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Review Article

Thermal and Mechanical Stability of Bismuth Doped Sn-Ag-Cu Lead-free Solder: A Comprehensive Review

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ABSTRACT

Expansion in technology urges for better advancement, thus resulting in miniaturization of electronic products with rising concern for the reliability of electronic packaging material. Lead-free solder, being one of the most prominent alternatives in the electronic packaging industry, is constantly exposed to harsh conditions, which are especially exacerbated with smaller solder joints and a closer pitch. Hence, with the effort of attaining a more reliable solder alloy, research has been intensively executed to overcome the hurdle of maximizing the potential of SAC solders. The scope of the review thus focuses on identifying the aptitude of bismuth-doped SAC solders by analyzing their microstructure evolution in isothermal aging while understanding their thermal and mechanical stability in different fatigue tests. In the earlier days, Bismuth was found to realize a better melting point when interacting with the tin matrix due to its unique solid solution-strengthening mechanism. Bismuth-doped solders can also induce a more robust solder joint with smaller IMC particles and a thinner interfacial layer that enables significant improvement in fatigue resistance compared to traditional SAC alloys. Therefore, the review concludes that bismuth-doped SAC solder tends to outshine the conventional alternative as well as offering immense advancement in thermal and mechanical properties, portraying them as a potential alternative for the assembly of high-reliability electronic products, especially in industries with extreme conditions such as aviation, automotive, and military.

Keywords: Aging, bismuth, mechanical cycling, micro-alloying, reliability, SAC, thermal cycling

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INTRODUCTION

Soldering is a process similar to welding, where two metals are joined together with the aid of a filler material. In the case of the soldering process, a solder such as tin-lead (Sn-Pb) is utilized (Darwish et al., 2000). According to historical records, soldering has been one of the most commonly practiced metal and artifact fabrication techniques since even thousands of years ago, during the Chinese dynasties. In the early 2000s, Sn-Pb solders were widely used in either first- or second-level interconnects for printed circuit boards (PCBs) in the manufacturing of electronic products due to their superior reliability, performance, and quality in actual service. Despite being one of the most economically friendly approaches, it exhibits optimum physical and mechanical properties due to the presence of lead (Pb). However, the increased concern for environmental issues and global health has led to a restriction on lead usage in electronic products due to its adverse effects on both environmental and human health since July 1, 2006. The mandatory prohibition of lead then begins to be enforced globally, first by the legislation and restrictions imposed by the European Union (EU) under the Restriction of Hazardous Substances (RoHS) Directive (Kanlayasiri & Sukpimai, 2016).

Hence, the shift in global trends and views on the soldering industry then fostered the development of lead-free solders as a replacement for Sn-Pb solders, which encouraged researchers to cultivate the potential of lead-free solders with ideal reliability and properties to be utilized in electronic applications in various industries. Lead-free solders can be classified into two categories depending on the number of elements involved in making up the composition of a solder system, typically with tin (Sn) as the primary matrix. In general, lead-free solders include either binary or ternary compounds depending on the number of alloying elements through mechanical alloying (Abtew & Selvaduray, 2000). Incorporating lead-free solders into high-reliability applications requires a thorough understanding and evaluation of a solder's properties, ranging from the melting point, wetting ability, and mechanical properties, to ensure a product's stability in real-world operation. Furthermore, the presence of Ag content in SAC solders tends to deteriorate a solder's resistance to mechanical stress due to the formation of unique IMC compounds such as Ag_3Sn.

Although it was proven that the atom-pinning effect of Ag_3Sn provides additional strength by inhibiting cracks, IMC compounds such as Ag_3Sn and Cu_6Sn_5 composites are prone to agglomerating when exposed to heat, which embrittles a solder under elevated working conditions (Bhavan et al., 2024). Therefore, it is crucial to seek improvement in the said solder to further enhance its credibility and better integrate it with modern applications, especially in industries with extreme operating conditions, such as the automotive, aviation, and military sectors. In some literature, increasing Ag content within ternary SAC alloy was deemed to be beneficial, as proven by Coyle et al. (2015), who achieved a better thermal fatigue property with SAC405 solder in comparison to its other peers with lower

Ag composition. Despite the possibility of coalescing and coarsening the Ag_3Sn atom in a solder space when exposed to heat, higher Ag content, in turn, incurs a greater cost on manufacturing and production.

Although one may say that the obstacle can be easily overcome by utilizing a ternary SAC solder with lower Ag content, reducing the Ag content compromises the solder's thermal fatigue resistance, which deviates from the initial motive. Therefore, to attain a better consequence without compromising either the thermal-mechanical or the drop impact strength of a SAC solder, some of the literature has been actively researching the possibility of introducing a fourth element into the solder matrix, such as indium (In) (Ren et al., 2023), gallium (Ga) (Zhang et al., 2023), bismuth (Bi) (Tarman et al., 2024), or even nanomaterials such as carbon nanotubes (CNT) (Dele-Afolabi et al., 2019) and graphene nanosheets (GNS). Li et al. (2021), for instance, reviewed the mechanical performance and properties of various lead-free solders when they interact with different elements ranging from metal particles to transition elements, with the primary objective of understanding and predicting the performance of the solder among modern PCBs. Bismuth, or Bi, in particular, was deemed to be exceptional thanks to its unique effect when coming into contact with the Sn atom. Differing from elements such as Ag, Bi tends to strengthen a Sn-based solder through its unique solid-solution strengthening mechanism that embeds itself into the molten Sn matrix during reflowing (Liu et al., 2024). The attribute, therefore, further pins down the movement of atoms and affects the growth kinetics of both the IMC compound and the IMC layer, which dictates the mechanical strength of a solder under isothermal aging.

In recent studies, researchers have focused on studying different micro- and nanoparticles and their potential in SAC solders. However, only a handful of suggested materials are viable for the current market with both advantages in cost and performance. Being one of the cheaper candidates, such as Bi, gains a great deal of interest, especially when it was discovered to enhance a solder's melting temperature. Therefore, to understand better the benefits of Bi in lead-free solders, the present study aims to study the effects of Bi addition on microstructure, isothermal aging, as well as thermal and mechanical stability of a SAC-Bi alloy, which is deemed to be essential, especially in the case of continuous miniaturization of technology that demands solder material with ideal resistance towards thermal and mechanical stresses.

MICROSTRUCTURE

Hodúlová et al. (2018) stated that a conventional SAC solder may consist of a network of dendritic structures made up of Sn dendrites encompassed by a eutectic region with Sn atoms and IMC compounds, as shown in Figure 1. Apart from the Sn solder matrix, a solder also comprises an IMC layer that occupies the interface between the pad and solder to provide robust joint strength. An IMC composite is typically formed from the interaction of elements from both the pad and within the solder matrix that migrate to form composites such as Cu_6Sn_5 or Ag_3Sn compounds. IMC particles may also occupy the space between dendrites to form a network that exhibits extra strength and stability toward the structural integrity of an SAC product. Since Ag_3Sn holds a significant role in refining the grain of the Sn matrix due to its immense presence in the eutectic region of a solder matrix, it helps in defining the thermal dependability of an SAC solder. Ag_3Sn atoms serve as the pining factor that regulates the movement of dislocation but tend to deteriorate with detrimental aging, especially during high-temperature operating conditions. Therefore, to refine the grain morphology and increase the solder's resistance to thermal-related testing, dopants such as Bi are often utilized to improve structural integrity and reliability.

