Differences in heat exposure degradation of Sn alloy platings joined with Ag-epoxy conductive adhesive

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Isotropic conductive adhesives (ICAs), which consist of various conductive powders (fillers) and thermoset adhesives (binders), have been intensively studied as alternatives to solders. Among them, Ag-epoxy series ICAs are a well established alternative because of their good mechanical properties, electrical conductivity, and excellent heat, chemical and oxidation resistances. However, the compatibility of Ag-epoxy series ICAs with Sn or Sn alloy-plated components, which are widely used in industry, worsens at elevated temperatures. Oxidation of metals becomes a factor in degradation under heat. The authors have also reported that the serious degradation of strength by heat exposure is caused by the preferential diffusion of Sn in the plating to Ag in the ICA [1].

Developments of Pb free components as well as solders are advancing; Sn-Bi [2–4], Sn-Ag [5, 6], Sn-Cu [6], Sn-Zn [7], and pure Sn platings are typical examples of alternatives to Sn-Pb plating on components. Various additives are needed for Sn-Ag, Sn-Cu, and Sn-Zn platings because of the large differences of standard electrode potential between Sn and each metallic element. However, Sn plating has a problem of whiskers [8], even though it has been used for a long time. Sn-Bi plating has been applied widely as a Sn alloy plating because it can be fabricated from even a simple salt bath and is compatible with the early Pb-free solders such as Sn-Ag-Bi and Sn-Zn-Bi.

This work was performed to investigate the differences in degradation between Sn-Pb and Sn-Bi platings. Moreover, the difference was discussed in respect to crystal direction and the self-diffusion of Sn.

Cu with different Sn alloy-platings was used as the electrode material. Cu blocks, 15 mm×15 mm×15 mm and 99.9 wt% pure were prepared and one of the faces to be joined was polished to an optical flatness. The Cu blocks were then plated with Ni and Sn alloys of Sn-10 wt%Pb (Sn-Pb) or Sn-3 wt%Bi (Sn-Bi); plating conditions are summarized in Table I. The ICA used in this work was a typical Ag-epoxy system, loaded 73 wt% Ag. Two Sn alloy-plated Cu blocks were joined with ICA by curing at 150 °C for 0.5 hr. The thickness of the adhesive layer was

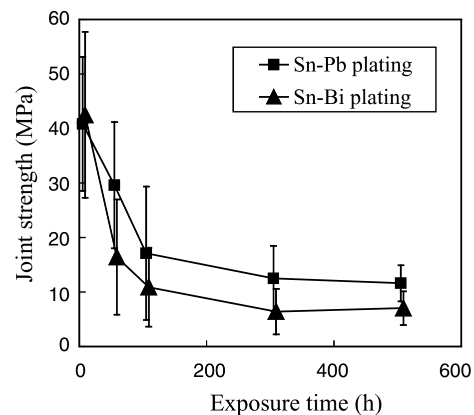

Figure 1 Joint strength change as a function of exposure time at 150 °C.

controlled to about 70 μm. Tensile tests were carried out in the same way as in our earlier work [1]. Joints were cut into rectangular tensile bars of 1 mm×3.5 mm×1 mm with the joint interface set to be vertical to the tensile axis. The tensile bars were subjected to heat exposure at 150 °C for up to 500 hr in air. Tensile tests were performed at room temperature at a crosshead speed of 0.5 mm/min. More than three specimens were tested for each data point. Microstructure observations and analyses were carried out using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The area percentages of voids on the Sn alloy platings were measured from microstructure observation of the fracture surface. JCPDS #4–673 [9] and #4–686 [10] were used to identify Sn and Pb.

Fig. 1 shows the changes in tensile strength of the Sn-Pb and Sn-Bi joints as a function of exposure time. The initial strengths of the joints were quite similar and were significantly degraded by heat exposure. However, the degradation rate of the Sn-Bi joints was faster than that of the Sn-Pb joints: the strength of the Sn-Bi joints degraded after a mere 50 hr at 150 °C. Before significant degradation the joints broke at the ICA/Sn alloy plating interface and inside of the ICA, but after significant degradation the joints broke only at the ICA/Sn alloy plating interface. The

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TABLE I Plating conditions

Plating	Ni under plating	Sn-10 wt%Pb plating	Sn-3wt%Bi plating
Cathode current density (A/dm^2)	2.0	4.0	5.0
Plating time (s)	360	380	260
Bath capacity (l)	2.0	2.0	2.0
Bath temperature (°C)	60	25	35
Agitating (rpm)	900	350	350
Average plating thickness (μm)	2.0	8 .8	8.4

TABLE II Joint Committee on Powder Diffraction Standards 4–673 [9]

Interplanar spacing: d (Å)	2θ (Cu-Kα) (°)	Relative intensity	Miller indices: *hkl*
2.915	30.649	100	200
2.793	32.015	90	101
2.062	43.874	34	220
2.017	44.904	74	211

authors have already reported the degradation mechanism by diffusion of Sn [1].

