

Interface Reaction and Mechanical Properties of Lead-free Sn–Zn Alloy/Cu Joints

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The interfacial reaction and mechanical properties of Sn–Zn lead-free alloys/Cu joints were investigated under thermal exposure conditions. In the solder layer, Zn phases reacted with Cu and were transformed to Cu–Zn compounds with increasing exposure time. The microstructure change caused decreasing Vickers hardness of the solder layer. At the joint interface, although Cu–Zn compounds formed first, the formation of Cu–Sn compounds occurred with increasing exposure time. Simultaneously, the disappearance of Cu–Zn compounds and void formation occurred. The activation energy of the growth of Cu–Zn compounds at the joint interface was determined to be approximately 70 kJ/mol. That value is close to the activation energy of the diffusion of Zn in Sn crystal.

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1. Introduction

Sn–Zn alloys have been expected to be used as a substitute for Sn–Pb eutectic solder, because the melting temperature (199°C for the Sn–9 mass% Zn eutectic composition) is much closer to that of the Sn–Pb eutectic solder (183°C) compared to other lead-free solders. In fact, many studies on Sn–Zn alloys have been performed¹⁾ and their application to reflow soldering has also been reported.²⁾ However, it is not easy to perform soldering with Sn–Zn alloys because Zn is an active metal. There are many issues which must be resolved before putting Sn–Zn alloys into practical use, such as developing wettability, preventing void formation in the solder joint and application to flow soldering. Although some reliability tests have been performed,¹⁾ they are not sufficient to evaluate the reliability of solder joints formed with Sn–Zn alloys. Moreover, Cu–Zn compounds form at the interfaces of Sn–Zn alloys and Cu.³⁾ This is different from the case of most other lead-free solders, which show Cu–Sn compounds formation at the joint interfaces. Cu–Zn compounds are not stable when heated. It has been reported that an interfacial morphology changed from Cu–Zn compounds to Cu–Sn compounds only after heating for 100 h at 150°C.⁴⁾ The instability of the reaction layer affects the joint reliability. Since the morphology change from Cu–Zn to Cu–Sn is also very interesting from an academic standpoint, studies on the interface reaction of Sn–Zn/Cu joints have been reported.^{3–7)} However, there are few works which have focused on the actual operating conditions of electronics products and which have systematically determined the effects of thermal exposure on the interface reaction. The aim of this study is to examine the interfacial reaction, microstructures and mechanical properties of Sn–Zn/Cu joints, under practical thermal exposure conditions.

2. Experimental Procedure

Solder pastes of Sn–9Zn and Sn–8Zn–3Bi(mass%) were prepared. Rods of the same solder materials were also pre-

Table 1 Solder type.

Solder type (mass%)	Solidus temp. (°C)	Liquidus temp. (°C)
Sn–9Zn	199	199
Sn–8Zn–3Bi	187	197

pared. Table 1 lists the solidus and liquidus temperatures for each solder material.

An FR-4 printed circuit board with Cu pads, which were designed for assembling surface mount devices, was prepared. The Cu pad size was $1.65 \times 0.3 \times 0.045 \text{ mm}^3$. A Cu plate of 99.99 mass% purity was also used as a substrate. The size of the Cu plate was $50 \times 50 \times 0.3 \text{ mm}^3$.

The solder paste was applied to the Cu pads of the FR-4 board by the conventional paste printing method. Soldering was carried out using a reflow furnace in nitrogen atmosphere (O_2 concentration: 1000 ppm). The peak reflow temperature was 213°C. The holding times above 199°C (melting point of Sn–9Zn), 197°C and 187°C (liquidus and solidus temperatures of Sn–8Zn–3Bi) were 34 s, 38 s and 56 s, respectively. For the Cu plate, a $10 \pm 1 \text{ mg}$ solder piece was cut from each solder rod, and applied to the Cu plate with flux. Soldering was performed in air at 230°C for 60 s using a hot plate. Samples were allowed to cool naturally after soldering.

