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Impact Properties of Lead-Free Sn-Ag-Cu-Ni-Ge Solder Joint with Cu Electrode

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The impact properties of solder ball joints with Sn-Ag-Cu-Ni-Ge lead-free solders and Cu electrodes were investigated in the aged conditions at 393 K. The impact properties evaluated was compared with Sn-Ag and Sn-Ag-Cu solder joints. The impact properties of Sn-Ag-Cu-Ni-Ge joints were superior to those of Sn-Ag and Sn-Ag-Cu joints. In the cases of Sn-Ag and Sn-Ag-Cu joints, fracture mainly occurred in the intermetallic compounds (IMC) layer formed in the joint interface regardless of aging treatment. On the contrary, main fracture mode was solder fracture in as-reflow Sn-Ag-Cu-Ni-Ge joints. Although the main fracture mode gradually changed from solder fracture to IMC fracture upon aging, Sn-Ag-Cu-Ni-Ge joints had excellent impact reliability compared with Sn-Ag and Sn-Ag-Cu joints even after aging at 393 K for 1000 h. [doi:10.2320/matertrans.MF200808]

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1. Introduction

A Sn-Ag-Cu-Ni-Ge lead-free solder has been developed to be used for various industry machines.^{1,2)} A supplement of a small amount of Ge in a Sn-Ag-Cu lead-free solder is effective to depress the oxidation of the solder in soldering.¹⁾ Moreover, a supplement of a small amount of Ni in the Sn-Ag-Cu solder is expected to refine matrix phases formed in the solder and the microstructure with such matrix phases is expected to be relatively stable under heat exposure conditions.²⁾ Although mechanical properties and microstructures of the Sn-Ag-Cu-Ni-Ge lead-free solder have been examined,^{2,3)} the researches on the reliability of the Sn-Ag-Cu-Ni-Ge solder joints are a little.

In the previous study, ball shear strength and microstructures of the solder ball joints with Sn-Ag-Cu-Ni-Ge solders and Cu electrodes have been investigated in the aged conditions.^{4,5)} From the investigation results of ball shear strength, it was clarified that the Sn-Ag-Cu-Ni-Ge solder joint has excellent heat resistance compared with those of the joints using the Sn-Ag and Sn-Ag-Cu solders.⁴⁾ Moreover, it has been reported that the supplement of a little amount of Ni into the Sn-Ag-Cu solder is effective to prevent the growth of the reaction layer formed in the joint interface.⁵⁾

For solder ball joints, the impact reliability is one of the crucial issues⁶⁾ besides thermal fatigue, heat resistance and so on. The purpose of this study is to investigate the impact properties of the Sn-Ag-Cu-Ni-Ge solder ball joints in the aged conditions. The effect of a supplement of Ni and Ag in the Sn-Ag-Cu-Ni-Ge lead-free solder on the impact properties of the solder ball joint was investigated. The solder ball joints with a eutectic Sn-Ag solder and a ternary Sn-Ag-Cu solder were also investigated for comparison.

Table 1 Chemical compositions of solder balls studied.

Solder type	Chemical composition (mass%)
SA	Sn-3.5Ag
SAC	Sn-3.5Ag-0.5Cu
SACNG	Sn-3.5Ag-0.5Cu-0.07Ni-0.01Ge
S3ACNG	Sn-3.0Ag-0.5Cu-0.07Ni-0.01Ge
SAC0.15NG	Sn-3.5Ag-0.5Cu-0.15Ni-0.01Ge
SAC0.25NG	Sn-3.5Ag-0.5Cu-0.25Ni-0.01Ge

2. Experimental

Four types Sn-Ag-Cu-Ni-Ge solder balls were prepared and Sn-3.5 mass%Ag and Sn-3.5 mass%Ag-0.5 mass%Cu solder balls were also prepared for comparison. Table 1 shows chemical compositions of solder balls used in this study. The diameter of each solder ball was 0.3 mm. Following the experimental procedure of the previous reports,^{4,5)} the solder ball was joined on a Cu pad on an FR-4 substrate by reflow soldering with non-clean flux. The diameter of the Cu pad was 0.2 mm and the surface of the Cu pad was finished with organic solderability preservative. The peak temperature and duration time over 493 K in reflow soldering were set to be 516 K and 44 s, respectively.^{4,5)} After reflow soldering, the subsequent aging treatment were conducted at 393 K for 300 h, 600 h and 1000 h.

