J Mater Sci (2011) 46:4896–4905
DOI 10.1007/s10853-011-5401-3

Effects of Co additions on electromigration behaviors in Sn–3.0 Ag–0.5 Cu-based solder joint

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Received: 21 November 2010 / Accepted: 16 February 2011 / Published online: 24 February 2011

Abstract As the miniaturization trend of electronic packing industry, electromigration (EM) has become a critical issue for fine pitch packaging. The EM effects on microstructure evolution of intermetallic compound layer (IMC) in Sn–3.0 Ag–0.5 Cu + XCo ($X = 0$, 0.05, 0.2 wt%) solder joint was investigated. Findings of this study indicated that current stressing of Sn–3.0 Ag–0.5 Cu–0.2 Co solder joint with 10^4 A/cm^2 at 50 °C for 16 days, no remarkable EM damages exhibited in solder matrix. Whereas, after current stressing at 150 °C for 1 and 3 days, Sn–3.0 Ag–0.5 Cu specimens showed obvious polarity effect between cathode and anode. Different morphology changes were also observed at both sides. After current stressing for 1 day, two IMC layers, Cu_6Sn_5 and Cu_3Sn, with wave type morphology formed at cathode. Sn phases were also observed inside in the IMC layer. However, only Cu_6Sn_5 formed in anode. Three days later, Sn phases were found in anode. Besides, Co additions, aging treatment, Ag_3Sn, and other IMCs improved the resistance of EM by the evidence of retarding polarity effect.

Introduction

Owing to the requirements for higher performance of portable devices, the dimension of solder bump continues decreasing and the current density keeps rising. Thereafter, the reliability issues associated with electromigration (EM) in interconnects of microelectronic packaging has earned more and more attentions [1–4]. EM was defined as the mass transportation of atoms driven by electric current and charge carriers. It can cause microstructural changes in solder joint through the movement of solders and intermetallic compound (IMC) layer. In Sn–Ag–Cu (SAC)-based alloys, such as polarity effect, void nucleation and propagation can be induced by EM [5–9]. It is well known that IMC layer plays an important role in realizing the function of bonding in solder joints [10]. Moreover, as reported by Chen et al. Sn was the dominant moving element in Sn/Cu, Sn/Ni, and Sn/Ag systems during EM process. The growth rate of IMC layer can be increased in anode and decreased in cathode in SAC solders [5]. As a consequence, the studies of EM should focus more consideration on such an interface in addition to the morphology variation of solder matrix. However, the current crowding and Joule heating effects induced by complicated geometry of solder bumps in actual electronic packaging industry hampered the understanding of EM [11, 12]. Some understandings about the microstructural evolutions observed from this type of bumps were over evaluated. There are two strategies to release or avoid current crowding and associated local Joule heating. One is the optimization of the configuration of the solder joint. Tu et al. diffused and spread electric current by introducing contact resistance [1]. However, the high current density in contact resistance might enhance the consumption of UBM. Nah et al. utilized the superb thermal conductivity of

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Cu column to eliminate hot-spots in solder [13]. The other one is the adjustment of solder materials. By using reinforcement particles or composition adjustment approaches to improve the resistance of solder materials for EM. Unfortunately, rare studies had mentioned on the view of this point.

Studies in single phase materials have been carried out a long period and proposed some solutions for EM, such as incorporating copper atoms in aluminum grain boundaries [14]. Knowledge gained from these studies can give inspiration in dealing with EM problems in multiphase materials. In order to suppress coarsening of solder matrix and growth of IMC layer between solder matrix and Cu substrate, fourth-element alloying approach has been widely used in electronic industry [15–17]. As one of the promising alloying elements, Co has been investigated by some of previous works. It even can act as diffusion barrier in Pb-free solder joint during soldering process [16, 17]. Therefore, it may be useful to retard the difference of IMC layers' thicknesses between anode and cathode. Then, a small amount of Co was added into Sn–Ag–Cu solder to understand its influence on EM behaviors.

This study examined the effects of different weight fractions of Co additions (0.05 and 0.2 wt%) on EM behaviors based on Sn–3.0 Ag–0.5 Cu solder alloy. The evolution of microstructural characterization of joint specimens under the current density of 10^4 A/cm^2 at different ambient temperature was observed. Besides eliminating current crowding effects, the solder joints with butt structure were used in this study. The changes of polarity effects on both anode and cathode sides of solder joint with or without Co have been analyzed.

Experimental procedures

The Sn–3.0 Ag–0.5 Cu–X Co ($X = 0$, 0.05, 0.2 wt%) solder alloys were fabricated by alloying method. Commercial available Sn–3.0 Ag–0.5 Cu solder paste and Co particles were used in this study. The size distribution of the solder particles and Co particles were 20–38 μm and 2–3 μm, respectively. The Co powder was mechanically mixed with the solder paste. During the alloying process, ceramic crucible was used as container. After the melting of the solder, the liquid was casted to a rod ingot. Then, the cast was rolled into 200 μm thick. A detailed description of this process is available in our previous publication [18].

