Microstructure evolution, IMC growth, and microhardness of Cu, Ni, Ag-microalloyed Sn–5Sb/Cu solder joints under isothermal aging

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ABSTRACT

In this work, various Cu, Ni, Ag-microalloyed Sn–5Sb/Cu joints, ordinary Sn–5Sb/Cu joints, and low-melting-point Sn–3Ag–0.5Cu (SAC305)/Cu (used for comparison) were prepared, focusing on the influence of Cu, Ni, and Ag on the microstructure evolution, interfacial IMC growth, and microhardness of Sn–5Sb/Cu joint under long-time isothermal aging process. Results showed that the microstructure of microalloyed joints consisted of b-Sn matrix, SbSn, and (Cu, Ni)₆Sn₅ and Ag₃Sn compounds. (Cu, Ni)₆Sn₅ compounds generated a coarsening effect in the aging microalloyed joints, yet its coarsening speed is significantly lower than the ordinary Sn–5Sb/Cu. Meanwhile, the total IMC layer thickness increased with the rising aging time. A single fine dendritic (Cu, Ni)₆Sn₅ IMC at the interface of microalloyed joint was observed and evolved into a larger scallop or layer-like duplex IMCs ((Cu, Ni)₆Sn₅ + Cu₅Sn) after the aging. Considering the combined effect of Cu, Ni, and Ag, the microalloyed joints exhibited the improved microstructure relative to ordinary counterparts and low-melting-point SAC305 materials, significantly inhibiting the interfacial IMC growth, especially Cu₅Sn. The Cu₅Sn IMC thickness and diffusion coefficient in the Sn–5Sb–0.5Cu–0.1Ni–0.5Ag/Cu joint were 0.71–2.81 μm and 0.96 × 10⁻⁶ μm²s⁻¹, respectively. Besides, the precipitation strengthening mechanism triggered by the microalloyed elements was extremely obvious and the soldering and aging joints revealed superior microhardness values of 20–35 HV. This could effectively improve the application range of Sn–5Sb-based materials in higher-temperature package conditions such as third-generation semiconductors.
1 Introduction

The third-generation semiconductors are considered as attractive new electronic components due to their large bandgap, high breakdown voltage, excellent thermal conductivity, high electron saturation drift rate, and strong radiation resistance, represented by silicon carbide (SiC) and gallium nitride (GaN) [1–3]. Therefore, they are widely favored in optoelectronic and lighting device, high-frequency communication (5G), high-power electronic supplier, and consumer electronics. With the development of current global COVID-19 virus pandemic, distance learning and home-based work have increased the further demands for advance electronic products. With the increase in working temperature owing to high-frequency and high-power working characteristics of third-generation semiconductors, it can easily cause device overheating and premature failure of microelectronic solder joints. At present, an effective method in improving the reliability of joints is to use appropriate high-melting-point and endured solder alloys, which can withstand higher temperature, ensure effective mechanical connection and electrical functions [4–7].

At present, high-melting-point solders on the market are typically high-Pb alloys and some lead-free alloy systems. Among them, high-Pb alloys have been used for the electronic products as a joint material for a long time [8, 9], due to good wettability and sufficient strength and high conductive/thermal conductivity. However, human health and environmental considerations alongside international legislation barring the use of venenous Pb in the electronic packaging industry have accelerated the development of feasible lead-free solder alloys [10–12]. From the perspective of high-temperature applications, a limited number of alloy systems are available, including Au–Sn alloys, Bi-based alloys, Sn–Sb alloys, and Zn-based alloys. These alloys are more or less inadequate with exorbitant price, brittleness, or poor wettability [13].

Sn–Sb alloys are one of the potential candidates for interconnect materials to meet the challenging high-temperature resistance and strength requirements of third-generation semiconductor packaging, replacing traditional high-Pb alloys, thereby facilitating the development of electronic packaging materials and technologies [14–18]. The several quality investigations [14, 18] have given physical and mechanical properties of Sn–Sb alloys, which reveals that Sn–5Sb (wt%) near peritectic alloy has favorable wettability, excellent electrical conductivity, and relatively high strength. Actually, Sn–Sb alloys have also recently obtained much attention on the application of lithium/potassium ion batteries (LIBs and PIBs) due to high-capacity anode and enhanced the cycling life of LIBs and PIBs [19–22].

However, Sn–Sb alloys exist a narrow melting range and interface brittleness, and the great concern of their development is to improve the working reliability of joints without affecting other properties [23]. The reliability of solder joints depends on the growth morphology of interface intermetallic compounds (IMCs) and the stability of matrix structure to avoid severe deformation of solder matrix as well as voids and cracks emerged at the interface during subsequent processing and use [6, 24, 25]. When joints are subjected to different thermal aging conditions during service, the formation of thick and irregular IMC layers exposes the solder joint to brittle fracture due to thermal expansion mismatch between the solder and substrate. Therefore, it is essential to deeply understand the microstructure evolution and the growth mechanism of IMCs during working for the design of Sn–Sb-based alloy.