The impact test of the solder ball joint was conducted at room temperature using Instron Micro Impactor.⁷⁾ Figure 1 shows a schematic of the impact test. The thickness of the Cu pad and the resist were 36 μm and 46 μm , respectively. The velocity before impact was set at 1 m/s. Figure 2 indicates an example of the result of the impact test with a Sn-3.5Ag-0.5Cu-0.07Ni-0.01Ge solder ball joint. In this study, energy to peak load was defined as E_p , and thus the impact shear strength (peak load) and the impact toughness (E_p) were investigated. Eight joints were tested under each condition,

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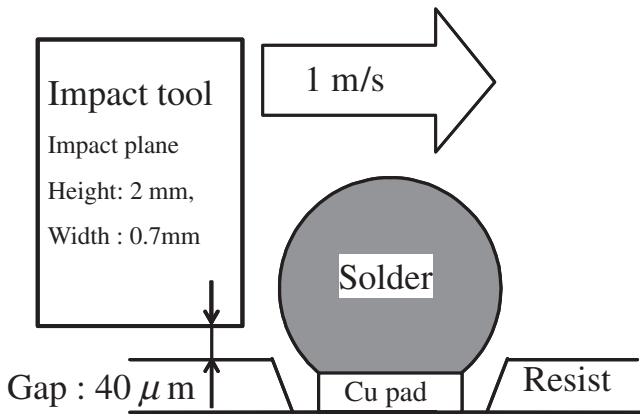


Fig. 1 Schematic of impact test for solder ball joint.

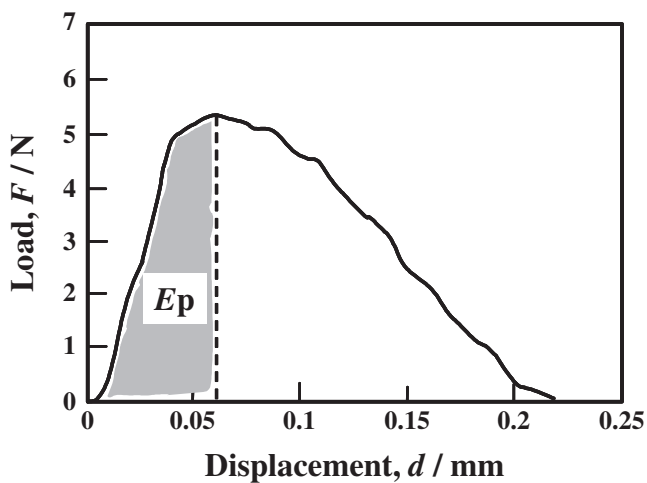


Fig. 2 Example of a result of impact test with a Sn-3.5Ag-0.5Cu-0.07Ni-0.01Ge solder ball joint (without aging).

and the averages of the peak load and E_p were evaluated by the data except maximum and minimum values. Fracture surfaces after the impact test were observed with an electron probe X-ray microanalyzer (EPMA) to investigate the fracture mode.

