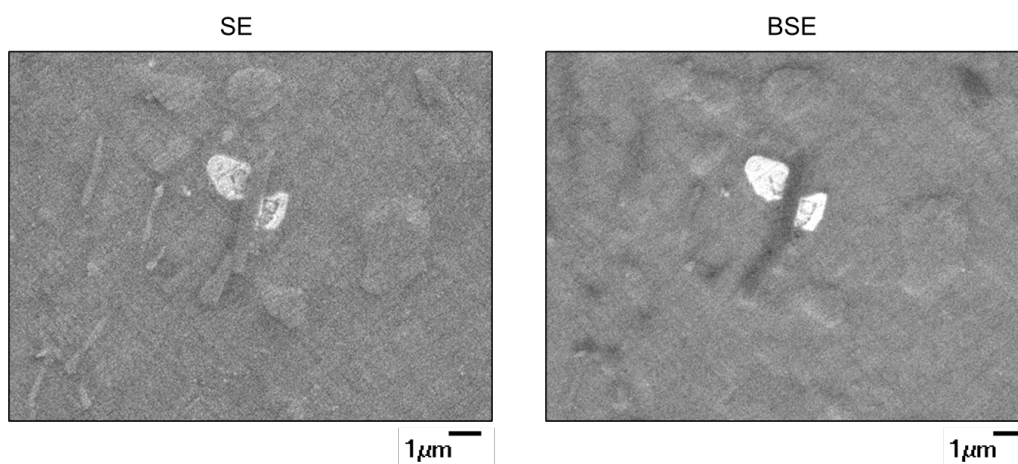


(a) Bi-rich Phases Aging at $125\text{ }^{\circ}\text{C}$

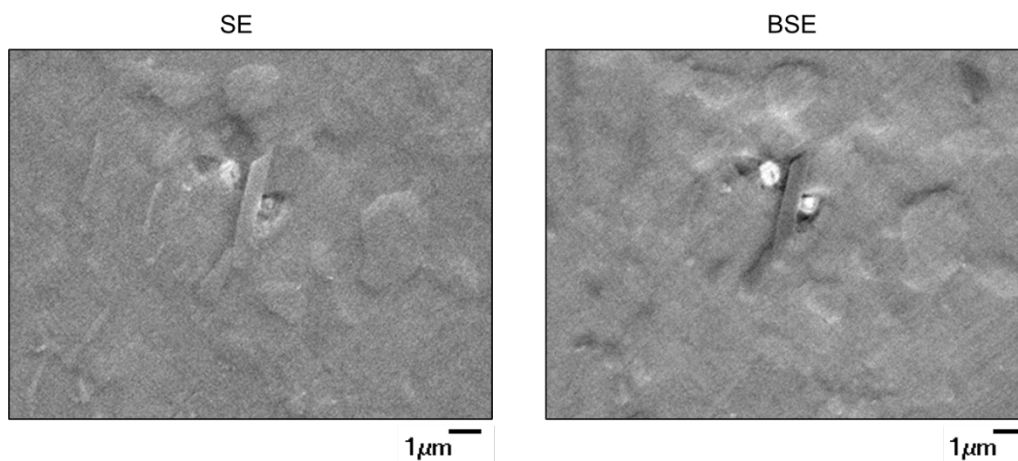


(b) Bi-rich Phases Aging at 100 °C

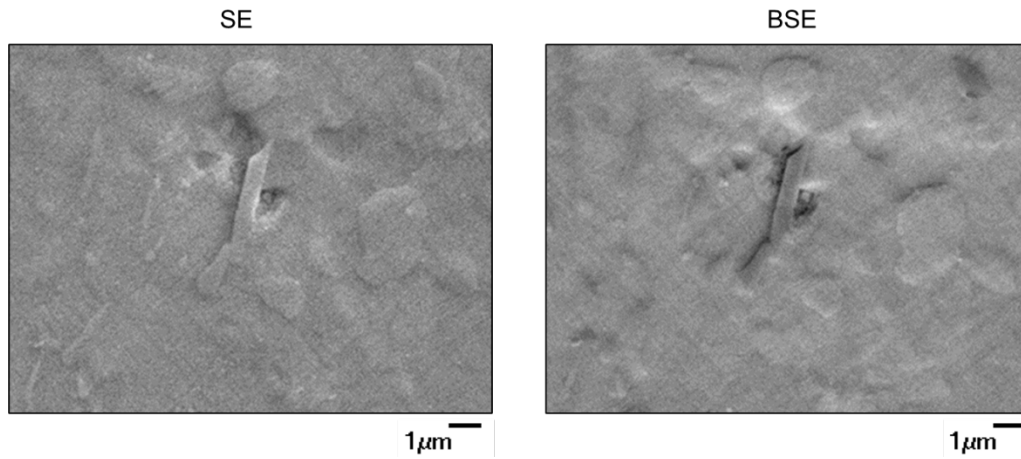
Figure 6.5 Dissolving of Bismuth Rich Phases During Aging



(a) No Aging

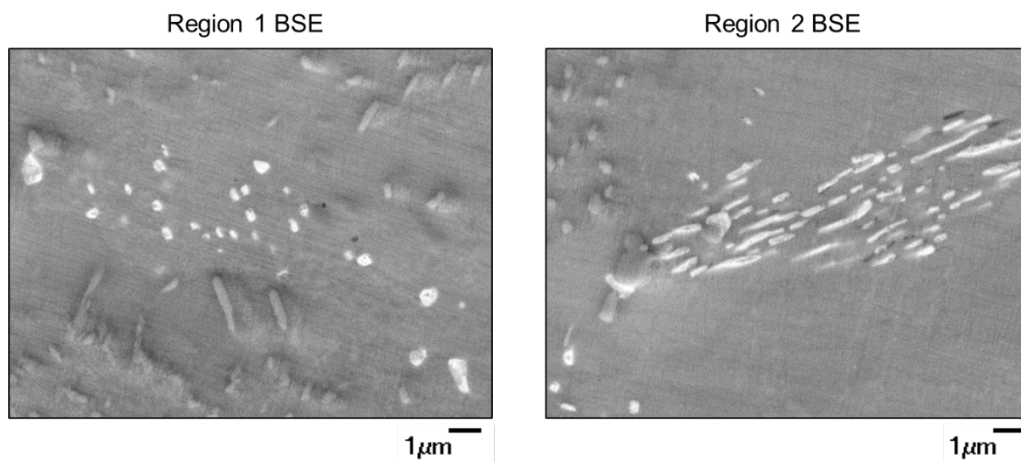


(b) 20 Minutes of Aging

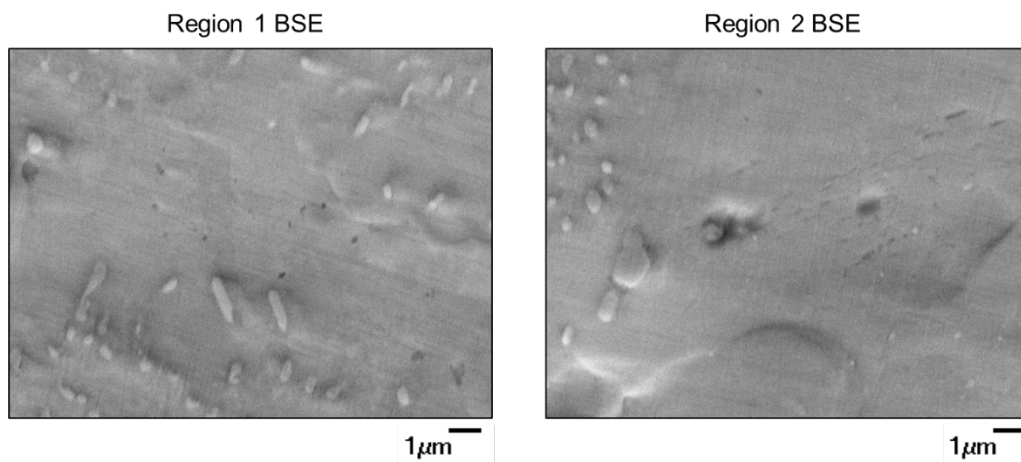


(c) 40 Minutes of Aging

Figure 6.6 Bi Rich Phase in SAC_Q (Aging at 125°C)



(a) No Aging



(b) 10 Hours of Aging

Figure 6.7 Bi Rich Phase in SAC_Q After Long Term Aging (Aging at 125°C)



(a) No Aging

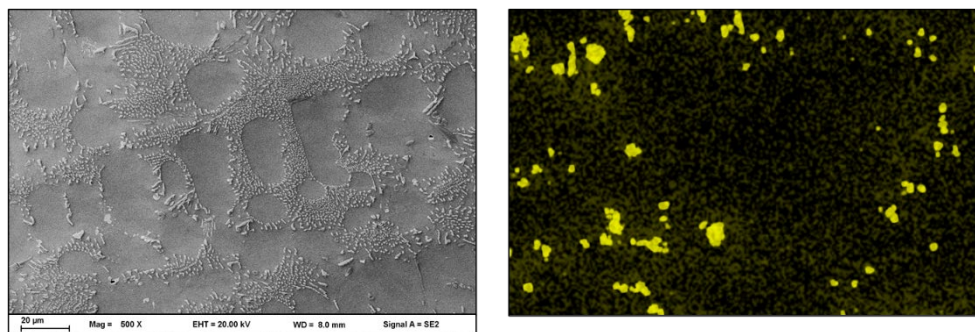


(b) 1 Hour of Aging at 125°C

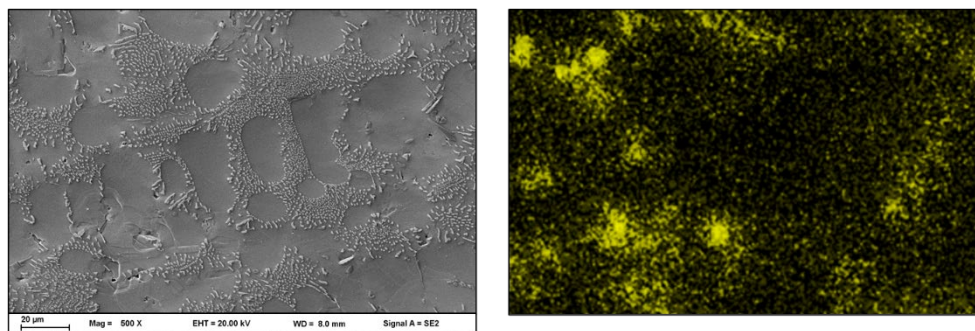
Figure 6.8 Bi Rich Phases for EDS

Table 6.3 Chemical Compositions of Bi Rich Phase

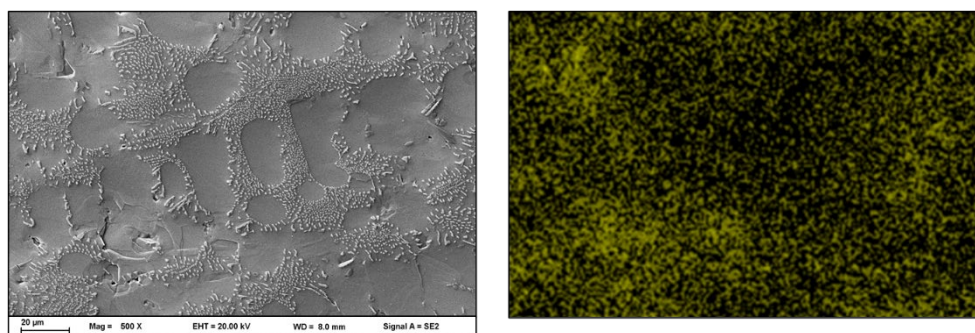
Element	Weight%	
	No Aging	1 Hour
Bi M	87.35	11.63
Sn L	12.65	88.37
Ag L	0.00	0.00



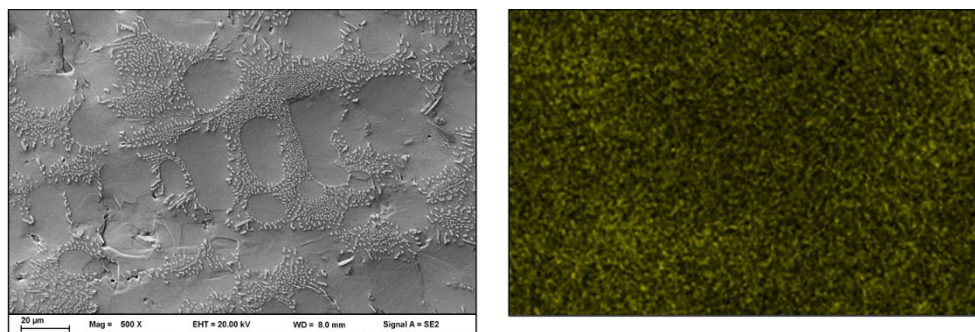
(a) No Aging



(b) 40 Minutes of Aging



(c) 2 Hours of Aging



(d) 8 Hours of Aging

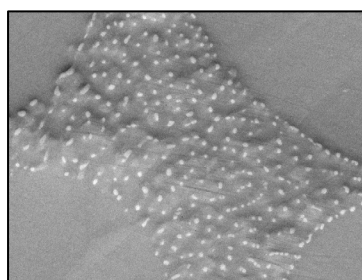
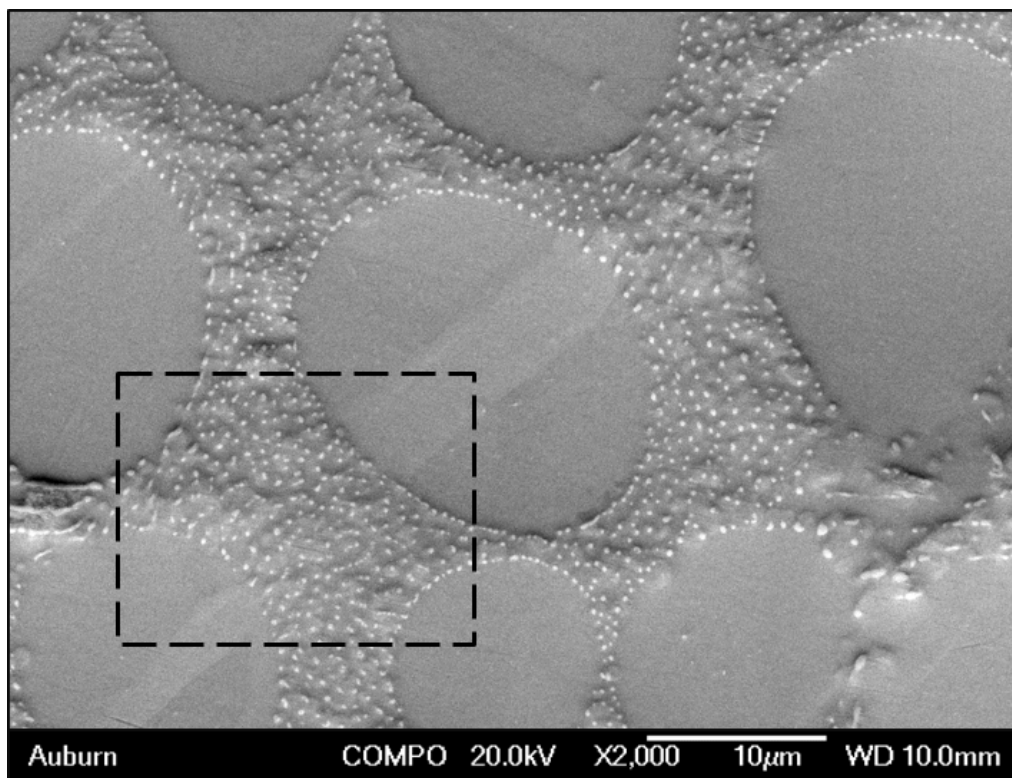
Figure 6.9 Example of SAC_Q Microstructural Evolution with Bi EDS Mapping of Aging at T = 100 °C

6.4 Comparison of Aging Degradation in SAC305 and SAC_Q Alloys

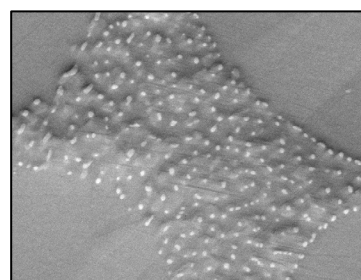
SEM analysis of the selected regions was then performed on the non-aged as-polished samples. The same samples were then aged at high temperatures ($T = 100$ and 125 °C) for different durations of aging. The microstructures of the selected regions were captured after each aging interval. SAC305 and SAC_Q solder joint were prepared for each of the three aging temperatures, and three regions were studied in each joint.

The SEM images of the selected regions at different aging conditions are shown in Figure 6.10 – 6.13. A diffusion-based IMC coarsening occurs, and larger particles are produced at the expense of smaller particles (Ostwald Ripening). Coarsening of intermetallic particles occurred due to aging. Some IMC particles grew in size, some split into several smaller particles, and some decreased in size and disappeared in the end. In other words, the number of IMC particles decreased, the average particle size increased, and the average particle separation distance increased. Also, the particles shifted to more spherical shapes. The shape and size of the dendrites remained nearly unchanged.

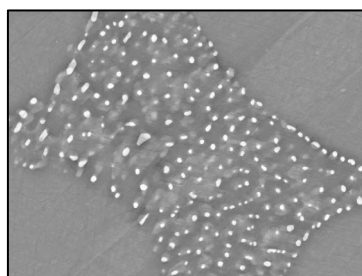
This coarsening and coalescing of IMC particles during aging is known to play a critical role in the degradations of solder mechanical properties. IMC particles will pin and block the movement of dislocations. However, aging leads to both a smaller number of larger IMC particles, and increased spacing between the particles. This results in dislocations being able to pass more easily through the material, decreasing both the yield stress and strength.



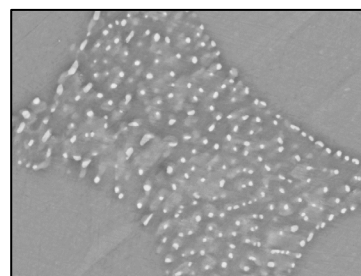
As Reflowed (Well-Polished)



Aging at 100°C for 4 hours

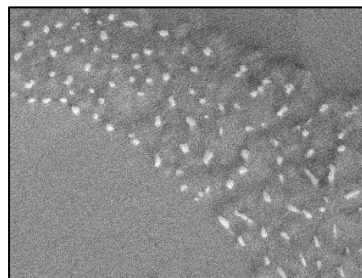
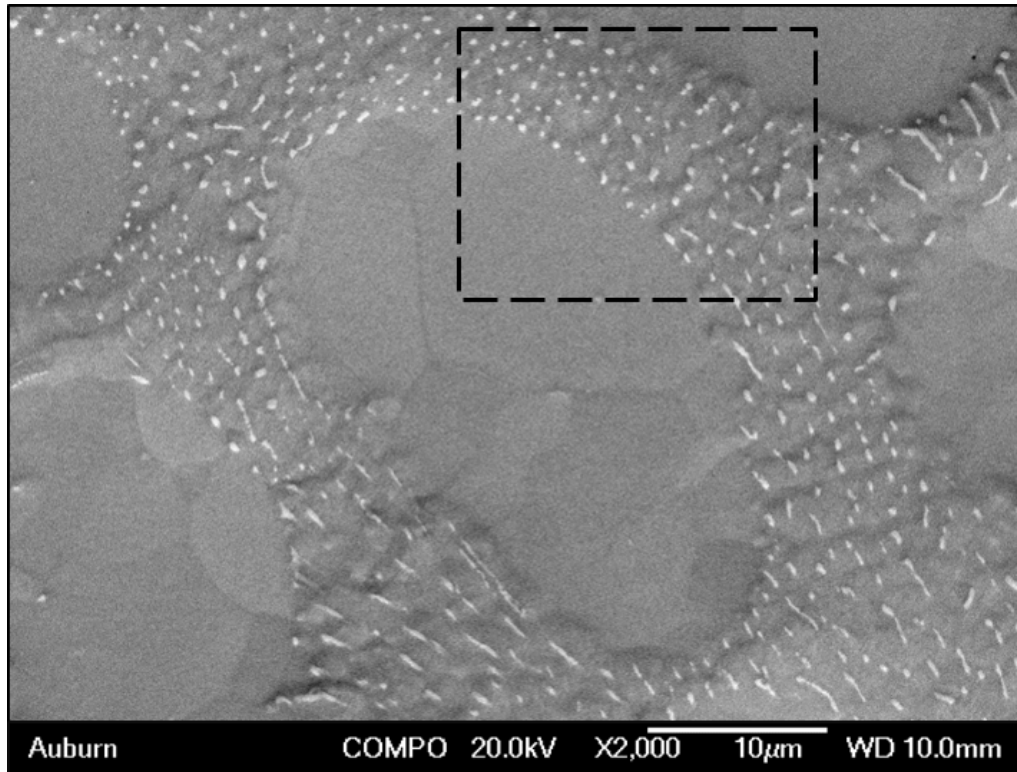


Aging at 100°C for 8 hours

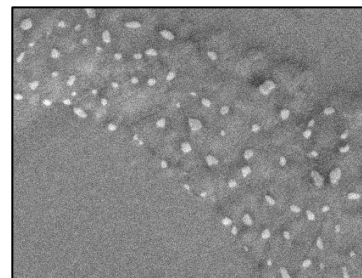


Aging at 100°C for 12 hours

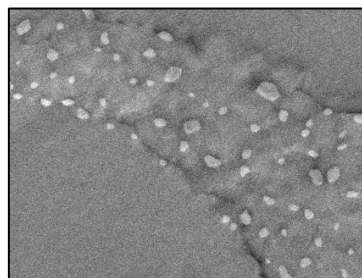
(a) Example Region of SAC305 Samples (Aging at $T = 100^\circ\text{C}$)



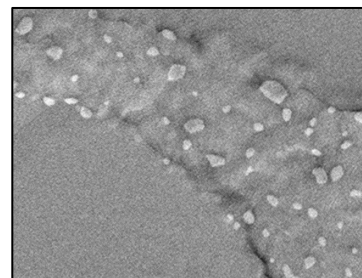
As Reflowed (Well-Polished)



Aging at 125°C for 4 hours



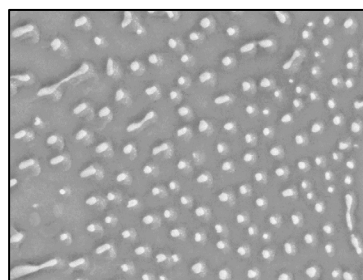
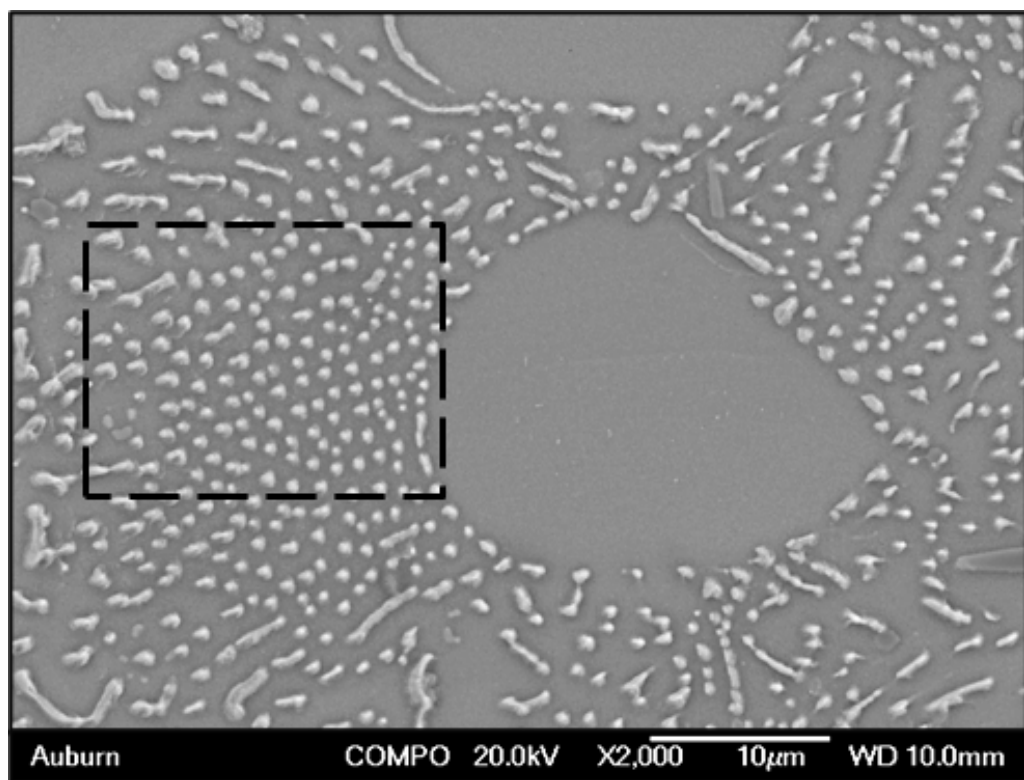
Aging at 125°C for 12 hours



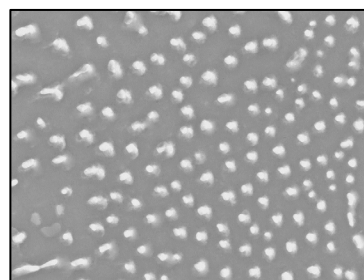
Aging at 125°C for 24 hours

(b) Example Region of SAC305 Samples (Aging at $T = 125^\circ\text{C}$)

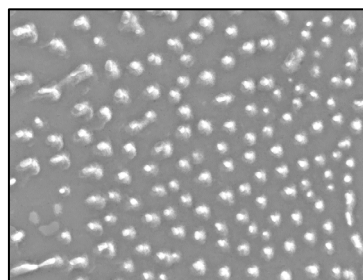
Figure 6.10 Microstructural Evolution in SAC305 Subjected to Isothermal Aging



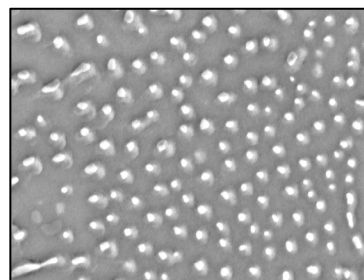
As Reflowed (Well-Polished)



