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**Synergistic effects of In nanoparticle doping and ultrasonic assistance on the interfacial
microstructure and reliability of Sn58Bi/Ni solder joints**

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Abstract

In this study, In nanoparticles (NPs) were doped into Sn58Bi solder and Sn58Bi- x In/Ni ($x = 0, 0.05, 0.1, 0.2, 0.4, 1.0$ wt%) solder joints were fabricated on Ni substrates using ultrasonic-assisted soldering. The effects of In doping on the wettability, interfacial reactions, microstructure evolution, mechanical properties, and thermal shock reliability of the solder joints were systematically investigated. The results showed that the contact angle exhibited a non-monotonic variation with increasing In content, reaching a minimum of 8.9° at 0.1 wt% In and increasing to 19.1° at 1.0 wt% In. Thermal analysis revealed that 0.1-0.4 wt% In narrowed the melting interval and lowered the liquidus temperature, whereas excessive In (1.0 wt%) broadened the melting interval and increased undercooling to 21.4°C . The synergistic effect of In addition and ultrasonic cavitation/acoustic streaming optimally refined the Bi-rich phase and solder matrix grains at 0.1 wt% In, reducing the average grain size to $1.33\text{ }\mu\text{m}$. The interfacial intermetallic compound(IMC) layer was identified as Ni_3Sn_4 , with In substituting Sn to form $\text{Ni}_3(\text{Sn}, \text{In})_4$, and its compactness was maximized at 0.2 wt% In, whereas higher In contents caused scalloped coarsening. The shear strength first increased and then decreased with increasing In content, peaking at 33.61 MPa at 0.1 wt% In, accompanied by ductile dimple fracture. excessive In (1.0 wt%) led to brittle cleavage-dominated failure and a sharp drop in strength to 22.15 MPa. Under thermal shock, the Sn58Bi-0.1In/Ni joint exhibited suppressed IMC growth and Bi-rich phase coarsening after 400 cycles.

Keywords: In nanoparticles(NPs), ultrasonic-assisted soldering, Ni substrate, intermetallic compound(IMC)

1. Introduction

With the rapid miniaturization and high integration of modern electronic devices, low-temperature soldering technology has become increasingly important in advanced packaging applications[1, 2]. Sn58Bi solder, characterized by its low melting point, good wettability and relatively low cost, is widely recognized as one of the most promising lead-free solders for low-temperature electronic assembly[3]. However, its inherent brittleness and poor mechanical reliability significantly limit its long-term service performance, especially under complex service conditions such as thermal cycling and mechanical loading[4, 5]. Therefore, improving the microstructure and mechanical properties of Sn58Bi-based solder joints remains a critical issue for

practical electronic packaging applications[6].

Substrate metallization plays a decisive role in the interfacial reaction and mechanical performance of solder joints[7, 8]. Compared with conventional Cu substrates, Ni substrates show superior oxidation resistance and favorable reactivity with Sn-based solders, and form a more stable IMC layer. This effectively suppresses excessive IMC growth and enhances joint reliability[9]. Nevertheless, Sn58Bi/Ni joints still suffer from coarse matrix structure and insufficient mechanical strength. In recent years, nanoparticle reinforcement has been proven as an effective strategy to refine microstructure, inhibit IMC coarsening, and enhance mechanical performance. Among various reinforcements, In NPs show good compatibility with Sn-based solders and potential to improve ductility and interfacial bonding[10].

Ultrasonic-assisted soldering has emerged as an efficient and environmentally friendly joining method in electronic packaging[11]. It relies on ultrasonic cavitation and acoustic streaming effects. Ultrasonic vibration generates numerous cavitation bubbles in the molten solder, which violently collapse under alternating pressure, producing localized high temperature, high pressure, intense shockwaves and microjets. These mechanical impacts effectively strip surface oxides, promote solder spreading, refine grains and accelerate interfacial reactions[12, 13].

In this work, In NPs were mechanically incorporated into Sn58Bi solder as reinforcements to prepare Sn58Bi- x In ($x = 0, 0.05, 0.1, 0.2, 0.4, 1.0, 2.0, 4.0, 10$ wt%) composite solders. Composite solder joints on Ni substrates were fabricated via ultrasonic-assisted soldering. The effects of In addition on the melting characteristics and wettability of Sn58Bi solder on Ni substrates were examined to evaluate solderability. The microstructure evolution and interfacial intermetallic compound growth of the Sn58Bi- x In/Ni joints under ultrasonic-assisted soldering were analyzed, while shear tests were performed to assess joint mechanical performance. The mechanical properties of In-reinforced joints were comprehensively investigated, and the underlying strengthening mechanisms were elucidated.

2. Experimental Procedures

2.1. Materials

The experimental flowchart is illustrated in Fig. 1. In this study, In NPs with an average diameter of 300 ± 100 nm (Zhongke Yannuo Technology Co., Ltd.) and commercial Sn58Bi solder paste (MLM Material Co., Ltd., China) were used as raw materials. The composite solders were

prepared by mechanically stirring the solder paste with the In NPs in a solder paste mixer (AT-1000S) for at least 30 min to ensure homogeneity, yielding Sn58Bi- x In($x = 0, 0.05, 0.1, 0.2, 0.4, 1.0, 2.0, 4.0, 10$ wt%) composite solders. The prepared composite solders were placed onto Ni substrates with dimensions of $20 \times 20 \times 0.5 \text{ mm}^3$ and $10 \times 5 \times 0.5 \text{ mm}^3$. Prior to soldering, the Ni substrates were ground with 400# SiC paper to remove surface oxides, followed by ultrasonic cleaning in ethanol for 2 min. During soldering, the samples were positioned on a precision graphite hot plate (LCS-35plus, Shanghai Lichen Bangxi Instrument Technology Co., Ltd.). The composite solder paste was applied onto both ends of the Ni strips, and a 500 g weight was placed on top to prevent the solder paste from being displaced by the heating and ultrasonic oscillation. The hot plate was gradually heated to 200 °C and held for 2 min, during which ultrasonic vibration (20 kHz, 200 W) was applied for 30 s with the ultrasonic horn positioned vertically beneath the sample. After soldering, the samples were allowed to cool naturally in air. A portion of the as-soldered samples was subsequently subjected to thermal shock testing in a thermal shock chamber (GDC-8010, Shanghai Mousse Experimental Equipment Co., Ltd.) to examine the morphological changes of the solder joints under thermal cycling conditions. The thermal shock test was conducted using a rapid temperature cycling chamber, which consisted of high-temperature and low-temperature zones. The solder joints and shear specimens were placed in the chamber and subjected to a series of thermal shock cycles ranging from 200 to 400 cycles. The temperature profile reached extremes of 125 °C and -55 °C, with a dwell time of 15 min at each extreme. Thus, the duration of a single thermal shock cycle was 30 min.

2.2. Characterization and shear test

The morphology of the In NPs was characterized by scanning electron microscopy (SEM, Sigma 500, Zeiss), as shown in Fig. 1 (a)-(b). The melting behavior of the composite solders was investigated using differential scanning calorimetry (DSC, METTLER TGA 2). Wettability tests were conducted on solder joints formed on Ni substrates of $20 \times 20 \times 0.5 \text{ mm}^3$, and the contact angles were measured using an optical contact angle analyzer (Model CA200, Guangdong Hokuto Instruments Co., Ltd.). Each test was repeated 8-10 times, and the average value was taken as the final result. Two sizes of Ni substrates: $20 \times 20 \times 0.5 \text{ mm}^3$ and $10 \times 5 \times 0.5 \text{ mm}^3$ were employed for microstructural and mechanical characterization, respectively. For the joints on $20 \times 20 \times 0.5 \text{ mm}^3$ substrates, the solder joints were cut in half from the middle to expose the cross-section, then

mounted in epoxy resin. The mounted samples were sequentially ground with 400#, 600#, 1000#, 1200# and 1500# SiC papers, followed by polishing with a wool cloth to a mirror-like finish. Finally, the cross-sections were etched with a solution containing 90% ethanol and 10% nitric acid for SEM observation of the interfacial microstructure and IMC layer. To observe the IMC grains, the joints on $20 \times 20 \times 0.5 \text{ mm}^3$ substrates were thinned by mechanical grinding and subsequently etched in an ultrasonic bath containing a solution of 80% ethanol and 20% nitric acid. The IMC grains were then examined by SEM, and the average grain size was determined using ImageJ software. The IMC thickness and grain size values reported here are averages calculated from measurements taken from five different regions per sample. For shear strength testing, lap shear tests were performed on specimens with dimensions of $10 \times 5 \times 0.5 \text{ mm}^3$ using a tensile testing machine (Model DR-508A, Dongguan Dongri Instrument Co., Ltd.) at a tensile speed of 2 mm/min. Each test was repeated 6-8 times, and the average value was adopted as the final result. The fracture surfaces were subsequently examined and analyzed by SEM.

