Reliability of Solder Joint with Sn–Ag–Cu–Ni–Ge Lead-Free Alloy under Heat Exposure Conditions

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The reliability of a solder ball joint with a Sn–Ag–Cu–Ni–Ge lead-free alloy, which is expected to be an advanced lead-free solder, was investigated under heat exposure conditions. Solder ball joints with a eutectic Sn–Ag alloy and a ternary Sn–Ag–Cu alloy were also prepared to compare with that of the Sn–Ag–Cu–Ni–Ge alloy. Microstructural observations of the cross sections of the solder ball joints were conducted to investigate microstructural evolutions in the solders and the growth kinetics of reaction layers formed at joint interfaces. The influence of heat exposure treatment on joint strength was investigated by ball shear test. Moreover, the influence of surface treatment of a Cu pad on the reliability of the solder joint was also investigated.

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1. Introduction

A Sn–Ag–Cu–Ni–Ge lead-free alloy is expected to be an advanced lead-free solder.¹,² Among lead-free solders, ternary Sn–Ag–Cu solders³–¹¹ are expected to be the substitute of a Sn–Pb eutectic solder, and have become widely spread in the manufacture of many electronic devices. However, the advanced lead-free solder, which has higher reliability than ternary Sn–Ag–Cu solders, is required to be used for various industry machines. A supplement of a small amount of Ge in the lead-free solder is effective to depress the oxidation of the solder in soldering.¹ Moreover, a supplement of a small amount of Ni is expected to refine matrix phases formed in the solder² and the microstructure with such matrix phases is expected to be relatively stable under heat exposure conditions. Although mechanical properties and microstructures of the Sn–Ag–Cu–Ni–Ge lead-free solder have been examined,²,¹² the researches on the reliability of the solder joint with the Sn–Ag–Cu–Ni–Ge solder are little. Thus, the purpose of this study is to investigate the reliability of the solder ball joint with the Sn–Ag–Cu–Ni–Ge solder under heat exposure conditions. In particular, the influence of a supplement of Ni and Ge in the Sn–Ag–Cu lead-free solder on the microstructure of the solder ball joint and joint strength was investigated. To compare with the solder ball joint with the Sn–Ag–Cu–Ni–Ge solder, solder ball joints using a eutectic Sn–Ag alloy and a ternary Sn–Ag–Cu alloy were also investigated.

2. Experimental Procedures

An FR-4 substrate, which has Cu pads with a diameter of 200 µm, was prepared. For the Cu pad, electroless Ni/Au-plated Cu pads were also prepared. The thicknesses of the Ni layer and the Au layer were 3 µm and 30 nm, respectively. The composition of the Ni layer was Ni–7.2 mass%P. Three types of solder ball were prepared; Sn–3.5 mass%Ag–0.5 mass%Cu–0.07 mass%Ni–0.01 mass%Ge (SACNG), Sn–3.5 mass%Ag–0.5 mass%Cu (SAC) and Sn–3.5 mass%Ag (SA).

Table 1 Solidus and liquidus temperatures for solders studied.

<table>
<thead>
<tr>
<th>Solder (mass%)</th>
<th>Solidus temp. (°C)</th>
<th>Liquidus temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn–3.5Ag</td>
<td>221</td>
<td>221</td>
</tr>
<tr>
<td>Sn–3.5Ag–0.5Cu</td>
<td>217</td>
<td>219</td>
</tr>
<tr>
<td>Sn–3.5Ag–0.5Cu–0.07Ni–0.01Ge</td>
<td>217</td>
<td>221</td>
</tr>
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Fig. 1 Temperature profile in reflow soldering.

mass%Ag–0.5 mass%Cu (SAC) and Sn–3.5 mass%Ag (SA). Table 1 shows the solidus and liquidus temperatures for solders studied. The diameter of the solder ball was 300 µm. The solder balls were set on the Cu pads and the electroless Ni/Au-plated Cu pads with non-clean flux, and soldering was conducted with a reflow furnace. Figure 1 shows the temperature profile in reflow soldering. After reflow soldering, a subsequent heat exposure treatment was conducted for the solder ball joints at 80, 100 and 120 °C for 1000 h. Microstructural observations were performed to the cross sections of the solder ball joints using scanning electron microscopy (SEM) and electron probe X-ray microanalysis (EPMA) to investigate the microstructures of the solder ball joints and the growth kinetics of reaction layers formed at joint interfaces. Moreover, ball shear test was performed to
investigate joint strength of the solder ball joint. The schematic of the test is shown in Fig. 2. The test speed of the ball shear test was 15 mm/min.

