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EFFECT OF Al ADDITION ON THE THERMAL AND MECHANICAL BEHAVIOR OF Sn-9Zn EUTECTIC Pb-FREE SOLDER ALLOY

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ABSTRACT

In the present study 1.0, 2.0 and 4.0 wt. % Al is added with the Sn-9Zn eutectic solder alloy to investigate the effect of Al as a third element on the microstructural and mechanical properties as well as thermal behavior of the newly developed ternary solder alloys. The results indicate that Al refines the microstructures and forms intermetallic compounds (IMC) with the eutectic solder alloy. The microstructures of newly developed ternary Sn-9Zn-xAl solder alloys were fine needle-like α-Zn phase with some IMCs dispersed in the β-Sn matrix. The compact shaped Al_6Zn_3Sn IMC uniformly distributed in the β-Sn phase which results in an increase in the tensile strength, due to the second phase dispersiod strengthening mechanism. As the Al content increases, the microhardness of the Sn-9Zn-xAl ternary solder alloys also improves due to the presence of harder IMC in the microstructure.

Keywords: Microstructure, Mechanical Properties, Thermal Behavior, Intermetallic Compounds.

1. 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 solder for various electronic attachment applications [1-3]. All alternatives to the standard eutectic tin–lead solder 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 solder has become highly recommended as a substitute for Sn-Pb eutectic solder due to its lower melting point [4]. Sn-Zn solder 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 solder is difficult to handle practically due to its highly active characteristics [5]. As reported by S. Vaynman et al. [6] Sn-9Zn eutectic solders 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-9Zn solder alloy.

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 $197^{O}C$ as reported by Sebaoun et al. [7], who discussed the diffusion paths of various Sn–Zn–Al systems at various isotherms. It has been reported that the Al-Zn-Sn solders have good wettability on Al [8]. The microstructures of the Sn-9Zn-0.45Al lead-free solders have been investigated using scanning electron microscopy [9].

Addition of a third element significantly changes Sn-9Zn 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 solder greatly improves its mechanical properties [10-12]. 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 temperature, microstructure, microhardness and tensile properties on Sn–9Zn eutectic solder alloy that may alter after addition of various amount of Al in it.

2. EXPERIMENTAL PROCEDURE

The Sn–9Zn, Sn-9Zn-1.0Al, Sn-9Zn-2.0Al and Sn-9Zn-4.0Al lead-free solders were prepared with commercially available pure tin, zinc, and copper (purity of 99 %). The constituent elements were melted in a furnace. The molten alloys (in the alumina crucible) were homogenized at $300^{O}C$ and then 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 melting temperatures of the solder alloys were determined with differential scanning calorimeter (DSC

Q 10). For DSC analysis, a piece of about 10 mg solder was placed into an Al pan. To obtain the data, the sample was initially scanned from 25^0C to 150^0C at a rate of 25 Kminute^{-1} and then at a rate of 5 Kminute^{-1} up to 250^0C under nitrogen gas atmosphere.

The as-cast solders were sectioned and polished according to non-ferrous metallography with 0.5μm Al_2O_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), which was followed by SEM. A Philips XL40 FEG scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analysis system was used to inspect and analyze the microstructure of the three different solders and to perform the semi quantitative analysis on those structures in order to determine the phases. The accuracy of the compositional measurement was about 5%. To determine the formula composition of the intermetallic compounds (IMCs), the chemical analyses of the EDX spectra were corrected by standard ZAF software. The backscattered electron imaging mode of the SEM was used for the microstructural study. EDX analysis has been done to support the phase identification of the structure. 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 and at least ten readings of different indentation were taken for each sample at room temperature to obtain the mean value.

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

Alloys	Sn	Zn	Al	Pb	Bi	Sb
Sn-9Zn	Bal.	8.69	-	0.35	0.23	0.01
Sn-9Zn -1.0Al	Bal.	8.68	0.98	0.34	0.25	0.02
Sn-9Zn -2.0Al	Bal.	8.60	2.01	0.35	0.25	0.01
Sn-9Zn -4.0Al	Bal.	8.63	3.96	0.34	0.26	0.01

The rectangular solder 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 25^0C to obtain data on the stress-strain curves which contain information of elongation at fracture and the UTS.