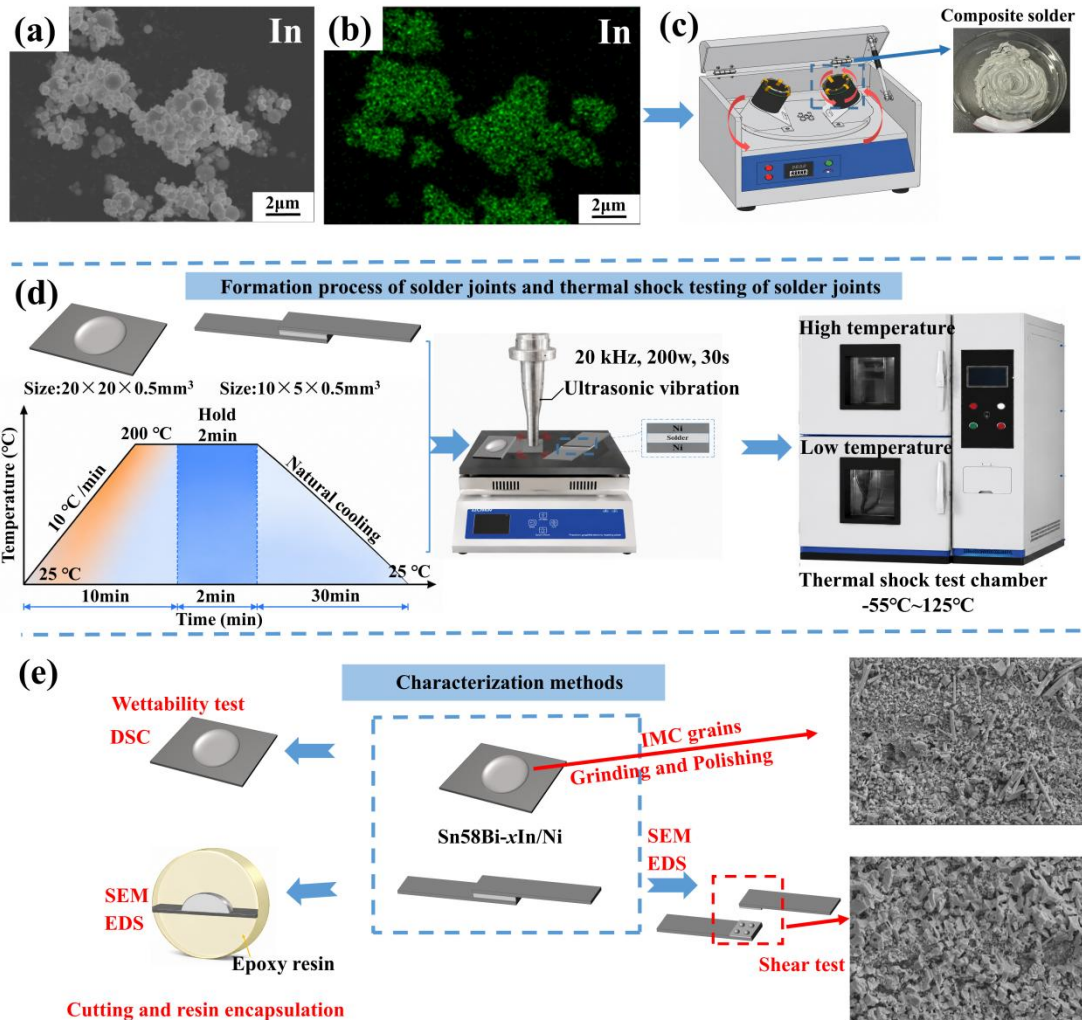


Fig. 1 Experimental Flowchart.(a)-(b) SEM morphology and EDS elemental distribution of In NPs. (c) Composite solder prepared by mechanical stirring of In NPs and Sn58Bi solder. (d) Formation process of solder joints and thermal shock test. (e) Characterization methods for as-welded joints and joints after thermal shock treatment.

3. Results and Discussion

3.1. Wettability

To identify the optimal In addition level, we first evaluated the wettability of the composite Sn58Bi solders. As shown in Fig. 2, the contact angle of Sn58Bi- x In solders on Ni substrates rises significantly from 13.1° to 68.8° when the In content increases from 0 wt% to 10 wt%, indicating a clear deterioration in wettability, which is likely caused by increased viscosity of the molten solder upon In addition. Focusing on the practical range of 0-1.0 wt% In, however, the contact angle follows a non-monotonic trend, it first decreases from 13.1° to a minimum of 8.9° at 0.1 wt% In, and then increases again to 19.1° at 1.0 wt% In. The initial drop at low In levels (≤ 0.1 wt%) is attributed to the surface-active nature of In, which reduces the surface tension and interfacial energy, promoting better wetting. The subsequent rise with higher In content is mainly due to increased melt viscosity and nanoparticle agglomeration, which hinder the spreading of the molten solder[14]. Given that contact angles of 20° or below are generally considered acceptable for practical applications[15], we selected 1.0 wt% as the maximum In addition level for the fabrication of composite Sn58Bi solder joints in subsequent experiments.

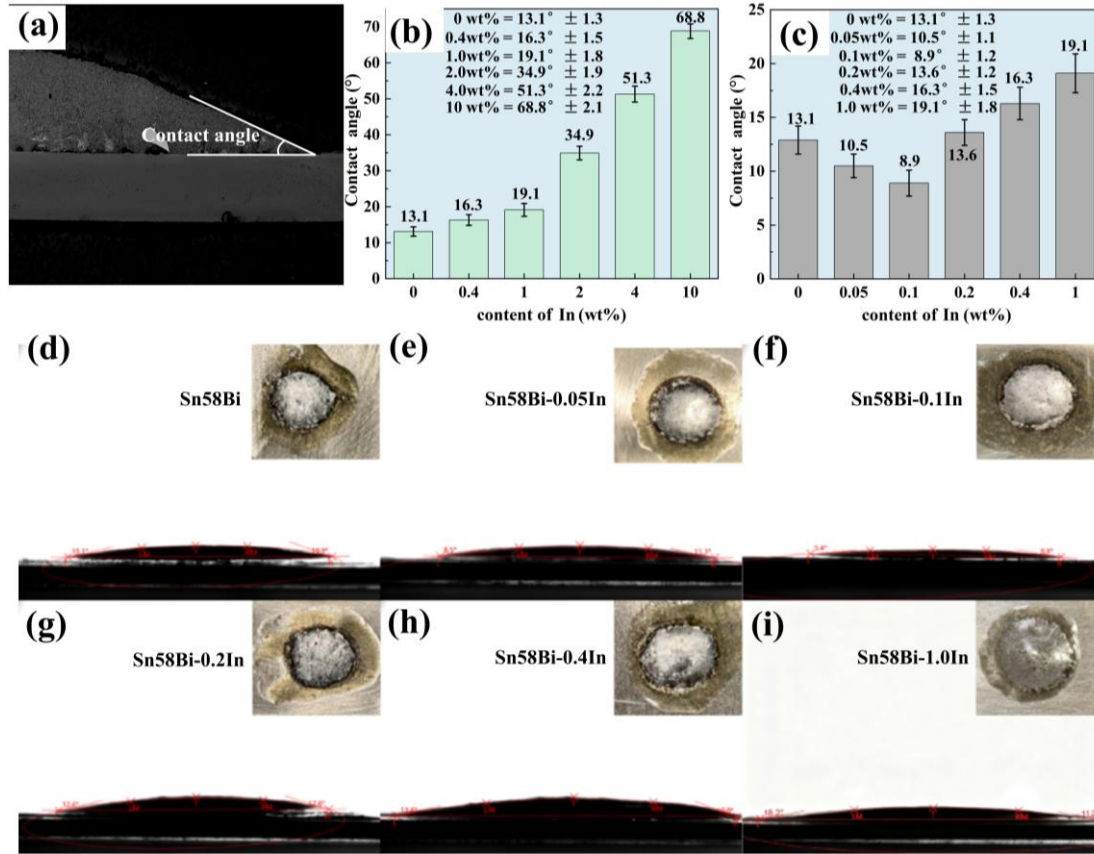


Fig. 2 Contact angle of Sn58Bi-xIn solders on Ni substrates. (a) Observation diagram of contact angle measured by optical contact angle measuring instrument under optical microscope. (b)-(c) Effects of In doping content on contact angle. (d)-(i) Wetting morphology of solders with different In addition amounts on Ni substrate.

3.2. Melting characteristics

The DSC results show that the melting and solidification behaviors of Sn58Bi composite solders can be effectively tuned by indium addition, especially under the combined effect of ultrasonic-assisted soldering on Ni substrates. As summarized in Table 1 and shown in Fig. 3 (a)-(f), pure Sn58Bi presents a melting onset temperature T_S of 138.2 °C and a peak temperature T_M of 144.3 °C, and low-level 0.05 wt% In addition slightly raises its melting peak to 146.2 °C along with mild increases in T_S and liquidus temperature T_L , which is closely associated with the solid-solution effect of In and the redistribution of Bi-rich phases driven by ultrasonic vibration. when In content rises to 0.1-0.4 wt%, the melting interval (T_L - T_S) is greatly narrowed from the original 12.2 °C to 7.1-7.3 °C and T_L decreases to 147.7-148.7 °C, proving better compositional uniformity inside the solder, since ultrasonic cavitation and acoustic streaming accelerate element diffusion to refine Sn-

Bi-In microstructure and interfacial reactions between solder and Ni substrate further optimize phase distribution and thermal response, whereas excessive 1.0 wt% In reverses this variation trend, lowering melting onset temperature to 135.8 °C and broadening melting interval to 14.6 °C due to the formation of local low-melting zones that damage thermal uniformity. In terms of solidification characteristics displayed in Fig. 2 (g)-(l), the crystallization onset temperature T_C stays stable at 121.0-122.1 °C with low and medium In doping content yet falls sharply to 114.6 °C at 1.0 wt% In, and the undercooling (T_S-T_C) gradually rises with increasing In content, peaking at 21.4 °C at 1.0 wt% In, this obvious undercooling originates from solute segregation of In and is further intensified by ultrasonic stirring, which restrains the nucleation of primary Bi-rich phase.