Various alloyed elements (e.g., Cu, Ag, In) are added into Sn–Sb alloys, which leads to the discovery of interesting features distinguished with Sn–Sb alloys. El-Daly et al. [14] study the effect of the individual 0.7%Cu and 0.7%Ag addition on the micromorphology and stretching behavior of Sn–5Sb alloy. It is found that Cu and Ag can refine the microstructure, while Cu is more effective than Ag in increasing the yield strength and ultimate tensile strength of matrix material. Esfandyarpour et al. [26] reported that 1.5% Bi addition as a major refiner to improve the ultimate tensile strength of matrix material, yet Bi reduces the impact resistance of joints. Similar results in the enhanced strength have also been reported by Alam et al. [27] when the addition of Ag and Au to Sn–5Sb alloys promotes the formation of AuSn4 and Ag3Sn IMCs and preserves the stability of microstructure. Zeng et al. [28] also reported that ternary Sn–Sb–Cu alloys with the increased liquidus temperature and improved electrical characteristics may be considered as attractive high-temperature lead-free solders due to the addition of Cu.
In our previous work [29], a comparative study was conducted on the wetting behavior and microstructure of Sn–5Sb–xCuNiAg/Cu solder joints and the initial Sn–5Sb/Cu. The Sn–5Sb–xCuNiAg/Cu joints showed excellent wettability and inhibited IMC growth relative to the Sn–5Sb/Cu joint. However, fewer researches have been reported about on microstructure features and mechanical strength for lead-free Sn–5Sb solder joints containing multiple alloy elements under aging conditions, especially the lack of extensive and systematic results on the internal connection of solder interface microhardness. For this purpose, considering not only a wide range of alloy composition, but also a long-time working environment of electronic devices, Sn–5Sb–xCuNiAg quinary alloys with different formulations were prepared. At the same time, Sn–5Sb and low-melting-point Sn–3Ag–0.5Cu (SAC305) alloys were prepared for a comparison with Sn–5Sb–xCuNiAg alloys. The microstructure evolution, IMC growth, and microhardness of novel Sn–5Sb–xCuNiAg microalloyed joints and Sn–5Sb and SAC305/Cu joints were systematically investigated and evaluated by the same long-time aging conditions. The combined effects of Cu, Ni, and Ag were proposed and the comprehensive influences of microstructure evolution and IMC growth on microhardness were discussed. The results are expected to push forward the further development of new solder alloys for different electronic packaging applications.

2 Experimental procedure

2.1 Materials preparation

In this study, microalloyed solder systems were developed by employing sample composition Sn–5Sb–xCuNiAg. This study is also compared them with Sn–5Sb (without extra elements addition) and SAC305 (low-melting-point solder). The specific composition and contents of above alloys are presented in Table 1. The solder alloys were prepared of Sn–5Sb, Sn–10Cu, Sn–5Ni, and Sn–20Ag interalloys with similar melting points to ensure the approximate solidification time and uniform chemical composition of microalloyed solder during the process.

The solder alloys were made in a graphite crucible heated by a high-frequency electromagnetic induction heating furnace (SM-25) for 15 min at a peak temperature of 650 °C under the whole protection of argon environment. The alloys were melted and overturned 3 times to further guarantee the uniformity. Thereafter, 0.015 g of each sample formulation was smelting in the glycerin solution to produce solder pellets with dimension of 760 ± 10 μm (diameter).

2.2 Microstructure characterization

The solder pellets (760 μm) were subjected to reflow soldering process on the Cu substrate (diameter of 610 μm) of printed circuit board (PCB) coated with flux according to the DSC results of solder alloys and wetting results on the Cu substrates [29]. The reflow soldering process was achieved by a constant heating platform with a peak temperature of 280 °C for 30 s. The samples were cooled down in air and were cleaned with alcohol and ultrasound to remove redundant flux. Then, the samples were put into a vacuum aging furnace at 150 °C for isothermal aging treatment of 504, 1008, 1512, and 2016 h, respectively.