3. Results and Discussion

3.1 Impact properties

Figures 3 and 4 show the results of the impact test. For specimens as reflow (without aging treatment), the joint with the SA solder shows similar impact shear strength to those of the Sn-Ag-Cu-Ni-Ge joints. On the contrary, the impact shear strength of the SAC joint is inferior to those of other joints. Moreover, the impact toughness of the SAC joint is much lower than those of other solder joints. It is approximately a half those of other solder joints. A similar tendency was observed in the previous report with Sn-3.5 mass%Ag and Sn-3.8 mass%Ag-0.7 mass%Cu solder joints.⁷⁾ For the Sn-Ag-Cu-Ni-Ge lead-free solder joints, the effect of Ni and Ag contents in the Sn-Ag-Cu-Ni-Ge solder on the impact properties is negligible.

With increasing aging time, the impact shear strength decreased in all solder joints. In particular, the decrease in the

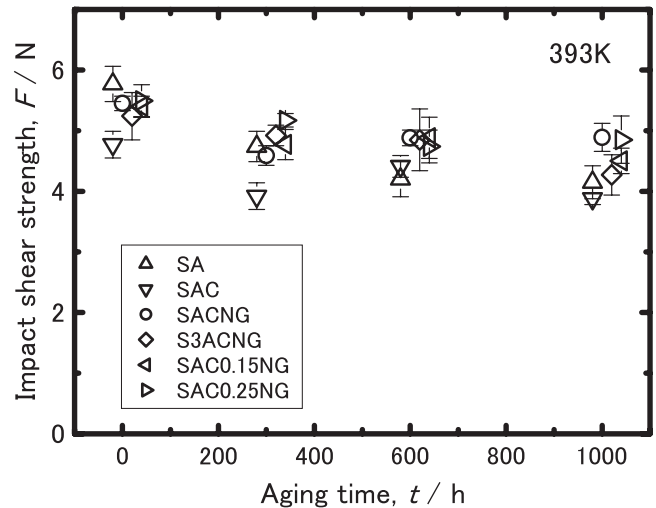


Fig. 3 Impact shear strength measurement result.

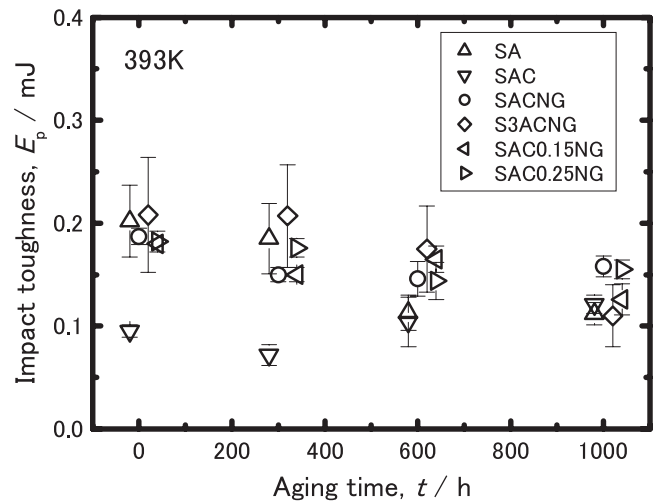


Fig. 4 Impact toughness (E_p) measurement result.

SA joint was remarkable, and its strength was the level similar to that of the SAC joint after aging at 393 K for 600 h. A similar tendency was observed in the impact toughness, although a little increase of the impact toughness was found in the SAC joint. It has been reported that Cu_6Sn_5 and Cu_3Sn layers form in the joint interfaces upon aging in all the joints investigated.⁸⁾ In particular, the growth rate of the Cu_3Sn layer in the SAC joint is the fastest among the joints investigated. As described later, fracture occurred in an intermetallic compounds (IMC) layer regardless of aging treatment in the SAC joint. When the Cu_3Sn layer grows in the interface between the Cu_6Sn_5 layer and the Cu pad, fracture could occur in the Cu_3Sn layer or the $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ interface. Therefore, the quick growth of the Cu_3Sn layer probably has an effect on the impact properties of the SAC joint. Further investigation to identify the fracture region is required to clarify the effect.

