Effect of aluminum addition on tensile properties of naturally aged Sn-9Zn eutectic solder

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The effects of the addition of aluminum and natural aging on the tensile properties of Sn-9Zn and Sn-9Zn-0.5Al were investigated in rapidly solidified bulk specimens. Because oxidation occurs from the eutectic cell boundary of the surface and grows simultaneously into the subsurface with increased aging time, the deterioration of the tensile properties of Sn-9Zn and Sn-9Zn-0.5Al specimens correspond to the number of days it is naturally aged. The fracture characteristics of tensile fracture surface change from ductile dimples to partially dimpled and partially intergranular. The intergranular fracture behavior is attributed to the tensile cracks initiated from the surface cell boundary, cracks caused by cell boundary oxidation. This result indicates the depth of boundary oxidation that can be promoted by alloyed 0.5% aluminum. © *2002 Kluwer Academic Publishers*

1. Introduction
Global restrictions will be placed on the use of lead-containing materials, including Pb-Sn solder alloy. Such restrictions necessitate the development of lead-free solder [1]. Sn-Zn eutectic alloy has recently been considered as one of the lead-free solder materials [2, 3]. The eutectic melting point of Sn-Zn alloy is 472 K [2, 4], close to the 456 K melting point of Pb-Sn alloy. Also, at the eutectic composition of 8.9 wt% Zn, the wettability is only slightly below that of Sn-40 wt% Pb alloy. Many studies on the wettability and corrosion resistance of Sn-Zn solder have been reported, with previous investigations indicating that alloying Al could improve the soldering property and corrosion resistance in electronic packaging parts [5, 6]; it also lowers the melting point of Sn-Zn alloy to 470 K [7]. However, little data are available in the literature on tensile properties of the Sn-Zn solder materials. This work aimed to investigate the effect of adding aluminum on the tensile properties of Sn-Zn solder in rapidly solidified bulk specimens. The tensile deformation and fracture behavior of Sn-9Zn-0.5Al solder specimens in terms of natural aging condition are compared with unalloyed Sn-9Zn solder specimens.

2. Experimental procedure
The Sn-9Zn eutectic alloy and 0.5 wt% Al-alloyed Sn-Zn alloy used in this study were prepared from pure Sn, pure Zn, and pure Al. A high frequency induction furnace was used to make the master alloy. In order to approximate the solidification rate of a soldering point, the master alloy was melted again and cast into a Y-shaped graphite chill-mold. The pouring temperature was 543 K, and the thickness of the plate was 2.4 mm. One of the samples contained 8.9 wt% Zn (Sn-9Zn), and the other 8.6 wt% Zn and 0.5 wt% Al (Sn-9Zn-0.5Al). The as-cast specimens were machined into the dimensions indicated in Fig. 1.

In addition, four groups of specimens were aged at a controlled room temperature (30°C) in normal atmosphere for 30, 60, 90, and 180 days before the tensile test. A comparison was made between the Sn-9Zn and the Sn-9Zn-0.5Al materials at each of these naturally aging days. Tensile tests were carried out in atmosphere at a cross head speed of 1.5×10^{-2} mm/s, which corresponds to the initial tensile strain rate of 7.5×10^{-4} mm/s. The fracture surface was observed by SEM, and EDS was used to examine the solidification cell boundary after natural aging of the solders.

3. Results
3.1. Effect of natural aging on tensile property of rapid solidified bulk specimen
Fig. 2 shows the typical microstructure of Sn-9Zn eutectic solder. Observation confirmed that there was little difference between unalloyed and Al-alloyed samples in an as-cast initial condition. Fig. 2b shows the morphological features that the Zn-rich phase homogeneously dispersed in the Sn-rich matrix.

