Retained ratio of reinforcement in SAC305 composite solder joints: Effect of reinforcement type, processing and reflow cycle

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Abstract

Purpose – The effect of reinforcement type, processing methods and reflow cycle on actual retained ratio of foreign reinforcement added in solder joints was systematically studied.

Design/methodology/approach – Two kinds of composite solders based on SAC305 (wt.%) alloys with reinforcements of 1 wt.% Ni and 1 wt.% TiC nano-particles were produced using powder metallurgy and mechanical blending method. The morphology of prepared composite solder powder and solder pastes were examined; retained ratios of reinforcement (RRoR) added in solder joints after different reflow cycles were analysed quantitatively using an Inductively Coupled Plasma optical system (ICP-OES Varian-720). The existence forms of reinforcement added in solder alloys during different processing stages were studied using SEM, XRD and EDS.

Findings –The obtained experimental results indicated that the RROR in composite solder joints decreased with the increase in the number of reflow cycles but a loss ratio diminished gradually. It was also found that the RRORwhich could react with the solder alloy were higher than that of the one that are unable to react with the solder. In addition, compared with mechanical blending, the RRORs in the composite solders prepared using power metallurgy were relatively pronounced.

Originality/Value –Present study offer a preliminary understanding on actual content and existence form of reinforcement added in a reflowed solder joint, which would also provide practical implications for choosing reinforcement and adjusting processing parameters in the manufacture of composite solders.

Key words: Electronic materials; Composite materials; Solder; Retained ratio; Reflow cycles

1. Introduction

Lead-containing solders have been continuously replaced in electronics packing because of the environmental and health concerns; thus, lead-free solders demonstrated a rapid development (Abtew and Selvaduray, 2000; Zhang *et al.*, 2012; Shen and Chan, 2009). To further enhance the performance of lead-free solder joints in harsh service conditions，incorporation of reinforcements into a solder matrix is widely regarded as a feasible method (Chellvarajoo, 2015; Fouda and Eid, 2015; El-Daly *et al.*, 2013; Hu *et al.*, 2013; Bukat *et al.*, 2013; Gao *et al.*, 2010).

At present, there are two common methods to prepare composite solders with added reinforcements: mechanical blending and powder metallurgy (Shen and Chan, 2009; Liu *et al.*, 2013; Tsao *et al.*, 2012). In the former, a solder paste and reinforcement are directly mixed together through mechanical stirring. In the latter, a solder powder and reinforcement are blended by ball milling before compacting, sintering and subsequent extrusion or rolling. However, no matter what method is used, most of the reinforcement added was excluded outside of solder joints in the soldering process (Liu *et al.*, 2008; Chen *et al.*, 2015). In such a case, the amount of reinforcement retained in the final state of solder joints is quite different from the initial one, leading to reduction of an enhancing effect due to limited doping with reinforcement. To date, although the effect of foreign reinforcement on microstructure

and performance of lead-free solders was widely studied, a retained ratio of reinforcement in composite solder joints was only mentioned in few works (Chen *et al.*, 2016; Haseeb *et al.*, 2014; Tay *et al.*, 2013; Haseeb *et al.*, 2011). It is expected that a type of reinforcements, a number of reflow cycles and a method of processing of composite solders have important impacts on RRoR in solder joints.

In this paper, Ni and TiC nanoparticles were chosen as reinforcements to strengthen a SAC matrix since Ni is known as an active reinforcement that could react with molten SAC solder, while TiC is a relatively inert reinforcement (Chellvarajoo, 2015; Tay *et al.*, 2013; Kennedy *et al.*, 2001). To understand the effect of processing and reflow cycles on RRoRs in solder joints, mechanical blending and powder metallurgic routes were adopted to produce composite solders while the number of reflow cycles was controlled when preparing solder joints. In addition, the microstructures and chemical compositions of prepared composite solders at different processing stages were contrastively investigated.

2. Experimental procedures

The SAC305 (wt.%) solder paste (Beijing Compo, China) and powders (Suzhou EUNOW Electronic Materials, China) were used as matrix materials, while the as-purchased nano-sized Ni (with an average diameter of 20 nm, JCNANO) and TiC (with an average diameter of 25 nm, JCNANO) were employed as reinforcement materials.

The initial weight fraction of both reinforcements was chosen as 1 wt. %. In this

paper, mechanical blending method (Method A) and a powder-metallurgy method (Method B) were utilised to prepare composite solders. Specifically, in Method A, the pre-weighed solder paste and the reinforcements were first mechanically blended prior to printing onto an aluminium oxide chip using a steel stencil and further soldering into solder balls in a reflow oven (see Fig 1a). In Method B, a mixture of a solder powder and reinforcements was first ball-milled for 20 hours before uniaxial compacting into solder billets and sintering at 180℃ for 3 hours under vacuum atmosphere. Subsequently, the sintered solder billets were rolled into solder foils (200 μm in thickness) and then cut into solder flakes with dimension of 1 mm×1 mm×0.2 mm using a rotary cutter; solder balls with an average diameter of 750 μm were prepared through the reflow process (see Fig. 1a). To ensure the stability of reflow process, same reflow parameters were adopted for both of method A and method B; the reflow curve is shown in Fig 1b. According to the type of reinforcement added and the processing method, these prepared composite solder balls are denoted as follows: SAC/Ni-A, SAC/Ni-B, SAC/TiC-A and SAC/TiC-B.