The impact properties of the SA joint were analogous to those of the Sn-Ag-Cu-Ni-Ge joints until aging time was 300 h. However, they degraded than those of the Sn-Ag-Cu-Ni-Ge joints when the aging time was over 600 h. For the Sn-Ag-Cu-Ni-Ge joints, significant difference was not observed

in the impact properties until the aging time was 600 h. When the aging time was 1000 h, the impact properties of the S3ACNG joint degraded compared with other Sn-Ag-Cu-Ni-Ge joints, and they were very close to those of SA and SAC joints.

Figure 5 shows ball shear strength for each solder joint evaluated by conventional ball shear test.^{4,5)} The test was conducted at shear speed of 15 mm/min (2.5×10^{-4} m/s). In the case of slow shear speed, SA, SAC and S3ACNG joints showed similar shear strength during aging at 393 K. Their values were lower than those of SACNG, SAC0.15NG and SAC0.25NG until the aging time was over 600 h, although the effect of solder composition on ball shear strength was slight when the aging time was 1000 h. Compared impact shear strength shown in Fig. 3 with conventional ball shear strength shown in Fig. 5, the impact shear strength of the SAC joint is less than those of other joints. Moreover, considering impact toughness shown in Fig. 4, it is clarified the impact properties of the SAC joint are inferior to those of other lead-free solder joints investigated. On the contrary, it was found that the Sn-Ag-Cu-Ni-Ge joints except the S3ACNG joint have excellent impact properties in the aged conditions at 393 K compared with SA and SAC joints.

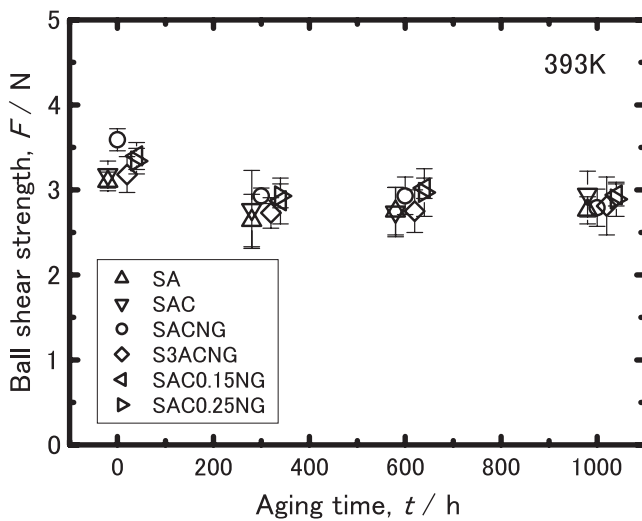


Fig. 5 Ball shear strength evaluated by conventional ball shear test.^{4,5)}

3.2 Fracture mode

Three fracture modes were observed in fracture surfaces after the impact test in this study. The examples of fracture modes are shown in Fig. 6. Figures 6(a), (b) and (c) show solder fracture, IMC fracture and their complex fracture, respectively. Figure 7 shows the change of the fraction of fracture mode upon aging for each solder joint. For the SAC joint, fracture occurred in the IMC layer regardless of aging treatment. Thus, the SAC joint seems to have poor impact properties as shown in Figs. 3 and 4.

For the SA joint, although the main fracture mode was IMC fracture, the solder fracture mode was also observed in as-reflow joints. Figures 8(a) and (b) show cross sectional views of as-reflow SA and SAC joints, respectively. In both joints, scallop-shape Cu-Sn IMC layers form in the joint interfaces. However, morphology of the IMC layers are somewhat different in both joints. The maximum length of protrusions formed in IMC layers are approximately 5 μ m and 10 μ m in SA and SAC joints, respectively. Nonuniform formation of the IMC layer has become noticeable in the SAC joint as shown in Fig. 8. In such a nonuniform IMC layer, crack formation could occur easily in the groove in the IMC layer when the impact shear force is loaded to the joint.⁹⁾