Similar to other micro- or nano-constituents, Bi helps in refining the grain structure of a SAC solder, which enhances its mechanical integrity and properties. Unlike the particle-strengthening mechanism, the inert Bi element is highly solid-soluble in Sn, as evidenced by Mahdavifard et al. (2015). Hence, Bi does not react with other constituents in an SAC

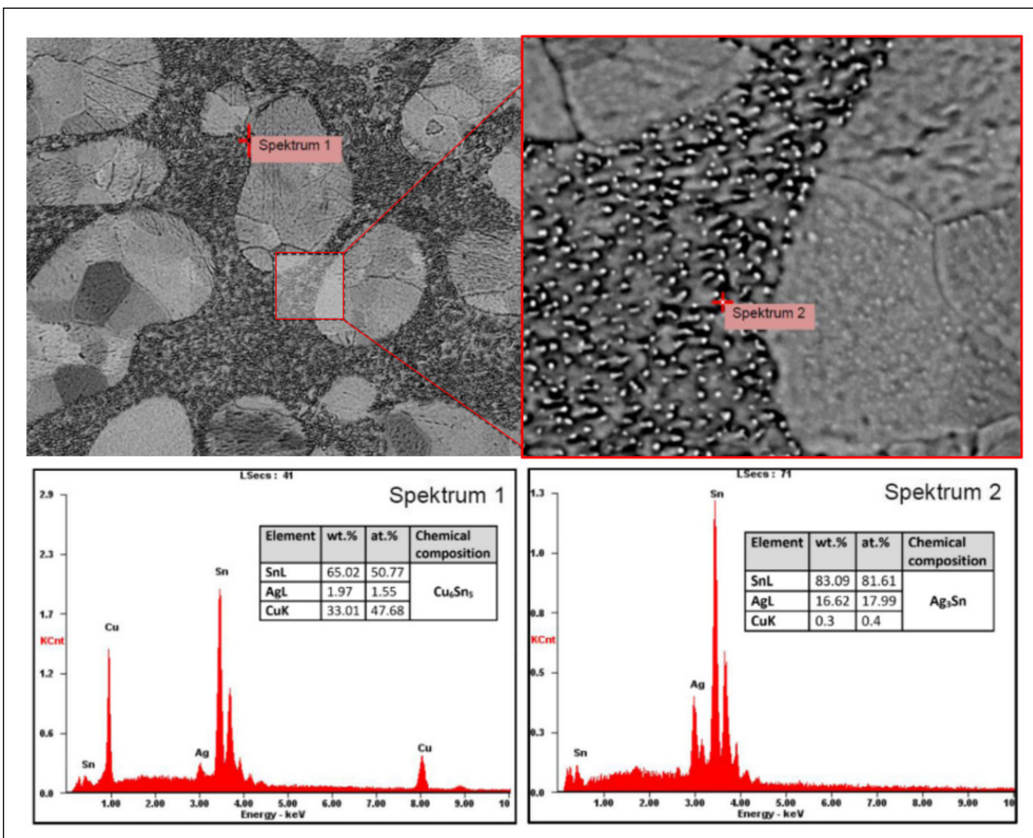


Figure 1. SEM Image and EDX analysis of SAC305 solder (Hodúlová et al., 2018)

solder matrix that could form a secondary composite, such as Ag_3Sn. From morphology, Bi atoms are capable of refining a solder's grain size and distributing the IMC compound within the eutectic region evenly. The effect increases with increasing Bi content, as Ali et al. (2024) demonstrated. Refinement of a solder's grain structure greatly relies on the size of the reinforcement material that helps in reconstructing the lattice structure of a solid solder whilst obstructing the movement of both particles and dislocations, as evidenced by Yang et al. (2022). The phenomenon identically occurs in the case of Bi atoms. A compositional analysis was carried out and validated the fact that SAC157 solder with a Bi composition of 0.5 and 5.0 wt.% displays a slight difference in particle distribution with the IMC compound, which is more uniformly spreads within the solder matrix in the case of higher Bi content (Figure 2). The result concurs with Gao et al. (2023), who observed a left shift in the XRD plot with increasing Bi content that was inferred to be a diminishment in grain size followed by a disturbance in the orderly management of the lattice structure (Figure 3).

The phenomenon results from the distortion of the crystal lattice of the Sn structure by the Bi atom, which also generates internal stress that hinders dislocation motion. A

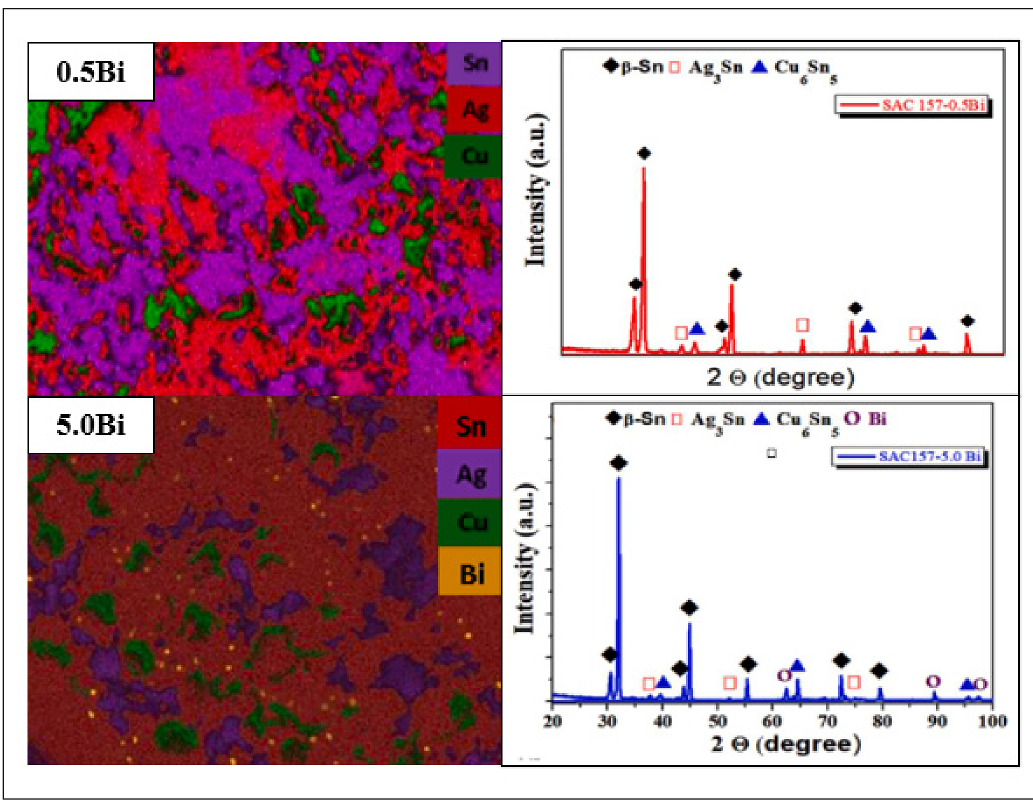


Figure 2. EMPA mapping and XRD analysis of SAC157 solder with 0.5 and 5.0 wt.% Bi (Ali et al., 2024)

smaller movement of atoms cuts down the interaction between different constituents, eventually diminishing the volume fraction of IMC compounds within the eutectic region of a solder matrix. A more homogeneous structure can then be attained within an SAC solder with a more uniformly distributed IMC compound along the grain boundary of the Sn dendrite and eutectic region. A homogeneous solder structure ensures mechanical stress is more well distributed, which prevents the formation of a single stress concentration point that negatively affects the mechanical strength of a solder alloy, which conceivably induces cracks when exposed to thermomechanical and mechanical stress. The noticeable enhancement was proven by Yang et al. (2022) through the enhancement of SAC105 alloy using various materials, including antimony (Sb), bismuth (Bi), and titanium (Ti), which portray a reduction in grain size that accompanies an improvement in mechanical tensile strength.