To study the characteristics of treated composite solder (including solder paste and powder) before reflow process, the morphology of and the distribution of reinforcements in composite solders were observed using an environmental scanning electron microscope (ESEM Quanta 200). To measure the extent of RRoRs in composite solder foils and pastes before sintering and reflow, 50 mg mixture for each solder were ultrasonically dissolved in aqua regia; the resultant solutions were tested using an ICP-OES Varian-720 with test precision at a ppm level. The RRORsin

reflowed solder joints were similarly tested using ICP-OES; 20 solder joints for each group were tested to ensure the reliability of testing data. The RRoRs were quantified based on an atomic weight fraction of Ni and Ti in the aqua regia solutions. For microstructural analysis, the samples at different treatment stages (including before sintering, after it and after reflowing) were mechanically grinded and polished for observation with ESEM. In addition, the chemical composition of solder balls and the phase composition of different composite solders was analysed with ICP-OES, energy Dispersive Spectrometer (EDS) and X-ray diffractometer (XRD) of Phillips XRD-X'Pert PRO.

3. Results and discussion

Fig 2 shows the morphology of both plain and composite solder powder before and after ball-milling process (namely, method B). It can be seen that SAC solder particles show a regular spherical shape before ball-milling, while the obvious collision deformation was observed on the surface of ball-milled solder particles. Similarly, this change in shape of solder particles was also found in composite solder particles containing Ni and TiC reinforcements. However, there are still some differences observed on the surface of different single solder particles (shown in Fig 2c, e and h). It can be observed that the ball-milled plain SAC solder particles present a relatively smooth surface. By contrast, the composite solder particles containing foreign reinforcements show a relatively rough surface with a large number of dents and small particles. EDS results shown in Fig 2f and i further confirmed these

particles adhered or embedded on surface of solder particles are the added reinforcements (namely, Ni and TiC).

The SEM images of plain and composite solder pastes prepared by Method Aare shown in Fig 3; spherical solder particles and flux can be found in plain SAC solder paste. In comparison to plain SAC solder paste, the reinforcements added can be observed in composite solder pastes containing Ni and TiC reinforcements, which were shown in Fig 3c, d e and f. Specifically, these reinforcements added not only adhere to the surface of solder particles but also exist in solder flux. To verify the existence and content of foreign reinforcements in solder pastes, six different areas selected were tested by EDS, relevant testing results are presented in Table 1. The EDS results confirmed the existence of reinforcements in composite solder pastes; it also reveals that most reinforcements added are more likely located at solder flux rather than surface of solder particles.

According to observation results of composite solder particles and pastes, it can be found that most of reinforcements added appear in the form of aggregations in composites matrices (no matter what processing methods used). Specifically, the size of reinforcements' aggregations adhered on surface of solder particles ranges from 100 to 800 nm (see Fig 2), while their size is approximately in the range of 0.1 to1 μm in composite solder pastes (see Fig 3). This phenomenon indicates that it is difficult to homogeneously disperse nano-sized reinforcements into solder particles or solder pastes using mainstream processing methods. A uniformly distribution of foreign reinforcements in composite materials matrix in their initial size has always been a

difficult topic. At present, although the effect of reinforcements on microstructures and solderability of solder alloys is widely studied, the actual distribution and exiting forms of reinforcements added in solder matrix still need further study. As for processing methods, it is necessary to point out that the retained ratio of foreign reinforcement in composite solders prepared by Method B might relatively lower than that of composites prepared by Method A.

This point of view was verified after testing the actual retained ratios of Ni and TiC in composite solder foils and pastes using ICP-OES; the ICP results are shown in Table 2. From the ICP testing data, it can be concluded that no matter what kinds of reinforcements added, actual retained ratios of reinforcements in composites prepared by Method A are higher than that made by Method B. For method B, the loss of reinforcement might be caused by two reasons. On the one hand, the reinforcements added would stick to the surface of ball-milling media (including milling jars and milling balls). On the other hand, in addition to the embed or adhered reinforcements on the surface of solder particles, a considerable part of reinforcements are more likely to drop from the surface of solder particles during ball-milling process since there was no enough strong bonding strength between solder particles and the added reinforcement (especially, the inert reinforcement). The drop of reinforcements from surface of solder particles also generates a large number of dents on the surface of solder particles. For Method A, as shown in Fig 3, the reinforcements added would uniformly blend with solder flux after stirring for a long enough time (>30min), leading to a higher retained ratio of reinforcement in composite solder paste.

