Five layer Cu-coated Zn/Al clad solder for die attachment

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Abstract
Zn/Al and Zn/Al/Cu clad materials have been developed for high-temperature die attachment. The clad structure is used in an attempt to improve the wettability of Zn-Al solder by preventing oxidation of Zn and Al. The materials were produced by clad-rolling of Zn, Al, and Cu strips, and they act as a solder following eutectic melting at temperatures above 382°C. The wettability, bondability, and reliability of the clad materials were evaluated. It was found that the Zn/Al/Cu clad material could be used under an atmospheric oxygen concentration of 100 ppm. In addition, the thermal cycle life of a chip-to-substrate joint formed using the Zn/Al/Cu clad material was longer than that using Pb-Sn-Ag solder.

Key words
Clad material, Die bonding, Oxidation resistance, Pb-free solder, SiC

I. Introduction
A great deal of effort has been undertaken to develop new bonding technologies that can replace conventional Pb-based solder in electronics. One of the motivations for this is to comply with environmental regulations such as the RoHS and ELV directives. Another is to improve the reliability and robustness of products. This is particularly important for future SiC and GaN power devices, which will operate at extreme temperatures above 200°C, because even conventional Pb-based solder cannot satisfy the reliability requirements for such devices.

Among the many novel bonding approaches that have been suggested are Au-, Bi-, and Zn-based solders, transition liquid phase diffusion bonding using Sn-Cu and Ag-In systems, and sintering bonding using Ag nanoparticles [1]-[13]. Although these methods have the potential to offer high reliability, they have not come into widespread use due to high materials and processing costs, as well as technical difficulties in achieving an ideal bonding state. On the other hand, Zn-Al solder is relatively inexpensive, exhibits a high thermal conductivity, and forms a stable bonding interface with Ni metallization [9]. However, a crucial drawback is its poor wettability due to oxidation of Zn and Al, and thus suitable countermeasures must be found before Zn-Al solder can be used in practical applications.

To overcome this problem, we have developed Zn/Al and Zn/Al/Cu multilayer clad materials for high-temperature die attachment [14]. The clad structure is used in an attempt to improve the wettability of Zn-Al solder by preventing oxidation of Zn and Al. The materials are produced by clad-rolling of Zn, Al, and Cu strips, and they act as a solder following eutectic melting at temperatures above 382°C. In the present study, the wettability, bondability, and reliability of the clad materials were examined.

II. Experimental

A. Zn/Al clad material
Cross-sectional schematic images of a three-layer Zn/Al/Zn clad material (ZAZ) and a conceptual bonding mechanism using the ZAZ is illustrated in Fig. 1. ZAZ was produced by clad-rolling of Zn strips and an Al strip. The total thickness of ZAZ is 0.1 mm and the ratios of the layers are Zn:Al:Zn=3:1:3. A ZAZ is expected to start to melt at the clad interface at a temperature of 382°C and act as a Zn-6Al eutectic solder. Because the Al layer is covered by outer Zn layers, the Al is prevented from oxidizing during storage and the heating process. Thus, ZAZ is expected to exhibit better

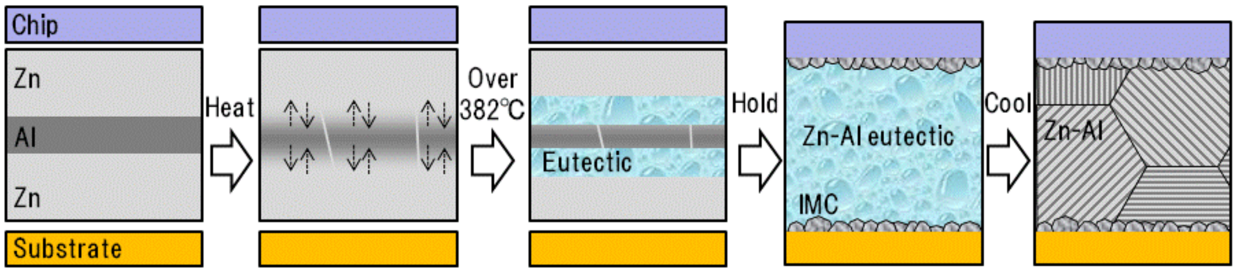
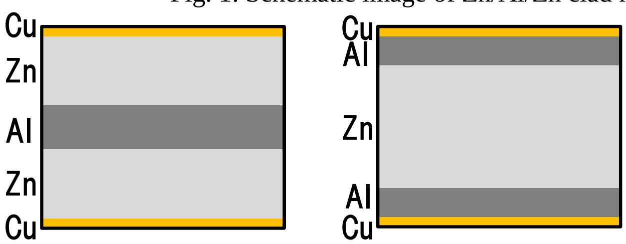


Fig. 1. Schematic image of Zn/Al/Zn clad material and its assumed bonding mechanism.