The joints of the FR-4 substrate were heat-treated at 105°C, 125°C and 150°C for 10 h, 120 h, 500 h and 1000 h. The joints of the Cu plate were heat-treated at 100°C, 125°C and 150°C for aging times ranging from 100 to 1000 h.

To investigate microstructures of the joints, the cross sections of the samples were observed with optical microscopy (OM), scanning electron microscopy (SEM) and an electron probe X-ray microanalyzer (EPMA). The Vickers hardness of the solder layer in the joint was also evaluated. A load of 0.098 N was applied to each solder layer for 10 s during the measurement.

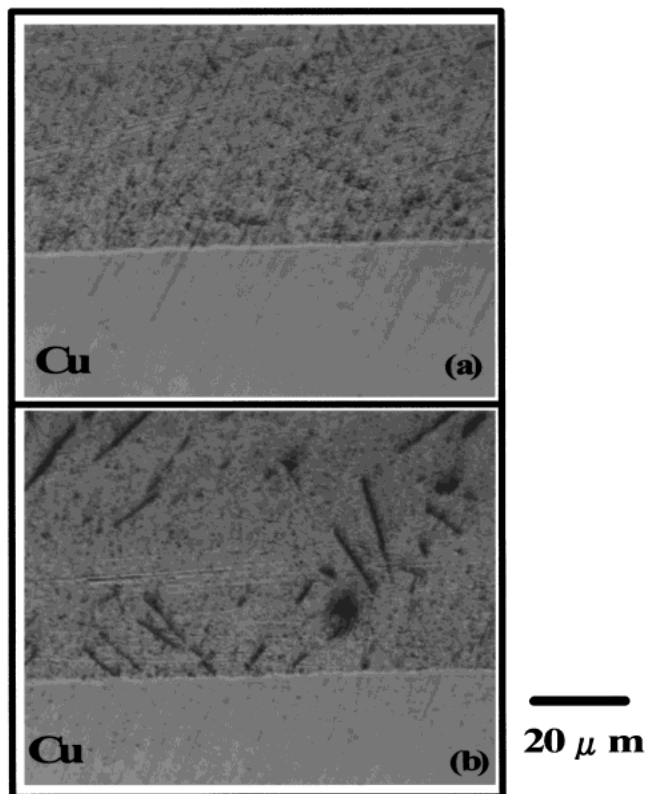


Fig. 1 Microstructures of initial solder joints. (a) Sn-9Zn/Cu, (b) Sn-8Zn-3Bi/Cu.

3. Results and Discussion

3.1 Initial microstructure

Figure 1 shows OM images of the initial microstructures of solder joints with Cu pads. The dispersion of Zn phases (dark-gray area) in a Sn matrix (bright-gray area) was observed in the solder layer. The dispersion of fine Zn phases was observed in the Sn-9Zn solder. On the other hand, rod-shaped Zn phases were dispersed in the Sn-8Zn-3Bi solder, and are coarser than those of Sn-9Zn. Since Sn-8Zn-3Bi is not eutectic in composition and has a freezing interval, primary Zn phases become rod-shaped phases in the solidification process. The formation of a reaction layer was observed at the joint interface. This layer was negligibly detected by EPMA analysis because the thickness of the layer was not sufficient to permit detailed investigation. Similar microstructures were observed in the case of solder joints with Cu plates.

3.2 Microstructure of the solder layer

Figure 2 shows OM images of solder joints with Cu pads after thermal exposure at 150°C. The growth of the reaction layer at the joint interface was observed in both joints after thermal exposure at 150°C for 10 h. When the heating time was over 120 h, accompanying the growth of the reaction layer at the joint interface, similar phases were also observed in the solder layer.

