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EFFECT OF VARIOUS AMOUNT OF Cu ON THE THERMAL AND MECHANICAL BEHAVIOR OF Sn-9Zn EUTECTIC Pb-FREE SOLDER ALLOY

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ABSTRACT

In this work, Cu content in the range between 0-1.0 wt.% with Sn-Zn eutectic system were examined in order to understand the effect of Cu addition on the microstructural and mechanical properties as well as the thermal behaviour of the solders. The melting temperature of Sn-9Zn eutectic solder alloy did not alter significantly with small amount of Cu addition. Only a 3^0C increase in melting temperature was observed with the 1.0 wt. % Cu addition. The flower shaped Cu_6Sn_5 and rod shaped Cu_5Zn_8 IMCs were found to be uniformly distributed in the β-Sn phase for Sn-9Zn-0.4Cu, which resulted in an increase in the tensile strength. It was also found that the microhardness of the solder alloy was increased with the addition of Cu up to a certain limit. Finally, it can be concluded that the addition of a little amount of Cu can improve the mechanical properties of Sn-9Zn eutectic solder alloy.

Keywords: Sn-Zn Eutectic Solder, Microstructure, Mechanical Property, Thermal Behavior, Intermetallic Compounds, Strengthening Mechanism.

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.

The addition of Cu may increase the melting point of solder alloy, as Cu has far higher melting point (1084^0C) than that of Sn-9Zn solder alloy (198^0C), thus increasing the alloy melting process. The Sn-Zn-Cu (SZC) solder had a near eutectic reaction in 214.93^0C [7]. By using midely active rosin (RMA) flux, the wetting angle of Sn-9Zn was found to be 89^0, and with addition of 4% Cu with 0.05% of rare earth, the alloy wetting angle was found to be minimum 49^0[8]. It had been proven that by alloying Cu with Sn-Zn-Al the melting temperature increases about 210^0C. Cu has the ability to stabilize Zn in the solder and controls the growth of the reaction layer [9]. With the addition of Cu in the Sn-Zn alloy, the Cu-Zn compound formed in the solder matrix prevent the Zn atoms to diffuse in the Cu foil, which causes the planar rod-shape Cu_5Zn_8 IMC at the interface change into scallop Cu_6Sn_5 IMC. It was observed that the IMC of Sn-Zn-xCu/Cu joint is mainly Cu_5Zn_8 when the content of Cu is 0-1%; when the content of Cu is 2%-6%, the IMC is Cu_6Sn_5 and Cu_5Zn_8 together; when the content of Cu is 8%, the IMC is Cu_6Sn_5. With the increasing of Cu in the Sn-Zn-xCu solder, the shear strength of the Sn-Zn-xCu/Cu solder joint is enhanced with the transformation of IMC type from planar Cu_5Zn_8 to scallop Cu_6Sn_5 at the interface [10].

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 [11-13]. 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 Cu 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 Cu in it.

2. EXPERIMENTAL PROCEDURE

The Sn–9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu and Sn-9Zn-1.0Cu 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 500^0C 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).

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

Alloys	Sn	Zn	Cu	Pb	Bi	Sb
Sn-9Zn	Bal.	8.692	-	0.346	0.253	0.009
Sn-9Zn-0.4Cu	Bal.	8.683	0.413	0.343	0.251	0.012
Sn-9Zn-0.7Cu	Bal.	8.601	0.682	0.346	0.252	0.010
Sn-9Zn-1.0Cu	Bal.	8.626	1.057	0.340	0.260	0.008

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.

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. The fracture surfaces of these lead-free alloys were also investigated under SEM to find the fracture mode.

3. RESULTS AND DISCUSSIONS

3.1 Melting Temperature

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-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu alloys on heating. With the addition of small amount of Cu, the melting temperatures changed slightly. The melting temperatures were found 199.33^0C, 200.13^0C and 200.28^0C for the Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu, respectively, as compared with 197.59^0C for Sn–9Zn eutectic alloy. Lee et al. [14] reported that the addition of Cu even up to 4% did not significantly alter the melting point of the Sn-9Zn alloy. For Cu addition here the melting temperature increases only 3^0C than that of Sn-9Zn binary eutectic alloy.