To investigate the microstructure of solder joint, each solder joint was fixed in a special inlay with high-temperature resistance and pressure resistance, which was made from a mixture of 13–16 portion of aluminate cement, 1 portion of methylhexahydrophthalic anhydride (MHHPA), 1 portion of methanoic anhydride (MNA), 3 portion of epoxy resin, and 1.5–4 portion of water (wt%), and cured at 150–160 °C for 24 h. The cross section of solder joint was grinding with metallographic water sand paper and polishing with 0.25 mm diamond spray polishing agent. After ultrasonic treatment, the samples were gently cleaned and etched with alcoholic hydrochloric acid solution with a volume ratio of 95:5 for 3–5 s. Then the optical microscope (OM) and scanning electron microscope

| Table 1 Chemical compositions (wt%) of the investigated solder alloys |
|--------------------------|--------------------------|------------------|------------------|
| Solder alloy             | Elements                 | Sn   | Sb   | Cu   | Ni   | Ag   |
| Sn–5Sb–0.5Cu–0.1Ni–0.1Ag| Balance                  | 5    | 0.5  | 0.1  | 0.1  |
| Sn–5Sb–1Cu–0.1Ni–0.1Ag  | Balance                  | 5    | 1    | 0.1  | 0.1  |
| Sn–5Sb–0.5Cu–0.1Ni–0.5Ag| Balance                  | 5    | 0.5  | 0.1  | 0.5  |
| Sn–5Sb                  | Balance                  | 5    | 0    | –    | –    |
| Sn–3Ag–0.5Cu (SAC305)   | Balance                  | –    | 0.5  | –    | 3    |
(SEM) were used to observe the solder bulk microstructure and IMC morphology. The energy-dispersive spectroscopy (EDS) method was used to identify the element and phases present of compounds in the bulk solder and IMC.

Moreover, the area and length of interfacial intermetallic compound (IMC) layer were measured directly by ImagePro and AutoCAD software. For per solder composition, the IMC layer thickness was averaged from five samples under the same condition using Eq. (1):

$$\delta = \frac{A}{L}$$  

where $\delta$ was the obtained IMC layer thickness, and $A$ and $L$ were the measured area and length of the IMC layer, respectively.

### 2.3 Microhardness testing

Microhardness testing of solder was performed using dynamic ultra-microhardness tester (SHIMADZU-DUH211). The primary loading–holding–unloading method was applied with an indentation loading force of 20 mN at load holding time of 10 s, with loading rate was 5 mN s$^{-1}$. The average hardness was taken as the actual measured value from 20 different locations of each sample.

Indentation hardness (HIT) was a measure indicator of the resistance to permanent deformation or damage, which was determined by measuring the diagonal lengths of an indentation. HIT value can be defined by using the following Eq. (2) for the triangular indenter with 115° tip angle (Berkovich indenter).

$$\text{HIT} = \frac{0.3565F}{h^2}$$  

where $F$ was the loading force (mN) and $h$ was an indentation depth (µm) in a sample. Indentation dynamic hardness HIT was correlated to Vickers hardness (HV) by using a suitable scaling factor from Eq. (3), for a Vickers indenter where the projected area function is known.

$$\text{HV} = 0.0924 \times \text{HIT}$$

It should be pointed that this HV was only for the comparison of hardness between the different solders, but the calculated results should not be used as a substitute for actual HV. Besides, the indentation morphologies were obtained by the camera fitted inside the dynamic ultra-microhardness tester.

### 3 Results and discussion

#### 3.1 Microstructure evolution

Figure 1 presents the solder bulk microstructure with a cross-sectional view of Sn–5Sb–xCuNiAg/Cu, Sn–5Sb/Cu, and SAC305/Cu solder joints after soldering. In Fig. 1a–c, the microstructure of three microalloyed Sn–5Sb–xCuNiAg/Cu joints contains β-Sn matrix and many SbSn phases (corresponding to the EDS spectrum in Fig. 2a), which is also clearly observed in the inset of Fig. 1a. Moreover, Cu, Ni, and Ag present in the solder bulk as microalloyed elements and chemically react with Sn–5Sb solder alloy to generate the floating (Cu, Ni)$_6$Sn$_5$ (Fig. 2b) and Ag$_3$Sn compounds (Fig. 2c). However, in the absence of alloyed Ni and Ag elements, the main intermetallic phases of Sn–5Sb/Cu bulk microstructure are SbSn and Cu$_6$Sn$_5$ in Fig. 1d (corresponding to the EDS spectrum in Fig. 2d). This is consistent with the microstructure of Sn–5Sb solder as El-Daly et al. [14] and Dele et al. [30] reported. In addition, the microstructure of SAC305Cu/Cu joints is manifested as β-Sn matrix and the fine and floating Cu$_6$Sn$_5$ and Ag$_3$Sn compounds in Fig. 1e.