Fig. 3 shows the 0.2% proof stress and elongation as a function of natural aging time. To investigate the effect of the Al addition, a comparison was made between the data of Sn-9Zn and Sn-9Zn-0.5Al. Fig. 3a shows a significantly higher 0.2% yield stress for the unaged Sn-9Zn-0.5Al specimen. It also shows that both specimens exhibited a continuous decrease in 0.2% yield stress with increasing natural aging days. After 30 days

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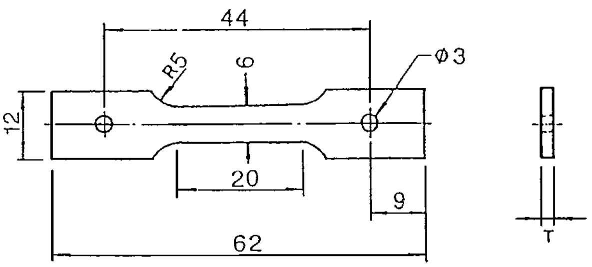

Figure 1 The dimension of tensile specimen (unit: mm).

natural aging, however, the yield stress of Sn-9Zn-0.5Al dropped drastically, and at 90 days, the drop equaled the level of the Sn-9Zn specimens. Fig. 3b shows that elongation decreased continuously from the first natural aging day, and that there was essentially a linear relationship between elongation and natural aging days. It should be noted that in contrast to the Sn-9Zn, the Sn-9Zn-0.5Al showed a drastic elongation drop from about 40% at 30 days of natural aging to 10% at 60 days.

The fracture surface was observed at all natural aging days investigated. Fig. 4a shows the fracture surface of the unaged Sn-9Zn specimen. A ductile dimple pattern can be seen clearly on the fracture surface, but Fig. 4b shows a significant difference in the fracture surface of the specimen aged for 180 days. The fracture surface changes to partially dimpled and partially intergranular. The location of intergranular fracture is near the specimen's surface. When the Sn-9Zn specimen fracture surface was compared with that of the Sn-9Zn-0.5Al specimen, the intergranular fracture pattern of the latter at 30 days was similar to that of the former at 180 days (Fig. 5). The intergranular fracture pattern could correspond to the rapidly solidified columnar structure perpendicular to the surface of the tensile specimen.

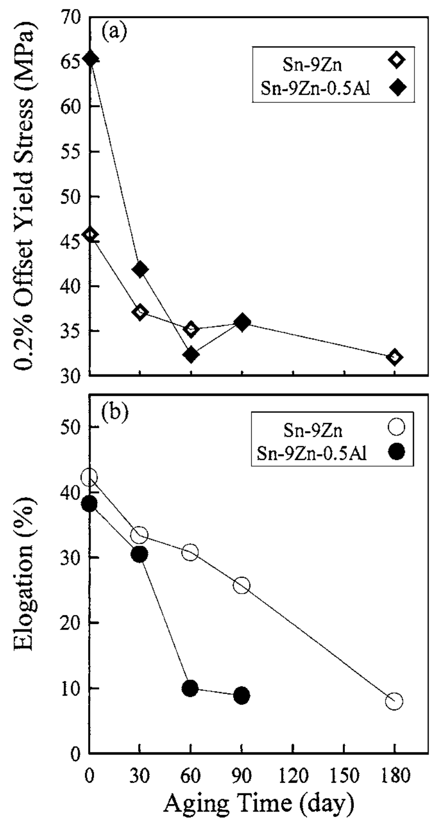

Figure 3 Tensile properties vs. aging time of Sn-9Zn and Sn-9Zn-0.5Al alloys: (a) 0.2% offset yield stress, (b) elongation.