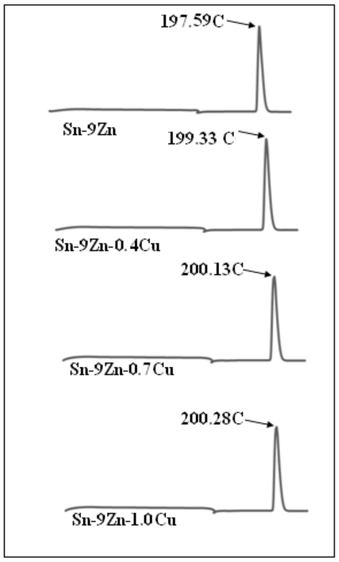

Fig 1. DSC curves of Sn-9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu alloys.

3.2 Microstructure and Elemental Analysis

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.

With the addition of 0.4% Cu, the eutectic Sn-9Zn alloy shows some precipitates distributed in the eutectic phase shown in Figure 2 (c and d). When 0.7% Cu is added with the eutectic Sn-9Zn alloy, the microstructure changes with some planar and flower shaped intermetallic compound distributed in the typical eutectic lamella as shown in Figure 3 (a and b). After the Cu addition increases to 1% the number of intermetallic also increase while eutectic phase decreases and at the same time IMC size become 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 flower or rod like dark grey phases. EDX analyses were carried out to clarify the composition of the dark grey phases. And interestingly it was found that Cu forms IMC of two different shapes reacting with both Zn and Sn. As can be seen in Figure 4 (a and b), the rod shaped dark gray phases revealed that the phases are composed of Cu and Zn and the Cu percentage of these phases are about 32 at. %. This observation implies that these rod shaped dark gray phases are actually γ-Cu_5Zn_8 IMC. From the EDX analysis of flower shaped dark gray phases as shown in Figure 4 (c and d) were found to be made of Cu and Sn. And from the stoichiometrical ratio it was found that these flower shaped IMCs were Cu_6Sn_5.

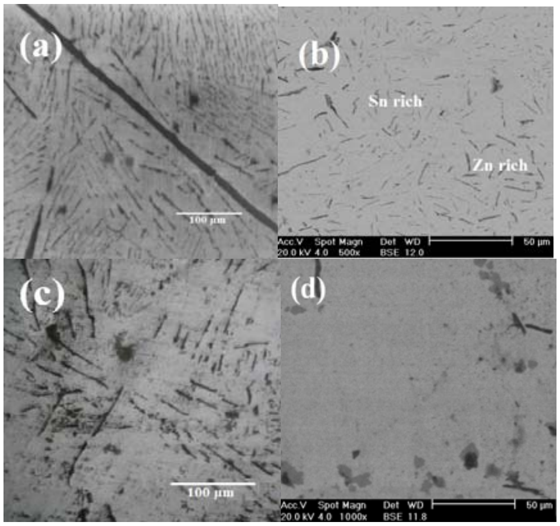

Fig 2. Optical and SEM micrograph respectively (a), (b) of Sn-9Zn and (c), (d) of Sn-9Zn-0.4Cu.

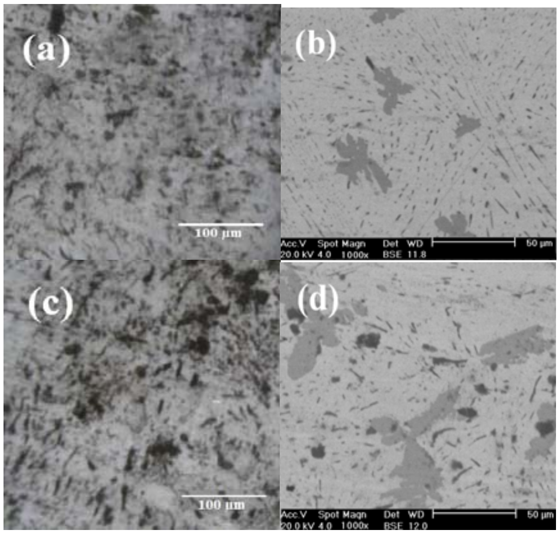

Fig 3. Optical and SEM micrograph respectively (a), (b) of Sn-9Zn-0.7Cu and (c), (d) of Sn-9Zn-1.0Cu.