Figure 3 reveals the solder bulk microstructure of the above joints after aging for 2016 h. It can be seen that similar phase compositions also appear in the microstructure of as-aged microalloyed solder joints (Fig. 3a–c). The difference is that a perceptible coarsening effect has occurred in the microstructure with the (Cu, Ni)$_6$Sn$_5$ and Ag$_3$Sn compounds by the Ostwald Ripening mechanism during the aging process. From the comparison of the grain size in the soldered and aged microstructure, the coarsening speed is not large. In the Sn–5Sb solder, the grain size of Cu$_6$Sn$_5$ compounds is only 2–5 µm after soldering (Fig. 1d), yet the grain size reaches about 20 µm (Fig. 3d). In short, the coarsening rate of Cu$_6$Sn$_5$ compounds in the Sn–5Sb/Cu joint is significantly higher than that of the microalloyed joints. It can be inferred that the coarsening of floating Cu$_6$Sn$_5$ compounds is inhibited by the addition of trace Cu, Ni, and Ag, thus contributing to the enhanced mechanical properties of solder joints under long-time working, such as the hardness mentioned later.

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analogous coarsening effect of the Ag₃Sn compounds in the SAC305/Cu joints is shown in Fig. 3e, and the grain size of Ag₃Sn phases reaches about 4 μm after aging for 2016 h.

In the alloyed enhancement systems, regardless of the soldering or aging joints, the smallest volume fraction and grain size of (Cu, Ni)₆Sn₅ compounds in the 0.5Cu–0.1Ni–0.1Ag/Cu, 0.5Cu–0.1Ni–0.5Ag/Cu, and SAC305/Cu joints after soldering. The insets in a and d show the amplified morphology of β-Sn + SbSn and/or Cu₆Sn₅ phases.

As shown in Fig. 4, the distribution of various elements and phases is shown more clearly. In the Sn–5Sb–0.5Cu–0.1Ni–0.5Ag solder, according to the distribution mapping results of Sn, Sb, Cu, and Ni elements after soldering and aging, (Cu, Ni)₆Sn₅ compounds exhibit irregularly bulk-like or granular shapes with small coarsening speed during the aging (Fig. 4a, b). Meanwhile, a clear aggregation has occurred with Ag element after aging, as shown in...
This also confirmed the coarsening of Ag₃Sn compounds. However, as shown in Fig. 4c and d, significant aggregation and coarsening of Cu element occur after aging in the Sn–5Sb solder, which results in the changing of Cu₆Sn₅ shapes from strip or cake to large bulk with size of 20 μm. Compared with Fig. 4a–d, it was again confirmed that the addition of Cu, Ni and Ag could inhibit the coarsening of floating Cu₆Sn₅ compounds [31–33]. Figure 4e and f clearly shows a similar coarsening procedure composing of cake-like Cu₆Sn₅ and rod-like Ag₃Sn phases after aging.

The worthy of note is all the solder bulk microstructure mentioned here is located near the ball center of the solder, while the bulk microstructure near the interface between the solder and Cu substrate is not considered. As shown in Fig. 4g, the coarsening effects of the compounds near the interface are very obvious, distinguishing from the ball center of solder. This can be explained by the diffusion mechanism (a volume diffusion mechanism also be confirmed from the later interfacial IMC growth kinetics). Due to the higher concentration of Cu between the Cu substrate/interface and the solder, a large number of Cu element will migrate from the substrate side to the solder bulk side, and massive Cu₆Sn₅ or (Cu, Ni)₆Sn₅ compounds emerge with Sn or Sn + Ni [31, 32]. Meanwhile, with the increasing distance from the substrate, the migration enrichment of Cu element is slower, thus a gradually decreasing content of the compounds from the interface to the center of solder appears in the microstructure of Fig. 4g.

In conclusion, the solder bulk microstructure of Sn–5Sb–xCuNiAg and SAC305 alloy exist a slower coarsening rate and finer compounds, compared with the microstructure of Sn–5Sb, which is associated with the formation of (Cu, Ni)₆Sn₅ and Ag₃Sn compounds.

### 3.2 Interfacial IMC growth

The reliability of solder joints is closely related to the morphology feature and thickness of the interfacial IMC between the solder and the substrate [34, 35]. Moreover, the thermal aging process also has a significant impact on the growth and failure behavior of the interfacial IMC [35]. Therefore, the growth behavior of the interfacial IMC in the microalloyed and general solder joints during the aging process is investigated next.

The OM interfacial microstructure of the Sn–5Sb–0.5Cu–0.1Ni–0.5Ag/Cu, Sn–5Sb/Cu, and SAC305/Cu joints under soldering and aging conditions is shown in Fig. 5a–c, respectively. It can be evidenced that the (Cu, Ni)₆Sn₅ IMC layer is formed at the interface between the microalloyed solder and Cu substrate after soldering (see Fig. 5a1). Yet an additional Cu₃Sn IMC with a deeply gray scale appears at the interface in the aged joints, as shown in Fig. 5a2–a5. Nevertheless, regardless of the soldering and aging conditions, two dominant interfacial IMC layers (Cu₆Sn₅ and Cu₃Sn phases) formed at the
interface in both the Sn–5Sb/Cu and SAC305/Cu joints, as shown in Fig. 5b and c.