Aging at 100°C for 4 hours

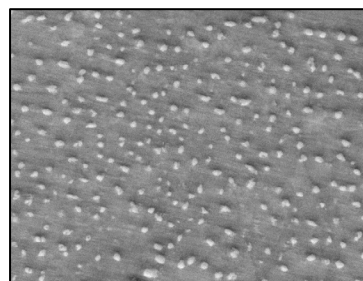
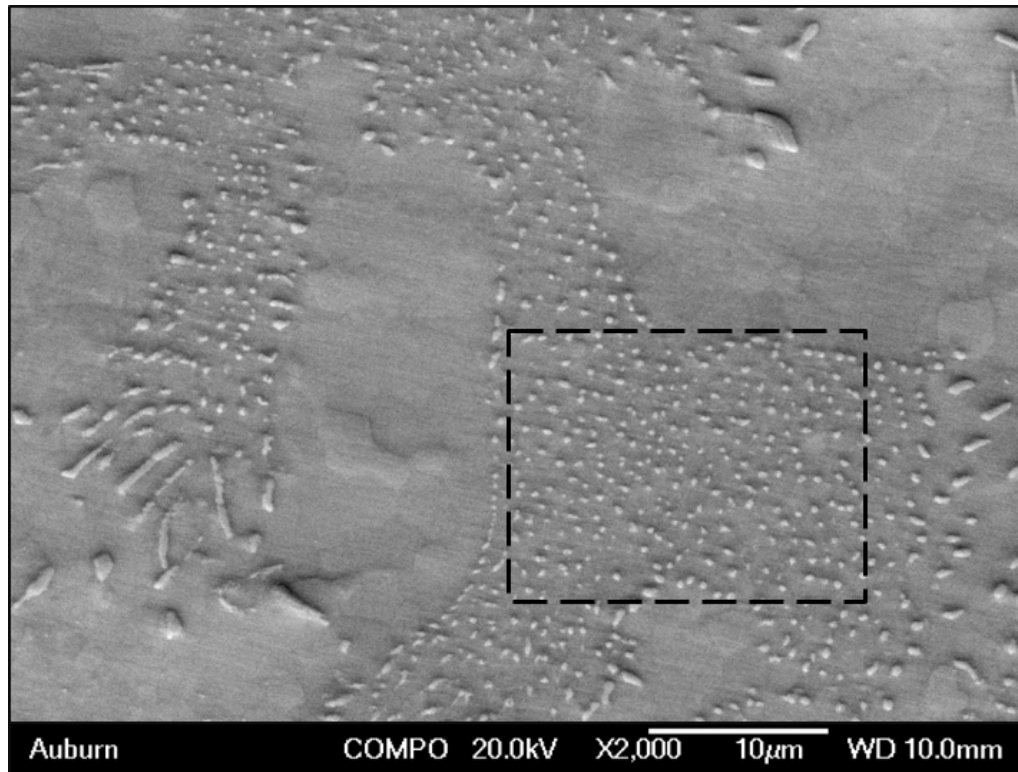


Aging at 100°C for 8 hours

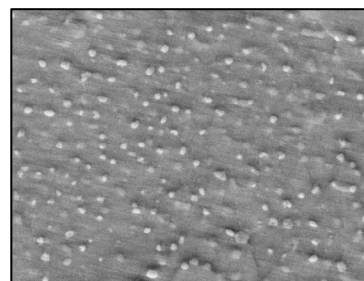


Aging at 100°C for 12 hours

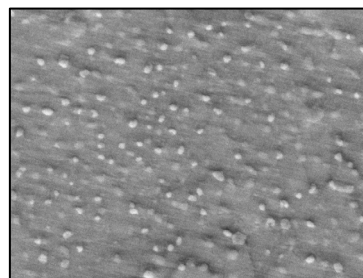
(a) Example Region of SAC_Q Samples (Aging at $T = 100\text{ }^{\circ}\text{C}$)



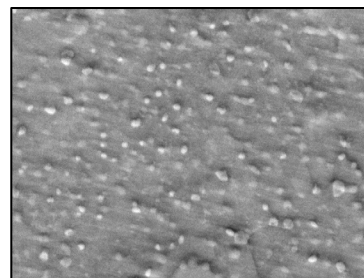
As Reflowed (Well-Polished)



Aging at 125°C for 8 hours



Aging at 125°C for 12 hours



Aging at 125°C for 24 hours

(b) Example Region of SAC_Q Samples (Aging at $T = 125\text{ }^{\circ}\text{C}$)

Figure 6.11 Microstructural Evolution in SAC_Q Subjected to Isothermal Aging

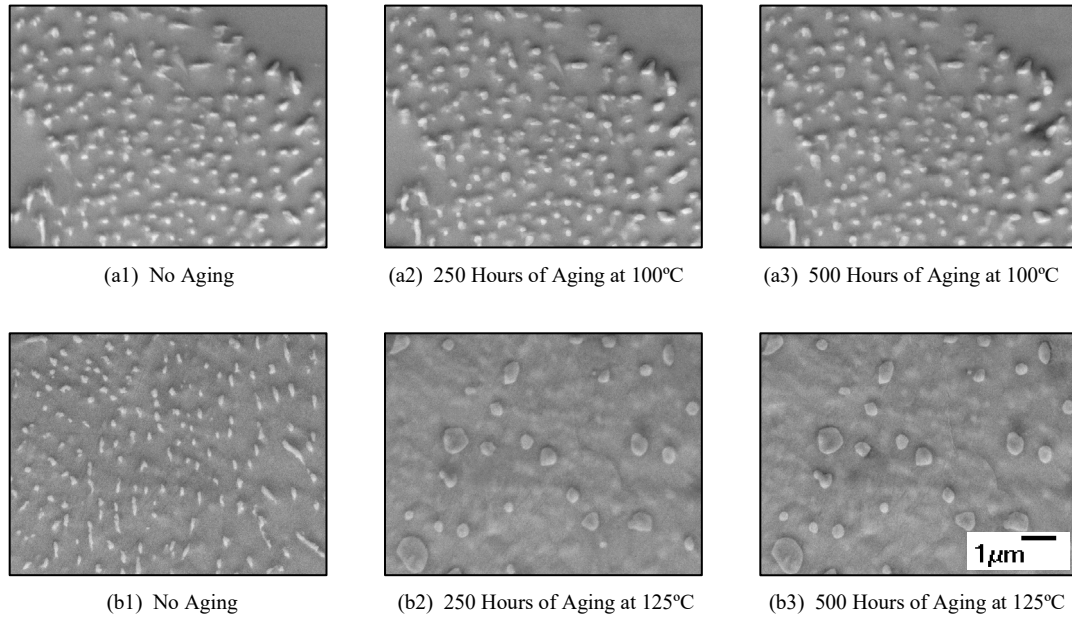


Figure 6.12 Aging Induced Evolution of SAC305 IMCs at 100 and 125 °C
(Aging Increment: 250 Hours)

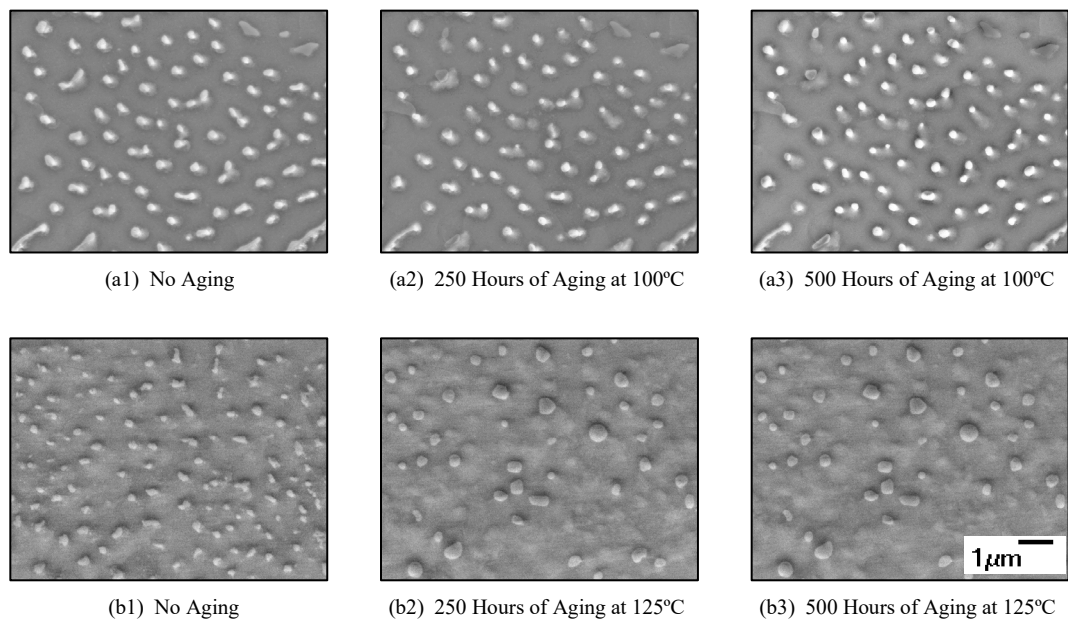


Figure 6.13 Aging Induced Evolution of SAC_Q IMCs at 100 and 125 °C
(Aging Increment: 250 Hours)

6.5 Comparison of Aging Degradation in SAC+Bi Alloys

Similar to prior results for SAC305 and SAC_Q, there is significant coarsening of the IMC particles during high temperature aging. The analyzed regions were typically chosen to be interdendritic regions with a heavy concentration of IMC particles. For example, the images shown in Figure 6.7 and Figure 6.8 contains zoomed-in high magnification views of the microstructure evolution for SAC+Bi Alloys of longer aging increment (250 hours up to 2000 hours) at 125°C. For longer aging time large aspect ratio particles tended to shift to more spherical shapes. Similar to our prior results for SAC_Q and SAC305, there is significant coarsening of the Ag₃Sn IMC particles during the first 250 hours of aging, while subsequent coarsening occurred at a very slow rate. As expected, aging at high temperature resulted in decreases in the number of IMC particles, and increases in the average particle size and average particle separation distance. Similar patterns of diffusion were observed for different temperatures and different alloys.

Quantitative analyses have been performed on the recorded SEM images to evaluate the size metrics for the Ag₃Sn IMC particle evolutions. For each aging temperature analysis, three such regions were digitally recorded to determine the average microstructural evolution. The area of each particle, the total area of all of the particles, and the total number of particles in each selected region and aging time were determined. These values were used to estimate the variation of the average particle diameter with aging time.

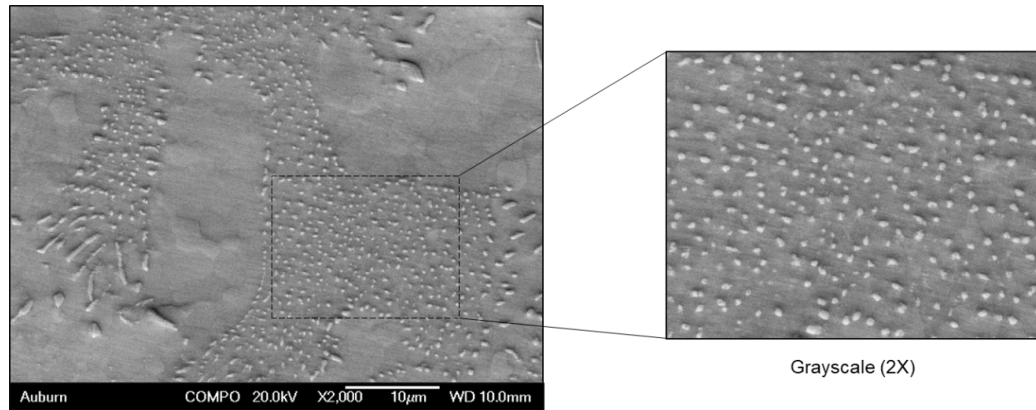


Figure 6.14 Sub-Region for Quantitative Analysis of Aging Effects on IMCs

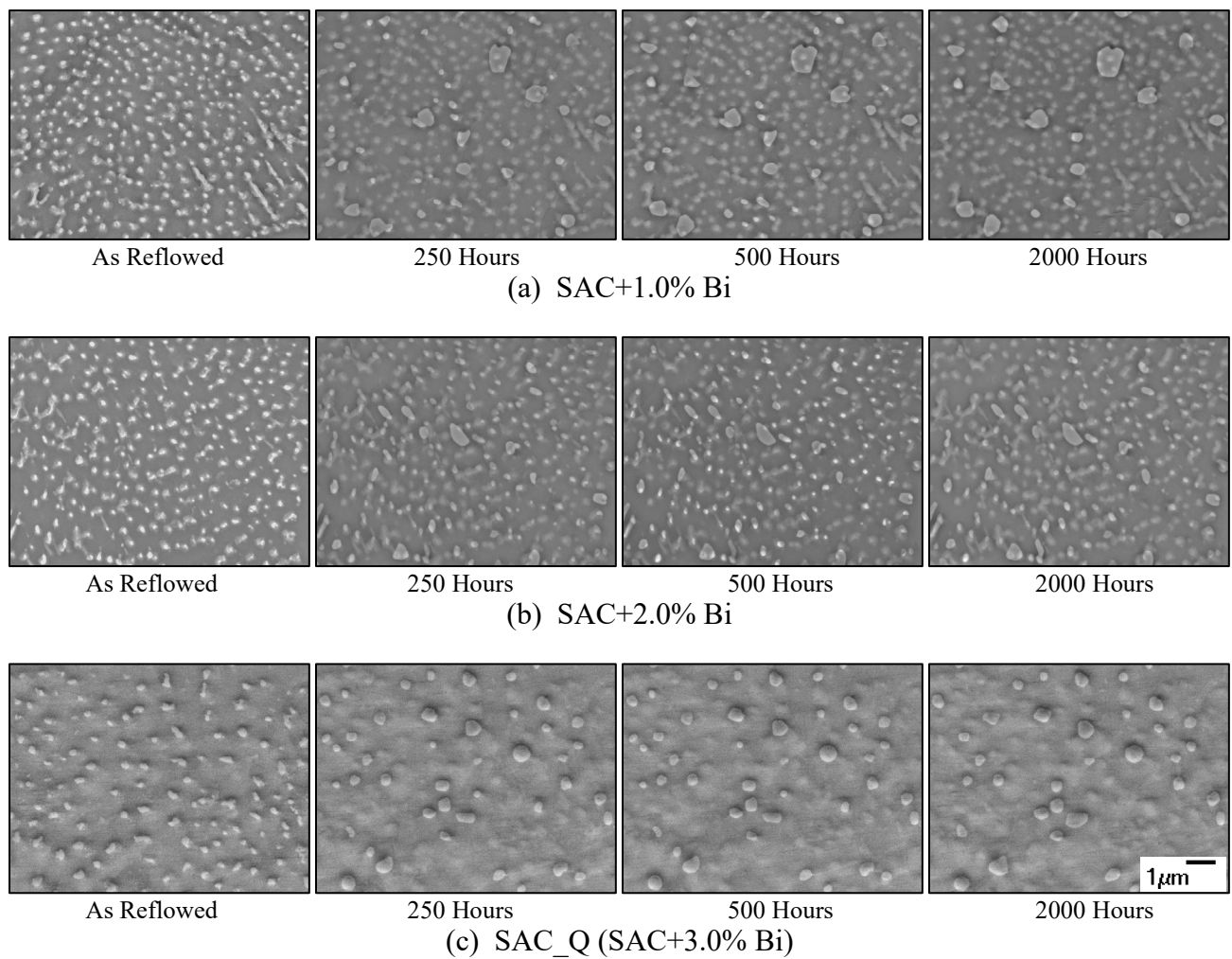


Figure 6.15 Example SAC+Bi Alloys Long Term Microstructural Evolution over 2000 Hours of Aging at $T = 125\text{ }^{\circ}\text{C}$ (Aging Increment: 250 Hours)

It is seen that the major changes in particle diameter occurred within the first 250 hours of aging ($t < 250$ hours). This matches our previous observations for the degradations in lead free solder mechanical behavior with aging [2-5, 29-33]. A plot of the variations of the average normalized IMC particle diameter with aging time for different SAC+Bi alloys compared with SAC305 are shown in Figure 6.10. During aging, intermetallic coarsening effects in SAC+Bi alloys are reduced relative to SAC305 because of adding bismuth. Under the same aging condition, the coarsening of SAC+1.0% Bi is more significant compared with SAC+2.0% Bi and SAC_Q. There is only slight difference of microstructure evolution in SAC+2.0% Bi and SAC_Q.

After 500 hours of aging at 125°C, the average IMC particle diameter increased by approximately 200% for SAC305 and approximately 120% for SAC_Q. There is also strong temperature dependence for the aging effect. After 500 hours of aging at $T = 100^\circ\text{C}$, the average IMC particle diameter increased by approximately 40% for SAC305 and approximately 10% for SAC_Q. Because all the alloys were formed using the same reflow profile, the initial IMC particles sizes were almost the same for the SAC305 and SAC+Bi joints. After same time of aging at high temperature, the aging induced degradation was strongly reduced in SAC+Bi alloys compared with SAC305. For the same alloy, the average particle diameter after aging at 125°C for 500 hours was almost ten times than aging at 100°C for 500 hours.

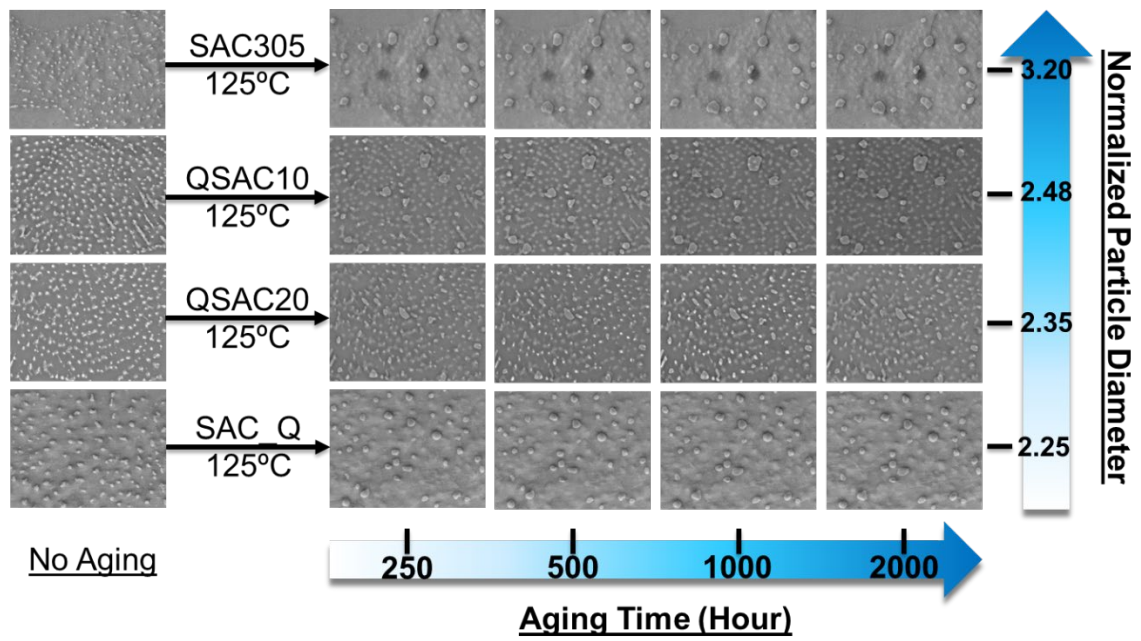


Figure 6.16 Example SAC+Bi Alloys Long Term Microstructural Evolution

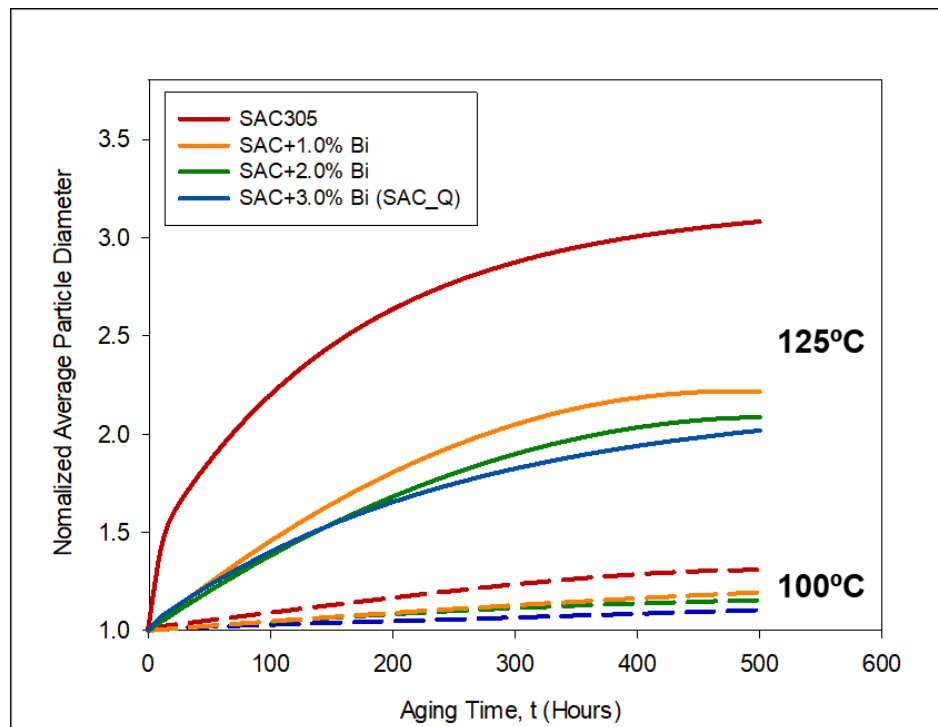


Figure 6.17 Variation of Normalized IMC Particle Diameter with Aging Time
(SAC305 and SAC+Bi; at 100 and 125 °C)

6.6 Discussion on Evolution of IMC Particles during Aging

Typically, IMC particles tend to become more round (spherical) with aging. Atoms on the surface of a particle have higher energy than the atoms inside a particle due to unsatisfied bonds in the surface atoms. A cylindrical or elongated particle has a higher fraction of surface atoms (or higher surface to volume ratio) compared to a spherical (round) particle with the same volume. As a result, the free energy per atom of an elongated particle or several small particle is higher than a big round particle with equal volume. This free energy difference is the driving force that causes the transition of IMC particles from smaller to a bigger size as seen in Figure 8.5.

This IMC coarsening phenomenon is also known as Ostwald Ripening. According to the Gibbs-Thompson effect [181, 182], an increase in particle size is accompanied by a decrease of the solute concentration in the matrix surrounding the particle. This leads to a concentration gradient, and solute atoms near smaller particles will diffuse towards the larger particles where the reductions in solute concentration has occurred. In addition, atoms from the smaller particles will go back into solution. The overall effects are shrinkage of smaller particles, and growth of larger particles. A schematic of the variation of solute concentration around a small and a large particles is shown in Figure 6.18. Since Ostwald Ripening is a diffusion-based process, use of higher aging temperatures will increase the rate of coarsening significantly.

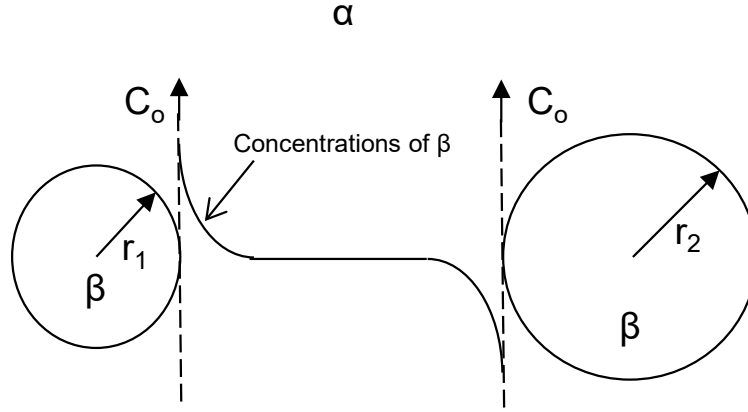


Figure 6.18 Schematic of Solute Concentration in Front of Particle [181].

The coarsening and coalescing of IMC particles during aging is known to play a critical role in the degradations of solder mechanical properties. IMC particles will pin and block the movement of dislocations. However, aging leads to both a smaller number of larger IMC particles and increased spacing between the IMC particles. The interparticle spacing λ can be calculated from the following equation:

$$\lambda = \frac{4(1-f)r}{3f} \quad (6.1)$$

where f is the volume fraction of the particles and r is the particle radius. Hence for a fixed volume fraction of the IMC particles, spacing between the particles increases with increasing particle diameter. Orowan proposed a mechanism that when a dislocation crosses incoherent precipitate particles (like the IMC particles in present case), it will bow and leave a loop of stress field around the particle [181, 182, 184]. A schematic of the interaction between a dislocation and IMC particles is shown in Figure 6.19.

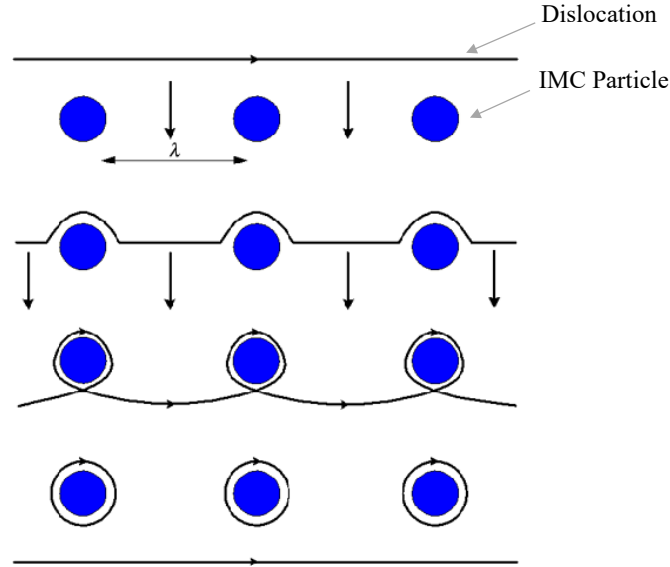


Figure 6.19 Schematic of a Dislocation Passing IMCs (Orowan Looping)

The yield stress and strength of a material depends on the shear stress (also known as the Orowan stress) that is required for a dislocation to pass through the particles. This shear stress will decrease as the inter-particle spacing increases during aging as shown in Equation 6.2 [180-182].

$$\tau_o = \frac{Gb}{\lambda} \quad (6.2)$$

where τ_o is the shear stress required for a dislocation to pass through the particles, G is the shear modulus, and b is the magnitude of the burgers vector. Therefore, aging leads to the coarsening of the IMC particles which causes to increase the interparticle spacing. The yield stress and strength of a material decrease after aging due to the increased interparticle spacing.

As Mentioned in section 4, the microstructure of SAC305 is mainly composed of a β -Sn matrix and two different intermetallic compounds (IMC) namely, Ag_3Sn and Cu_6Sn_5 .

The reduction of strength of SAC305 after aging can be attributed to 2 major facts. First, aging causes coarsening of the Ag_3Sn and Cu_6Sn_5 intermetallic compounds and hence reduces their ability to block dislocation movements. Second, the $\beta\text{-Sn}$ phase also coarsens/grows with aging, and hence reduces the strength of the alloy.

For the SAC-Bi alloy, the additional Bi content doesn't form any IMC with Sn. Therefore, the only IMCs that should present in microstructure of SAC_Q and Innolot are Ag_3Sn and Cu_6Sn_5 . However, Bi remains as a separate phase in the microstructure enhance the strength of the SAC-Bi alloys. Also, from the Sn-Bi phase diagram, it is observed that Bi has a good ($\sim 1.8\%$) solid solubility in Sn at room temperature. Hence Bi contributes more enhancement in strength of the SAC-Bi alloy before aging by the solid solution strengthening mechanism.

As seen in phase diagram, the solid solution solubility of Bi increases from 1.8% at $T = 25\text{ }^\circ\text{C}$, to about 17% at $125\text{ }^\circ\text{C}$. Thus, the Bi present in the as solidified microstructure of SAC-Bi alloys as a separate Bi phase will have the tendency to go into the solution with the $\beta\text{-Sn}$ matrix during aging. This will lead to additional solid solution strengthening of the SAC-Bi alloy. A hypothesis was developed to explain the experimental observation. According to the hypothesis, the observed negligible variations in strength of SAC+Bi before and after aging is due to the increases in strength from solid solution strengthening exceeding any reductions in strength caused by the evolution of microstructure during high temperature aging.

6.7 Summary

SEM and EDS have been utilized to examine aging induced microstructural changes occurring within different SAC+Bi lead free solder. Microstructural evolution has been studied for several different regions from several different SAC+Bi joints, and different aging time and aging temperatures have been performed. The size metrics for each IMC particle were tracked during the aging processes.

