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## Effect of Al addition on the microstructural and mechanical behavior of Bi doped Sn-Zn alloy

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### ABSTRACT

In the present study 1.0, 2.0 and 4.0 wt. % Al was added with the Sn-8Zn-3Bi eutectic alloy to investigate the effect of Al as a fourth element on the microstructural and mechanical properties of the newly developed quaternary alloys. The solidification behavior of the quaternary alloys with the cooling rate was also investigated as well. The results indicated that Al refined the microstructure and formed intermetallic compounds with the quaternary alloy. The microstructures of newly developed quaternary Sn-8Zn-3Bi-xAl alloys had fine needle-like  $\alpha$ -Zn phase with some IMC dispersed in the  $\beta$ -Sn matrix. The compact shaped IMCs uniformly distributed in the  $\beta$ -Sn phase which resulted in an increase in the mechanical properties, due to the second phase dispersion strengthening mechanism. As the Al content increased, both the microhardness and macrohardness of the Sn-8Zn-3Bi-xAl quaternary alloys improved due to the presence of harder IMC in the microstructure. With further employing faster cooling rate, the mechanical properties were also promoted.

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### KEYWORDS

Sn-zn-bi eutectic alloy;  
Al addition;  
Microstructure;  
Mechanical properties;  
Thermal behavior;  
Intermetallic compounds;  
Cooling rate.

### INTRODUCTION

The ban of lead in electronic products will occur in most industrialized countries before the end of this decade. Extensive investigations have been on-going over the last few years to find an acceptable Pb-free alloy for various low temperature attachment applications<sup>[1-3]</sup>. All alternatives to the standard eutectic tin-lead alloy investigated so far are based on tin alloys with a tin content significantly

over 90 wt. % in combination with copper, silver, antimony, bismuth, or zinc. Among the binary alloys, recently, Sn-Zn alloy has become highly recommended as a substitute for Sn-Pb eutectic alloy due to its lower melting point<sup>[4]</sup>. Sn-Zn alloy can also be used without replacing the existing manufacturing lines or electronic components. Again, Sn-Zn is advantageous from an economic point-of-view because Zn is a low cost metal. However, Sn-Zn eutectic alloy is difficult to handle practically due to its highly

TABLE 1 : Chemical composition of starting materials (wt. %)

Alloys	Sn	Zn	Al	Pb	Bi	Sb
Sn-8Zn-3Bi	Bal.	7.89	-	0.34	3.05	0.01
Sn-8Zn-3Bi-1.0Al	Bal.	7.68	0.88	0.34	2.85	0.01
Sn-8Zn-3Bi-2.0Al	Bal.	7.60	1.91	0.34	2.75	0.01
Sn-8Zn-3Bi-4.0Al	Bal.	7.42	3.87	0.34	2.86	0.01

active characteristics<sup>[5]</sup>. As reported by S. Vaynman et al.<sup>[6]</sup> Sn-8Zn eutectic alloys have limited commercial viability due to its serious oxidation and wetting problems. Addition of alloying elements is an effective way to improve oxidation resistance and wetting behavior of eutectic Sn-8Zn alloy. The addition of Bi in Sn-Zn near eutectic solder can improve the soldering properties<sup>[7-9]</sup>. Shohji et al. proved that the creep resistance of Sn-8Zn-3Bi is superior to that of Sn-37Pb<sup>[7]</sup>.

Al has been incorporated with Zn to enhance the atmospheric corrosion resistance of the conventional galvanizing coating for steel. The Al may form solid solutions with Zn and Sn and has a eutectic point at 197°C as reported by Sebaoun et al.<sup>[10]</sup>, who discussed the diffusion paths of various Sn-Zn-Al systems at various isotherms. It has been reported that the Al-Zn-Sn alloys have good wettability on Al<sup>[11]</sup>. The microstructures of the Sn-9Zn-0.45Al alloys have been investigated using scanning electron microscopy<sup>[12]</sup>.

