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Significant Inhibition of IMCs Growth between an Electroless Ni-W-P Metallization and SAC305 Solder During Soldering and Aging

XU Tao[1], HU Xiaowu[1, 2*], LI Yulong[1], JIANG Xiongxin[1], YU Xiao[1]

(1. Key Lab for Robot & Welding Automation of Jiangxi Province, Mechanical & Electrical Engineering School, Nanchang University, Nanchang 330031, China; 2. State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China)

Abstract: The formation and growth behavior of intermetallic compound (IMC) layers after introducing an electroless Ni-W-P metallization into the Sn-3.0Ag-0.5Cu (SAC305) solder joint during soldering and aging were investigated. The soldering was performed at 250 ℃ for 10 min, followed by air cooling and aging treatment at 150 ℃ up to 15 days. The results show that the scallop-like Cu_6Sn_5 IMC layer and planar-like Cu_3Sn formed between solder and Cu substrate during soldering and aging. The Ni_3P and $(Ni,Cu)_3Sn_4$ compounds were formed between electroless Ni-W-P layer and solder, and Cu substrate was not damaged and kept a smooth interface. When the isothermal aging treatment was applied, the total thickness of IMCs which formed at the SAC305/Cu and SAC305/Ni-W-P/Cu interface increased with increasing aging time. Kirkendall voids emerged at the Cu_3Sn and the Ni_3P layers, but the voids emerged at the Ni_3P layer in the form of crack. The amount of Kirkendall voids increased and the crack elongated with increasing aging time. The Cu_6Sn_5 and $(Ni,Cu)_3Sn_4$ grains grew by merging adjacent grains. In the process of growth, the growing interfacial compounds filled the free space, and new columnar dendrite grain of $(Ni,Cu)_3Sn_4$ constantly generated during aging treatment. After 15 days aging, the Ni-W-P barrier layer was still remained, which indicated that the Ni-W-P layer can be a good barrier layer between the solder alloys and Cu substrate.

Key words: lead-free solder; intermetallic compound; electroless Ni-W-P; interfacial reaction; isothermal aging

1 Introduction

Under bump metallization (UBM) is proposed as a good combination, which can protect the substrate from reacting with solder[1]. It is well know that cooper plate will drasticly react with Sn-based solders during reflow process and there are intermetallic compounds (IMCs) come into being at the interface. During the reflow process, the growth of IMC will cause fracture, open circuit and stress concentration near the joint.

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XU Tao (徐涛): E-mail: xutaofromyjt@163.com

*Corresponding author: HU Xiaowu (胡小武): Assoc. Prof.; Ph D; E-mail: huxiaowu@ncu.edu.cn

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In the past, various tin-lead alloys have been applied to electronic packaging field. However, there is a ban on the usage of electronic devices containing toxic lead and other hazardous wastes[2-4]. Therefore, it is necessary to find out some appropriate alternatives for Sn-Pb solders. Among several candidate alloys, the Sn-Ag-Cu alloy system is believed to be the first choice with the combination of other alloys such as Sn-Bi, Sn-Zn and Sn-Cu, *etc*[5]. The ternary Sn-Ag-Cu alloy which has excellent wettability and mechanical properties is regarded as the most promising alternative of Sn-Pb. Among the Sn-Ag-Cu lead-free solders, the Sn-3.0Ag-0.5Cu (SAC305) solder is the most common one used in microelectronic packaging[6-8].

Many studies have been carried out in the past and reported that Ni and its alloys which have a slower reaction rate with Sn than Cu and Cu alloys[9-12]. Soldering reaction between lead-free solders and electroless Ni-P, in terms of IMC morphology and growth kinetics have been well understood[5].

Nevertheless, the growth of intermetallic compounds of $(Ni,Cu)_3Sn_4$ and Ni_3P, which results from the reaction between tin-rich solder and electroless Ni-P layer during liquid reflow or solid aging, would make the brittle fracture of the solder joints. There is a possible way to improve the properties of Ni-P layer by add W element. Ni-W-P coating is considered as a good diffusion barrier since W possesses well wear resistance and stability.

In this paper, the IMC layer were formed by the reaction between lead-free solder of Sn-3.5Ag-0.5Cu and cooper which has electroless Ni-W-P coating. We reported our experimental results of solid state reaction between Ni-W-P UBM and lead-free Sn-3.5Ag-0.5Cu alloy. We concentrate on the study of microstructural evolution, the effect of aging time on the morphology of IMCs and growth kinetics of the IMC layer in the SAC305/Ni-W-P/Cu system during soldering and prolonged solid-state aging.

2 Experimental

The Sn-3.5Ag-0.5Cu lead-free alloy was used for the solder and 99.99% pure Cu plate with dimensions of 10×10×2 mm^3 was used for the substrate. Some Cu substrates were ecletroless plated with Ni-W-P on the surface, as shown in Fig.1. In Fig.1, a uniform film of Ni-W-P with thickness of 7.2 μm was observed on the surface of copper plate. After polishing, the Cu plates were degreased in a 30% water solution of hydrochloric acid HCl, followed by cleaning in acetone and drying in air. When the cleaned Cu substrates were prepared, they were divided into two groups. One group applied SAC305 soldering with prepared Cu substrate; while the other group was disposed with activates fluid (5 % water solution of HNO_3) one minute. The Ni-W-P will be electroless plated on the surface of the worked substrate by chemical reaction with a pH level of 7.0 in water bath at 80 ℃ for 150 minutes. The chemicals in the plating bath were listed in Table 1; the Ni-W-P layer contains P since sodium hypophosphite is used as a reducing agent.

Two groups of samples were placed equivalently on SAC305 solders and then sent into reflow oven to complete the soldering. The process of soldering was preceded at temperature of 250 ℃ for 10 minutes. Air cooling was applied after brazing. Some of soldered SAC305/Cu and SAC305/Ni-W-P/Cu couples were subjected to isothermal aging treatment at 150 ℃ for 24, 120, 240 and 360 h in air, respectively.

After reflowing and isothermal aging, two samples that derived from the single soldered sample by wire cutting were prepared to study each parameter by observing the cross-sectional structure and top view (direction perpendicular to the interface) of the IMC morphology under scanning electron microscope (SEM). One was mounted in epoxy and polished to remove the skin layer to reveal the cross-sectional microstructure; the other was immersed in corrosive liquid (20 vol% HNO_3 solution) with ultrasonic waves to dissolve away the excess solder and expose the three-dimensional IMC feature.