(a) CZA (b) CAZ

Fig. 2. Schematic image of Zn/Al/Cu clad materials.

wettability than Zn-Al solder. The melting point of ZAZ was examined using differential scanning calorimetry (DSC) with a heating rate of 10°C/min in air.

B. Zn/Al/Cu clad material (CZA and CAZ)

Cross-sectional schematic images of a five-layer Cu/Zn/Al/Zn/Cu (CZA) and Cu/Al/Zn/Al/Cu (CAZ) are illustrated in Fig. 2. Both were produced by the clad-rolling of Cu, Zn, and Al strips with strip thicknesses of 0.1 mm. The purpose of the outer Cu layers is to prevent both the Zn and Al layers from oxidizing.

C. Wettability test and boning procedure

A wettability test was performed by the following process. ZAZ, CZA, and CAZ were placed on Ni/Au-plated Cu substrates. Then, the samples were heated to 385°C at a heating rate of 100°C/min and maintained for 3 min in N_2 atmosphere using an infrared furnace. Wetting behavior and wet area were evaluated. Pb-5Sn-1.5Ag solder sheet and Zn-6Al eutectic solder sheet were also examined for comparison.

In the bonding process, a clad material was placed on a Ni-plated Cu substrate, and a Si chip and then a 0.8 g weight were stacked. The samples were heated following the same process described above except that N_2+4%H_2+0-100 ppm O_2 atmosphere was also used. For ZAZ, the surfaces were polished using #4000 emery papers. A comparison sample bonded using a Pb-5Sn-1.5Ag solder sheet was formed using the same process as above except that the maximum bonding temperature was set to 360°C.

D. Reliability test

A thermal cycle test between -55°C and 150°C was performed using the Si-to-Ni-plated Cu substrate joints fabricated by the above process. Bonding state was estimated using scanning acoustic microscopy.

III. Results and Discussion

A. Wettability and bondability of Zn/Al/Zn claded material

Fig. 3 shows DSC traces of ZAZ. The ZAZ melted at 382°C, which is the eutectic temperature of Zn-Al alloy. This indicates that the ZAZ started eutectic melting at the Zn/Al clad interface as shown in Fig. 1.

Fig. 4 shows optical images of Zn-6Al eutectic solder and ZAZ after a wetting test in N_2 atmosphere. Dashed circles in Fig. 4 indicate the shape of each solder sheet before melting. The Zn-6Al eutectic solder did not entirely wet on Ni/Au-plated Cu substrate. In addition, a mass of the Zn-6Al fell down when the substrate was turned over. This means that the Zn-6Al solder did not bond to the substrate due to its surface Zn and Al oxide films. In contrast, for ZAZ, the liquid was wet and spread widely on the substrate. Therefore, the wettability of ZAZ is better than that of Zn-6Al eutectic solder.