A butt solder joint was used to ensure a uniform distribution of current density in solder joint. A specially designed aluminum die was used to help the fix of the Cu/solder/Cu solder joint structure [19]. The two copper substrates were cross headed. Before soldering, Cu substrates were precleaned with 30% nitric acid solution and acetone to remove the oxidation layers and other contaminations. Furthermore, the melting and solidifying behaviors of solder alloys were examined by differentials canning calorimeter (DSC) analysis. It was found that the melting point of solder alloys with or without Co was similar. Consequently, the same reflow profile was applied to all specimens. The joints were soldered to a maximum temperature of 280 °C, and then cooled down to room temperature in the air. Figure 1a described the solder joint after mounted in epoxy resin. At this step, the hypotenuse was used as datum plane. Moreover, in order to guarantee a uniform current density in solder joint, the ends of two Cu substrates, 5 mm away from the solder joint, were bent an angel and act as down-lead for the application of electric current. Then, the sample was ground to a triangular prism structure. The dimensions of solder joint were shown in Fig. 1b. If the width of hypotenuse of the triangular prism was 447 μm, the area of cross section of solder joint was 5×10^{-4} cm^2. When 5 A direct current (DC) passed through the solder joints, an average current density of 10^4 A/cm^2 would be generated in solder joint.

Synthetical influences of temperature and electric current on the microstructure development of solder joint were investigated by comparing isothermal aging and current stressing conditions. During the test, the specimens were placed into a convection oven. The temperatures were 50, 100, and 150 °C, respectively. A constant direct current of 5 A was applied in solder joint to producing a current density of 10^4 A/cm^2. After current stressing for a chosen period of time, specimens were polished and examined by scanning electron microscope (SEM). The average

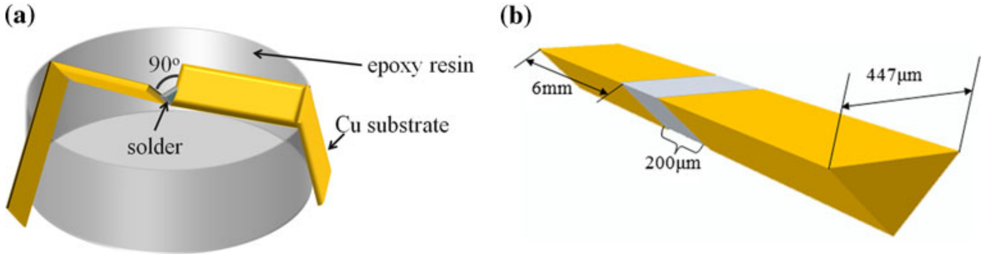


Fig. 1 Structure and dimensions of solder joint. **a** Joint mounted in epoxy resin, **b** dimensions and structure of joint

thickness of IMC layer between solder matrix and Cu substrate was measured through ImageTool® software. Energy dispersive X-ray spectrum (EDS) was used to identify chemical compositions in different phases and intermetallic layers.

Results and discussion

Microstructural characterizations of as reflowed SAC-based solder joints

It was demonstrated that the microstructural characterizations of as reflowed solder joints had a uniform and finely dispersed ternary eutectic phases as illustrated in Fig. 2. Except for the morphology changes of IMC layer, which transformed from scallop type to planar type, 0.05 wt% Co additions in solder matrix exhibited no remarkable influence on microstructure as compared to Sn–3.0 Ag–0.5 Cu solder joint. However, after the weight fraction of Co increased to 0.2%, amount of intermetallic compounds were examined in solder matrix. Their size and morphology were different with each other. EDS analysis revealed that the composition of these IMCs were similar with (Cu, $Co)_6Sn_5$. Considering that the solubility of Co in Sn was very low (0.04 wt%) [20, 21], the Co substituted some of Cu in Cu_6Sn_5 and formed $(Cu, Co)_6Sn_5$ in solder matrix. The thickness of IMC layers of these three solder joint, ranged from 2.64 to 3.31 μm, were nearly same.

Microstructure of solder joints after current stressed at 50 °C

The influence of ambient temperature and electrical current stressing was investigated by comparing the microstructures development under isothermal aging condition in Sn–3.0 Ag–0.5 Cu–0.2 Co. As compared to Fig. 3a and b, isothermal aging treatment for 16 days at 50 °C had no

