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Corresponding Author	Family Name	**Liu**
	Particle	
	Given Name	**Changqing**
	Suffix	
	Division	Wolfson School of Mechanical
	Organization	Electrical and Manufacturing Engineering, Loughborough University
	Address	Loughborough, UK
	Email	C.Liu@lboro.ac.uk
	ORCID	
Corresponding Author	Family Name	**Wu**
	Particle	
	Given Name	**Fengshun**
	Suffix	
	Division	State Key Laboratory of Materials Processing and Die and Mould Technology
	Organization	Huazhong University of Science and Technology
	Address	Wuhan, 430074, China
	Email	fengshunwu@hust.edu.cn
	ORCID	
Author	Family Name	**Chen**
	Particle	
	Given Name	**Guang**
	Suffix	
	Division	State Key Laboratory of Materials Processing and Die and Mould Technology
	Organization	Huazhong University of Science and Technology
	Address	Wuhan, 430074, China
	Division	Wolfson School of Mechanical
	Organization	Electrical and Manufacturing Engineering, Loughborough University
	Address	Loughborough, UK
	Email	
	ORCID	
Author	Family Name	**Liu**
	Particle	
	Given Name	**Li**
	Suffix	

	Division	Wolfson School of Mechanical
	Organization	Electrical and Manufacturing Engineering, Loughborough University
	Address	Loughborough, UK
	Email	
	ORCID	
Author	Family Name	**Du**
	Particle	
	Given Name	**Juan**
	Suffix	
	Division	Wolfson School of Mechanical
	Organization	Electrical and Manufacturing Engineering, Loughborough University
	Address	Loughborough, UK
	Email	
	ORCID	
Author	Family Name	**Silberschmidt**
	Particle	
	Given Name	**Vadim V.**
	Suffix	
	Division	Wolfson School of Mechanical
	Organization	Electrical and Manufacturing Engineering, Loughborough University
	Address	Loughborough, UK
	Email	
	ORCID	
Author	Family Name	**Chan**
	Particle	
	Given Name	**Y. C.**
	Suffix	
	Division	Department of Electronic Engineering
	Organization	City University of Hong Kong
	Address	Tat Chee Avenue, Kowloon Tong, Hong Kong
	Email	
	ORCID	

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Abstract	In this work, SAC305 lead-free solder reinforced with 0.1 wt. % fullerene nanoparticles was prepared using a powder metallurgy method. A lab-made setup and a corresponding Cu/solder/Cu sample for thermo-migration (TM) test were designed and implemented. The feasibility of this setup for TM stressing was further verified with experimental and simulation methods; a temperature gradient in a solder seam was calculated as 1070 K/cm. Microstructural evolution and mechanical properties of both plain and composite solder alloys were then studied under the condition of TM stressing. It was shown that compared to unreinforced SAC305 solder, the process of diffusion of Cu atoms in the composite solder seam was remarkably suppressed. After the TM test for 600 h, Cu/solder interfaces in the composite solder seam were more stable and the inner structure remained more intact. Moreover, the addition of fullerene reinforcement can considerably affect a distribution of Cu_6Sn_5 formed as a result of dissolution of Cu atoms during the TM test. Hardness data across the solder seam were also found notably different because of the elemental redistribution caused by TM.

Footnote Information

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Thermo-migration behavior of SAC305 lead-free solder reinforced with fullerene nanoparticles

Guang Chen[1,2], Li Liu[2], Juan Du[2], Vadim V. Silberschmidt[2], Y. C. Chan[3], Changqing Liu[2,*], and Fengshun Wu[1,*]

[1] State Key Laboratory of Materials Processing and Die and Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China
[2] Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, UK
[3] Department of Electronic Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong

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ABSTRACT

In this work, SAC305 lead-free solder reinforced with 0.1 wt. % fullerene nanoparticles was prepared using a powder metallurgy method. A lab-made setup and a corresponding Cu/solder/Cu sample for thermo-migration (TM) test were designed and implemented. The feasibility of this setup for TM stressing was further verified with experimental and simulation methods; a temperature gradient in a solder seam was calculated as 1070 K/cm. Microstructural evolution and mechanical properties of both plain and composite solder alloys were then studied under the condition of TM stressing. It was shown that compared to unreinforced SAC305 solder, the process of diffusion of Cu atoms in the composite solder seam was remarkably suppressed. After the TM test for 600 h, Cu/solder interfaces in the composite solder seam were more stable and the inner structure remained more intact. Moreover, the addition of fullerene reinforcement can considerably affect a distribution of Cu_6Sn_5 formed as a result of dissolution of Cu atoms during the TM test. Hardness data across the solder seam were also found notably different because of the elemental redistribution caused by TM.

Introduction

SAC305 (wt. %) lead-free solder is widely used in electronic interconnections, thanks to its outstanding mechanical properties and good reliability under service conditions [1–3]. However, with fast developments in miniaturization and integration density in high-density electronic packages, electro- and thermo-migration (TM) failures induced by a high current density and large thermal gradients have become a main problem which would threaten the reliability of SAC305 solder interconnections [4–8]. The microstructural and mechanical evolution together with failure modes of solder joints under TM and EM stressing were also reported in previous studies [9–14]. Abdulhamid et al. [9] comprehensively

Address correspondence to E-mail: C.Liu@lboro.ac.uk; fengshunwu@hust.edu.cn

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investigated the damage mechanics of 95.5Sn4Ag 0.5Cu (SAC405) lead-free solder joints under TM stressing. After 1156 h TM stressing, they found that the Cu concentration in cold side is significantly higher than in hot side, while vacancy migration and Sn grain coarsening are in the opposing direction. In order to deeply understand the TM process, a fully coupled thermo-mechanical model is introduced by Basaran et al. [10]; the TM induced strength degradation and grain coarsening effects were both analyzed. Further, they also comparatively studied the migration mechanism in solder joints under EM and EM/TM stressing [12].It was also reported that TM is more likely to lead to failures of solder joints in some cases [15]. Therefore, with the trend of decreasing interconnection height, lead-free solder interconnections will face with reliability challenges related to electro-migration (EM) and in particular, TM.

According to previous studies, mechanical properties and solderability of existing lead-free solders could be improved by adding some foreign reinforcement (including metals, ceramics, and carbon-based materials) into a solder matrix to prepare a composite solder [16–21]. In addition, some researchers also attempted to investigate an effect of foreign reinforcement on EM in solder joints; it was reported that a suitable type and an appropriate amount of reinforcement added showed a positive effect on suppressing EM in solder joints [22–27]. However, to date, a systematic study of TM behavior of composite solder interconnections containing foreign reinforcement under large temperature gradient is still lacking.