The obtained testing results mentioned above clearly show that actual RROR in solder pastes are higher than solder foils. However, from a practical point of view, actual retained ratio and distribution form of reinforcement in a reflowed solder joint are more implicational to understand the effect of doping of foreign reinforcements on performance of solder joints. Table 3 lists the retained ratio of reinforcements added in solder joints prepared by different processing methods after different reflow cycles. The ICP-OES results demonstrate a decrease of the RRoRs with the number of reflow cycles for all the studied groups. Further, the retained ratios of all the groups decreased significantly after the first reflow cycle. Specifically, the levels of RRoRs in the solder joints for SAC/Ni-A, SAC/Ni-B, SAC/TiC-A, and SAC/TiC-B decreased from the initial magnitude of 0.823%，0.762%，0.809% and 0.736% to 0.245%, 0.365%, 0.145%, and 0.176%, respectively. In particular, the retained ratio of TiC reinforcement in the SAC-TiC-A group showed the most considerable reduction after reflow process (the loss ratio of TiC reached up to 82.1%). However, the RRoRs saw only a slight decrease when solder joints were subjected to more reflow cycles.

In addition to these trends, two other findings from the ICP-OES results are worth mentioning. On the one hand, for the same kind of reinforcement, its loss ratio in the composite solder prepared with Method B was lower than that for Method A after soldering. This phenomenon could be associated with the solder paste which contained flux, most of the reinforcement added was excluded from the paste as the flux volatilized in the early stage of soldering, causing a substantial decline in the RRoR in the final state of solder joints. However, this process of flux volatilization

was avoided in preparation of composite solders with Method B. Thus, the RRoR in the composite solder prepared with powder metallurgy was higher after the first reflow cycle.

On the other hand, after comparing the ICP results of two different types of reinforcements, for any method employed to prepare the composite solder, the retained ratio of active reinforcement (e.g. Ni) in the final solder balls were obviously higher than that of inert reinforcements (e.g. TiC). Specifically, the level of RRoR of Ni was always higher than that of TiC in solder balls under the same conditions. A possible reason for this phenomenon is that Ni reacts readily with molten Sn-Ag-Cu alloy, forming Ni-containing intermetallic compounds (IMCs). By contrast, as a ceramic material, TiC is difficult to wet reactively by the molten Sn-based solder during the reflowing process; a relatively higher interfacial tension between TiC reinforcement and the molten solder caused the TiC reinforcements to be expelled from the solder joints. It is also believed that a part of Ni reinforcement reacted with SAC solder powder (resulting in Sn-Ni IMCs) at the compacting and sintering stages. This part of Ni reinforcement was thus retained in solder joints in the form of these IMCs. In addition, another part of Ni reinforcement that did not react during sintering is expected to react with molten solder during the reflow process and form new Sn-Ni and Sn-Ni-Cu IMCs. The XRD patterns of a SAC/Ni-B solder billet at different treating stages (Fig. 4a) also validated this finding. However, as seen in Fig. 4b, there were no new Ti-containing IMCs formed in SAC/TiC-B samples at the same treating stages.

In addition, to further understand the existing form of reinforcements in composite solders prepared by method B, the microstructures of SAC/Ni-B and SAC/TiC-B composite solders were examined using SEM. The obtained SEM images for two composite solders before and after sintering are shown in Fig 5 and Fig 6, respectively. It can be seen in Fig 5b that there are some small grey particles with spherical shape formed on the surface of Ni aggregation. These newly formed particles are regarded as Sn-Ni IMCs, which were generated from inter-diffusion between Sn and Ni atoms during compacting process. By contrast, in addition to the initial added TiC reinforcement, no new phases were formed in SAC/TiC-B solder matrix before sintering. This statement can also be confirmed by XRD results shown in Fig 4.

Additionally, to further study the transformation of reinforcements added in composite solders' matrices, microstructures of composite solders after sintering were also investigated using SEM and EDS (see Fig 6). According to Fig 6, the distribution forms of foreign reinforcements in solder matrices could be mainly grouped into three types: a. located at crevice between three solder particles (shown in Fig 6a and d); b. located at the boundary between two solder particles (shown in Fig 6b and e); c. inevitably aggregated at the defect location resulted from the irregular shape of solder particles after ball-milling. From the obtained SEM images, the initial distribution forms of added reinforcements (especially, the active reinforcement - Ni) would largely affect their existing form in solder matrices after sintering. For the first two distribution forms, Ni reinforcements are more likely to entirely transform into Sn-Ni