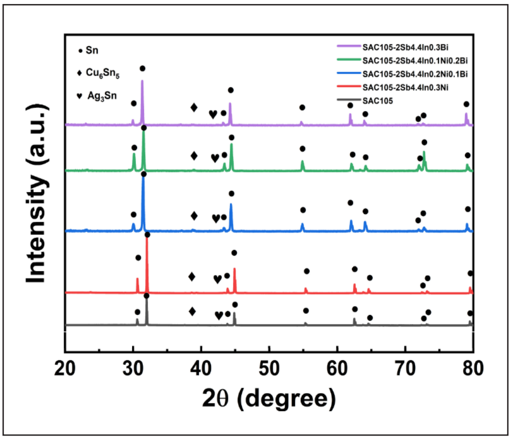


Figure 3. Compositional XRD Analysis for SAC105 solder with different reinforcement materials where a left shift in the plot was noticed as a result of distortion in the crystal lattice structure of the Sn matrix (Gao et al., 2023)

Interestingly, white spots, which were deduced to be Bi-rich phases, were found to separate and reside on the surface of the Sn dendritic structure in the case of Wu et al. (2019). The exceptional solid solubility of Bi allows Bi to freely diffuse along the grain boundaries of the β-Sn dendrite; thus, when the content exceeds a certain limit, phase separation occurs, and white Bi particles may then resurface above the Sn matrix of the SAC solder. The threshold limit typically falls at a range of 3 to 7 wt.%. The XRD graph presented further verifies the threshold limit of Bi in SAC alloy to be at a range not exceeding 4 wt.%. The theoretical understanding explains the peak of Bi content detected when a Bi content of 5 wt.% was incorporated into the SAC157 alloy. By studying the Sn-Bi phase diagram, the solid solubility limit of Bi in Sn elements typically increases with increasing temperature, which thus explains the ability of Bi to enhance the mechanical integrity of an Sn-based alloy when exposed to high-temperature aging.

The reaction between the Sn atom and other constituents, such as Cu and Ag, also brings about the formation of the IMC layer that exists at the interface between the metal pad and a solder bulk. Depending on the metal element, the IMC layer normally consists of a thermal unstable Cu_6Sn_5 that is most likely to degenerate to form a brittle Cu_3Sn layer that affects the reliability and structural integrity of a solder alloy. Cu_3Sn can either be formed from the dissolution of Cu_6Sn_5 or from the interfacial solid-state diffusion of Cu and Sn that reacts and remains at the solder-to-pad interface region. During aging, Cu_3Sn starts to grow and embrittles the entire solder alloy. Opposing what was expected, Bi does not play a significant role in inhibiting the growth of Cu-based IMC layer during as-cast conditions such as other elements, including Sb (Miao et al., 2024) or nickel (Ni) that directly participate and control the atomic diffusion of Cu and Sn during the solidification process.

For instance, Ni atoms interact with free IMC composites to form an alternative Cu-based composite that acts as the barrier in regulating the diffusion of both Cu and Sn atoms. The idea was proved from the SEM image presented by Sivakumar et al. (2021), where the thickness of SAC-Bi Ni solder does not vary much from a pure SAC405 alloy during as-reflowed conditions. This occurrence results from the characteristic of the Bi element, which is insoluble in other constituents besides the Sn atom. Despite that, knowing that Bi is highly soluble in the Sn matrix, the presence of Bi leads to the formation of a finer grain structure with a more finely dispersed IMC compound. This behavior thus slows down the diffusivity of the Sn atom, which reduces the growth rate of the IMC layer due to its pinning effect similar to those of Ag_3Sn particles. Apart from noticing an improvement in fatigue resistance for the case of Bi-doped solder, Jian, Hamasha, Alahmer, Wei et al. (2023) also noticed a betterment in IMC layer condition to grow more uniformly compared to a pure SAC solder despite achieving an increased thickness in Cu_6Sn_5 layer. The ability of Ag present in a SAC solder, along with the addition of Bi element, further inhibits the movement of particles and dislocations, which regulates the aging effect when exposed to elevated temperature.

During aging, Ag_3Sn plates start to coalesce and coarsen, thus losing their pinning effect, which reduces the hardness of a Sn-based solder. The presence of Bi atom, in turn, solid solution hardens the solder matrix, thus increasing the hardness of a SAC solder with preliminary aging. Although the Bi atom may seem trivial in the participation of regulating IMC layer thickness, it shines tremendously in high-temperature working conditions due to its distinctive feature.

ISOTHERMAL AGING

Isothermal aging is a process in which soldiers are exposed to temperatures higher than their real-life operating temperature for an extensive period to understand the tested solder's mechanical and microstructural behavior, which helps identify its durability, reliability, and stability. The interaction between the solder and substrate results in the formation of a thin IMC layer near the interface, which provides additional strength to the solder structure in an as-reflowed condition, especially with the presence of Cu_6Sn_5, which serves as a key factor in the improvement of lead-free solder systems (Ramli et al., 2022). However, with prolonged aging, Cu_6Sn_5 compounds are prone to dissolution, thus resulting in the formation of their weaker counterparts, known as Cu_3Sn, that are naturally brittle in strength (Dele-Afolabi et al., 2019). Hence, various researchers have sought different ways to understand the growth kinetics of the IMC layer in lead-free solders to counteract the detrimental effect of a thick IMC layer, primarily through the utilization of dopants. Bismuth, for instance, not only proved to be beneficial in decreasing the melting point of solder but was found to be highly stable under high-temperature exposure due to its exceptional pinning effect.

In accordance with Zhong et al. (2022), although reflowed solder for pure and Bi-doped SAC solder attained identical IMC layer thickness and composition, elements such as In and Bi are potential candidates that have the capability of substituting Sn in IMC to form an alternative compound given as Cu_3(Sn, In) or Cu_3(Sn, Bi), respectively. The observation can be inferred as the competency of Bi in not only hindering the movement of dislocations and IMC particles, which diminishes the Ostwald Ripening effect but also acting as a protective barrier similar to those nickel-contained IMC compounds that assist in limiting the diffusion rate of Cu atoms from either the solder matrix or the metal substrate. Apart from that, Sn-Bi lead-free solder bumps are also often utilized along with SAC solder paste to form composite solders that provide additional fortification, which was discerned to show positive results at different reflow temperatures (Shen et al., 2019). The result was proved by Zhang et al. (2024), who investigated the fracture behavior of the SAC305/Sn-Bi solder composite in the presence and absence of Co particles and the influence of different surface finishes. In the early 2000s, the improvement was found to be achieved along with the implementation of 1% Bi in SAC305 solder, especially in inhibiting the formation of thick IMC layers during isothermal aging, as demonstrated by Rizvi et al. (2006).