As a zero-dimensional carbon-based nanomaterial, a unique molecular structure of fullerene determines its physical stability, low density as well as its excellent electrical, thermal, and mechanical properties [28–32]. Hence, it was usually used as reinforcing phase in preparing polymer- and metal-based composite materials [33, 34]. Chernogorova et al. [33] reported that tensile strength and microhardness of an aluminum/C60 composite alloy were significantly improved with the addition of C60 reinforcement. Watanabe et al. [34] fabricated an Mg–Al-Zn/fullerene (C60) composite alloy with a powder metallurgy method; the produced material demonstrated superelasticity under 548 K (with 256 % elongation). Our research group also prepared a SAC305/fullerene (mixture of C60 and C70) composite solder with a powder metallurgy method; the influence of fullerene on microstructure and mechanical properties on SAC solder joints were also systematically studied. It was found that addition of a proper amount of fullerene was effective in microstructural refinement and improvement in mechanical properties of solder joints [35]. To study further the effect of fullerene reinforcement on thermo-migration behavior of solder joints, in this paper, a SAC/fullerene composite solder reinforced with nano-sized fullerene particles was similarly prepared with the powder metallurgy method. Cu/Solder/Cu-structured interconnections were then formed for subsequent thermo-migration tests. It is widely reported that TM in Sn-based solder joints can be triggered when a temperature gradient and an environmental temperature reach at least 1000 K/cm and 100 °C, respectively [36]. Therefore, for TM tests, to achieve a large enough thermal gradient and environmental temperature without involving EM factor, a TM setup based on a heating plate with constant temperature and a Peltier thermoelectric cooler was designed and prepared. Feasibility of the as-designed setup and corresponding samples was also further verified in this work.

After progressively prolonged TM tests, evolution of interfacial intermetallics (IMCs) at the hot and cold ends and microstructure at the center of both plain and composite solder seams were comparatively studied. Additionally, the dissolution of Cu atoms into the solder seams was quantitatively evaluated. Moreover, the change in mechanical properties of the solder seams as a result of redistribution of elements during the TM test was also investigated. The findings in this work could promote our understanding of the impact of thermal gradient and environmental temperature on reliability of composite solder joints without the effect of current. It can also facilitate future studies on mitigating failures in solder joints induced by thermo-migration.

Experimental

Preparation of composite solder

SAC305 (wt. %) lead-free solder powder (with diameter of 25–45 μm, Beijing Compo, China) and a mixture of fullerene nanoparticles (approximately 80 % C60 and 20 % C70 with an average diameter of 30 nm, JCNANO Materials Tech, China) were utilized as original materials. For preparation of

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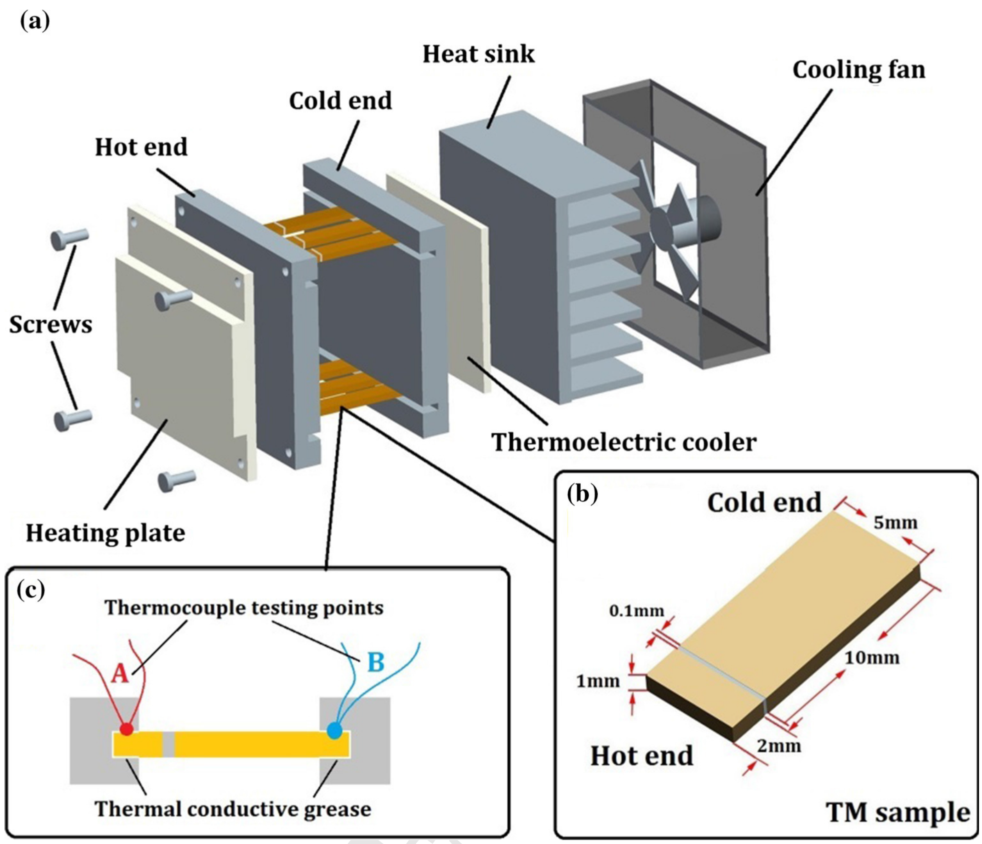

Figure 1 Schematic diagram of TM setup (**a**), TM samples (**b**), and thermocouple positions (**c**).

composite solder, the preweighted solder powder (99.9 wt %) and fullerene particles (0.1 wt. %) were homogenously blended in a planetary ball mill for 20 h. The mixed powder was then uniaxially compacted into solder billets (24 mm × 8 mm × 3 mm). These compacted solder billets were then sintered at 180 °C for 3 h in a vacuum sintering furnace before rolling into solder foils (with thickness of 100 μm) to prepare TM samples.

Design and preparation of TM setup and sample

To achieve a large enough thermal gradient across solder seams, a lab-made TM test setup was designed and prepared (as shown in Fig. 1a). The TM setup consisted of a constant-temperature heating plate with a temperature of 250 ± 5 °C as the heat resource and a Peltier thermoelectric cooler for cooling. A stable initial temperature (0 ± 2 °C) of the thermoelectric cooler was guaranteed by a temperature controller, while a heat sink and cooling fan were used to ensure its proper functioning during current stressing. The heating and cooling components were fixed on corresponding Cu bases with grooves (they were also the hot and cold sides in the TM tests). The spacing between two Cu bases was kept as 10 mm, while rectangular grooves with depth of 1 mm for placing TM samples were also produced on both hot and cold Cu bases with wire-electrode cutting. According to the difference of coefficients of heat conduction for different materials, the sample for TM was designed as an asymmetrical structure with a shorter hot end (2 mm) and a longer cold end (10 mm); a Cu plate (with thickness of 1 mm and width of 5 mm) was used as substrate material for both hot and cold sides of the sample. For sample preparation, end surfaces of the Cu substrates of both sides were well polished before soldering. A solder foil with dimensions of 5 mm × 1 mm × 0.1 mm was then clamped between two Cu substrates; finally, the clamped Cu substrates and the solder foil together with the clamp were placed in a reflow oven to prepare a sample of Cu/solder/Cu sandwich-like structure. The width of solder seams in reflowed solder samples remained similar to the thickness of the initial solder foils (namely, 100 μm); schematic diagram of a reflowed sample is shown in Fig. 1b. For

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the TM tests, the hot and cold ends of the prepared sample were correspondingly embedded in the above-mentioned grooves on both hot and cold Cu bases; the embedded depth was approximately 1 mm. To ensure good thermal conduction, thermal silicone grease was applied on each contact surface between different parts in the tests. In order to know the levels of temperature gradient and environmental temperature in the solder seam, experimental measurements and finite-element modeling were employed to evaluate the feasibility of the TM setup and the samples. A finite-element model was built with ANSYS 15.0 according to the actual dimensions of the setup and sample. To get good modeling results for a temperature distribution across the solder seam, thermocouples were first utilized to obtain the real temperature at points A and B during current stressing (the distances from A and B to the solder seam were 1 mm and 9 mm, respectively, as illustrated in Fig. 1c). The obtained average temperatures for points A and B were recorded when the temperature difference reached a balance; the recorded data were then set as the loading temperatures of the two ends for the subsequent modeling.