As expected, the results have shown that all of the SAC+Bi alloys demonstrate superior resistance to aging effects relative to SAC305. During aging, the bismuth was observed to go into solution within the beta-Sn dendrites and in the intermetallic rich regions between dendrites. It was observed that the coarsening of the intermetallic compounds was greatly mitigated in the SAC+Bi alloys relative to that observed in SAC305. The resistance to aging and microstructure evolution were found to be directly proportional to the amount of Bi present in the SAC+Bi alloy. The aging induced degradation of the SAC+Bi alloy will be greatly reduced compared with those for SAC305 for all aging times if the level of Bi is at least 1%. Under the same aging condition, the coarsening of SAC+1.0% Bi is more significant compared with SAC+2.0% Bi and SAC_Q. There is only slight difference of microstructure evolution in SAC+2.0% Bi and SAC_Q. The FIB results show that the IMC particle size underneath the surface and above the exposed surface are quite similar.

CHAPTER 7

EFFECTS OF HIGH TEMPERATURE AGING ON THE MECHANICAL BEHAVIOR OF SAC305 AND SAC_Q SOLDER ALLOYS

7.1 Introduction

Solder joint reliability in harsh environment applications are big concerns in the electronic packaging industry. The reliabilities of electronic packages used in various products depend on the environmental conditions experienced during field use. Consumer electronics are typically designed using maximum operating temperatures of 100 °C or less. However, prolonged exposures of lead free solders at high temperatures will cause aging effects, which involve evolution (coarsening) of the intermetallic compound (IMC) particles in microstructure resulting in further degradations of their mechanical properties. So it is important to make accurate predictions of solder joint reliability at high Temperature.

In this chapter, SAC305 and SAC_Q lead free solder alloys, recommended for high reliability applications have been chemically analyzed and then mechanically tested in order to determine the temperature dependent mechanical properties of these alloys. Before testing, the solder uniaxial specimens were aged (preconditioned) at the extreme high temperature of either $T = 125\text{ }^{\circ}\text{C}$. Several durations of aging were considered including 0, 2, 6, 12, and 24 hours. Tensile stress-strain tests were performed at 0.001sec^{-1}

strain rates on the aged specimens. For each alloy, the stress-strain curve shape and high temperature tensile properties (initial modulus and ultimate tensile strength) of the solder alloys were measured and compared.

7.2 Stress-Strain Data for Various Aging Conditions

The recorded experimental tensile test results for SAC305 solder alloy with different test temperatures and aging durations (Aging $T = 125\text{ }^{\circ}\text{C}$) are plotted in Figure 7.1. Results for SAC_Q is shown in Figure 7.2. Graphs in each plot shows the temperature dependent uniaxial stress-strain behavior of SAC305 solder alloy at a particular aging duration (0, 2, 6, 12, or 24 hours.), with the various colored curves representing the different aging conditions with blue= no aging, green= 2 hours of aging, yellow= 6 hours of aging, orange= 12 hours of aging, and red= 24 hours of aging. We found a significant degradation of mechanical properties with the increase in aging time for both alloys. Similar behavior has been observed at extreme high temperature aging as well (aging at $T = 200\text{ }^{\circ}\text{C}$).

The uniaxial tensile test results between SAC305 and SAC_Q have been shown in the same plot for comparison (Figure 7.3). Each of the graphs shows a comparative analysis of the uniaxial stress-strain behavior of both alloys at test temperature, with the various colored curves representing the different aging durations with blue= no aging, green= 2 hours of aging, yellow= 6 hours of aging, orange= 12 hours of aging, and red= 24 hours of aging at $T = 125\text{ }^{\circ}\text{C}$).

The results are grouped in two sets of curves in each graph. The first set (top four curves) shows the aging dependent stress-strain behavior of SAC_Q, and the second set

(bottom four curves) represents the same for SAC305. For each material, the top (blue) curve represents the average stress-strain curve for no aging, and the bottom (red) curve shows the average stress-strain curve at 24 hours of aging.

At the same test condition, SAC_Q exhibited the best mechanical properties, and typically both the ultimate tensile strength (UTS) and effective elastic modulus (E) of SAC_Q were twice as large of the corresponding values for SAC305. Furthermore, the SAC305 alloy demonstrated large aging induced degradations with significant drop in mechanical properties after only 1 day of high temperature aging, while the SAC_Q alloy appeared to have negligible aging effects for all aging durations.

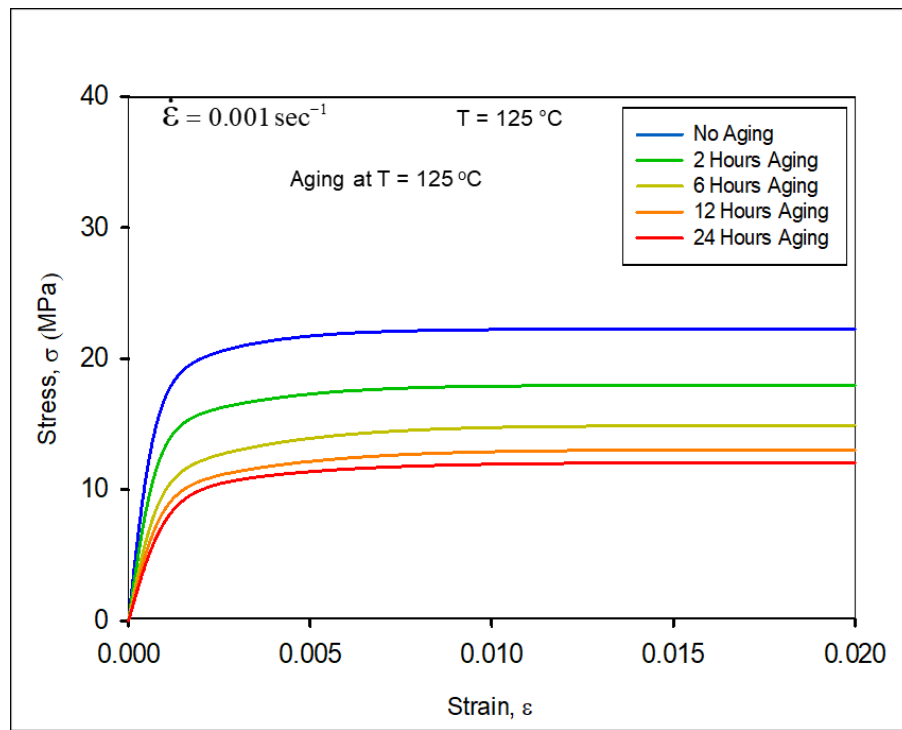


Figure 7.1 Stress-Strain Curves for SAC305

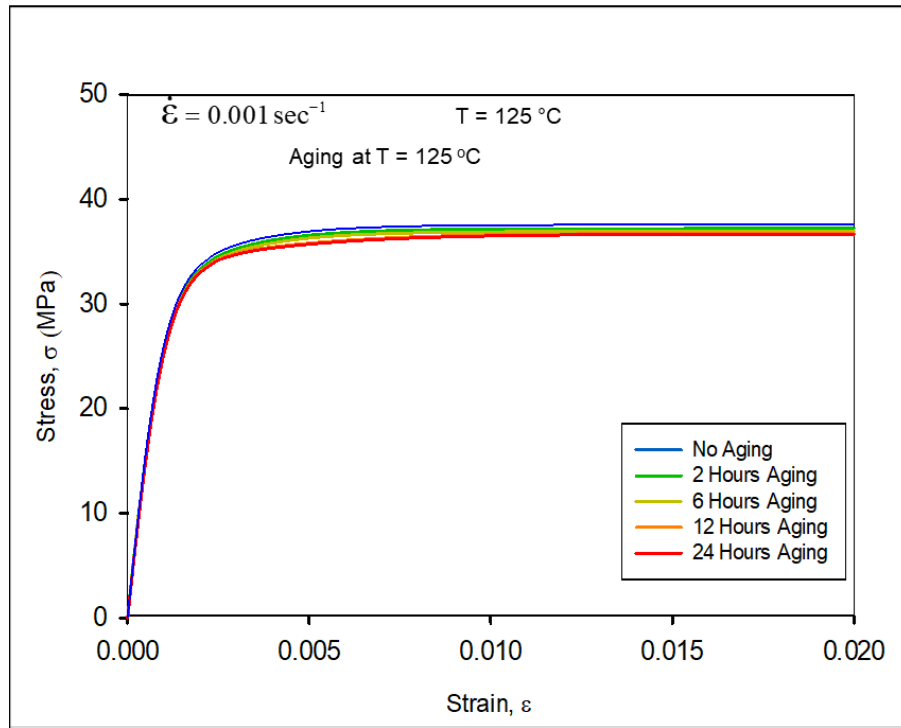


Figure 7.2 Stress-Strain Curves for SAC_Q

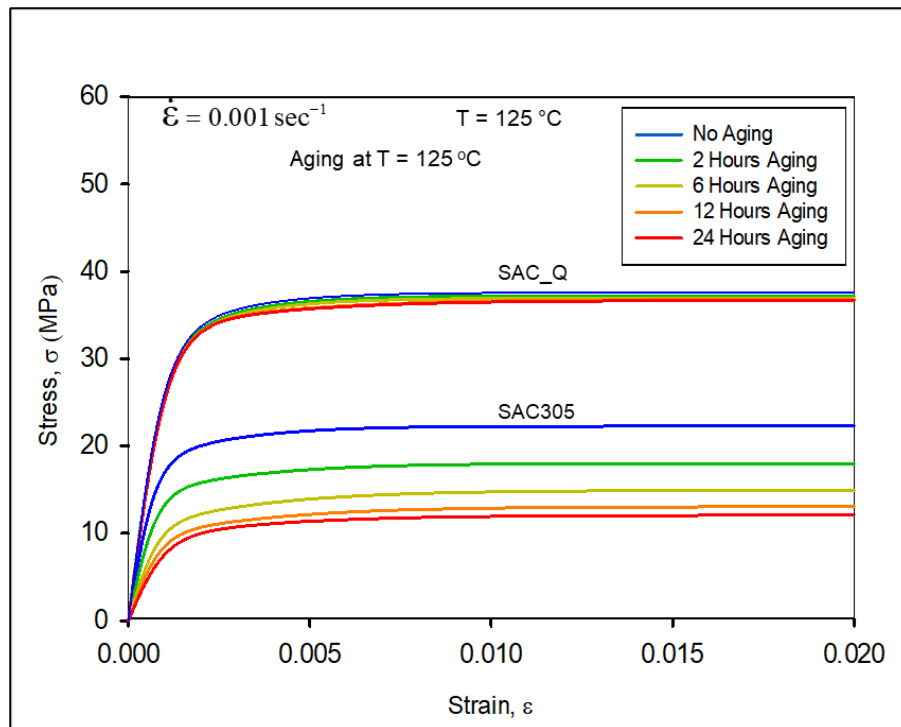


Figure 7.3 Comparison of Stress-Strain Curves for SAC305 and SAC_Q

(Aging and Testing at $T = 125^\circ\text{C}$)

7.3 Mechanical Properties

The mechanical properties of the three alloys have been extracted from the measured stress-strain data and tabulated in Tables 7.1. These properties, such as, initial effective elastic modulus and ultimate tensile strength have been included. By comparing the analogous results for the same aging temperature and testing temperature, but different alloys, it has been observed that compared with SAC_Q, the effective elastic modulus and ultimate tensile strength for SAC305 both decreases. Large aging induced degradations are evident for SAC305 with a significant drop in properties after 1 day of aging at 125°C. After that point, the properties degrade at a much slower rate. Conversely, the properties of SAC_Q were found to degrade very slowly or remain nearly constant at all aging conditions.

Table 7.1 Comparison of Effective Modulus and Ultimate Tensile Strength (UTS)

Alloy	Effective Modulus, E (GPa)					Ultimate Strength, UTS (MPa)				
	No	2	6	12	24	No	2	6	12	24
	Aging	Hours	Hours	Hours	Hours	Aging	Hours	Hours	Hours	Hours
SAC305	25.9	19.6	14.1	11.7	9.8	22.4	18.1	15.0	13.2	12.1
SAC_Q	34.1	33.4	33.0	32.9	32.7	37.6	37.2	36.9	36.7	36.6

7.4 Comparison of Aging Degradation in SAC305 and SAC_Q Alloys

At each aging condition, SAC_Q exhibited the best mechanical properties, and typically both the ultimate tensile strength (UTS) and effective elastic modulus (E) of SAC_Q were twice as large of the corresponding values for SAC305. Furthermore, the SAC305 alloy demonstrated large aging induced degradations with significant drop in mechanical properties after only 2 hours of high temperature aging, while the SAC_Q alloy appeared to have negligible aging effects for all aging durations.

Correlations between the reductions in effective modulus and ultimate tensile strength with the increase in IMC particle diameter as a function of aging time are shown in Figure 7.4 and 7.5, respectively, for both SAC305 and SAC_Q. The mechanical properties of these same solder alloys aged at for longer durations at $T = 125\text{ }^{\circ}\text{C}$ have been included as well. Large aging induced degradations are evident for SAC305 with a significant drop in properties after 5 days of aging at $T = 125\text{ }^{\circ}\text{C}$. After that point, the properties degrade at a much slower and steady rate. Conversely, the properties of SAC_Q were found to degrade very slowly or remain nearly constant at all aging conditions.

It is clear that the evolution of the mechanical strength of the solder alloys is closely linked to variation in IMC particle diameter, and that the effects of aging are much greater for SAC305 than SAC_Q. The bismuth present as a dopant in SAC_Q made it relatively insensitive to aging induced degradations by a combination of the solid solution strengthening mechanism and a slower coarsening of the Ag_3Sn IMC particles. The aging induced presence of bismuth in solution within the beta-Sn matrix provided an increased resistance to the Ostwald ripening diffusion process that coarsens the IMC particles.

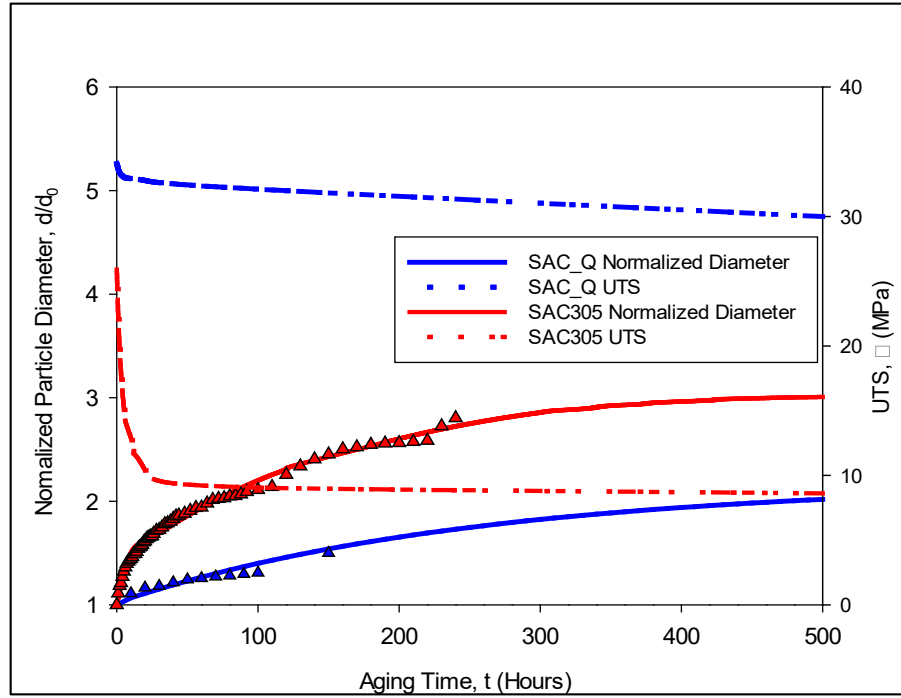


Figure 7.4 Variations of IMC Diameter and UTS with Aging Time
(SAC305 and SAC_Q; Aging at 125 °C)

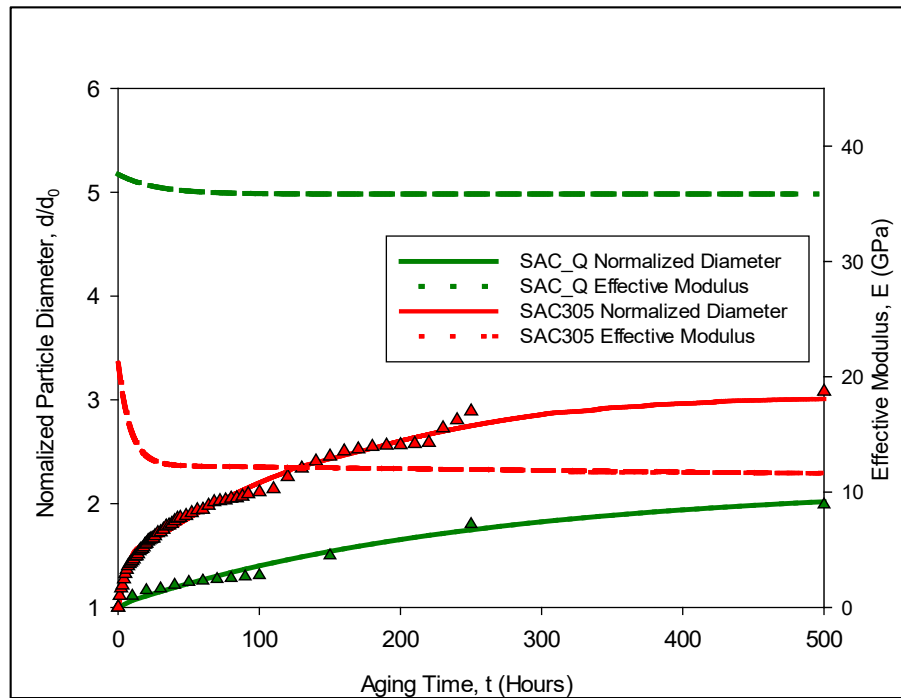


Figure 7.5 Variations of IMC Diameter and Modulus with Aging Time
(SAC305 and SAC_Q; Aging at 125 °C)

7.5 Summary and Discussion

A comparative study of the aging dependent mechanical behavior of SAC305 and SAC_Q solder alloys at high temperatures ($T = 125\text{ }^{\circ}\text{C}$) were investigated. Before testing, the solder uniaxial specimens were aged (preconditioned) at $T = 125\text{ }^{\circ}\text{C}$, and several different durations of aging were considered (no aging, and 2 hours, 6 hours, 12 hours and 24 hours of aging). Stress-strain tests were then performed on the aged specimens. Using the measured data, the evolutions of the stress-strain behaviors were determined as a function of aging time, and models describing the evolution of the mechanical properties (effective elastic modulus and ultimate tensile strength) with aging time were established.

Our experimental measurements show that a 40-50% drop in strength and modulus occurred at $T = 125\text{ }^{\circ}\text{C}$. Comparisons between SAC305 and SAC_Q indicate that the SAC_Q alloy was found to have significantly better high temperature mechanical properties relative to SAC305 at all prior aging conditions. In particular, the initial modulus and ultimate tensile strength of SAC305 experienced large degradations during high temperature aging, whereas the same properties of SAC_Q changed only slightly. These changes in mechanical behavior correlated well with the observed increases in the average IMC particle diameter and decreases in the number of IMC particles. The microstructural and material property degradations were especially large for SAC305 during the initial 50 hours of aging.

CHAPTER 8

CONCLUSIONS

8.1 Literature Review

Literature review has been done on Sn-Ag-Cu lead free solders, effects of aging on solder mechanical properties and microstructure, various influential factors on solder mechanical behavior, and effects of isothermal aging on solder microstructure.

The mechanical properties of a solder are strongly influenced by its microstructure, which is controlled by its thermal history including its solidification rate and thermal exposures after solidification. Aging of lead free solders leads to degradations in their constitutive and failure behaviors. For example, research in the literature has shown that aging leads to large reductions in solder material properties including shear strength, elastic modulus, nanoindentation joint modulus and hardness, high strain rate mechanical behavior, creep response, and Anand model parameters. Other studies have shown that aging causes severe degradations in uniaxial cyclic stress-strain curves and fatigue life, shear cyclic stress-strain curves and fatigue life, fracture behavior, drop reliability, and thermal cycling reliability.

Aging has a strong effect on mechanical properties of lead free solders, as they have high homologous temperatures in most product applications. It has been found that aging is universally detrimental to solder constitutive and failure behaviors. The changes in solder mechanical behavior are a result of the evolution of the solder microstructure that occurs during aging. The most well-known and widely observed microstructural changes are coarsening of the Ag_3Sn and

Cu₆Sn₅ IMCs present in the eutectic regions between β -Sn dendrites. In many studies on the effects of aging on solder microstructure, observations were made on two different solder joints (one non-aged and one aged). There are limited investigations that have involved the monitoring of evolving microstructure in a fixed region in a single solder sample.

Dopants have been found to strongly influence the properties and behaviors of lead free solders. For Example, Bi helps to reduce solidification temperature, increases strength by means of precipitation hardening, helps to reduce IMC (Intermetallic Compound) layer thickness, and also reduce aging induced degradation of mechanical properties in lead free solder materials. Ni helps to improve thermal fatigue life and drop test performance by refining Sn grain size and reducing the IMC layer formation near the Cu pad. The effects of rare earth (RE) elements and nanoparticle addition on the properties of lead free solder was also discussed in this chapter.

The changes in solder mechanical behavior are a result of the evolution of the SAC solder microstructure that occurs during aging. The most well-known and widely observed changes are coarsening of the Ag₃Sn and Cu₆Sn₅ intermetallic compounds (IMCs) present in the eutectic regions between beta-Sn dendrites. Several researchers have proposed empirical models to describe the growth of these secondary phase particles as a function of aging temperature and aging time, and related this growth to mechanical property changes.

8.2 Experimental Procedures

All the experimental procedures and the data processing steps were presented in chapter 3. Micro-scale uniaxial tensile specimens were prepared in a rectangular shaped hollow glass tube using a vacuum suction method. Typical dimension of the uniaxial tensile specimens was 80 (length) $\times$ 3 (width) $\times$ 0.5 (height) mm. Uniaxial tensile tests were performed using a micro tension

torsion testing system. Nanoindentation experiments were conducted on actual solder joints which were typically extracted from 14 x 14 mm PBGA assemblies (0.8 mm ball pitch, 0.46 mm ball diameter). Nanoindentation experiments were performed using Hysitron TI950 TriboIndenter.

To study the solder microstructural changes during aging, SAC305 solder samples were formed with RF and WQ cooling profiles and resulting initial microstructures, and then microscopy cross-sections were prepared. After polishing, small indentation marks were added to the cross-sections to facilitate locating the identical regions of interest. Then the microstructural changes in the fixed regions during aging were examined using SEM.

8.3 Investigation of Aging Induced Evolution of the Microstructure of SAC305 Lead Free Solder

In this investigation, Scanning Electron Microscopy (SEM) has been utilized to examine aging induced microstructural changes occurring within lead free solders. Unlike many prior studies, fixed regions in the solder joint cross-sections were monitored throughout the aging process, rather than examining different samples and/or different regions after the various aging exposures. Nanoindentation marks were added to the cross-sections at certain locations to facilitate locating the fixed regions of interest. Two aging increments (1 hour and 10 days) and two solidification profiles (RF and WQ) have been examined. After preparation of suitable cross-sectional samples, the samples were then aged at $T = 125\text{ }^{\circ}\text{C}$, and the microstructures were observed and recorded in the selected regions after various aging exposures using SEM. With this approach, time-lapse imagery of the microstructure evolution in a particular region of a solder joint has been recorded as a function of the aging time.

Using the recorded images, migration, coalescence, and coarsening of intermetallic compounds were visualized. It has been found that the number of IMC particles decreased, while the average size of the particles and average particle separation distance increased significantly with aging. The early aging period features the most rapid and dramatic changes in microstructure. Compared with RF SAC305, WQ SAC305 had much finer initial IMC particles but they coarsened to a greater degree during isothermal aging. For small aging times up to 11 hours at $T = 125\text{ }^{\circ}\text{C}$, experimentally recorded movies of microstructural evolution during aging have been made to visualize those aging phenomena.

Additionally, the coarsening of IMC particles in fixed regions during aging has been quantitatively analyzed. Particularly, the aging induced evolutions of number of IMCs, total area of all IMCs, average particle area, and average particle diameter have been quantified. For instance, during the first 11 hours of aging at $125\text{ }^{\circ}\text{C}$, the average IMC particle diameter increased by approximately 62% for RF SAC305 and 227% for WQ SAC305. After 50 days of aging, the average diameter increased by around 157% and 781% for RF SAC305 and WQ SAC305, respectively.

8.4 Quantitative Analysis of the Aging Induced Evolution of IMC Particles in Fixed Regions

Multiple regions were observed in several different RF and WQ solder joint samples. At last, the coarsening of IMC particles in fixed regions during aging has been recorded as a function of the aging time. Particularly, the aging induced evolutions of number of IMCs, total area of all IMCs, average particle area, and average particle diameter have been quantified. Some researchers have proposed empirical models to describe the growth of these secondary phase particles as a

function of aging temperature and aging time and related this growth to mechanical property changes.

For instance, during the first 12 hours of aging at 125 °C, the average IMC particle diameter increased by approximately 62% for RF SAC305 and 230% for WQ SAC305. After 50 days of aging, the average diameter increased by around 157% and 781% for RF SAC305 and WQ SAC305, respectively. Nanoindentation methods and FIB were used to explore the microstructure of the SAC305 alloys. The FIB results show that the IMC particle size underneath the surface and above the exposed surface are quite similar.

8.5 Investigation and Comparison of Aging Effects in SAC+Bi Solders Exposed to High Temperatures

In present work, three SAC+Bi lead free solder materials recommended for high reliability applications have been chemically analyzed and then observed after aging. The alloys are referred to as SAC_Q (3.0% Bi), SAC+2.0% Bi, and SAC+1.0% Bi. Solder joints have been extracted from SAC+Bi assemblies and subjected to aging exposures up to 2000 hours at high temperatures ($T = 100$ and 125 °C). After each aging time, we were able to quantitatively analyze the evolution of Ag_3Sn and other IMCs with aging. Specifically, the aging induced changes in number of IMCs, total area of all IMCs, average area of particles, average diameter of particles and the normalized diameter were quantified in the fixed regions. In addition, the Energy Dispersive Spectroscopy (EDS) mapping was used to visualize the diffusion of Bi in SAC+Bi alloys after aging.

As expected, the results have shown that all of the SAC+Bi alloys demonstrate superior resistance to aging effects relative to SAC305. During aging, the bismuth was observed to go into solution within the beta-Sn dendrites and in the intermetallic rich regions between dendrites. It

was observed that the coarsening of the intermetallic compounds was greatly mitigated in the SAC+Bi alloys relative to that observed in SAC305. The resistance to aging and microstructure evolution were found to be directly proportional to the amount of Bi present in the SAC+Bi alloy. The aging induced degradation of the SAC+Bi alloy will be greatly reduced compared with those for SAC305 for all aging times if the level of Bi is at least 1%. Under the same aging condition, the coarsening of SAC+1.0% Bi is more significant compared with SAC+2.0% Bi and SAC_Q. There is only slight difference of microstructure evolution in SAC+2.0% Bi and SAC_Q.