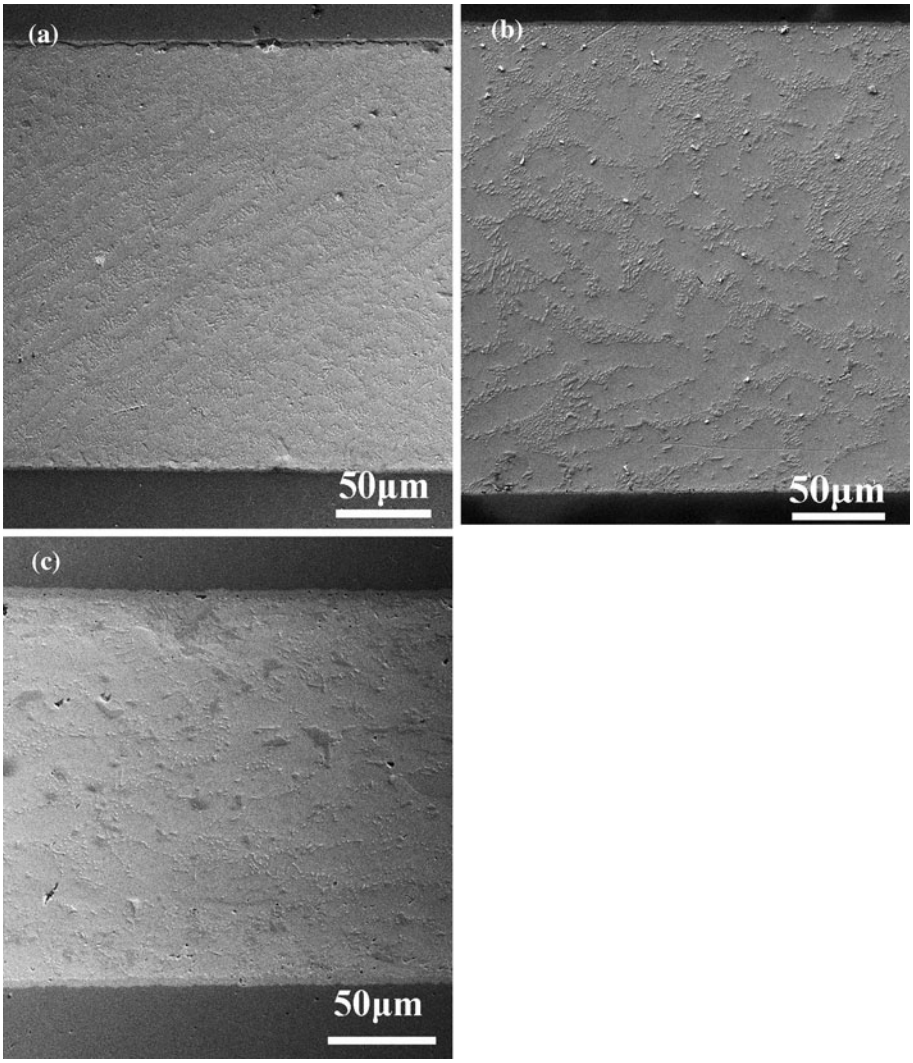


Fig. 2 SEM micrographs of solder joints as reflowed condition. **a** SAC (305), **b** SAC–0.2 Co, **c** SAC–0.05 Co