Figure 3 shows the microstructure and EPMA analysis results of a Sn-9Zn/Cu pad joint after heat exposure at 150°C for 120 h. The reaction phase in the solder layer was identified as a Cu-Zn compound, whose composition was Cu-41Zn-4Sn (at%). Zn phases were negligibly observed in the

solder layer; most of the Zn phases had transformed into Cu-Zn compounds. From the Cu-Sn-Zn ternary phase diagram⁸⁾ shown in Fig. 4, it is found the Cu-41Zn-4Sn phase consists of Cu, CuZn and Cu₅Zn₈. The diffusion constant of Cu or Zn atom in Sn crystal is significantly larger than that of the self-diffusion of Sn. Moreover, the diffusion constant of Cu atom in Sn is approximately a thousand times as large as that of Zn.^{9,10)} With increasing thermal exposure time, Zn phases react with Cu atoms, which diffuse from the Cu pad, and transform into Cu-Zn compounds.

Although the formation of Cu-Zn compounds was observed in both Sn-9Zn/Cu and Sn-8Zn-3Bi/Cu joints, some differences were observed in the process of transformation of each microstructure. In the case of Sn-9Zn, fine Zn phases transformed into Cu-Zn compounds first, and the growth of these Cu-Zn compounds was observed. On the other hand, rod-shape Zn phases spheroidized first in the Sn-8Zn-3Bi/Cu joint. The spherical Zn phases continuously transformed into Cu-Zn compounds, and the growth of these phases occurred. The microstructural change strongly affects the mechanical properties of the solder layer, as discussed later (refer to section 3.5). Similar tendencies of microstructural change were observed at 105°C and 125°C, although the transformation rate is slower with decreasing holding temperature. A similar tendency of microstructural change was observed in the joint with the Cu plate.

3.3 Interface microstructure of the Sn-Zn/Cu joint

As shown in Fig. 3, formation of the Cu-Zn compound layer was observed over almost the entire joint interface after the thermal exposure at 150°C for 120 h. The Cu-Zn compound layer was identified as Cu-31Zn-11Sn (at%) by EPMA analysis, which is a Cu₅Zn₈ layer considering the Cu-Sn-Zn ternary phase diagram shown in Fig. 4. Cu-Sn compounds were also observed locally at the joint interface. The Cu-Sn compounds formed at the interface of the Cu-Zn compound layer and Cu, and their phases grew into Cu. From EPMA analysis results, the Cu-Sn compound phase was identified as Cu-34Sn-2Zn (at%). Since multiphases were found in the Cu-Sn phase in Fig. 3, the Cu-Sn phase probably consisted of various phases. For the joints with Cu pads, the formation of the Cu-Sn compound was observed after the thermal exposure at 150°C for 120 h, 125°C for 500 h and 105°C for 1000 h. Table 2 shows the relationship between the formation of the Cu-Sn compound and the thermal exposure condition in the joints with Cu plates. The results are similar to those for the joints with Cu pads. When the exposure temperature was 125°C, the formation of the Cu-Sn compound occurred after the thermal exposure for 300 h. In the case of exposure to 150°C, the formation of the Cu-Sn compound was already observed upon thermal exposure for 100 h. Then, the joints with the Sn-9Zn/Cu plate and those with the Sn-8Zn-3Bi/Cu plate were heat-treated at 150°C for 50 h, and microstructural observation was performed. The results revealed that the formation of the Cu-Sn compound at the Cu-Zn compound/Cu interface occurred in both samples. Consequently, it was found that the formation of the Cu-Sn compound at the joint interface of the Cu-Zn compound layer and Cu can occur within a very short time at 150°C.