On the contrary, nonuniform formation of the IMC layer is inhibited in the SA joint compared with the SAC joint. Thus, frequency of crack formation in the IMC layer could reduce in the SA joint. Moreover, it was found from the result of tensile test using micro size specimens that tensile strength of an as-cast Sn-3.5 mass%Ag solder is higher than that of an as-cast Sn-3.5 mass%Ag-0.7 mass%Cu solder.¹⁰⁾ Due to higher strength of the solder and lower frequency of crack formation in the IMC layer, the as-reflow SA joint showed higher impact shear strength than the SAC joint. With aging, the fraction of IMC fracture increased and other modes were not observed when the aging time was over 600 h. Due to the change of the fracture mode to IMC fracture, the impact properties of the SA joint degraded to the level similar to those of the SAC joint. In SA and SAC joints, the Cu-Sn IMC layer, which has a scallop shape, forms in the joint interface by reflow soldering (refer to Figs. 8(a) and (b)) and the layer grows upon aging.⁴⁾ The growth rates of the Cu-Sn IMC layers at 393 K are analogous in SA and SAC joints.⁴⁾ Therefore, similar impact properties are obtained in SA and

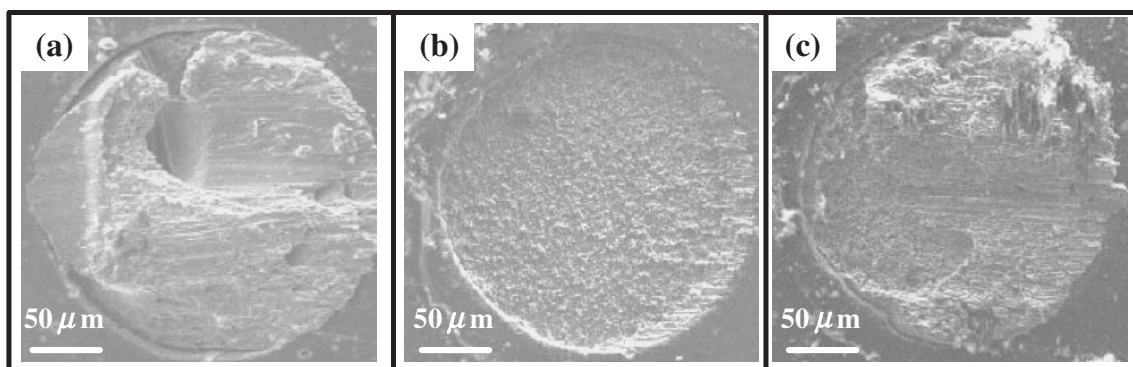


Fig. 6 Secondary electron images of fracture surfaces for as-reflow joints. (a) solder fracture in the SA joint, (b) IMC fracture in the SAC joint, (c) complex fracture in the SACNG joint.