8.6 Effects of High Temperature Aging on the Mechanical Behavior of SAC305 and SAC_Q Solder Alloys

A comparative study of the aging dependent mechanical behavior of SAC305 and SAC_Q alloys at high temperatures ($T = 125^{\circ}\text{C}$) were investigated. Before testing, the solder uniaxial specimens were aged (preconditioned) at the high temperature of $T = 125^{\circ}\text{C}$, and several different durations of aging were considered (no aging, and 2 hours, 6 hours, 12 hours, and 24 hours of aging). Stress-strain tests were then performed on the aged specimens. Using the measured data, the evolutions of the stress-strain behaviors were determined as a function of aging time, and models describing the evolution of the mechanical properties (effective elastic modulus and ultimate tensile strength) with extreme aging were established.

Our experimental measurements show that a 40-50% drop in strength and modulus occurred at high temperature $T = 125^{\circ}\text{C}$. Comparisons between SAC305 and SAC_Q indicate that SAC_Q had significantly better mechanical properties at all test temperatures and prior aging conditions. Substantial degradations of the mechanical properties (initial modulus, ultimate tensile

strength) occur in SAC305 during high temperature aging, whereas, SAC_Q exhibited relatively small variations in its properties during aging.

Recommendations for Future Work

Following future work can be performed to extend the findings of this dissertation:

- High temperature stress-strain behavior of SAC and SAC+Bi alloys subjected to aging at various high temperatures can be explored.
- The microstructure evolution study presented in this dissertation can be extended to a higher aging time. Based on the short and long term aging induced IMC coarsening data, a mathematical model can be developed to predict solder joint reliability as a function of aging time and temperature.
- The evolution of the microstructure of SAC+Bi alloys with aging can also be performed to understand how the changes in the microstructure making them resistant to aging induced degradations.
- The effects of aging on grain size and grain orientation of lead free solders can be quantified in the same region using SEM, polarized light microscope and EBSD.

REFERENCES

- [1] Ma, H., Suhling, C. J., "A Review of Mechanical Properties of Lead-Free Solders for Electronic Packaging," *J Mater Sci*, Vol. 44, pp. 1141-1158, 2009.
- [2] M. Abtew and G. Selvaduray, "Lead-Free Solders in Microelectronics," *Materials Science and Engineering: R: Reports*, vol. 27, no. 5, pp. 95-141, 2000.
- [3] Lee, N. C., "Getting Ready for Lead-Free Solders," *Soldering & Surface Mount Technology*, Vol. 9(2), pp. 65-69, 1997
- [4] Turbini, L. J., Munie, G. C., Bernier, D., Gamalski, J., Bergman, D. W., "Examining the Environmental Impact of Lead-free Soldering Alternatives," *IEEE Transactions on Electronics Packaging Manufacturing*, Vol. 24, pp. 4-9, 2001.
- [5] IPC Roadmap: *A Guide for Assembly of Lead-Free Electronics*, IPC, Northbrook, IL 2000.
- [6] Wood, E. P., Nimmo, K. L. "In Search of New Lead-free Electronic Solders," *Journal of Electronic Materials*, Vol. 23(8), pp. 709-713, 1994.
- [7] Hwang, J. S., *Implementing Lead-Free Electronics*, McGraw-Hill, 2004.
- [8] Allenby, B. R., Ciccarelli, J. P., "An Assessment of the Use of Lead in Electronic Assembly," *Proceedings of Surface Mount International Conference*, IEEE, pp. 1-28, San Jose, CA, 1992.
- [9] http://www.ameslab.gov/files/LeadFreeSolder_Foundation.pdf
- [10] Nimmo, K., "Alloy Selection," Chapter 3 of *Lead-free Soldering in Electronics: Science, Technology and Environmental Impact*, edited by K. Suganuma, New York, Marcel Dekker, pp. 61-62, 2004.
- [11] Gebhardt, E., Petzow, G., "The Constitution of the Ag–Cu–Sn System," *Z. Metallkd*, Vol. 50, pp. 597-605, 1959.
- [12] Miller, C. M., Anderson, I. E., Smith, J. F., "A Viable Sn-Pb Solder Substitute: Sn-Ag-Cu," *Journal of Electronic Materials*, Vol. 23(7), pp.595-601, 1994.
- [13] Loomans, M. E., Fine, M. E., "Tin-Silver-Copper Eutectic Temperature and Composition," *Metallurgical and Materials Transactions A*, Vol. 31(4), pp. 1155-1162, 2000.
- [14] Moon, K. W., Boettinger, W. J., Kattner, U. R., Biancaniello, F. S., Handwerker, C. A., "Experimental and Thermodynamic Assessment of Sn-Ag-Cu Solder Alloys," *Journal of Electronic Materials*, Vol. 29, pp. 1122-1136, 2000.

- [15] Snugovsky, L., Perovic, D. D., Rutter, J. W., "Solidification of Ternary Eutectic and Near-Eutectic Alloys in the Ag-Cu-Sn System," *TMS Meeting*, San Diego, CA, March 2003.
- [16] Cai, Z., "Reduction of Lead Free Solder Aging Effects Using Doped SAC Alloys," *Ph. D. Dissertation*, Auburn University, 2012.
- [17] <http://www.metallurgy.nist.gov/phase/solder/agcusn-ll.jpg>
- [18] Tsai, I., Tai, L.J., Yen, S.F., Chuang, T.H., Wu, E., Lo, R. and Ku, T., Wu, E., "Identification of Mechanical Properties of Intermetallic Compounds on Lead Free Solder," *Proceedings of the 55th Electronic Components and Technology Conference*, IEEE; Vol. 55(1), pp. 687-691, 2005.
- [19] Fields, R. J., Low, S. R., Lucey, G. K., "Physical and Mechanical Properties of Intermetallic Compounds Commonly Found in Solder Joints," *The Metal Science of Joining*, pp.165-174, 1991.
- [20] Zhu, Q. S., Zhang, L., Wang, Z. G., Wu, S. D., Shang, J. K., "Effect of Intermetallics Ag₃Sn on the Tensile Property of Sn_{3.8}Ag_{0.7}Cu Solder Alloy," I, Vol. 43(1), pp. 41-46, 2007.
- [21] Ganesan, S., Pecht, M., Lead-free Electronics, *Wiley-Interscience Publication*, pp. 51-52, 2006.
- [22] Lee, B. Z., Lee, D. N., "Spontaneous Growth Mechanism of Tin Whiskers," *Acta Materialia*, Vol. 46(10), 1998.
- [23] Pearson, W. B., *A Handbook of Lattice Spacings and Structure of Metals and Alloys*, Vol. 2, Pergamon Press, London, 1958.
- [24] S. Wiese et al., "Constitutive behaviour of lead-free solders vs. lead-containing solders-experiments on bulk specimens and flip-chip joints," *Proceeding of the 51st Electronic Components and Technology Conference*, pp. 890-902, 2001
- [25] R. J. McCabe and M. E. Fine, "Athermal and thermally activated plastic flow in low melting temperature solders at small stresses," *Scripta Materialia(USA)*, vol. 39, no. 2, pp. 189-195, 1998.
- [26] H. Ma and J. C. Suhling, "A review of mechanical properties of lead-free solders for electronic packaging," *Journal of Materials Science*, vol. 44, no. 5, pp. 1141-1158, 2009.
- [27] J. H. Lau and Y.-H. Pao, Solder joint reliability of BGA, CSP, flip chip, and fine pitch SMT assemblies, *McGraw-Hill*, New York, 1997.

- [28] R. W. Hertzberg, R. P. Vinci, and J. L. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, Wiley New York, 1996.
- [29] A. C. Fischer-Cripps, *Nanoindentation*, Third ed. Springer, 2011.
- [30] K. Zeng and K.-N. Tu, "Six cases of reliability study of Pb-free solder joints in electronic packaging technology," *Materials Science and Engineering: R: Reports*, vol. 38, no. 2, pp. 55-105, 2002.
- [31] K. Nogita, "Stabilisation of Cu₆Sn₅ by Ni in Sn-0.7 Cu-0.05 Ni Lead-Free Solder Alloys," *Intermetallics*, vol. 18, no. 1, pp. 145-149, 2010.
- [32] F. X. Che, J. E. Luan, and X. Baraton, "Effect of Silver Content and Nickel Dopant on Mechanical Properties of Sn-Ag-Based Solders," *Proceedings of the 58th IEEE Electronic Components and Technology Conference*, pp. 485-490, 2008.
- [33] F. Guo, J. Lee, S. Choi, J. P. Lucas, T. R. Bieler, and K. N. Subramanian, "Processing and Aging Characteristics of Eutectic Sn-3.5 Ag Solder Reinforced with Mechanically Incorporated Ni Particles," *Journal of Electronic Materials*, vol. 30, no. 9, pp. 1073-1082, 2001.
- [34] Z. G. Chen, Y. W. Shi, Z. D. Xia, and Y. F. Yan, "Study on the Microstructure of a Novel Lead-Free Solder Alloy SnAgCu-Re and Its Soldered Joints," *Journal of Electronic Materials*, vol. 31, no. 10, pp. 1122-1128, 2002.
- [35] F. Gao, S. Mukherjee, Q. Cui, and Z. Gu, "Synthesis, Characterization, and Thermal Properties of Nanoscale Lead-Free Solders on Multisegmented Metal Nanowires," *Journal of Physical Chemistry C*, vol. 113, no. 22, pp. 9546-9552, 2009.
- [36] C. M. T. Law and C. M. L. Wu, "Microstructure Evolution and Shear Strength of Sn-3.5 Ag-Re Lead-Free BGA Solder Balls," *Proceedings of the 6th IEEE CPMT Conference on High Density Microsystem Design and Packaging and Component Failure Analysis*, pp. 60-65, 2004.
- [37] N.-C. Lee, "Lead-Free Soldering-Where the World Is Going," *Advancing Microelectronics*, vol. 26, no. 5, pp. 29-35, 1999.
- [38] Ding, Y., Wang, C. Q., Tian, Y. H., Li, M. Y., "Influence of Ageing Treatment on Deformation Behavior of 96.5Sn3.5Ag Lead Free Solder Alloy During In-Situ Tensile Tests," *Journal of Alloys and Compounds*, Vol. 428, pp. 274-285, 2007.

- [39] Xiao, Q., Bailey, H. J., Armstrong, W. D., "Aging Effects on Microstructure and Tensile Property of Sn3.9Ag0.6Cu Solder Alloy," *Journal of Electronic Packaging*, Vol. 126(2), pp. 208-212, 2004.
- [40] Hasegawa, K., Noudou, T., Takahashi, A., Nakaso, A., "Thermal Aging Reliability of Solder Ball Joint for Semiconductor Package Substrate," *Proceedings of the 2001 SMTA International*, pp. 1-8, 2001.
- [41] Wang, Q., Johnson, R. W., Ma, H., Gale, W. F., "Properties of Lead-Free Solder Alloys as a Function of Composition Variation," *10th Electronic Circuit and World Convention Conference (ECWC 10)*, 2005.
- [42] Vianco, P. T., "Fatigue and Creep of Lead-free Solder Alloys: Fundamental Properties," Chapter 3 Lead-free Solder Interconnect Reliability, Edited by D. Shangguan, *ASM International*, pp. 67-106, 2006.
- [43] R. W. Johnson, J. L. Evans, P. Jacobsen, J. R. Thompson, and M. Christopher, "The Changing Automotive Environment: High-Temperature Electronics," *IEEE Transactions on Electronics Packaging Manufacturing*, vol. 27, no. 3, pp. 164-176, 2004.
- [44] M. Hattori, "Needs and Applications of High-Temperature Lsis for Automotive Electronic Systems," *Proceedings of the International Conference on High Temperature Electronics*, pp. 37-43, 1999.
- [45] B. Parmentier, O. Vermesan, and L. Beneteau, "Design of High Temperature Electronics for Well Logging Applications," *Proceedings of the International Conference on High Temperature Electronics*, 2003.
- [46] H. Ma, J. C. Suhling, P. Lall, and M. J. Bozack, "Reliability of the Aging Lead Free Solder Joint," *Proceeding of the 56th IEEE Electronic Components and Technology Conference*, pp. 849-864, 2006.
- [47] H. Ma, J. C. Suhling, Y. Zhang, P. Lall, and M. J. Bozack, "The Influence of Elevated Temperature Aging on Reliability of Lead Free Solder Joints," *Proceeding of the 57th IEEE Electronic Components and Technology Conference*, pp. 653-668, 2007.
- [48] Y. Zhang, Z. Cai, J. C. Suhling, P. Lall, and M. J. Bozack, "The Effects of Aging Temperature on SAC Solder Joint Material Behavior and Reliability," *Proceedings of the 58th IEEE Electronic Components and Technology Conference*, pp. 99-112, 2008.

- [49] I. E. Anderson and J. L. Harringa, "Elevated Temperature Aging of Solder Joints Based on Sn-Ag-Cu: Effects on Joint Microstructure and Shear Strength," *Journal of Electronic Materials*, vol. 33, no. 12, pp. 1485-1496, 2004.
- [50] I. E. Anderson, J. W. Walleiser, J. L. Harringa, F. Laabs, and A. Kracher, "Nucleation Control and Thermal Aging Resistance of near-Eutectic Sn-Ag-Cu-X Solder Joints by Alloy Design," *Journal of Electronic Materials*, vol. 38, no. 12, pp. 2770-2779, 2009.
- [51] Z. Cai, Y. Zhang, J. C. Suhling, P. Lall, R. W. Johnson, and M. J. Bozack, "Reduction of Lead Free Solder Aging Effects Using Doped SAC Alloys," *Proceedings of the 60th IEEE Electronic Components and Technology Conference*, pp. 1493-1511, 2010.
- [52] S. Choi, T. R. Bieler, J. P. Lucas, and K. N. Subramanian, "Characterization of the Growth of Intermetallic Interfacial Layers of Sn-Ag and Sn-Pb Eutectic Solders and Their Composite Solders on Cu Substrate During Isothermal Long-Term Aging," *Journal of Electronic Materials*, vol. 28, no. 11, pp. 1209-1215, 1999.
- [53] C. M. Chuang, T. S. Lui, and L. H. Chen, "Effect of Aluminum Addition on Tensile Properties of Naturally Aged Sn-9Zn Eutectic Solder," *Journal of Materials Science*, vol. 37, no. 1, pp. 191-195, 2002.
- [54] R. Darveaux, "Shear Deformation of Lead Free Solder Joints," *Proceedings of the 55th IEEE Electronic Components and Technology Conference*, pp. 882-893, 2005.
- [55] R. Darveaux and K. Banerji, "Fatigue Analysis of Flip Chip Assemblies Using Thermal Stress Simulations and a Coffin-Manson Relation," *Proceedings of the 41st IEEE Electronic Components & Technology Conference*, pp. 797-805, 1991.
- [56] Y. Ding, C. Wang, Y. Tian, and M. Li, "Influence of Aging Treatment on Deformation Behavior of 96.5Sn3.5Ag Lead-Free Solder Alloy During in Situ Tensile Tests," *Journal of Alloys and Compounds*, vol. 428, no. 1, pp. 274-285, 2007.
- [57] I. Dutta, D. Pan, R. A. Marks, and S. G. Jadhav, "Effect of Thermo-Mechanically Induced Microstructural Coarsening on the Evolution of Creep Response of SnAg-Based Microelectronic Solders," *Materials Science and Engineering: A*, vol. 410-411, pp. 48-52, 2005.
- [58] T.-C. Hsuan and K.-L. Lin, "Effects of Aging Treatment on Mechanical Properties and Microstructure of Sn-8.5Zn-0.5Ag-0.01Al-0.1Ga Solder," *Materials Science and Engineering: A*, vol. 456, no. 1, pp. 202-209, 2007.

- [59] K.-S. Kim, C.-H. Yu, and J.-M. Yang, "Aging Treatment Characteristics of Solder Bump Joint for High Reliability Optical Module," *Thin Solid Films*, vol. 462-463, pp. 402-407, 2004.
- [60] B. Lampe, "Room Temperature Aging Properties of Some Solder Alloys," *Welding Journal*, vol. 55, no. 10, pp. 330-340, 1976.
- [61] X. Luhua, J. H. L. Pang, K. H. Prakash, and T. H. Low, "Isothermal and Thermal Cycling Aging on IMC Growth Rate in Lead-Free and Lead-Based Solder Interface," *IEEE Transactions on Components and Packaging Technologies*, vol. 28, no. 3, pp. 408-414, 2005.
- [62] A. S. Medvedev, "Aging of Tin-Lead Solders and Joints Soldered by Them," *Metallovedenie I Obrabotka Metallov*, vol. 7, pp. 16-23, 1956.
- [63] K. Mysore, D. Chan, D. Bhate, G. Subbarayan, I. Dutta, V. Gupta, J. Zhao, and D. Edwards, "Aging-Informed Behavior of Sn3.8Ag0.7Cu Solder Alloys," *Proceedings of IEEE ITherm*, pp. 870-875, 2008.
- [64] J. H. L. Pang, T. H. Low, B. S. Xiong, X. Luhua, and C. C. Neo, "Thermal Cycling Aging Effects on Sn–Ag–Cu Solder Joint Microstructure, IMC and Strength," *Thin Solid Films*, vol. 462-463, pp. 370-375, 2004.
- [65] S. Wiese and K. J. Wolter, "Creep of Thermally Aged SnAgCu-Solder Joints," *Microelectronics Reliability*, vol. 47, no. 2, pp. 223-232, 2007.
- [66] Q. Xiao, H. J. Bailey, and W. D. Armstrong, "Aging Effects on Microstructure and Tensile Property of Sn3.9Ag0.6Cu Solder Alloy," *Journal of Electronic Packaging*, vol. 126, no. 2, pp. 208-212, 2004.
- [67] J.-W. Yoon, C.-B. Lee, and S.-B. Jung, "Growth of an Intermetallic Compound Layer with Sn-3.5Ag-5Bi on Cu and Ni-P/Cu During Aging Treatment," *Journal of Electronic Materials*, vol. 32, no. 11, pp. 1195-1202, 2003.
- [68] Y. Zhang, "The Effects of Aging on the Mechanical Behavior of Lead Free and Mixed Formulation Solder Alloys," PhD, Mechanical Engineering, Auburn University, Auburn, AL, 2010.
- [69] Y. Zhang, Z. Cai, J. C. Suhling, P. Lall, and M. J. Bozack, "The Effects of SAC Alloy Composition on Aging Resistance and Reliability," *Proceedings of the 59th IEEE Electronic Components and Technology Conference* pp. 370-389, 2009.

- [70] S. L. Allen, M. R. Notis, R. R. Chromik, and R. P. Vinci, "Microstructural Evolution in Lead-Free Solder Alloys: Part I. Cast Sn–Ag–Cu Eutectic," *Journal of Materials Research*, vol. 19, no. 5, pp. 1417-1424, 2004.
- [71] A. Bansal, T. Lee, K. Liu, and J. Xue, "Effects of Isothermal Aging and in-Situ Current Stress on the Reliability of Lead-Free Solder Joints," *Proceedings of 60th IEEE Electronic Components and Technology Conference*, pp. 1529-1535, 2010.
- [72] S. Chavali, Y. Singh, P. Kumar, G. Subbarayan, I. Dutta, and D. R. Edwards, "Aging Aware Constitutive Models for SnAgCu Solder Alloys," *Proceedings of the 61st IEEE Electronic Components and Technology Conference* pp. 701-705, 2011.
- [73] W. M. Chen, P. McCloskey, and S. C. O'Mathuna, "Isothermal Aging Effects on the Microstructure and Solder Bump Shear Strength of Eutectic Sn37Pb and Sn3.5Ag Solders," *Microelectronics Reliability*, vol. 46, no. 5, pp. 896-904, 2006.
- [74] R. Gagliano, "Shear Testing of Solder Joints: The Effect of Various Parameters on the Maximum Shear Stress of Eutectic Tin-Lead Solder," *Advanced Materials for the 21st Century: Proceedings of the 1999 Julia R. Weertman Symposium*, pp. 107-116, 1999.
- [75] M. Hasnine, M. Mustafa, J. C. Suhling, B. C. Prorok, M. J. Bozack, and P. Lall, "Characterization of Aging Effects in Lead Free Solder Joints Using Nanoindentation," *Proceedings of the 63rd IEEE Electronic Components and Technology Conference*, pp. 166-178, 2013.
- [76] S. W. R. Lee, Y.-K. Tsui, X. Hunag, and E. C. C. Yan, "Effects of Room Temperature Storage Time on the Shear Strength of PBGA Solder Balls," *International Mechanical Engineering Congress and Exposition*, pp. 259-262, 2002.
- [77] Y. Miyazawa and T. Ariga, "Influences of Aging Treatment on Microstructure and Hardness of Sn-(Ag, Bi, Zn) Eutectic Solder Alloys," *Materials Transactions*, vol. 42, no. 5, pp. 776-782, 2001.
- [78] M. Mustafa, Z. Cai, J. C. Suhling, and P. Lall, "The Effects of Aging on the Cyclic Stress-Strain Behavior and Hysteresis Loop Evolution of Lead Free Solders," *Proceedings of the 61st IEEE Electronic Components and Technology Conference*, pp. 927-939, 2011.
- [79] J. Wilde, A. R. Fix, and W. Nüchter, "Microstructural Changes of Lead-Free Solder Joints During Long-Term Ageing, Thermal Cycling and Vibration Fatigue," *Soldering & Surface Mount Technology*, vol. 20, no. 1, pp. 13-21, 2008.

- [80] M. Motalab, M. Mustafa, J. C. Suhling, J. Zhang, J. Evans, M. J. Bozack, and P. Lall, "Correlation of Reliability Models Including Aging Effects with Thermal Cycling Reliability Data," *Proceedings of the 63rd IEEE Electronic Components and Technology Conference*, pp. 986-1004, 2013.
- [81] J. Zhang, Z. Hai, S. Thirugnanasambandam, J. L. Evans, M. Bozack, R. Sesek, Y. Zhang, and J. C. Suhling, "Correlation of Aging Effects on Creep Rate and Reliability in Lead Free Solder Joints," *Journal of SMT*, vol. 25, no. 3, pp. 19-28, 2012.
- [82] T. Lee and H. Ma, "Aging Impact on the Accelerated Thermal Cycling Performance of Lead-Free BGA Solder Joints in Various Stress Conditions," *Proceedings of the 62nd IEEE Electronic Components and Technology Conference*, pp. 477-482, 2012.
- [83] L. Yin, M. Meilunas, B. Arfaei, L. Wentlent, and P. Borgesen, "Effect of Microstructure Evolution on Pb-Free Solder Joint Reliability in Thermomechanical Fatigue," *Proceedings of the 62nd IEEE Electronic Components and Technology Conference*, pp. 493-499, 2012.
- [84] T. Zhang, J. Evans, C. Mitchell, Z. Z. Li, E. Crandall, a. J. Ridenour, and F. Xie, "Reliability of Lead-Free BGA with SnPb Solder Paste for Harsh Environments," *Proceedings of SMTA/CAVE Symposium on AIMS Harsh Environment Electronics*, 2009.
- [85] M. Hongtao, J. C. Suhling, P. Lall, and M. J. Bozack, "Reliability of the Aging Lead Free Solder Joint," *Peoceedings of the 56th IEEE Electronic Components and Technology Conference*, pp. 849-864, 2006.
- [86] Z. Yifei, C. Zijie, J. C. Suhling, P. Lall, and M. J. Bozack, "The Effects of Aging Temperature on SAC Solder Joint Material Behavior and Reliability," *Proceedings of the 58th IEEE Electronic Components and Technology Conference*, pp. 99-112, 2008.
- [87] R. J. Coyle, P. P. Solan, A. J. Serafino, and S. A. Gahr, "The Influence of Room Temperature Aging on Ball Shear Strength and Microstructure of Area Array Solder Balls," *Proceedings of the 50th IEEE Electronic Components and Technology Conference*, pp. 160-169, 2000.
- [88] T.-K. Lee, H. Ma, K.-C. Liu, and J. Xue, "Impact of Isothermal Aging on Long-Term Reliability of Fine-Pitch Ball Grid Array Packages with Sn-Ag-Cu Solder Interconnects: Surface Finish Effects," *Journal of Electronic Materials*, vol. 39, no. 12, pp. 2564-2573, 2010.

- [89] M. A. Whitmore, A. C. Chilton, and W. B. Hampshire, "Fatigue Failure in a Model SMD Joint," *Soldering & Surface Mount Technology*, vol. 1, no. 3, pp. 21-24, 1989.
- [90] L. Ming, K. Y. Lee, D. R. Olsen, W. T. Chen, B. T. C. Tan, and S. Mhaisalkar, "Microstructure, Joint Strength and Failure Mechanisms of SnPb and Pb-Free Solders in BGA Packages," *IEEE Transactions on Electronics Packaging Manufacturing*, vol. 25, no. 3, pp. 185-192, 2002.
- [91] J.-M. Koo and S.-B. Jung, "Effect of Displacement Rate on Ball Shear Properties for Sn–37Pb and Sn–3.5Ag BGA Solder Joints During Isothermal Aging," *Microelectronics Reliability*, vol. 47, no. 12, pp. 2169-2178, 2007.
- [92] R. Darveaux, "Shear Deformation of Lead Free Solder Joints," *Proceedings of the 55th Electronic Components and Technology Conference*, pp. 882-893, 2005.
- [93] J. R. Oliver, J. Liu, and Z. Lai, "Effect of Thermal Ageing on the Shear Strength of Lead-Free Solder Joints," *Proceedings of the International Symposium on Advanced Packaging Materials Processes, Properties and Interfaces*, pp. 152-157, 2000.
- [94] H. L. J. Pang, K. H. Tan, X. Q. Shi, and Z. P. Wang, "Microstructure and Intermetallic Growth Effects on Shear and Fatigue Strength of Solder Joints Subjected to Thermal Cycling Aging," *Materials Science and Engineering: A*, vol. 307, no. 1, pp. 42-50, 2001.
- [95] T. Lee, B. Zhou, and T. R. Bieler, "Impact of Isothermal Aging and Sn Grain Orientation on the Long-Term Reliability of Wafer-Level Chip-Scale Package Sn–Ag–Cu Solder Interconnects," *IEEE Transactions on Components, Packaging and Manufacturing Technology*, vol. 2, no. 3, pp. 496-501, 2012.
- [96] R. C. J. Smetana, P. Read, R. Popowich, D. Fleming, and T. Sack, "Variations in Thermal Cycling Response of Pb-Free Solder Due to Isothermal Preconditioning," *Proceedings of SMTA International Conference*, pp. 641-654, 2011.
- [97] L. Anand, "Constitutive Equations for Hot-Working of Metals," *International Journal of Plasticity*, vol. 1, no. 3, pp. 213-231, 1985.
- [98] S. B. Brown, K. H. Kim, and L. Anand, "An Internal Variable Constitutive Model for Hot Working of Metals," *International Journal of Plasticity*, vol. 5, no. 2, pp. 95-130, 1989.
- [99] J.-P. Clech, "An Obstacle-Controlled Creep Model for Sn-Pb and Sn-Based Lead-Free Solders," *Proceedings of SMTA International Conference*, 2004.