Bondability of ZAZ in N_2+100 ppm O_2 is shown in Fig. 5. In

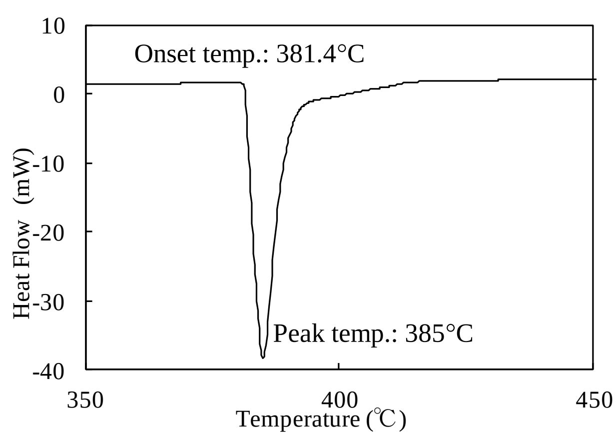
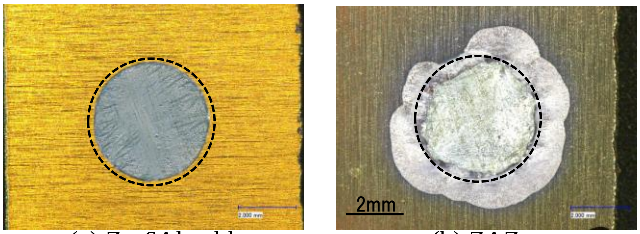
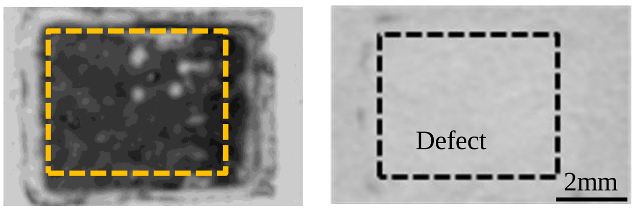


Fig. 3. DSC traces of Zn/Al/Zn clad material with a heating rate of 10°C/min in air atmosphere.



(a) Zn-6Al solder (b) ZAZ

Fig. 4. Optical images of wettability test.



(a) With polish (b) Without polish

Fig. 5. Ultrasonic acoustic images of chip-to-substrate joint using Zn/Al/Zn clad material bonded in an atmospheric oxygen concentration of 100 ppm.

this figure, dashed rectangles indicate the shape of Si chip. The black area within the rectangle is the bonded area, whereas the white area is void or unbonded area. In the case that ZAZ was polished, most of the area under the Si chip was successfully bonded, as shown in Fig. 5(a). On the other hand, in the case that ZAZ was not polished, the chip was not bonded at all, as shown in Fig. 5(b). It may be assumed that the difference was caused by the roughness of ZAZ. Non-polished ZAZ was not able to bond due to the thick flat oxide film over the outer Zn layers, which grew thicker in the heating process in the atmospheric oxygen concentration of 100 ppm, and a Zn-6Al liquid created from the ZAZ was enclosed in the thick Zn oxide. In contrast, the surfaces of the polished ZAZ were scratched and uneven. Therefore, the thick oxide films were finely fractured by the eutectic melting of the ZAZ, and a Zn-6Al liquid leaked through gaps of the fractured oxides. Consequently, bonding is achieved even at high oxygen concentration.

According to the above results, ZAZ successfully prevents oxidation of the Al layer by virtue of the outer Zn layer, and exhibits better wettability than Zn-6Al eutectic solder. However, the outer Zn layers oxidize easily, and thick Zn oxides inhibit bonding. Therefore, ZAZ requires initial polishing, and low oxygen concentration should be maintained in the bonding atmosphere. Unfortunately, those requirements are costly and far from practical for its utilization.

B. Effects of Cu layer of Zn/Al/Cu clad materials

Si-to-Ni/Au-plated Cu substrate joints were formed using CZA and CAZ in atmospheres of N_2+4% H_2, N_2+4%H_2+50 ppm O_2, and N_2+4%H_2+100 ppm O_2. Cross-sectional observations of microstructure revealed defects from the

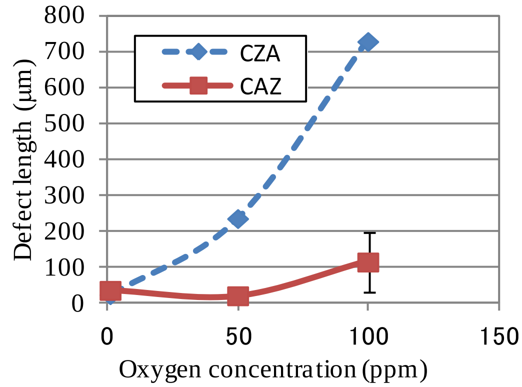


Fig. 6. Relation between defect length and atmospheric oxygen concentration of each clad material.

edge of the joints toward the center. It is suspected that the defects are oxide films. Fig. 6 shows the relation between the length of the defects and atmospheric oxygen concentrations. For CZA, the defect length increased with increasing oxygen concentration. In contrast, for CAZ, the effect of the atmosphere was slight.