Table 1 Melting parameters of composite solder alloys.

Solders	T_S (°C)	T_M (°C)	T_L (°C)	T_C (°C)	T_L-T_S (°C)	T_S-T_C (°C)
Sn58Bi	138.2	144.3	150.4	123.0	12.2	15.2
Sn58Bi-0.05In	139.8	146.2	152.2	121.4	12.4	18.4
Sn58Bi-0.1In	141.4	145.2	148.7	121.0	7.3	20.4
Sn58Bi-0.2In	140.6	144.2	147.7	119.3	7.1	21.3
Sn58Bi-0.4In	141.4	145.2	148.7	122.1	7.3	19.3
Sn58Bi-1.0In	135.8	144.0	150.4	114.6	14.6	21.4

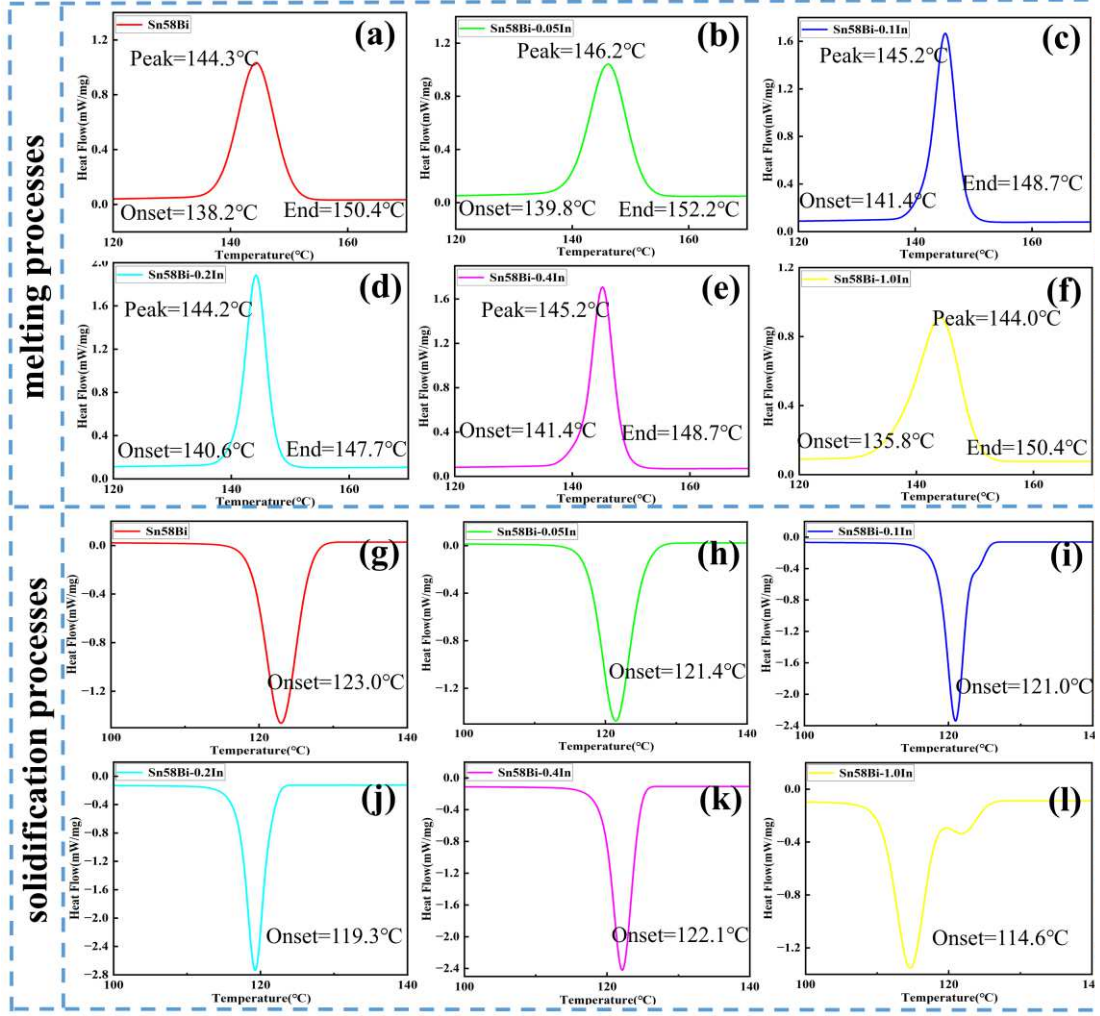


Fig. 3 DSC image analysis of Sn58Bi-xIn. (a)-(e) and (g)-(l) are the melting process and solidification process, respectively.

3.3. Microstructure

The morphological evolution of the Bi-rich phase in ultrasonic-assisted Sn58Bi-xIn solder joints fabricated on a Ni substrate is presented in Fig. 4. The undoped Sn58Bi solder exhibits coarse and irregular Bi-rich phase domains with uneven distribution, and ultrasonic treatment alone is insufficient to eliminate these intrinsic coarse structures, as confirmed by the magnified view in Fig. 4 (a1). A low In addition of 0.05 wt% yields only a marginal refining effect through the coupling of In modification and the ultrasonic field, whereas the synergistic action is remarkably optimized at 0.1 wt% In, generating significantly refined and uniformly dispersed Bi-rich phase (Fig. 4 c1). The underlying refinement mechanisms are schematically illustrated in Fig. 5. As shown in Fig. 5 (a), during the solidification of pure Sn58Bi solder, the Bi-rich phase grows freely into large, irregular structures without solute modification or external field intervention. In contrast, with In addition

(Fig. 5 b), In atoms segregate at the solidification front to promote fine-grain nucleation. When combined with ultrasonic vibration (Fig. 5 c), the cavitation effect generates high-pressure shockwaves and micro-jets that physically fragment the growing Bi-rich phase structures, while acoustic streaming induces forced melt convection to further homogenize solute distribution and restrict the continuous growth of Bi-rich phases, preventing the formation of large-scale connected frameworks[16]. The dynamic behavior of cavitation bubbles can be described by the modified Rayleigh-Plesset equation(1)[17, 18]:

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho} \left[\left(P_0 + \frac{2\sigma}{R_0} \right) \left(\frac{R_0}{R} \right)^{3n} - P_A - P_0 - \frac{2\sigma}{R} - \frac{4\mu}{R} \dot{R} \right] \quad (1)$$

where R is the instantaneous radius of the cavitation bubble, $\dot{R}$ and $\ddot{R}$ are the radial velocity and acceleration of the bubble wall, respectively, ρ is the density of the molten Sn58Bi solder, P_0 is the ambient hydrostatic pressure in the liquid, R_0 is the initial radius of the cavitation nucleus, σ is the surface tension of the molten solder, n is the polytropic index of the gas inside the bubble, P_A is the amplitude of the applied ultrasonic pressure, and μ is the dynamic viscosity of the molten solder. Further increasing the In content to 0.2-0.4 wt% maintains the refined microstructure without additional structural improvement, indicating that the synergistic refining effect reaches saturation. However, excessive In doping of 1.0 wt% markedly coarsens the Bi-rich morphology, where large and irregular Bi-rich phase structures reappear even under continuous ultrasonic excitation (Fig. 4 f1). Such structural deterioration originates from the increased melt viscosity caused by superfluous In solute, which severely attenuates bubble oscillation, weakens cavitation collapse intensity and acoustic streaming agitation efficiency, and ultimately enables the regrowth of coarse Bi-rich phases.