- [100] Y. Hong, P. Deane, P. Magill, and K. L. Murty, "Creep Deformation of 96.5Sn-3.5Ag Solder Joints in a Flip Chip Package," *Proceedings of the 46th IEEE Electronic Components and Technology Conference*, pp. 1136-1142, 1996.
- [101] X. Q. Shi, Z. P. Wang, Q. J. Yang, and H. L. J. Pang, "Creep Behavior and Deformation Mechanism Map of Sn-Pb Eutectic Solder Alloy," *Journal of Engineering Materials and Technology*, vol. 125, no. 1, pp. 81-88, 2002.
- [102] S. Wiese, M. Roellig, and K. Wolter, "Creep of Eutectic SnAgCu in Thermally Treated Solder Joints," *Proceedings of the 55th IEEE Electronic Components and Technology Conference*, vol. 2, pp. 1272-1281, 2005.
- [103] H. Ma, J. C. Suhling, Y. Zhang, P. Lall, and M. J. Bozack, "The Influence of Elevated Temperature Aging on Reliability of Lead Free Solder Joints," *Proceedings of the 57th IEEE Electronic Components and Technology Conference*, pp. 653-668, 2007.
- [104] J. H. Lau, "Solder Joint Reliability of Flip Chip and Plastic Ball Grid Array Assemblies under Thermal, Mechanical, and Vibrational Conditions," *IEEE Transactions on Components, Packaging, and Manufacturing Technology: Part B*, vol. 19, no. 4, pp. 728-735, 1996.
- [105] W. K. Jones, Y. Q. Liu, M. A. Zampino, and G. L. Gonzalez, "The at-Temperature Mechanical Properties of Lead-Tin Based Alloys," in *Microelectronic Interconnections and Assembly*, Springer Netherlands, pp. 53-58, 1998.
- [106] Y. L. W. K. Jones, M. A. Zampino, G. Gonzalez, and M. Shah, "Design and Reliability of Solders and Solder Interconnections," *TMS Annual Meeting*, 1997.
- [107] X. Q. Shi, W. Zhou, H. L. J. Pang, and Z. P. Wang, "Effect of Temperature and Strain Rate on Mechanical Properties of 63Sn/37Pb Solder Alloy," *Journal of Electronic Packaging*, vol. 121, no. 3, pp. 179-185, 1999.
- [108] F. Lang, H. Tanaka, O. Munegata, T. Taguchi, and T. Narita, "The Effect of Strain Rate and Temperature on the Tensile Properties of Sn-3.5Ag Solder," *Materials Characterization*, vol. 54, no. 3, pp. 223-229, 2005.
- [109] L. H. Dai and S.-W. R. Lee, "Characterization of Strain Rate-Dependent Behavior of 63sn-37Pb Solder Alloy," *Proceedings of ASME InterPACK*, pp. 307-313, 2001.

- [110] H. Nose, M. Sakane, Y. Tsukada, and H. Nishimura, "Temperature and Strain Rate Effects on Tensile Strength and Inelastic Constitutive Relationship of Sn-Pb Solders," *Journal of Electronic Packaging*, vol. 125, no. 1, pp. 59-66, 2003.
- [111] W. J. Plumbridge and C. R. Gagg, "Effects of Strain Rate and Temperature on the Stress–Strain Response of Solder Alloys," *Journal of Materials Science: Materials in Electronics*, vol. 10, no. 5, pp. 461-468, 1999.
- [112] J. H. L. Pang, B. S. Xiong, and F. X. Che, "Modeling Stress Strain Curves for Lead-Free 95.5Sn-3.8Ag-0.7Cu Solder," *Proceedings of the 5th International Conference on Thermal and Mechanical Simulation and Experiments in Microelectronics and Microsystems*, pp. 449-453, 2004.
- [113] J. G. Harper, L. A. Shepard, and J. E. Dorn, "Creep of Aluminum under Extremely Small Stresses," *Acta Metallurgica*, vol. 6, no. 7, pp. 509-518, 1958.
- [114] F. Garofalo and D. B. Butrymowicz, "Fundamentals of Creep and Creep-Rupture in Metals," *Physics Today*, vol. 19, no. 5, pp. 100-102, 1966.
- [115] L. Anand, "Constitutive Equations for the Rate-Dependent Deformation of Metals at Elevated Temperatures," *Journal of Engineering Materials and Technology*, vol. 104, no. 1, pp. 12-17, 1982.
- [116] F. X. Che, H. L. J. Pang, W. H. Zhu, W. Sun, and A. Y. S. Sun, "Modeling Constitutive Model Effect on Reliability of Lead-Free Solder Joints," *Proceedings of the 7th International Conference on Electronic Packaging Technology*, pp. 1-6, 2006.
- [117] M. Pei and J. Qu, "Constitutive Modeling of Lead-Free Solders," *Proceedings of International Symposium on Advanced Packaging Materials: Processes, Properties and Interfaces*, pp. 45-49, 2005.
- [118] K. Mysore, G. Subbarayan, V. Gupta, and R. Zhang, "Constitutive and Aging Behavior of Sn3.0Ag0.5Cu Solder Alloy," *IEEE Transactions on Electronics Packaging Manufacturing*, vol. 32, no. 4, pp. 221-232, 2009.
- [119] M. Motalab, Z. Cai, J. C. Suhling, and P. Lall, "Determination of Anand Constants for SAC Solders Using Stress-Strain or Creep Data," *Proceedings of IEEE ITherm*, pp. 910-922, 2012.

- [120] N. Bai, X. Chen, and H. Gao, "Simulation of Uniaxial Tensile Properties for Lead-Free Solders with Modified Anand Model," *Materials & Design*, vol. 30, no. 1, pp. 122-128, 2009.
- [121] M. Amagai, M. Watanabe, M. Omiya, K. Kishimoto, and T. Shibuya, "Mechanical Characterization of Sn–Ag-Based Lead-Free Solders," *Microelectronics Reliability*, vol. 42, no. 6, pp. 951-966, 2002.
- [122] Y. Kim, H. Noguchi, and M. Amagai, "Vibration Fatigue Reliability of BGA -IC Package with Pb-Free Solder and Pb–Sn Solder," *Microelectronics Reliability*, vol. 46, no. 2, pp. 459-466, 2006.
- [123] M. L. Huang and L. Wang, "Effects of Cu, Bi, and in on Microstructure and Tensile Properties of Sn-Ag-X(Cu, Bi, in) Solders," *Metallurgical and Materials Transactions A*, vol. 36, no. 6, pp. 1439-1446, 2005.
- [124] M. Matahir, L. Chin, K. Tan, and A. Olofinjana, "Mechanical Strength and Its Variability in Bi-Modified Sn-Ag-Cu Solder Alloy," *Journal of Achievement in Materials and Manufacturing Engineering*, vol. 46, pp. 50-56, 2011.
- [125] R. S. Pandher, B. G. Lewis, R. Vangaveti, and B. Singh, "Drop Shock Reliability of Lead-Free Alloys - Effect of Micro-Additives," *Proceedings of the 57th IEEE Electronic Components and Technology Conference*, pp. 669-676, 2007.
- [126] Z. Zhenqing, W. Lei, X. Xiaoqiang, W. Qian, and L. Jaisung, "The Influence of Low Level Doping of Ni on the Microstructure and Reliability of SAC Solder Joint," *Proceedings of International Conference on Electronic Packaging Technology & High Density Packaging*, pp. 1-5, 2008.
- [127] I. d. Sousa, D. W. Henderson, L. Parry, S. K. Kang, and D. Shih, "The Influence of Low Level Doping on the Thermal Evolution of SAC Alloy Solder Joints with Cu Pad Structures," *Proceedings of the 56th IEEE Electronic Components and Technology Conference*, pp. 1454-1461, 2006.
- [128] J. H. Lee, S. Kumar, H. J. Kim, Y. W. Lee, and J. T. Moon, "High Thermo-Mechanical Fatigue and Drop Impact Resistant Ni-Bi Doped Lead Free Solder," *Proceedings of the 64th IEEE Electronic Components and Technology Conference*, pp. 712-716, 2014.

- [129] T. Yeung, H. Sze, K. Tan, J. Sandhu, C. Neo, and E. Law, "Material Characterization of a Novel Lead-Free Solder Material — SACQ," *Proceedings of the 64th IEEE Electronic Components and Technology Conference*, pp. 518-522, 2014.
- [130] L. Sun and L. Zhang, "Properties and Microstructures of Sn-Ag-Cu-X Lead-Free Solder Joints in Electronic Packaging," *Advances in Materials Science and Engineering*, vol. 2015, no. 639028, 2015.
- [131] M. Sadiq, R. Pesci, and M. Cherkaoui, "Impact of Thermal Aging on the Microstructure Evolution and Mechanical Properties of Lanthanum-Doped Tin-Silver-Copper Lead-Free Solders," *Journal of Electronic Materials*, vol. 42, no. 3, pp. 492-501, 2013.
- [132] H. Lee, Y. Chen, T. Hong, K. Shih, and C. Hsu, "Microstructural Evolution of Sn-3.5Ag Solder with Lanthanum Addition," *International Conference on Electronic Packaging Technology & High Density Packaging*, pp. 617-622, 2009.
- [133] H. Hao, Y. Shi, Z. Xia, Y. Lei, and F. Guo, "Microstructure Evolution of SnAgCu Lead-Free Solders under High Temperature Aging," *Journal of Electronic Materials*, vol. 37, no. 1, pp. 2-8, 2008.
- [134] D. Witkin, "Influence of Microstructure on Mechanical Behavior of Bi-Containing Pb-Free Solders," *Proceedings of IPC APEX EXPO Conference and Exhibition*, vol. 1, pp. 540-560, 2013.
- [135] A. Delhaise, D. Perovic, and P. Snugovsky, "The Effects of Bi and Aging on the Microstructure and Mechanical Properties of Sn-Rich Alloys," *Proceedings of the International Conference on Soldering and Reliability*, 2015.
- [136] R. R. Chromik, R. P. Vinci, S. L. Allen, and M. R. Notis, "Measuring the Mechanical Properties of Pb-Free Solder and Sn-Based Intermetallics by Nanoindentation," *JOM*, vol. 55, no. 6, pp. 66-69, 2003.
- [137] X. Deng, N. Chawla, K. K. Chawla, and M. Koopman, "Deformation Behavior of (Cu, Ag)-Sn Intermetallics by Nanoindentation," *Acta Materialia*, vol. 52, no. 14, pp. 4291-4303, 2004.
- [138] F. Gao, H. Nishikawa, T. Takemoto, and J. Qu, "Mechanical Properties Versus Temperature Relation of Individual Phases in Sn-3.0Ag-0.5Cu Lead-Free Solder Alloy," *Microelectronics Reliability*, vol. 49, no. 3, pp. 296-302, 2009.

- [139] Y. D. Han, H. Y. Jing, S. M. L. Nai, L. Y. Xu, C. M. Tan, and J. Wei, "Temperature Dependence of Creep and Hardness of Sn-Ag-Cu Lead-Free Solder," *Journal of Electronic Materials*, vol. 39, no. 2, pp. 223-229, 2010.
- [140] M. Hasnine, J. C. Suhling, B. C. Prorok, M. J. Bozack, and P. Lall, "Exploration of Aging Induced Evolution of Solder Joints Using Nanoindentation and Microdiffraction," *Proceedings of the 64th IEEE Electronic Components and Technology Conference*, pp. 379-394, 2014.
- [141] M. Hasnine, J. C. Suhling, B. C. Prorok, M. J. Bozack, and P. Lall, "Nanomechanical Characterization of SAC Solder Joints - Reduction of Aging Effects Using Microalloy Additions," *Proceedings of the 65th IEEE Electronic Components and Technology Conference*, pp. 1574-1585, 2015.
- [142] M. Hasnine, J. C. Suhling, B. C. Prorok, M. J. Bozack, and P. Lall, "Anisotropic Mechanical Properties of SAC Solder Joints in Microelectronic Packaging and Prediction of Uniaxial Creep Using Nanoindentation Creep," *Experimental Mechanics*, vol. 57, no. 4, pp. 603-614, 2017.
- [143] S. Lotfian, J. M. Molina-Aldareguia, K. E. Yazzie, J. Llorca, and N. Chawla, "Mechanical Characterization of Lead-Free Sn-Ag-Cu Solder Joints by High-Temperature Nanoindentation," *Journal of Electronic Materials*, vol. 42, no. 6, pp. 1085-1091, 2013.
- [144] V. M. F. Marques, C. Johnston, and P. S. Grant, "Nanomechanical Characterization of Sn-Ag-Cu/Cu Joints—Part 1: Young's Modulus, Hardness and Deformation Mechanisms as a Function of Temperature," *Acta Materialia*, vol. 61, no. 7, pp. 2460-2470, 2013.
- [145] V. M. F. Marques, B. Wunderle, C. Johnston, and P. S. Grant, "Nanomechanical Characterization of Sn-Ag-Cu/Cu Joints—Part 2: Nanoindentation Creep and Its Relationship with Uniaxial Creep as a Function of Temperature," *Acta Materialia*, vol. 61, no. 7, pp. 2471-2480, 2013.
- [146] H. Rhee, J. P. Lucas, and K. N. Subramanian, "Micromechanical Characterization of Thermomechanically Fatigued Lead-Free Solder Joints," *Journal of Materials Science: Materials in Electronics*, vol. 13, no. 8, pp. 477-484, 2002.
- [147] M. Sadiq, J.-S. Lecomte, and M. Cherkaoui, "Individual Phase Mechanical Properties at Different Temperatures of Sn-Ag-Cu Lead-Free Solders Incorporating Special Pileup

- Effects Using Nanoindentation," *Journal of Electronic Packaging*, vol. 137, no. 3, pp. 031005-031005-5, 2015.
- [148] Y. Sun, J. Liang, Z.-H. Xu, G. Wang, and X. Li, "Nanoindentation for Measuring Individual Phase Mechanical Properties of Lead Free Solder Alloy," *Journal of Materials Science: Materials in Electronics*, vol. 19, no. 6, pp. 514-521, 2008.
 - [149] J. L. Hay and G. M. Pharr, "Instrumented Indentation Testing," *Mechanical Testing and Evaluation*, vol. 8, 2000.
 - [150] K. O. Kese, Z. C. Li, and B. Bergman, "Method to Account for True Contact Area in Soda-Lime Glass During Nanoindentation with the Berkovich Tip," *Materials Science and Engineering: A*, vol. 404, no. 1, pp. 1-8, 2005.
 - [151] M. Cabibbo, D. Ciccarelli, and S. Spigarelli, "Nanoindentation Hardness Measurement in Piling up SiO₂ Coating," *Physics Procedia*, vol. 40, pp. 100-112, 2013.
 - [152] G. J. S. Chou, "Microstructure Evolution of Snpb and SnAg/Cu BGA Solder Joints During Thermal Aging," *Proceedings of the 8th International Advanced Packaging Materials Symposium*, pp. 39-46, 2002.
 - [153] R. L. J. M. Ubachs, P. J. G. Schreurs, and M. G. D. Geers, "Microstructure Evolution of Tin-Lead Solder," *IEEE Transactions on Components and Packaging Technologies*, vol. 27, no. 4, pp. 635-642, 2004.
 - [154] U. Sahaym, B. Talebanpour, S. Seekins, I. Dutta, P. Kumar, and P. Borgesen, "Recrystallization and Ag₃Sn Particle Redistribution During Thermomechanical Treatment of Bulk Sn–Ag–Cu Solder Alloys," *IEEE Transactions on Components, Packaging and Manufacturing Technology*, vol. 3, no. 11, pp. 1868-1875, 2013.
 - [155] M. Maleki, J. Cugnoni, and J. Botsis, "Isothermal Ageing of SnAgCu Solder Alloys: Three-Dimensional Morphometry Analysis of Microstructural Evolution and Its Effects on Mechanical Response," *Journal of Electronic Materials*, vol. 43, no. 4, pp. 1026-1042, 2014.
 - [156] A. U. Telang, T. R. Bieler, J. P. Lucas, K. N. Subramanian, L. P. Lehman, Y. Xing, and E. J. Cotts, "Grain-Boundary Character and Grain Growth in Bulk Tin and Bulk Lead-Free Solder Alloys," *Journal of Electronic Materials*, vol. 33, no. 12, pp. 1412-1423, 2004.

- [157] P. Kumar, B. Talenbanpour, U. Sahaym, C. H. Wen, and I. Dutta, "Microstructural Evolution and Some Unusual Effects During Thermo-Mechanical Cycling of Sn-Ag-Cu Alloys," *Proceedings of IEEE ITherm*, pp. 880-887, 2012.
- [158] P. Chauhan, S. Mukherjee, M. Osterman, A. Dasgupta, and M. Pecht, "Effect of Isothermal Aging on Microstructure and Creep Properties of SAC305 Solder: A Micromechanics Approach," *Proceedings of ASME InterPACK*, pp. V001T07A009, 2013.
- [159] W. Yang, R. W. Messler, and L. E. Felton, "Microstructure Evolution of Eutectic Sn-Ag Solder Joints," *Journal of Electronic Materials*, vol. 23, no. 8, pp. 765-772, 1994.
- [160] C. Tz-Cheng, Z. Kejun, R. Stierman, D. Edwards, and K. Ano, "Effect of Thermal Aging on Board Level Drop Reliability for Pb-Free BGA Packages," *Proceedings of the 54th IEEE Electronic Components and Technology Conference*, vol. 2, pp. 1256-1262, 2004.
- [161] S. Ahat, M. Sheng, and L. Luo, "Microstructure and Shear Strength Evolution of SnAg/Cu Surface Mount Solder Joint During Aging," *Journal of Electronic Materials*, vol. 30, no. 10, pp. 1317-1322, 2001.
- [162] W. K. Choi and H. M. Lee, "Effect of Soldering and Aging Time on Interfacial Microstructure and Growth of Intermetallic Compounds between Sn-3.5Ag Solder Alloy and Cu Substrate," *Journal of Electronic Materials*, vol. 29, no. 10, pp. 1207-1213, 2000.
- [163] A. M. Z. Akhtar, K. H. Wirda, I. S. R. Aisha, and I. Mahadzir, "Microstructure Evolution at the Solder Joint During Isothermal Aging," *Proceedings of the 36th International Electronics Manufacturing Technology Conference*, pp. 1-5, 2014.
- [164] M. Berthou, P. Retailleau, H. Frémont, A. Guédon-Gracia, and C. Jéphos-Davennel, "Microstructure Evolution Observation for SAC Solder Joint: Comparison between Thermal Cycling and Thermal Storage," *Microelectronics Reliability*, vol. 49, no. 9, pp. 1267-1272, 2009.
- [165] W. C. Oliver and G. M. Pharr, "An Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments," *Journal of Materials Research*, vol. 7, no. 6, pp. 1564-1583, 1992.
- [166] D. Tabor, *The Hardness of Metals*, Oxford University Press, 2000.
- [167] M. Motalab, Z. Cai, J. C. Suhling, J. Zhang, J. L. Evans, M. J. Bozack, and P. Lall, "Improved Predictions of Lead Free Solder Joint Reliability That Include Aging Effects,"

- Proceedings of the 62nd IEEE Electronic Components and Technology Conference*, pp. 513-531, 2012.
- [168] M. Motalab, M. Mustafa, J. C. Suhling, J. Zhang, J. Evans, M. J. Bozack, and P. Lall, "Correlation of Reliability Models Including Aging Effects with Thermal Cycling Reliability Data," *Proceedings of the 63rd IEEE Electronic Components and Technology Conference*, pp. 986-1004, 2013.
 - [169] D. Herkommer, J. Punch, and M. Reid, "A Reliability Model for SAC Solder Covering Isothermal Mechanical Cycling and Thermal Cycling Conditions," *Microelectronics Reliability*, vol. 50, no. 1, pp. 116-126, 2010.
 - [170] G. Z. Wang, Z. N. Cheng, K. Becker, and J. Wilde, "Applying Anand Model to Represent the Viscoplastic Deformation Behavior of Solder Alloys," *Journal of Electronic Packaging*, vol. 123, no. 3, pp. 247-253, 2001.
 - [171] D. Bhate, D. Chan, G. Subbarayan, T. C. Chiu, V. Gupta, and D. R. Edwards, "Constitutive Behavior of Sn3. 8Ag0. 7Cu and Sn1. 0Ag0. 5Cu Alloys at Creep and Low Strain Rate Regimes," *IEEE Transactions on Components and Packaging Technologies*, vol. 31, no. 3, pp. 622-633, 2008.
 - [172] M. Motalab, Z. Cai, J. C. Suhling, and P. Lall, "Determination of Anand Constants for SAC Solders Using Stress-Strain or Creep Data," *Proceedings of ITherm*, pp. 910-922, 2012.
 - [173] N. J. Chhanda, J. C. Suhling, and P. Lall, "Experimental Characterization and Viscoplastic Modeling of the Temperature Dependent Material Behavior of Underfill Encapsulants," *Proceedings of ASME InterPACK* no. 44625, pp. 749-761, 2011.
 - [174] M. Mayo and W. Nix, "A Micro-Indentation Study of Superplasticity in Pb, Sn, and Sn-38 Wt% Pb," *Acta Metallurgica*, vol. 36, no. 8, pp. 2183-2192, 1988.
 - [175] M. Mayo, R. Siegel, A. Narayanasamy, and W. Nix, "Mechanical Properties of Nanophase TiO₂ as Determined by Nanoindentation," *Journal of Materials Research*, vol. 5, no. 5, pp. 1073-1082, 1990.
 - [176] P. Borgesen, "Microstructurally Adaptive Constitutive Relations and Reliability Assessment Protocols for Lead Free Solder," in "SERDP Project WP-1752 Final Report," 2015.

- [177] I. Dutta, "A Constitutive Model for Creep of Lead-Free Solders Undergoing Strain-Enhanced Microstructural Coarsening: A First Report," *Journal of Electronic Materials*, vol. 32, no. 4, pp. 201-207, 2003.
- [178] I. Dutta, P. Kumar, and G. Subbarayan, "Microstructural Coarsening in Sn-Ag-Based Solders and Its Effects on Mechanical Properties," *JOM*, vol. 61, no. 6, pp. 29-38, 2009.
- [179] P. Kumar, Z. Huang, S. C. Chavali, D. K. Chan, I. Dutta, G. Subbarayan, and V. Gupta, "Microstructurally Adaptive Model for Primary and Secondary Creep of Sn-Ag-Based Solders," *IEEE Transactions on Components, Packaging and Manufacturing Technology*, vol. 2, no. 2, pp. 256-265, 2012.
- [180] G. E. Dieter and D. J. Bacon, *Mechanical Metallurgy*, 3rd ed., Mc Graw-Hill New York, 1986.
- [181] R. Boistelle and J. P. Astier, "Crystallization Mechanisms in Solution," *Journal of Crystal Growth*, vol. 90, no. 1, pp. 14-30, 1988.
- [182] R. E. Smallman, *Modern Physical Metallurgy*, 4th ed., Elsevier, 2016.
- [183] D. A. Porter, K. E. Easterling, and M. Sherif, "Phase Transformations in Metals and Alloys, (Revised Reprint)," CRC press, 2009.
- [184] Y. D. Han, H. Y. Jing, S. M. L. Nai, C. M. Tan, J. Wei, L. Y. Xu, and S. R. Zhang, "A Modified Constitutive Model for Creep of Sn-3.5Ag-0.7Cu Solder Joints," *Journal of Physics D: Applied Physics*, vol. 42, no. 12, p. 125411, 2009.

Appendix

A.1 Suggested Polishing Method for Struers Automatic Polisher

(<https://www.struers.com/en/Knowledge/Grinding-and-polishing#grinding-polishing-how-to>)

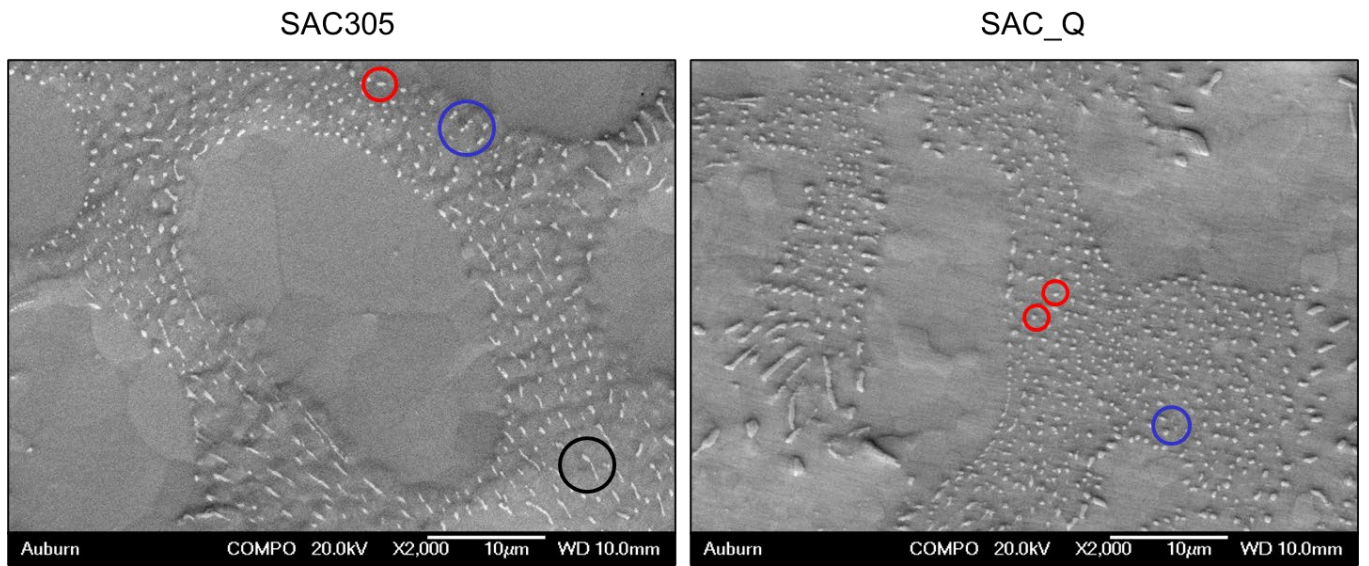
Grinding

 Step	 PG	 FG
 Surface	SiC-Foil	MD-Largo
 Abrasive	SiC	DiaPro AllegroLargo 9
 Grit/ Grain size	# 320	9 μm
 Lubricant	Water	
 Rotational speed [rpm]	300	150
 Force[N]/ specimen	25	40
 Time [min]	Until plane	3

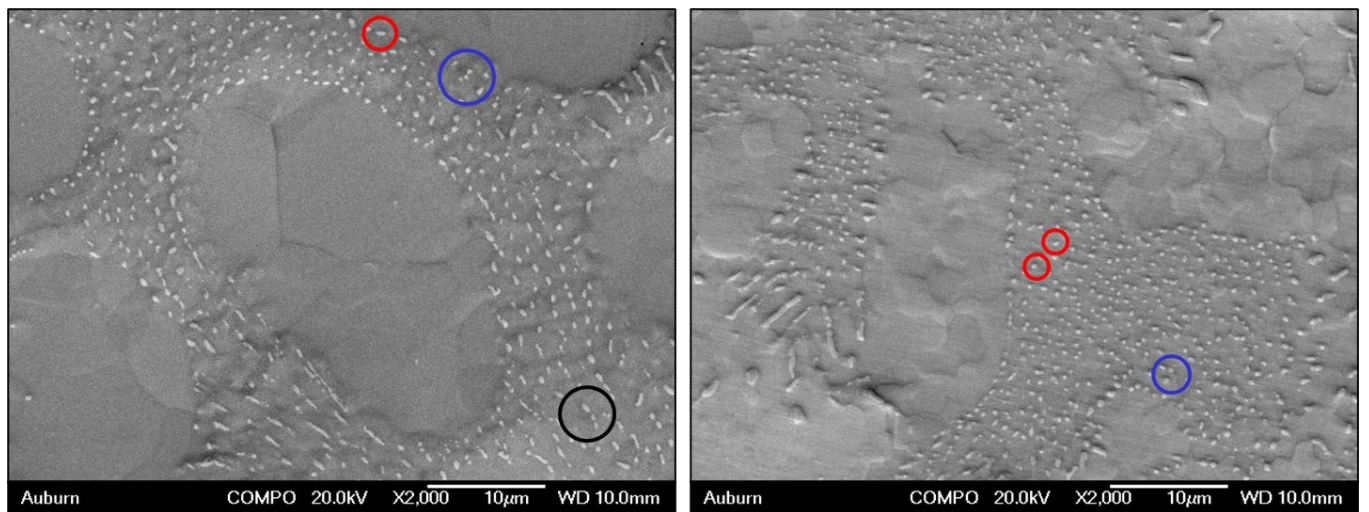
Polishing

 Step	 DP	 OP
 Surface	MD-Mol	MD-Nap or MD-Chem
 Abrasive	DiaPro Mol R3	OP-S NonDry
 Grain size	3 μm	0.25 μm
 Lubricant		
 Rotational speed [rpm]	150	150
 Force[N]/ specimen	25	10
 Time [min]	5	Unitil Ready