The above phases of the interfacial IMC layer are identified in the EDS spectra of Fig. 6. For example, in the aged Sn–5Sb–0.5Cu–0.1Ni–0.5Ag/Cu joint of Fig. 6a, region E: atomic contents of Cu, Ni, and Sn are 45.08%, 2.74%, and 50.64%, respectively. (Cu + Ni):Sn ≈ 6:5, assuming that this IMC layer is the (Cu, Ni)\textsubscript{6}Sn\textsubscript{5} phase (Fig. 6a1). This finding agrees well with the investigations of previous investigations \[29, 31\]. For region F, the atomic contents of Cu and Sn are 75.54% and 22.93%. (Cu + Ni):Sn ≈ 3:1, inferred that the other IMC layer is the Cu\textsubscript{3}Sn phase (Fig. 6a2). The phases are determined in other joints by similar methods.

Different interfacial phases appear in the three joints after soldering, which is related to the alloyed elements contained in the solder. In the microalloyed Sn–5Sb/Cu joint, the reduced concentration gradient of Cu on both sides of the interface can inhibit the formation of Cu\textsubscript{3}Sn IMC (higher Cu ratio), comparing with the (Cu, Ni)\textsubscript{6}Sn\textsubscript{5} or Cu\textsubscript{3}Sn IMC with lower Cu ratio. Hence, only a single (Cu, Ni)\textsubscript{6}Sn\textsubscript{5} exists at the interface after welding. It is noteworthy that the total IMC thickness of the SAC305/Cu joint is thinner than the microalloyed Sn–5Sb/Cu joint under the
soldering condition (Fig. 5b1 and c1). This can be rationalized by the view of Xu et al. [25], where many 
Ag3Sn granular compounds in the high-Ag SAC solder embedded into the valley position of the 
scallop-like interface to prevent the growth of the interfacial IMC during the soldering. Besides, this 
view can also further explain why the total IMC thickness of microalloyed Sn–5Sb/Cu joints is less 
than that of Sn–5Sb/Cu joints by the effect of Ag. It is also highlighted that Ni is an effective trace additive 
and can provide a diffusion barrier between Cu and Sn at the interface, then inhibit the formation of the 
Cu6Sn5 and Cu3Sn IMCs [36, 37].

Regardless of the solders, with the increasing of 
aging time, the initial fine dendritic or scallop-like 
joints after a, c, e soldering and b, d, f aging at 150 °C for 2016 h, 
g the macro-morphology of Sn–5Sb–0.5Cu–0.1Ni–0.5Ag/Cu joints 
Cu6Sn5 IMC layer gradually changes to a wider scallop-like and layer-like IMC, especially when the 
aging time is 1512 h and 2016 h. Meanwhile, the total IMC thickness gradually increased during the aging 
process, where the thickness of the Cu3Sn IMC layer increased rapidly. The evolution of the Cu3Sn IMC 
layer in the aging samples agrees with the findings of Wang et al. [38, 39], who reported on Cu3Sn IMC 
formation and growth in the SAC305/Cu joints doped by Cu-CNTs or -CNBs under the aging at 
150 °C.

However, it should be pointed out that the growth 
mechanism of Cu3Sn after the long-time aging is 
different from the short-time aging condition. The 
interfacial IMC thickness is small in the short-time
aging process, mainly the short-range diffusion reaction with Sn atoms and Cu atoms at the interface germinates to form the Cu$_3$Sn IMC layer (e.g., Fig. 5b2). This reaction is expressed as $3\text{Sn} + \text{Cu} \rightarrow \text{Cu}_3\text{Sn}$. Instead, the short-range diffusion reaction is not easily accessible in the long-time aging process because of the apparently increasing IMC thickness and the far diffused distance. Simultaneously, massive Cu atoms diffuse more readily toward the thermodynamically unstable Cu$_6$Sn$_5$ IMC phase at sufficient time \[ \geq 30, 40 \]. Therefore, under this condition, the Cu$_3$Sn IMC is mainly synthesized from Cu and Cu$_6$Sn$_5$ IMC by the $9\text{Cu} + \text{Cu}_6\text{Sn}_5 \rightarrow 5\text{Cu}_3\text{Sn}$ reaction. Finally, the thickness of the Cu$_3$Sn IMC is higher than the Cu$_6$Sn$_5$ IMC layer in the Sn–5Sb/Cu and SAC305/Cu joints (Fig. 5b5 and c5). Only in the microalloyed joints, the combinative action of the elements inhibited the diffusion of Sn atoms and the growth of the Cu$_3$Sn IMC (Fig. 5a5). The Cu$_3$Sn IMC layer has the similar scallop-peak and scallop-valley morphology with the Cu$_6$Sn$_5$ IMC layer in Fig. 5b4–b5 or c4–c5, which is evidenced that the second growth mechanism of Cu$_3$Sn IMC under the long-time aging.

