Grain growth sequence of Cu_3Sn in the Cu/Sn and Cu/Sn–Zn systems

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A B S T R A C T

Transmission electron microscopy (TEM) technique is used to figure out the growth mechanism of Cu_3Sn in the systems of Cu/Sn and Cu/Sn–Zn where Cu is polycrystalline. After reflow in Cu/Sn system, a layer of equiaxed Cu_3Sn grains is already present. During solid-state aging initial equiaxed Cu_3Sn grains become columnar and newly formed equiaxed Cu_3Sn grains nucleate at the triple junction sites of the interfaces between Cu/Cu_3Sn and two adjacent Cu_3Sn grains. After prolonged aging large columnar and equiaxed Cu_3Sn grains are present with several voids near the Cu side. Sn–0.5 wt.%Zn solders are prepared to react with Cu for comparison. The result shows that Cu_3Sn grains in this system are constrained to be equiaxed without progressive columnar growth after long time aging.

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1. Introduction

In modern electronics, Sn-based solder interconnections which provide electrical, mechanical and physical connections are widely used. The conducting substrates are commonly made by Cu and Sn is the major element in Sn-based solders to react with Cu substrates [1,2]. Therefore the chemical reaction between Sn and Cu is an important issue. There are plenty of studies about the chemical reaction between Cu and Sn-based solders such as pure Sn, Sn–Ag, Sn–Pb, Sn–Zn, Sn–Bi, Sn–Ag–Cu, Sn–Ag–Bi, etc. [1–23]. In the above-mentioned systems the two general intermetallic compounds (IMCs), Cu_3Sn and Cu_6Sn_5, may be present. The formation of these two IMCs is closely related to the mechanical and electrical properties of devices [3,4]. Thus it is necessary to put much emphasis on these two IMCs.

The growth mechanism transition of Cu_6Sn_5, form scallop-type (initial wetting reaction condition) to layer-type (subsequent solid-state aging condition), has been reported before [5,6]. However, the growth mechanism of Cu_3Sn is rarely concerned because the thickness of Cu_3Sn is too thin to be studied in many cases. Transmission electron microscopy (TEM) technique provides a good approach to figure out the growth mechanism of Cu_3Sn phase. Shang et al. reported the directional growth of Cu_3Sn between eutectic SnBi solder and (1 0 0) single crystal Cu [7]. The interfacial reaction on Cu (1 0 0) plane resulted in a columnar growth of Cu_3Sn along Cu [1 0 0]

with a crystallographic relationship. They also pointed out that the columnar growth and the crystallographic relationship observed in their study had not been reported before for Cu_3Sn. In recent years studies on correlation between single crystal Cu and Sn-based solders have already been published [1,7,8]. However, polycrystalline Cu substrates are widely used in modern electronics [1]. Shang et al. prepared the reactions of eutectic SnBi solder on both single crystal and polycrystalline Cu substrates later [9]. Since the aggregation of Bi fine particles at Cu/Cu_3Sn interface is possible to influence the diffusion behavior between Cu and Cu_3Sn [10] and the kinetics of Cu_3Sn growth [2,10], pure Sn used in the present work could serve as a fundamental to state the growth behavior of Cu_3Sn.

Addition of several elements is able to retard the thickness of IMCs during interfacial reactions between Sn-based solders and Cu. It is reported that the growth of Cu_3Sn would be retarded due to adding Zn atoms into solders [11,12]. However, the microstructure observation of the retarded Cu_3Sn by TEM is never reported. In this present work Sn–0.5 wt.%Zn solders were also prepared to react with polycrystalline Cu. The growth of Cu_3Sn grains in Sn–0.5 wt.%Zn/Cu system were observed by TEM to compare with that in pure Sn/Cu system. The present work is aimed to observe the growth of Cu_3Sn not only in pure Sn/polycrystalline Cu system but also in Sn–0.5 wt.%Zn/polycrystalline Cu system. Both as-reflowed and aged samples were prepared to investigate the microstructure of Cu_3Sn grains during nucleation and growth.