3. Results and Discussion

3.1 Initial microstructures of solder ball joints

Figure 3 shows secondary electron images of the cross sections of the solder ball joints after reflow soldering. At the interface between the SA solder and the Cu pad, the reaction layer does not uniformly form and partially grows up to several-micron meters. Fine granular phases with diameters of sub-micron meters are dispersed with a network structure in the SA solder. Such fine granular phases are Ag$_3$Sn and those are dispersed in β-Sn matrix. Similar microstructure is observed at the interface between the SAC solder and the Cu pad. In contrast, the reaction layer uniformly forms in the joint of the SACNG solder and the Cu pad, compared with those formed in the joints with the SA and SAC solders. Moreover, fine granular phases and some larger phases with diameters of a few micron meters are observed in the SACNG solder. The fine granular phases seem to be Ag$_3$Sn. For even the larger phases, they were not sufficient to permit detailed investigation by EPMA quantitative analysis. Thus, EPMA analysis was performed to phases in the solder which grew by heat exposure treatment. The result is described in next paragraph.

In the case of the joints with the Ni/Au-plated Cu pad, the reaction layers do not uniformly form at the joint interfaces in all the solders. However, the thicknesses of the reaction layers formed at the joint interfaces are relatively smaller than those of the joint using the Cu pad. For the SAC and SACNG solders, similar microstructures, which are more refinement than that in the SA solder, are observed in the solders. When soldering is performed to the Ni/Au-plated Cu pad, a small amount of Ni is dissolved in the molten solder and thus the composition of the molten solder becomes Ni-rich. Therefore, the supplement of a small amount of Cu and Ni in the Sn–Ag system alloy is effective to refine the microstructure. For the joint using the SACNG solder, however, a few micron-meters phases are also observed, as well as the joint using the Cu pad. For such phases, EPMA analysis was performed after heat exposure treatment due to the same reason described above. The result of the EPMA analysis is described in next paragraph.

Figure 4 shows low magnified secondary electron images of the cross sections of the solder ball joints shown in Fig. 3. Although microstructures in the vicinity of the joint interface are refined, those located at some distance from the joint interface are dendritic in the all joints. Similar dendritic microstructures were observed in the as-cast specimens of SA, SAC and SACNG solders. In the vicinity of the joint interface, the electrode material is diffused in the molten solder and thus the concentration of such electrode material in the solder is relatively higher. Moreover, the cooling rate in the reflow soldering process seems to be relatively higher near the joint interface due to higher thermal conductivity of the Cu pad. Therefore, the higher concentration of electrode material in the molten solder and higher cooling rate in soldering cause the refinement of the microstructure in the vicinity of the joint interface.
3.2 Microstructures of solder ball joints after heat exposure treatment

Figure 5 shows secondary electron images of the cross sections of the solder ball joints after heat exposure treatment at 120°C for 1000 h. In the joints with Cu pads, the reaction layers grow up to approximately 5 µm regardless of the solder type. Table 2 shows EPMA analysis results for the reaction layers formed at the joint interfaces. For EPMA analysis, mapping analysis was performed first and subsequent quantitative analysis was performed to elements detected by the mapping analysis. The reaction layers formed at the joint interfaces with the SA and SAC solders are Cu–Sn compounds. For the reaction layer formed at the joint interface with the SACNG solder, the layer is Cu–Sn compound included a few atomic percent Ni atoms.

For the joint with the Ni/Au-plated pad, the thickness of the reaction layer is at most a few micron meters, and the growth of the reaction layer by heat exposure treatment is negligible regardless of the solder type (refer to Figs. 3 and 5). The reaction layer is Ni–Sn–P compound in the joint with the SA solder. For the joint with the SAC and SACNG
solders, the reaction layers are Ni–Sn–Cu–P compounds. Ito et al.\textsuperscript{14} have identified the reaction layers formed at the joint interface between the Sn–3.5 mass\%Ag–0.75 mass\%Cu solder and the electroless Ni/Au-plated Cu pad using transmission electron microscopy. They have reported that Ni–Sn–P, Ni\textsubscript{3}P and (Cu,Ni)\textsubscript{6}Sn\textsubscript{5} layers form at the joint interface from the Ni–P plating layer to the solder. Therefore, Ni–Sn–Cu–P compounds observed by EPMA in this study are probably composed of Ni–Sn–P, Ni\textsubscript{3}P and (Cu,Ni)\textsubscript{6}Sn\textsubscript{5} layers.

For all the specimens, the network structure with fine Ag\textsubscript{3}Sn phases in the solder disappears after heat exposure treatment. Such a microstructure evolution decreases strength of the solder. Moreover, dendritic microstructures, which are similar to those shown in Fig. 4, were not observed in the solder ball joints. Microstructures after heat exposure treatment at 120°C for 1000 h were analogous to the microstructures in the vicinity of the joint interfaces, which are shown in Fig. 5, in the whole solder ball joints.