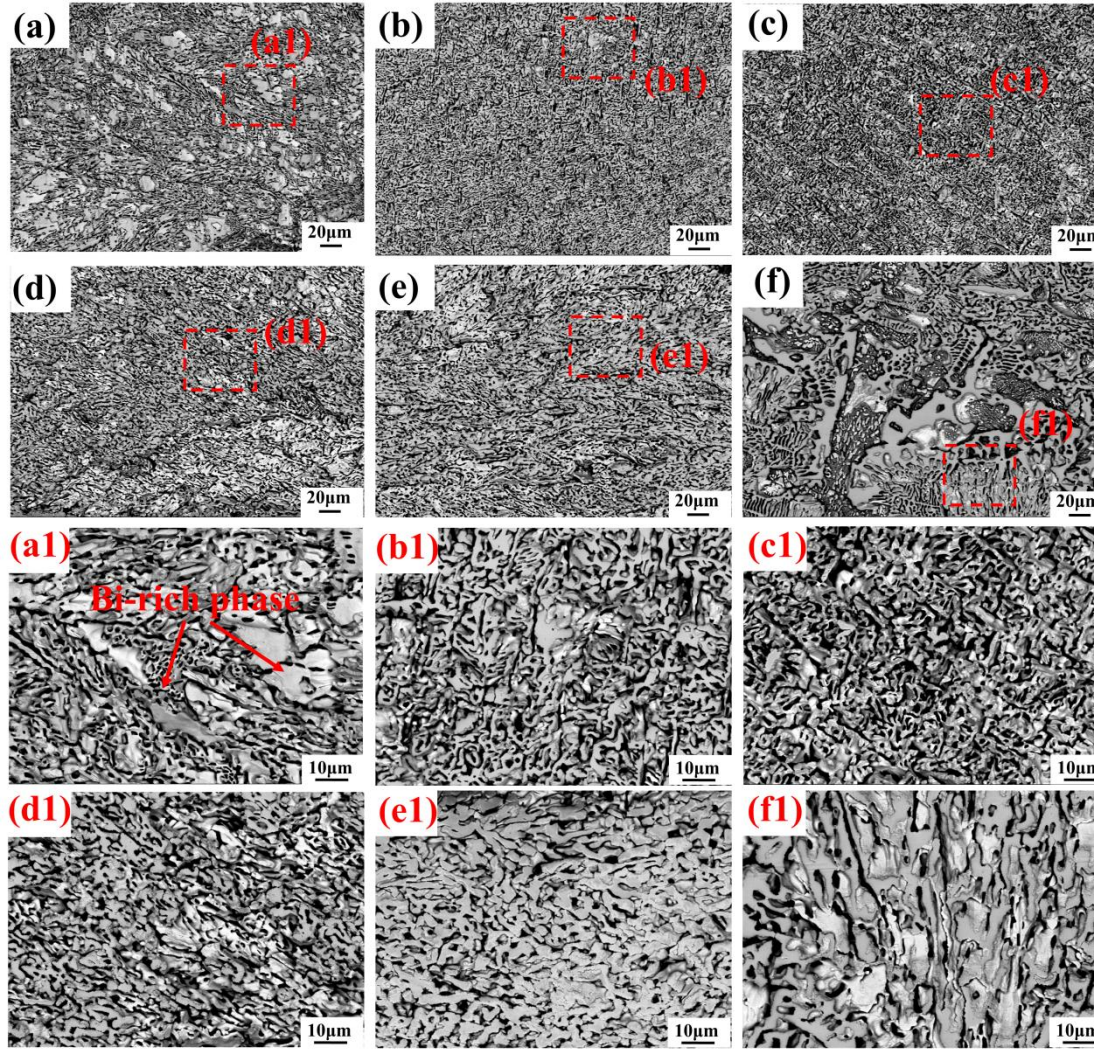


Fig. 4 Microstructure of Sn58Bi-xIn/Ni solder joints. (a)-(f) show the microstructures of composite solder joints with In contents of 0, 0.05, 0.1, 0.2, 0.4, and 1.0 wt%, respectively. (a1)-(f1) are the corresponding magnified views of the selected regions.

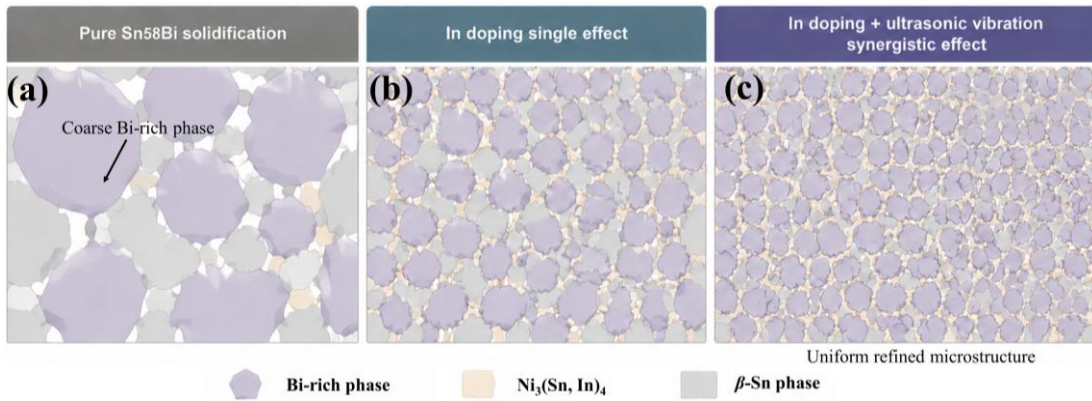


Fig. 5 Schematic mechanism of microstructure evolution of Sn58Bi solder joints under

combined In doping and ultrasonic action. (a)Pure Sn58Bi solidification (b)In doping single effect (c)In doping and ultrasonic vibration synergistic effect.

3.4. Interfacial layer and grains

Fig. 6 and 7 systematically present the IMC morphology evolution and the corresponding elemental distributions of Sn58Bi/Ni solder joints with varying In contents under ultrasonic-assisted soldering conditions. Under the influence of the ultrasonic field, the evolution of the IMC layer depends not only on the In content but is also significantly modulated by ultrasonic cavitation and acoustic streaming effects[19]. As the In content increases from 0 to 1.0 wt%, the IMC layer exhibits pronounced changes in both thickness and uniformity. In the In-free joint (Fig. 6 a, a1), the IMC layer is relatively thin and irregularly shaped, which is attributable to the fact that although ultrasonic action can disrupt the initial interfacial oxides and promote wetting, the IMC growth rate is suppressed in the absence of In addition[14, 20]. With the addition of 0.05 wt% In (Fig. 6 b, b1), the layer becomes more continuous and uniform. This improving trend continues up to 0.2 wt% In (Fig. 6d, d1), at which point the IMC layer reaches its maximum compactness and thickness, indicating a synergistic strengthening effect between ultrasonic-assisted soldering and an appropriate amount of In doping—the acoustic streaming promotes rapid transport of In atoms toward the interface, while the addition of In further stabilises the IMC growth front by reducing the interfacial energy[21]. However, when the In content is further increased to 0.4 and 1.0 wt% (Fig. 6 e, f and Fig. 6 e1, f1), the IMC layer exhibits coarsening, appearing as a scalloped and uneven interface, suggesting that excessive In disrupts the interfacial reaction of the IMC[22]. Moreover, the mechanical impingement of the ultrasonic field may exacerbate interfacial perturbation in the presence of excess solute. To gain a deeper understanding of the IMC growth kinetics, the thickness evolution of the IMC layer can be described by the classical diffusion-controlled growth model equation(2)[23, 24] :

$$X = X_0 + A \cdot t^n \cdot e^{\left(-\frac{Q}{RT}\right)} \quad (2)$$

where X is the IMC layer thickness at time t , X_0 is the initial IMC thickness, A is a pre-exponential constant, n is the time exponent, Q is the activation energy for IMC growth,

R is the ideal gas constant, and T is the absolute temperature. The time exponent n serves as a critical indicator of the growth mechanism: when $n \approx 0.5$, the growth is diffusion-controlled. when $n \approx 1$, it is interfacial reaction-controlled[23]. In the present work, the calculated n values for the In-free and low-In (<0.2 wt%) joints are approximately 0.5, suggesting that the IMC growth is governed by atomic diffusion. However, upon increasing the In content to 1.0 wt%, the n value deviates significantly from 0.5, implying a transition in the rate-controlling step—possibly toward interfacial reaction control—as excessive solute accumulation may alter the local chemical potential gradient at the reaction front.