Fig. 2 shows the fracture surfaces of the Sn-Bi joints from the start to after 500 hr heat exposure, and Fig. 3 shows the changes in the area percentage of voids as a function of exposure time. The voids on fracture surfaces grew with the increase in time of heat exposure. The growth of voids on the Sn-Bi plating was faster than that on the Sn-Pb plating: the area percentage of the Sn-Bi plating after 50 hr heat exposure was similar to that of the Sn-Pb plating after 100 hr heat exposure. Differences in the degradation rates of the tensile strength in Fig. 1 fits the area percentages of voids on each of the Sn alloy platings in Fig. 3.

Fig. 4 shows the XRD patterns obtained from the Sn-Pb and Sn-Bi platings before being joined, and Table II summarizes the JCPDS of β-Sn [9]. From Fig. 4a, Sn and Pb were identified and the (2 0 0) Sn face, which is the fourth peak in relative intensity from the JCPDS, was the strongest peak. While, from Fig. 4b, only Sn was identified and the (2 1 1) Sn face was the strongest. Thus, it is shown that these platings are oriented in a certain crystal direction.

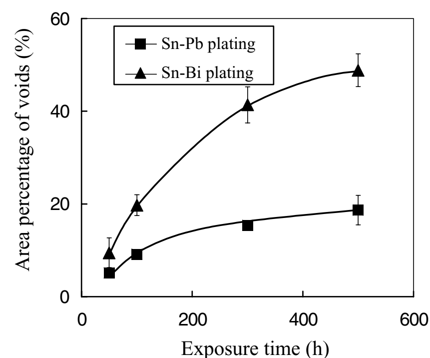

Figure 3 Area percentage changes on the fracture surfaces of Sn alloy plating side as a function of exposure time at 150 °C.

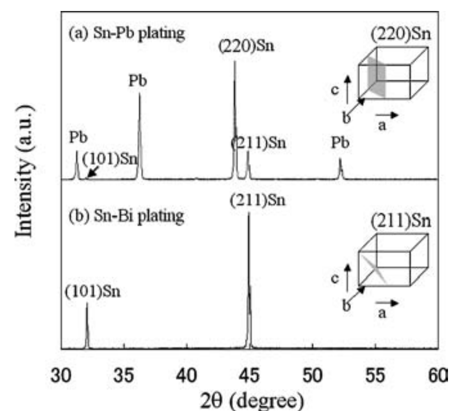

Figure 4 The XRD patterns of (a) Sn-Pb and (b) Sn-Bi platings before being joined.