In the SACNG solder, the formation phases in the solder grow up to several-micron meters after heat exposure treatment. Figure 6 shows EPMA mapping analysis results for the cross section of the solder ball joint with the SACNG solder and the Cu pad after heat exposure treatment. Cu, Sn and Ni atoms are detected in dark-gray phases observed in a back-scattered electron image. Since such phases have similar microstructures to that of the reaction layer formed at the joint interface, the phases are probably Cu–Sn compounds with a few atomic percent Ni atoms. In contrast, similar Cu–Sn compounds were scarcely observed in the joint with the SA and SAC solders and the Cu pads. It means that the supplement of a small amount of Ni in the Sn–Ag–Cu solder induces the growth of Cu–Sn compounds in the solder under heat exposure conditions. This is because Ni atoms become the nucleation sites of the formation of Cu–Sn compounds and many nuclei of Cu–Sn compounds are already existed in the solder joints after reflow soldering.

In the joint with the Ni/Au-plated Cu pad and the SACNG solder, the growth of the Cu–Sn compound layer with a few atomic percent Ni atoms was observed only beside the joint interface. As shown in Table 2, the Ni–Sn–Cu–P or Ni–Sn–P compound layers form at the joint interface in the case of the joint using the Ni/Au-plated pad. Since Ni atoms are consumed in interfacial reaction, the formation of Cu–Sn compounds with a few atomic percent Ni atoms does not wide occur in the solder. For the joints with the Ni/Au-plated Cu pads and the SA and SAC solders, the formation of Cu–Sn compounds in the solder were scarcely observed, as well as the joints with the Cu pads.

In this study, segregation or precipitation of Ge and its compounds was not observed by EPMA analysis in all the specimens before and after heat exposure treatment. Therefore, it was clarified that the supplement of a small amount of Ge in the SAC solder scarcely influences microstructure formation of the solder ball joint.

### 3.3 Growth kinetics of reaction layers

From the results of EPMA analysis and microstructural observation by back-scattered electron images following annealing treatment, the reaction layer seems to be not changed by annealing in this study. That is, Cu–Sn compounds grow in the joints with the SA and SAC solders and the Cu–Sn compound included a few atomic percent Ni atoms grows in the joint with the SACNG solder in the case of the Cu pad. For the joint with the Ni/Au-plated Cu pads, Ni–Sn–P and Ni–Sn–Cu–P compounds grow in the joint with the SA solder and in the joints with the SAC and SACNG solders, respectively.

Figure 7 shows the relationship between the thickness of the reaction layer and the root of heat exposure time. As described above, the growth rate of the reaction layer in the joint with the Cu pad is faster than that with the Ni/Au-plated pad in all the solders. From the results shown in Fig. 7, the
The growth kinetics of the reaction layers formed in the joint interfaces obey the following relationship:

\[ X = (Kt)^{1/2} + X_0 , \quad K = kD \]

where \( X \) is the thickness of the reaction layer, \( X_0 \) is the thickness of the reaction layer before heat exposure treatment, \( K \) is the growth rate constant, \( t \) is the heat exposure time, \( D \) is the diffusion coefficient and \( k \) is constant. As also observed in Fig. 5, the influence of the solder type on the growth kinetic of the reaction layer is negligible in the heat exposure conditions investigated. It means that the supplement of a small amount of Ni and Ge in the Sn–Ag system solder scarcely influences on the growth of the reaction layer formed at the joint interface.

The activation energy of the growth of the reaction layer can be calculated by an Arrhenius plot for \( K \), which is evaluated from the slope of the line shown in Fig. 7. Figure 8 indicates Arrhenius plot results for the growth of the reaction layers formed at the joint interfaces. For the joint with Cu pads, the activation energies of the growth of the reaction layers were investigated 92.5, 98.3 and 65.7 kJ/mol for the SA, SAC and SACNG solders, respectively. The values are close to those of previous works; 64–89 kJ/mol for the reaction layers formed at the Sn–3.5Ag/Cu and the Sn–3.5Ag–0.75Cu/Cu interfaces.\(^{15} \) For the joint with Ni/Au pads, the activation energies of the growth of the reaction layers were investigated 29.4, 12.9 and 12.9 kJ/mol for the SA, SAC and SACNG solders, respectively. The values are much smaller than those of the joints with Cu pads, and are close to the activation energies for the grain boundary diffusion in solders.\(^{16} \) In the case of the joint with the electroless Ni/Au-plated pad, the P-rich layer forms between the Ni–P layer and the Ni–Sn reaction layer following the growth of the reaction layer.\(^{17} \) In such case, the P-rich layer prevents Ni atoms from diffusing from the Ni–P layer to the reaction layer. Thus, the growth of the Ni–Sn reaction layer would be controlled mainly due to the diffusion of Ni atoms which exist in the solder beside the joint interface. Since the solubility of Ni atoms in the solder is very low, the growth of the reaction layer was very slow under the heat exposure condition investigated.