As shown in Fig. 3, the disappearance of the Cu-Zn com-

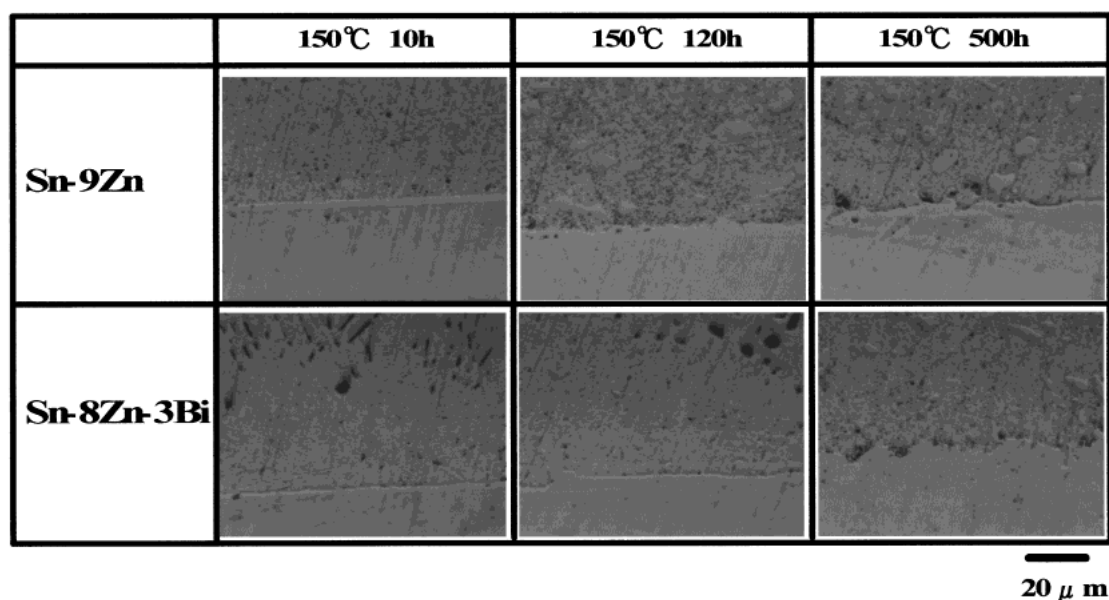


Fig. 2 Microstructures adjacent to joint interfaces after heat exposure at 150°C.

Table 2 Relationship between Cu–Sn compound formation and heat exposure condition in Sn–Zn alloy/Cu plate joints.

Solder type temp. (°C)	Heat exposure time (h)									
	100	200	300	400	500	600	700	800	900	1000
Sn–9Zn										
100	no	no	no	no	no	no	no	no	no	no
125	no	no	yes	yes	yes	yes	yes	yes	yes	yes
150	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
Sn–8Zn–3Bi										
100	no	no	no	no	no	no	no	no	no	yes
125	no	no	yes	yes	yes	yes	yes	yes	yes	yes
150	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes

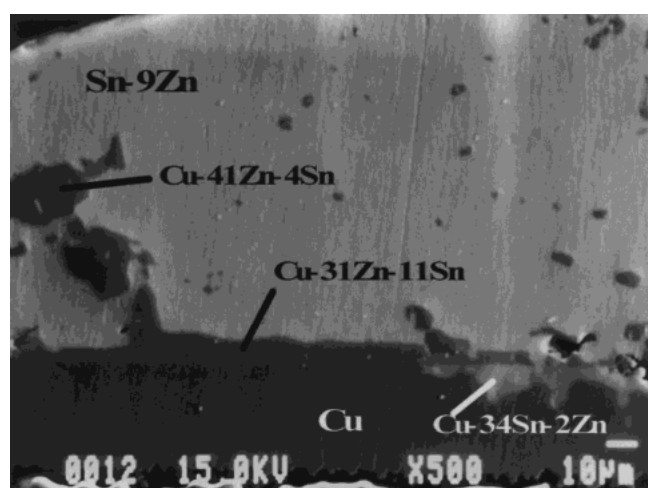
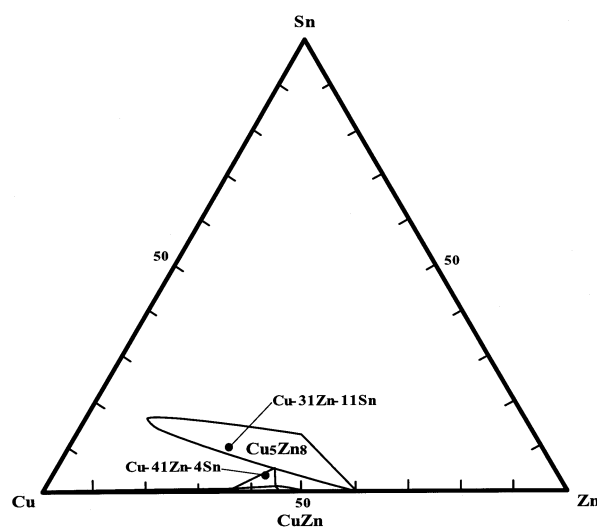


Fig. 3 Microstructure and EPMA analysis results of a Sn–9Zn/Cu pad joint after heat exposure at 150°C for 120 h.