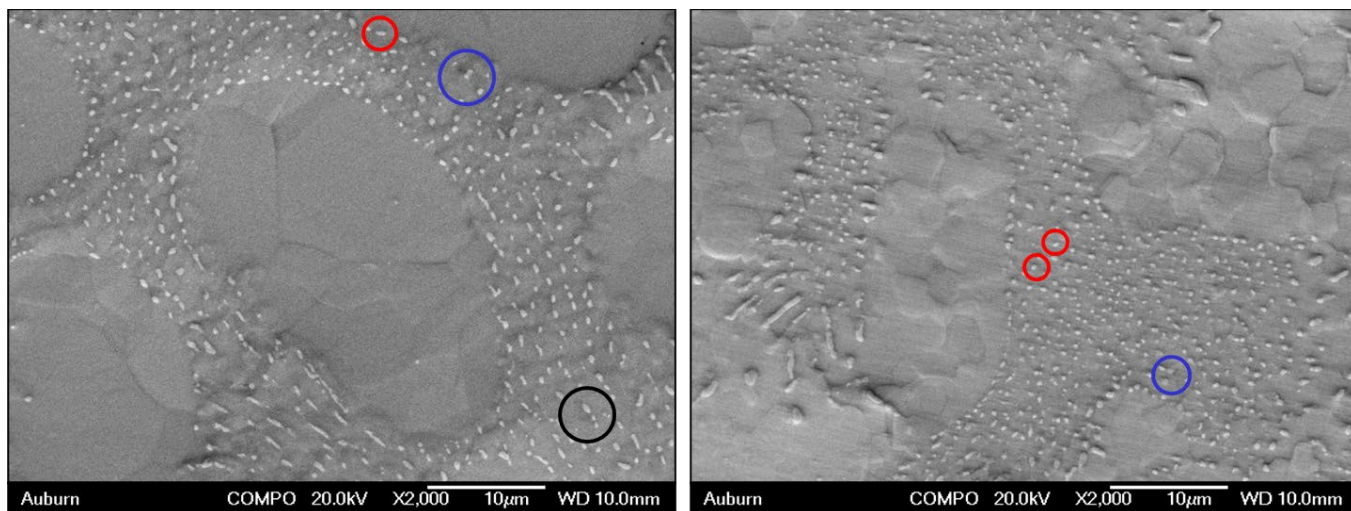
A.2 SEM Images of SAC305 and SAC_Q



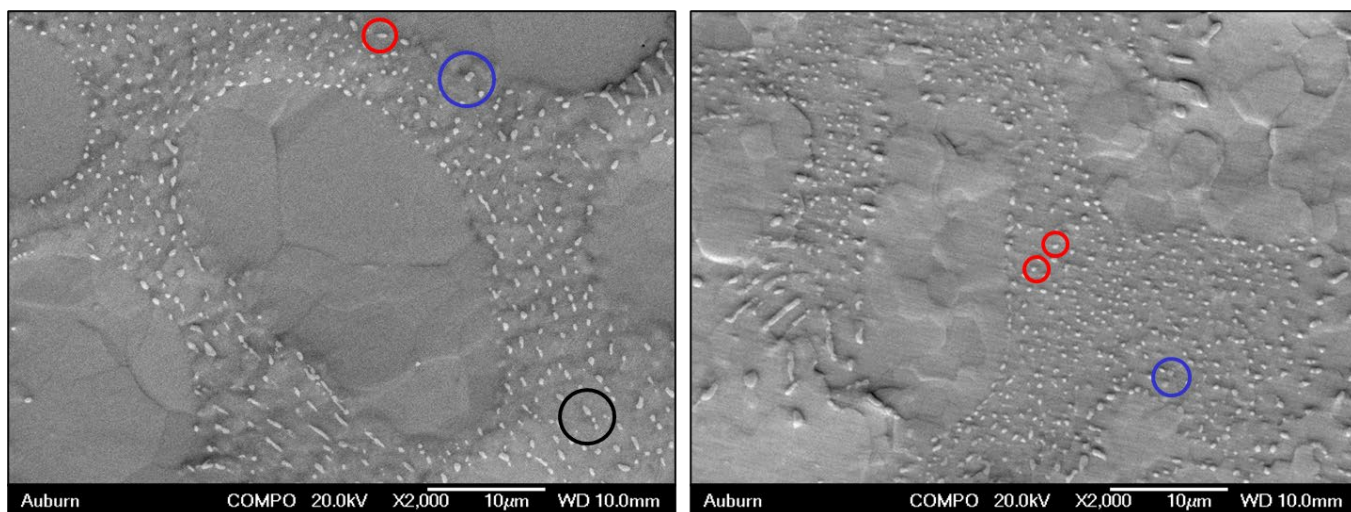
(a) No Aging



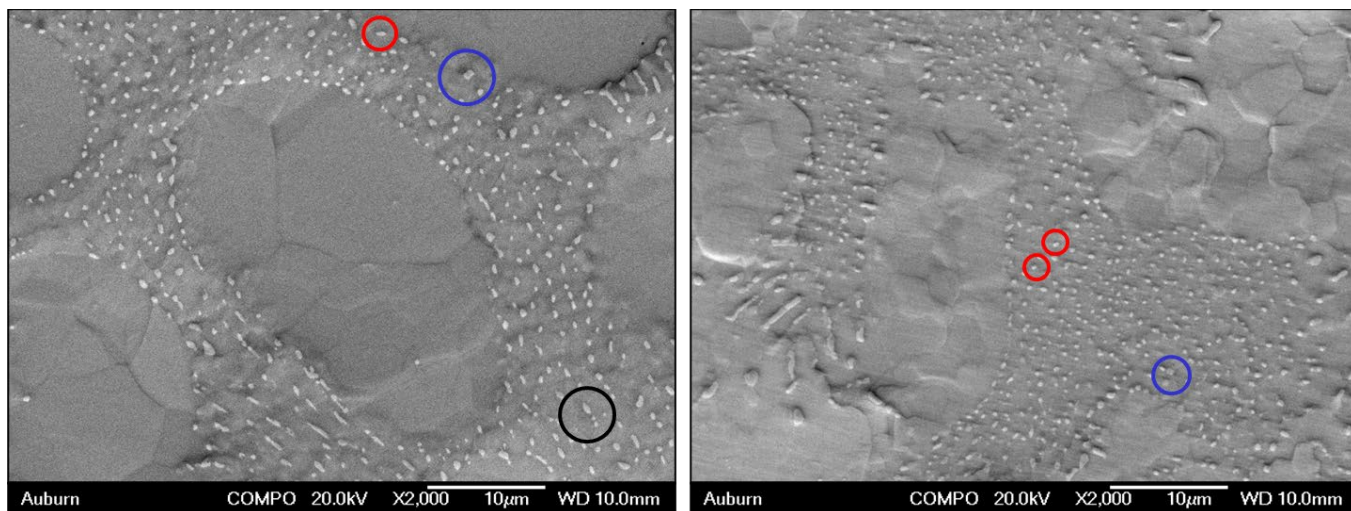
(b) 1 Hour of Aging



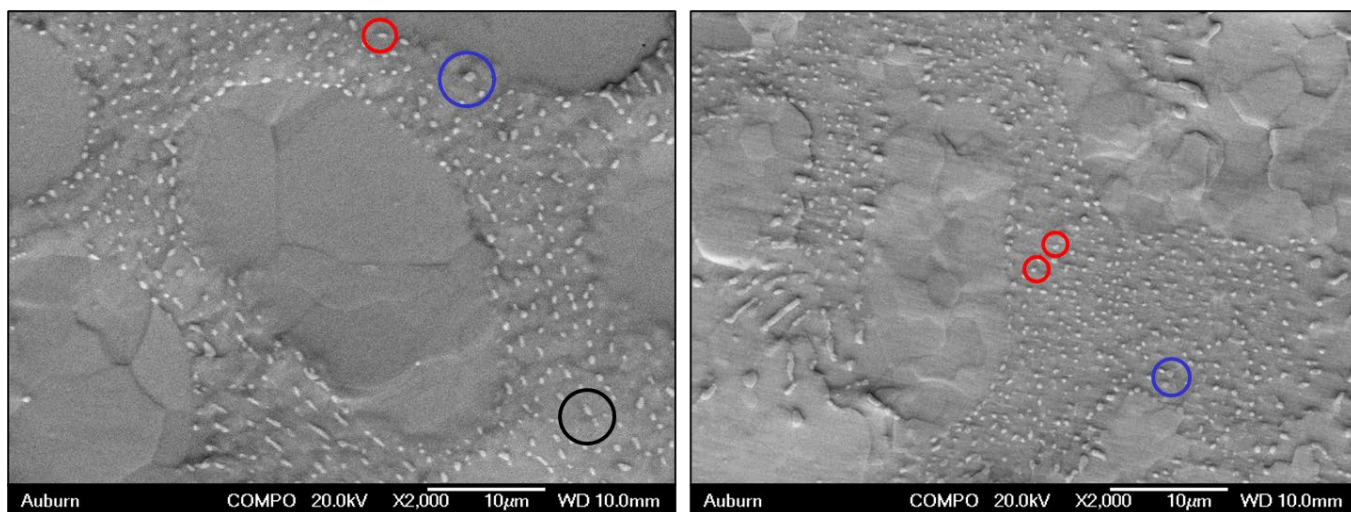
(c) 2 Hours of Aging



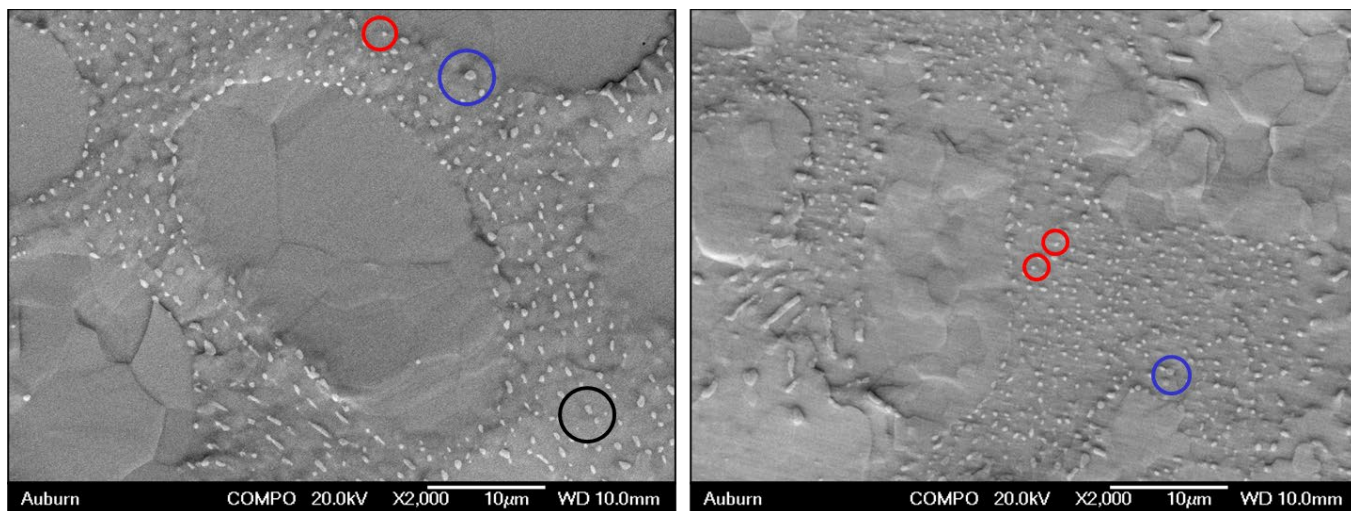
(d) 3 Hours of Aging



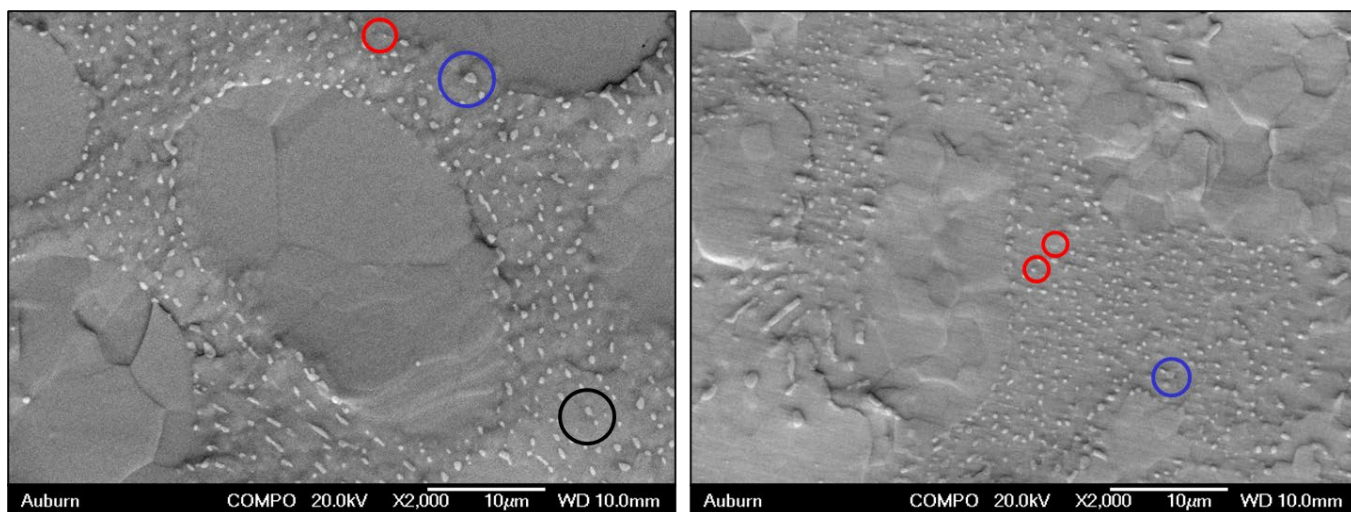
(e) 4 Hours of Aging



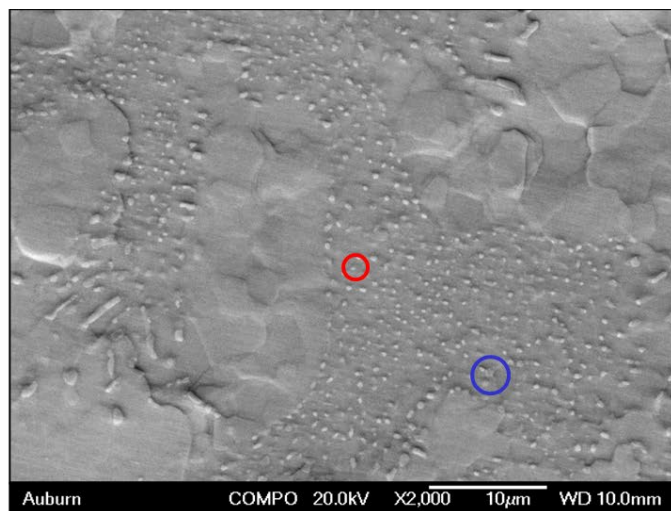
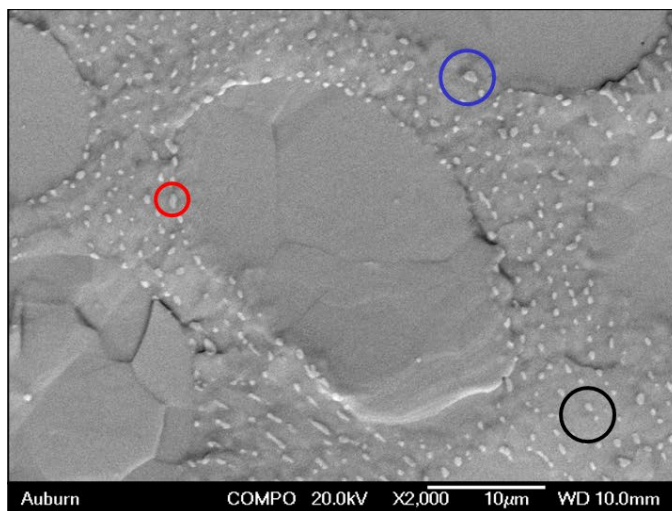
(f) 5 Hours of Aging



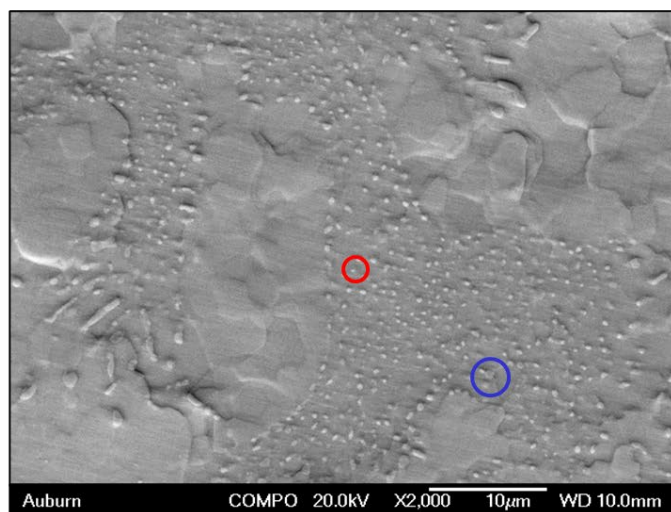
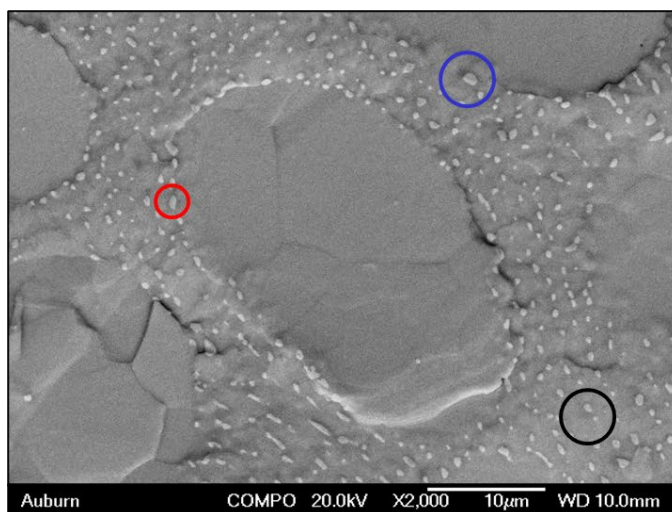
(g) 6 Hours of Aging



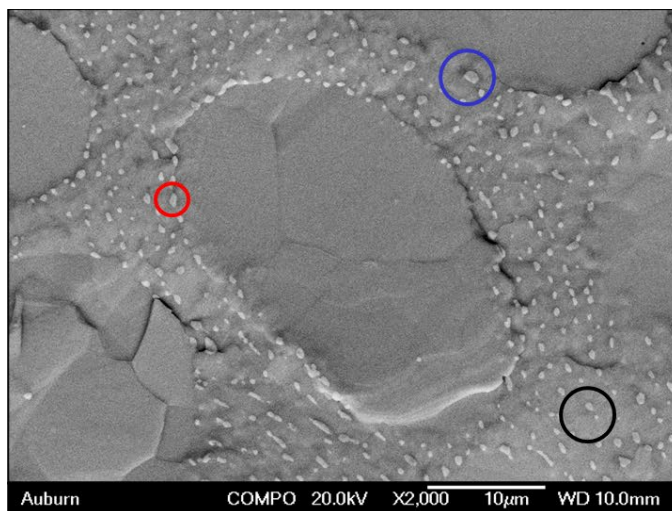
(h) 7 Hours of Aging



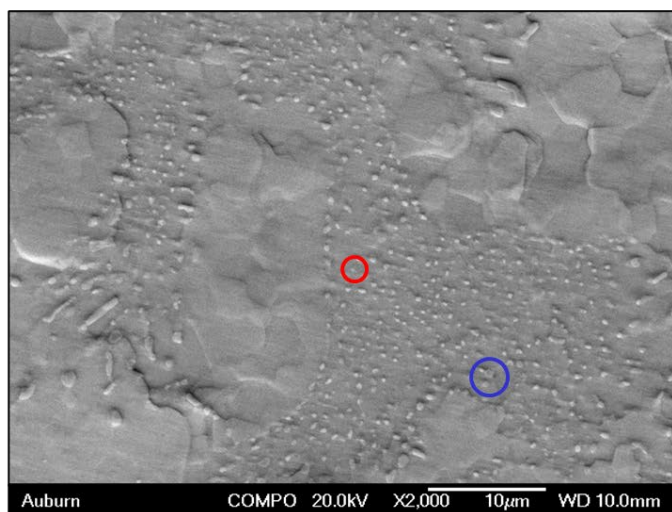
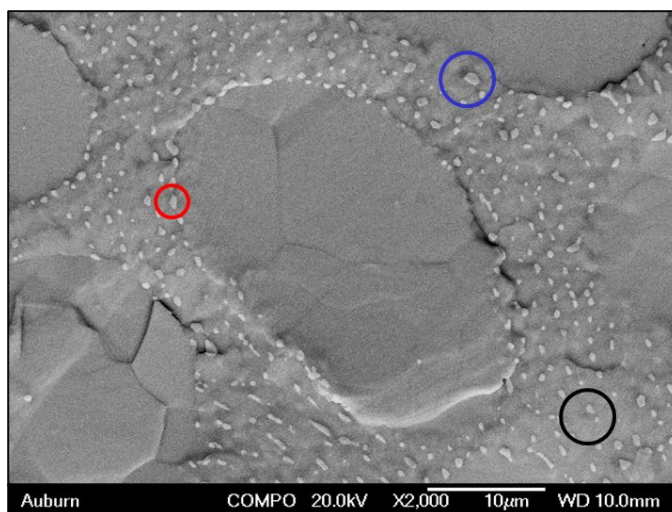
(i) 9 Hours of Aging