Addition of a fourth element significantly changes Sn-8Zn-3Bi eutectic binary alloys microstructure, and mechanical properties have a large extent of dependency on mechanical properties. It has already proven that addition of a third element in the Sn-9Zn

eutectic greatly improves its mechanical properties<sup>[13-15]</sup>. Thus, the objective of this study is to find out the relation between the microstructure and mechanical properties that alters with the formation of IMCs for various amount of Al addition. This study concerns with the melting microstructure, microhardness and macrohardness on Sn-9Zn eutectic alloy that may alter after addition of various amount of Al in it.

### EXPERIMENTAL PROCEDURE

The Sn-8Zn-3Bi, Sn-8Zn-3Bi-1.0Al, Sn-8Zn-3Bi-2.0Al and Sn-8Zn-3Bi-4.0Al lead-free alloys were prepared with commercially available pure tin, zinc, copper and aluminium (purity of 99 %). The constituent elements were melted in a furnace. The molten alloys (in the alumina crucible) were homogenized at 300°C and then a portion of the molten metal poured in a graphite mold. The rest of the molten metal poured in a steel mold to prepare the chill cast ingot. Consequently, chemical analyses were done by volumetric method to determine the exact composition of the casting ingots. The chemical compositions of the alloys were listed in TABLE 1.

The as-cast alloys were sectioned and polished

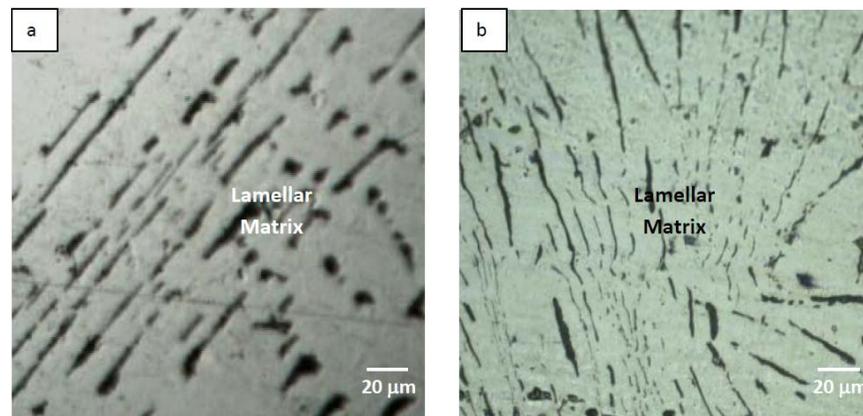


Figure 1 : Optical micrographs of as cast sample of a) slow cooled and b) fast cooled at a magnification of 400 X

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according to non-ferrous metallography with  $0.5\mu\text{m}$   $\text{Al}_2\text{O}_3$  particles in order to obtain the microstructure. After cleaning with acetone and alcohol, the samples were investigated by an optical microscope with digital camera (LEICA-MZFLIII) Grinding and polishing were necessary to obtain polished, smooth and flat parallel surface before indentation testing. Thus, the polished samples were placed in a Vickers Shimadzu microhardness tester to measure the microhardness. The applied load was 50g for 10s. The macrohardness was measured with Brinell hardness tester. The applied load was 1.0 kN for 30 sand at least 10 readings of different indentations were taken at room temperature to obtain the mean value.

The rectangular cast ingots were then mechanically machined into tensile specimens with a gauge length marked 32.00 mm for each samples, the width and thickness of the samples were 6.00 mm and 5.00 mm respectively. Tensile tests were carried out with a tensile testing machine (Instron 3369 Universal Testing Machine) at a strain rate of 1.00 mm/min at  $25^\circ\text{C}$  to obtain data on the stress-strain curves which contain information of elongation at fracture and the UTS.

## RESULTS AND DISCUSSIONS

### Microstructure and elemental analysis

The optical micrographs of the Sn-8Zn-3Bi in Figure 1 (a and b) show the typical lamella of eutectic microstructures for both the slow and fast cooled samples. It was established that the eutectic Sn-8Zn-3Bi alloy consists of  $\hat{\alpha}$ -Sn, Bi rich phase and Zn-rich phase. In the micrograph, the bright regions are the  $\hat{\alpha}$ -Sn phase and the primarily solidified phases; the dark phases are fine needlelike Zn-rich phase in  $\hat{\alpha}$ -Sn matrix. Also some Zinc spheroids were observed in the microstructure. The Bi rich phase was not identified with the optical resolution. In the slowly cooled Sn-Zn-Bi eutectic alloy, the eutectic lamella was thicker than that in the fast cooled one and the amount of lamella seemed to suppressed as well in the fast cooled Sn-Zn-Bi eutectic alloy.