3. RESULTS AND DISCUSSIONS

DSC analysis was carried out in order to investigate the fundamental thermal reactions on heating of these alloys. figure 1 shows the typical DSC curves obtained for Sn-9Zn, Sn-9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al alloys on heating. With the addition of small amount of Al, the melting temperatures changed slightly. The melting temperatures were found 201.710C, 203.150C and 205.400C for the Sn-9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al, respectively, as compared with 197.590C for Sn–9Zn eutectic alloy. Das et al. [13] reported that the addition of a small amount of Al did not significantly alter the melting point of the Sn-9Zn alloy. For 4% Al addition here the melting temperature increases only 8^oC than that of Sn-9Zn binary eutectic alloy.

Table 2: Melting temperature and mechanical properties of Sn-9Zn, Sn-9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al alloys.

Alloys	Melting Temp. (^{O}C)	Micro hardness BHN	Tensile Strength (MPa)	Elon -gation (%)
Sn-9Zn	197.59	16.80	41	48.00
Sn-9Zn -1.0Al	201.71	18.10	51.24	24.53
Sn-9Zn -2.0Al	203.13	19.15	52.57	32.67
Sn-9Zn -4.0Al	205.40	20.15	55.55	27.06

The optical and SEM micrograph of the Sn-9Zn in figure 2 (a and b) shows the typical lamella of eutectic microstructure. It has been mentioned that the eutectic Sn-9Zn alloy consists of β-Sn and Zn-rich phases. In the micrograph, the bright regions are the β-Sn phase and the primarily solidified phases; the dark phases are fine needlelike Zn-rich phase in β-Sn matrix. Also some Zinc spheroids are observed in the microstructure.

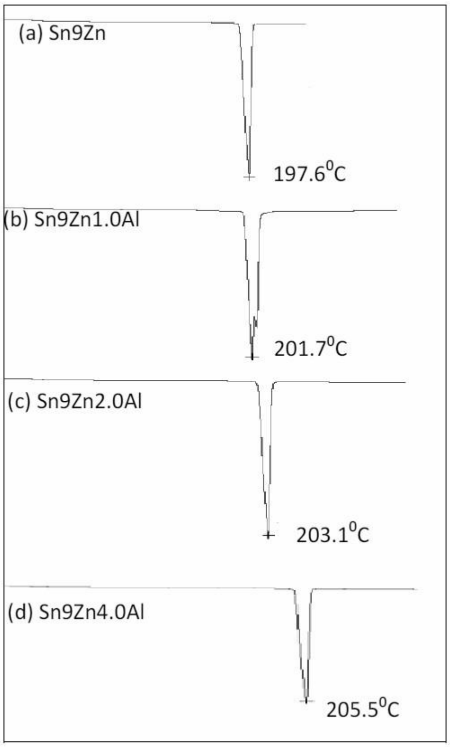

Fig 1. DSC curves of Sn-9Zn, Sn-9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al alloys

With the addition of 1% Al, the eutectic Sn-9Zn alloy shows some precipitates distributed in the eutectic phase shown in figure 2 (c and d). When 2% Al is added with the eutectic Sn-9Zn alloy, the microstructure changes with globular shaped intermetallic compound distributed in the typical eutectic lamella as shown in figure 3 (a and b). After the Al addition increases to 4% the number of intermetallics also increases while eutectic phase decreases and at the same time IMC size become little larger, as shown in figure 3 (c and d). The micrograph of the ternary alloys can be distinguished into three phases, i.e. the matrix β-Sn, the needle-like eutectic α-Zn, and the globular dark grey phases. EDX analyses were carried out to clarify the composition of the dark grey phases. As can be seen in figure 4 (a and b), the dark gray phases revealed that the phases are composed of Al, Sn and Zn and the Al percentage of these phases are about 57 at. %. This observation implies that these dark gray phases are actually Al_6Zn_3Sn IMC.

Thus, we can see when a third element Al is added with the Sn-9Zn eutectic alloy, the α-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-9Zn-2.0Al and Sn-9Zn-4.0Al deprived of thick Zn-rich eutectic lamella and consists of fine eutectic colonies dispersed with large Al_6Zn_3Sn compounds.

The microhardness of a solder alloy depends on the motion of dislocation, growth and configuration of grains. The processes are more sensitive to the microstructure of the solder alloy than its chemical composition. So the mechanical property such as the microhardness depends especially on the microstructure, processing temperature, the composition, etc. [14]. 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 solders 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 of the other phases increases as there are more alloying elements in solder. The same trend was confirmed for Sn-9Zn and Sn-9Zn-xAl alloys; the average hardness value increases when small amount of Al is added to the Sn-9Zn eutectic alloy as a third alloying element, as shown in figure 5.