Table 1 Composition of the plating bath for electroless Ni-W-P

Components of plating bath	Concentration/(g/L)
$NiSO_4·6H_2O$	30
$NaH_2PO_2·H_2O$	35
$Na_3C_6H_5O_7·2H_2O$	30
$CH_3CH(OH)COOH$	16
NH_4Cl	50
$Na_2WO_4·2H_2O$	35

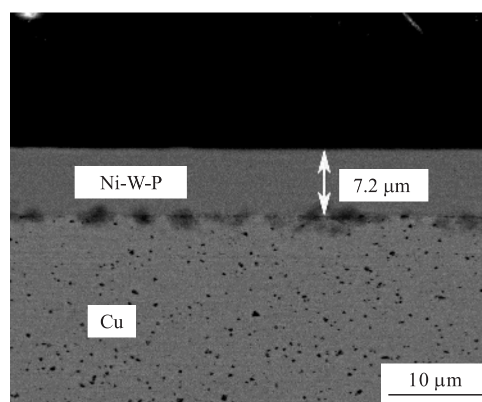

Fig.1 Cross-sectional images of electroless Ni-W-P on the Cu substrate

In order to get accurate thickness data of the IMCs, the microstructure of interfacial reaction region between solder and substrate was investigated by SEM (QUANTA 200F) at a voltage of 20 keV. Detailed morphologies of the top-view surface were revealed using back scatter.

The IMC equivalent thickness was measured using the SEM images of the metallographic cross-sections and the following image analysis procedure. (1) A SEM image of each sample was obtained at the appropriate magnification. (2) The grayscale SEM image was enhanced using Adobe Photoshop image analysis software to clearly identify the interfaces between the different layers and their pixels. (3) The mean equivalent thickness (L_{IMC}) of the individual layer was calculated using the following equation:

$$L_{IMC}=(N_{IMC}/N_{SEM})\times L_{SEM} \quad (1)$$

where L_{SEM} is the actual height of the individual SEM image, and N_{IMC} and N_{SEM} are the number of pixels in the IMC layers and the entire SEM image, respectively. To improve the statistical reliability of the IMC layer-thickness data, at least 15 SEM images covering numerous grains in the middle of the interface were analyzed for each sample. The errors of each IMC equivalent thickness were obtained by using the standard deviation function from the measured data[2].

3 Results and discussion

3.1 Morphology of IMCs of SAC305/Cu samples

Interfacial micrographs of all SAC305/Cu solder joints were observed by SEM with the same

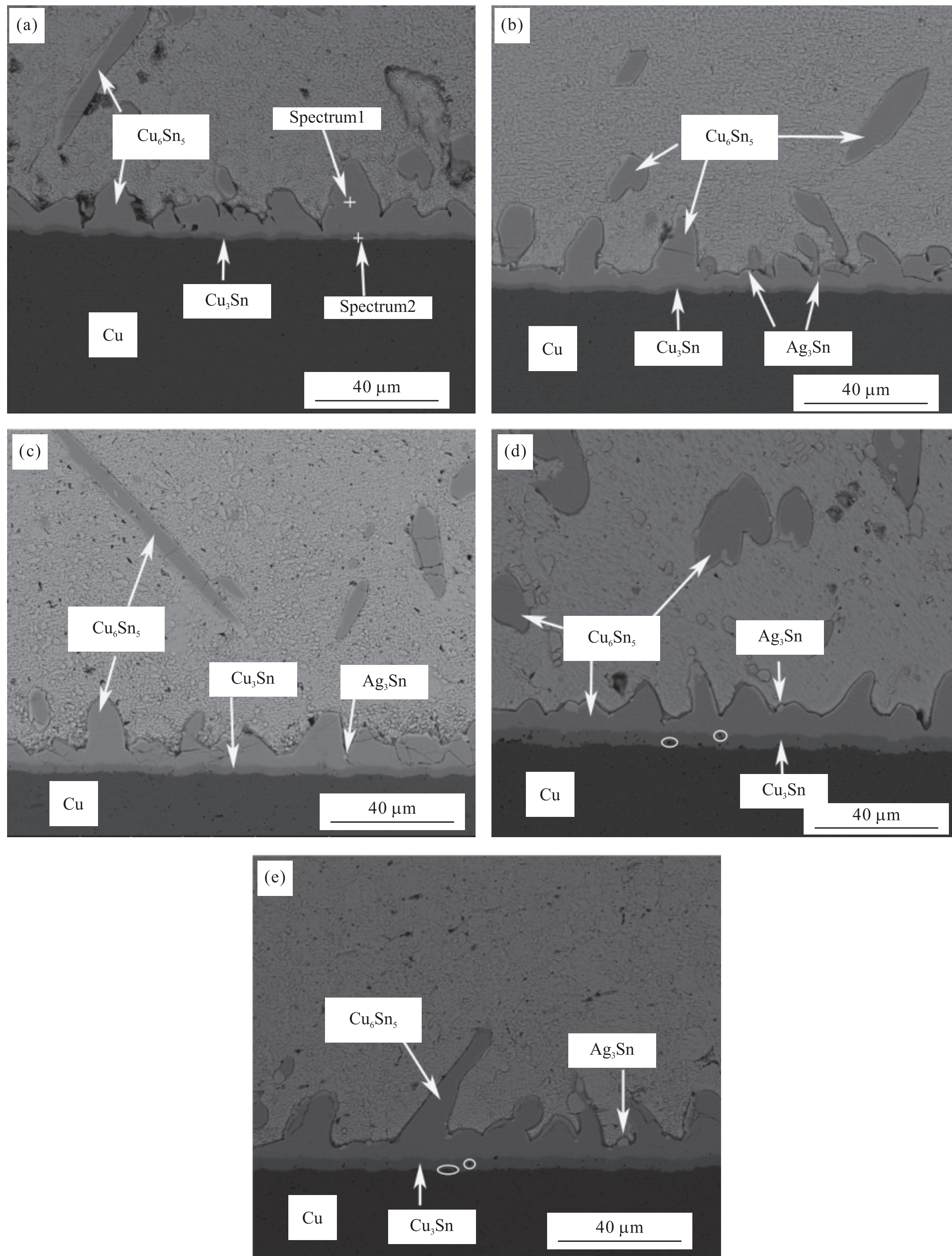

Fig.2 Cross-sectional images of SAC305/Cu interfaces reflowed at 250 ℃ for 10 min: (a) aged at 150 ℃ for 0 day; (b) aged at 150 ℃ for 1 day; (c) aged at 150 ℃ for 5 days; (d) aged at 150 ℃ for 10 days; (e) aged at 150 ℃ for 15 days