Bi comes along with high solid solubility and a solid strengthening mechanism; the growth rate of IMC thickness in the case of SAC-1Bi was much slower and in a linear manner when compared with pure SAC305 solder, which was further proven by other researchers who not only discovered the exceptional aging ability but also reported the embrittlement of SAC solder with high Bi content that subsequently affects the fatigue life of the as-reflowed solder (Kanchanomai et al., 2002; Li & Shi, 2006; Zhao et al., 2009). On the other hand, Ramli et al. (2022) reviewed the performance of different elements when added to a SAC solder matrix. They found that, apart from the great reliability of indium addition, the incorporation of 3 wt.% Bi, along with 0.05 wt.% erbium, helps in refining the thickness of the IMC layer during isothermal aging. As aforementioned, the formation of a brittle Cu_3Sn layer near the interface of a bare copper pad on the package or substrate side can be bestowed on the contribution of copper atoms from either the metal pad itself or from the dissolution of Cu_6Sn_5 compounds that react partially with Sn atoms to form their brittle Cu_3Sn form (Dele-Afolabi et al., 2020). Correspondingly, Sivakumar et al. (2021) were able to present results that concur with the statement despite achieving a thicker Cu_6Sn_5 IMC layer for the case of SAC-Bi, Ni solder ball, the Cu_3Sn layer was much thinner in the said solder compared to pure SAC405 samples due to the fact of a higher migration rate of Cu in SAC405 during thermal aging.

Apart from its marvelous ability in controlling the growth of the IMC layer, bismuth was also found to be capable of regulating the coarsening effect of IMC particles that reside within the eutectic region. For instance, Ali et al. (2021) investigated the microstructure behavior of as-cast and thermally aged solder with bismuth compositions ranging from 1 wt.% to 3 wt.%. In the case of SAC-3Bi solder, the grain boundaries were found to be less scattered with a more refined Sn grain structure even under aging temperatures of 100°C and 200°C, which indicates the aptitude of bismuth particles in the movement of dislocation and IMC particles. Wu et al. (2021) studied the effect of different bismuth content and aging temperature on the IMC particle diameter. They found that apart from increasing particle diameter with increasing aging temperature due to an increase in diffusion rate and Ostwald ripening effect, the normalized particle diameter size of SAC-3Bi was the smallest in all cases, as shown in Figure 4. The author explained that the amount of bismuth that resides within the eutectic region of an SAC305 solder decreases as it gradually propagates toward the direction of the dendritic structure with increasing aging time. Initially, three different structures with distinct colors, including grey tin dendrites, black IMCs, and white bismuth, were observed in an as-reflowed bismuth-doped SAC305 solder bulk structure. However, with increasing aging periods, larger brittle IMC particles, particularly Ag_3Sn compounds, start to form at the expense of their smaller forms, which are portrayed as depicted in Figure 5.

Bismuth was thus deemed to be extremely beneficial in the SAC solder system, partially due to its non-reactivity with other constituents but also due to its high solid solubility in molten tin upon heating, which helps in anchoring the movement of dislocations and IMC compounds and encourages the formation of solder with comparatively better strength and structural integrity. Similar work was carried out by Ahmed et al. (2016), and it was discovered that by assimilating merely 2.4 wt.% of bismuth into SAC105 solder, the solder achieved improved performance in stress-strain behavior with higher resistance towards aging compared to the pure condition. Both authors were able to achieve a lower degree of Ostwald ripening effect along with the presence of bismuth, which verifies the pinning ability of bismuth atoms comparable to Ag_3Sn particles. All in all, the performance of SAC-Bi solder in isothermal aging proves its suitability and potential in high-temperature applications.

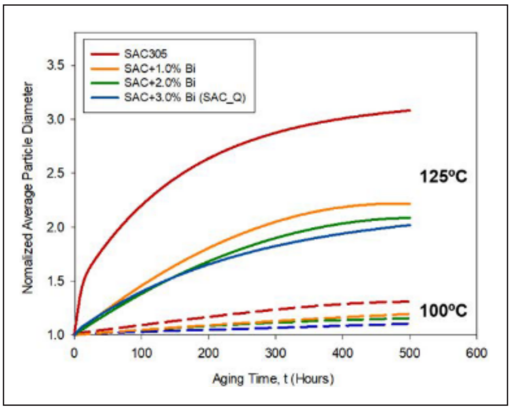


Figure 4. The normalized particle diameter of IMC particles at various conditions (Wu et al., 2021)

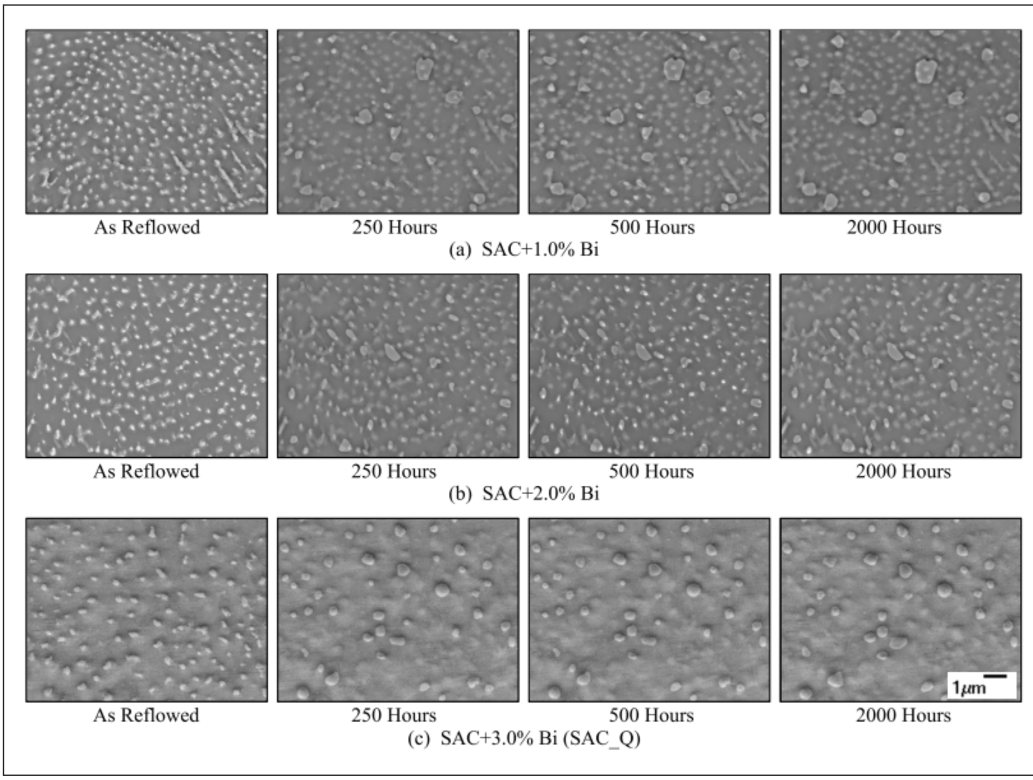


Figure 5. Microstructural evolution of SAC405 solders with different bismuth content after aging for 2000 hours at 125°C (Wu et al., 2021)

THERMAL CYCLING

Thermal cycling, as the name implies, is the fluctuation of heat a material is exposed to in its working environment. In the case of lead-free solders, thermal fatigue is often viewed as the most damaging factor that causes a connected solder joint to lose its structural integrity and electrical connectivity. Moreover, under exposure to either constant heat or thermal fluctuations, SAC solders tend to exhibit features that affect the reliability of an electronic device. The presence of an IMC layer or IMC precipitates within the solder matrix adversely affects morphology when exposed to heat, which explains the reason for lead-free solders with low ductility and creep resistance in operating conditions with high temperatures (Depiver et al., 2021). During thermal fatigue, the repeating changes in temperature cause iterating expansion and contraction of the mounted device and PCB at a different rate due to a dissimilar coefficient of thermal expansion (CTE).