In addition, after a long-time aging at 1512–2016 h, a large quantity of the (Cu, Ni)$_6$Sn$_5$ or Cu$_6$Sn$_5$ IMCs at the interface diffuses into the solder, as shown by the red arrows in Fig. 5, and large bulk or cake-like floating IMCs generate in the solder near the interface. This also causes a dynamic balance of the (Cu, Ni)$_6$Sn$_5$ or Cu$_6$Sn$_5$ IMC at the interface, resulting in little thickness growth of the interfacial (Cu, Ni)$_6$Sn$_5$ or Cu$_6$Sn$_5$ IMC after long aging (e.g. Fig. 5a4, a5).

**Fig. 5** OM interfacial microstructure of a Sn–5Sb–0.5Cu–0.1Ni–0.5Ag/Cu, b Sn–5Sb/Cu, and c SAC305 joints. Subscripts 1–5 represent the soldering condition, aging for 504 h, 1008 h, 1512 h, and 2016 h, respectively.
Table 2 summarizes the IMC layer thickness values in the microalloyed Sn–5Sb/Cu joint, and the ordinary Sn–5Sb/Cu and SAC305/Cu joints at different aging time intervals are summarized. As shown in the Table, the total IMC layer thickness for all joints increases with the aging time. Relative to the

Table 2 SEM interfacial microstructure of a Sn–5Sb–0.5Cu–0.1Ni– 0.5Ag/Cu, b Sn–5Sb/Cu, and c SAC305/Cu solder joints aged at 150 °C for 2016 h, and EDS spectra of the interfacial IMC.

Subscripts 1 and 2 represent (Cu, Ni)₅Sn₅/Cu₆Sn₅ IMC and Cu₃Sn IMC, respectively.
ordinary Sn–5Sb/Cu joint (~ 11.51 µm at 2016 h), a significant growth inhibition is observed in the total IMC thickness of the microalloyed Sn–5Sb–0.5Cu–0.1Ni–0.5Ag/Cu joint (~ 10.63 µm at 2016 h), which exists little difference from widely commercial SAC305/Cu joints (9.96 µm at 2016 h). The lower IMC layer growth values are attributed to the formation of fine (Cu, Ni)₆Sn₅ and Ag₃Sn in the microalloyed Sn–5Sb/Cu joint, which inhibits the atomic diffusion on both sides of the interface and disrupts the continuation of the rapid reaction between Sn and Cu atoms during the aging process. This is consistent with some studies [41, 42], where Cu and Ag significantly inhibited the diffusion of the Sn and Cu atoms at the interface.

It is worth highlighting here that the thickness changing of Cu₃Sn IMC in the microalloyed Sn–5Sb–0.5Cu–0.1Ni–0.5Ag/Cu joint is far lower than the other two joints after aging. The Cu₃Sn IMC thickness is about 2.81 µm after aging at 2016 h in the microalloyed joint, whereas in the Sn–5Sb/Cu and SAC305/Cu joints, it reaches 3.4 µm and 3.14 µm after aging at 504 h as well as 5.98 µm and 4.9 µm at 2016 h. Much research [43, 44] indicates that the formation of Cu₃Sn phase relative to the Cu₆Sn₅ phase produces a larger volume contraction at the interface, in turn visible Kirkendall voids appear inside the interface layer. This will potentially trigger a premature breakage at the interface of the joint under the long-time working. Therefore, in this respect, a more obvious effect on the enhanced reliability of the joints is achieved by inhibiting the growth of Cu₃Sn IMC.

Generally, the IMC growth during the aging process is mainly controlled by volume diffusion. The IMC layer thickness can be represented using an empirical growth model [45]:

$$\delta_t - \delta_0 = Dt^{1/2} \quad (4)$$

where \(\delta_t\) is the average IMC thickness at time \(t\), \(\delta_0\) is the average IMC thickness of the joint after soldering, and \(D\) is the growth rate constant (also known as the diffusion coefficient). Therefore, the IMC growth in the joint should follow the square root of the power-law relation.