magnification to ensure the thickness of the measured precisely. Fig.3 show the interfacial microstructures of SAC305/Cu solder joints after reflowing at 250 ℃ for 10 minutes and aging at 150 ℃ for 24, 120, 240 and 360 h, respectively. As shown in Fig.3(a) and 3(b), a continuous bi-layer IMC consisting of a scallop-shaped Cu_6Sn_5 IMC layer (solder side) and a planar-like Cu_3Sn layer (Cu side) at the soldered joints interface were observed. The Cu_6Sn_5 and Cu_3Sn layer were confirmed by EDS analyses as shown in Fig.5(a) and (b). With the increasing aging time, there were dramatically increases in thicknesses of Cu_6Sn_5 and Cu_3Sn layers, as shown in Fig.2(c)-2(e). Three remarkable phenomena showed up in this group experiment. The first one is the chunk-like Cu_6Sn_5 appeared in all solders bulk images. The SAC305 solder contains 0.5% Cu element which could result in crystal nucleus of Cu_6Sn_5 IMC. The nucleus of IMC would conduct spontaneous nucleation

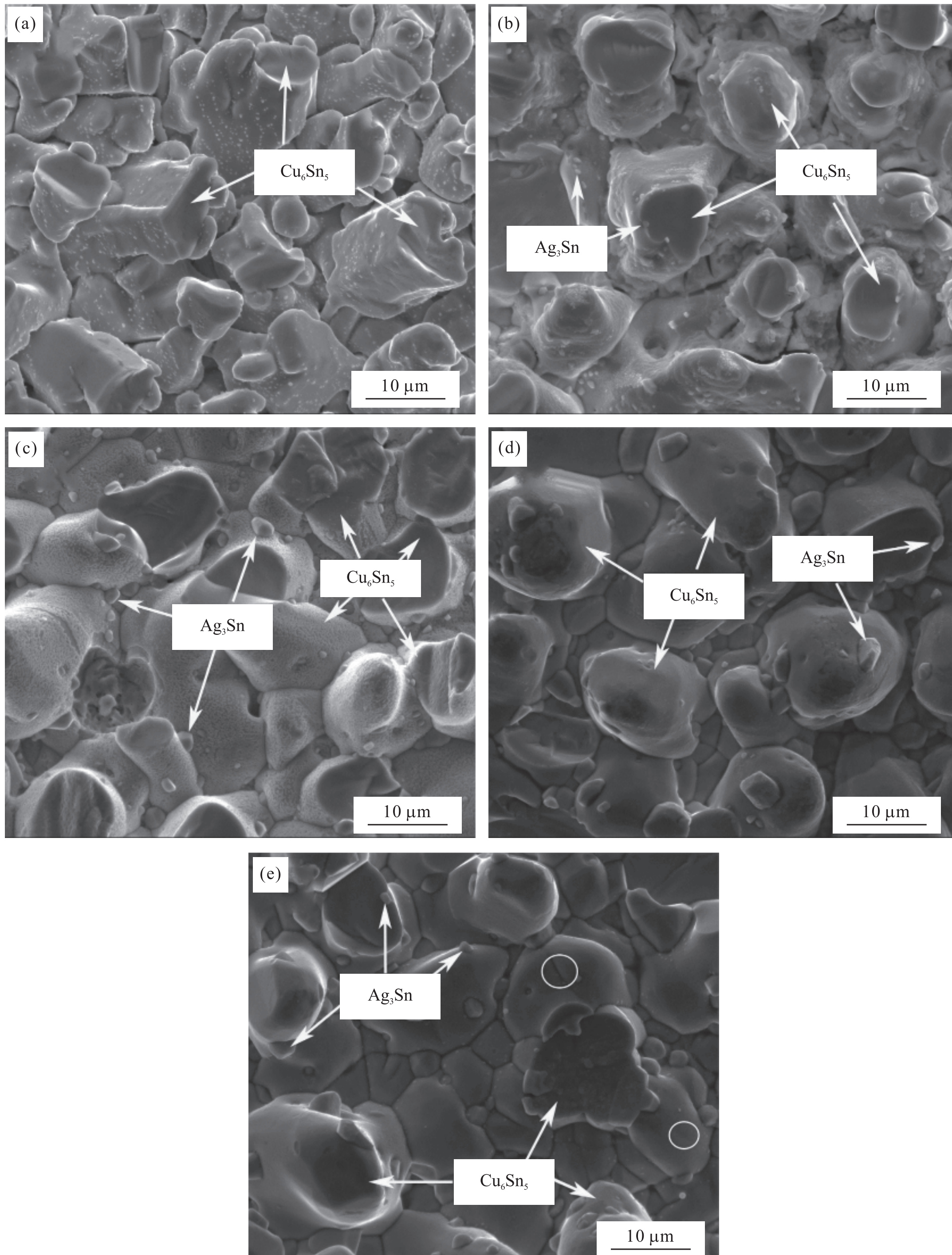

Fig.3 Top view of SAC305/Cu interfacial Cu_6Sn_5 grain reflowed at 250 ℃ and aged at 150 ℃ for different time: (a) reflowed only; (b) aged for 24 h; (c) aged for 120 h; (d) aged for 240 h; (e) aged for 360 h

and growth during the solidification of solder. The second phenomenon is that kirkendall voids[13-16] (black voids as displayed in Fig.3(c)-3(e)) were observe at the interface of Cu_3Sn/Cu (as shown in Fig.3(c) and 3(d)) and inside the Cu_3Sn layer (Fig.2(e)). This is in agreement with the results developed by Xiaowu Hu *et al*[2] and Xiao Yu *et al*[17]. The formation of kirkendall voids can give rise to concentration of stress in solder joints during the process of service, leading to weakening the reliability of mechanical properties of soldered joints and shrinkage working life of products. The third phenomenon is that a large number of cracks appear within Cu_6Sn_5 IMC layer. The cracks in Figs.3(c) and 3(e) indicated that the fracture mode of Cu_6Sn_5 was brittle fracture during aging, and that can be the major reason of failure behavior of solder joints in the process of service.