Therefore, along with the miniaturization of technology and increasing solder density, understanding thermal cycling in terms of the solder's microstructural and mechanical behavior is extremely crucial in improving an electronic product's reliability and sustainability in different environments and circumstances. To understand the behavior and prevent malfunctioning of developed boards, industrial manufacturers typically carry out reliability testing prior to product delivery. Reliability testing is the process in which the assembled boards are given a series of harsh trials to ensure that they are able to handle various working situations without failing. Correspondingly, for thermal cycling reliability testing, second-level assembled boards are exposed to extreme temperature fluctuations, typically within the -40°C to 125°C range, with a holding time of 10 to 15 minutes at each extremity and a ramping rate commonly below 10°C/min in accordance with the IPC9701 standard (Romdhane et al., 2022). However, Hokka et al. (2013) explained that the characteristic life of a lead-free solder may somehow differ depending on not only the constituents but also the cycle parameters. The author thus concluded that the most appropriate parameters should be selected based on the industries and applications involved. Nevertheless, lead-free solders were proven to creep and deform when exposed to intense conditions, which causes cracks to initiate and propagate along the misoriented grains resulting from prior recovery and recrystallization phases. Therefore, doping was viewed as a viable approach to fostering a solder with durable and reliable joint strength to improve its microstructural behavior and reduce the coarsening of second-phase particles.

From the context of microstructural behavior, Libot et al. (2018) investigated the thermal fatigue behavior of a SAC305 solder by understanding its microstructural changes. Thermal fatigue-induced creep in a lead-free solder typically follows a sequential process starting from recovery and recrystallization before an intergranular crack is observed. In general, thermal cycling generates thermal stresses that excite the movement of particles such as Ag_3Sn and dislocations, which is often known as the recovery phase. The movement of dislocations disrupts the arrangement of grains and introduces grain boundaries with misoriented angles, causing the grain angle to increase. The grain continues to grow to a higher angle as the thermal stress accumulates, resulting in the commencement of the recrystallization phase. Continuous expansion and contraction of PCB and module thus employ thermomechanical stress on the solder, which causes cracks to propagate along the designated path created by the recrystallized grains. In modern technology, SAC305 has proven to achieve a good performance that even surpassed the traditional Sn-Pb solders in terms of thermal cycling reliability (Arfaei et al., 2015). Despite being one of the environmentally friendly candidates, the SAC solder displays better thermal creep fatigue resistance than the traditional Sn-Pb alternative due to its stable microstructure and the presence of Ag and Cu elements.

As previously mentioned, Ag_3Sn and Cu_6Sn_5 IMC composites are two common particles that can be detected in a SAC solder matrix, whereas the IMC composites of Sn-Pb alloy rely on the type of adjacent metal that a solder is attached to and typically comprise only of Cu_6Sn_5. Although the Ag-based solder is prone to coalesce and coarsens with heat, Ag_3Sn does serve as a good pinning factor that assists in resisting thermal-induced failure.

However, Ag_3Sn may eventually agglomerate and even pin it to the misoriented grain boundaries, which encourages the nucleation of new grains that exacerbates the thermal cycling defect. This encourages the discovery of third-generation alloys such as Innolot to be utilized in industries with harsh environments and necessitates zero failure during service. The adaptation of Innolot opens the chapter for the potential of Bi in elevated temperatures and to delve deeper into its possibility in large temperature ranges.

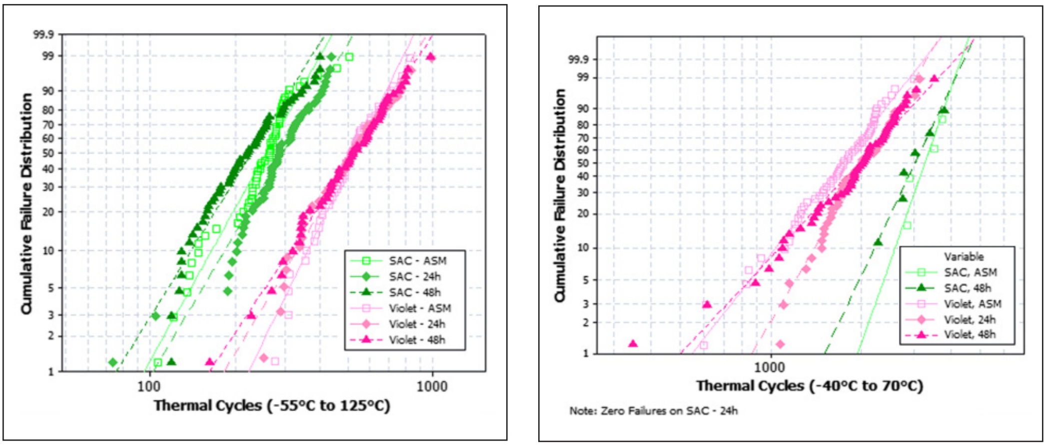
From the morphology, it was observed that Bi is highly solid-soluble in molten Sn, which enhanced the mechanical and microstructural properties of an SAC alloy during solidification. For instance, the Sn-58Bi alloy was able to attain an exceptionally low melting temperature thanks to the distinctive capability of Bi. The positive benefits of Bi also improve the thermal fatigue performance of a Sn-based alloy, as Tian et al. (2022) demonstrated by investigating the interaction between SAC305 nanoparticles in the Sn-58Bi alloy. Furthermore, by looking into SAC-Bi, Innolot (SAC407 with 0.15 wt.% Ni, 1.40 wt.% Sb, and 3.00 wt.% Bi addition), SAC-In, SAC-305, and SAC-Mn solders, the bismuth-containing SAC-Bi and Innolot soldiers were found to achieve a better characteristic life at above 3,000 cycles for all cases when compared with their relative peers (Akkara et al., 2022). Similar to other thermally related testing, Bi serves an identical purpose as Ag_3Sn particles that help impede the movement of grains, particles, and dislocations, slowing down the thermal cycling-induced alterations. Bi elements behave similarly to Sb and Ni, which embed themselves in the Sn matrix, and solid-solution strengthens a Sn-based solder.