As summarized in Table 2 the VHN of eutectic Sn-9Zn was 16.8, while those of Sn-9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al were 17.89, 19.15 and 20.15 respectively. The hardness increases for Sn-9Zn eutectic alloy after addition of a third element can be understood by dissolution of Al atoms for Sn-9Zn-xAl ternary alloys and formation of IMC particles in the solder matrix to promote precipitation hardening. This may also be explained by the microstructural observations for the corresponding ternary alloy. Fig. 3 represents that all the Sn-9Zn-xAl alloys are composed of three different phases; the matrix β-Sn, small amount of needle-like eutectic α-Zn, and the dark gray phases of IMCs, while the Sn-9Zn eutectic alloy consists of only first two phases with some Zn spheroids in it.

The ultimate tensile strength (UTS) is the maximum engineering stress, which a material can withstand in tension, on the engineering stress-strain curve. The yield stress is the stress level at which plastic deformation begins. For solder alloys, the yield stress is commonly defined by the stress on the stress-strain curve at 0.2% strain offset. The effect of third alloying additives on mechanical properties of Sn-9Zn eutectic solder alloy can be seen from the strain–stress curves shown in Fig. 6. The ultimate tensile strength (UTS) and elongation values are listed in Table 2. The tensile strength of the Sn–9Zn, 9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al were 48.78, 51.24, 52.57 and 55.55 MPa, respectively. The elongation at failure of the Sn–9Zn, 9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al were 48, 24.5, 32.6 and 27%, respectively. The Sn–9Zn–4.0Al alloy had the higher UTS and Sn–9Zn alloy exhibit higher elongation, while Sn–9Zn had the lowest UTS. As per dispersion strengthening theory [15], the strength must increase with the addition of a second phase particle in the matrix. 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 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.