To further understand the growth behavior of

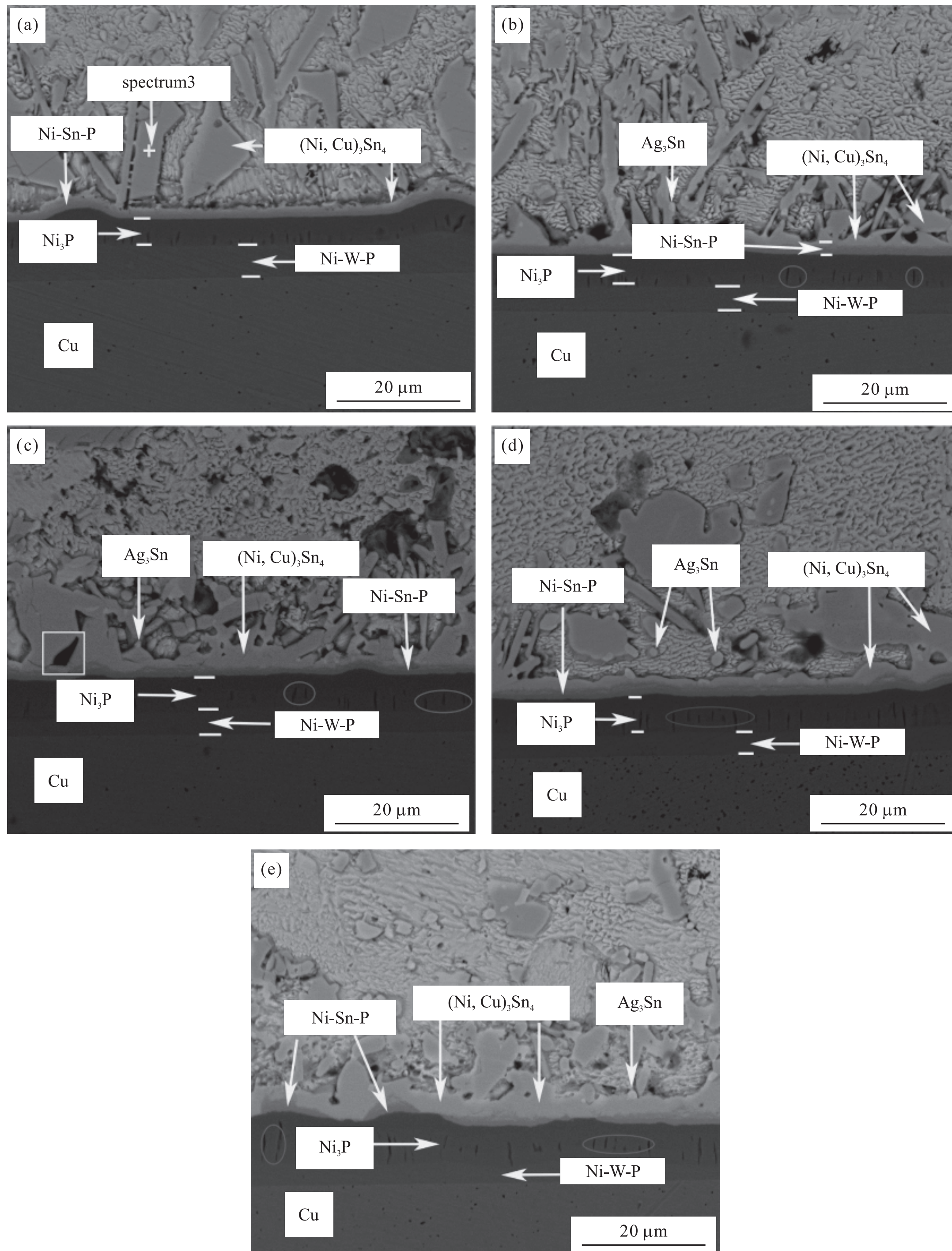

Fig.4 Cross-sectional images of SAC305/Ni-W-P/Cu interfaces reflowed at 250 ℃ for 10 min: (a) aged at 150 ℃ for 0 day; (b) aged at 150 ℃ for 1 day; (c) aged at 150 ℃ for 5 days; (d) aged at 150 ℃ for 10 days; (e) aged at 150 ℃ for 15 days

the interfacial IMC grains, a well know reaction of formation and growth of Cu_3Sn is given as Eq.(2):

$$Cu_6Sn_5 + 9Cu \rightarrow 5Cu_3Sn \tag{2}$$

During isothermal aging, the thicker IMC indicated that there were new IMC grains formation and growth, and this new IMC grains could be come from the product that amounts of Cu atoms reacted with solder, as shown in Fig.3. In this reaction process, a lot of grooves among the interfacial IMCs acted as well channels for Cu atom to pass through the IMCs[2].

Top-views of interfacial IMCs morphology of SAC305/Cu solder joints after reflowing and aging are shown in Fig.3. As shown in Fig.3(a), the branch-type Cu_6Sn_5 with cross section of triangular prism protruded from bottom was observed. After aging for 24 h, the branch-type Cu_6Sn_5 expanded in root and the cross section of triangular prism turned into round shape obviously, as indicated in Fig.3(b). Meanwhile, a number of particles of Ag_3Sn occurred and those particles would transform to chunk-like during the subsequent aging. Both of ovoid-type Cu_6Sn_5 grains and Ag_3Sn particles enlarged with prolonged aging time, and their morphologies still remained ovoid during this period, as shown in Fig.3(c)-3(e). In addition, with the increasing aging time, flat and compact geography formed on the top of interface, and this kind of morphology resulted from cross growth of Cu_6Sn_5 grains as shown in Fig.3(e).

Fig.3 shows the secondary electron micrographs of the SAC305/Cu couples during isothermal aging at 150 ℃ for various times. A series of apparent transformations can be found. The first change is that the branch-type Cu_6Sn_5 with cross section of triangular prism expanded in root and turned into ovoid shape. The second is that the surface of IMC turned from rugged into flat and compact as shown in Fig.3(e). The third variation is that the Ag_3Sn particles arose and grew as aging time goes by. The fourth transformation is that two adjacent grains exhibited matching crystal structures and merged together as shown in Fig.3(e) drew by the white circles. All of these changes result from the growth of interfacial compounds. The Cu_6Sn_5 grains become ovoid and thick by merged adjacent grains, and formed a flat and compact surface. The Ag_3Sn particles also expanded during the aging treatment.