This phenomenon thus explains the increase in characteristic life or longevity of bi-doped solder when compared to a conventional SAC alloy. It is essential to investigate the microstructural changes that the Bi element causes to a pure SAC alloy to evaluate the thermal fatigue performance of an SAC solder. Fundamentally, the Ag_3Sn precipitates define the performance of a solder's thermal fatigue resistance (Belhadi, Wei, Vyas et al., 2022). From the SEM images of as-cast solder, Ag and Sn interact to form a large network that holds the Sn dendrites in place while pinning the movement of dislocations. With subsequent thermal cycling, the Ag_3Sn precipitates begin to coarsen in both pure and bi-doped BGA but were found to be more severe in the case of pure SAC and Sn-Pb solder. The presence of Bi atoms improved the microstructure integrity of the entire solder bulk, which reduces the Ostwald-Ripening effect of Ag_3Sn particles that contribute to the formation of recrystallized grains. The growth kinetics of the IMC layer were also enhanced in the bi-doped SAC alloy case, especially under additional reinforcement material, including Sb and Ni elements, which regulate the diffusivity of Cu and Sn atoms.

Since the IMC layer acts as the localized stress area that triggers the formation of microcracks, a thinner Cu_3Sn layer, in the case of SAC-Bi alloy, also discouraged cracks from propagating and thus increased a solder's working life. The betterment of a solder's lifespan can also correlate to an improvement in mechanical strength under thermal cycling reliability testing, which simulates a real-life working condition that a solder may be exposed to. When exposed to thermal-induced stress for an extensive period, solder tends to soften and eventually crack due to a deterioration in mechanical strength. Bi-doped SAC solder, on the other hand, helps enhance the microstructural integrity of a solder and improve the mechanical strength of an SAC solder from a long-term perspective. For instance, Hassan et al. (2020) discovered that the mechanical strength of a SAC405 solder can be greatly improved with the incorporation of merely 3 wt.% Bi. The mechanical degradation of SAC-3Bi under various thermal cycling conditions was found to decrease more steadily than a pure SAC solder. Material is bound to degrade when exposed to different forms of stress due to the accumulation of stress that results in microstructural changes within the material matrix.

Despite having a steady drop in elastic modulus for the case of SAC-3Bi, an abrupt fall was observed in the case of SAC405 alloy, thus concurring with the positive effect of Bi in regulating thermal cyclic failure whilst maintaining a considerably optimal mechanical strength in spite of long-term thermal cycling. In real-life circumstances, it is common for solders to be exposed to both thermal stresses and mechanical loads, such as in the case simulated by Belhadi, Wei, Qasaimeh et al. (2022). Due to the benefits of Bi in the Sn matrix, the tested SAC-3Bi solder was able to achieve betterment in resistance towards not only thermal cycling but also creep-induced deformation. Similar to the effect of Ag in resisting thermal cycling, Bi greatly reduces the creep extension of solder due to its solid solution and precipitate hardening mechanism. Interestingly, increasing Ag content also assists in the formation of more refined networks of grain with smaller interparticle spaces, thus reducing the chances of grain boundary sliding caused by either thermal cycling or creep deformation.

Nevertheless, a considerable addition of Ag is essential to diminish the Ostwald Ripening effect of the primary Ag_3Sn precipitates, potentially aggravating thermal-induced failure. The phenomenon was proven by Liu et al. (2024) by improving the fatigue life of SCN-Bi solder compared to Ag-rich SAC-Bi alloy. However, the presence of foreign atoms such as Bi, Ge, and Co further refines the morphology of the involved solder, which not only improves the solder's thermal fatigue life but enhances its hardness and mechanical strength. Furthermore, it was observed that SAC-Bi actually outperformed SAC solder in a more severe thermal cycling condition with a larger temperature range but instead portrays a weaker behavior in shorter temperature extremes, as shown in the life prediction of the solder in Figure 6 (Delhaise et al., 2020). Stacking fault energy (SFE) generally indicates the energy required for dislocation to climb and glide. Higher SFE indicates that a material has a narrower stacking fault and allows dislocation to slide between atoms more easily than lower SFE, typically observed in alloy systems such as SAC-Bi.



(a) (b)

Figure 6. The Weibull plot shows that the characteristic life of SAC405-6Bi ('Violet') was higher in the case of (a) high-temperature cycling and lower in the case of (b) low-temperature cycling (Delhaise et al., 2020)

As previously mentioned, thermal cycling causes strain accumulation, which triggers systems to release the accumulated damage in any possible way, either through recovery (dislocation movement) or recrystallization (grain restructure). In the scenario with higher ΔT, a larger strain causes both systems to spend less time in the plastic region; thus, the recrystallization phase occurs relatively sooner. However, in the case of smaller ΔT, the SAC solder with lower SFE spends a longer time in the recovery phase due to its ductile property, whereas SAC-Bi, despite achieving better strength, tends to recrystallize sooner due to wider stacking faults that hinder dislocation movement. Therefore, in spite of aging being a detrimental process, preliminary aging at a moderate level positively enhanced the thermal fatigue life of a doped system, such as the case of SAC-Bi solder. Comparatively to clarification by Cai et al. (2021), homogeneous Sn-Bi structure actually exceeds the longevity of SAC/Sn-Bi composite during thermal cycling tests that regulate the nucleation of grain that causes cracks to propagate in an undesirable manner.

Therefore, this further signifies the importance of achieving ideal homogeneity (Swanson & Anselm, 2023). From the presented morphology, as shown in Figure 7, the solder typically encounters failure at the solder's neck. An intergranular fracture that propagates along the recrystallized grain may often be observed and typically focuses on the area close to the package or substrate side. Table 1 summarizes the achievement of Bi in solder reliability of various types of SAC solder. Clearly, from the highlighted studies, Bi serves as an excellent reinforcement material due to its essential solid-solution strengthening mechanism, which contributes to its exceptional solid-solubility in Sn, which especially outshines the pure solder alternative in extreme temperature conditions that cater to industries operating in harsh environments.

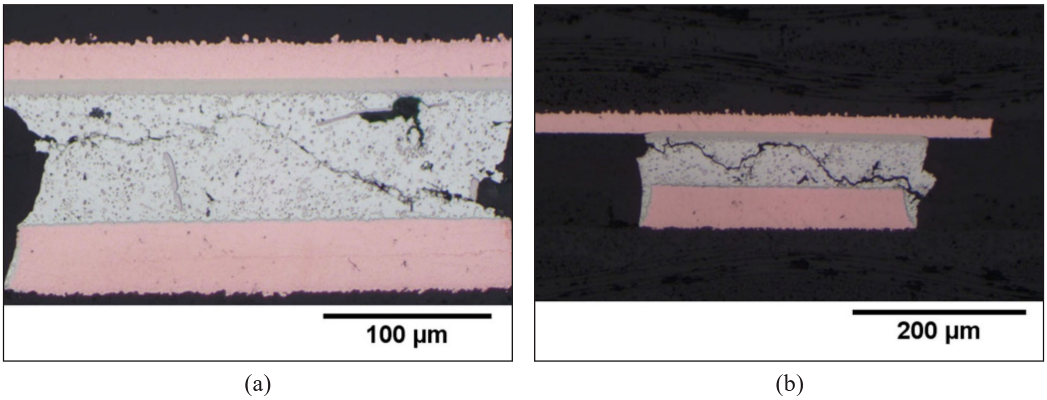


Figure 7. Solder morphology of both (a) SAC305 and (b) Violet under temperature cycling of -40°C to 70°C, with the latter showing a larger factor of recrystallization (Delhaise et al., 2020)