TM tests and characterization

In the TM tests, five samples for each kind of solder (plain and composite) were tested to satisfy different testing purposes. Specifically, microstructural evolution of one selected sample for each kind of solder was continuously observed a using scanning electron microscope (SEM QURTA 200) every 200 h; the total stressing time of the TM tests was designed as 600 h. The rest of samples that experienced the same TM stressing process were used for mechanical and compositional analysis. A focused ion beam (FIB) system was employed to study the distribution of Cu-Sn IMCs within a subsurface layer of the studied solder seams, while features of the inner structure were studied with an X-ray Micro-CT scanner (Metris XT H 160Xi) before and after the TM tests. Mechanical properties of the solder seams before and after the TM tests were also evaluated with a nanoindenter (Hysitron Ti750) at a constant load rate of 10 mN and a dwell time of 5 s. To know the difference in mechanical properties in different areas, in nanoindentation tests, each solder seam was evenly divided into three areas, denoted as A, B, and C at different positions between cold and hot ends. Five randomly selected locations for each area were tested to ensure reliability of the test results. In addition, to evaluate quantitatively the process of dissolution of Cu atoms into the solder seams under a large temperature gradient, the seams were cut off from the TM samples after different TM stressing times. After that, residual Cu at the surface of the solder seams was removed by fine polishing. The treated solder seams were then ultrasonically dissolved in aqua regia solution for elemental analysis using an inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian-720) with test precision at PPM level.

Results and discussion

Feasibility evaluation of TM setup and sample

Evolution of measured temperature at points A and B with the stressing time in the TM test is shown in Fig. 2. It can be seen from the curves that the temperature saw a continual increase at the hot end after current stressing, while the temperature of the cold end demonstrated a small decrease first and then increased gradually; after approximately 7 min of the stressing, the temperature difference between the hot and cold ends reached equilibrium. During this stable stage, the average temperatures of the hot (point A) and cold (point B) ends were measured as 206.7 and 40.3 °C, respectively.

The temperature data obtained from the TM sample were used as original temperature parameter for finite-element modeling (FEM). The calculated temperature distributions in the TM setup and the solder seam are presented in Fig. 3. According to the simulation results, the temperature of hot side of the solder seam reached 181.4 °C, while the temperature of the cold side could reach 170.7 °C. In such a case, the temperature difference in the solder seam could achieve 1070 K/cm, since the width of the solder seam was 100 μm; the average environmental temperature at the solder seam was approximately 176 °C. According to previous studies [37], TM in lead-free solders can be triggered when the temperature gradient and the environmental temperature reach at least 1000 K/cm and 100 °C, respectively. In this work, it is clear that the obtained levels of temperature gradient and environmental temperature in the solder seam properly meet these requirements.

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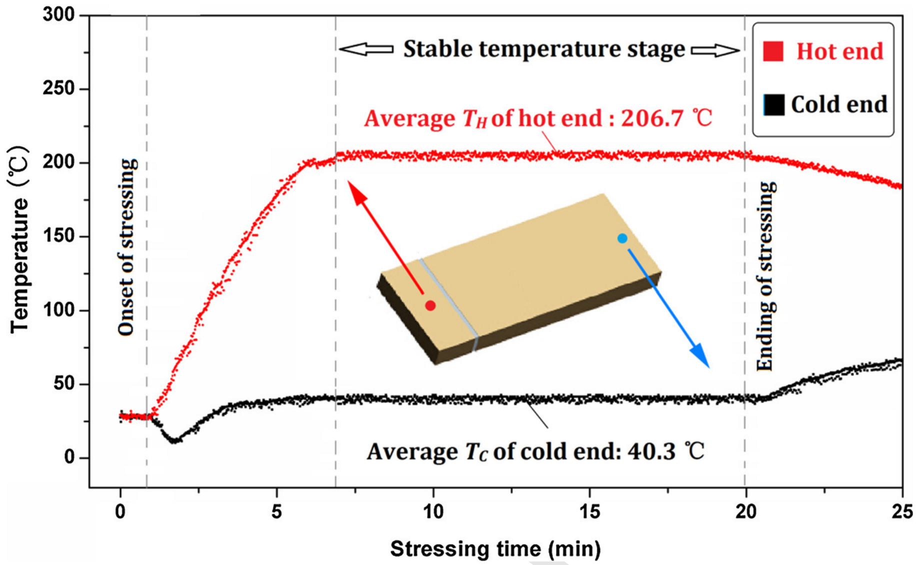

Figure 2 Evolution of temperature at points A and B with stressing time.

Thus, the TM setup and the produced sample are feasible for the TM tests.

Microstructural evolution

The microstructures of both plain and composite solder seams after different TM stressing times are shown in Figs. 4 and 5; the variation in thickness of interfacial Sn-Cu IMCs during TM testing is plotted in Fig. 6. It can be found from images of the solder seam before the TM test that β-Sn, Ag_3Sn IMC and Cu_6Sn_5 IMC were present in both kinds of solder seams. It is worth noting that the sizes of β-Sn phase and Ag_3Sn IMCs in the fullerene-reinforced composite solder seam were found to be apparently smaller than that in the plain SAC305 solder seam. This phenomenon can be explained in the following way: the added foreign reinforcement provided more nucleation sites during the solidification process; they also could impede the growth of grains by hindering atomic diffusion [35]. With the TM stressing time increasing, large quantities of bulky Cu-Sn IMCs can be found in both plain and composite solder seams; these Cu-Sn IMC are a mixture of the initial Cu_6Sn_5 in the SAC305 solder and the newly formed Cu_6Sn_5 as a result of dissolution and migration of Cu atoms coming from the Cu substrates. However, it is apparent that the size and quantity of these Cu-Sn IMCs in the plain SAC305 solder seam were larger than those in the composite solder seam, as shown in Figs. 4d, g, j and 5d, g, j. For the unreinforced SAC305 sample, it was found that Cu-Sn IMCs formed first at the hot end and the central position of the solder seam after 200 h stressing. With the stressing time increasing, the amount of Cu-Sn IMCs continued to grow, and these oval-shaped IMCs were also gradually distributed in the whole solder seam (after 400 h stressing). After 600 h TM stressing, most of the Cu-Sn IMCs were observed to locate at the central position and the cold end of the solder seam. By contrast, after 200 h TM stressing, although the formation and location of Cu-Sn IMCs in the fullerene-reinforced solder seam are similar to those in the plain solder seam, the size of these newly formed IMCs was clearly smaller when compared to their counterparts in the unreinforced SAC305 solder seam after the same stressing time. In addition, there is also a big difference in microstructures for two solder seams after 400 h and 600 h of TM stressing. Specifically, Cu-Sn IMCs formed as result of Cu diffusion were found in both solder seams at the early stressing stage (0–200 h); however, compared to the obvious migration of Cu-Sn IMCs in the plain solder seam, the changes of location of these IMCs in the composite solder seam were not that evident over time. Furthermore, most of IMCs in the composite solder seam were still located at the hot end and the central position after 400 h and 600 h stressing; only a small part of these IMCs were found at the position closed to the cold end, since the distribution of reinforcement added in the composite solder seam might not relatively uniform after reflow process.