2. Experimental

TEM samples were fabricated as follows. Cu foils (99.9 wt.%) were firstly ground and polished mechanically and then ultrasonically cleaned in ethanol. Afterward the Cu foils were deoxidized by 5 vol.% nitric acid solution and then put on a commer-

cial rosin flux. The reflow process is that the pretreated Cu foils were immersed into molten Sn (99.9 wt.%) and Sn–0.5 wt.%Zn solders with infinite quantity at 250 °C for 90 s and then quenched in iced water. The Sn ingots immersed into the Cu foil were sliced into several sheets which were then aged at 160 °C isothermally for 2–2000 h. The as-reflowed and aged sheets were mechanically thinned to less than 20 μm. These thinned sheets were then glued to Ni rings with commercial G1 epoxy. Furthermore ion-milling treatment with liquid nitrogen cold stage was done at 4.5 keV and with an inclination of 2–6°. Conventional TEM was used at an accelerating voltage of 200 kV. Composition measurement was performed by energy dispersive X-ray (EDX) analysis on TEM.

3. Results and discussion

3.1. Morphology of Cu_3Sn in as-reflowed and as-aged pure Sn/Cu samples

The microstructure of the as-reflowed samples is shown in Fig. 1(a). The two IMCs, Cu_6Sn_5 and Cu_3Sn, are present. Fig. 1(a) also shows that the interfaces of Cu/Cu_3Sn and Cu_3Sn/Cu_6Sn_5 are non-planar. This is due to large driving force, resulting from extended concentration profile, for the dissolution and diffusion of Cu into liquid Sn [13,14]. In general soldering process, Cu_6Sn_5 is the first phase to form at the Cu/liquid Sn interface by experimental observation and thermodynamic calculation [14–16]. Hence the formation of Cu_6Sn_5 is accompanied by the formation of non-planar Cu/Cu_6Sn_5 interface. Cu_3Sn will form between Cu and Cu_6Sn_5 and the formation of non-uniform Cu_3Sn layer here is believed to inherit the non-planar interface of Cu/Cu_6Sn_5. It has been reported that there are orientation relationships between Cu and Cu_6Sn_5 as (1 0 0) single crystal Cu is used to react with molten Sn-based solders [1,8]. They expected that there is a lower interfacial energy between Cu_6Sn_5 and (1 0 0) single crystal Cu. Therefore as long as (1 0 0) single crystal Cu is used these two interfaces of Cu/Cu_3Sn and
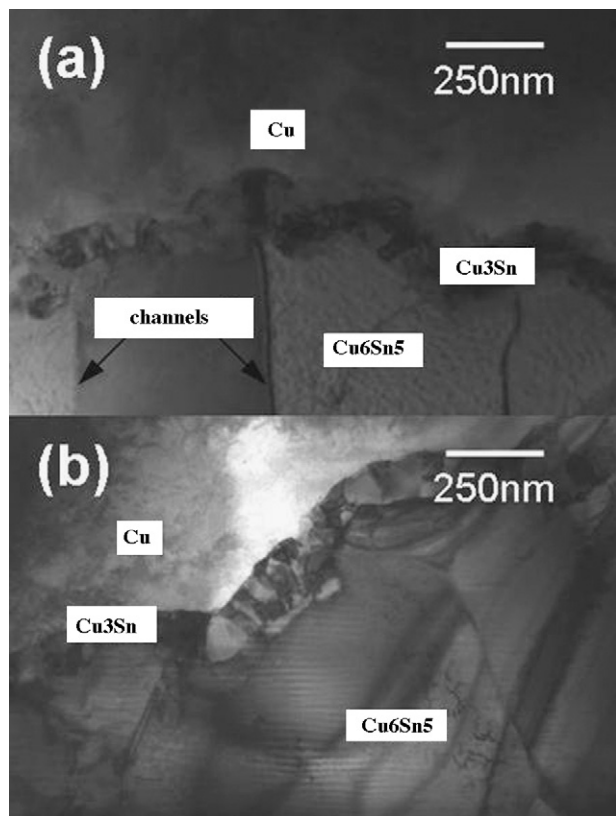