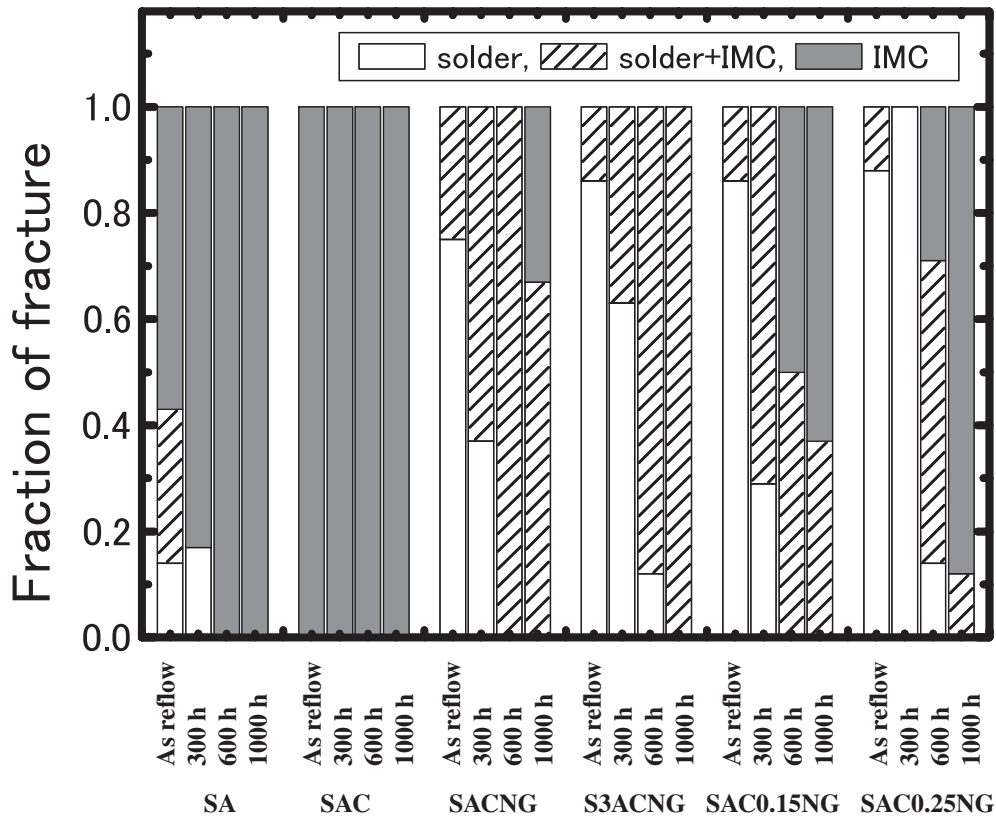


Fig. 7 Fracture mode change upon aging at 393 K.

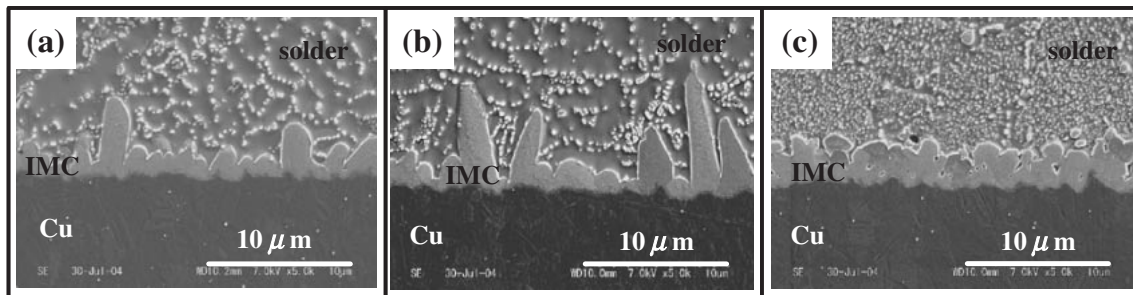


Fig. 8 IMC formation in the joint interfaces by reflow soldering (secondary electron images). (a) SA joint, (b) SAC joint, (c) SACNG joint.

SAC joints when IMC fracture is dominant upon aging.

On the other hand, the Sn-Ag-Cu-Ni-Ge joints have relatively excellent impact properties compared with SA and SAC joints (shown in Figs. 3 and 4). For the Sn-Ag-Cu-Ni-Ge joints, the main fracture mode is solder fracture until the aging time is 300 h, although the main fracture mode changes to IMC fracture or complex fracture over the aging time of 600 h. This change of the fracture mode causes the degradation of the impact properties of the joints. However, except the S3ACNG joint, the Sn-Ag-Cu-Ni-Ge joints have superior impact properties to SA and SAC joints even after aging at 393 K for 1000 h. In the Sn-Ag-Cu-Ni-Ge joints, a Cu-Sn-Ni IMC layer, which is an accumulation of granular phases, forms in the joint interface by reflow soldering^{4,5)} (refer to Fig. 8(c)). The IMC layer is not densely compared with the Cu-Sn IMC layer formed in SA and SAC joints and