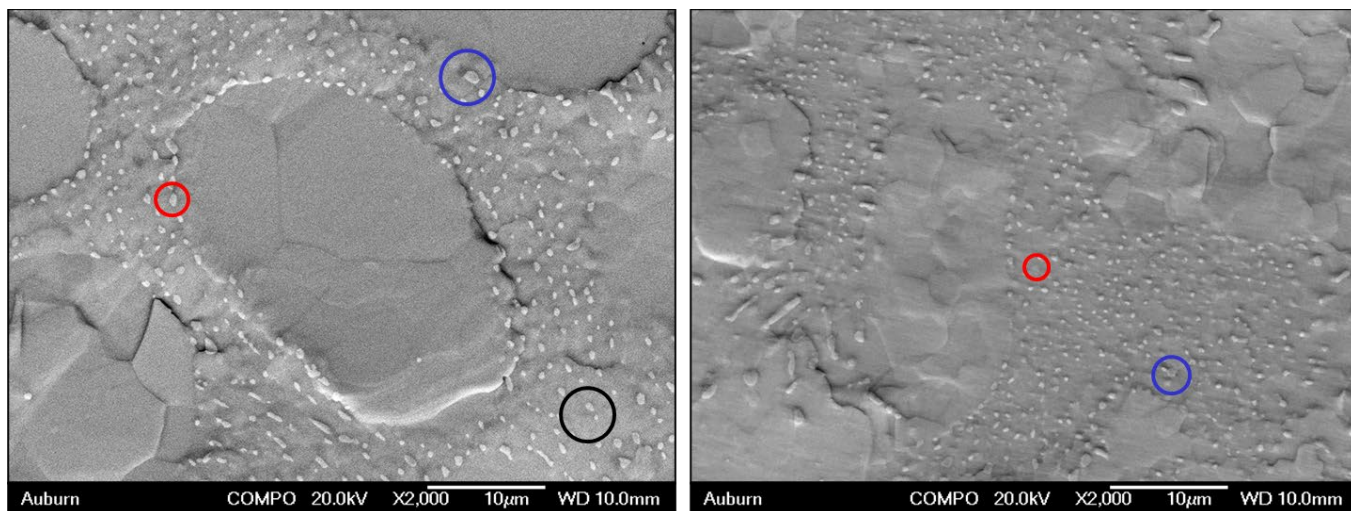
(j) 10 Hours of Aging



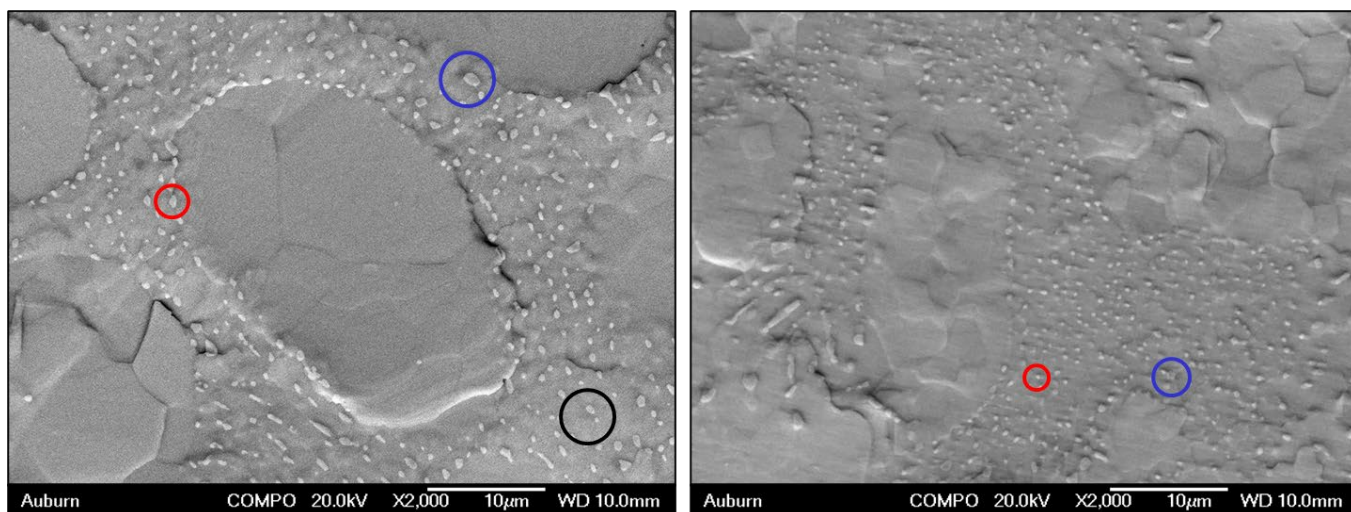
(k) 11 Hours of Aging



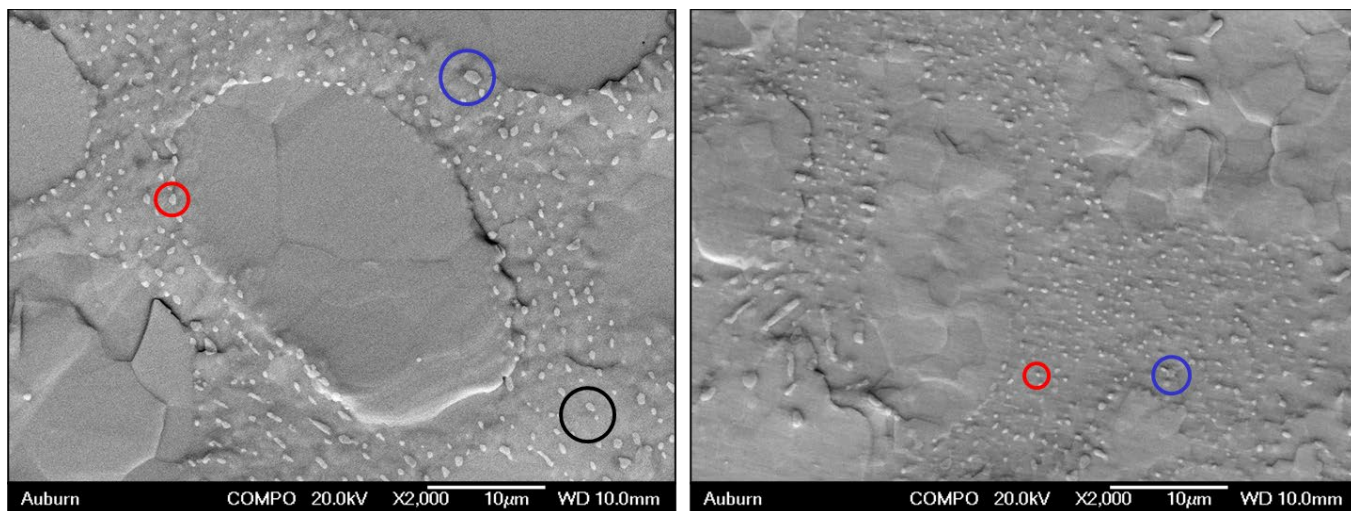
(l) 12 Hours of Aging



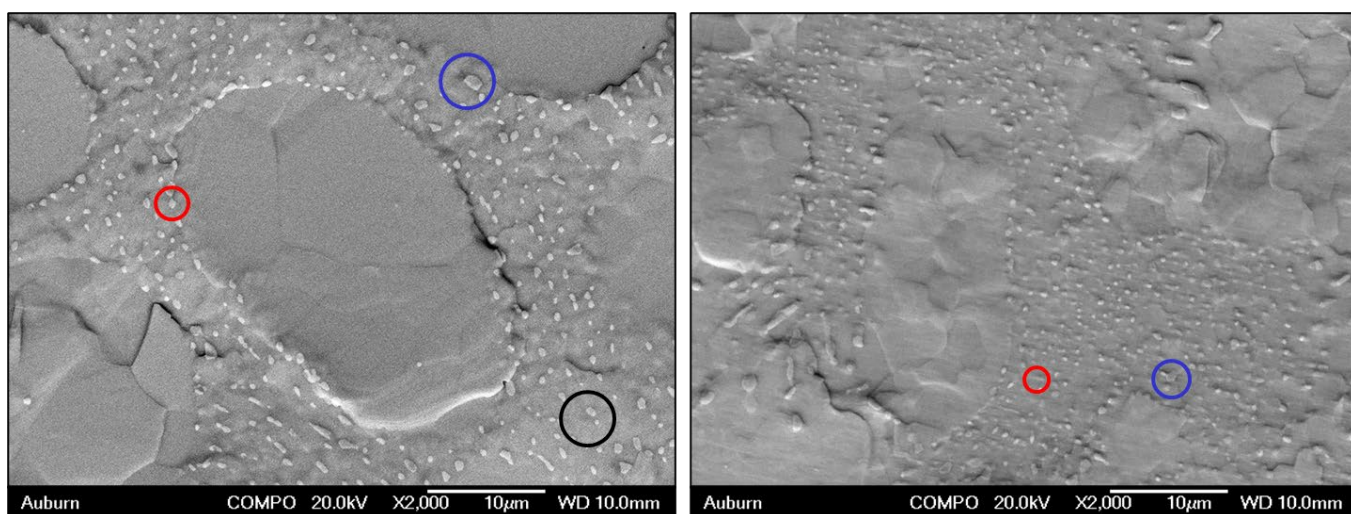
(m) 14 Hours of Aging



(n) 16 Hours of Aging



(o) 18 Hours of Aging



(p) 24 Hours of Aging

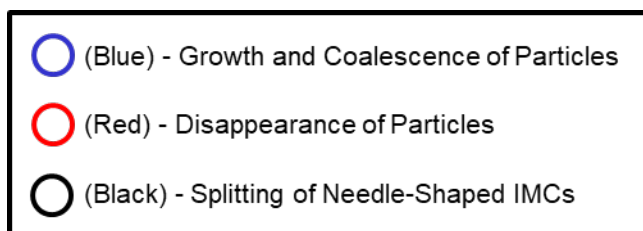
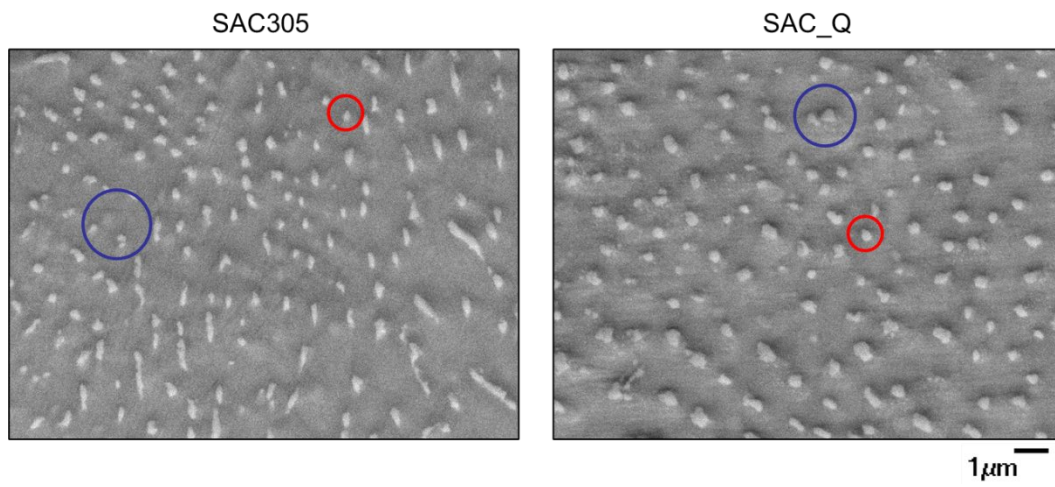
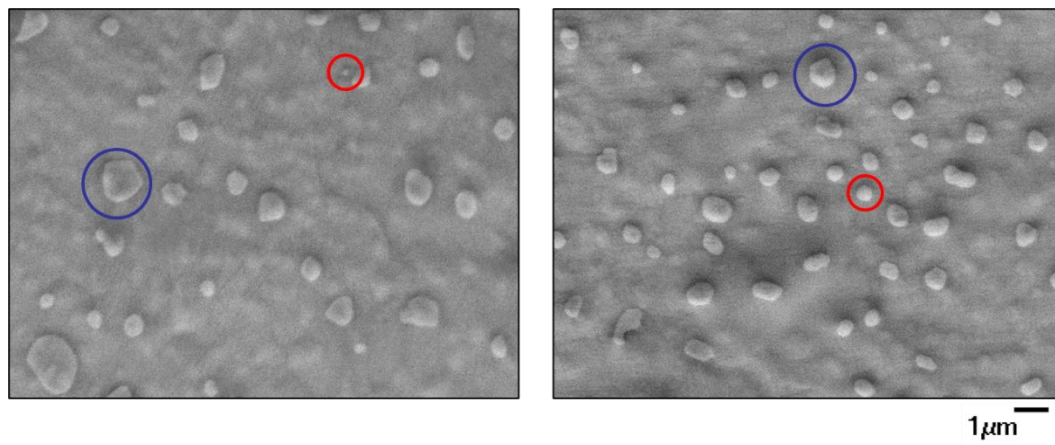


Figure A.1 Short term aging induced microstructural evolution of SAC305 and SAC_Q by SEM
microscopy (Aging at $T = 125\text{ }^{\circ}\text{C}$)

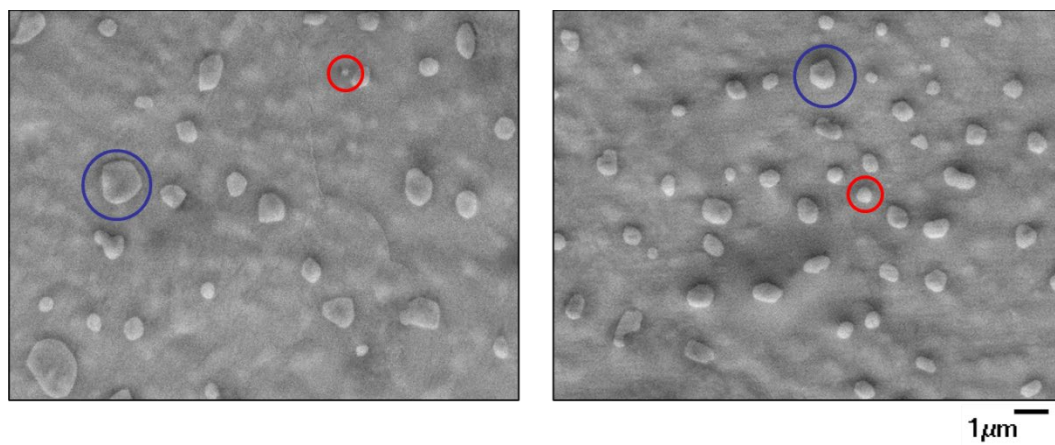
A.3 SEM Images of IMC Particles in SAC305 and SAC_Q



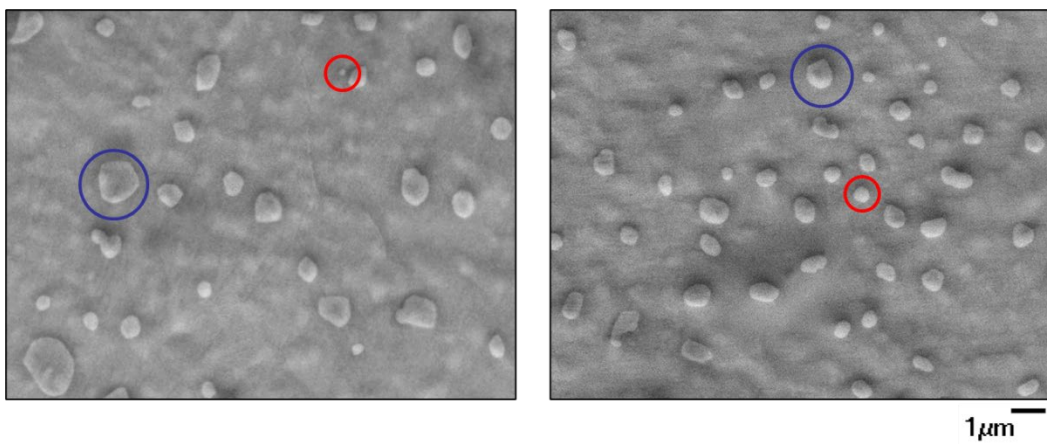
(a) No Aging



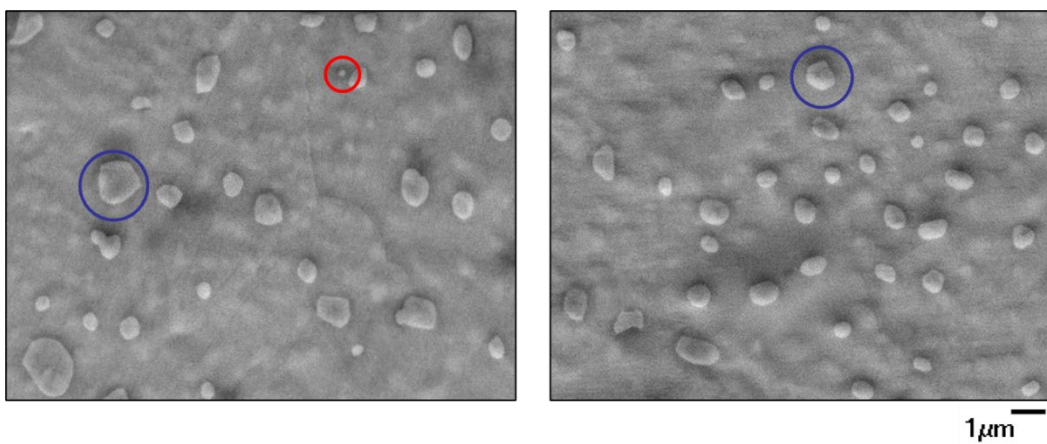
(b) 250 Hours of Aging



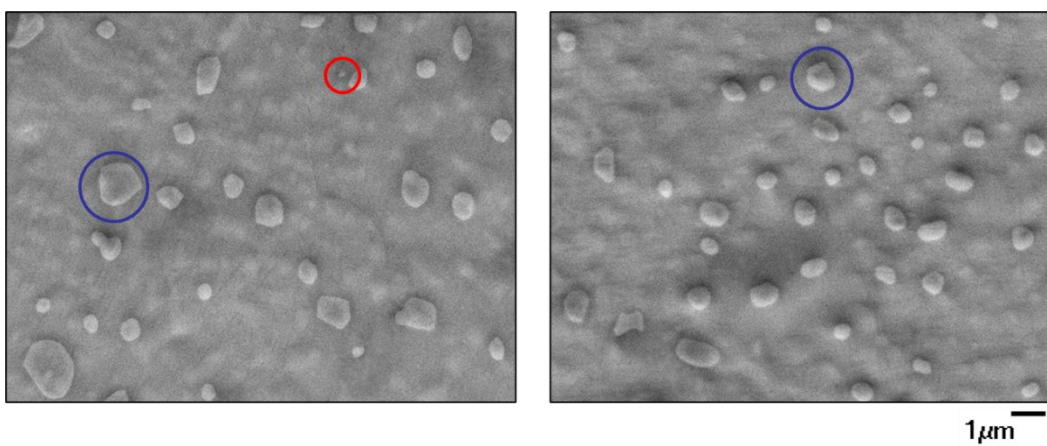
(c) 500 Hours of Aging



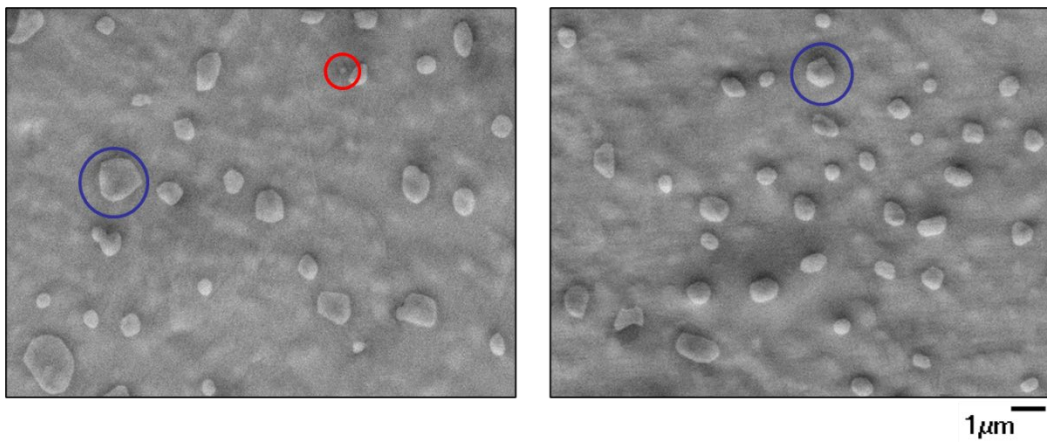
(d) 750 Hours of Aging



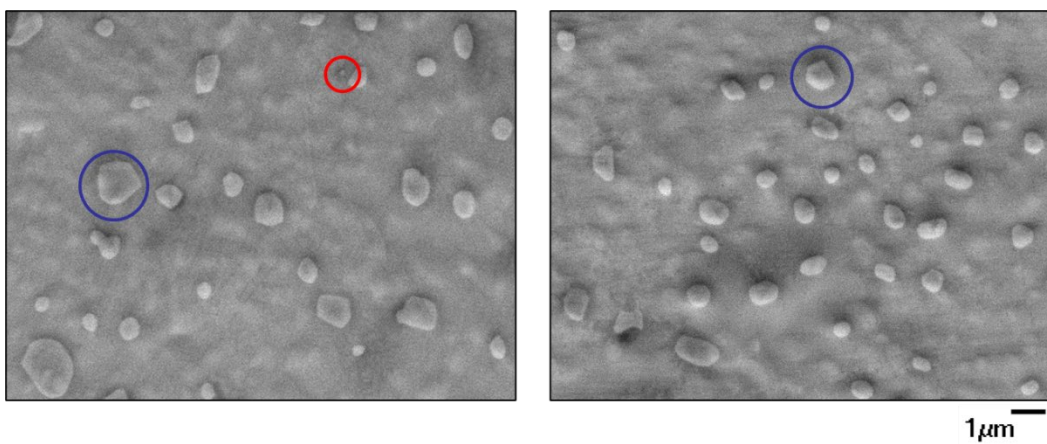
(e) 1000 Hours of Aging



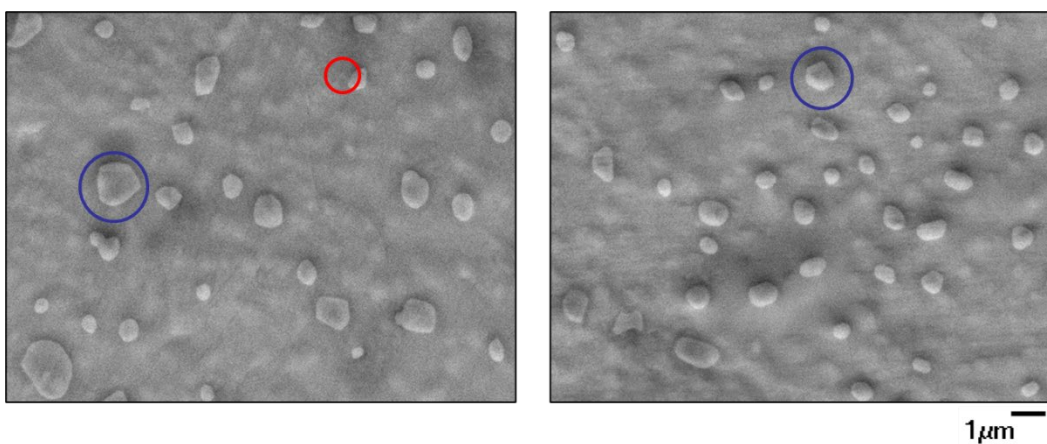
(f) 1250 Hours of Aging



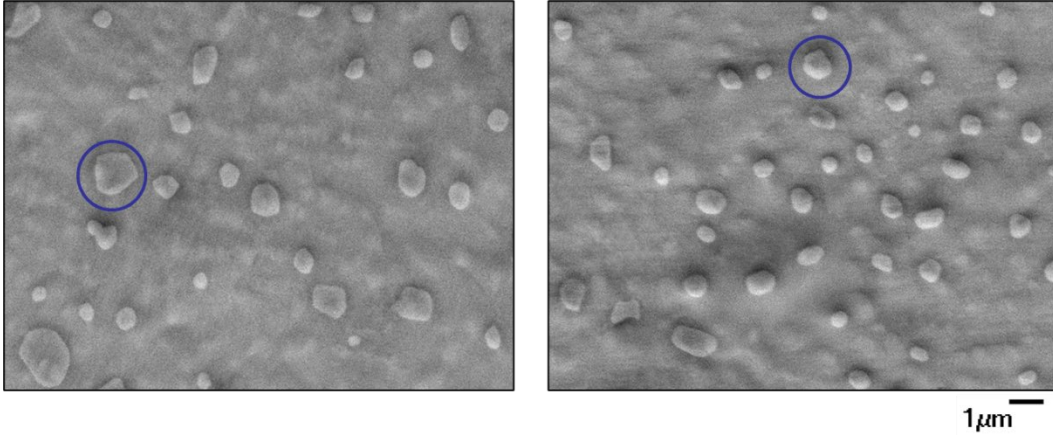
(g) 1500 Hours of Aging



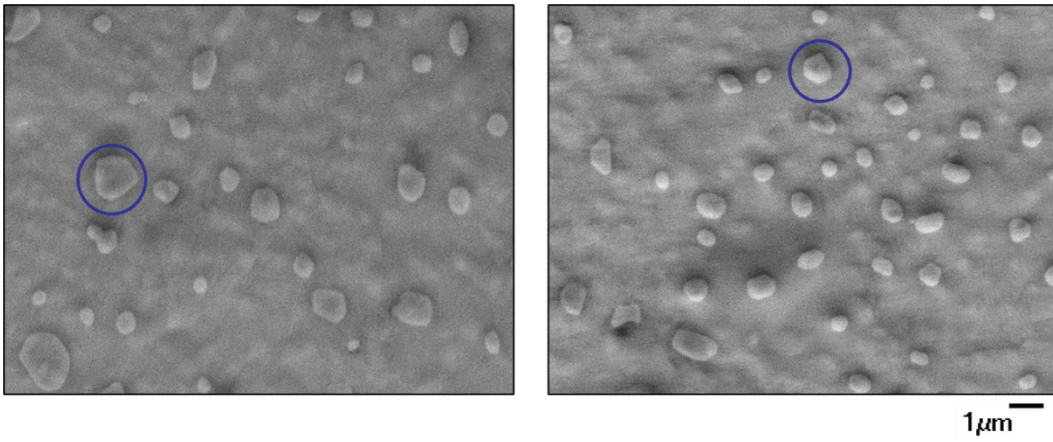
(h) 1750 Hours of Aging



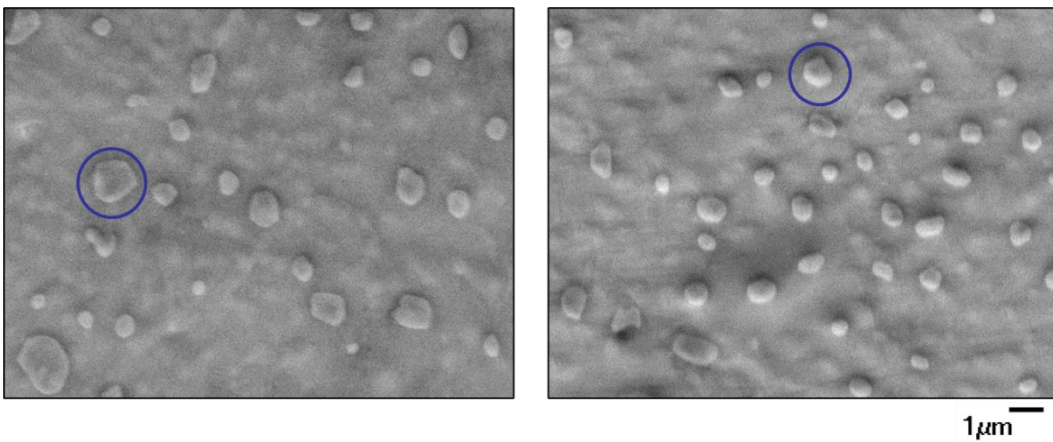
(i) 2000 Hours of Aging



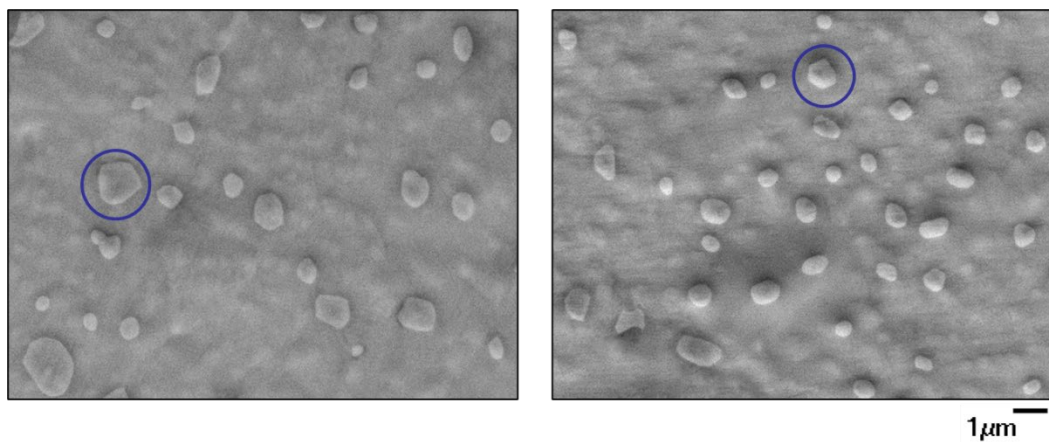
(j) 2250 Hours of Aging



(k) 2500 Hours of Aging



(l) 2750 Hours of Aging



(m) 3000 Hours of Aging

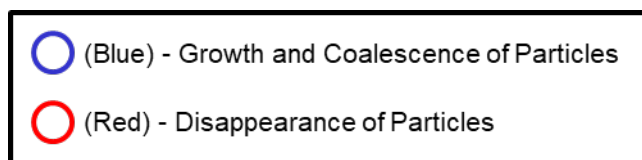
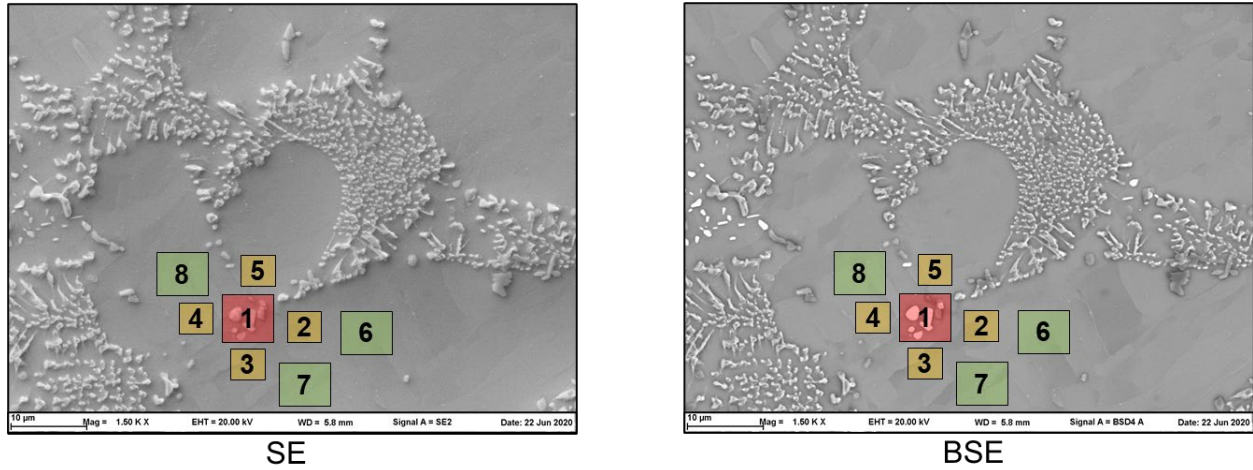
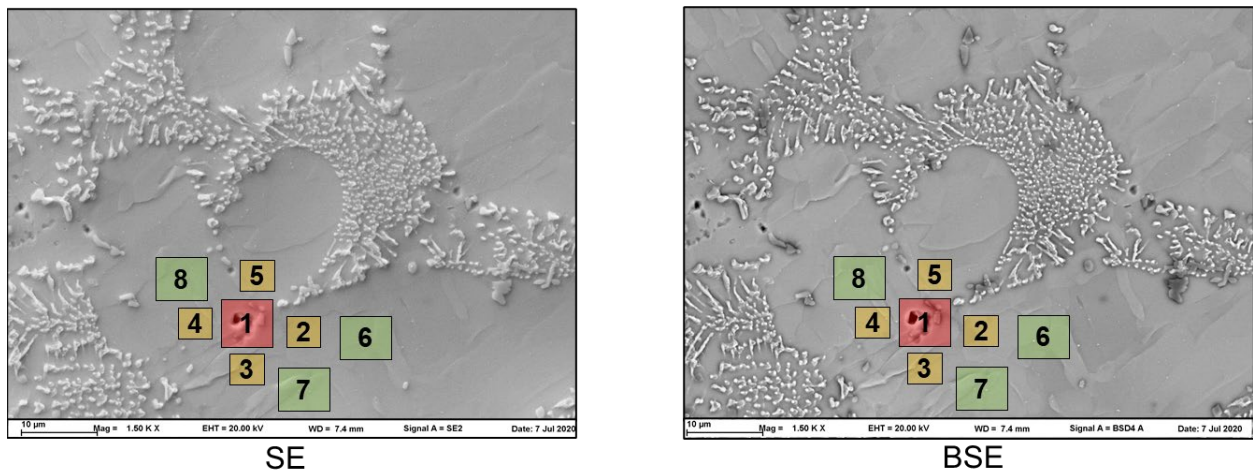