Table 1
The effect of Bi dopants in conventional Sn-based solder

Solder	Findings	Reference
SAC-Bi SCN-Bi	SCN-Bi solder was able to display astonishingly high characteristic life despite the absence of Ag. This phenomenon clarifies that despite Ag being beneficial in enhancing fatigue life, a high amount of incorporation encourages Ag_3Sn coarsening, which reduces the significance of its positive effect in LFS.	Liu et al., 2024
SAC-2Bi	Bi helps lower the acceleration factor (AF) of the SAC solder in thermal cycling, thus implicating the ability of the solder to resist fatigue life degradation in extreme loading conditions.	Jeon et al., 2023
SAC-3Bi	Doping of elements including Bi, Sb, In, and Ni greatly enhances the fatigue life of a SAC solder, which even surpasses the traditional Sn-Pb in thermal cycling.	Belhadi, Wei, Vyas et al., 2022
Innolot SAC-3Bi	ENIG surface finishing provides the best result due to the presence of Ni atoms. Conversely, when elements such as Ni, Sb, and Bi were added to a pure SAC solder, the solder was strengthened as a solid solution, which increased its fatigue life.	Akkara et al., 2022
SAC405 (1 – 4% Bi)	A lower failure rate indicating a better characteristic life was attained for SAC405 added with 3 to 4 wt.% of Bi. Similar to Bi, a small addition of Sb further enhanced the reliability of the solder, especially in high-temperature cycling.	Zou et al., 2021
Sn-Bi	Homogeneous Sn-Bi solder displays better fatigue life compared to SAC solder and mixed SAC/Sn-Bi solder.	Cai et al., 2021
SAC205 -6Bi	Bi addition enhances the performance of SAC solder in thermal cycling with a larger range between -40°C to 125°C but is weaker when compared to SAC305 at a smaller range between -40°C to 70°C.	Delhaise et al., 2020
SAC405-3Bi	The material property degradation of SAC-Bi solder was much steadier compared to pure SAC solder at various conditions, including thermal cycling, thermal shock, and isothermal aging, which indicates the capability of Bi to enhance a solder's thermal fatigue life.	Hasan et al., 2020

MECHANICAL CYCLING

Thermal cycling has been playing a significant role in identifying the reliability of solder joints in the second level of interconnects for an electronic assembly. However, similar to aging, thermal cycling lacks efficiency due to its extensive testing period. With the fact that thermal cycling is a well-established testing practice with restricted standards, acceleration of the said method can only be achieved by either increasing the temperature swing or shortening the cycle time by augmenting the ramp rate, which potentially changes the failure mode of a tested solder and questions the credibility of the obtained results for the life prediction of a solder's lifespan. According to Graver et al. (2009), a thermal cycling test with a temperature range between 0°C and 100°C requires around half a year for the tested lead-free solder-jointed board to exhibit failure. To enhance efficiency, the author proposed the idea of utilizing mechanical cycling as a four-point bending test. This practice is often common in industry to create an environment that a solder structure may experience, which helps understand a solder's behavior holistically.

For instance, testing approaches such as mechanical vibration are occasionally designed to be carried out along with thermal cycling. By doing so, board manufacturers and reliability engineers were able to identify the weaknesses of a designed product more easily, thus enabling subsequent improvements. Through coherent testing of mechanical vibration and thermal cycling, Borgesen et al. (2019) were able to concur with the idea by clarifying that the behavior of SAC and Sn-Bi solders may differ from thermal cycling tests. Introducing an additional type of stress further exacerbates the damage intensity that accumulates within the solder matrix, which results in different microstructural and mechanical behavior. Consequently, different approaches have also been actively researched by correlating the aging effect with mechanical simulated thermal strain by cycling with tests that exert flexural stress (Vandevelde et al., 2017; Wang et al., 2009; Wang et al., 2020), tensile stress (Maruf et al., 2024), and shear stress (Hoque et al., 2021; Su et al., 2020). Different from conventional thermal cycling tests, isothermal mechanical cycling tests can be carried out either with thermal and mechanical stress introduced simultaneously or through the utilization of preliminary aged solder. However, the absence of thermal-induced strain results in a lower degree of grain, and IMC coarsening triggers the recovery and recrystallization stage in a thermal cycling test, thus removing the adverse effect that causes microstructure instability within a solder bulk. The occurrence causes the failure mode to be slightly different during isothermal mechanical testing in spite of essentially achieving an analogously identical fracture mode that cracks in the form of an intergranular crack along the IMC layer within the interface region.

SAC solder, as aforementioned, is often doped with dissimilar-size particles to enhance its mechanical and thermal properties. Similar to thermal-related testing, SAC-Bi was presumed to outperform a pure SAC alloy in a mechanical cycling test. Unlike the inverse relationship of Ag content with the mechanical stability of a solder in a lead-free solder, the presence of Bi solution strengthens the overall mechanical properties of an SAC (El-Daly et al., 2015). Higher Bi content typically helps in fortifying the mechanical strength of an SAC solder, as demonstrated by Belhadi et al. (2019) when investigating solders including SAC305, SAC-3Bi, and SAC-6Bi. At the as-reflowed condition, an increment of Bi content provides additional support to the ductile solder through the means of a solid-solution strengthening mechanism. Bi plays an essential role in enhancing the thermal and mechanical stability of a solder by mitigating the detrimental effect attributable to dislocation movement. The betterment in shear strength was achieved in the case of SAC-6Bi in unaged conditions. However, it regularly deteriorated with an increasing aging period that eventually outshined the SAC-3Bi solder in severe aging circumstances. Since aging encourages agglomeration of particles, the excess number of Bi atoms acting as the solute of the entire system tends to coalesce and coarsen when the solvent atoms (Sn matrix) are fully occupied and redundant.

Coagulation of the Bi atom causes its brittle nature to dominate and thus embrittles the SAC system at higher aging hours, even though a low strain rate was utilized during the testing of SAC-6Bi solder with a preliminary aging of 1000 hours. From Figure 8, increasing stress amplitude generally leads to a lower characteristic life of both pure and bi-doped SAC solders. Comparatively, the Bi element was again proven to mitigate the adverse effect of aging and help attain a solder with enhanced strength and lower ductility. Furthermore, Bi refines the solder grain, elevating the mechanical stability of a SAC solder. This was proven by Al Athamneh and Hamasha (2020), where despite both solders failing at the approximately identical cyclic range, the bi-doped solder was able to withstand a higher stress amplitude thanks to its improvement in fatigue resistance. Furthermore, Jian, Hamasha, Alahmer, Hamasha et al. (2023) demonstrated that SAC-Bi generally displays a betterment in fatigue resistance, especially when cycled within moderate and high-stress conditions. The presence of Ag and Bi atoms refines the Sn grain size and increases the phase boundaries of a solder morphology. Both the Ag_3Sn particles that formed from the interaction of Ag and Sn atoms, as well as the Bi-rich phases that surround the eutectic region of a solder matrix, further obstruct the movement of dislocation, which adversely catalyzes the softening of a metal alloy.