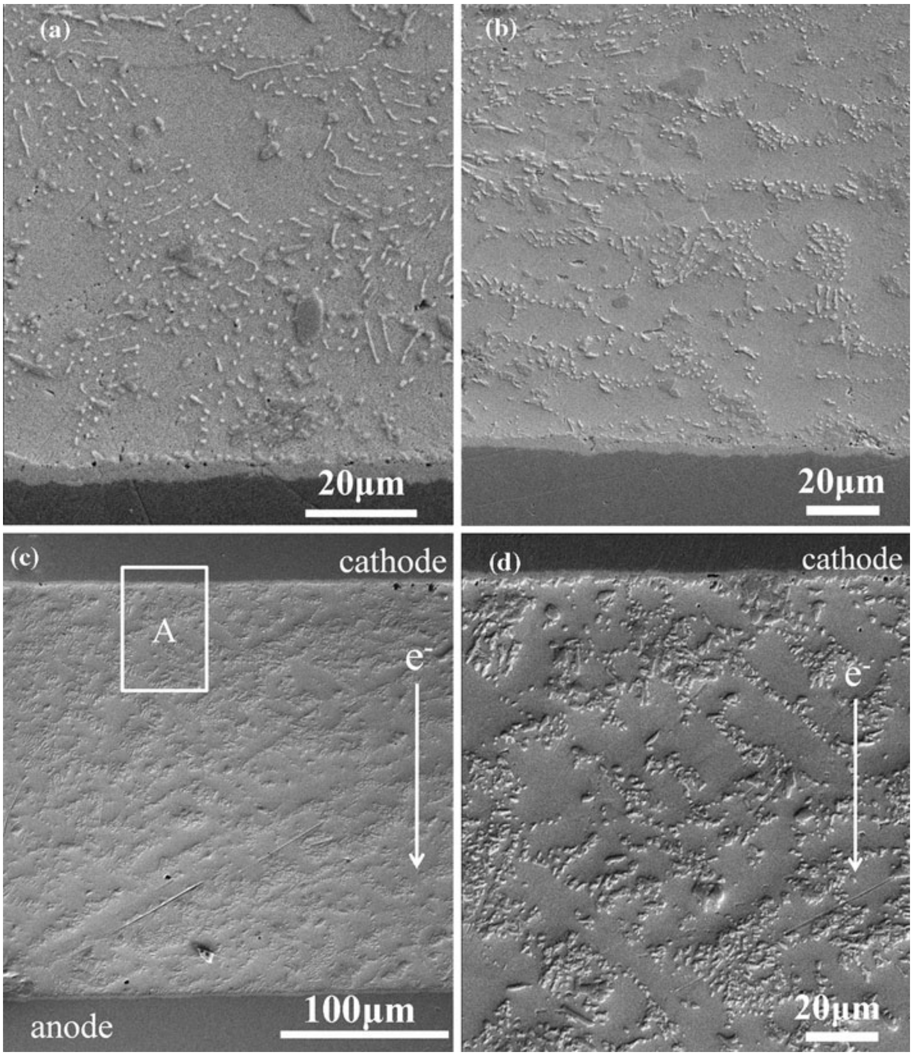


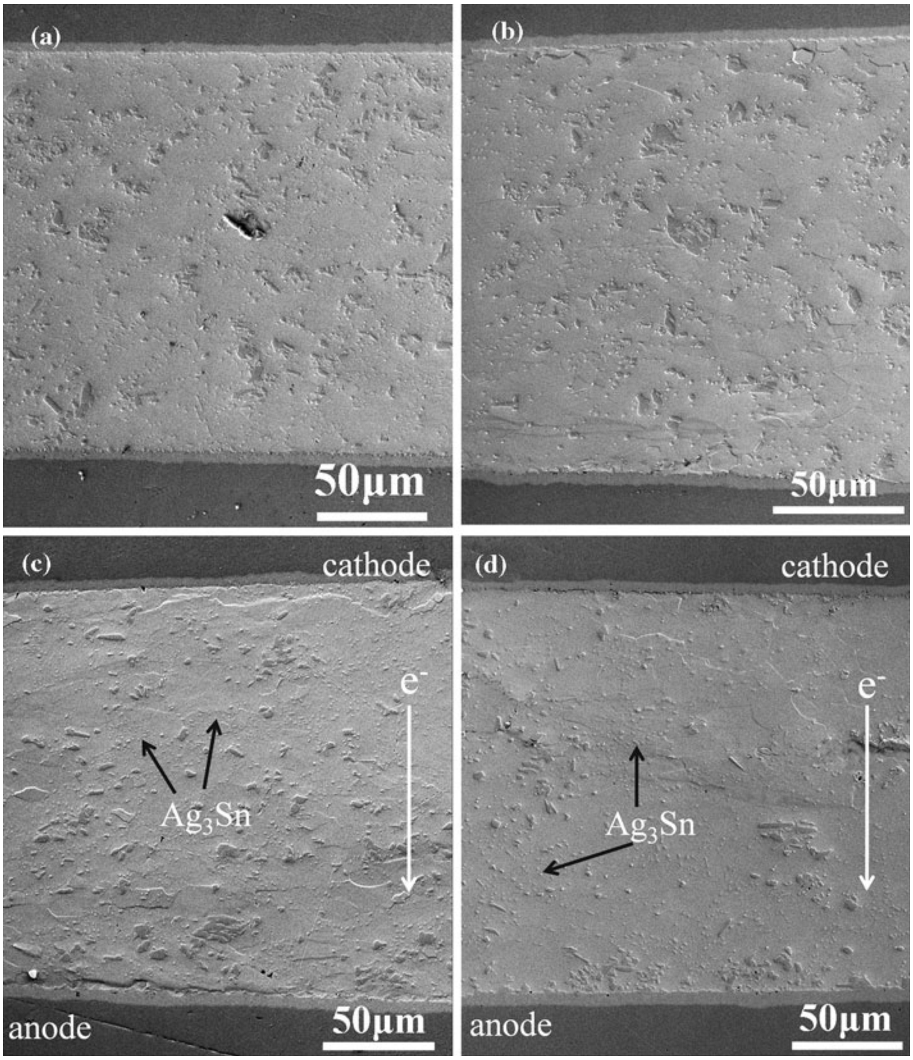
Fig. 3 SEM images of Sn–3.0 Ag–0.5 Cu–0.2 Co solder joint. **a** as reflowed, **b** aging at 50 °C for 16 days, **c** EM for 16 days at 50 °C, **d** amplification of cathode side

obvious effects on microstructure of the solder joint. Figure 3c and d shows the SEM images of solder joint's microstructures after applied electric current at the same ambient temperature for 16 days. It was implied that there were no visible EM damages or microstructure coarsening in the joint. These results were similar to the finds of Lin et al. [22]. On one hand, it was supposed that the stability of the microstructure had been improved by adding of Co [16]. On the other hand, it suggested that EM not easily happened in SAC-based solder joint at 50 °C, even if the current density had arrived at 10^4 A/cm^2. Therefore, it was suggested that the threshold of EM in different solder alloys held different relevant parameters. If a fixed current density was applied to a solder joint, there existed a corresponding critical ambient temperature for the threshold of EM. As long as the temperatures are lower than the critical point, EM effects can be ignored when mentioned to evaluate the life time of solder joint. That is, the relationship between temperature and current density must be the key factors to determine EM effects on microstructure evolutions during current stressing.

Microstructure of solder joints after current stressed at 150 °C

In order to induce EM in SAC–0.2 Co solder joint, the ambient temperature was enhanced to 150 °C. Figure 4 shows the comparison of SEM images of SAC–0.2 Co solder joint after treatments with or without current stressing at 150 °C. The microstructure of SAC–0.2 Co solder joints was coarsened after isothermal aging for 1 and 3 days as demonstrated in Fig. 4a and b. It is worth to note that the growth tendency of IMC layer was not as obvious as that of Sn–3.0 Ag–0.5 Cu solder joint. Figure 4c and d shows the micrographs of SAC–0.2 Co solder joints with current stressing of 10^4 A/cm^2 at 150 °C for 1 and 3 days. EM was observed as an evidence of a slightly difference of the thickness of IMC layers between anode and cathode

Fig. 4 SEM images of Sn–3.0 Ag–0.5 Cu–0.2Co solder joint with or without current stressing of 10^4 A/cm^2 at 150 °C. **a** aging for 1 day, **b** aging for 3 days, **c** EM for 1 day, **d** EM for 3 days



sides. That was polarity effect of IMC layer under EM condition. However, after current stressing for 3 days, the thickness of IMC layer of anode side was 8.62 μm. It was not only lower than the report of Gan et al. [6], but 5 μm lower than the EM results of Sn–3.0 Ag–0.5 Cu solder joint in this article. This observation confirmed the reinforcement effects of Co additions in SAC-based solder matrix. That is, a suitable addition of Co suppressed the growth of IMC layer and retarded the polarity effect under EM conditions. Besides, it was interesting to note that Ag_3Sn held an unparalleled stability in all treatment conditions. It was believed that Ag_3Sn played an important role in preventing the movement of solder and also retarding EM. Besides, according to Anderson et al., the number and the size of IMCs can be increased and decreased, respectively, after introducing minor Co in solder matrix [16]. The more IMCs can be produced in the grain boundaries. Thereafter, the EM can be retarded more effectively in SAC–Co solders than SAC solders.