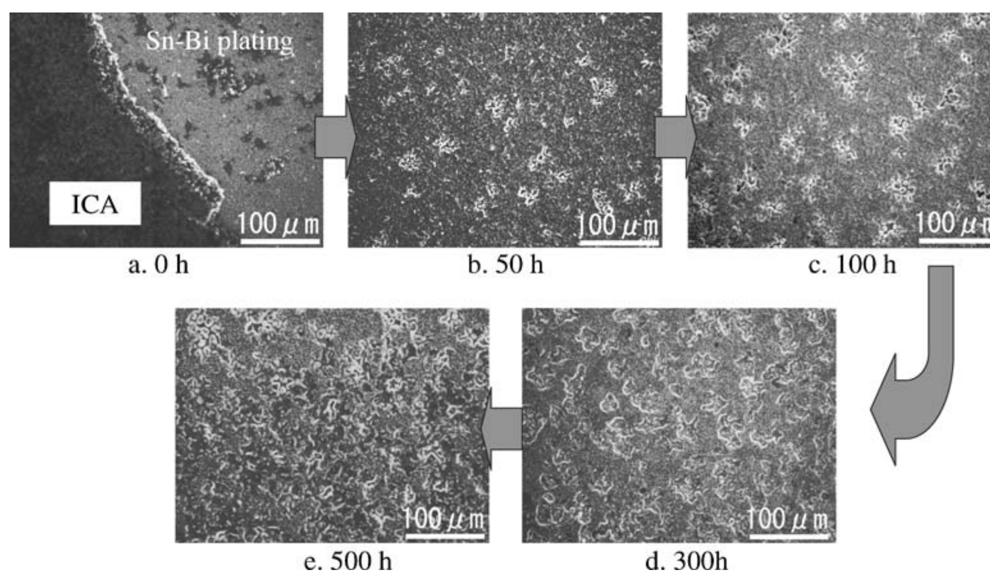

Figure 2 Fracture surfaces of the Sn-Bi joints (Sn-Bi plating side except a).

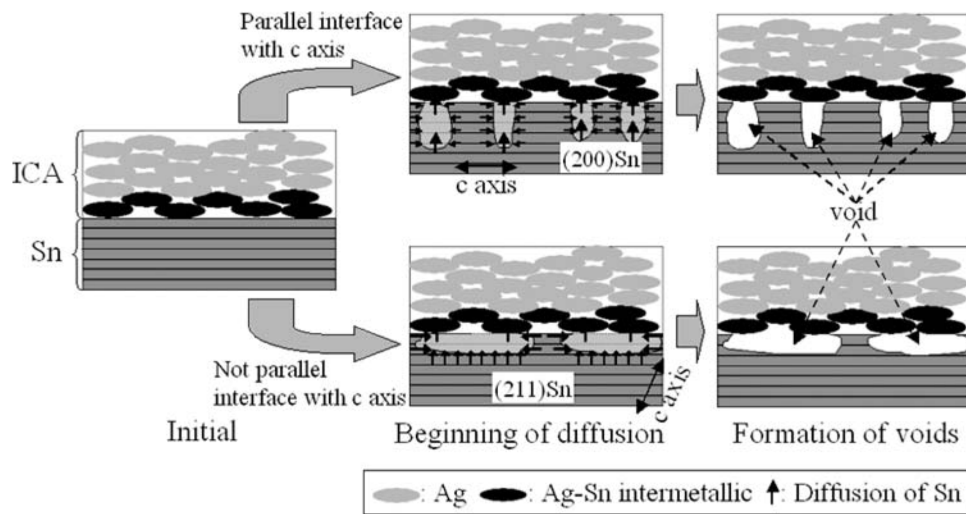

Figure 5 Schematic illustrations of the difference in void formations for each crystal direction of the plating (The actual ICA/plating interface of "Not parallel interface with *c* axis" decreases more than that of "Parallel interface with *c* axis".).

Table III summarizes the self-diffusion rates D of β-Sn at 150 °C calculated with the Arrhenius equation

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

where D_0 is the frequency factor, Q is the activation energy, R is a gas constant (8.31 J/Kmol) and T is the absolute temperature. The crystal structure of β-Sn is tetragonal and the self-diffusion rate parallel with the c axis of the crystal at 150 °C is 4.37×10^{-9}, which is less than half the 9.52×10^{-9} of that in the vertical direction. This Sn-Pb plating is oriented to (2 2 0) which is parallel with the c axis of the crystal. Therefore, it seems that Sn can easily diffuse in the vertical direction at a plating/ICA interface in Sn-Pb plating, resulting in delaying the increase of the area percentage of voids at the interface, and the difference in heat degradation with the Sn-Bi plating, as shown in Fig. 5. It is expected that more data on various crystal directions and the amounts of the addition metals can turn this degradation model into a general mechanism.

The difference in heat exposure degradation of Sn alloy platings joined by Ag-epoxy ICA was investigated and discussed from the point of view on crystal direction and self-diffusion of β-Sn. The results can be summarized as follows:

TABLE III Self-diffusion parameters of β-Sn [11]

Diffusion direction	Frequency factor: D_0 (m^2/s)	Activation energy: Q (J/mol)	Diffusion rate at 150 °C: D (m^2/s)
$\parallel$c	1.28×10^5	1.09×10^5	4.37×10^{-9}
$\perp$c	2.10×10^5	1.08×10^5	9.52×10^{-9}

1. Sn-Pb plating joints degraded after 100 hr heat exposure, while Sn-Bi plating joints did so after only 50 hr.
2. The strength of the degradation related to the increase in the area percentage of voids.
3. Differences in the increases of the area percentage of voids were explained based on crystal direction and self-diffusion of β-Sn.

Acknowledgments

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