218 or Sn-Ni-Cu IMCs after sintering, which can be seen in Fig 6a and b. However, for
219 the third distribution form, the Ni reinforcements added would not entirely transform
220 into Ni contained IMCs due to the relatively large size of Ni aggregation. In this case,
221 Ni contained IMCs would be formed from outside to inside around the Ni aggregation
222 (see Fig 6c). EDS results of selected points in Fig 6 are listed in Table 4. According to
223 Fig 6a, b and EDS results of point 1, 2 and 3 shown in Table 4, it can be known that
224 the IMCs formed at solder particles' boundaries are mainly Ni_3Sn_4 or Ni_3Sn_2, which
225 resulted from a fully reaction between Ni reinforcements and Sn-based solder during
226 sintering. However, for the Ni aggregation with lager size, the centre of the
227 aggregation is the non-reacted Ni reinforcements, which are surrounded by newly
228 formed Ni-contained IMCs. The content of Ni element in inner sider of the IMCs
229 layer is proved higher than in outer sider (see EDS results of point 4, 5, 6 and 7). In
230 contrast, the TiC reinforcement remains its initial morphology and distribution forms
231 in SAC/TiC composite solder matrix without new IMCs formed, which could also be
232 evidenced by relevant XRD, SEM and EDX results. By comparing the SEM images
233 of the two studied solder alloys after reflowing (shown in Fig 7), it can also be found
234 that blocky Ni-Sn-Cu IMCs were formed in the matrix of the SAC/Ni composite
235 solder alloy, indicating that Ni remained in the solder joints in the form of
236 Ni-containing IMCs. Still, no similar phenomenon was found in the reflowed
237 SAC/TiC solder alloy, and the TiC reinforcement exists in the solder matrix in its
238 initial state without any new phase formed

239 The big difference in transformation of Ni and TiC reinforcements in solder

matrices during compacting, sintering and reflowing process could be explained by different physical attributes of two reinforcements. As mentioned above, Ni is an active metal reinforcement, which is much easier to react with solid or molten Sn-based solder alloy by atom diffusion under mechanical loading or heating condition. On the contrary, as a typical ceramic material, TiC reinforcement can hardly build a reliable bonding with solid or molten solder alloy due to the non-wetted interface and relatively higher interfacial tension during processing process (especially, sintering and reflowing). Essentially, the relatively stable interface between TiC and solder matrix is mainly determined by the difference in chemical bond structure between ceramic materials and metal materials. Actually, in addition to the proposed factors in the present study (including type of reinforcement, processing methods and reflow cycles), other factors such as density of reinforcements, modification of reinforcement, alloy elements and soldering approaches might also have important effects on retained ratio of foreign reinforcements in solder interconnections; these aspects would be also valuable and instructive in follow-up study.

4. Conclusions

The retained ratios of two kinds of reinforcement in the SAC based composite solder joints decrease with the reflow cycles. The loss the reinforcements reached their maximum after the first reflow for both reinforcements. In addition, the loss ratios showed a much slower decline for the subsequent reflow cycles. For the same

reinforcement, the levels of its retained ratio in the composite solder prepared with powder metallurgy were higher than those prepared with the solder-paste blending method. For the same processing method, the retained ratio of active reinforcement – Ni – that could react with the solid and molten solder was higher than that of TiC reinforcement which is unable to react with solder alloy.

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Reference

Abtew, M and Selvaduray, G. (2000), “Lead-free solders in microelectronics”, *Mater Sci Eng R*, Vol. 27, pp. 95-141.

Zhang, L., He, C.W., Guo, Y.H., Han, J.G., Zhang, Y.W. and Wang, X.Y. (2012), “Development of SnAg-based lead free solders in electronics packaging”, *Microelectron Reliab*, Vol. 52, pp. 559-578.

Shen, J. and Chan, Y.C. (2009), “Research advances in nano-composite solders”,

281 *Microelectron Reliab*, Vol. 49, pp. 223-234.

282 Chellvarajoo, S., Abdullah, M.Z. and Khor, C.Y. (2015), "Effects of diamond
283 nanoparticles reinforcement into lead-free Sn–3.0Ag–0.5Cu solder pastes on
284 microstructure and mechanical properties after reflow soldering process", *Mater*
285 *Design*, Vol. 82, pp. 206-215.

286 Fouda, A.N. and Eid, E.A. (2015), "Influence of ZnO nano-particles addition on
287 thermal analysis, microstructure evolution and tensile behavior of Sn–5.0wt%Sb–
288 0.5wt% Cu lead-free solder alloy", *Mater Sci Eng A*, Vol. 632, pp. 82-87.

289 El-Daly, A.A., Hammad, A.E., Fawzy, A. and Nasrallh, D. A. (2013), "Microstructure,
290 mechanical properties, and deformation behavior of Sn–1.0Ag–0.5Cu solder after
291 Ni and Sb additions", *Mater Design*, Vol. 43, pp. 40-49.

292 Hu, X., Chan, Y.C., Zhang, K.L. and Yung, K.C. (2013), "Effect of graphene doping
293 on microstructural and mechanical properties of Sn–8Zn–3Bi solder joints
294 together with electromigration analysis", *J Alloy Compd*, Vol.580, pp.162-171.

295 Bukat, K., Sitek, Janusz., Koscielski, M., Niedzwiedz, W., Mlozniak, A. and
296 Jakubowska, M. (2013), "SAC solder paste with carbon nanotubes. Part II: carbon
297 nanotubes' effect on solder joints' mechanical properties and microstructure",
298 *Solder* Surf Mt *Tech*, Vol. 25, pp. 195-208.