Fig. 1. The microstructure of the sample which is (a) as-reflowed and (b) aged at 160 °C for 2 h. The interfaces of Cu/Cu_3Sn and Cu_3Sn/Cu_6Sn_5 are getting planar and the striation within Cu_6Sn_5 grains is changed from wavy to parallel after aging.
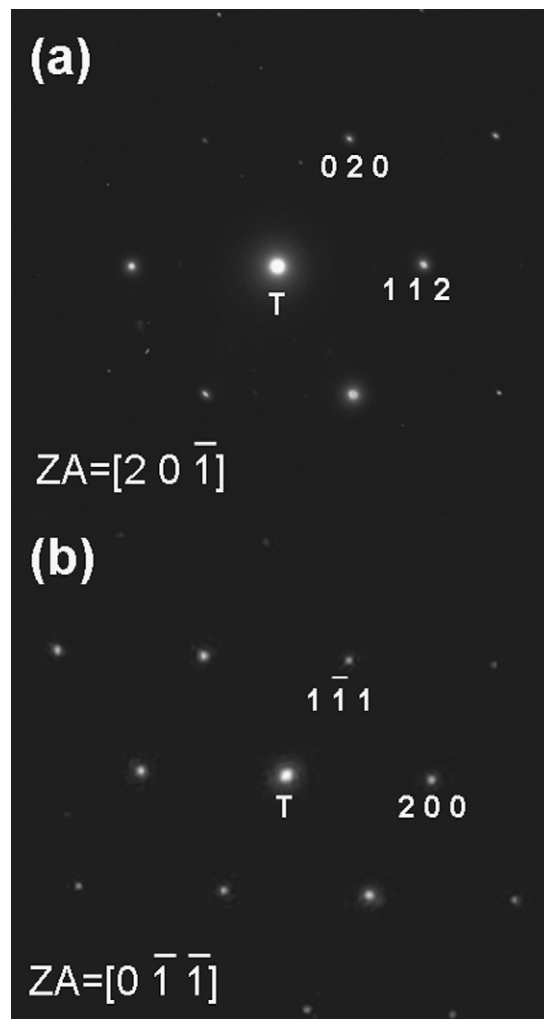

Fig. 2. The selected area electron diffraction patterns of (a) Cu_6Sn_5 and (b) Cu_3Sn. The zone axis of Cu_6Sn_5 and Cu_3Sn is $[20\bar{1}]$ and $[0\bar{1}\bar{1}]$, respectively.

Cu_3Sn/Cu_6Sn_5, which inherit that of Cu/Cu_6Sn_5, would be smooth [9]. Laurila et al. [14] suggested that the grain structure of the Cu substrates has an effect on the dissolution rate of Cu and then on interface morphology. This suggestion is verified by the above experimental results.

Fig. 1(b) shows the microstructure of the samples aged at 160 °C for 2 h. Due to the diffusion of reacting species, the concentration profile decreases between Cu and Cu_6Sn_5, introducing lower driving force, and then the interfaces of Cu/Cu_3Sn and Cu_3Sn/Cu_6Sn_5 becomes planar. Striations in the Cu_6Sn_5 grains can be clearly seen as reported by Liu et al. [17]. The striation is wavy or randomly distributed in the as-reflowed stage but parallel during solid-state aging as shown. Fig. 2(a) is a selected area diffraction pattern (SADP) of Cu_6Sn_5 with $[20\bar{1}]$ zone axis and Fig. 2(b) is that of Cu_3Sn with $[0\bar{1}\bar{1}]$ zone axis. Composition measurements are performed by TEM-EDX. The average composition of Cu_6Sn_5 is 59.7 at.% Cu + 40.3 at.% Sn and that of Cu_3Sn is 75.2 at.% Cu + 24.8 at.% Sn. Cu_6Sn_5 has two structural forms, η-Cu_6Sn_5 with $P2_1/c$ space group [18] and η'-Cu_6Sn_5 with $C2/c$ space group [19], in the solid state with an allotropic transformation at 186 °C. Laurila et al. [14] pointed out that in the as-quenched samples metastable high temperature η-Cu_6Sn_5 will be retained at room temperature. If the ambient temperature is higher (~150 °C), the time for η-$Cu_6Sn_5 \rightarrow \eta'$-$Cu_6Sn_5$ transformation will decrease significantly. In this case, Cu_6Sn_5 should be η' phase in the as-aged (160 °C for 2 h)