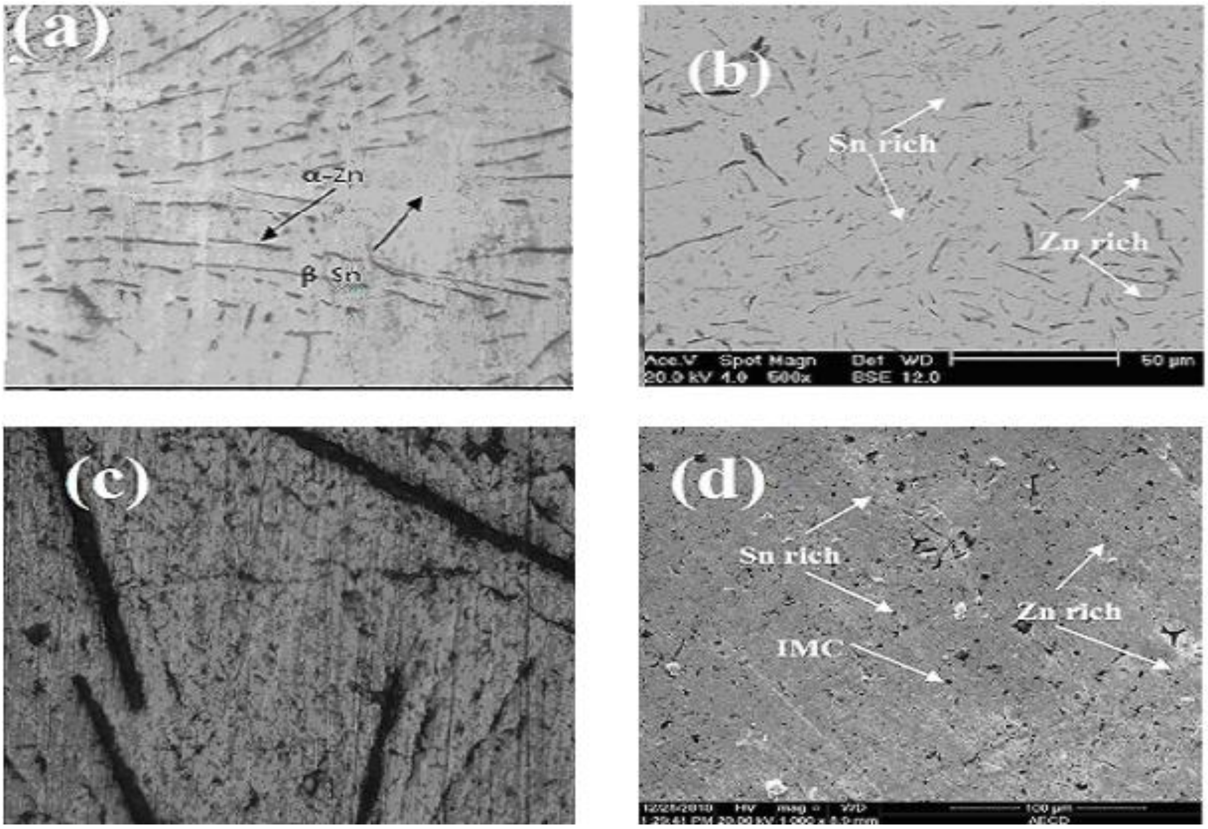

Fig 2. (a) Optical micrograph of Sn-9Zn (b) SEM micrograph of Sn-9Zn (c) Optical micrograph of Sn-9Zn-1.0Al (d) SEM Micrograph of Sn-9Zn-1.0Al

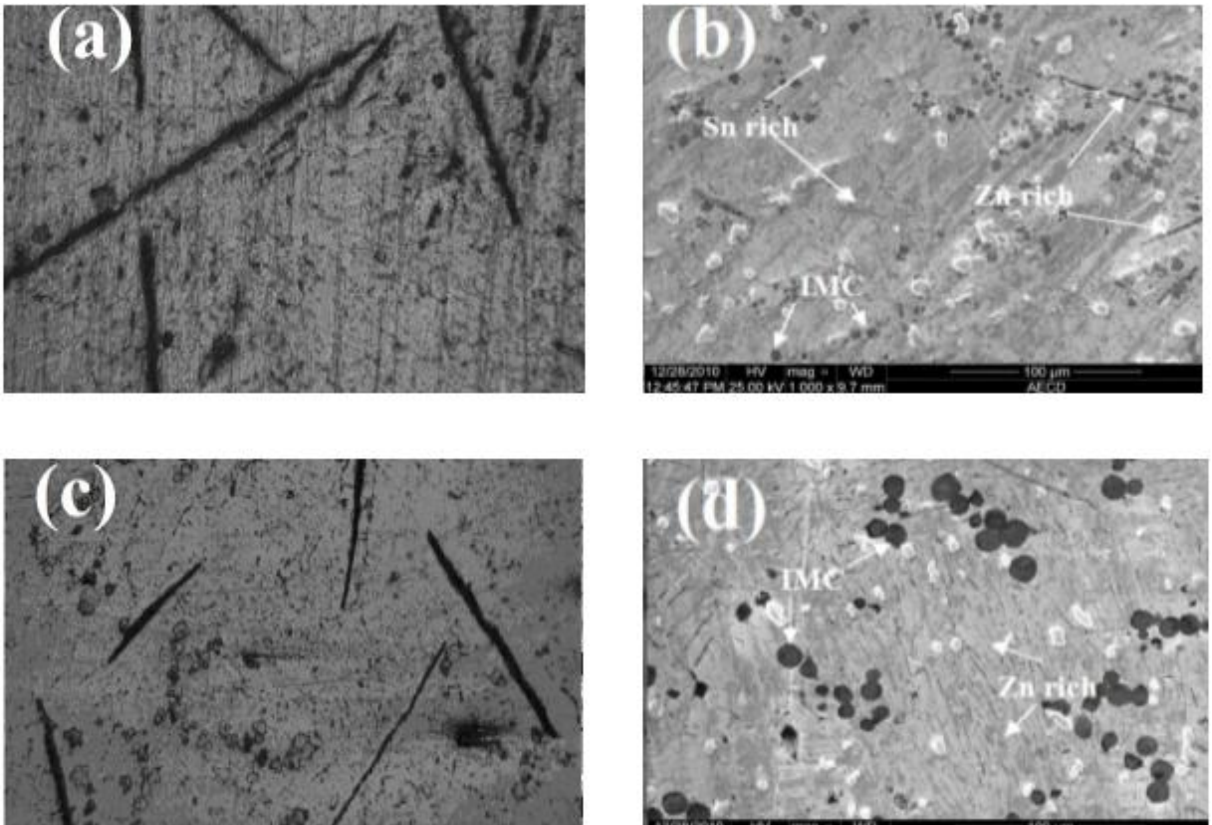

Fig. 3. (a) Optical micrograph of Sn-9Zn-2.0Al (b) SEM micrograph of Sn-9Zn-2.0Al (c) Optical micrograph of Sn-9Zn-4.0Al (d) SEM micrograph of Sn-9Zn-4.0Al