In addition to the difference in microstructural evolution for two solder seams, the growth

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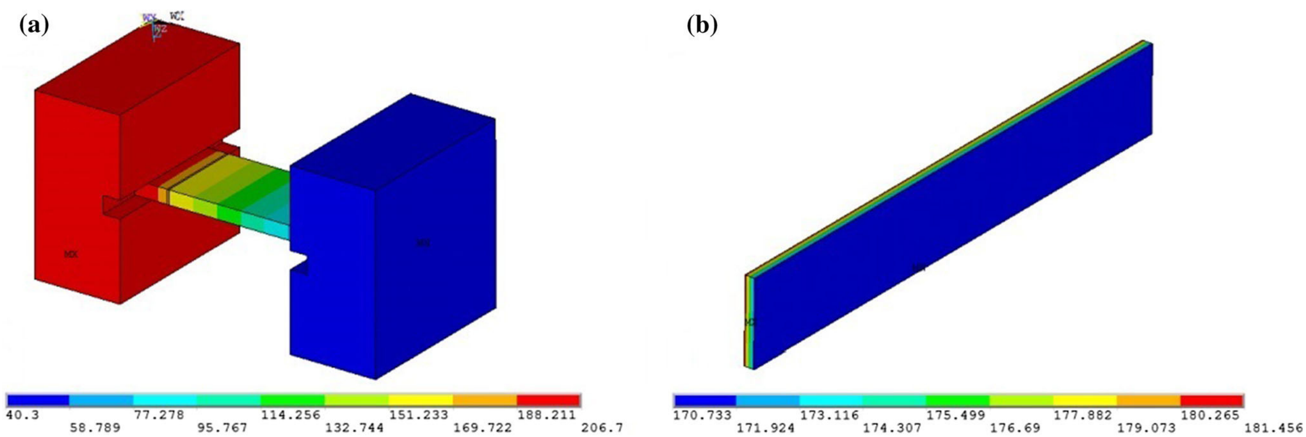

Figure 3 Temperature distributions in TM setup (**a**) and solder seam (**b**).

characteristics of interfacial IMCs of two types of samples were also different during TM stressing. For the plain solder seam, as shown in Fig. 4, the thickness of interfacial IMCs at the cold end obviously increased with the stressing time. The measured data for thickness shown in Fig. 6a also confirmed this trend; the thickness of interfacial IMCs at the cold end increased from the initial 2.12 μm to 8.96 μm after 600 h stressing, i.e., approximately 323 %. In addition, the morphological evolution of interfacial IMC at hot end also worth noting. It can also be found from Fig. 4 that the thickness of interfacial IMCs at the hot end similarly showed a gradually increasing trend during the first 400 h of stressing; the thickness increased from 2.51 μm to 3.36 μm, as shown in Fig. 6a. However, the thickness variation of interfacial IMC at hot end was not that pronounced compared to that for the cold end. Further, some Kirkendall voids were found in interfacial IMCs at the hot end after 400 h of TM stressing (see Fig. 4i). After 600 h of stressing, it can be seen that the initial interface at the hot end was damaged; only a very thin layer of IMC retained on the Cu substrate. The interfacial damage at the hot end can be attributed to considerable diffusion and migration of Cu atoms from the substrate into the solder seam during the TM stressing process; this interfacial damage also further blocked diffusion pathways for Cu atoms. As to the cold end, some granular Ag_3Sn phase with light gray color was also observed in Cu_6Sn_5 interfacial IMC after 600 h of TM stressing. The observed formation, migration, and location of Cu-Sn and Sn-Ag IMCs in the SAC305 solder seam during TM stressing illuminate that both Cu and Ag atoms migrate from the hot end to the cold one under the large temperature gradient; this finding in the present study is consistent with the current research results obtained by other researchers [15, 38].

In contrast, the growth of interfacial IMCs between the composite solder seam and the Cu substrates was mitigated considerably during TM stressing. Specifically, the thickness of interfacial IMCs at the cold end similarly showed an increase with the stressing time, from initial 1.86 to 4.86 μm after 600 h (Fig. 6b). The thickness increment for interfacial IMC at the cold end was approximately 161 %, significantly less than that in the plain SAC305 solder seam. In addition, no Ag_3Sn phase was found in interfacial IMCs at the cold end after 400 h or 600 h of TM stressing. For the hot end, the thickness of interfacial IMCs also increased with the stressing time, from initial 2.14 to 3.52 μm after 600 h. However, in contrast to serious damage happened at the hot interface in the plain SAC305 solder seam, morphology of interfacial IMCs at the hot end in the composite solder seam remained intact even after 600 h stressing, except that only a few of Kirkendall voids were found in this area. Thus, it is believed that incorporation of fullerene reinforcement inhibited the dissolution process of the Cu substrate, formation, and migration of Cu-Sn IMCs as well as the growth of interfacial IMCs. Based on the microstructural comparison between the plain and composite solder seams after TM stressing, the retardation of growth and migration of IMCs in the solder seam can be explained as follows. Fullerene is a nonreactive, noncoarsening material, when appearing in grain boundaries; present fullerene might hinder the migration of atoms

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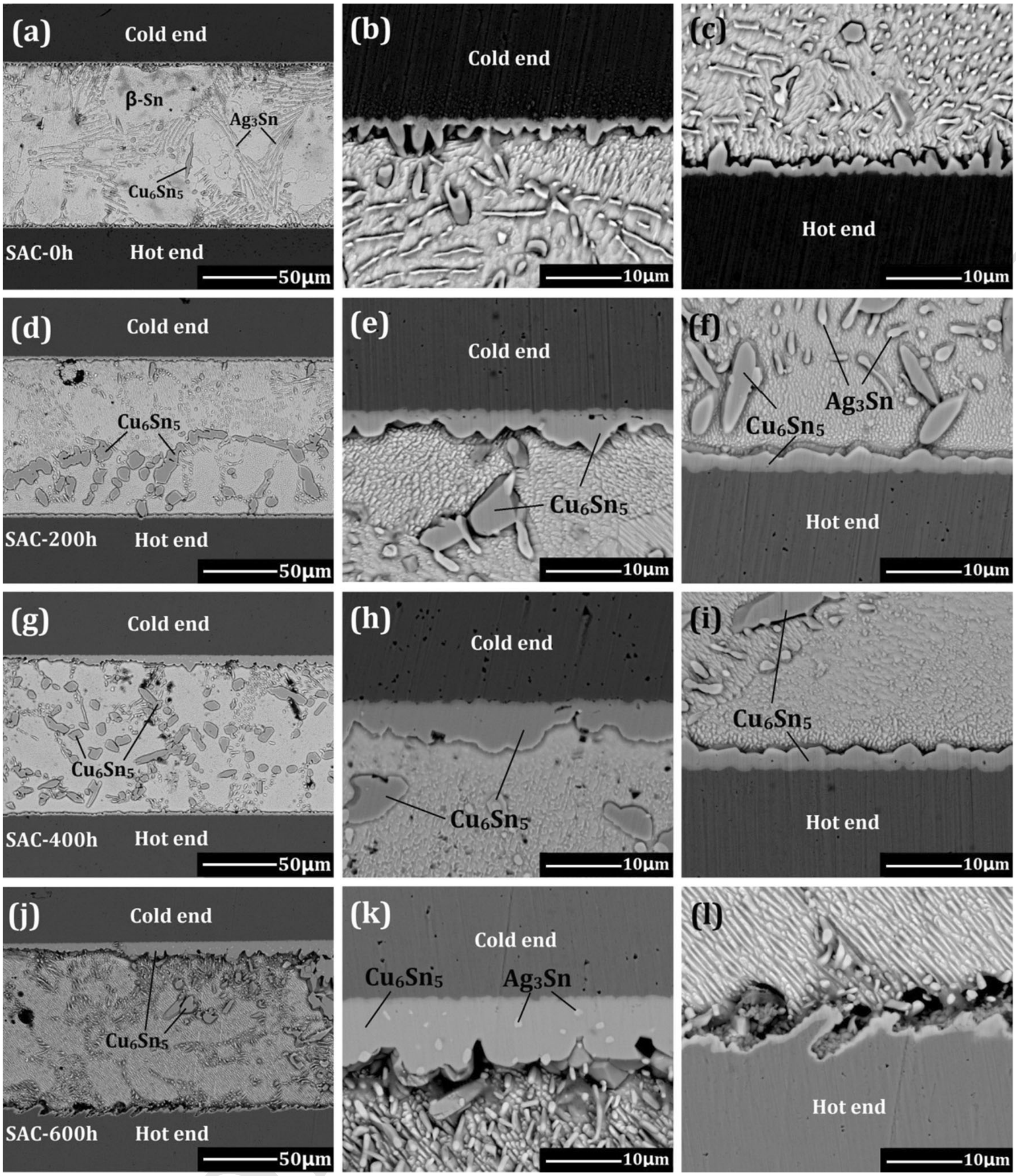