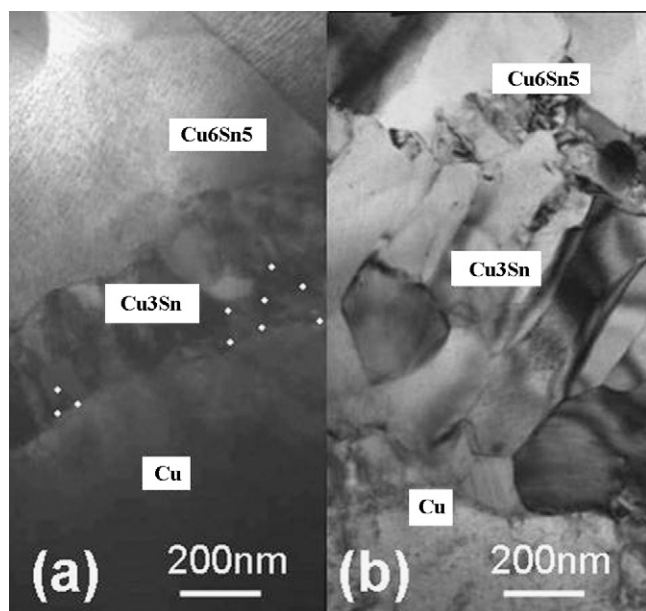**Fig. 3.** (a) Newly formed Cu_3Sn grains nucleate at the triple point sites at the interfaces between Cu/Cu_3Sn and two adjacent Cu_3Sn grains after aging at 160 °C for 48 h. (b) Newly formed Cu_3Sn grains grow into equiaxed after aging at 160 °C for 144 h.

samples. Cu_3Sn has a crystal structure with orthorhombic unit cell which constitutes a superstructure to the hexagonal structure [20].

3.2. Columnar growth of initial Cu_3Sn layer and newly formed equiaxed Cu_3Sn layer

Fig. 3(a) reveals the microstructure of the samples aged at 160 °C for 48 h. The initial Cu_3Sn grains (layer 1) become columnar. Moreover, the newly formed Cu_3Sn grains nucleate at the triple point sites of the interfaces between Cu/Cu_3Sn and the two adjacent Cu_3Sn. Such columnar nature indicates that the grain boundary diffusion controls Cu_3Sn formation or that there is strong anisotropy in the growth of Cu_3Sn [14]. Grain boundary diffusion would induce grain boundary sliding to straighten the wavy grain boundaries [21]. In the Cu_3Sn phase the interdiffusion fluxes of Cu and Sn are controlled by volume diffusion in the temperature range of 150–225 °C [14]. The aging temperature in our study is 160 °C and thus volume diffusion mechanism is suggested to be dominant. Shang et al. [7] performed their solid-state aging at 393 K and thus the grain boundary diffusion mechanism was suggested to be dominant in the Cu_3Sn phase [14]. Whether volume diffusion or grain boundary diffusion is dominant, the nature of columnar growth of Cu_3Sn is unchanged. Consequently, it is suggested that the anisotropy growth of Cu_3Sn itself is strongly controlling the columnar growth of Cu_3Sn. Several orientated growth nature of Cu_3Sn has been reported before [20,22].

Large driving force for the formation of Cu_3Sn causes the difficulty in nucleation of new Cu_3Sn grains. Once nucleated, the anisotropy growth mechanism of Cu_3Sn will start gradually and the morphology of Cu_3Sn is going to be columnar [7]. During solid-state aging, diffusion flux of Cu is higher than that of Sn in the Cu_3Sn phase, that is, Kirkendall effect, and thus excess vacancies would be left behind in the Cu_3Sn phase. The formation of these vacancies would increase the internal stress which will disturb the balance of surface tension at the triple point site between Cu/Cu_3Sn and two adjacent Cu_3Sn grains. Hence newly formed Cu_3Sn grains will nucleate at this triple point sites to form more grain boundaries and then release not only internal stress but also excess vacancies. Fig. 3(b) reveals the microstructure of the samples aged at
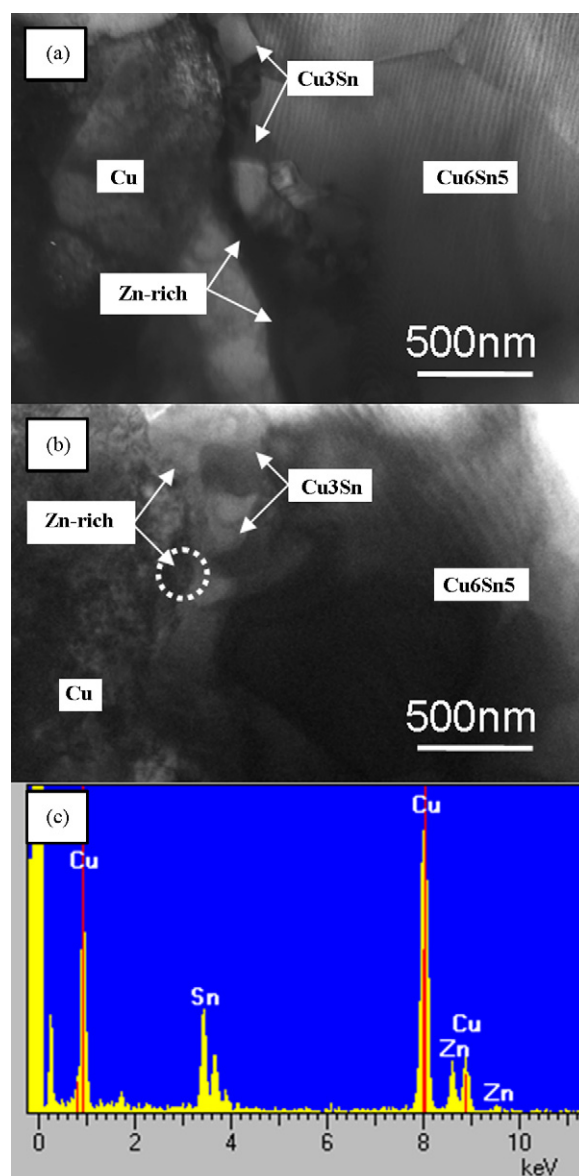