As a comparison, EM effects on microstructure changes of Sn–3.0 Ag–0.5 Cu solder joint under current stressing of 10^4 A/cm^2 at 150 °C were detected. Figure 5a and c displayed the changes of microstructures of solder joint after current stressed for 1 and 3 days. The polarity effect was far more visible than that of the solder joint with reinforced 0.2 wt% Co additions or that of the joints just current stressing at 50 °C. The difference of thickness between anode and cathode became more evident with the increase of time as compared with Fig. 5a and c. There are a few interesting features in Fig. 5. Figure 5b and d shows the microstructures of cathode side and anode side of solder joint after EM for 1 and 3 days, respectively. It was clear that two IMC layers were formed at cathode side, but one at the anode side as shown in Fig. 5a and b. Contrary to the former literatures [16], the morphology of IMC layer exhibited a wave type at the cathode. It was not scallop type or planar type. Besides, the morphology of the interface was sprouted to Cu substrate but not solder matrix.

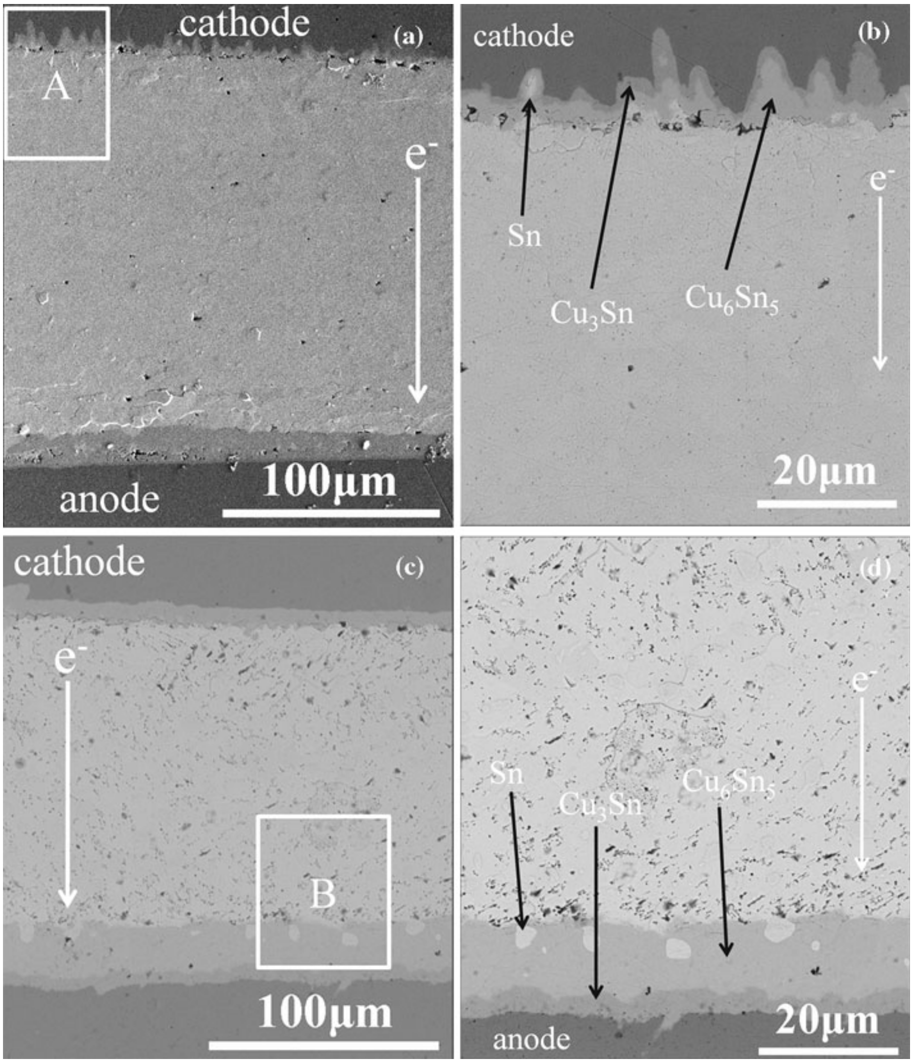


Fig. 5 SEM images of Sn–3.0 Ag–0.5 Cu solder joint with current stressing of 10^4 A/cm^2 at 150 °C. **a** 1 day, **b** cathode EM for 1 day, **c** 3 days, **d** anode EM for 3 days

Some of the Sn phases were also found interior of this IMC layer. After current stressing for 3 days, the numbers of IMC layers and their shape were changed as illustrated in Fig. 5c and d. At the cathode side, the wave type of the IMC layer changed to planar type. Two IMC layers combined to one and no Sn phases existed in cathode side. However, at the anode side, Cu_3Sn formed between Cu_6Sn_5 and Cu substrate. Interior of this side IMC layer, Sn phases were observed. Moreover, voids were also found at the cathode side. That is because of the movement and condensation of vacancies, which moved away from anode to cathode, voids formed at this side as the effect of electric current [6].