Fig. 4 Cu–Sn–Zn ternary phase diagram (298 K).⁸⁾

pound layer and the void formation were frequently observed at the joint interface when the Cu–Sn compound formed. The formation of voids causes crack formation and thus the joint reliability is degraded.⁵⁾ As for the mechanism of the mor-

phology change from Cu–Zn to Cu–Sn, it has not been clarified, although a theory based on the diffusion of Sn atoms has been proposed.⁷⁾ The phenomenon is similar to that of the formation of Au–Sn compounds at the interface of Au/AuIn₂ in

the Au/In–48Sn joint.¹¹⁾ Further study is required in order to elucidate the mechanism of the transformation and suppress void formation.

3.4 Growth of reaction layer at the joint interface

Figure 5 shows the thickness of the reaction layer in the joints with Cu plates plotted against the thermal exposure time. The thickness of the reaction layer was measured from the area devoid of the Cu–Sn compound. When the exposure temperature was 150°C, the formation of the Cu–Sn compound and the disappearance of the Cu–Zn layer were observed at most of the joint interfaces. At such an interface, it is difficult to measure the thickness of the Cu–Zn compound layer. Thus, Fig. 5 shows the growth of the Cu–Zn compound layer at the joint interface until the interface morphology changes from Cu–Zn to Cu–Sn. It is found that the thickness of the Cu–Zn reaction layer is proportional to the square root of the thermal exposure time for both solder materials. This means that the growth kinetics of the Cu–Zn compound layer obeys the parabolic law. The growth rate constant, k , was determined from the slope of the linear relation in Fig. 5. The growth rate constant k was plotted against the inverse of the exposure temperature in Fig. 6 to determine the activation energy Q for k . The activation energies were calculated to be 64.3 kJ/mol and 70.1 kJ/mol for the growth of the Cu–Zn compound in Sn–9Zn/Cu and Sn–8Zn–3Bi/Cu, respectively. These values are very close to the activation energies of the diffusion of Zn in Sn crystal, which are 50.4 kJ/mol in the “ a ” axis direction and 89.5 kJ/mol in the “ c ” axis direction.¹⁰⁾ In the system currently studied, Zn phases transform into Cu–Zn compounds because Cu atoms diffuse rapidly in the Sn–Zn solders. Considering that an adequate number of Cu atoms were supplied in the solder layer due to their rapid diffusion, the diffusion of Zn toward the joint interface controls the growth of the Cu–Zn compound layer at the joint interface. This is the reason why the measured activation energies of the growth of the Cu–Zn compound layers are close to those of the diffusion of Zn in Sn crystal.

In this work, the joints with Cu pads designed for use as surface mount technology (SMT) components were also investigated, but detailed evaluation of activation energy from these results could not be performed due to insufficient experimental data. In the case of micro-joints, which are smaller in size than the joints with a Cu plate, the transformation of the Zn phase into the Cu–Zn compound can occur in a shorter time. Following the formation of the Cu–Zn compound, Zn phases in the solder disappear. Since the Cu–Zn compound is stable in the solder layer, few Zn atoms diffuse to the joint interface. In the final stage, the growth of the Cu–Zn compound layer was suppressed due to a shortage of Zn atoms diffusing from the solder layer. Thus, the growth rate of the Cu–Zn reaction layer strongly depends on the solder volume in the joint area.