Fig. 4. The microstructure of the Sn–0.5 wt.%Zn/Cu samples reflowed at 250 °C for 1 h and then aged at 160 °C for (a) 0 h and (b) 750 h, respectively. (c) The EDX spectrum of the Zn-rich layer circled in (b).

160 °C for 144 h. The shape of newly formed Cu_3Sn grains (layer 2) is equiaxed. Two kinds of Cu_3Sn morphology, columnar and nodular grains, have been observed before by SEM [23]. An alternative explanation is that triple points were locations with a lower nucleation activation energy than grain boundaries for heterogeneous nucleation [24].

3.3. Comparison of Cu_3Sn morphology between pure Sn/Cu and Sn–Zn/Cu systems

It is widely reported that the growth of Cu_3Sn would be retarded when Zn atoms are added into solders [11,12]. The mechanism for retardation of Cu_3Sn growth is suggested that a Zn-rich layer is located at the interface of Cu/Cu_3Sn and this Zn-rich layer is able to retard the supply of Cu. This result is confirmed experimentally [12] and theoretically [25]. Fig. 4(a) reveals the microstructure of the as-reflowed Sn–0.5 wt.%Zn/Cu samples (250 °C for 1 h). Afterwards, the samples are aged at 160 °C for 750 h and the microstructure is shown in Fig. 4(b). A Zn-rich layer which EDX spectrum is shown
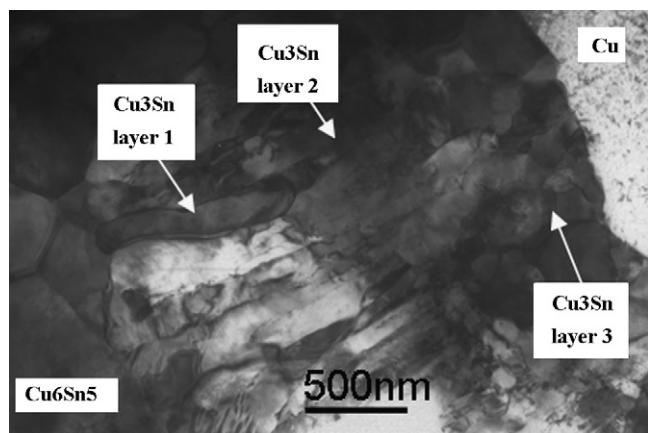
Fig. 5. Cu_3Sn grains separate into three parts after aging at 160 °C for 400 h. Cu_3Sn layer 1 is the initial Cu_3Sn with larger columnar shape. Cu_3Sn layer 2 which is equiaxed originally becomes columnar. Cu_3Sn layer 3 is the newly formed Cu_3Sn region with equiaxed grains.