Figure A.2 Long term aging induced microstructural evolution of SAC305 and SAC_Q by SEM microscopy (Aging at $T = 125\text{ }^{\circ}\text{C}$)

A.4 Bi Diffusion in SAC_Q at High Temperature



(a) No Aging



(b) 10 Minutes of Aging

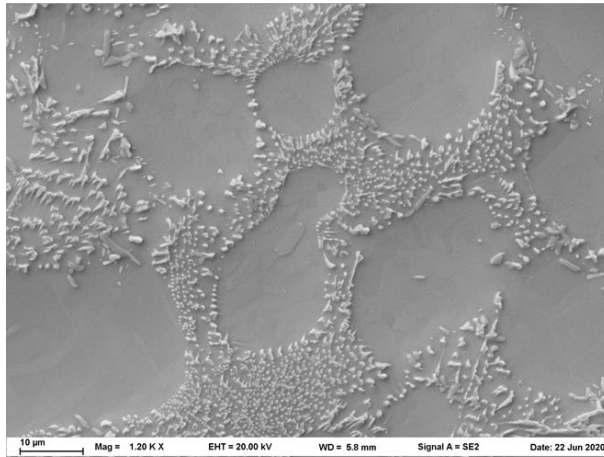
Figure A.3 EDS Small Region Results for SAC_Q Aging at 150°C

	S1	S2	S3	S4	S5	S6	S7	S8
No Aging	15.9	1.6	1.5	2.8	1.4	1.3	1.6	1.5
After Aging	3.5	2.5	3.2	3.9	2.3	1.9	3.9	2.5

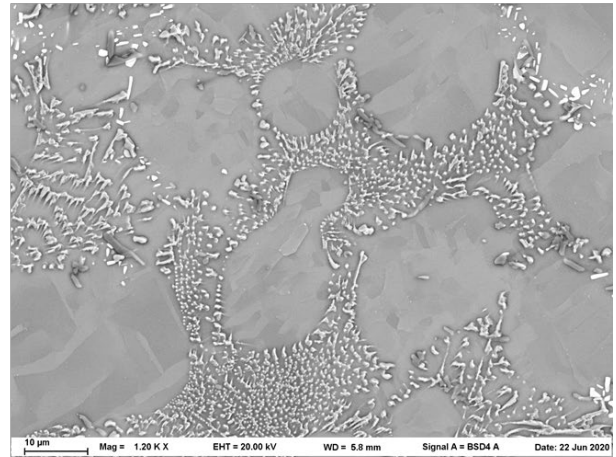
Table A.1 EDS Results for Regions in Figure A.3

A.5 EDS Mapping Results for SAC_Q Aging at 150°C

No Aging

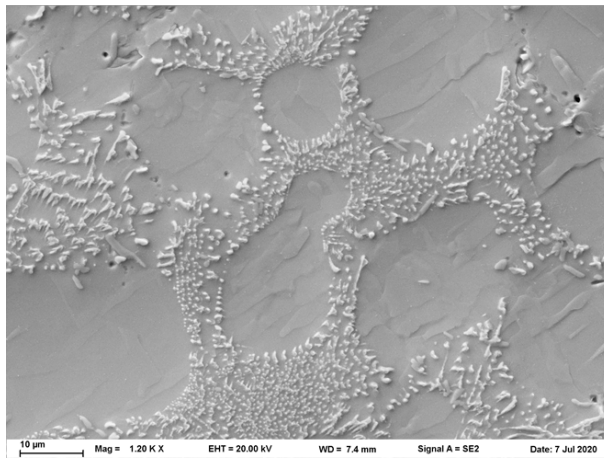


SE

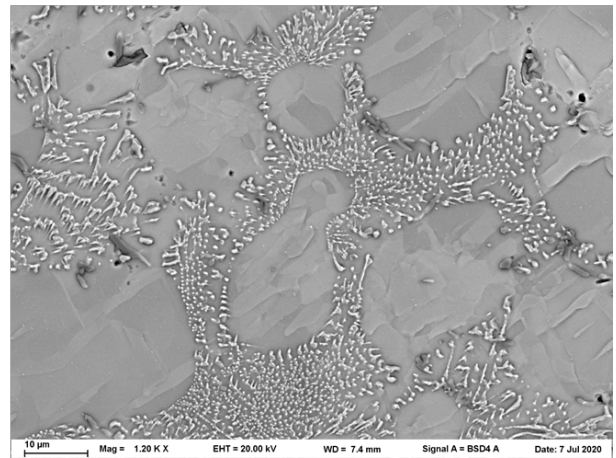


BSE

10 Minutes of Aging at 150 °C



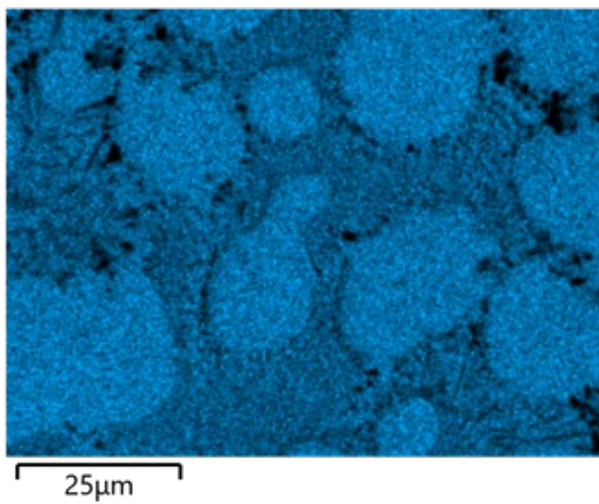
SE



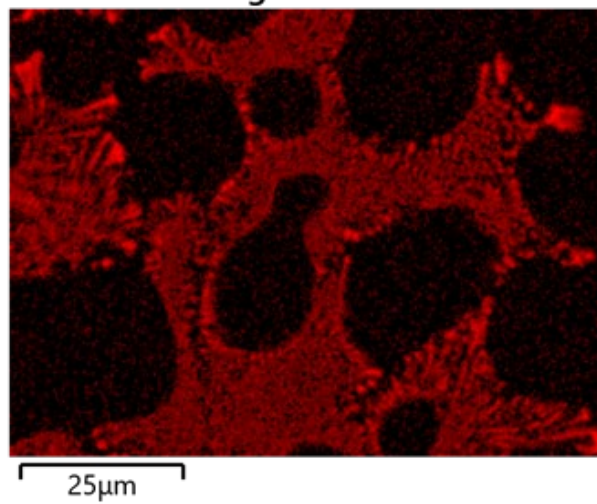
BSE

Figure A.4 SEM Images of SAC_Q Aging at 150°C

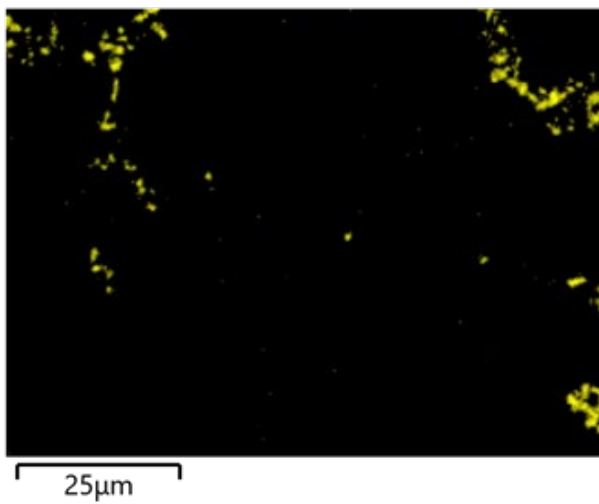
Sn L series



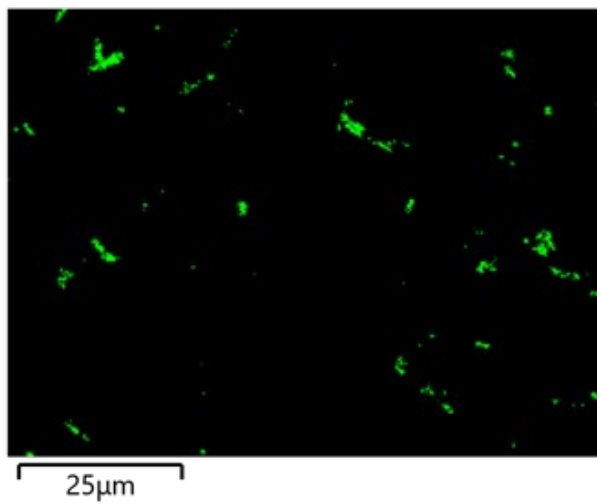
Ag L series



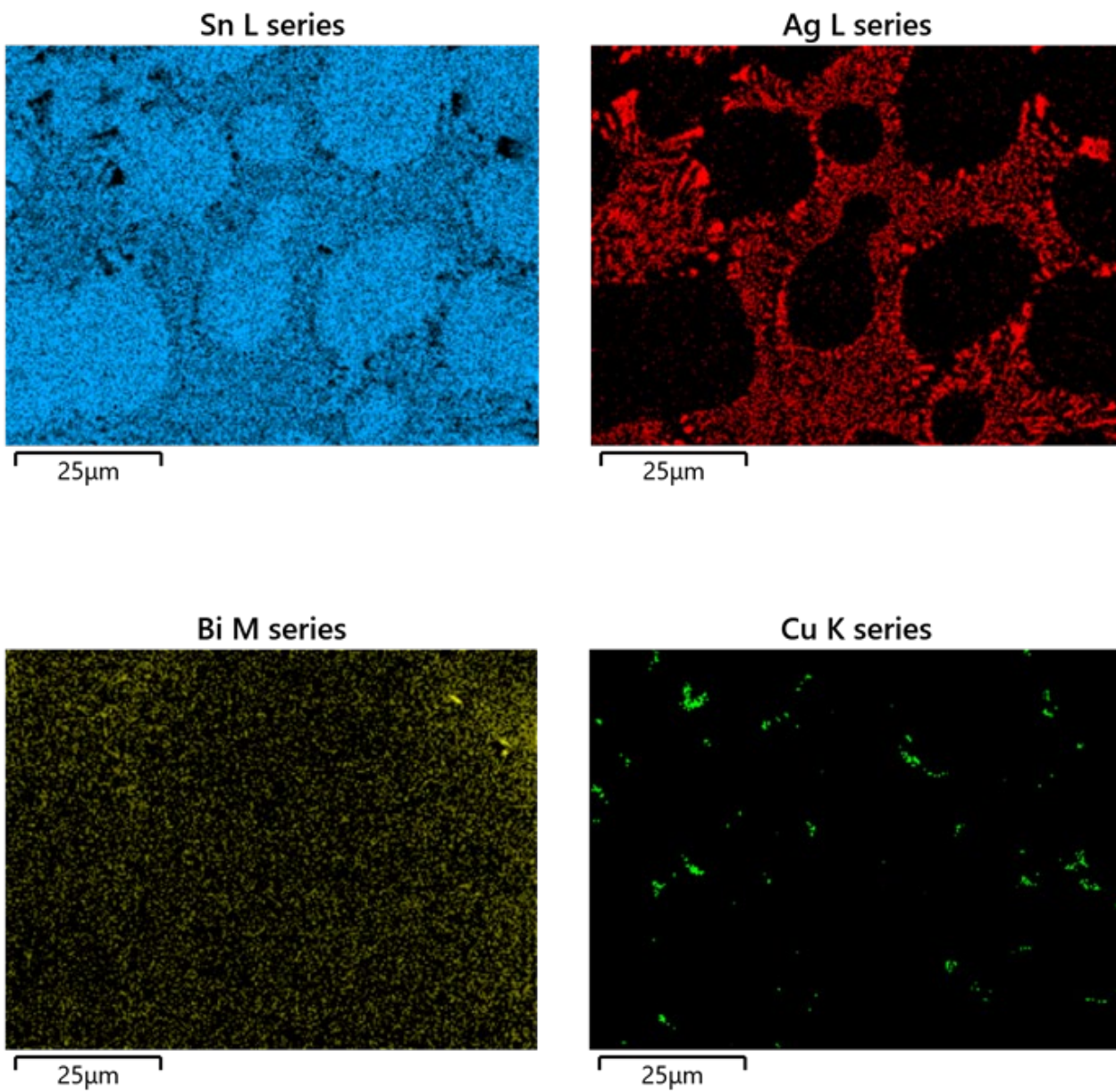
Bi M series



Cu K series



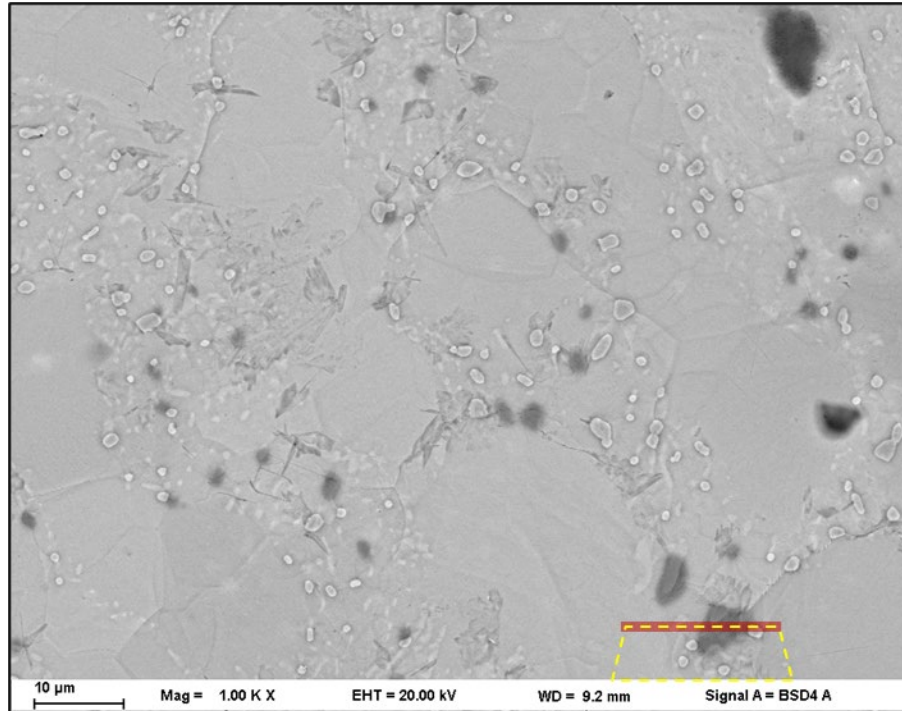
(a) No Aging



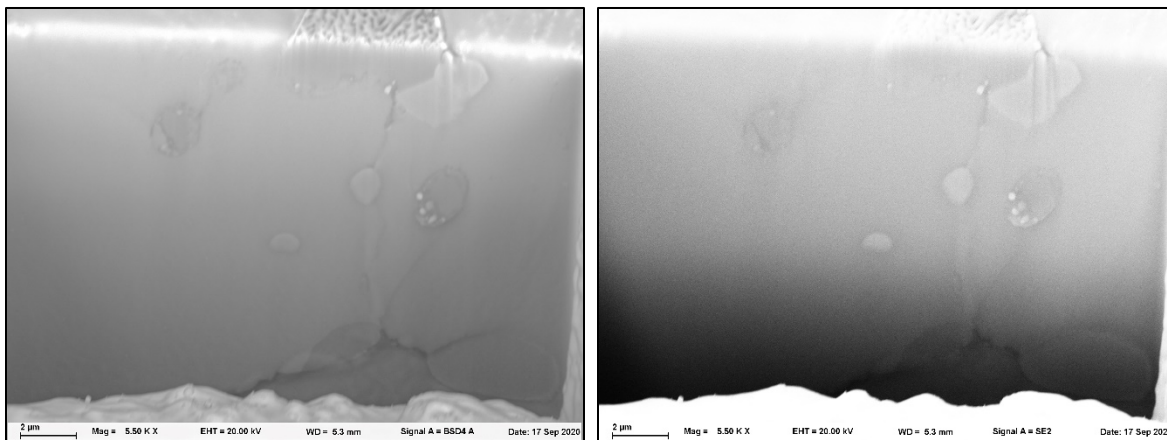
(b) 10 Minutes of Aging at 150 °C

Figure A.5 EDS Mapping Results of SAC_Q Aging at 150°C

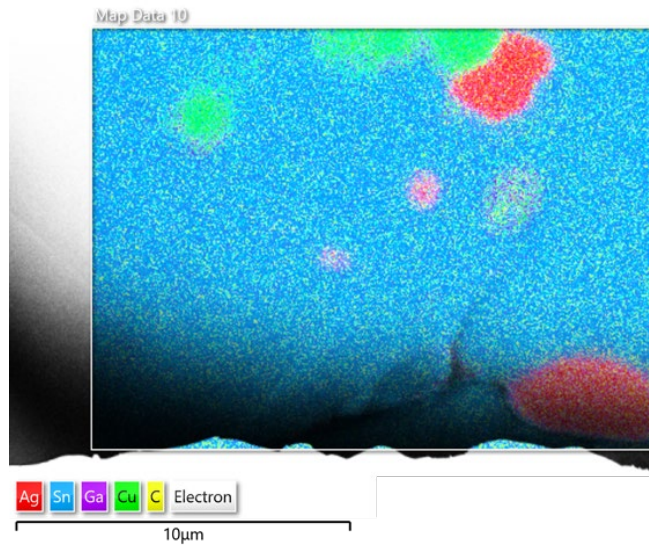
A.5 FIB Results in Other Regions



(a) Location of the FIB

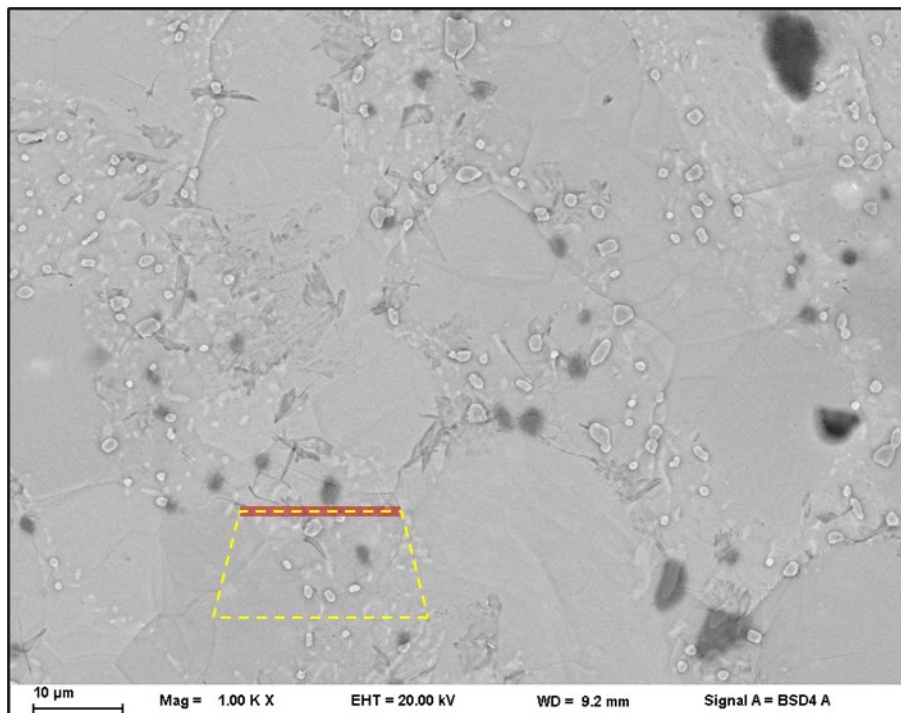


(b) SEM Images of the Cross Section (Left:BSE, Right:SE)

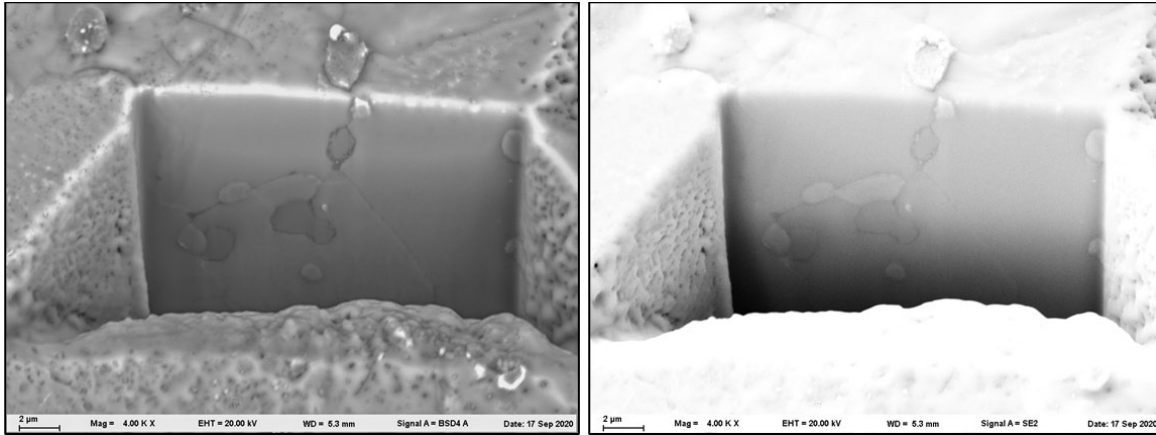


(c) EDS Mapping of the Cross Section

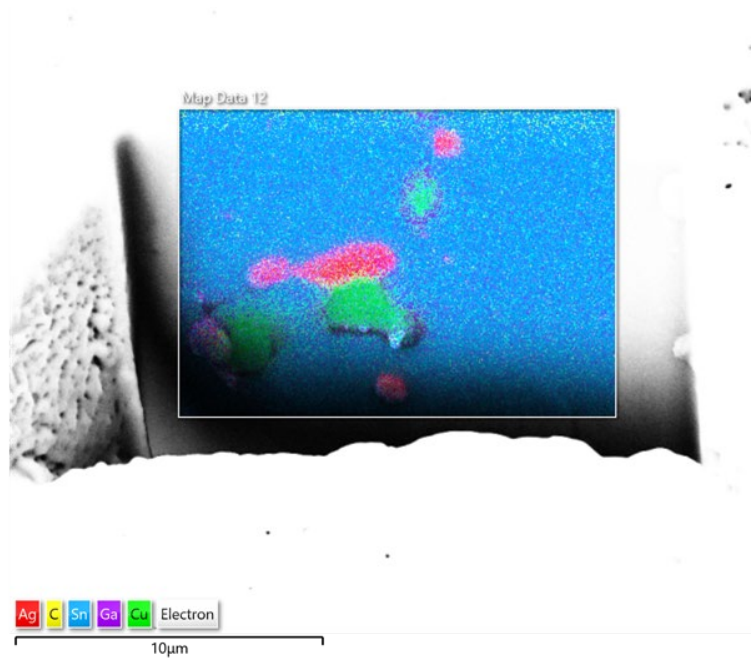
Figure A.6 FIB and EDS Results of Region 2 (SAC305 after 7000 Hours of Aging at 125 °C)



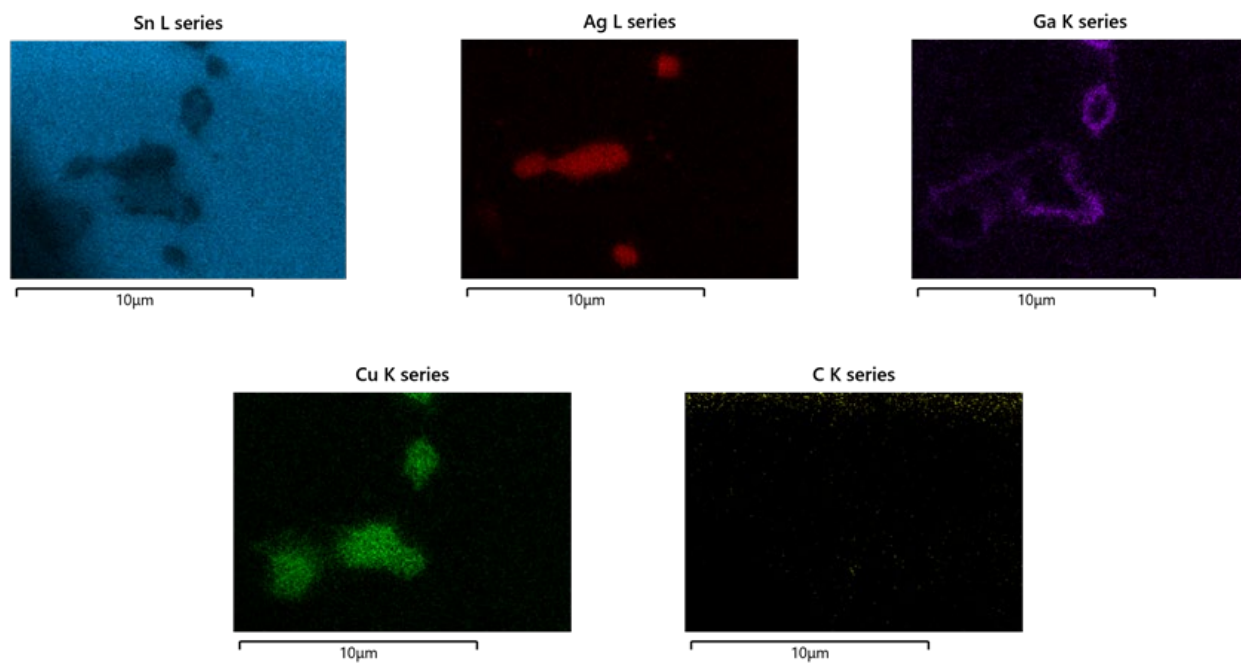
(a) Location of the FIB



(b) SEM Images of the Cross Section (Left:BSE, Right:SE)



(c) EDS Mapping of the Cross Section



(e) EDS Element Mapping

Figure A.7 FIB Results of Region 3 (SAC305 after 7000 Hours of Aging at 125 °C)