3.2 Morphology of IMCs in the as-reflowed and as-aged SAC305/Ni-W-P/Cu samples

The cross-sectional micrograph of as-reflowed and

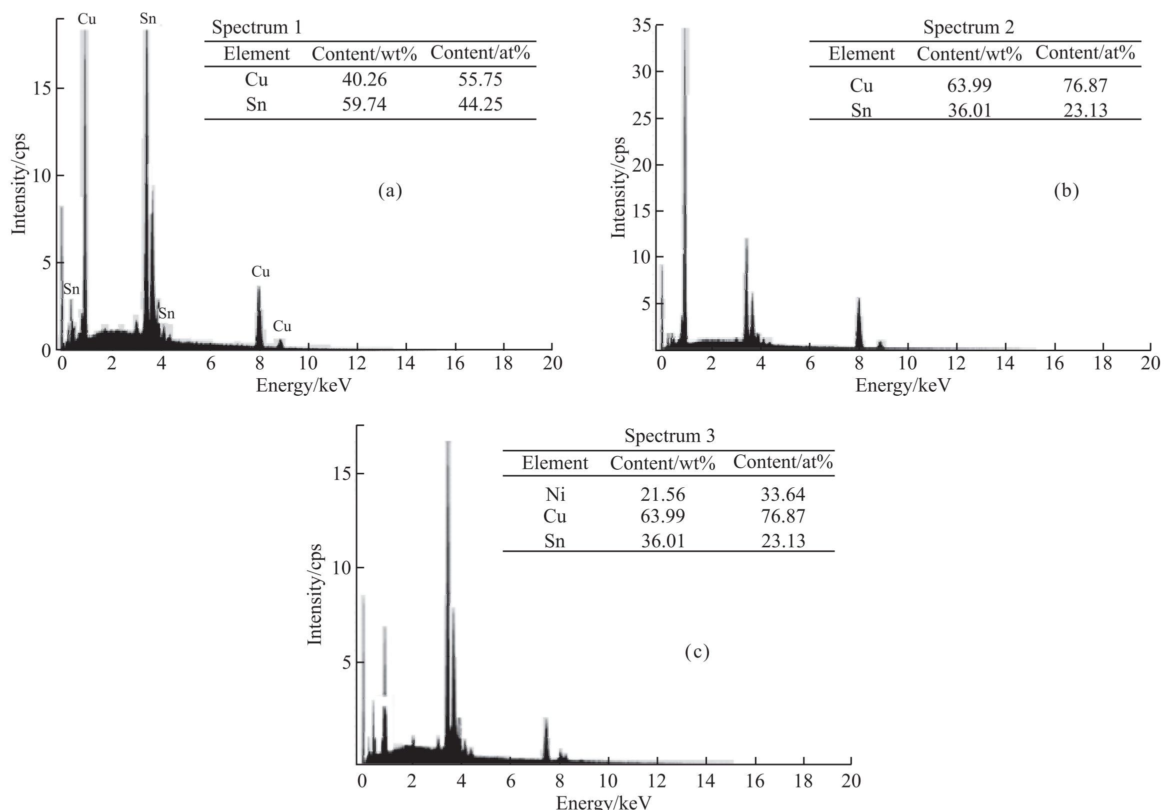

Fig.5 EDS analysis of IMCs grain in Figs. 3 and 4: (a) spectrum 1; (b) spectrum 2; (c) spectrum 3

as-aged SAC305/Ni-W-P/Cu solder joints are shown in Fig.4. After brazed, a ternary Ni-Sn-P compound which was also formed at the interface[18-21] comes out between solder and Cu substrate. And in this study, an apparent appearance that the Ni-Sn-P compounds grew up during solid-state aging was found as shown in Fig.4. Under the back scattering, a gray layer existed in the top of ternary compound as shown in Fig.4(a) has been identified as the $(Ni,Cu)_3Sn_4$, which was confirmed by EDS analyses as shown in Fig.5(c). This is in agreement with the results developed by Aditya Kumar *et al*[18], who thought the branch-type and bulky compounds in solder were $(Ni_{1-x}Cu_x)_3Sn_4$, which were a mixed composition of compounds. What's more, many long and black voids which stand at the interface of Ni-W-P/Ni_3P have been marked with circles as shown in Fig.4. It was reported that the Ni_3P layer could act as a fast diffusion path for Ni atoms with a