in Fig. 4(c) is located between Cu_3Sn and Cu in these samples. The thickness of Cu_3Sn aged at 160 °C for 750 h is thinner in comparison with that of pure Sn/Cu samples aged at 160 °C for 400 h (shown in Fig. 5). Such Cu_3Sn phase with thinner thickness is called retarded Cu_3Sn in the present literature. It is noted that the morphology of the retarded Cu_3Sn phase keeps the original shape (i.e., equiaxed shape), even though the aging time reaches 750 h. The retarded Cu_3Sn grains do not transform to be columnar but just increase grain size with the original equiaxed shape. The increase in thickness of Cu_3Sn is attributed to the grain coarsening. The columnar growth of this retarded Cu_3Sn is like to be stopped even though grain growth still continues. However, in pure Sn/Cu samples aged at 160 °C for 400 h a large amount of Cu_3Sn grains are already highly columnar and these highly columnar Cu_3Sn grains are beneficial to increase the total thickness of Cu_3Sn. Thus, it is believed that the interfacial reaction between Zn-bearing solders and Cu is able to retard the columnar growth of Cu_3Sn which mainly contributes to the thickness increase of Cu_3Sn (discussed later).

3.4. Growth generation of Cu_3Sn layers

Fig. 5 shows the microstructure of the pure Sn/Cu samples aged at 160 °C for 400 h. Cu_3Sn layer 1 (the oldest) becomes larger and more columnar. The original equiaxed Cu_3Sn layer 2 becomes columnar. The newest Cu_3Sn grains (layer 3) with equiaxed shape form between Cu and Cu_3Sn layer 2. With extending the aging time newly formed equiaxed Cu_3Sn nucleates and then becomes columnar and old columnar Cu_3Sn becomes larger and more columnar. Shang et al. [9] pointed out that in eutectic SnBi solder/polycrystalline Cu system newly formed Cu_3Sn will also nucleated at the Cu_3Sn/Cu_6Sn_5 interface. However, in the present work (pure Sn solder/polycrystalline Cu) this phenomenon

is obscure especially to the samples with long time aging. Fig. 6 reveals the microstructure of pure Sn/Cu samples aged at 160 °C for 2000 h. It shows that the Cu_3Sn/Cu_6Sn_5 interface is totally occupied by large columnar Cu_3Sn and no small equiaxed Cu_3Sn grains are found. Bi segregation is found at the SnBi solder/Cu_6Sn_5 interface [9] or at Cu/Cu_3Sn interface [10]. It is likely due to that this segregation at interfaces would influence the interfacial property and the kinetics of Cu_3Sn growth [2,10].

3.5. Void formation in the Cu_3Sn phase

The samples are undergone prolonged aging at 160 °C for 2000 h and the resulting microstructure is shown in Fig. 6. The thickness of equiaxed Cu_3Sn is only a little bit thicker than that of samples aged at 160 °C for 400 h. This result implies that the increase of total thickness of Cu_3Sn is attributed to the columnar Cu_3Sn grains. Additionally, this result also implies that the increase rate of equiaxed Cu_3Sn thickness is slower. The other notable feature is that many voids exist in the Cu_3Sn phase especially close to the Cu_3Sn/Cu interface. Many workers have pointed out that the presence of voids accompanies the Cu_3Sn formation [10,14,17,26]. Some of them indicated these voids as Kirkendall voids; however, there are some other discussions and the root cause of the void formation is likely to be more complex [14,26]. To date, the major suggested mechanism of void formation is Kirkendall effect, that is, unbalanced diffusion fluxes (Cu flux > Sn flux) in the Cu_3Sn phase and then introduce excess vacancies. Additionally, the formation of these voids is also related to the existence of the impurities or additives in the solders or Cu substrates. The impurities and additives act as the heterogeneous nucleation sites of the voids and act as diffusion barriers since some of them are easily aggregated to retard the diffusion of reacting species. The above suggestion is fulfilled with the lower "quality" systems demonstrated by most experimental observations but not with high purity systems.