Thus, we can see when a third element Cu 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 Cu. Cu also reacts with Sn as well to form intermetallic compound. And due to the high reactivity of Cu (electro negativity: -1.90), the microstructure of Sn-9Zn-0.7Cu and Sn-9Zn-1.0Cu deprived of thick Zn-rich eutectic lamella and consists of fine eutectic colonies dispersed with large Cu_5Zn_8 and Cu_6Sn_5.

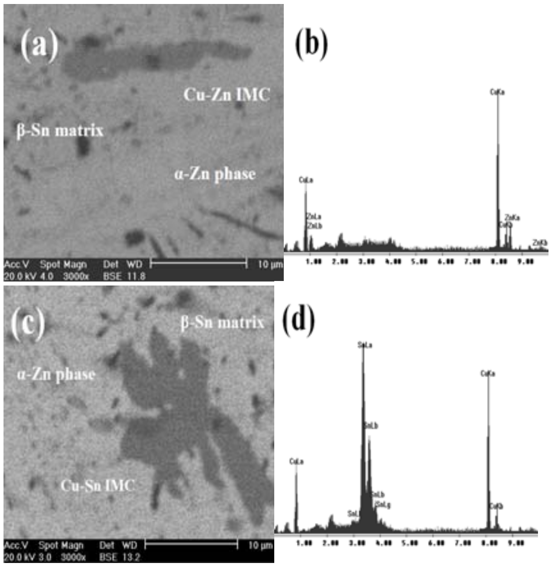

Fig 4. The dark gray phases and their quantitative analyses with EDX for Sn-9Zn-0.4Cu alloy (a), (b); (c), and (d).

3.3 Microhardness

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. [15]. 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, the higher the hardness. 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-0.4Cu alloys; the average hardness value increases when small amount of Cu is added to the Sn-9Zn eutectic alloy as a third alloying element, as shown in Figure 5.

In Figure 5, it can be seen that the VHN of eutectic Sn-9Zn was 16.8, while those of Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu were 21, 16.6 and 15.5 respectively. The hardness increases for Sn-9Zn eutectic alloy after addition of a third element can be understood by dissolution of Cu atoms for Sn-9Zn-xCu 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. Figure 3 represents that all the Sn-9Zn-xCu 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. And also the amount of eutectic α-Zn phase quantity is high and thick compared to that of the Zn-rich phases of the ternary alloys, which in turns results in a lower hardness value. Unfortunately for higher amount of Cu addition the hardness value starts to decrease gradually. This happens due to the formation of large IMC in the β-Sn matrix, which consumes more Zn and Sn from original bulk solder and eventually develops some sort of weak interface with the parent matrix.

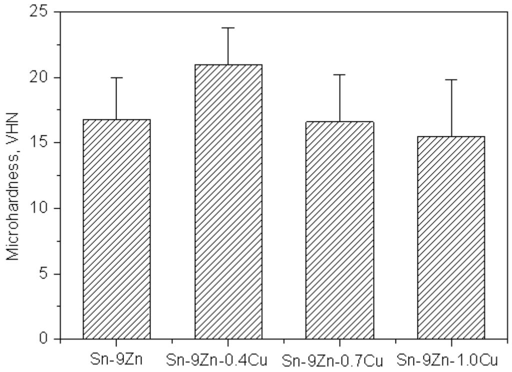

Fig 5. Graphical representation of Vickers Hardness Number (VHN) with Standard-deviation for Sn-9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu alloys.

3.4 Tensile Properties

The ultimate tensile strength (UTS) is the maximum engineering stress, which a material can withstand in tension, on the engineering stress-strain curve [16]. 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 Figure 6. The tensile strength of the Sn–9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu were 52, 53, 48 and 43 MPa, respectively. The elongation at failure of the Sn–9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu were 62, 47, 38 and 38%, respectively. The Sn–9Zn–0.4Cu alloy had the higher UTS and Sn–9Zn alloy exhibit higher elongation, while Sn–9Zn–1.0Cu had the lowest UTS and elongation. In the tensile stress-strain curves shown in Figure 6, after the peak tensile stresses are reached at □0.05 strain, the binary Sn–9Zn alloy has a less steep slope than the Sn–9Zn–xCu alloys. This steeper slope indicates that the eutectic structure becomes a hypoeutectic structure. The formation of Cu-Sn and Cu-Zn compound occurs at the expense of the Zn-rich phase. The variation in Sn content renders the eutectic structure into a hypoeutectic structure.