includes solder phases. Thus, IMC fracture does not occur easily in the as-reflow Sn-Ag-Cu-Ni-Ge joints. Moreover, since the IMC layer grows with coarsening of granular IMC phases by aging, the growth rate is slower than those of the Cu-Sn IMC layer in SA and SAC joints.^{4,5)} Therefore, the change of fracture mode to IMC fracture upon aging is delayed due to slow growth of the IMC layer. Consequently, the Sn-Ag-Cu-Ni-Ge joints have relatively superior impact properties to SA and SAC joints after aging at 393 K for 1000 h.

For the S3ACNG joint, impact properties similar to those of SA and SAC joints were obtained after aging at 393 K for 1000 h. As shown in Fig. 5, the S3ACNG joint has lower ball shear strength similar to those of SA and SAC joints at a slow shear speed.⁵⁾ Moreover, it has been reported that as-cast hypoeutectic Sn-Ag-Cu solders, which have lower Ag

content than Sn-3.5 mass%Ag-0.7 mass%Cu, have lower tensile strength than that of the as-cast Sn-3.5Ag-0.7Cu solder and such a tendency is kept after aging at 393 K for 504 h.¹⁰⁾ Thus, the S3ACNG solder would have lower strength than those of other Sn-Ag-Cu-Ni-Ge solders after aging. After aging at 393 K for 1000 h, IMC fracture was observed in the Sn-Ag-Cu-Ni-Ge joints except the S3ACNG joint. On the contrary, IMC fracture was not observed but complex fracture of the solder and the IMC was observed in the S3ACNG joint after the aging. In such complex fracture including solder fracture, the lower strength of the aged S3ACNG solder seems to cause impact properties of the joint to degrade. Consequently, the impact properties of the S3ACNG joint were inferior to those of other Sn-Ag-Cu-Ni-Ge joints and similar to those of SA and SAC joints after aging at 393 K for 1000 h. When aging time is under 600 h, the S3ACNG joint has the impact properties similar to those of other Sn-Ag-Cu-Ni-Ge joints. In such conditions, solder fracture is dominant and thus impact properties of the solder itself have an effect on those of the solder joint. Therefore, the investigation of the impact properties of the solder is required to elucidate the effect.

4. Conclusions

The impact properties of the solder ball joints with Sn-Ag-Cu-Ni-Ge solders and Cu electrodes were investigated. Moreover, the comparison with Sn-Ag and Sn-Ag-Cu solders was also conducted. The results obtained are summarized as follows.

- (1) The impact properties of the Sn-Ag-Cu-Ni-Ge solder joints are superior to the Sn-3.5Ag-0.5Cu solder joint in the aged conditions investigated.
- (2) For the Sn-3.5Ag-0.5Cu joint, IMC fracture occurred regardless aging treatment and thus the impact properties degraded.
- (3) For the Sn-3.5Ag joint, impact properties similar to those of Sn-Ag-Cu-Ni-Ge joints were observed in as-reflow joints. Fraction of IMC fracture increased upon aging and thus impact properties degraded to the level

similar to those of the Sn-3.5Ag-0.5Cu joint after aging at 393 K for 600 h.

- (4) The main fracture mode was solder fracture in as-reflow Sn-Ag-Cu-Ni-Ge joints. With aging, the main fracture mode changed from solder fracture to IMC fracture.
- (5) Since the IMC layers formed in the Sn-Ag-Cu-Ni-Ge joints are not densely and the growth rates of the layers upon aging are slow, IMC fracture does not occur easily and thus the impact properties of the Sn-Ag-Cu-Ni-Ge joints are superior to those of Sn-3.5Ag and Sn-3.5Ag-0.5Cu joints after aging at 393 K for 1000 h.

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