Figure 4 Microstructural evolution of SAC305 solder seam under temperature gradient of 1072 K/cm: **a**–**c** initial; **d**–**f** 200 h; **g**–**i** 400 h; **j**–**l** 600 h.

which could otherwise accelerate the process of IMC formation. Thus, the relationship between the growth rates for different crystal orientations of IMCs changed, leading to restrictions on growth and migration of IMCs. It is also widely believed that the diffusion coefficient of Cu atoms in the Sn matrix is relatively large [39]. Thus, combined diffusion between Cu and Sn atoms determined the growth of the interfacial Cu-Sn IMC phase at the solder/copper interface. According to our previous study on location of fullerene added in the solder matrix [35], it is supposed that some fullerene reinforcement stuck around the Cu-Sn phases, acting as barriers for diffusion of Sn to the Cu substrate or even obstructing formation of Cu_6Sn_5, inhibiting the growth of an interfacial IMC layer.

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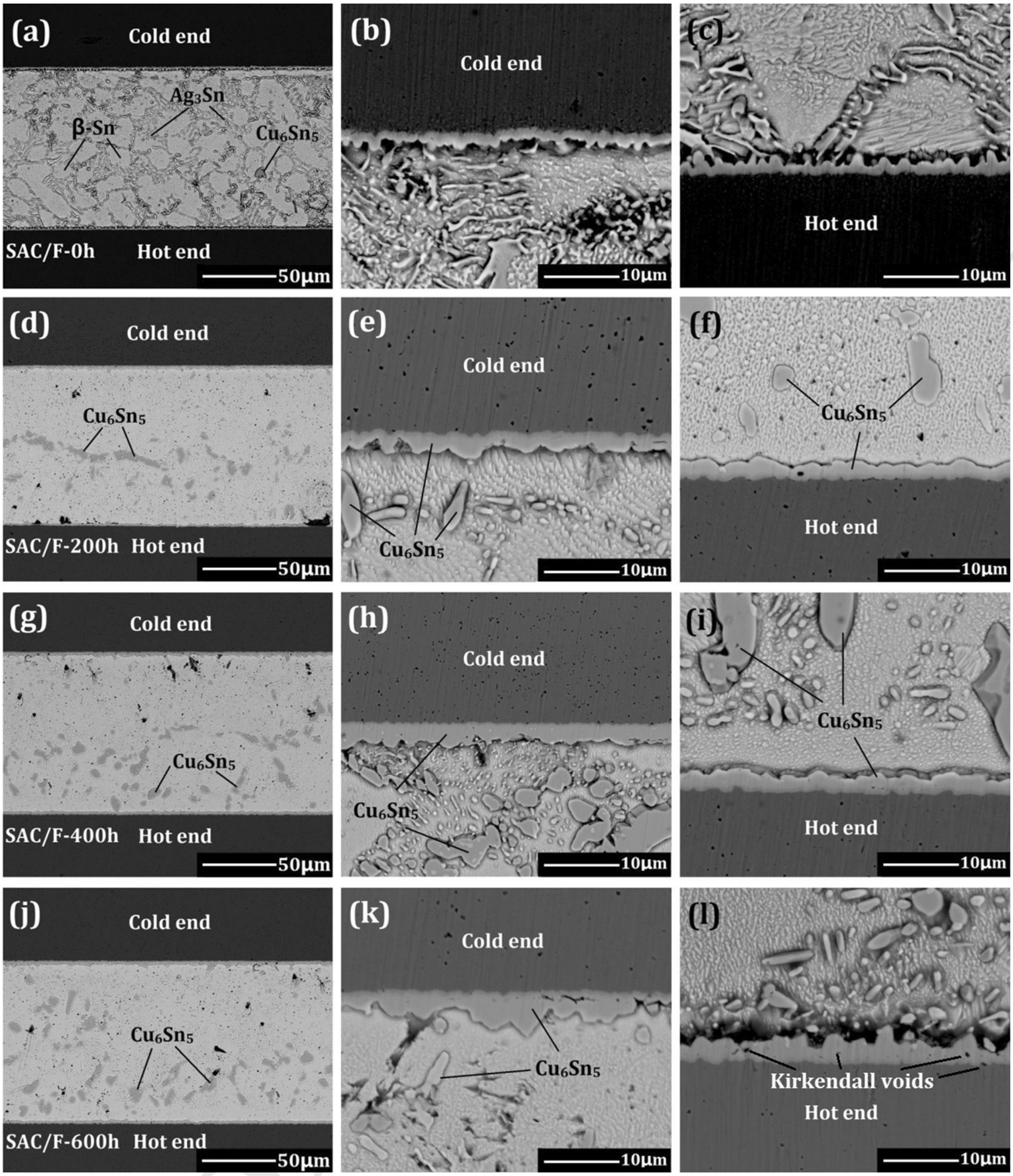

Figure 5 Microstructural evolution of SAC305/F composite solder seam under temperature gradient of 1072 K/cm: **a**–**c** original; **d**–**f** 200 h; **g**–**i** 400 h; **j**–**l** 600 h.