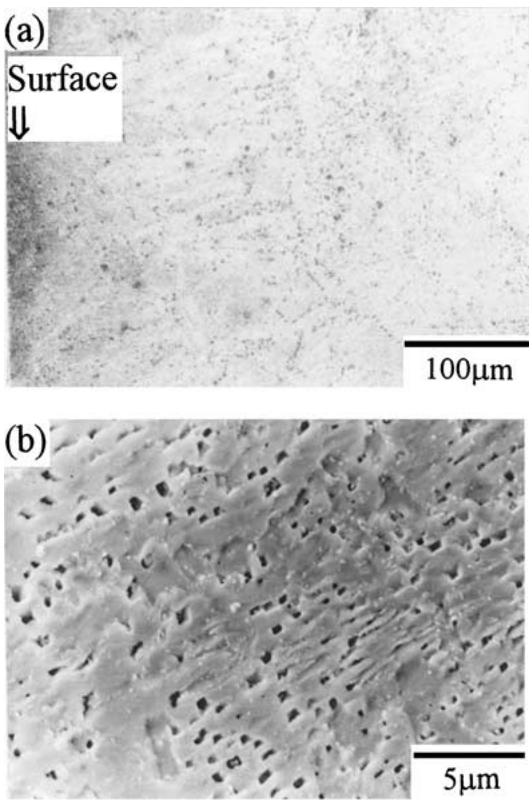

Figure 2 Microstructure of as-cast Sn-9Zn specimen: (a) OM, and (b) SEM.

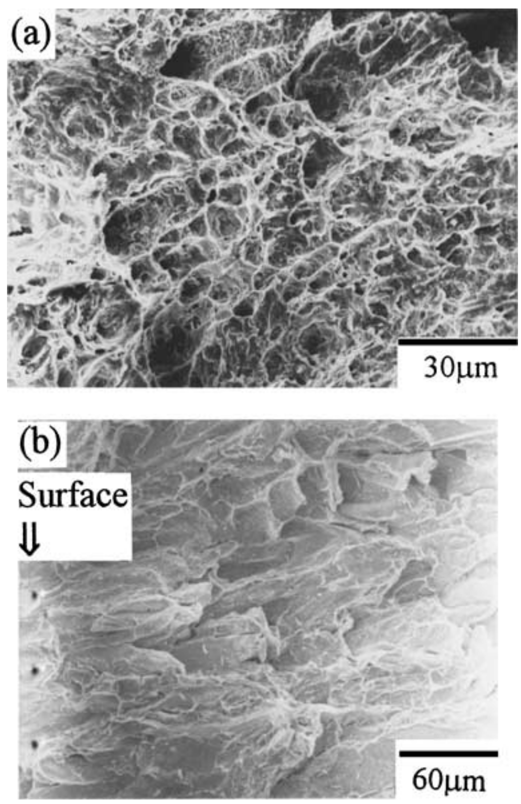

Figure 4 Fracture surface of Sn-9Zn: (a) as-cast, and (b) aged for 180 days.

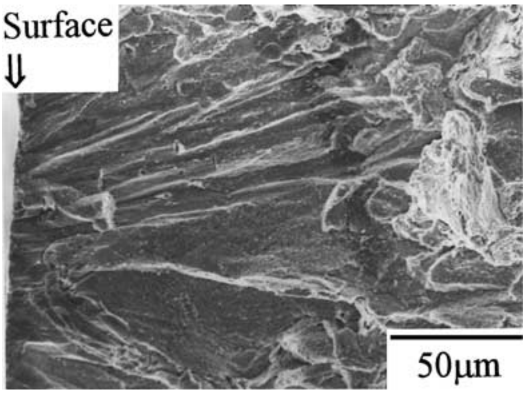

Figure 5 Fracture surface of Sn-9Zn-0.5Al aged for 30 days.

3.2. Oxidation of the solidification cell boundary

To investigate the effect of natural aging days on the ductility deterioration of Sn-Zn solders, examination of the microstructure aged for 180 days shows that boundary inclusions formed on the subsurface of the specimen grew along the cell boundary as far as about 310 μm (Fig. 6). There was little evidence of an observable cell boundary in unaged specimens (Fig. 2a). The SEM/EDS evidence showed the composition of the eutectic cell-boundary and the inside of the cell (Fig. 7). It can be seen that the eutectic cell boundary contains a certain amount of Zn and oxygen. Fig. 7b also shows a significant difference in the amount of Zn between the inside of the grain and at the grain boundary. Examination of the naturally aged microstructure by SEM and OM shows evidence that the eutectic-cell-boundary oxidation observed began at the surface and grew along the grain boundary in all specimens investigated.