### 3.4 Ball shear strength

Figures 9 and 10 show results of the ball shear tests for the joints with the Cu pads and the Ni/Au-plated Cu pads, respectively. With increasing heat exposure time, ball shear strength decreases gradually regardless of test temperature, solder type and pad type. The reduction ratio of joint strength following the heat exposure treatment increases with increasing test temperature in all the specimens.

For the joints with Cu pads, the ball shear strength of the
joint with the SACNG solder is a little larger than those of the joints with the SA and SAC solders. Figure 11 shows secondary electron images of fracture surfaces of solder ball joints after ball shear test. In this study, fracture occurred in the solder located at a distance of approximately 10 \(\mu\)m from the joint interface in all the joints. Therefore, the ball shear strength corresponds to strength of each solder. As shown in Figs. 3, 5 and 6, Ag\(_3\)Sn and Cu–Sn compounds with a few atomic percent Ni atoms disperse in the SACNG solder, and thus the solder strength of the SACNG solder is relatively higher than those of the SA and SAC solders. From the tensile test results using dog-bone-type specimens, it was reported the tensile strength of the SACNG solder is a little lower than those of the SA\(^{18}\) and SAC\(^{2}\) solders. For the
specimen used in such a test, the microstructure is dendritic as shown in Fig. 4. As described above, the microstructure in the vicinity of the joint interface is different from the dendritic one due to the diffusion of the electrode materials into the molten solder. Moreover, Cu–Sn compounds with a few atomic percent Ni atoms form in the solder joint using the SACNG solder and the Cu pad, and thus the SACNG solder is strengthened by the compound formation in the solder. Since fracture occurred near the joint interface in this study, the joint strength of the SACNG seems to be higher than those of the SA and SAC solders.

However, the ball shear strength becomes almost the same level after heat exposure at 120°C for 1000 h regardless of solder type. Since Cu–Sn compounds, which disperse in the SACNG solder, coarsen after heat exposure at 120°C for 1000 h, the ball shear strength seems to decrease at the same level as the SA and SAC solders.

In the case of the joint using the Ni/Au-plated pad, the ball shear strength of the joint with the SACNG solder is approximately as same as that of the joint with the SAC solder at 80°C. The joint strength is higher than that of the joint with the SA solder. As shown in Fig. 3, the SAC and SACNG solders have refined microstructures and thus the joint strength is higher than that of the SA solder. At 100 and 120°C, similar tendency is observed until 300 h. However, the ball shear strength saturates on the same level in all the solders when the heat exposure time is over 600 h.

As shown in Fig. 5, microstructure coarsening occurs easily following the heat exposure treatment at higher temperature. Moreover, the effect of the supplement of a small amount of Ni in the solder becomes negligible because the dissolution of Ni from the Ni/Au-plated pad in the molten solder occurs in reflow soldering. Therefore, analogous ball shear strength is obtained under long-term heat exposure conditions at higher temperature regardless of solder type.

4. Conclusions

The reliability of the solder ball joint with the Sn–3.5Ag–0.5Cu–0.07Ni–0.01Ge solder was investigated under heat exposure conditions and compared with those of the joints with the Sn–3.5Ag and Sn–3.5Ag–0.5Cu solders. The summary is as follows.

1) Cu–Sn compounds included a few atomic percent Ni disperse in the joint with the Sn–3.5Ag–0.5Cu–0.07Ni–0.01Ge solder and the Cu pad after reflow soldering.

2) The ball shear strength of the joint with the Sn–3.5Ag–0.5Cu–0.07Ni–0.01Ge solder and the Cu pad is relatively higher than those of the joints using the Sn–3.5Ag and Sn–3.5Ag–0.5Cu solders.

3) In the case of the joint using the electroless Ni/Au-plated Cu pad, the influence of the supplement of a small amount of Ni in the Sn–Ag–Cu solder on the ball shear strength was negligible.

4) Regardless of both solder type and pad type, the ball shear strength became at approximately same level after heat exposure treatment at 120°C for 1000 h.

5) The growth kinetics of the reaction layers formed at the joint interfaces have similar tendency regardless of whether or not the supplement of a small amount of Ni and Ge in the Sn–Ag–Cu solder.

REFERENCES