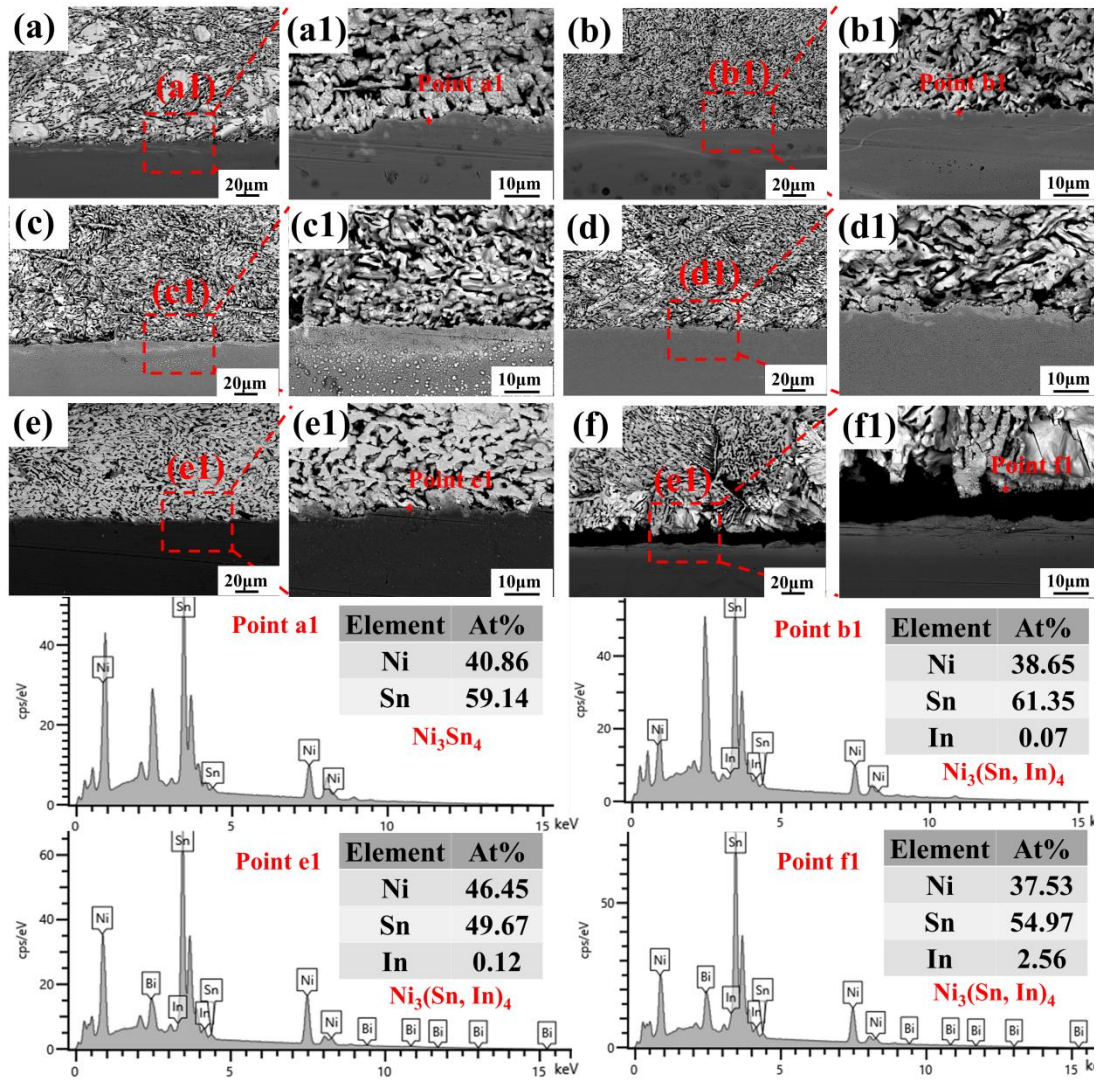


Fig. 6 IMC layer of Sn58Bi-xIn/Ni solder joints. (a)-(f) display the interfacial IMC morphology of solder joints prepared with composite solders containing 0, 0.05, 0.1, 0.2, 0.4 and 1.0 wt% In, respectively. (a1)-(f1) are the corresponding enlarged views of IMC layers. The EDS analysis at points

a1, b1, e1 and f1 is performed on the regions marked in (a1), (b1), (e1) and (f1).

EDS point analyses conducted at positions Fig. 6 a1, b1, e1 and f1 (marked in the corresponding magnified images) confirm that the IMC phase consistently maintains a Ni_3Sn_4 matrix, with In substituting Sn to form a $\text{Ni}_3(\text{Sn}, \text{In})_4$ solid solution. The In contents measured at these points are 0, 0.07, 0.12 and 2.56 at%, respectively, while the Ni/Sn atomic ratio consistently remains close to 3:4, indicating that In preferentially occupies the Sn sublattice. This substitution behaviour is corroborated by the EDS mapping results in Fig. 7. For all joints, the Ni and Sn signals overlap precisely at the interfacial region, confirming that this layer is a Ni-Sn IMC. Notably, in the specimens containing 0.1 and 1.0 wt% In, the In elemental maps show clear enrichment within the IMC zone, which is in good agreement with the point analysis data. In contrast, the Bi distribution (Fig. 7 a2-c2) remains uniformly dispersed in the solder matrix, with no detectable segregation at the IMC layer, indicating that Bi does not participate in the interfacial reaction and that its partitioning behaviour is not influenced by either In addition or ultrasonic-assisted soldering[25]. In addition, the acoustic streaming effect introduced by ultrasonication significantly enhances the spreading ability of the molten solder on the Ni substrate, leading to a more uniform enrichment of In atoms at the interface[26].

The grain structure of the solder matrix and its average grain size variation are illustrated in Fig. 8 (a)-(g). The In-free joint exhibits relatively coarse and irregular grains (Fig. 8 a), whereas under ultrasonic-assisted soldering conditions, the cavitation effect itself already exerts a certain grain-refining influence[19]. With increasing In addition, the grains gradually refine and become more equiaxed under the coupled effect of the ultrasonic field and In doping[22], reaching a minimum average size of 1.33 μm at 0.1 wt% In, compared with 1.65 μm for the undoped solder. This indicates that the transient high-energy impact provided by ultrasonication promotes the detachment and dispersion of numerous fine IMC particles, which together with the In addition provide abundant heterogeneous nucleation sites[27], thereby achieving an optimal grain refinement effect. Beyond this optimal content, however, the grain size increases monotonically to 1.50 μm at 0.4 wt% In and further to 1.74 μm at 1.0 wt% In (Fig. 8 g). This non-monotonic behaviour suggests that an appropriate amount of In (0.1 wt%) in synergy with ultrasonic-assisted soldering provides the most effective grain refinement, whereas higher In concentrations promote grain coarsening.

This is likely because excess solute atoms weaken the intensity of ultrasonic cavitation while simultaneously enhancing atomic diffusion rates, resulting in a prevailing grain growth tendency[1, 28]. The EDS analysis at point f marked in Fig. 8 (f) confirms the presence of Ni, Sn and In, indicating that the elongated grains are $\text{Ni}_3(\text{Sn}, \text{In})_4$. This ternary phase can serve as heterogeneous nucleation sites during solidification, and the mechanical vibration effect of ultrasonication further promotes its uniform dispersion in the matrix, thereby significantly enhancing the refinement efficiency. In summary, the synergistic effect of ultrasonic-assisted soldering and an appropriate amount of In doping achieves the optimal interfacial microstructure regulation at 0.1 wt% In, whereas excessive doping leads to coarsening and regression of both the IMC layer and the grain structure, owing to the combined influence of nonlinear ultrasonic effects and solute supersaturation.

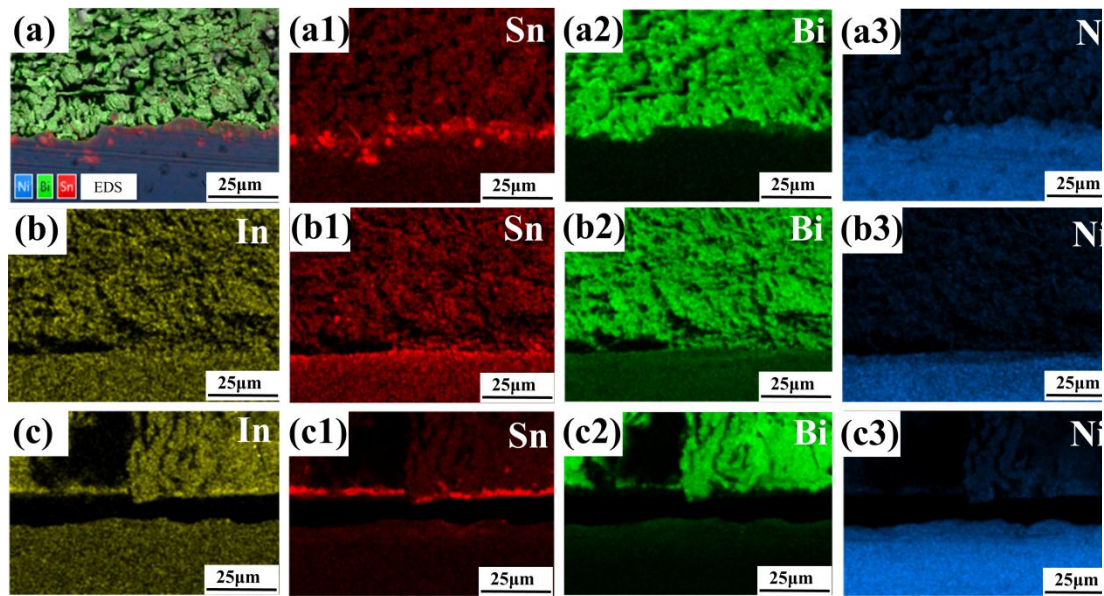


Fig. 7 EDS elemental distribution mappings of interfacial IMC layers. (a)-(a3), (b)-(b3), (c)-(c3) represent joints soldered by Sn58Bi solders containing 0, 0.1 and 1.0 wt% In.