It should be noted that a certain number of days of natural aging are required for the oxidation to begin and then to grow into the subsurface of the specimen. Fig. 8 shows significant grain-boundary oxidation in the Al-alloy specimens compared with the Al-unalloyed specimens after natural aging for fewer days. Fig. 9 shows the depth of boundary oxidation of Sn-9Zn and Sn-9Zn-0.5Al. There is a significant difference in boundary oxidation depth between the Sn-9Zn-0.5Al and the Sn-9Zn specimens aged up to 90 days; after 90 days, however, the oxidation depths are quite similar. The early boundary oxidation in the Sn-9Zn-0.5Al specimens was promoted by the addition of alloyed 0.5 wt% aluminum.

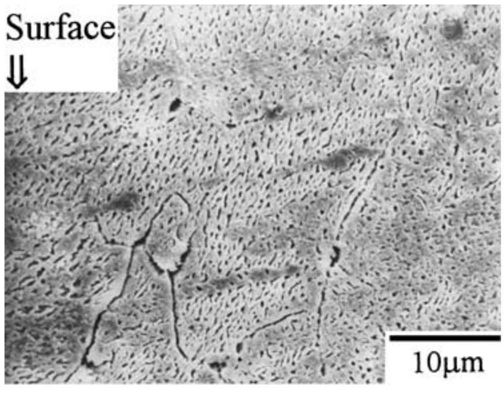

Figure 6 Morphology of Sn-9Zn after aged for 180 days.

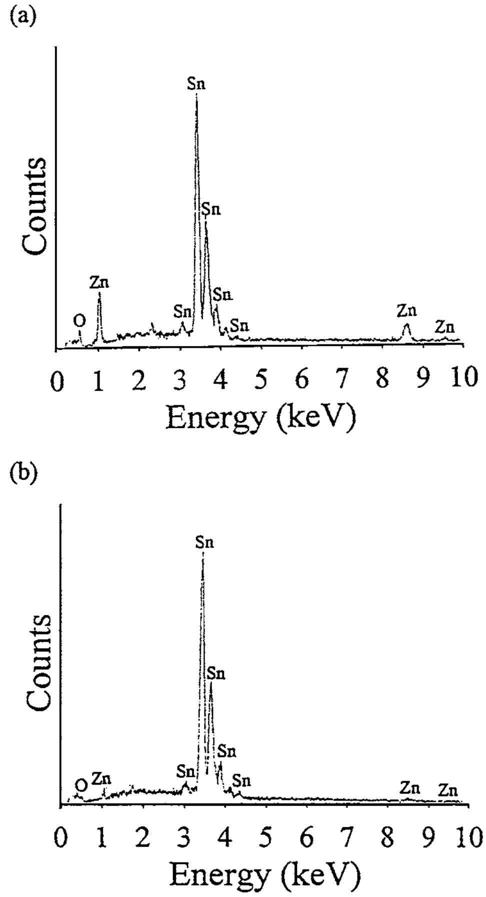

Figure 7 Typical EDS spectrum of Sn-9Zn after aged for 180 days: (a) in eutectic cell boundary, and (b) inside of eutectic grain.

To investigate the effect of the addition of Al, an examination of the grain boundary oxidation was conducted by EDS (Fig. 10). A certain amount of oxygen, zinc, and aluminum can be recognized in the eutectic cell boundary.

4. Discussion

The most important effect on the microstructure and tensile properties of the addition of aluminum to Sn-9Zn solder was the promotion of oxidation at the solidification cell boundary. In atmosphere, longer natural aging of Sn-9Zn solder may cause a deepening in oxidation depth and a deterioration of ductility. Figs 8 and 9 suggest that although there was a similarity in boundary oxidation between our Sn-9Zn and Sn-9Zn-0.5Al samples, it should be noted that the oxidation rate from the surface was significantly different. Eutectic-cell boundary oxidation, however, is a common phenomenon occurring from the first natural aging day and continuing as natural aging increases. It would, therefore, be very useful for the improvement of the mechanical properties of Al-alloyed solders if the boundary oxidation problem could be suppressed.