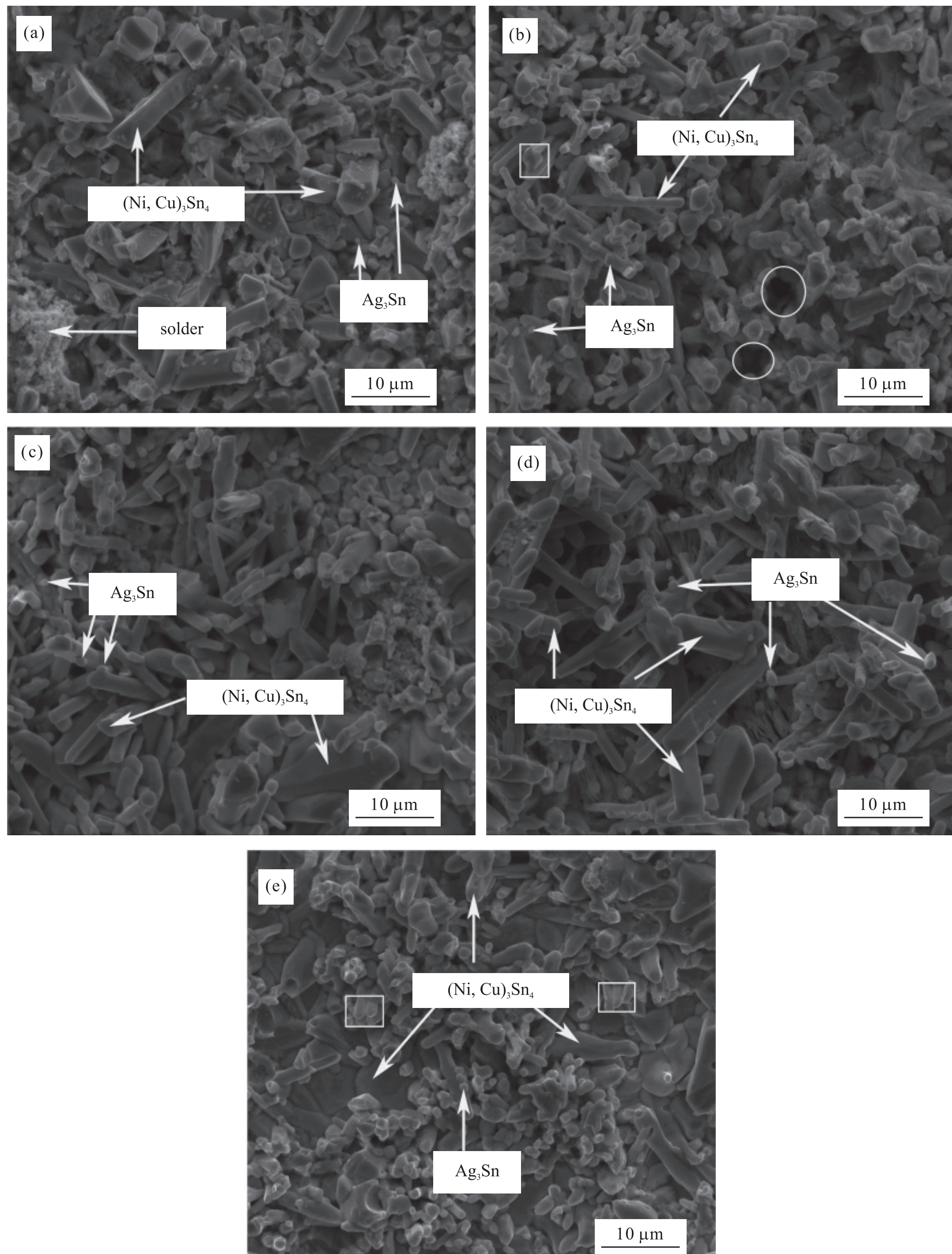

Fig.6 Top view of SAC305/Ni-W-P/Cu interfacial $(Ni,Cu)_3Sn_4$ columnar dendrite grain reflowed at 250 ℃ and aged at 150 ℃ for different time: (a) reflowed only; (b) aged for 24 h; (c) aged for 120 h; (d) aged for 240 h; (e) aged for 360 h

fine columnar structure. So, many long and black voids emerged in the Ni_3P layer resulted from the formation of vacant sites which was caused by the diffusion of Ni atoms through Ni_3P layer but there were not enough compensation from other elements.

After 24 h aged, a new kind of compound named Ni-Sn-P appeared between $(Ni,Cu)_3Sn_4$ and Ni_3P as shown in Fig.4(b). This kind of new compound was inferred as a reaction intermediate by some other compounds transformed. Some black regions had been marked by the rectangle as shown in Fig.4(c) around $(Ni,Cu)_3Sn_4$. With the aging time increasing, there were a few black regions in Fig.4(d) and 4(e), that could be resulted from the growth and combination of $(Ni,Cu)_3Sn_4$. In addition, a lot of particles of Ag_3Sn also occurred in Fig.4(b) and enlarged in the latter aged.

Four different compound layers exist between solder and Cu substrate. From top to bottom are $(Ni,Cu)_3Sn_4$, Ni-Sn-P, Ni_3P, Ni-W-P, respectively. After a period of duration, the layer of Ni-Sn-P experiences two stages. The thickness of Ni-Sn-P layer firstly increases, which is clearly seen in Fig.4(a)-4(d), then decreases because of the consumption which is contributed to the growth of $(Ni,Cu)_3Sn_4$, as shown in Fig.4(e). Through this change in trend, the mechanism of transformation of compounds and diffusion track of Ni element could be explained as follows:

$$\text{Ni-W-P} \rightarrow Ni_3P \rightarrow \text{Ni-Sn-P} \rightarrow (Ni,Cu)_3Sn_4 \quad (3)$$

The above formula indicates that the Ni element diffuses from electroless Ni-W-P layer into solder, which results into various compounds. The layer of Ni-Sn-P attenuated could be resulted from the generation of $(Ni,Cu)_3Sn_4$ by consuming itself as a transition layer. In the early period of aging, a large amount of Ni diffused from the Ni-W-P layer lead to the formation of those kinds of compounds and turned into thicker layers and IMCs. But in the later stage of aging, the $(Ni,Cu)_3Sn_4$ grew by consuming transition layer of Ni-Sn-P to acquire the desired Ni. The continuous attenuation of electroless Ni-W-P declined diffusion rate of Ni. The driving force for Ni element diffusion in this process is the Ni concentration difference between the solder and electroless Ni-W-P layer.

Top-views of interfacial IMCs morphology of SAC305/Ni-W-P/Cu after reflow are shown in Fig.6. Mainly two kinds of compounds which were observed clearly in pictures are $(Ni,Cu)_3Sn_4$ and Ag_3Sn, respectively. As shown in Fig.6(a), some stunted columnar $(Ni,Cu)_3Sn_4$ appeared, and Ag_3Sn particles were adhered on the columnar $(Ni,Cu)_3Sn_4$ compound. The phenomenon has been mentioned in previous research[5]. The black region which has been marked by the rectangle in Fig.4(c) and circles in Fig.6. This kind of spare room exists both on top-views and cross-sectionals indicating that the preferential growth orientation of $(Ni,Cu)_3Sn_4$ crystal was perpendicular to SAC305/Ni-W-P/Cu interface. The $(Ni,Cu)_3Sn_4$ crystal growth pattern can be defined as columnar crystal growing by oriented growth from Fig.4 and Fig.6. Along with aging, only a black region can be observed. It demonstrates the $(Ni,Cu)_3Sn_4$ crystal filled the free space by enlarging the size of intermetallic compound. And in the bottom of interface, a lot of huge diameter $(Ni,Cu)_3Sn_4$ branches and grains occurred as shown in Figs.6(d), 6(e). When it combines with discoveries which are marked with rectangle in Figs.6(b), 6(e), there are a good explanation that two or more thin branches coalesced into bigger and huge branch or bulk. After reflowed, only some stunted columnar $(Ni,Cu)_3Sn_4$ appeared. After another 24 h aging at 150 ℃, there were many thin columnar $(Ni,Cu)_3Sn_4$ distributed and became larger along with aging as shown in Figs.6(b)-6(e).