299 Liu, X.D., Han, Y.D., Jing, H.Y., Wei, J. and Xu, L.Y. (2013), "Effect of graphene
300 nanosheets reinforcement on the performance of Sn–Ag–Cu lead-free solder",
301 *Mater Sci Eng A*, Vol.562, pp.25-32.

302 Gao, L.L., Xue, S.B., Zhang, L., Sheng, Z., Ji, F., Dai, W., Yu, S.L. and Zeng, G.

303 (2010), “Effect of alloying elements on properties and microstructures of SnAgCu
304 solders”, *Microelectron Eng*, Vol. 87, pp. 2025-2034.
305 Tsao, L.C., Huang, C.H., Chung, C.H. and Chen, R.S. (2012), “Influence of TiO2
306 nanoparticles addition on the microstructural and mechanical properties of
307 Sn0.7Cu nano-composite solder” *Mater Sci Eng A*, Vol.545, pp.194-200.
308 Liu, J., Andersson, C., Gao, Y. and Zhai, Q. (2008), “Recent development of
309 nano-solder paste for electronic interconnect applications”, Proceedings of the
310 10th Electronics Packaging Technology Conference, Singapore, pp. 84–93.
311 Chen, G., Wu, F.S., Liu, C.Q. and Chan, Y.C. (2015), “Effect of fullerene-C60&C70
312 on the microstructure and properties of 96.5Sn-3Ag-0.5Cu solder”, 65th
313 Electronic Components & Technology Conference, U.S., pp.1262-1267.
314 Chen, G., Huang, B.M., Liu, H., Chan, Y.C., Tang, Z.R. and Wu, F.S. (2016), “An
315 investigation of microstructure and properties of Sn3.0Ag0.5Cu-XAl2O3
316 composite solder”, *Solder* Surf Mt *Tech*, Vol. 28, pp. 84-92.
317 Haseeb, A.S.M.A., Leong, Y.M. and Arafat, M.M. (2014), “In-situ alloying of
318 Sne3.5Ag solder during reflow through Zn nanoparticle addition and its effects on
319 interfacial intermetallic layers”, *Intermetallics*, Vol. 54, pp. 86-94.
320 Tay, S.L., Haseeb, A.S.M.A., Johan, M.R., Munroe, P.R. and Quadir, M.Z. (2013),
321 “Influence of Ni nanoparticle on the morphology and growth of interfacial
322 intermetallic compounds between Sne3.8Ag0.7Cu lead-free solder and copper
323 substrate”, *Intermetallics*, Vol. 33, pp. 8-15.
324 Haseeb, A.S.M.A. and Leng, T. S. (2011), “Effects of Co nanoparticle addition to

Sn-3.8Ag-0.7Cu solder on interfacial structure after reflow and ageing", *Intermetallics*, Vol. 12, pp. 707-712.

Kennedy, A.R. and Wyatt, S.M. (2001), "Characterizing particle–matrix interfacial bonding in particulate Al–TiC MMCs produced by different methods", *Compo Pt A*, Vol. 32, pp. 555-559.

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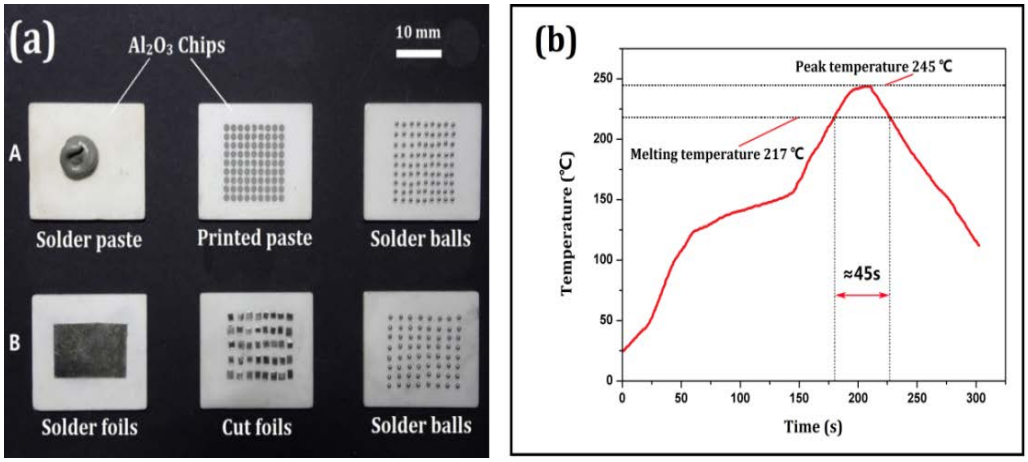

Fig. 1 (a) Schematic diagram of processing methods (b) Reflow condition for preparing solder balls