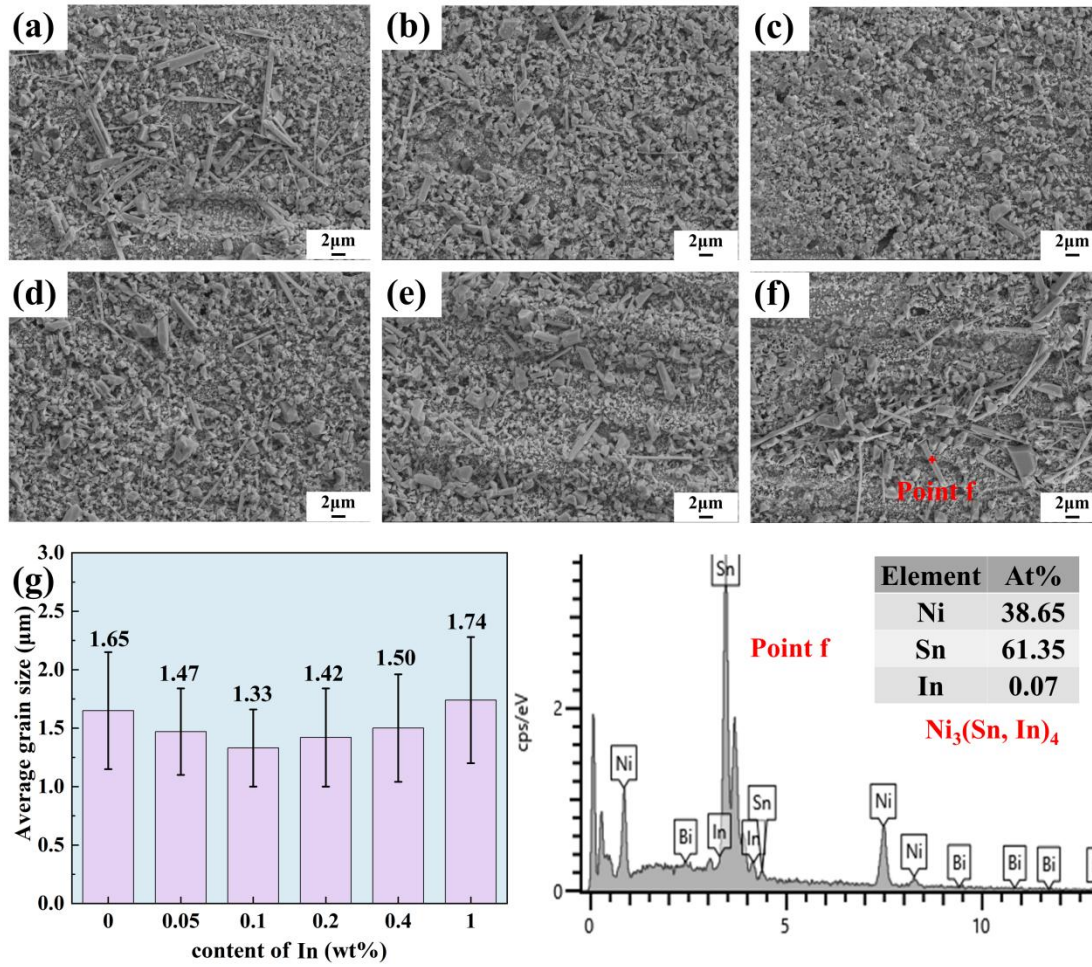


Fig. 8 Grain microstructure of soldered joints. (a)-(f) correspond to solders doped with 0, 0.05, 0.1, 0.2, 0.4 and 1.0 wt% In. (g) illustrates the average grain size. The marked Point f in (f1) was characterized by EDS.

3.5. Mechanical properties and fracture morphology

The mechanical performance and fracture behavior of Sn58Bi- x In/Ni solder joints are presented in Fig. 9 and Fig. 10, respectively. The average shear strength initially increases from 30.44 MPa for the In-free joint to 31.89 MPa at 0.05 wt% In, reaching a maximum of 33.61 MPa at 0.1 wt% In. Further addition to 0.2, 0.4 and 1.0 wt% In causes a continuous decrease to 29.92, 26.73 and 22.15 MPa, respectively (Fig. 9). This non-monotonic variation is directly reflected in the fracture morphologies (Fig. 10). The In-free joint (Fig. 10 a) displays a relatively flat fracture surface with shallow dimples, suggesting a mixed ductile-brittle failure mode. At 0.05 wt% In (Fig. 10b) and particularly at 0.1 wt% In (Fig. 10 c), the fracture surfaces become rougher and covered with a dense network of fine, deep dimples (Fig. 10 b1, c1), indicative of predominantly ductile fracture

where cracks propagated through the solder matrix accompanied by substantial plastic deformation—consistent with the highest strength at 0.1 wt% In. In contrast, at In contents of 0.2 wt% and above (Fig. 10 d-f), the fracture surfaces gradually flatten and feature fewer and shallower dimples. At 0.4 wt% In (Fig. 10 e, e1) and especially at 1.0 wt% In (Fig. 10 f, f1), cleavage-like facets and interfacial debonding become apparent, signalling a transition toward brittle fracture with crack propagation preferentially along the IMC layer or the IMC/solder interface. The EDS analysis at point b2 (Fig. 10 b2) confirms the presence of Ni, Sn and In with the stoichiometry of $\text{Ni}_3(\text{Sn}, \text{In})_4$, indicating that the IMC phase remains the dominant reaction product even at the fracture surface. The further magnified images in Fig. 10 a2, b2 and f2 provide additional microstructural details: in the In-free joint (Fig. 10 a2), the dimples contain a mixture of exposed and embedded grains, suggesting incomplete separation along grain boundaries. At 0.05 wt% In (Fig. 10 b2), the dimples are densely populated with well-defined, plump grains, reflecting extensive plastic deformation and good ductility. At 1.0 wt% In (Fig. 10 f2), however, the dimples appear conspicuously sparse, with significantly fewer and less distinct grains, indicating a reduction in ductility and a shift toward brittle failure, which directly accounts for the dramatic strength drop at this composition.

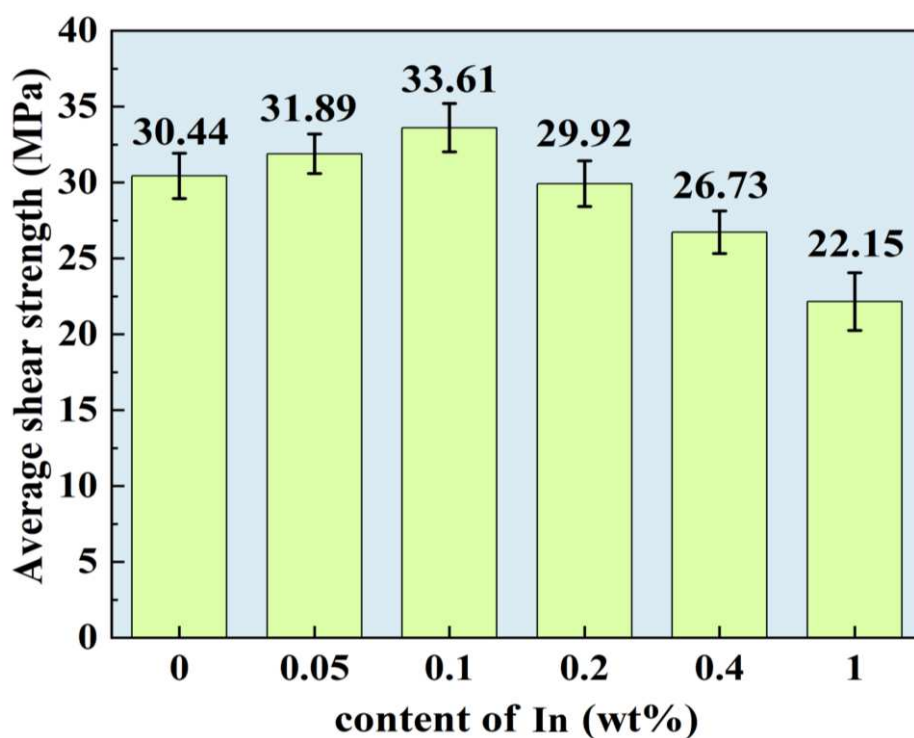


Fig. 9 The average shear strength of Sn58Bi-xIn/Ni solder joints.

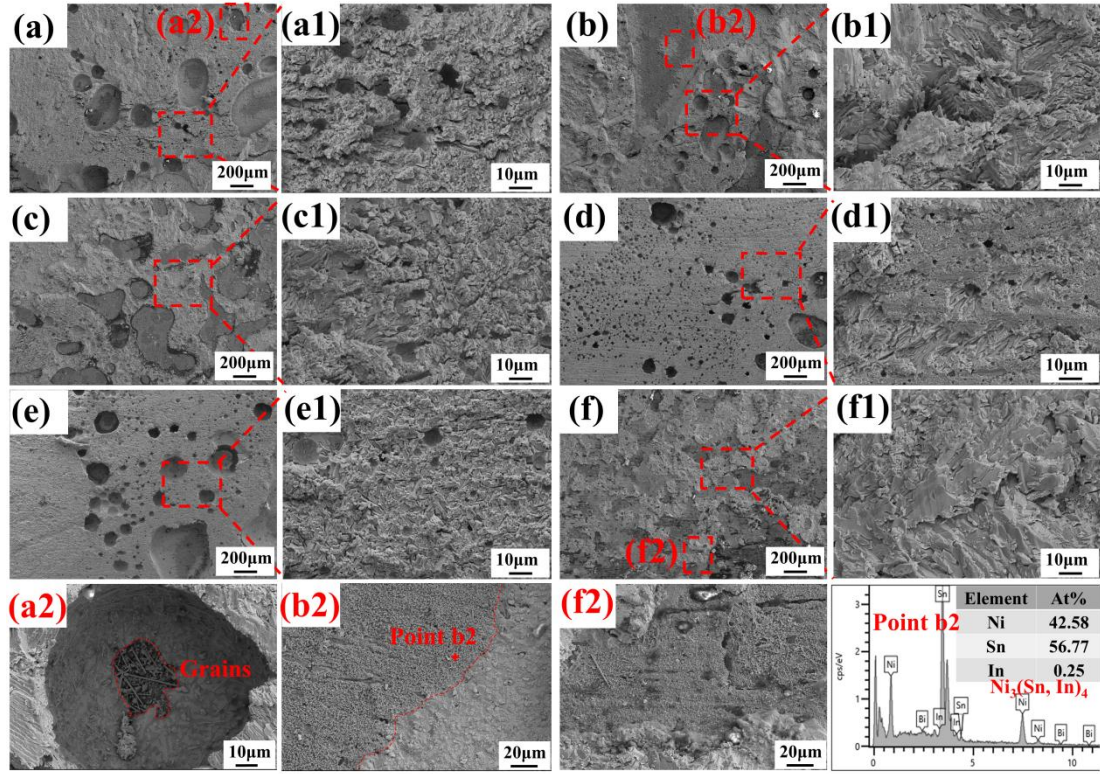


Fig. 10 Fracture morphology of Sn58Bi-xIn/Ni solder joints. (a)-(f) Fracture morphologies of solder joints doped with 0, 0.05, 0.1, 0.2, 0.4 and 1.0 wt% In, respectively. (a1)-(f1) Corresponding magnified views of the regions marked in (a)-(f). (a2), (b2) and (f2) Further magnified views of the regions in (a), (b) and (f), respectively.