Since the mechanism of void formation suggested above is identical whether low or high quality system is considered, voids should also be detected in high quality system. As shown in Fig. 6 we can see obviously many voids exist in the Cu_3Sn phase. Following the formation of grain boundary of newly formed Cu_3Sn grains that could release the excess vacancies, the reason for void formation is believed to be related to the difficulty in the formation of newly formed Cu_3Sn grains. During prolonged aging, the increase rate of equiaxed Cu_3Sn thickness is slower as-mentioned above. The possible reasons why newly formed Cu_3Sn grains are difficult to form are listed in the following. First, with increasing the aging time enlarged Cu_6Sn_5 grains and Cu_3Sn layer 1 reduce the grain boundaries (rapid diffusion paths) for supplying the reacting species. Due to the shortage of reacting species especially Sn, new Cu_3Sn grains are difficult to form. Second, the curvature of the growth front interface (Cu_6Sn_5/Cu_3Sn) is also worthy to note. The interface of growth front is highly concave toward Cu_6Sn_5 after long time aging but not during short time aging. This result means that the formation of Cu_3Sn itself is unfavorable after long time aging so that the nucle-
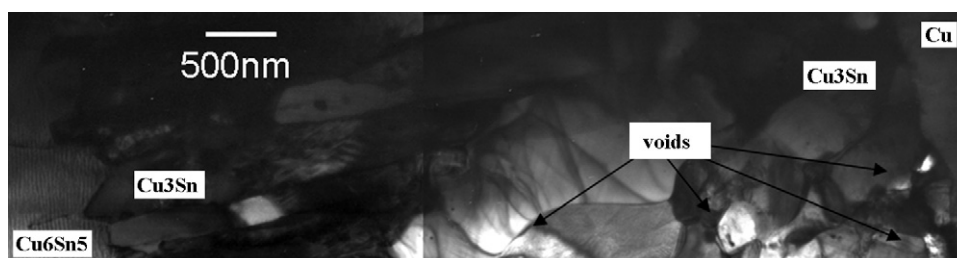

Fig. 6. The microstructure of the Sn/Cu samples aged at 160 °C for 2000 h. The increase of equiaxed Cu_3Sn thickness is not obvious. Several voids are present in the Cu_3Sn phase near the Cu side.

ation of newly formed Cu_3Sn grains is suppressed. The percentage of newly formed equiaxed grains is decreased as shown. Afterward, voids appear in the Cu_3Sn phase especially close to the Cu_3Sn/Cu interface.

4. Summary

Finally it is to summarize all the above results. In the as-reflowed stage (275 °C for 90 s), the two IMCs, Cu_6Sn_5 and Cu_3Sn are present. Since there is no orientation relationship as long as polycrystalline Cu is used, non-planar interfaces of Cu/Cu_3Sn and Cu_3Sn/Cu_6Sn_5 are present. These two interfaces are believed to inherit non-planar Cu/Cu_6Sn_5 interface since Cu_6Sn_5 is the first phase to form in the Cu–Sn system. The nature of Cu_3Sn columnar growth indicates that the grain boundary diffusion controls Cu_3Sn formation or that there is strong anisotropy in the growth of Cu_3Sn. Since the former condition is not confirmed in our study, the latter one is suggested to be dominant. Newly formed equiaxed Cu_3Sn grains would nucleate at the triple point sites of the interfaces between Cu/Cu_3Sn and the two adjacent Cu_3Sn grains to release internal stress and excess vacancies result from unbalanced diffusion fluxes of Cu and Sn atoms in the Cu_3Sn phase. The columnar Cu_3Sn layer 1 becomes larger and more columnar upon increasing the aging time, the original equiaxed Cu_3Sn layer 2 becomes columnar and the newly formed equiaxed Cu_3Sn layer 3 nucleates and grows between Cu and Cu_3Sn layer 2. The formation of newly formed equiaxed Cu_3Sn at the Cu_3Sn/Cu_6Sn_5 interface is obscure in the present work especially during long time aging. The growth of Cu_3Sn in Sn–0.5 wt.%Zn/Cu system is taken for a comparison. In this system equiaxed Cu_3Sn grains form during reflow and keep the same shape after long time aging. The interfacial reaction between Zn-bearing solders and Cu is able to retard the columnar growth of Cu_3Sn which mainly contributes to the thickness increase of Cu_3Sn. The thickness increase in this retarded Cu_3Sn is attributed to the grain coarsening of equiaxed grains. During prolonged aging in pure Sn/Cu system many voids are present in the Cu_3Sn phase due to the

difficulty in the formation of newly formed Cu_3Sn grains to release excess vacancies. The difficulty in the formation of newly formed Cu_3Sn grains is due to the shortage of reacting species and that the formation of Cu_3Sn itself becomes unfavorable.

Acknowledgement

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