In addition, to understand further the distribution position of Cu-Sn IMCs in a subsurface layer of the solder seam, a dovetail groove with depth of 10 μm was prepared on the solder seams after 600 h of stressing using FIB, and the respective images are shown in Fig. 7. It can be known that after a long-term TM stressing, most of Cu-Sn IMCs formed by Cu diffusion were found to locate at the central position and the cold end of the plain SAC305 solder seam; the size and location of these IMCs were consistent with the SEM results as shown in Fig. 4. Similarly, the observed location and size of Cu-Sn IMCs in the composite solder seam using FIB were almost the same as the results shown in Fig. 5. The

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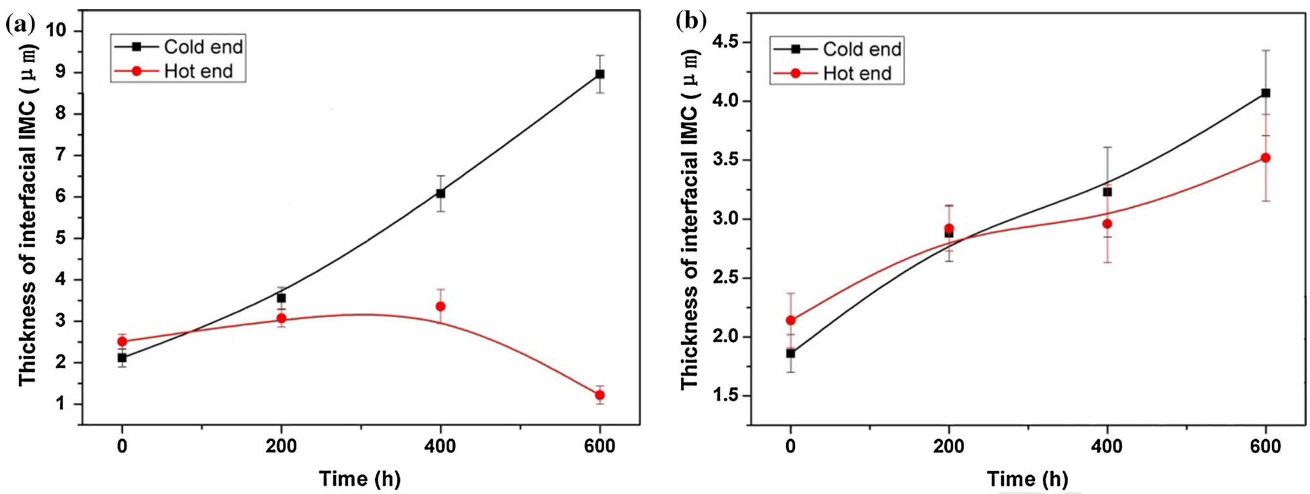

Figure 6 Evolution of thickness of Cu-Sn IMCs at the Cu/SAC305/Cu (**a**) and Cu/SAC305-F/Cu (**b**) with TM stressing time.

difference of location of Cu-Sn IMCs in the subsurface layer of two kinds for solder seams further indicates that the presence of foreign reinforcement can not only retard the migration of atoms on surface of the solder seam but also mitigate this diffusion in the inner of the solder seam.

To quantitatively measure the effect of addition of fullerene on diffusion of Cu atoms from the Cu substrate to the solder seams, the weight percentages of Cu in the solder seams were analyzed after different TM stressing times using ICP. For the ICP tests, in order to meet the testing requirements (the weight of sample is at least 100 mg) as well as to understand the Cu content as precise as possible, four treated samples (cut and polished solder seams; the weight of each solder seam was approximately 38 mg) were chosen for each kind of solder. The average Cu content for each solder was used as the testing result for comparative analysis; the ICP results are shown in Fig. 8. Although the cutting and polishing processes can cause errors in measuring the content of Cu in the solder seams, the obtained results shown in Fig. 8 revealed an obvious difference in the Cu content in two types of solder seams after different stressing times. Specifically, it increased with the TM stressing time; however, the increase rate in the plain SAC305 solder was much higher seam during whole stressing process than that in the composite solder seam. After 600 h of stressing, the average Cu content in the former reached 4.55 wt %, about 9 times higher than its initial value of 0.52 wt %. In contrast, the average Cu content in the composite solder seam after 600 h stressing was 2.09 wt %; only about 4 times higher than its initial value of 0.51 wt %. It is also worth noting that the increase rate of Cu in the plain SAC305 showed a decreasing trend in the interval from 400 h to 600 h. This phenomenon can also be explained by the fact that the diffusion and migration paths of Cu atoms at the Cu/solder interface were damaged due to a long-term TM stressing; this found change in the Cu content agrees well with the observed results as shown in Fig. 4. To avoid the error caused by the above-described phenomenon, only the data for times below 400 h were used to calculate the dissolution rate of Cu atoms during TM stressing. This rate was calculated employing the following formula:

$$v = \frac{M(w_2 - w_1)}{T}, \qquad (1)$$

where v is the dissolution rate of Cu atoms, M is the average weight of the solder seam, T is the stressing time, w_1 and w_2 are the weight percentages of Cu in the solder seams after 0 h and 400 h stressing, respectively. After 400 h stressing, the net increase of Cu in the SAC305 solder seam was 3.27 wt %; since the weight of the solder seam was 38 mg, 1.24 mg of Cu was dissolved into the solder seam during 400 h of stressing. Due to the fact that the experimental parameters, including the temperature gradient and environmental temperature within the solder seam were relatively stable, the dissolution rate of Cu atoms form the substrate to the solder seam can thus be calculated as 3.1×10^{-6} g/h. By comparison, the increment of Cu content was only 0.488 mg in the composite solder seam after 400 h stressing; the

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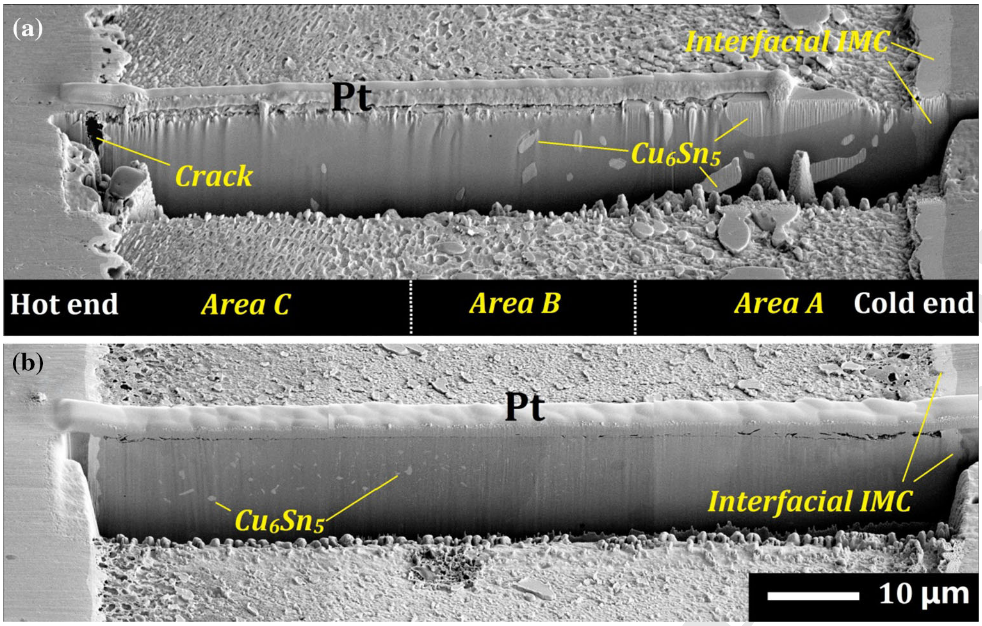

Figure 7 SEM images of FIB-cut trenches on subsurface layer of SAC305 (**a**) and SAC305/F (**b**) solder seams.

dissolution rate of Cu atoms was calculated as 1.22×10^{-6} g/h, which is only about a half of that in the plain solder seam. The ICP results and the calculated dissolution rates of Cu atoms clarify that addition of fullerene reinforcement contributed to mitigation of the diffusion from the Cu substrate into the solder seam under TM conditions.