Both the boundaries and formed composites act as a robust barrier that mitigates the chances of crack initiation that results from the formation of defects such as grain boundaries, voids, and other surface defects. The phenomenon explains the achievement of SAC-3.3Bi in achieving a higher characteristic life when compared with Sn-Cu-Bi solder during shear cycling in various aging conditions in spite of utilizing a higher Bi content. Fundamentally, Kaimkuriya et al. (2024) highlighted where harder materials tend to be more susceptible to plastic deformation, which thus results in lower fatigue life. Material with higher strength is typically associated with lower ductility, such as what was observed in the case of SAC-Bi solders. The presence of Bi atoms strengthens the structure of the soft, ductile SAC solder by means of a solid solution strengthening mechanism. Bi atom alters the atomic structure, which causes a material to induce less plastic deformation work per cycle. The material accumulates damage over time during fatigue cycling by absorbing and dissipating energy. Higher plastic deformation work per cycle results in microstructural changes that benefit crack initiation and propagation, which signifies a lower fatigue life within a solder material with higher ductility.

Figure 9 records the comparison in the hysteresis loop (left) and average work per cycle (right) among various solder alloys during shear cycling. A larger hysteric loop of SAC solder with 0.08 wt.% of Bi element denotes that the solder alloy experiences a larger plastic deformation work during the cyclic test. On the other hand, Su et al. (2020) again

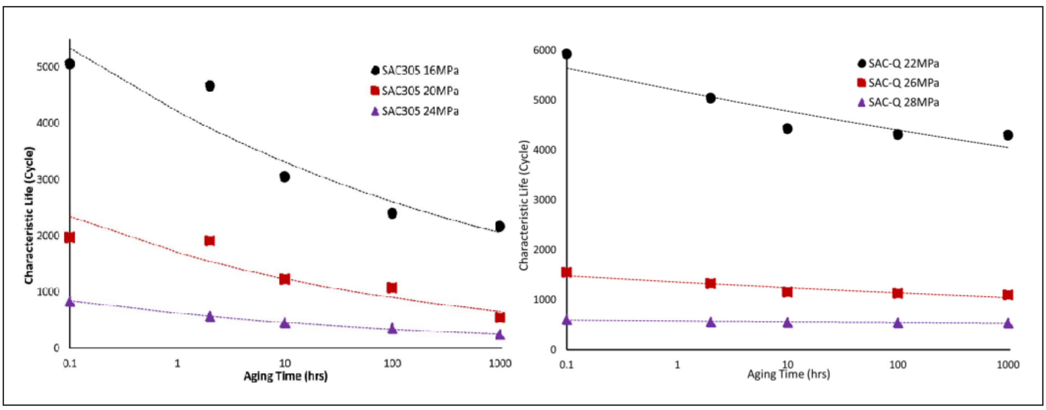


Figure 8. Comparison in characteristic life of SAC305 and SAC-3.3Bi at various stress amplitudes and aging time (Al Athamneh & Hamasha, 2020)

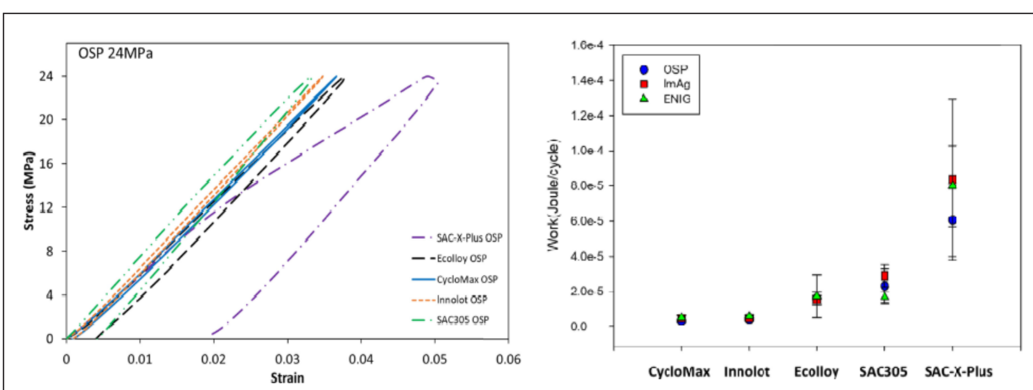


Figure 9. Comparison in hysteresis loop and average plastic deformation work per cycle for various alloys with different surface finishes (Su et al., 2020)

proved that a strong and brittle alloy can be achieved with lower average plastic work per cycle when an adequate addition of Bi particles at a range of 2 to 3 wt.% was added to a pure SAC system. Apart from that, to understand and correlate the difference in tensile properties between pure and bismuth-doped SAC solder, Ahmed et al. (2016) utilized a six-axis load cell testing machine to identify the stress-strain behavior of SAC105 and SAC105-Bi solder when placed within a thermal chamber with different temperature ranges between 25°C and 125°C. Thanks to the capability of Bi to resist aging, the SAC-Bi alloy achieved an improvement in mechanical stability, making it optimal to be incorporated in low-Ag content solder. By utilizing an adequate amount of Bi to replace Ag in low-Ag alloys, the coarsening effect of IMC composites can be diminished, which alleviates aging-related degradation while augmenting its fatigue resistance towards both mechanical and thermal stresses.

Moreover, Haq et al. (2022) and their respective peers were able to study the effect of mechanically cycled SAC405 solder with bismuth compositions of 1 wt.%, 2 wt.%, and 3 wt.%. However, a lower fatigue life was attained for the case of SAC-3Bi due to the embrittlement of Bi when integrated with the SAC solder matrix. The phenomenon concurs with the idea that an appropriate amount of Bi is required, and further research is needed to cultivate a solder structure with excellent strength and reliability whilst minimal sacrifice on ductility that adversely causes cracks to initiate and propagate when exposed to stresses in real-world situations.

CONCLUSION

Lead-free solders have been gaining great attention among industrial experts due to their exceptional sustainability and reliability, along with their ability to achieve greener technology that benefits both the environment and human health, making them a good candidate for competing with traditional Sn-Pb solders. Taking the renowned SAC solder as an example, despite its great achievement in nurturing strong and robust joints for electrical connection of devices to PCBs at the second interconnect assembly level, its relatively high melting temperature of approximately 217°C to 220°C has led to several complications, including complex IMC as well as difficulty in the design and consolidation of electronic packages. Hence, the doping of third-party alloys, for instance, bismuth, is often considered to not only achieve a breakthrough in mechanical strength but also primarily to attain a more ideal melting temperature that is compatible with both the glass transition temperature and the decomposition temperature of the PCB and to-be mounted device, respectively.

However, because of its brittle nature, the ductility of the aforementioned system tends to deteriorate eventually, which serves as the main reason for promoting a soldering system with weak reliability in response to thermal and mechanical stresses. Due to the high solid solubility of bismuth in tin solvent when exposed to heat, the bismuth atom tends to reside within the dendritic structure. It restricts the movement of dislocations as well as particles that potentially contribute to particle coarsening with prolonged heating, which ultimately leads to thermal fatigue fracture, which thus explains its exceptional performance in aging. Nonetheless, in the future, work should be focused on understanding a bismuth-enhanced lead-free solder system in thermal cycling and mechanical cycling reliability to understand the behavior of bismuth when reacting with a tin-based solder matrix such as the SAC system, thus assisting in cultivating the potential of bismuth in real-life industries and preventing unprecedented situations from happening in the future due to immature results.

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