3.6. Interface layer and microstructure after thermal shock

As shown in Fig. 11, the interfacial IMC layer of the Sn58Bi/Ni solder joint exhibits significant coarsening and thickening with increasing thermal shock cycles. After 400 cycles, the IMC layer becomes highly irregular and even shows signs of localized cracking, indicating a clear degradation in interfacial stability. In contrast, the Sn58Bi-0.1In/Ni joint shows considerably retarded IMC growth under the same conditions. even after 400 cycles, the IMC layer remains relatively thin and continuous, suggesting that the addition of 0.1 wt% In effectively suppresses excessive interfacial reaction[29]. This suppression is further supported by the EDS mapping results in Fig. 12, which reveal a more uniform elemental distribution at the interface of the In-containing solder, with reduced segregation of Sn and Bi. The presence of In likely modifies the interfacial energy and atomic diffusivity, thereby inhibiting the rapid formation of Ni-Sn IMC. Meanwhile, the cavitation effect of ultrasound promotes initial wetting and the formation of a thin, continuous IMC layer,

while its acoustic streaming effect facilitates a more homogeneous dispersion of In NPs in the molten solder, ensuring that the In-induced suppression of IMC growth is sustained throughout the subsequent thermal shock exposure[14, 30]. As a result, the combined effect of In doping and ultrasonic treatment endows the solder joint interface with enhanced stability under thermal shock.

Fig. 13 presents the evolution of the internal Bi-rich phase morphology and the corresponding shear strength of both solder joints. For the Sn58Bi/Ni joint, thermal shock gradually coarsens the Bi-rich phase and makes its distribution increasingly non-uniform. after 400 cycles, the Bi-rich phase shows clear aggregation and localized segregation (Fig. 13 a-c). The excessive growth and cracking of the interfacial IMC layer, together with the coarsening and segregation of the internal Bi-rich phase, jointly contribute to the decrease in shear strength from 30.46 MPa to 27.24 MPa after 400 cycles. In the Sn58Bi-0.1In/Ni joint, by contrast, the Bi-rich phase retains a finer size and more uniform distribution even after prolonged thermal shock, with significantly less coarsening (Fig. 13 d-f). meanwhile, the interfacial IMC layer does not exhibit obvious overgrowth or cracking. Its shear strength drops from 33.58 MPa to 29.85 MPa after 400 cycles. This improved microstructural stability and interfacial integrity can be attributed to the refining effect of In, which suppresses Bi segregation and coarsening, while the ultrasonic vibration during soldering further promotes uniform dispersion of In NPs and refines the overall matrix structure[30, 31]. The synergy between the two effectively mitigates thermal fatigue damage, thereby preserving both interfacial integrity and mechanical reliability of the solder joint under thermal shock conditions.

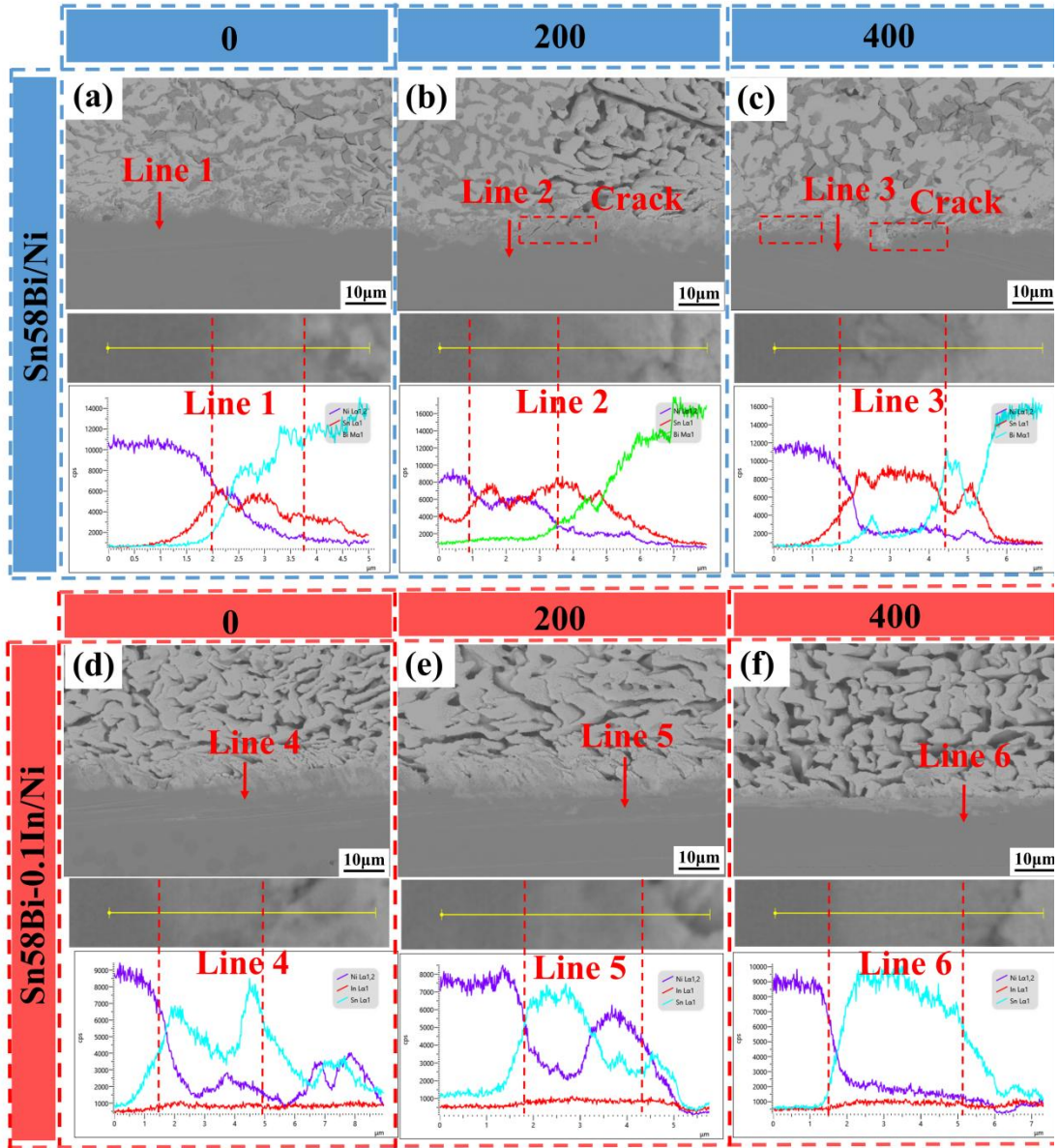


Fig. 11 IMC layer of Sn58Bi-xIn/Ni solder joints under thermal shock. (a) - (c) represents the 0, 200, and 400 cycles of Sn58Bi/Ni solder joints under thermal shock. (d) - (e) represents the 0, 200, and 400 cycles of Sn58Bi-0.1In/Ni solder joint under thermal shock.