To further access the effect of TM on inner structure of the solder seams, MCT nondestructive scanning was employed to analyze the solder seam area; the scanning results are shown in Fig. 9. Apparently, solder seam areas of both types of samples appear rather intact, without apparent defects before TM stressing (see Fig. 9a and c). However, big differences in inner structures were found for two solder seams after 600 h of TM stressing. Specifically, voids and cracks caused by elemental migration were found at both hot and cold interfaces of the plain SAC305 solder seam; further, large amounts of Cu-Sn IMCs (dark-gray areas) can also be observed at both sides of the solder seam (Fig. 9b). In contrast, the inner structure of the composite solder seam after long-term stressing seems to be less affected when compared with the SAC305 solder seam; only few voids were found. The newly formed Cu-Sn IMCs (dark-gray areas) are mainly distributed at the hot side of the solder seam, while only a small quantity of these IMCs were found at the cold side (Fig. 9d). The scanning results illustrate that addition of fullerene reinforcement into solder seam could help to maintain this structural integrity, extending the service life of solder interconnections exposed to a large temperature gradients.

Mechanical properties

In most previous studies, hardness of composite solder joints containing foreign reinforcements was evaluated using an automatic digital microhardness tester or a Vickers microhardness tester [11, 40–43]. Some researchers tested hardness and modulus of solder joints by employing a nanoindenter [44, 45]. By investigating hardness distribution in solder joints after current stressing, Ren et al. [46] reported that the hardness data showed a gradient distribution within a solder joint from an anode side to a cathode. However, by now, no studies mentioned the effect of thermal gradient on mechanical properties of composite solder joints containing foreign reinforcement. Therefore, in this investigation, to study the mechanical strength of small areas in solders seams, nanoindentor was used to assess a variation in hardness of different solder seams before and after 600 h TM stressing. A constant loading rate of 10 mN and a dwell time of 5 s were set as the operating parameters for these tests. Continuous monitoring of

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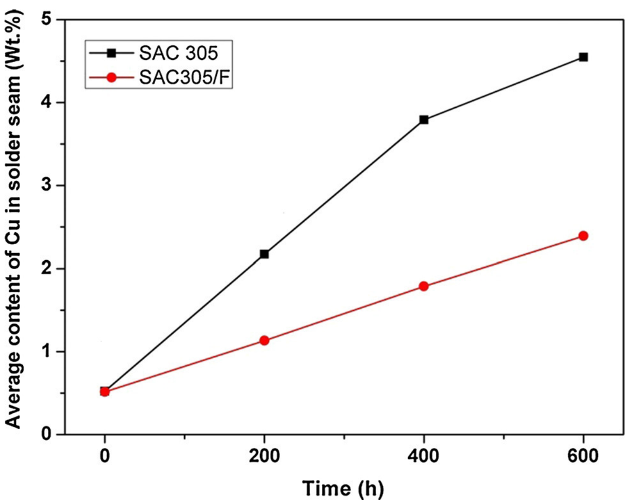

Figure 8 Evolution of weight percentage of Cu in solder seams with stressing time.

the constant applied load, constant dwell time, and indenter's depth displacement was applied to identify the hardness of different solder seams. In nanoindentation test, five points were randomly selected for both plain and composite solder seam before TM stressing. For the solder seams after 600 h stressing, as mentioned in the experimental part, five points were also randomly chosen from A, B, and C areas for each types of solder seams; the partitioning of areas A, B, and C is shown in Fig. 7.

All load–displacement diagrams for indentation points and the relevant hardness data for different samples are shown in Figs. 10 and ~~11~~ Table 1. By comparing diagrams for the plain and composite solder seams before stressing, it is clear that the average indentation depth for the former (1338 nm) is larger than that for the later (1263 nm). This finding indicates that the resistance to deformation and hardness of the fullerene-reinforced composite solder were higher than those of the plain SAC305 solder. Improved mechanical strength can be explained as follows. On the one hand, the reduction in the maximum depth was due to the decrease in the grain sizes of the plain solder after doping with 0.1wt. % of fullerene nanoparticles (see Figs. 4a, 5a). On the other hand, a dispersion-strengthening effect as well as a pinning effect caused by introduction of foreign reinforcement also makes a considerable contribution. AQ1 The calculated hardness data shown in ~~Fig. 11~~ Table 1 also confirms this point of view; the average hardness of the fullerene-reinforced composite solder seam was 0.256 ± 0.05 GPa, AQ2 0.2562 GPa which is 21.9 % higher than that of the plain SAC solder. However, it was found that a scatter in load–displacement diagrams for the composite solder seam was larger than that for the plain solder. This phenomenon indicates that the distribution of fullerene in the solder matrix might not be homogeneous. As well known, foreign reinforcement, especially, inert particles (including ceramics and carbon-based materials), are hard to be wetted reactively by the molten solder; there is a large interfacial free energy between the molten solder and the reinforcement. Thus, most of the added reinforcement might be excluded out of the molten solder during the soldering process, leading to a loss of reinforcement and inhomogeneous distributions of reinforcement in solder joints. This problem need to be further studied in the future to facilitate the application of composite solders in the electronic industry.

From Fig. 10b and d as well as the hardness data shown in Table 1, an obvious difference in indenter depths and distributions of hardness data can be found for the two studied types of TM stressed solder seams. These results vividly demonstrate that the hardness data of the plain SAC solder seam after 600 h stressing gradually decreased from its cold end (area A) to the hot end (area C), from the average value of 0.2534 GPa for area A to 0.1932 GPa for area C. This phenomenon can also be explained using migration and redistribution of different elements in the solder seam caused by TM stressing. During this process, a large amount of Cu atoms dissolved into the solder seam, forming Cu-Sn IMCs; these newly formed Cu-Sn IMCs were then continually pushed toward the cold end by the reverse thrust resulted from migration of Sn atoms from the cold end to the hot one [15]. In addition, like Cu atoms, Ag atoms were also confirmed to move in the same direction when the solders were subjected to a large temperature gradient. The migration and redistribution of Sn, Ag, and Cu during TM stressing would finally lead to an increase of Cu-Sn and Ag-Sn IMCs at the cold end and the central position of the solder seam. This point of view also agrees with the observed results as shown in Figs. 4 and 7a. The elemental redistribution caused by the temperature gradient would largely determine the hardness distribution in the solder seams. According to previous reports, the hardness values of the β-Sn, Ag_3Sn, and Cu_6Sn_5 phases are estimated as 0.35 ± 0.04 GPa [47], 2.9 ± 0.2 GPa [48], and 6.10 ± 0.53 GPa [49], respectively. It is apparent