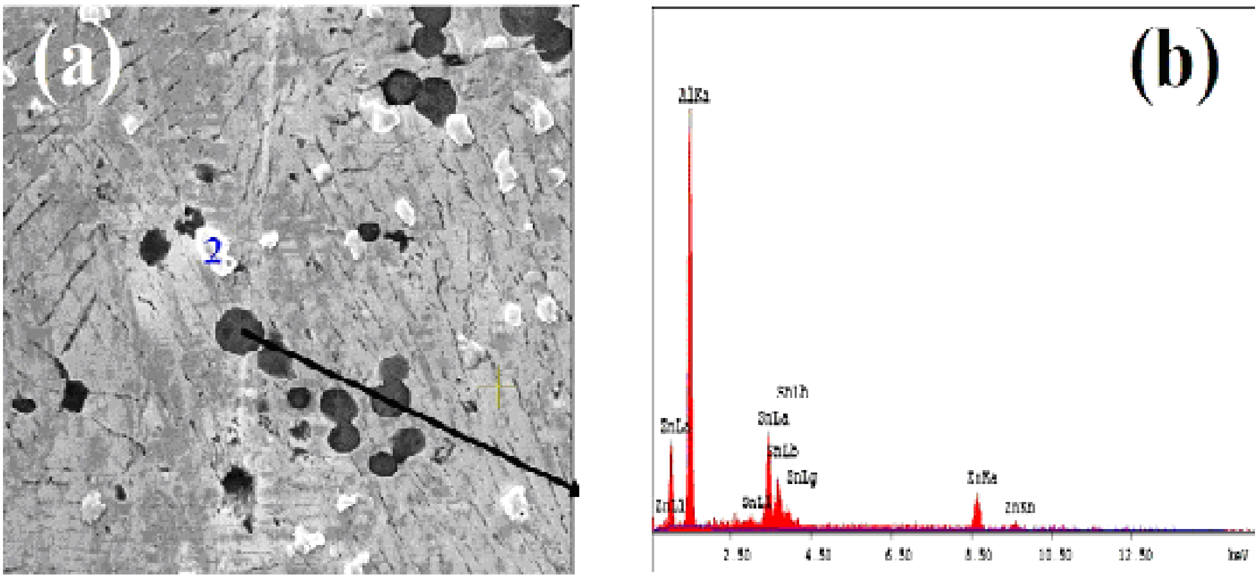

Fig 4. (a) The dark gray phases for Sn-9Zn-2.0Al alloy and (b) their quantitative analyses with EDX

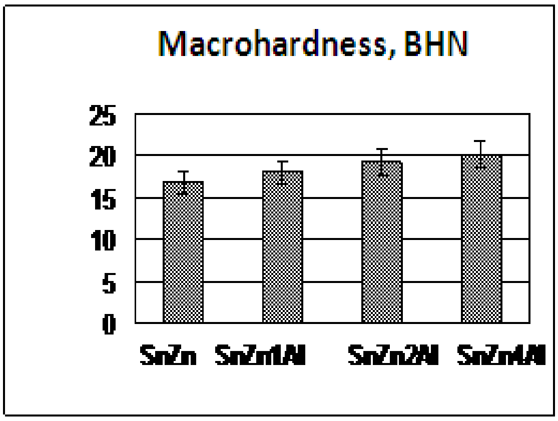

Fig 5. Brinell Hardness Number (BHN) for Sn-9Zn, Sn-9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al alloys.

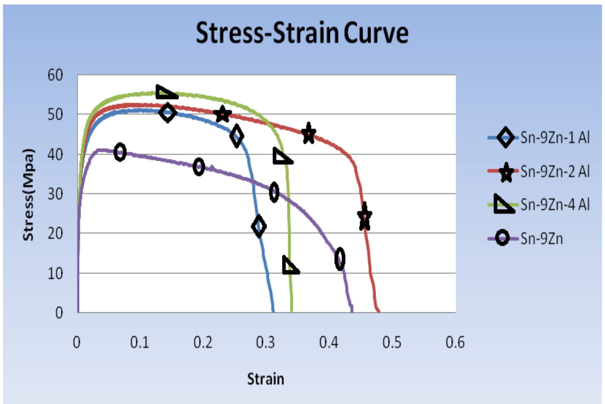

Fig 6. Tensile Stress-Strain curves of Sn-9Zn, Sn-9Zn-1.0Al, Sn-9Zn-2.0Al, and Sn-9Zn-4.0Al alloys.