3.5 Vickers hardness of solder layer

Figure 7 shows Vickers hardness measurement results for the solder layer of the Sn–Zn alloy/Cu pad joints. In the case of the Sn–9Zn solder, the hardness decreases with increasing holding time. Since Zn phases transform into Cu–Zn compounds in the solder layer as shown in Fig. 2, the hardness of

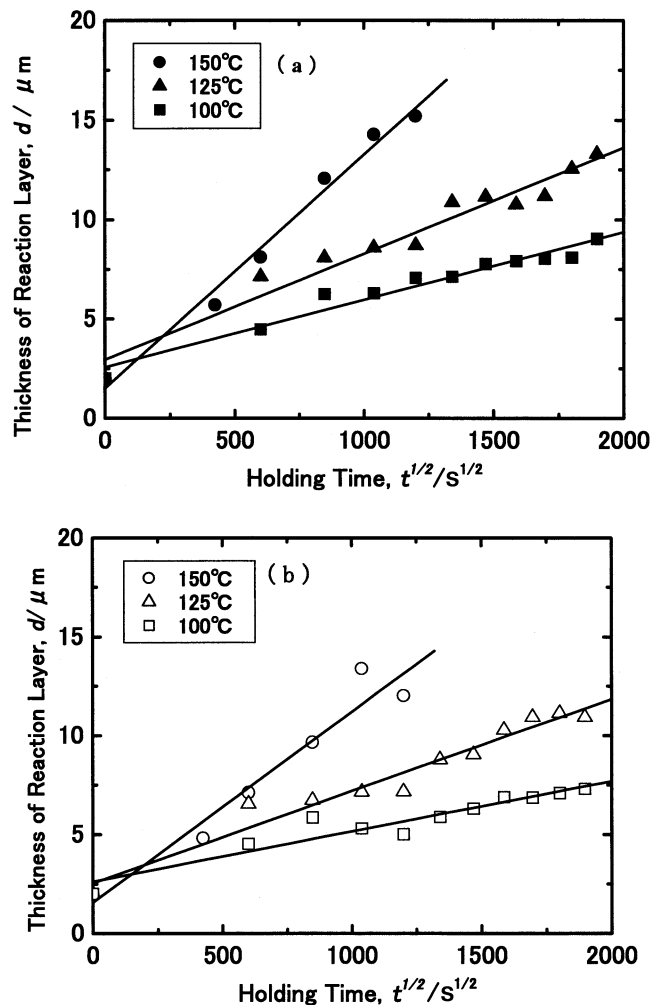


Fig. 5 Reaction layer growth at the joint interface. (a) Sn–9Zn, (b) Sn–8Zn–3Bi.

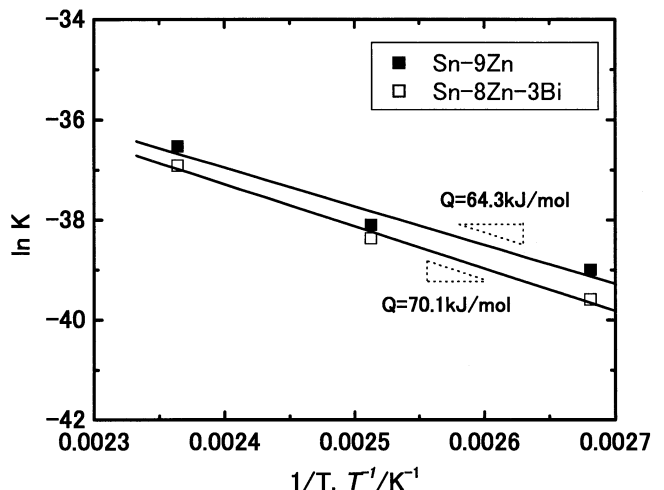


Fig. 6 Arrhenius plot of growth rate constant k .

the Cu–Zn compound is probably less than that of Zn. On the other hand, the hardness of the Sn–8Zn–3Bi solder layer initially increases with increasing exposure time, and decreases beyond an exposure time of approximately 500 h. The change of hardness can be explained by the microstructural change as shown in Fig. 2. That is, the spheroidization of the rod-shaped Zn phase initially causes the hardening due to a dispersion ef-