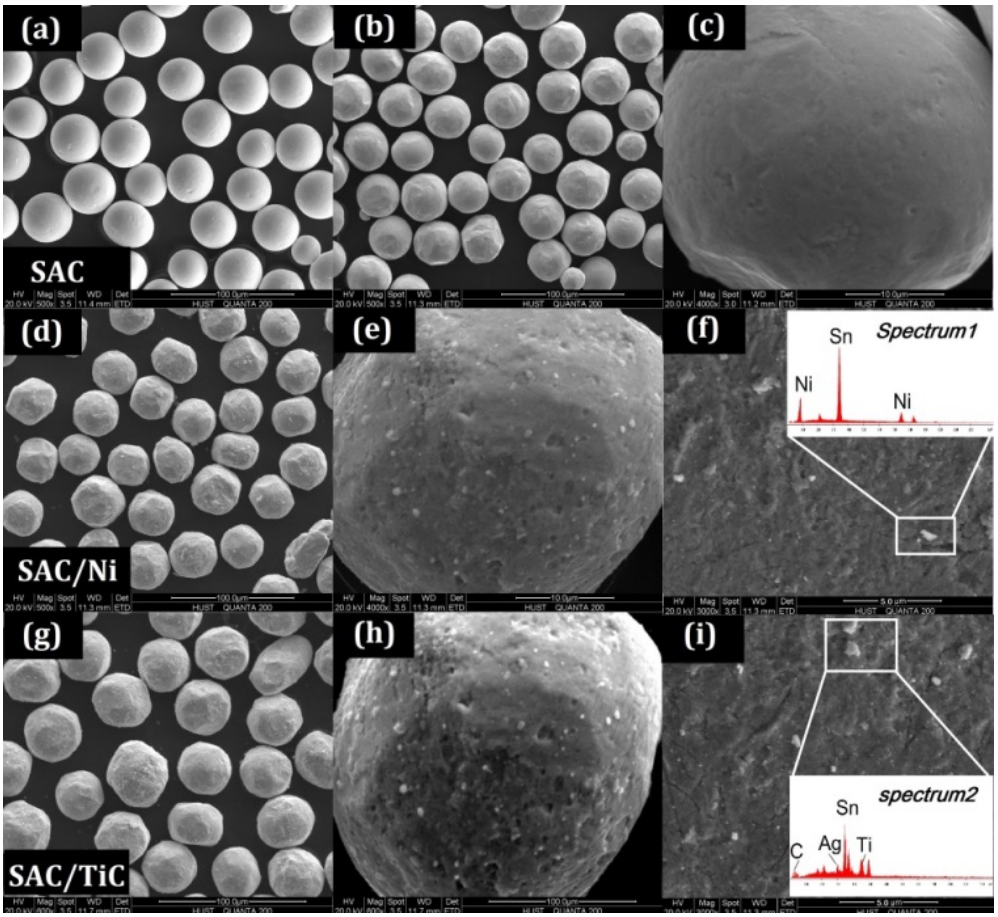

Fig 2 morphology of both plain and composite solder powder after ball-milling process: (a-c) for SAC, (d-f) for SAC/Ni and (g-i) for SAC/TiC.

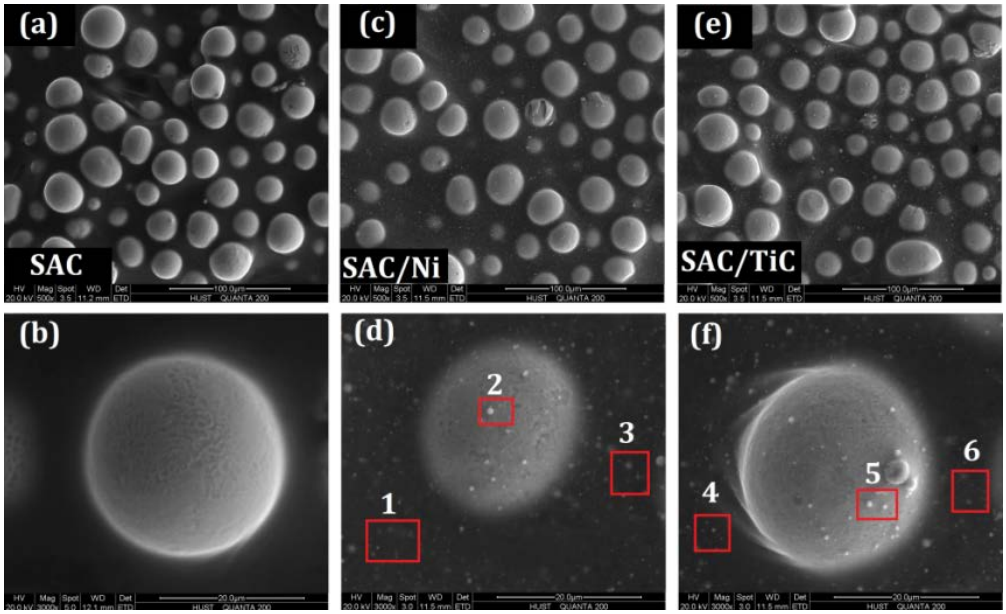

Fig 3 Morphology of both plain and composite solder pastes: (a-b) for plain SAC, (c-d) for SAC/Ni and (e-f) for SAC/TiC.