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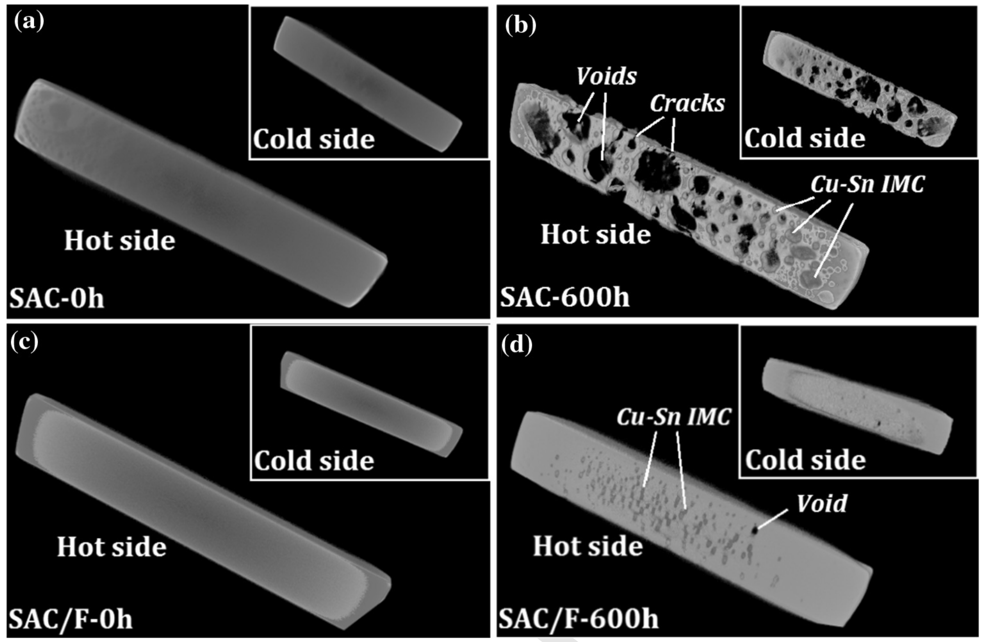

Figure 9 MCT scanning results for plain (**a**, **b**) and composite (**c**, **d**) solder seams before (**a**, **c**) and after (**b**, **d**) 600 h stressing.

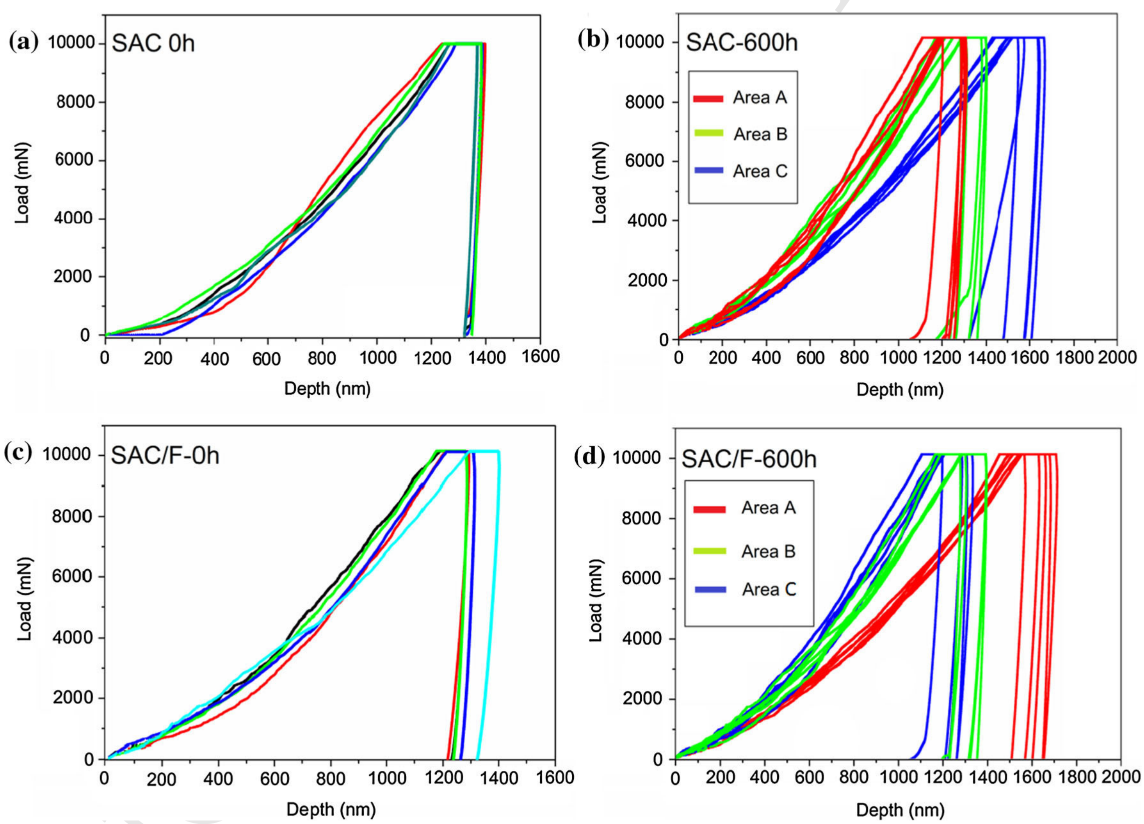

Figure 10 Testing results of indentation points for plain (**a**, **b**) and composite (**c**, **d**) solder seams before (**a**, **c**) and after (**b**, **d**) TM for 600 h.

that the enrichment of some rigid phase (including Cu-Sn and Ag- Sn IMCs) at the cold end gave a rise to an improvement of hardness in this area.

In contrast, the distribution of hardness values in the composite solder seam showed an opposite result: the hot end (area C) demonstrated a higher

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Table 1 Calculated hardness data for plain (a) and composite (b) solder seams before and after 600 h TM stressing

	Plain SAC solder (GPa)	Composite solder (GPa)
Reference Hardness (0 h)	0.2102	0.2562
Area A (600 h)	0.2534	0.2026
Area B (600 h)	0.212	0.2544
Area C (600 h)	0.1932	0.2634

hardness value than the cold end (area A). In consideration of the migration features of different elements as well as the obtained results shown in Figs. 5 and 7b, it can be concluded that the migration rate of all elements in the composite solder seam was diminished due to the addition of foreign reinforcement. As described in Sect. 3.2, most of the newly formed Cu-Sn IMCs were located at the central position and the hot end of the solder seam (namely, areas C and B); this was also the main reason for higher hardness values in these areas than in other areas. As for the cold end, although it was also exposed to a large temperature gradient during TM stressing, it was affected more like an isothermal aging process, since the migration rate of elements was largely mitigated. During the stressing period, the decline in hardness resulting from coarsening of the β-Sn and Ag_3Sn phases might exceed the enhancement effect caused by enrichment of Cu-Sn and Ag-Sn IMCs, leading to the overall decrease in hardness.

Conclusions

The SAC305/0.1F lead-free composite solder was produced through the powder metallurgy route. A temperature difference generator and relevant TM samples were designed and prepared; the evaluated temperature gradient in the solder seam in the setup was 1070 K/cm. After TM stressing, diffusion of Cu from the substrate to the solder seam was found in both plain and composite solders; this phenomenon was particularly prominent in the unreinforced solder seam. After 600 h of TM stressing, the interface at the hot end was damaged considerably, while a significant increase in the thickness was found in interfacial IMCs at the cold end. Although interfacial IMCs in the composite solder seam also showed an increasing trend during TM stressing, the interfacial structure remained intact compared with that of the plain solder seam. According to ICP results, the dissolution rate of Cu in the plain SAC305 solder under the employed experimental condition was 3.1×10^{-6} g/h; while for the composite solder, it was only 1.22×10^{-6} g/h. In addition, the scanning MCT results revealed that fullerene reinforcement helped to maintain integrity of the inner structure. The nanoindentation results demonstrated that hardness of the solder alloy obviously improved thanks to the doping of fullerene nanoparticles; moreover, mitigated elemental migration caused by the presence of the reinforcement could alter the distribution of hardness values in a solder seam under TM stressing. The findings of this study indicate that addition of fullerene could mitigate the negative effect of TM; hence, composite solders containing foreign reinforcement have a potential for a use under harsh service conditions.

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Compliance with ethical standards

Conflict of Interest We declare that no conflict of interest exits in the present manuscript.

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