To search for a cause, surfaces of CZA and CAZ were investigated during the heating process. Fig. 7 shows the surface color changes of the CZA and CAZ surfaces. It is found that the surface of the CZA changed gradually from orange to gray at around 200°C., whereas the CAZ remained orange up to 382°C, at which temperature it melted and showed a metallic luster. From analyses of microstructures, the gray surface of the CZA was identified as an intermetallic compound of $CuZn_4$, and the orange surface of the CAZ was identified as Cu. In short, during a heating process, the Cu layers of CZA completely disappear, and the underslab Zn layer is exposed to atmosphere. Subsequently, the Zn quickly oxidizes and the bondability of CZA deteriorates in a high oxygen concentration atmosphere. In contrast, the Cu layers of CAZ are present up to the melting temperature of 382°C. Initial Cu oxides of the CAZ surface are able to deoxidize during heating by H_2. When the CAZ melts, it is believed that no oxides are present, so that its bondability is maintained even under 100 ppm O_2 atmospheric conditions.

Next we consider the behavior of CZA and CAZ with respect to interdiffusion between layers. Diffusion distances of each layer were calculated using the following equations:

$$X = \sqrt{2Dt} \tag{1}$$

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

where X is the diffusion distance, D is the diffusion coefficient, D_0 is a prefactor, t is the diffusion time, Q is the activation energy, R is a gas constant, and T is absolute temperature [15]. Diffusion distances were calculated assuming that CZA and CAZ were heated at 380°C for 1 min. The results are shown in Fig. 8. Zn in the case of CZA and Al

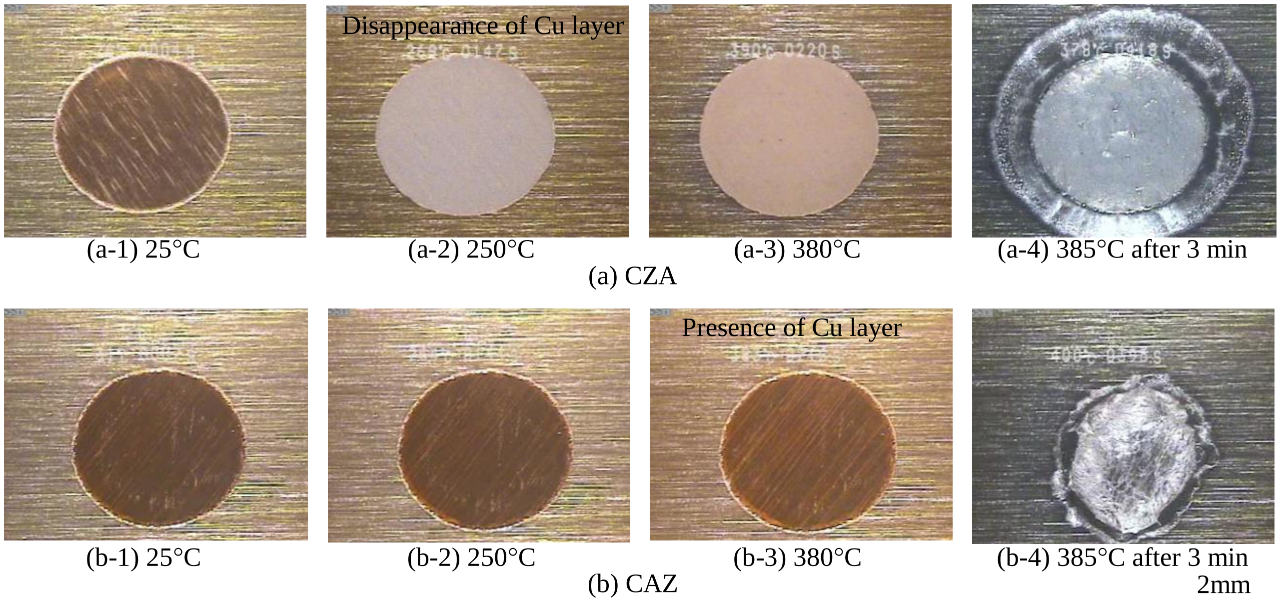


Fig. 7. Optical images of surface of each clad material for a heating rate of 100°C/min in N_2 atmosphere.