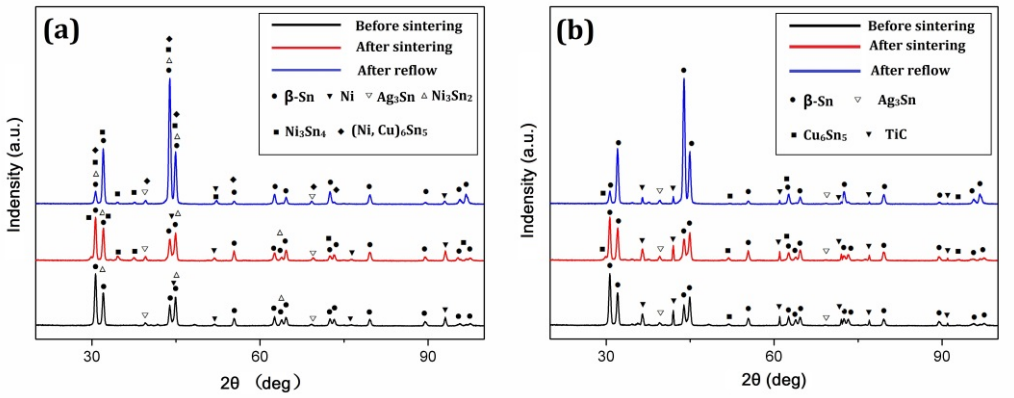

Fig. 4 XRD patterns of SAC/Ni (a) and SAC/TiC (b) composite solders at different treating stages

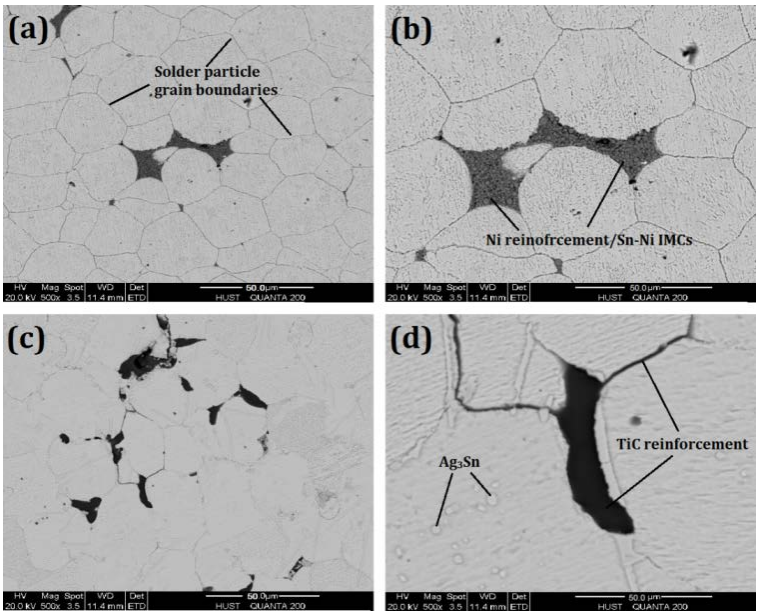

Fig 5 Microstructures of (a-b) SAC/Ni and (c-d) SAC/TiC composite solders prepared through method B before sintering