To further systematically discuss the ability of the CuNiAg microalloyed Sn–5Sb/Cu joint to inhibit the IMC layer growth, the growth kinetics of the IMC layer formed in the joint under the long-time isothermal aging condition are shown in Fig. 7, taking the IMC thickness as a function of the square root of time. In the three joints, the growth procedure of the total IMC layer satisfies a linear relationship with the square root of the aging time, verifying that the above growth model of Eq. 4 is still followed under the long-time aging condition. The growth rate constant \(D\) is obtained from the slope of the linear fitting plots in Fig. 7, which is listed below in Table 2. The results show that the growth rate value of the total IMC layer in the microalloyed Sn–5Sb/Cu joint (6.79 \(\times\) 10⁻⁶ µm s⁻²) is lower than the Sn–5Sb/Cu joint (8.3 \(\times\) 10⁻⁶ µm s⁻²), which is consistent with the expected ability of Cu, Ni, and Ag microalloyed in inhibiting IMC growth. For single Cu₃Sn IMC layer, the microalloyed Sn–5Sb/Cu joint reveals the least growth rate value of 0.96 \(\times\) 10⁻⁶ µm s⁻² for the Cu₃Sn IMC layer, which is dramatically lower than the Sn–5Sb/Cu joint of 3.49 \(\times\) 10⁻⁶ µm s⁻² and the SAC305/Cu joint of 2.16 \(\times\) 10⁻⁶ µm s⁻².

As observed in Figs. 5 and 6, the microalloyed solder joint exhibits the low Cu₃Sn growth values relative to the other two materials. Due to the combined effects of Cu, Ni, and Ag, the fine (Cu, Ni)₆Sn₅ and Ag₃Sn form in the solder and act as pinning phases of the boundary, more effectively suppressing the diffusion between the solder and the Cu substrate, especially the supply of Cu atoms required for the growth of the IMC layer. Thus, it can be argued that the (Cu, Ni)₆Sn₅ IMC layer significantly contributes to the overall IMC growth of the microalloyed enhanced Sn–5Sb/Cu joint under the isothermal aging, while, on the contrary, the Cu₃Sn IMC with higher Cu content in the ordinary Sn–5Sb and SAC305/Cu joints contributes more to the total IMC growth.

Besides, putting into consideration the aging temperature of 150 °C belongs to a high-temperature aging only for the SAC305 solder (melting point of 217 °C), the Sn atoms in the solder and the Cu atoms in the substrate can obtain enough energy to overcome the energy barrier during the long high-temperature aging process [45, 46], leading to a rapid growth of Cu₃Sn IMC (Fig. 7d). Meanwhile, the investigation [47] also observes that many Sn atoms can diffuse into the Cu₃Sn IMC in the reaction with high-Ag solder, further promoting the formation of Cu₃Sn IMC. Although a thin interfacial IMC layer is still obtained in the soldered SAC305/Cu joint, the unduly thick interfacial Cu₃Sn IMC under the aging condition greatly improves the brittleness of the SAC305/Cu joint and the adapted reliability cannot
be guaranteed. This solder joint was unfit for packaging environments at higher temperatures.

### 3.3 Microhardness

The service life of the joint heavily depends on the mechanical strength to avoid the severe deformation of the electronic device occurring during the

![Fig. 7](image-url)  
**Fig. 7** a Total IMC thickness of the solder joints at the different aging time, and plot of the b total, c (Cu, Ni)$_6$Sn$_5$/Cu$_6$Sn$_5$, d Cu$_3$Sn IMC thickness against the square root of aging time for the solder joints aged at 150 °C

| Aging time (h) | Sn–5Sn–0.5Cu–0.1Ni–0.5Ag/Cu | Sn–5Sb/Cu | SAC305/Cu |
|----------------|-------------------------------|------------|------------|
|                | Total                        | (Cu, Ni)$_6$Sn$_5$ | Cu$_3$Sn  | Total | Cu$_6$Sn$_5$ | Cu$_3$Sn  | Total | Cu$_6$Sn$_5$ | Cu$_3$Sn  |
| 0              | 3.61                         | 3.44       | 0.17       | 3.75 | 2.8        | 0.95    | 3.07 | 2.13        | 0.94    |
| 504            | 6.32                         | 5.56       | 0.76       | 7.62 | 4.22       | 3.4     | 6.59 | 3.45        | 3.14    |
| 1008           | 6.72                         | 5.86       | 0.86       | 8.43 | 5.02       | 3.41    | 6.91 | 3.67        | 3.24    |
| 1512           | 9.38                         | 7.28       | 2.1        | 9.93 | 5.47       | 4.46    | 8.96 | 4.95        | 4.01    |
| 2016           | 10.63                        | 7.82       | 2.81       | 11.51| 5.53       | 5.98    | 9.96 | 5.06        | 4.90    |
| Growth rate / $\times 10^{-6}$ μm s$^{-2}$ | 6.79                         | 2.64       | 0.96       | 8.3  | 1.03       | 3.49    | 6.54 | 1.18        | 2.16    |
installation and subsequent use [48, 49]. However, one of the simplest and most immediate methods for estimating the mechanical strength of any metal material is the measurement of microhardness [50]. Figure 8 displays the microhardness values of the microalloyed, ordinary Sn–5Sb/Cu and SAC305/Cu solder joints subjected to the soldering and isothermal aging conditions, where the red color represents higher microhardness values and blue-purple color indicates lower hardness values. In spite of the composition of the microalloyed solders, a rapid increase of microhardness value is observed with the increase of the aging time. This is caused by sufficient diffusion between the elements and the growth of the compounds. A further evidence can be out forward from the indentation images of Fig. 9, in which the smaller residual indentation in the aging joints (Fig. 9b) confirmed the increased hardness than the soldered joints (Fig. 9a).