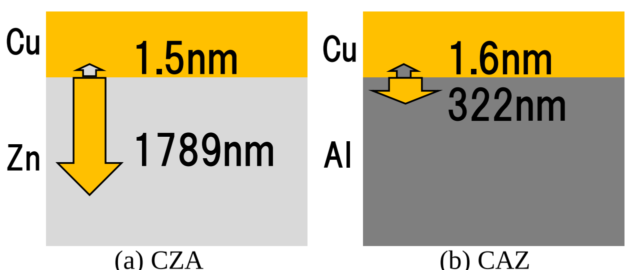


Fig. 8. Calculated diffusion distance of each layer at 380°C for 1 min.

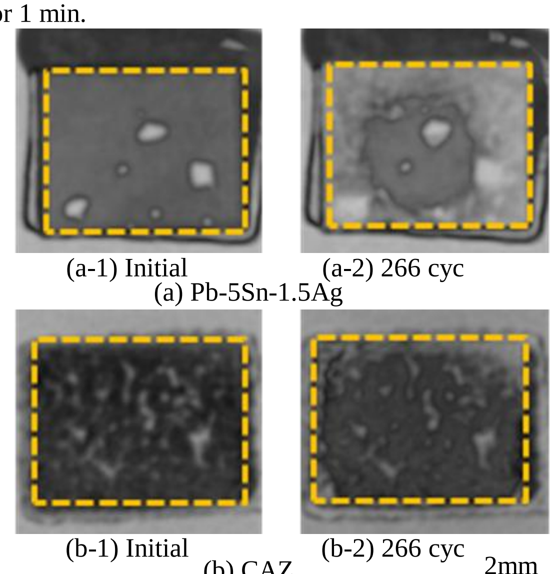


Fig. 9. Ultrasonic acoustic images of chip-to-substrate joints using each solder before and after a thermal cycle test between -55°C and 150°C.

in the case of CAZ rarely diffuse into the outer Cu layer. However, Cu in the CZA case easily diffuses into the underslab Zn layer, whereas Cu in the CAZ case did not substantially diffuse into the underslab Al layer. In short, the underslab Al layers of the CAZ act as diffusion barriers between the Cu and Zn layers.

Summarizing the above, for CAZ, the outer Cu layers prevent the Zn and Al from oxidation, and the underslab Al layers prevent the Cu layers from disappearing by acting as diffusion barriers. Therefore, CAZ is able to exhibit superior bondability even in a high oxygen concentration atmosphere. The CAZ structure creates an oxide-free Zn-Al-Cu solder immediately after its melting.

C. *Thermal cycle reliability*

Thermal cycle reliability of the Si-to-Ni-plated Cu substrate joints formed using CAZ and Pb-5Sn-1.5Ag solder was examined. This is a highly accelerated test, because the joints were not molded with epoxy resin and the bonded layer is loaded to produce extreme strain.

Crack propagation behavior is shown in Fig. 9, wherein white areas are voids or cracks. Cracks of both CAZ and Pb-based solder propagated from the edge region toward the center. Cracking speed for the CAZ was slower than that for Pb-based solder. In addition, there was no apparent change in void size for CAZ, although that for Pb-based solder grew. Therefore, Zn-Al joints formed using CAZ have a longer lifetime than conventional Pb-based solder.

IV. Conclusion

ZAZ, CZA, and CAZ clad materials have been developed for die-attach solder for the purpose of improving the usability of Zn-Al solder. We obtained the following conclusions:

(1) A three-layer Zn/Al/Zn clad material exhibits better wettability than Zn-6Al solder. However, surface polishing and low atmospheric oxygen concentration are required for bonding.
(2) A five-layer Cu/Al/Zn/Al/Cu clad material exhibits superior bondability without polishing even under an atmospheric oxygen concentration of 100 ppm. The outer Cu layers prevent the oxidation of Zn and Al, and the underslab Al layers act as diffusion barriers between the Cu and Zn layers.
(3) Joints formed using CAZ have a longer thermal cycle lifetime than those formed using conventional Pb-based solder.
Based on these results, the Cu/Al/Zn/Al/Cu clad material is a promising candidate for replacing Pb-based solder.

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