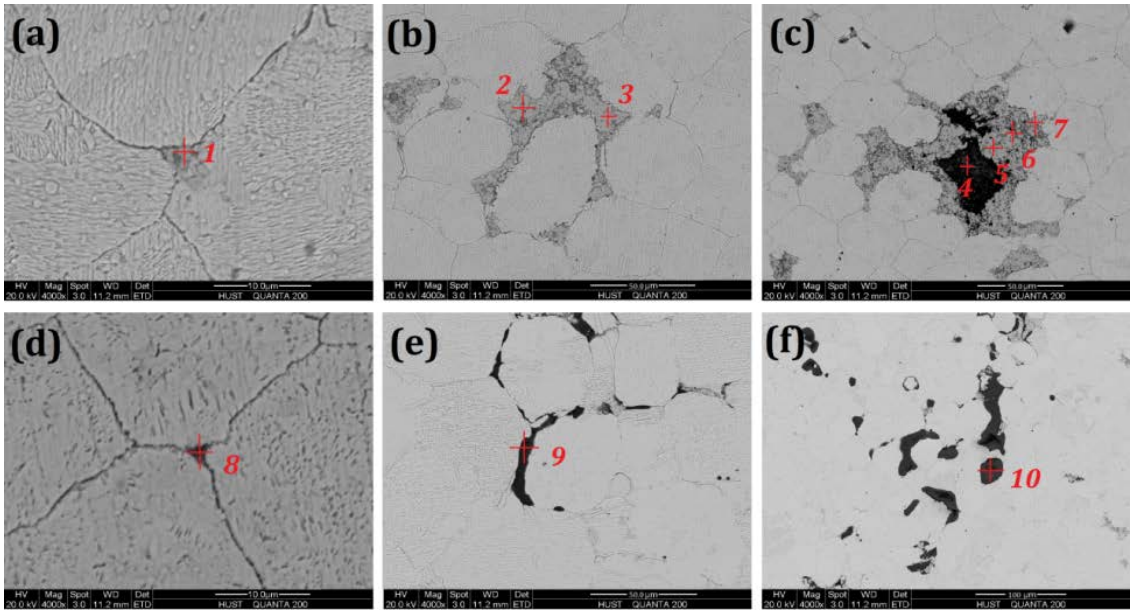

Fig 6 Microstructures of (a-c) SAC/Ni and (d-f) SAC/TiC composite solders prepared through method B after sintering.

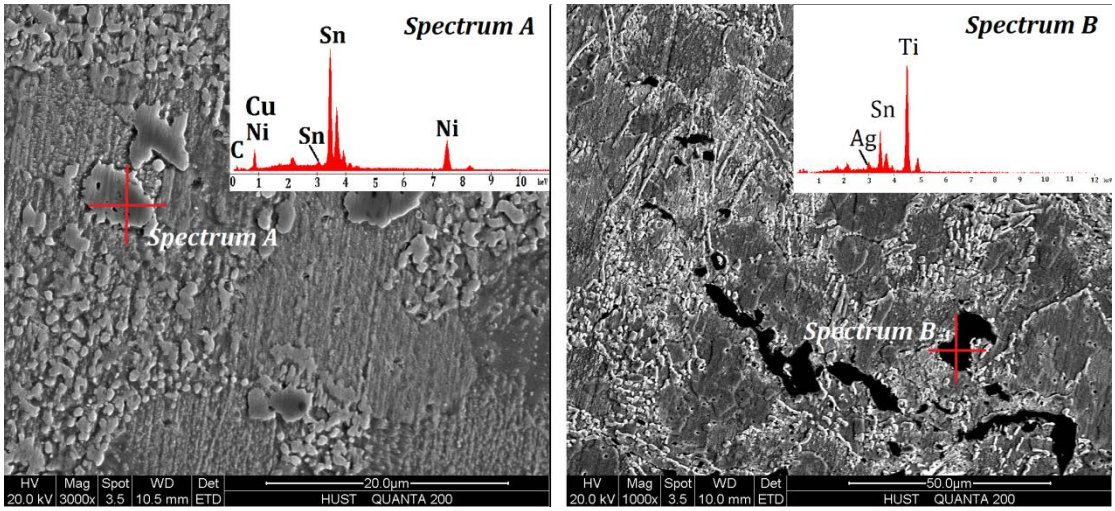

Fig. 7 Microstructures of (a) SAC/Ni and (b) SAC/TiC composite solders after reflow.

Table 1 Weight percentage of different Elements of selected areas in Fig 3

	Sn (wt. %)	Ag (wt. %)	Cu (wt. %)	Ni (wt. %)	C (wt. %)	Ti (wt. %)
#1	9.82	—	—	7.38	82.8	—
#2	79.3	1.8	0.27	1.2	17.43	—
#3	8.89	—	—	6.92	84.19	—
#4	7.78	0.07	—	—	87.8	4.35
#5	83.6	2.1	0.06	—	13.19	1.05
#6	8.92	—	—	—	88.7	2.38

Table 2 Actual weight fraction of reinforcements in composite solder foils and pastes before reflow

	Wt .% of Ni		Wt .% of TiC	
Solder type	SAC/Ni-A	SAC/Ni-B	SAC/TiC-A	SAC/TiC-B
Reference	1	1	1	1
RROR	0.823	0.762	0.809	0.736

Table 3 Reinforcement elements in different solder balls tested by ICP-OES

Solder types	Reflow cycles		
	1	**2**	**3**
SAC/Ni-A	0.245%	0.186%	0.162%
SAC/Ni-B	0.365%	0.276%	0.262%
SAC/TiC-A	0.145%	0.118%	0.102%
SAC/TiC-B	0.176%	0.14%	0.128%

Table 4 Atoms percentage of different elements of selected points in Fig 8

	Sn (At. %)	Ag (At. %)	Cu (At. %)	Ni (At. %)	C (At. %)	Ti (At. %)
#1	55.47	1.08	0.24	43.21	—	—
#2	56.12	1.24	0.83	41.81	—	—
#3	57.11	1.48	0.63	40.78	—	—
#4	35.46	0.72		63.82	—	—
#5	41.21	0.28	0.19	58.32	—	—
#6	44.89	1.84	1.10	52.13	—	—
#7	68.34	1.67	0.54	29.45	—	—
#8	50.31	0.21	0.08	—	22.67	26.73
#9	48.24	0.93	0.53	—	24.58	25.12
#10	48.76	0.82	0.41	—	23.52	26.47