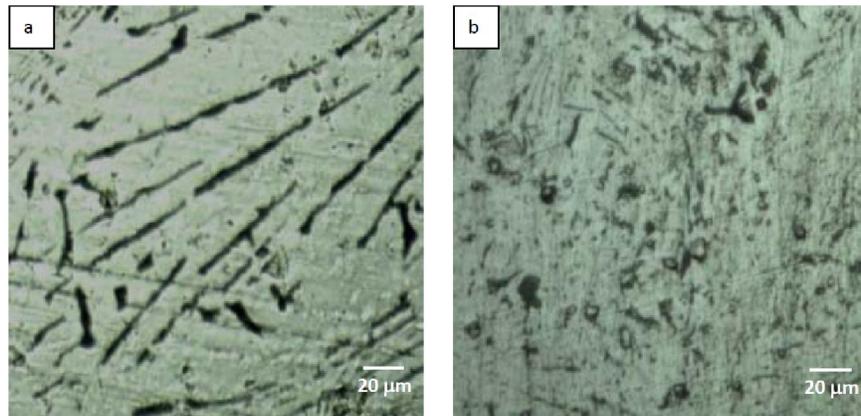
With the addition of 1% Al, the eutectic Sn-8Zn-

3Bi alloy showed some precipitates distributed in the eutectic phase shown in Figure 2. When 2% Al is added with the eutectic Sn-8Zn-3Bi alloy, the microstructure changed with globular shaped intermetallic compound distributed in the typical eutectic lamella as shown in Figure 3. After the Al addition increased to 4% the number of intermetallics also increased while eutectic phase decreased and at the same time IMC size became little larger, as shown in Figure 3 and Figure 4. The micrographs of the quaternary alloys were well distinguished into three phases, i.e. the matrix  $\hat{\alpha}$ -Sn, the needle-like eutectic  $\hat{\alpha}$ -Zn, and the globular dark grey phases. Another important thing is that for the fast cooled samples the distribution of the IMCs is homogenized, the formation of intermetallic compounds seemed increased and the formation of eutectic lamella was further suppressed (Figure 2b, 3b and 4b).

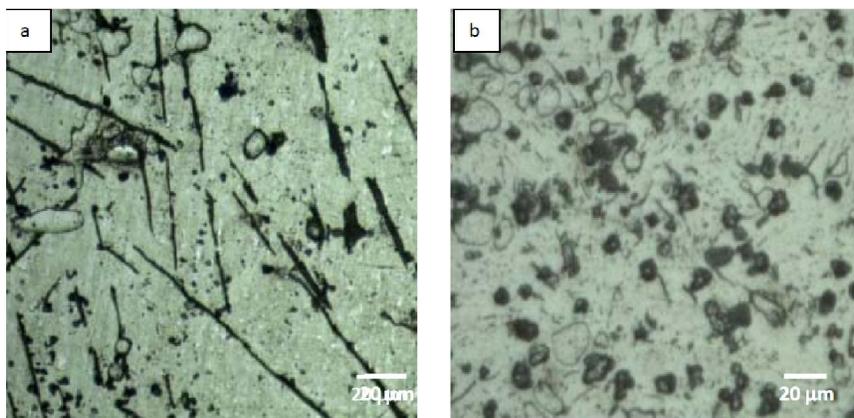
Thus, we can see when a fourth element Al is added with the Sn-8Zn-3Bi eutectic alloy, the  $\hat{\alpha}$ -Zn phases decreased and changes to finer structure. As Zn is a very reactive material (electro negativity: -1.65), it forms compound with the Al. And due to the high reactivity of Al (electro negativity: -1.90), the microstructure of Sn-8Zn-3Bi-2.0Al and Sn-8Zn-3Bi-4.0Al deprived of thick Zn-rich eutectic lamella and consists of fine eutectic colonies dispersed with large intermetallic compounds.