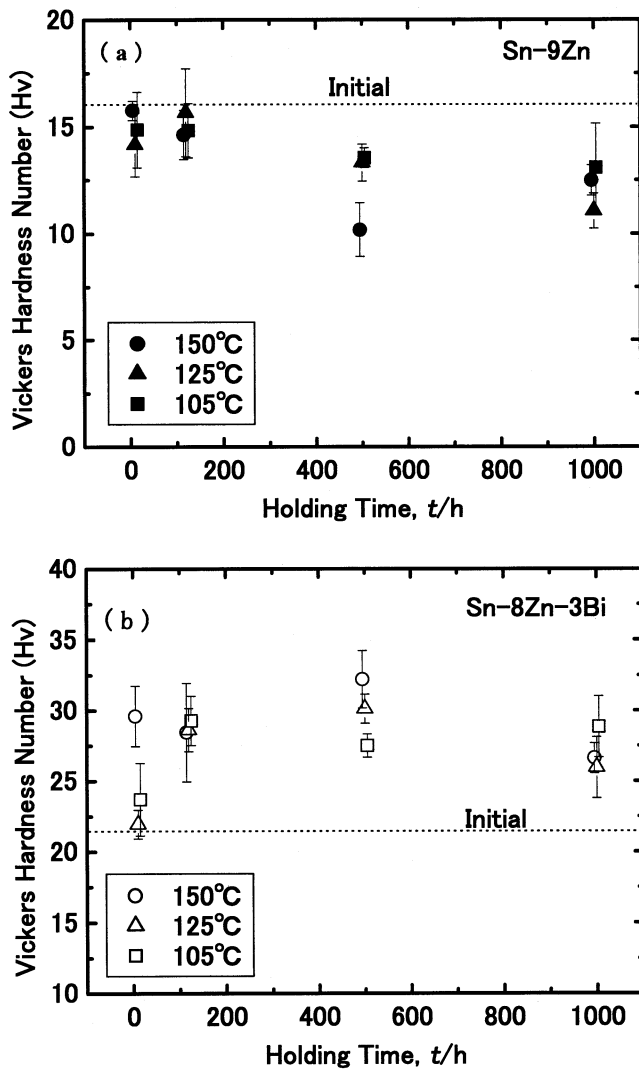


Fig. 7 Vickers hardness measurement results. (a) Sn–9Zn, (b) Sn–8Zn–3Bi.

fect of finer phases. When the holding time exceeds approximately 500 h, Zn phases transform into Cu–Zn compounds and thus the hardness of the solder decreases.

4. Conclusions

In this work, the evolution of joint microstructures and the mechanical properties of Sn–Zn alloy/Cu joints were investigated after the thermal exposure test. The results are summarized as follows.

- (1) Zn phases transformed into Cu–Zn compounds with

increasing heat exposure time.

- (2) The Vickers hardness of the Sn–9Zn solder decreased following the transformation of Zn phases into Cu–Zn compounds.

- (3) In the case of Sn–8Zn–3Bi, the rod-shaped Zn phases spheroidized when the heat exposure time was less than 500 h, and the Vickers hardness of the solder increased. After the heat exposure time of more than 500 h, the Vickers hardness decreased due to the transformation of spherical Zn phases into Cu–Zn compounds.

- (4) At the joint interface, the Cu–Zn compound layer formed immediately after soldering and this layer grew with increasing exposure time. Additional thermal exposure caused the formation of Cu–Sn compounds at the interface of the Cu–Zn compound and Cu. This compound grew into the Cu layer.

- (5) When Cu–Sn compounds formed at the joint interface, both the disappearance of the Cu–Zn compound layer and void formation occurred locally at the interface.

- (6) The activation energy of the Cu–Zn compound growth at the joint interface was evaluated as being approximately 70 kJ/mol. This value is close to that of the diffusion of Zn in Sn crystal.

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