The formation of wave type IMC layer at cathode was due to the initial morphology of IMC layer, the difference of interdiffusion velocities between solder matrix and substrate and electric current. Actually, a very thin Cu_3Sn IMC layer was formed between Cu_6Sn_5 and Cu substrate after reflowed condition. The concentration gradient and high temperature induced the interaction between solder matrix and Cu substrate during solid state diffusion. However, if the interdiffusion process was interfered by electric current, the growth tendency of IMC layer at both interfaces would become different. It was known that scallop type IMC layer formed as reflowed condition. Tu et al. [23] demonstrated that Cu flux would like to diffuse through the valley areas between two neighbors of scallops from Cu substrate to solder matrix. Thereafter, these valley areas were firstly preferred to fulfilling by Cu_6Sn_5 IMCs. Nevertheless, at the areas between scallops and Cu substrate, Cu flux could not easily diffuse through this barrier during a short time. It was difficult to allow the diffusion of Cu atom due to the preformed thicker IMC layer (scallops). During the initial stage of EM, if the ambient temperature and current density as high as enough, there must have amount of Cu atoms tended to diffuse to solder matrix through scallops. Then, the Cu atoms were supersaturated at the interface areas between Cu substrate and scallops, but diffused smoothly at the valley areas. Furthermore, the difference of interdiffusion velocities at different positions and the aggradation tendency of Cu atoms at the interface were accelerated by electron wind force at cathode. As a result, a strong interdiffusion was caused between scallops and Cu substrate. Then, a wave type Cu_3Sn IMC layer, extruded to Cu substrate, formed at the cathode. Furthermore, the rapid diffusion of Cu flux form substrate to solder, the interdiffusion between two neighbors of scallops, the barrier effect of scallops, and the electric current made the diffusion velocities and its orientations more complicated. During the ripening reaction, the different diffusion velocities with stochastic orientations between two scallops made Sn phases, like isolated lands, remained in IMC layer. That was the reason why Sn phases can be examined in these two IMC layers. At anode side, due to the electron wind force, the diffusion velocity of Cu flux form substrate to solder was reduced and the Sn flux from solder to substrate was accelerated. It resulted in the growth rate of Cu_3Sn slower than that of the cathodes side. Besides, the sufficient availability of Cu atoms, migrated from cathode, ensured the repaid growth of Cu_6Sn_5 at anode. Therefore, after current stressing for 1 day, only a Cu_6Sn_5 layer can be observed in anode.

After current stressing for 3 days, solder joint had a sufficient diffusion time, the difference of diffusion velocities was balanced same at the cathode. In order to decrease the energy of interface, the wave type IMC layer was finally changed to planar type. This is because the wave type IMC has a larger interfacial area than planar type interface. Under the help of electric current, the Cu flux diffused through cathode easily and the Cu flux should continuously move to anode. Therefore, only Cu_6Sn_5 remained at cathode. At anode side, although, the Cu flux was decreased by the of electron flow, it still moved toward solder matrix due to the chemical potential gradient and the Cu_3Sn layer grow up enough to observe. The exhibition of Sn phases inside IMC layer was resulted from the different formation rate of Cu_6Sn_5 which nearby the interface of IMC/solder.

In order to find out the effects of different weight fraction of Co additions on microstructure of solder joint under same EM conditions. The SEM images of SAC–0.05 Co solder joint with current stressing 10^4 A/cm^2 at 150 °C for 3 days were exhibited in Fig. 6. Polarity effect had been observed as the evidence of EM. Besides, the voids condensed at the cathode side and propagated a crack at the interface between IMC layer and solder matrix. Compared with SAC–0.2 Co specimen, these changes were related to the different weight fractions of Co. As shown in Fig. 2b, when 0.2 wt% Co added into solder matrix, amount of bulk IMCs were formed during solidification process. These IMCs can effectively prevent the movement of vacancies from anode to cathode during current stressing process. As a result, the formation time of voids had been prolonged. However, 0.05 wt% Co additions were relatively too small to change solder joint's microstructure as illustrated in Fig. 2c. That is, the introducing of 0.05 wt% Co was not enough to retard the formation of voids. The reason for no crack emerged at the cathode side of Sn3.0Ag0.5Co solder joint after current stressing for 3 days was due to the formation of wave type IMC layer. It also prolonged the formation of voids at cathode. It was worth to note that the Co contained IMCs which near by the interfacial layer would prevent the Cu being available for the IMC layer and block the growth of IMC layer. A thinner thickness of IMC layer lead to Cu flux diffusion easily. Besides, the introducing of Co made the scallop IMC layer changed to planar layer. This change minimized the difference of diffusion velocities. These two factors avoid the formation of crack