As shown in Fig.6(e), the flat $(Ni,Cu)_3Sn_4$ grains whose shape is like bulk are pointed out by arrow, and a large amount of thin columnar $(Ni,Cu)_3Sn_4$ compounds emerged. In the period of aging, there still exists a process that Ni element diffused into solder reacting to form new thin columnar $(Ni,Cu)_3Sn_4$ compounds. As long as the process proceeds, fresh thin columnar $(Ni,Cu)_3Sn_4$ grains generate. Abundant Ag_3Sn particles adhered on the columnar $(Ni,Cu)_3Sn_4$ compound, and Ag_3Sn particle become bigger than before. It can be found that the Ag_3Sn particles will grow with aging.

3.3 IMCs growth kinetics at the SAC305/Cu interface and SAC305/Ni-W-P/Cu interface

In Fig.7, four mean thicknesses of interfacial IMC layers are plotted against the square root of aging time during 150 ℃ aging process. Fig.7 represents the IMC layer thickness of as-aged SAC305/Cu and SAC305/Ni-W-P/Cu which were aged at the same condition of isothermal 150 ℃ for 24, 120, 240, and 360 h, respectively. The standard deviation which was measured from the mean thickness of the interfacial layer according to Eq.(1) was quoted in this figure to make error bars more accurate. Relations of thicknesses of four different IMC layers are presented in Fig.7, which indicates the Cu_6Sn_5 phase, Cu_3Sn phase and

$(Ni,Cu)_3Sn_4$ phase all follow a linear relationship with the square root of the aging time. That implies that the diffusion mechanism in the growth of total IMC is a predominant factor.

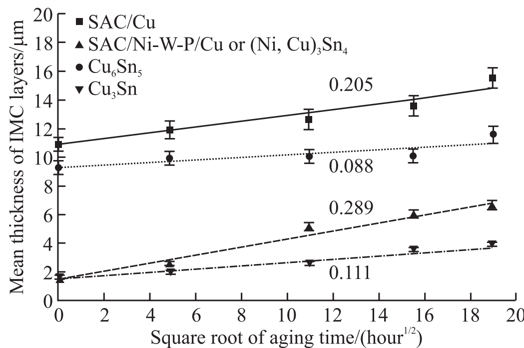

Fig.7 Mean thickness of IMC layers formed at SAC305/Cu interface and SAC305/Ni-W-P/Cu interface *versus* the square root of the aging time

Generally, the growth kinetic parameters of an IMC layer can be determined by plotting its measured thickness as a function of the aging time at given temperature. It has been reported[4, 22] the growth kinetic of the interfacial IMC layer follows the square root time law expressed in the equation below[2]:

$$L_t = L_0 + kt^{1/2} \tag{4}$$

where L_t is the average thickness of the IMC layer at aging time t, L_0 is the initial thickness before aging, k is the growth rate constant, which is strongly related to the diffusion coefficient of atomic elements of the IMCs, and can be obtained from the linear regression line in this figure[2]. The diffusion-controlled mechanism could express with this equation during aging process. From this equation, the value of k related to the total thickness of IMC layer at 150 ℃ for SAC305/Cu and SAC305/Ni-W-P/Cu solder joints brazed at 250℃ for 10 min was found to be 0.205 09 and 0.289 4 $\mu m/h^{1/2}$ (equal to 5.697×10^{-17} and 8.03×10^{-17} m^2/s), respectively, as shown in Fig.7 and Table 2. Under the same condition, the values of k related to the Cu_6Sn_5 and Cu_3Sn layers are 0.088 4 and 0.110 67 $\mu m/h^{1/2}$ (equal to 2.456×10^{-17} and 3.074×10^{-17} m^2/s), as shown in Fig. 7 and Table 2.

It's obviously seen that the growth rate of Cu_3Sn layer is higher than Cu_6Sn_5 layer from the slope in Fig.7 and data in Table 2. As mentioned in Eq.(2), the Cu_3Sn comes from the product of interfacial Cu_6Sn_5 reacted with Cu atom. In consequence, the Cu atom diffusing to the interface of Cu_6Sn_5/solder is greatly reduced. This certifies that Cu_3Sn grows by consuming Cu_6Sn_5 at the interface of Cu_6Sn_5/Cu_3Sn on one hand, and Cu_6Sn_5 grains can't obtain enough Cu atoms to support the growing on the other hand. Besides, there are two directions that Cu_3Sn layer can expand, not only develop at the Cu_3Sn/Cu interface towards Cu substrate but also at the Cu_6Sn_5/Cu_3Sn interface towards the Cu_6Sn_5. For these reasons, the Cu_3Sn layer grows faster than the Cu_6Sn_5 layer as shown in Fig.7. For prolonged aging, the Cu_3Sn layer will be thicker than the Cu_6Sn_5 layer and dominates the interfacial IMCs growth[2]. Kirkendall voids originally formed in the Cu_3Sn layer, as marked by circles in Fig.2(d) and 2(e).

Table 2 Results of statistical analysis for the mean IMC thickness in the SAC305/Cu and SAC305/Ni-W-P/Cu samples

Aging time/day	IMC thickness/μm			
	SAC305/Cu			SAC305/Ni-W-P/Cu
	Total IMC	Cu_6Sn_5	Cu_3Sn	Total IMC /$(Ni,Cu)_3Sn_4$
0	11	9.3	1.7	1.48
1	11.9	9.93	1.97	2.62
5	12.7	10.1	2.6	5.19
10	13.62	10.12	3.5	6.06
15	15.5	11.6	3.9	6.66
Growth rate constant /(μm $hour^{-1/2}$)	0.205	0.289	0.111	0.088

Table 3 Measured thickness of various compound for SAC305 /Ni-W-P/Cu samples

Aging time/day	Metallic compound thickness/μm		
	SAC305/Ni-W-P/Cu		
	Ni-Sn-P	Ni_3P	Ni-W-P
0	1.22	4.3	5
1	1.48	4.9	3.87
5	1.38	5.57	3.49
10	1.42	5.74	3.2
15	1.08	6.42	2.79

It's clearly seen that the total IMC thickness of SAC305/Cu is higher than that of SAC305/Ni-W-P/Cu from Table 2. After prolonged aging, an abnormal phenomenon that the growth rate of SAC305/Cu IMC layer is lower than that of the SAC305/Ni-W-P/Cu (or $(Ni,Cu)_3Sn_4$) layer appeared in Fig.7. This kind of phenomenon could be explained by that the Ni-W-P layer were not entirely reacted and continuously generated $(Ni,Cu)_3Sn_4$ compounds which made the total thickness of IMC increased. But in the SAC305/Cu samples, the initial thicker IMC resulted from the drastic reaction of solder with Cu substrate. The procedure is slow in the subsequent aging. After reflow

soldering, the total thickness of IMC existed at the SAC305/Ni-W-P/Cu interface only was 1.48 μm; the Ni_3P layer was 4.3 μm; the rest layer Ni-W-P and Ni-Sn-P was 5 and 1.22 μm, respectively. Meanwhile, the total thickness of IMC whose main component are Cu_6Sn_5 and Cu_3Sn compounds at the SAC305/Cu interface was 11 μm. We know that Cu_6Sn_5 and Cu_3Sn also consume the Cu substrate to grow up, that can bring about various defects and cause thermal expansion coefficient mismatch. After comparing the experimental data, it shows that the Ni-W-P layer plays a barrier role and effectively blocks the diffusion of Cu atom. There is no copper compound generated at the interface. The melt solder reacted with solid state cooper during soldering, and Ni-W-P barrier layer succeeded with protecting substrate.