In rapidly solidified solder, the oversaturation of the Zn element in the Sn-rich phase, it should be noted, may cause natural aging of a freshly solidified material at room temperature (300 K). In addition, because

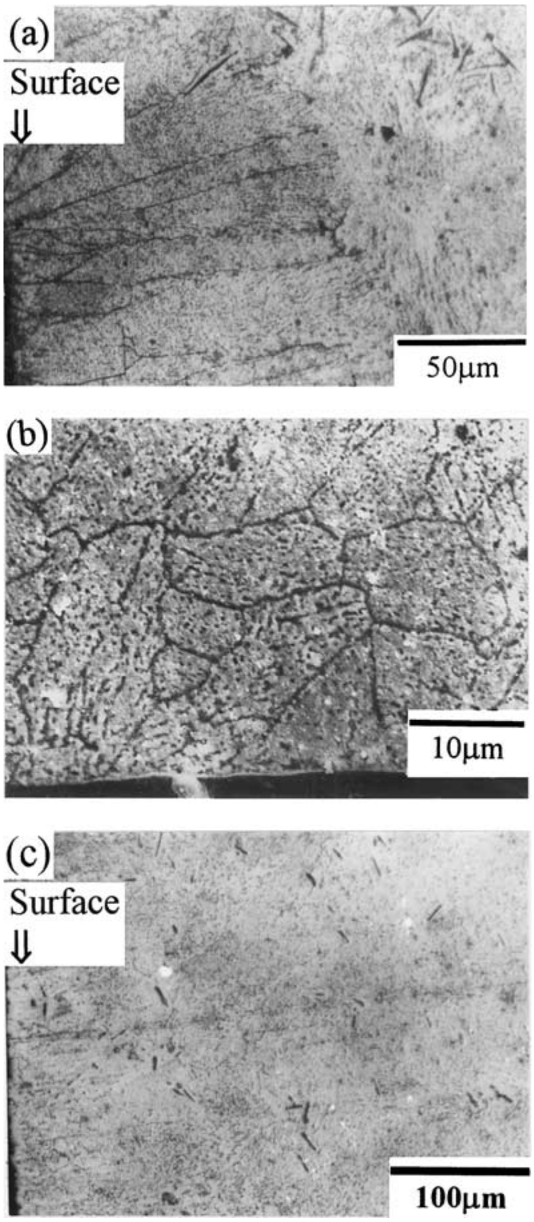

Figure 8 Morphology of Sn-9Zn-0.5Al aged 30 days (a) OM, (b) SEM, and of Sn-9Zn aged 30 days (c) OM.

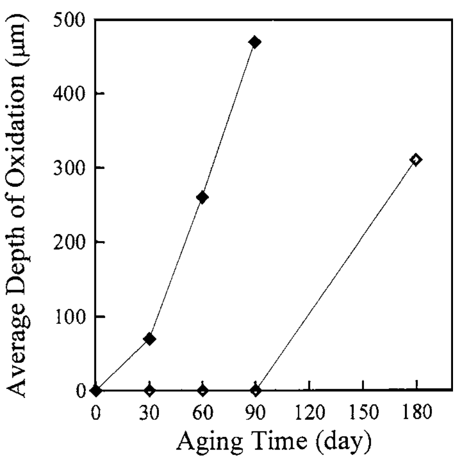

Figure 9 The depth of grain boundary oxidation of Sn-9Zn and Sn-9Zn-0.5Al.