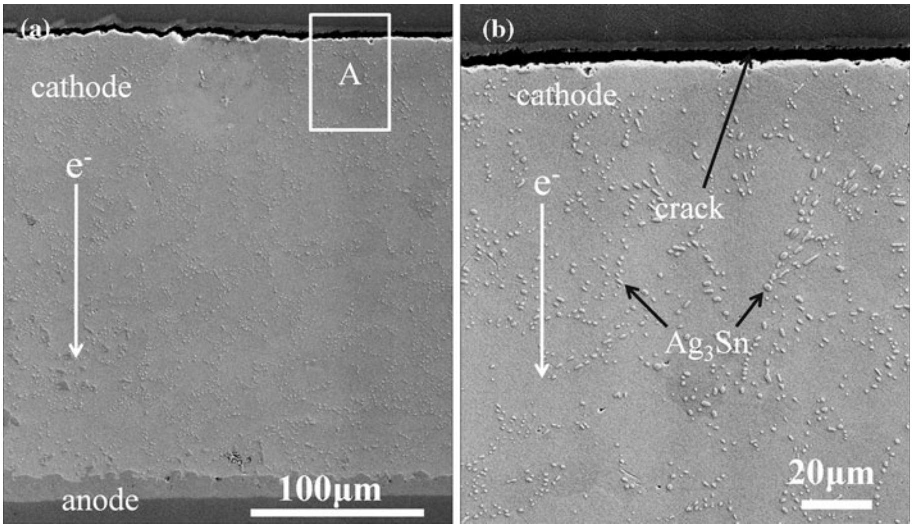


Fig. 6 SEM images of Sn–3.0 Ag–0.5 Cu–0.05 Co solder joint with current stressing of 10^4 A/cm^2 at 150 °C. **a** 3 days, **b** amplification of cathode

during current stressing for 3 days. It was also very important to point that Ag_3Sn still remain its initial morphology. It assumed that the finely dispersed IMCs improved the resistance of EM in solder matrix by retarding the polarity effect, but a too thinner thickness of IMC layer was harmful to the reliability issues of solder joint under current stressing conditions. Figure 7 summarized the IMC layers' thicknesses of different solder joints under same EM conditions at 150 °C. It was demonstrated that the polarity effect has been retarded effectively by adding Co into the solder.

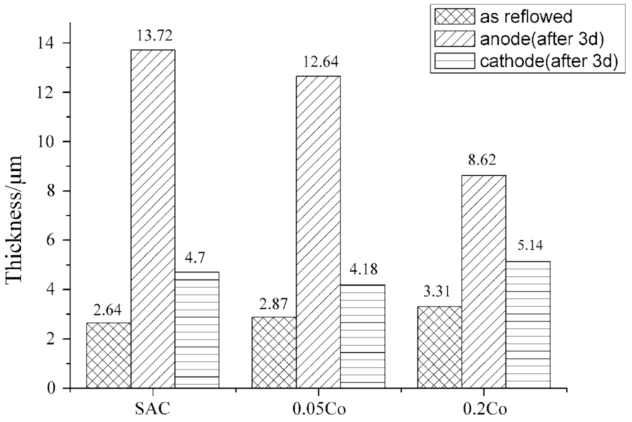
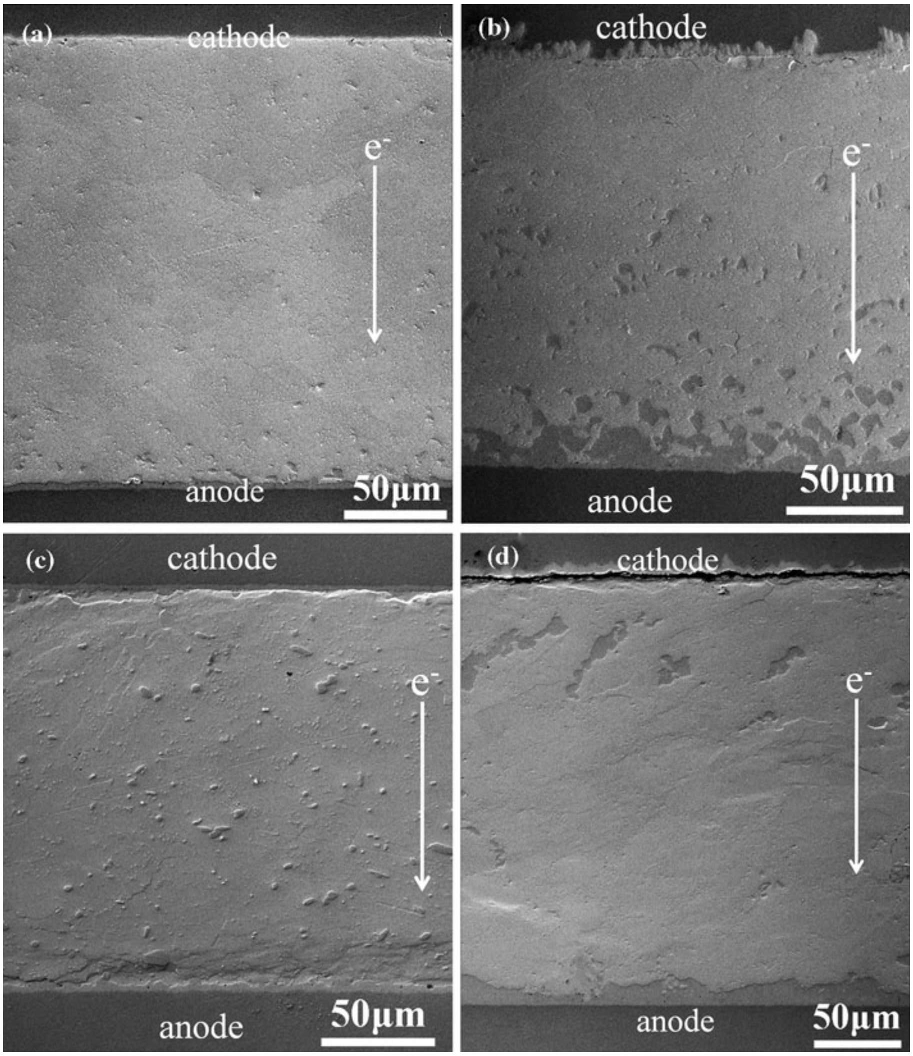