### Macrohardness

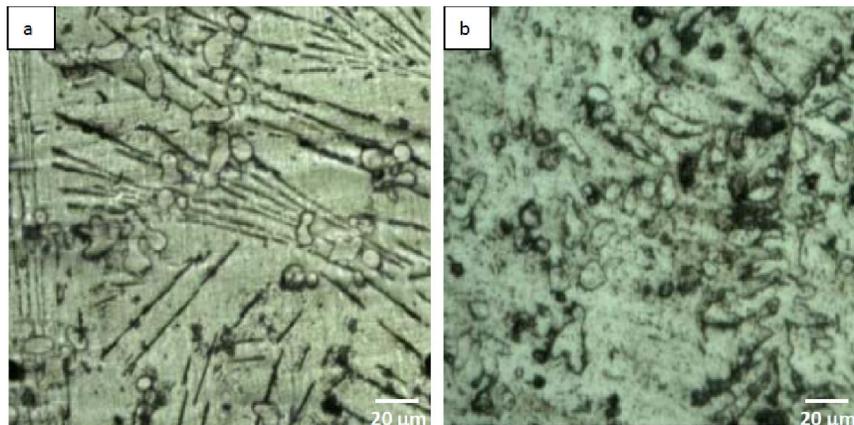
The microhardness of an alloy depends on the motion of dislocation, growth and configuration of grains. The processes are more sensitive to the microstructure of the alloy than its chemical composition. So the mechanical property such as the microhardness depends especially on the microstructure, processing temperature, the composition, etc<sup>[14]</sup>. In the present study the microhardness test was performed to observe the change of mechanical properties associated with the microstructural changes. Figure 5 shows the microhardness results with standard deviation as a function of alloy composition. In general, the hardness of Sn-based strongly depends on the alloying elements; the more the alloying elements there are, the higher the hardness is. This is attributed to the fact that the volume fraction



**Figure 2 :** Optical micrographs of as cast sample of a) slow cooled and b) fast cooled Sn-Zn-3Bi-1Al alloy at a magnification of 400 X



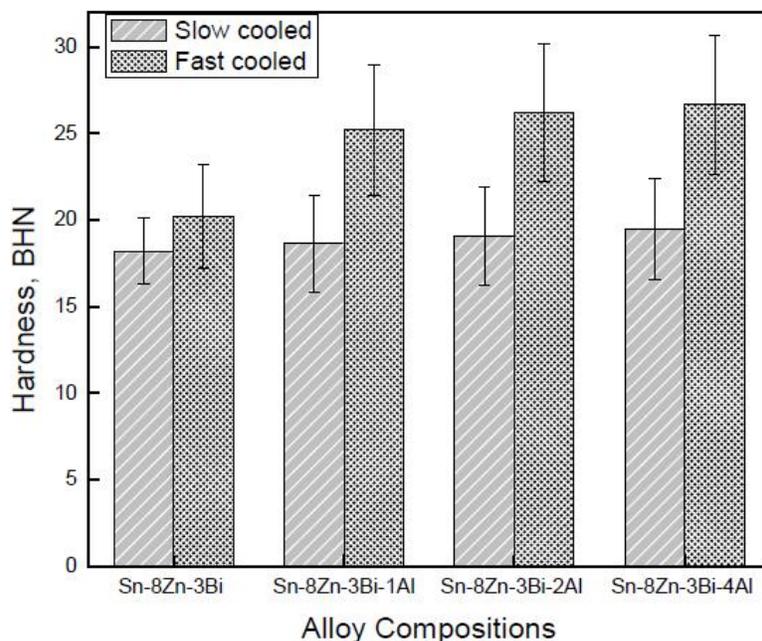
**Figure 3 :** Optical micrographs of as cast sample of a) slow cooled and b) fast cooled Sn-Zn-3Bi-2Al alloy at a magnification of 400 X



**Figure 4 :** Optical micrographs of as cast sample of a) slow cooled and b) fast cooled Sn-Zn-3Bi-4Al alloy at a magnification of 400 X

of the other phases increases as there are more alloying elements. The same trend was confirmed for Sn-8Zn-3Bi and Sn-8Zn-3Bi-xAl alloys; the average hardness value increases when small amount of Al is added to the Sn-8Zn-3Bi eutectic alloy as a fourth alloying element, as shown in Figure 5.