4. CONCLUSIONS

Addition of a third element can promote the mechanical and thermal property of Sn-9Zn solder alloy in various ways. The melting temperature of Sn-9Zn eutectic solder alloy doesn't alter significantly after small amount of Al in it, only a 8^0C increase is observed up-to 4.0 wt. % Al addition. The volume fraction of IMCs in Sn-9Zn-xAl ternary alloys nucleates in contrast to that of the eutectic α-Zn phase, which decreased with increasing addition of Al. At the same time the eutectic α-Zn phase converts into fine needle-like structures rather than thick rod-like lamella. Again in the microstructures of newly developed ternary alloys some new phases are observed compared to Sn-9Zn eutectic solder alloy. For different amount of Al addition the new phases found to be globular shaped precipitate of Al_6Zn_3Sn. As the microhardness is strongly depend on the microstructure, thus the microhardness value increases for Al addition in the eutectic Sn-9Zn solder alloy. The tensile strength of Sn-9Zn-xAl is found to be higher compared to the Sn-9Zn eutectic solder alloy; on the other hand elongation drops. Finally, it can be concluded that the addition of Al can improve the mechanical properties of Sn-9Zn eutectic solder alloy.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. K. Suganuma, "Preface-Special Issue on Lead-Free Soldering in Electronics," Mater. Trans. 45 (2004) 605-605.
2. K. Zeng and K.N. Tu, "Six cases of reliability study of Pb-free solder joints in electronic packaging technology," Mater Sci Eng R. 38 (2002) 55–105.
3. M. Abtew and G. Selvaduray, "lead-free solders in microelectronics," Mater Sci Eng R 27 (2000) 95–141.

4. J. M. Song and Z.M. Wu, “Variable eutectic temperature caused by inhomogeneous solute distribution in Sn–Zn system,” Scripta Metall. 54 (2006) 1479-1483.
5. K.S. Kim, J.M. Yang, C.H. Yu, I.O. Jung, and H.H. Kim, “Analysis on interfacial reactions between Sn–Zn solders and the Au/Ni electrolytic-plated Al pad,” J. Alloys and Compounds 379 (2004) 314-318.
6. S. Vaynman and M. E. Fine, “Development of fluxes for lead-free solders containing zinc” Scr. Mater. 41, (1999) 1269-1271.
7. A. Sebaoun, D. Vincent, D. Treheux, “Al-Zn-Sn phase diagram isothermal diffusion in ternary system” Mater. Sci. Technol. 3 (1987) 241-248.
8. K. Suganuma, T. Murata, H. Noguchi, Y. Toyoda, “Heat resistance of Sn--9Zn solder/Cu interface with or without coating” J. Mater. Res. 15 (2000) 884-891.
9. S. P. Yu, M. C. Wang, M.H. Hon, “Formation of Intermetallic compounds in Eutectic Sn-Zn-Al-solder hot-dipped on Cu substrate” J. Mater. Res. 16 (2001) 76-82.
10. D. Soares, C. Vilarinho, J. Barbosa, R. Silva, M. Pinho and F. Castro, “Effect of the Bi content on the mechanical properties of a Sn-Zn-Al-Bi solder alloy”, Mater. Sci. Forum 455-456 (2004) 307-311.
11. C. M. Chuang, T. S. Lui, L. H. Chen, “Effect of aluminum addition on tensile properties of naturally aged Sn-9Zn eutectic solder”, J. Mater. Sci. 37 (2002) 191-195.
12. C. M. L. Wu, and Y. W. Wong, “Rare-earth additions to lead-free electronic solders”, J. Mater. Sci.: Mater. Electron. 18 (2007) 77-91.
13. 13. S. K. Das, A. Sharif, Y. C. Chan, N. B. Wong and W. K. C. Yung, Influence of small amount of Al and Cu on the microstructure, microhardness and tensile properties of Sn-9Zn binary eutectic solder alloy, J. Alloys and Compounds, 481 (2009) 167-172.
14. D. Frear, H. Morgan, S. Burchett, J. Lau, “The Mechanics of Solder Alloy Interconnects”, Van Nostrand Reinhold, New York (1994).
15. G. E. Dieter, “Mechanical Metallurgy”, McGraw-Hill Book Co., New York (1986).

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