Fig. 7 The summarization of IMC layers' thicknesses in different solder joints after current stressing for 3 days at 150 °C

Microstructure of solder joints after current stressed at 100 °C

Figure 8a and b showed the microstructures of Sn–3.0 Ag–0.5 Cu–0.05Co solder joint with current stressing of 10^4 A/cm^2 at 100 °C for 1 and 3 days, respectively. It was suggested that polarity effect has happened after electric current applied for 1 day. After 3 days, the characterizations of microstructure were similar to that of SAC(305) solder joint with current stressing of 10^4 A/cm^2 at 150 °C for 1 day. The lower temperature decreased the EM damage on microstructure during a same current stressing period.

Fig. 8 SEM images of Sn–3.0 Ag–0.5 Cu–0.05 Co solder joint with current stressing of 10^4 A/cm^2 at 100 °C. **a** 1 day, **b** 3 days, **c** aging for 5 days followed electric current for another 5 days, **d** two circles of electric current for 2 days followed another aging for 3 days



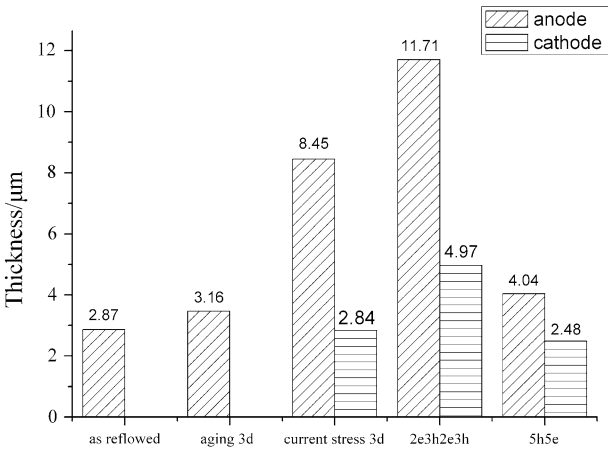


Fig. 9 The summarization of IMC layers' thicknesses in SAC–0.05 Co solder joints after different treatments at 100 °C

Besides, some other comparison experiments were also carried out in this study. Figure 8c exhibited the microstructure of solder joint which firstly experienced a aging treatment for 5 days at 100 °C then applied electric current for another 5 days (5h5e) at the same ambient temperature. It was clear that a relatively thicker IMC layer with planar type morphology can help to suppress the migration of metal atoms diffusion through the IMC layer. Therefore, polarity effect has been alleviated by aging treatment. However, the alternative treatments, 2-day current stressing at 100 °C and come up with 3-day aging then experienced another circle (2e3h2e3h), was very harmful to the reliability issues of solder joint. Not only was the wave type IMC layer formed, the crack was also propagated at the cathode side. The formation of wave type IMC layer was due to the first 2-day current stressing. Moreover, the thickness of IMC layer became thicker and Cu_3Sn layer also formed at this step. If the electric current was withdrawn, the solid state diffusion would dominate the reaction of solder joint. In order to support the growth of Cu_6Sn_5, Cu atoms departed from Cu_3Sn and left vacancies at the interface between these two layers. After experienced another treatment circle, the voids formed crack. Thereafter, before current stressing, appropriate aging treatment can help to improve the resistance of EM, but the alternation treatments, on the order of electric current and aging, accelerated the formation of voids at the cathode side. Figure 9 summarized the thicknesses of IMC layers of SAC–0.05 Co solder joints after different treatments at 100 °C. This results well supported the view have been mentioned above.

Conclusions

In this article, effects of small amount of Co additions on EM behavior of Sn–3.0 Ag–0.5 Cu-based solder joints were investigated with current density of 10^4 A/cm^2 at 50, 100, and 150 °C, respectively. The conclusions were as follows:

1. Under the same current stress, temperature was likely the dominant factor which determined EM damage on solder joint. Current stressing of Sn–3.0 Ag–0.5 Cu solder joint with 10^4 A/cm^2 at 150 °C for 1 day, two IMC layers with wave type morphology formed at the cathode side. Sn phases were also found in this side IMC layer. However, after current stressing for 3 days, Sn phases were examined in anode.
2. The IMC layer which held a planar type and appropriate thickness improved the resistance of EM effects by retarding the polarity effect. Ag_3Sn and the IMCs which finely dispersed in solder matrix and aging treatment also alleviated the effects of electric current for the solder joint.
3. The relationship between ambient temperature and current density determined the development of microstructure under EM conditions. Some complicated changes on evolution of microstructure have been achieved by variation of these two factors.

Acknowledgements The authors acknowledge the support of this work from Beijing Natural Science Foundation Program and Scientific Research Key Program of Beijing Municipal Commission of Education (KZ200910005004).

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