From Figure 5, the BHN of the slowly cooled eutectic Sn-8Zn-3Bi was 16.8, while those of Sn-8Zn-3Bi-1.0Al, Sn-8Zn-3Bi-2.0Al, and Sn-8Zn-3Bi-4.0Al were 18.2, 18.7, 19.1 and 19.6 respectively. The BHN of the fast cooled eutectic Sn-8Zn-3Bi was 16.8, while those of Sn-8Zn-3Bi-1.0Al, Sn-8Zn-3Bi-



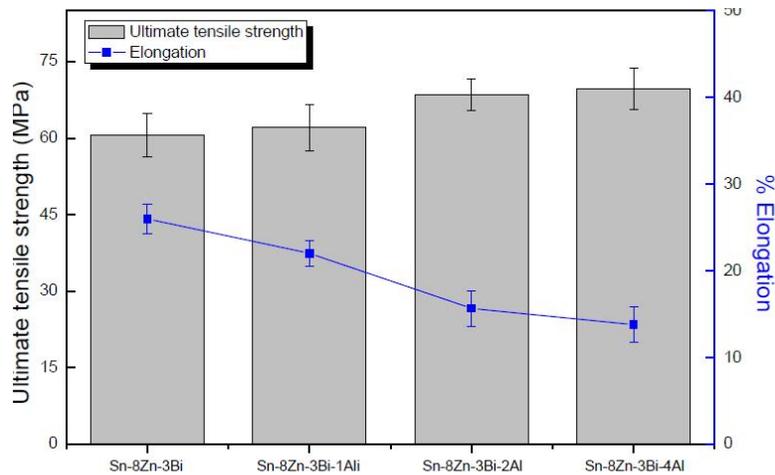
**Figure 5 :** Brinell hardness of Sn-8Zn-3Bi, Sn-8Zn-3Bi-1.0Al, Sn-8Zn-3Bi-2.0Al and Sn-8Zn-3Bi-4.0Al alloys

2.0Al, and Sn-8Zn-3Bi-4.0Al were 20.1, 25.2, 26.1 and 26.7 respectively. The hardness increases for Sn-8Zn-3Bi eutectic alloy after addition of a fourth element can be understood by dissolution of Al atoms for Sn-8Zn-3Bi-xAl quaternary alloys and formation of IMC particles in the matrix to promote precipitation hardening. This may also be explained by the microstructural observations for the corresponding quaternary alloy. Figure 2-4 represents that all the Sn-8Zn-3Bi-xAl alloys are composed of three different phases; the matrix  $\alpha$ -Sn, small amount of needle-like eutectic  $\alpha$ -Zn, and the dark gray phases of IMCs, while the Sn-8Zn-3Bi eutectic alloy consists of only first two phases with some Zn spheroids in it. The difference in hardness increase was more pronounced in fast cooled samples.

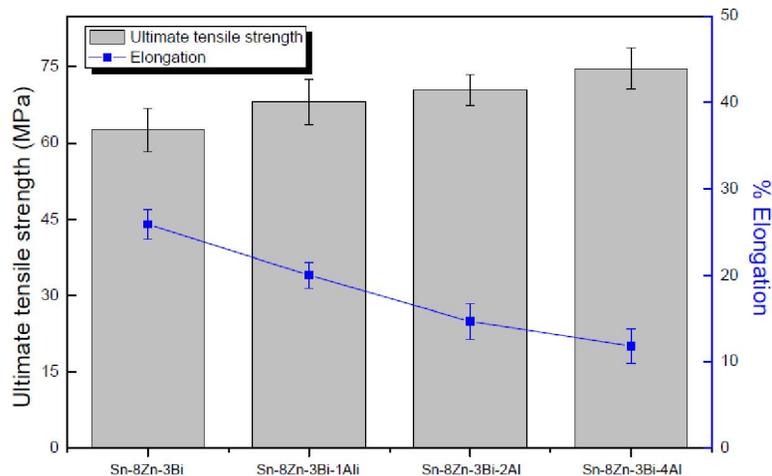
### Tensile strength

The ultimate tensile strength (UTS) is the maximum engineering stress, which a material can withstand in tension, on the engineering stress-strain curve<sup>[16]</sup>. The yield stress is the stress level at which plastic deformation begins. For alloys, the yield stress is commonly defined by the stress on the stress-strain curve at 0.2% strain offset. The effect of fourth alloying additives on mechanical properties of Sn-8Zn-3Bi eutectic alloy can be seen from the strain-stress curves shown in Figure 6 and Figure 7. The