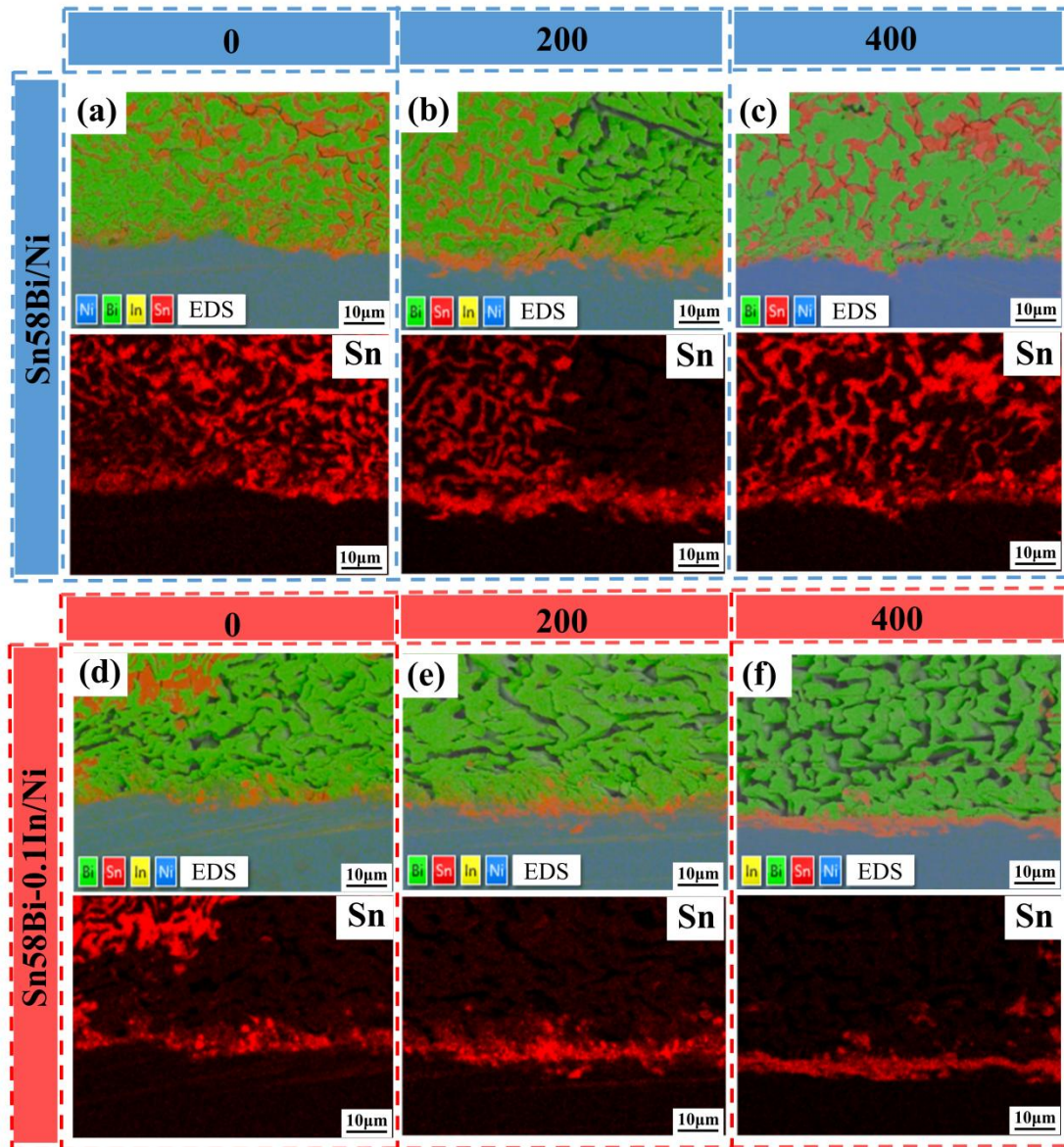


Fig. 12 EDS analysis of IMC layer of Sn58Bi-xIn/Ni solder joint under thermal shock, corresponding to Fig. 11.

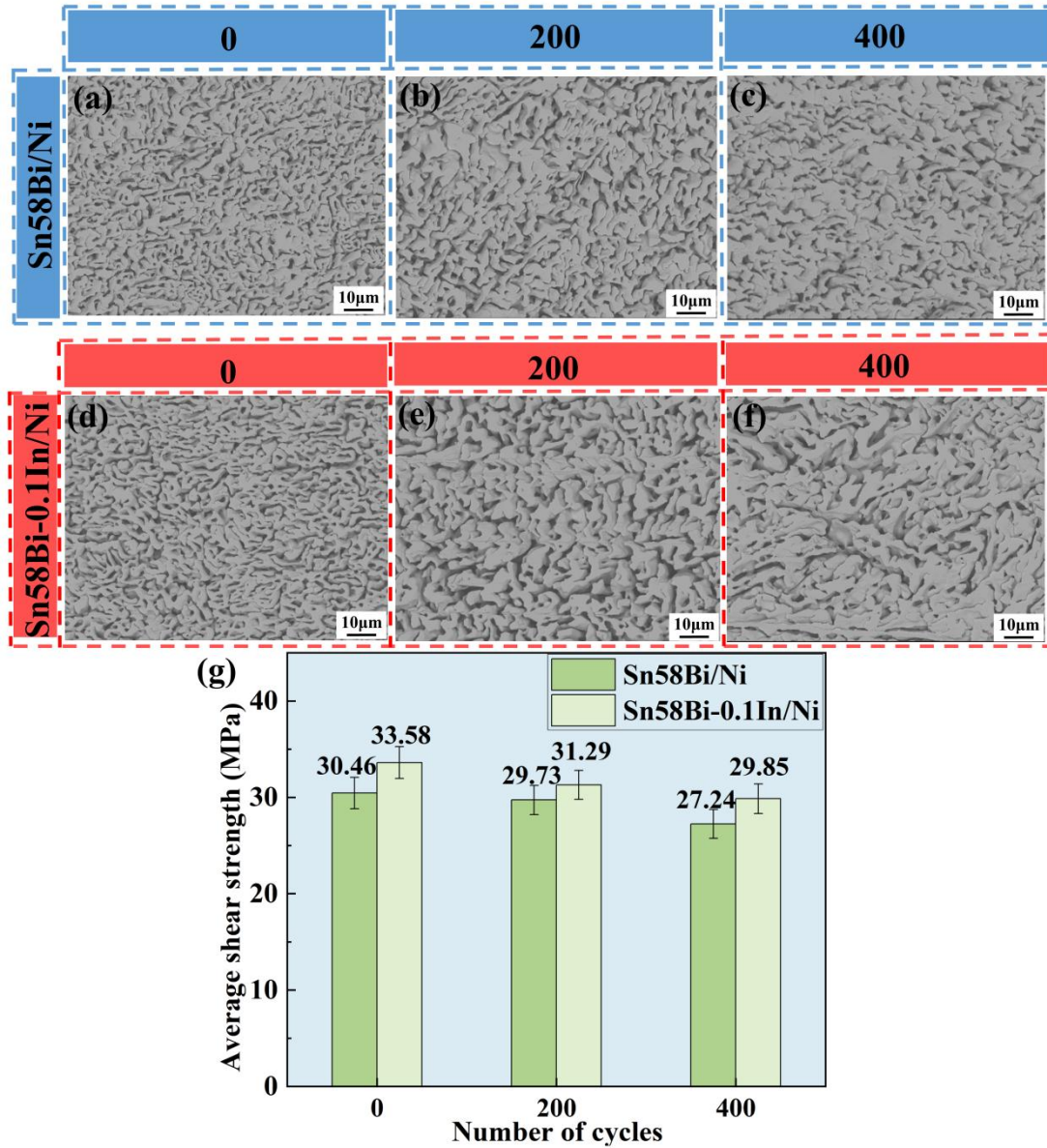


Fig. 13 Microstructure of Sn58Bi-xIn/Ni solder joints under thermal shock. (a) - (c) represents the 0, 200, and 400 cycles of Sn58Bi/Ni solder joints under thermal shock. (d) - (f) represents the 0, 200, and 400 cycles of Sn58Bi-0.1In/Ni solder joint under thermal shock. (g) the average shear strength of each solder joint under different numbers of thermal shocks.

4. Conclusion

In this study, we systematically investigated the effects of In NPs doping and ultrasonic-assisted soldering on the wettability, interfacial microstructure, IMC evolution, mechanical properties, and thermal stability of Sn58Bi/Ni solder joints:

- (1) With increasing In content, the contact angle initially decreases and then increases, reaching a

minimum of 8.9° at 0.1 wt% In. Thermal analysis reveals that 0.1-0.4 wt% In narrows the melting interval and lowers the liquidus temperature, while 1.0 wt% In broadens the melting interval and increases undercooling.

(2) The Bi-rich phase in Sn58Bi/Ni solder joints is significantly refined and uniformly dispersed at 0.1 wt% In through the synergy of In-induced nucleation and ultrasonic cavitation/acoustic streaming, whereas excessive In (1.0 wt%) causes coarsening due to increased melt viscosity that weakens cavitation intensity. The refining effect saturates at 0.2-0.4 wt% In without further improvement.

(3) The IMC layer in Sn58Bi/Ni solder joints reached its maximum compactness at 0.2 wt% In due to the synergy of ultrasonic acoustic streaming and In-induced interfacial energy reduction, while excessive In (≥ 0.4 wt%) caused scalloped coarsening. EDS analyses confirmed that In substituted Sn in the Ni_3Sn_4 lattice to form $\text{Ni}_3(\text{Sn}, \text{In})_4$, with Bi remaining uniformly distributed without interfacial segregation. Grain refinement was optimized at 0.1 wt% In (1.33 μm), whereas higher In contents weakened cavitation intensity and promoted coarsening.

(4) The shear strength of Sn58Bi-xIn/Ni solder joints exhibits a non-monotonic trend with In content, peaking at 33.61 MPa for 0.1 wt% In and then declining to 22.15 MPa at 1.0 wt% In. Fracture surface analysis reveals a transition from ductile dimple fracture at low In levels to brittle cleavage-dominated failure at high In contents, consistent with the strength variation. The $\text{Ni}_3(\text{Sn}, \text{In})_4$ phase remains the dominant interfacial reaction product across all compositions.

(5) The Sn58Bi-0.1In/Ni joint exhibits significantly suppressed IMC growth and Bi-rich phase coarsening under thermal shock compared with the In-free joint, maintaining a more uniform interfacial structure. Consequently, its shear strength decreases only moderately from 33.58 MPa to 29.85 MPa after 400 cycles, whereas the In-free joint drops from 30.46 MPa to 27.24 MPa. This enhanced thermal stability is attributed to the combined effects of In-induced refinement and ultrasonic-assisted uniform dispersion.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Data Availability Statement

The raw and processed experimental data that support the findings of this study are not publicly available

due to internal laboratory constraints. Reasonable requests for data can be directed to the corresponding author.

Author Contribution declaration

Xiao-bin Zhang: Conceptualization, Investigation, Writing-Original Draft, Formal Analysis, Review & Editing;

Liang Zhang: Methodology, Supervision, Review & Editing;

Wei-min Long: Investigation, Formal Analysis;

Yu-hao Chen: Visualization, Data Curation;

Yu-jing Qiu: Formal Analysis, Validation;

Tao Liu: Methodology, Review & Editing

Highlights

(1) With increasing In content, the contact angle initially decreases and then increases, reaching a minimum of 8.9° at 0.1 wt% In. Thermal analysis reveals that 0.1-0.4 wt% In narrows the melting interval and lowers the liquidus temperature, while 1.0 wt% In broadens the melting interval and increases undercooling.

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