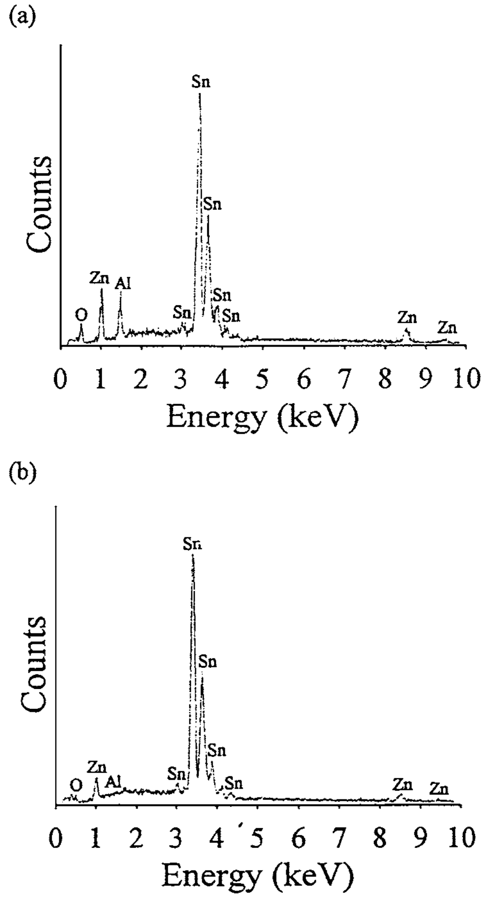

Figure 10 Typical EDS spectrum of Sn-9Zn-0.5Al after aged 90 days: (a) in eutectic cell boundary, and (b) inside of eutectic grain.

300 K is already half the melting point of eutectic Sn-9Zn solder, Fig. 3a indicates that a 0.2% flow stress drop as natural aging days increase can be correlated with the tempering effect. This aged softening phenomenon for Sn-9Zn solder occurring in the present case is in substantial agreement with the results of most research on Pb-Sn solder [8]. But, as shown in Fig. 3b, the elongation data for Sn-9Zn solder continuously dropped as the natural aging days increased, and there was an even sharper drop in the elongation data of Sn-9Zn-0.5Al solder. Based on this experimental evidence, a possible reason for this ductility deterioration of eutectic Sn-9Zn solder should include grain boundary oxidation; there was little evidence of boundary precipitation. The difference between the Sn-9Zn-0.5Al solder and the Al-unalloyed Sn-9Zn solder appears to have been caused by the promotion of the boundary oxidation rate.

A reference is given in Table I [9] showing the oxidation potential of Zn is higher than that of Sn. It should be noted that there is good agreement account for a certain days. In addition, because the oxidation potential is significantly higher for Al than for the other elements,

TABLE I Standard electromotive force potentials [9]

Reaction	Standard potential, (volts)
$Al = Al^{3+} + 3e^-$	1.662
$Zn = Zn^{2+} + 2e^-$	0.763
$Sn = Sn^{2+} + 2e^-$	0.136

TABLE II As-cast tensile properties of this present solder and traditional solder

	0.2% Yield stress (MPa)	Total elongation (%)
60Sn-40Pb	38	38
Sn-9Zn	46	41
Sn-9Zn-0.5Al	65	39

and because of the resulting similarity in oxidation behavior, as shown in Fig. 8, Figs 9 and 10 explain the coincidence in the boundary oxidation phenomenon. On the other hand, the present study's tensile tests were performed using rapidly solidified bulk specimens with a microstructure similar to that of solder joints, to provide an understanding of the differences in mechanical properties between Sn-9Zn solder and Pb-Sn solder prepared under identical conditions. The details of tensile properties are listed in Table II.

Cell boundary oxidation, it should be noted that can be characterized as an additional problem with Al-alloyed Sn-9Zn solder compared to traditional Pb-Sn solder. It is necessary to overcome this boundary oxidation problem because the tensile cracks were found to initiate from the surface and grow simultaneously into the subsurface along solidification cell boundaries (Figs 4 and 5). The preceding discussion demonstrates that boundary oxidation can cause severe deterioration of fatigue strength. Additional work is needed to identify the reliability of Sn-9Zn eutectic solders.

5. Conclusions

1. The effects of the addition of aluminum on the microstructure of Sn-9Zn eutectic solder are (1) a similarity in the solidification cell boundary oxidation behavior in terms of natural aging days, and (2) the boundary oxidation rate was promoted by the alloyed aluminum.

2. Both Sn-9Zn and Sn-9Zn-0.5Al specimens exhibit a continuous decrease in 0.2% yield stress and elongation with increasing natural aging days. The Al-alloyed specimen showed more severe deterioration after 30 natural aging days.

3. The deterioration of the tensile properties of both eutectic Sn-9Zn solder materials, the corresponding natural aging days, and boundary oxidation depth resulted in an apparent difference in tensile properties.

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