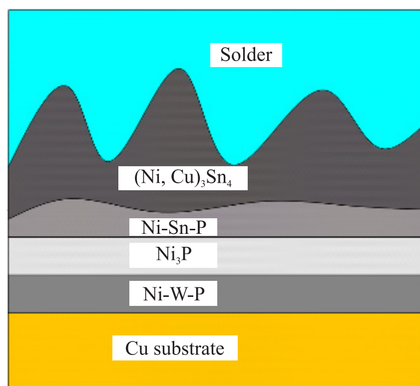

Fig.8 Schematic diagram of SAC305/Ni-W-P/Cu joints

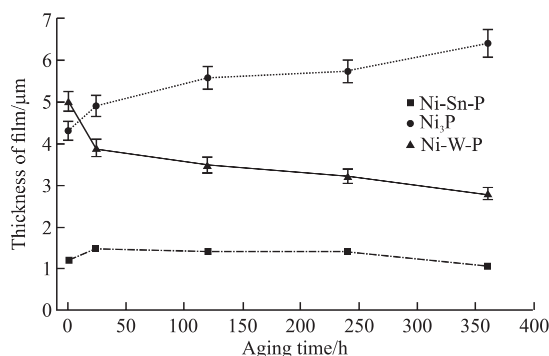

Fig.9 Relationships of various solid solutions with aging time

Schematic diagram of SAC305/Ni-W-P/Cu joints is shown in Fig.8. During the aging, the thickness of IMC of SAC305/Cu interface became thicker by consuming Cu atom and the crack occurred within Cu_6Sn_5 phase as shown in Fig.2(b) and 2(c). However, crack rarely occurred within the $(Ni,Cu)_3Sn_4$ phase in the SAC305/Ni-W-P/Cu solder joints. Brittle fracture only formed at branch's cross-section of $(Ni,Cu)_3Sn_4$. The same duration and condition were adopted during aging, and the Ni-W-P barrier layer still existed after a long time aging as shown in Fig.4, but Cu substrate had been dissolved. It indicates that the Ni-W-P layer was extremely tardy in reaction with solder and no response with Cu substrate. And it is suitable for a good barrier layer.

Another interesting phenomenon appeared on the interface of $(Ni,Cu)_3Sn_4$ and Ni_3P as shown in Fig.4. After soldering, Ni-Sn-P layer emerged but not obvious on the interface. For further aging, the thickness of Ni-W-P layer becomes thinner; the thickness of Ni_3P layer sustained the growth; the thickness of Ni-Sn-P layer first increased and then decreased as shown in Fig.9. The broken line shows change of thickness of Ni-Sn-P layer in Fig.9. In Fig.4(e), only a thin layer of Ni-Sn-P existed. By consuming transition layer of Ni-Sn-P, the Ni was desired. Moreover, this kind of growth mechanism will delay the consumption of Ni-W-P layer and the Cu substrate will be protected before the Ni-W-P layer fades away.

4 Conclusions

The present work has examined the effect of Ni-W-P barrier layer growth behavior of the interfacial IMCs layer in SAC305/Ni-W-P/Cu solder joints during reflowing at 250 ℃ and aging at 150 ℃ for 24, 120, 240 and 360 h, respectively. The following conclusions can be summarized:

a) During soldering, solder reacted with Cu substrate to form scallop-like Cu_6Sn_5 grains and planar-like Cu_3Sn in Cu substrate. The Ni_3P layer and $(Ni,Cu)_3Sn_4$ compounds were formed between electroless Ni-W-P layer and solder, and Cu substrate was not damaged and kept a smooth interface since Ni-W-P barrier layer prevent the Cu substrate dissolution.

b) During aging at 150 ℃ for 360 h, scallop-like Cu_6Sn_5 grains tended to become planar and the total thickness of interfacial IMC layer increased with increasing aging time. Incidentally, the Cu_3Sn layer can benefit from its growth mechanism to increase much faster than the Cu_6Sn_5 layer. The thickness of Ni_3P and $(Ni,Cu)_3Sn_4$ also increased with increasing aging time, but the thickness of Ni-Sn-P layer increased at first and decreased later, that resulted from the $(Ni,Cu)_3Sn_4$ layer growth by consuming transition layer of Ni-Sn-P to acquire the desired Ni atom.

c) Under the same aging conditions, the brittle fracture occurred within IMC of SAC305/Cu interface but barely within IMC of SAC305/Ni-W-P/Cu interface. After 360 h aging, the barrier layer of Ni-W-P

still remained at the interface and Cu substrate was not dissolved. Besides, kirkendall voids emerged both within the Cu_3Sn layer and the Ni_3P layer, but the voids emerged within the Ni_3P layer in the form of crack, the amount of kirkendall voids increased, and the crack elongated with increasing aging time.

d) The Cu_6Sn_5 grains and $(Ni,Cu)_3Sn_4$ crystal which formed at SAC305/Cu interface and SAC305/Ni-W-P/Cu interface were both coarsened by merging adjacent grains. In the process of growth, the growing interfacial compounds filled the free space, and new columnar dendrite grains of $(Ni,Cu)_3Sn_4$ constantly generated during aging treatment. During aging process, the thickness of IMCs layer (including Cu_6Sn_5, Cu_3Sn and $(Ni,Cu)_3Sn_4$ crystal) increased linearly with the square root of aging time, and their growth rate constants are 2.456×10^{-17}, 3.074×10^{-17}, and 8.03×10^{-17} m^2/s, respectively.

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