tensile strength of the slowly cooled Sn-8Zn-3Bi, Sn-8Zn-1.0Al, Sn-8Zn-3Bi-2.0Al, and Sn-8Zn-3Bi-4.0Al were 60.55, 62.10, 68.57 and 69.66 MPa, respectively. The elongation at failure of the Sn-8Zn, Sn-8Zn-1.0Al, Sn-8Zn-3Bi-2.0Al, and Sn-8Zn-3Bi-4.0Al were 26, 22, 15.6 and 13.6%, respectively for the slowly cooled samples. The tensile strength of the fast cooled Sn-8Zn-3Bi, Sn-8Zn-1.0Al, Sn-8Zn-3Bi-2.0Al, and Sn-8Zn-3Bi-4.0Al were 62.30, 64.25, 68.57 and 74.56 MPa, respectively. The elongation at failure of the Sn-8Zn, Sn-8Zn-1.0Al, Sn-8Zn-3Bi-2.0Al, and Sn-8Zn-3Bi-4.0Al were 23.3, 19.2, 13.5 and 11.8%, respectively for the slowly cooled samples. The Sn-8Zn-3. Bi-4.0Al alloy had the higher UTS and Sn-8Zn-3Bi alloy exhibit higher elongation, while Sn-8Zn-3Bi had the lowest UTS. As per dispersion strengthening theory<sup>[15]</sup>, the strength must increase with the addition of a second phase particle in the matrix. And for the case of small amount of Al addition in Sn-8Zn-3Bi the theory proved right, while for the amount of Al increases the theory contradicts with the results. These contradictory results can be explained from the microstructure and tensile fracture surface of the alloys very clearly. The both phenomenon of tensile strength and elongation can be clearly explain by the dispersion strengthening theory; i.e. the second phase formed by Al generates obstacle for the dislocation



**Figure 6 :** Variation of average ultimate tensile strengths and % elongation of slow cooled Sn-8Zn-3Bi, Sn-8Zn-3Bi-1.0Al, Sn-8Zn-3Bi-2.0Al and Sn-8Zn-3Bi-4.0Al alloys



**Figure 7 :** Variation of average ultimate tensile strengths and % elongation of fast cooled Sn-8Zn-3Bi, Sn-8Zn-3Bi-1.0Al, Sn-8Zn-3Bi-2.0Al and Sn-8Zn-3Bi-4.0Al alloys

at the grain boundary (the maximum region of mismatch), dislocation piles up results in a increase in tensile strength, the term also called precipitation strengthening. On the other hand due to movement restriction of dislocation densities the slip planes cannot find their suitable direction to move freely results lack in ductility; i.e. elongation decreases.

## CONCLUSIONS

Addition of a fourth element can promote the mechanical and thermal property of Sn-8Zn-3Bi alloy in various ways. The volume fraction of IMCs in Sn-8Zn-3Bi-xAl quaternary alloys nucleates in contrast to that of the eutectic  $\alpha$ -Zn phase, which decreased with increasing addition of Al. At the same time the eutectic  $\alpha$ -Zn phase converts into fine needle-

like structures rather than thick rod-like lamella. Again in the microstructures of newly developed quaternary alloys some new phases are observed compared to Sn-8Zn-3Bi eutectic alloy. For different amount of Al addition the new phases found to be globular shaped precipitate of intermetallic compounds. As the microhardness is strongly depend on the microstructure, thus the microhardness value increases for Al addition in the eutectic Sn-8Zn-3Bi alloy. The tensile strength of Sn-8Zn-3Bi-xAl is found to be higher compared to the Sn-8Zn-3Bi eutectic alloy; on the other hand elongation drops. As the amount of Al in Sn-8Zn-3Bi increases, the tensile strength increases and elongation drops. Finally, it can be concluded that the addition of Al can improve the mechanical properties of Sn-8Zn-3Bi eutectic alloy.

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