The hardness values of the microalloyed Sn–5Sb/Cu joints (> 20 HV) are significantly higher than the ordinary Sn–5Sb/Cu and SAC305/Cu joint under the soldering conditions. A reasonable explanation for this phenomenon is that the strengthening effect is improved by the precipitation of more (Cu, Ni)_6Sn_5 and Ag_3Sn compounds in the microalloyed solder. After aging for 2016 h, the three microalloyed Sn–5Sb/Cu joints still exhibit superior microhardness values of 32–35 HV, yet the microhardness value is about 28 HV in the Sn–5Sb/Cu joint. It is evident that the comprehensive addition of trace Cu, Ni, and Ag is highly efficient for the strengthening the Sn–5Sb/Cu joints. And the microhardness value of the SAC305/Cu joint is only about 20 HV. The low microhardness values in both the Sn–5Sb and SAC305 solder alloys
and the coarsening of the Cu$_6$Sn$_5$ and Ag$_3$Sn compounds cause locally severe plastic deformation of the solder joint during the aging/service process. Taking into account the high price of Ag and the excellent microstructure and microhardness values exhibited by the microalloyed joints, it seems that the combined addition of 0.5Cu–0.1Ni–0.5Ag is a most reasonable option for satisfying the higher temperature package in the three microalloyed solders.

4 Conclusions

In this work, the microalloyed lead-free Sn–5Sb/Cu, ordinary Sn–5Sb/Cu, and SAC305/Cu joints were prepared. The microstructure evolution, interfacial IMC growth behavior, and microhardness of the above solder joints were investigated under the same long-time aging condition. The major conclusions are as follows:

The solder bulk microstructure of the microalloyed Sn–5Sb/Cu joints obviously presented β-Sn matrix, various compounds of SbSn, (Cu, Ni)$_6$Sn$_5$ and Ag$_3$Sn after soldering. A visible coarsening effect of (Cu, Ni)$_6$Sn$_5$ and Ag$_3$Sn compounds occurred undergoing the long-time aging process, which yet maintained a slow coarsening speed and a fine bulk microstructure compared with the ordinary Sn–5Sb/Cu joint.

Under the reflux welding process, a significant single fine dendritic Cu$_6$Sn$_5$ IMC existed at the interface between the microalloyed solder and the Cu substrate. After the isothermal aging, a duplex IMC structure containing the scallop-like Cu$_6$Sn$_5$ and the layer-like Cu$_3$Sn IMC emerged at the interface between the microalloyed solder and the Cu substrate. However, regardless of the soldering and aging conditions, the duplex IMC structure exhibited at the interface of Sn–5Sb/Cu and SAC305/Cu joints.

The total thickness of the interfacial IMC layer rose with the increase of the aging time for all solder joints. Relative to the ordinary solder joints, A significant decline of the total IMC growth in the microalloyed joint was obtained; in particular, the relatively Cu$_3$Sn IMC layer grew slower than the (Cu, Ni)$_6$Sn$_5$ IMC layer.

The combined effect of Cu, Ni, and Ag elements added into the solder inhibited the growth of the floating Cu$_6$Sn$_5$ compound and fine (Cu, Ni)$_6$Sn$_5$ and Ag$_3$Sn compounds were generated. These compounds acted as pinning phases at the grain boundary and more efficiently inhibited diffusion between the solder and the Cu substrate, especially the supply of Cu atoms required for the IMC layer growth, thus leading to a finer microstructure and a thinner interfacial Cu$_3$Sn IMC.

The microhardness of the solder gradually increased with the rising aging time. The addition of alloyed elements has an excellent precipitation strengthening effect on the Sn–5Sb/Cu joint, improving the microhardness of 32–35 HV under the aging condition for 2016 h, especially the elemental combination of 0.5Cu–0.1Ni–0.5Ag. The inhibitory effect on the interfacial IMC and the enhanced microhardness of the solder can effectively alleviate the premature deformation failure under the high-temperature service, which is beneficial to the interconnection performance and application of the advanced third-generation semiconductor.

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Author contributions

All authors made equal contributions to researching data, discussion, and analysis of the content of the manuscript. MX designed the experiment and wrote the article. XW discussed the results and wrote the article. FS supervised the project and reviewed/edited the manuscript before submission.

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Data availability
The data that support the findings of this study are not openly available and are available from the corresponding author upon reasonable request.

Declarations
Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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