Figure 7 shows the tensile properties for Sn-9Zn, Sn–9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu alloys. An increase in 2% proof strength is observed for 0.4% Cu addition in Sn-9Zn alloy, while a 24% drop in elongation is observed for it. For 0.7 and 1.0% Cu addition both proof strength and elongation decreases in larger extent. As per dispersion strengthening theory [17], the strength must increase with the addition of a second phase particle in the matrix. And for the case of small amount of Cu addition in Sn-9Zn the theory proved right, while for the amount of Cu 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.

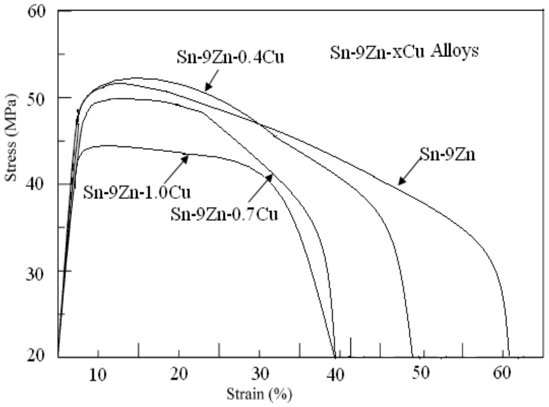

Fig 6. Tensile stress-strain curves of Sn-9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu alloys.

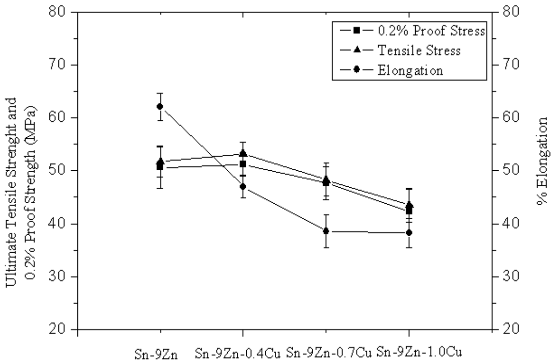

Fig 7. Tensile properties of Sn-9Zn, Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu, and Sn-9Zn-1.0Cu alloys.

3.5 Fracture Mode

Figure 8 shows the fractography of the alloys after tensile tests. All alloys displayed a typical ductile fracture mode. The dimpled pattern is represented in all fracture surfaces. The dimple size of the alloys varies for different element content. The dimples size for Sn-9Zn-0.4Cu is much finer compared to others. For Sn-9Zn-0.4Cu, Sn-9Zn-0.7Cu and Sn-9Zn-1.0Cu alloys, some Cu-Sn and Cu–Zn compounds were observed in the fracture surfaces. The fracture surface of the Sn-9Zn-0.4Cu alloy shows many fine dimple structures (Figure 8b). On the other hand, the fracture surfaces of the Sn-9Zn-0.7Cu and Sn-9Zn-1.0Cu alloys exhibit some cleavage patterns, as shown in Figure 8 (c and d). Thus, Sn–9Zn–0.7Cu and Sn-9Zn-1.0Cu alloy undergoes a complex fracture pattern. From the results of tensile tests on Sn–9Zn–0.4 Cu alloy, the formation of small size of Cu-Sn and Cu-Zn compounds promote tensile strength and deteriorate elongation slightly, while the tensile tests for Sn–9Zn–0.7Cu and Sn-9Zn-1.0Cu alloys reveal that the large intermetallic compounds deteriorates both tensile strength and elongation.

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. For higher amount of Cu in Sn-9Zn eutectic solder alloy tensile properties deteriorates. The fall of tensile strength is believed for the weak interface formed between the IMC and the matrix, which in turn decrease the tensile strength. According to Dieter [17], the second phase element increases the tensile strength up to a certain extent and beyond that the precipitate starts to grow non-coherently which results in the decrease of the overall strength. And for the case of Sn-9Zn-0.7Cu and Sn-9Zn-1.0Cu alloys the IMCs growth is beyond that limit which results in a decrease in the tensile strength. Also from figure 3 (a), (c) and 4 (a), (c), it can be observed that the flower and rod shaped IMCs have several edges, which may acts as crack initiators during tensile loading. Thus, rather than ductile cup-cone, complex cleavage type fracture surface is exposed after tensile test. The reduction of elongation for Cu addition may also be related to the weak interface between the large IMCs with the β-Sn matrix.

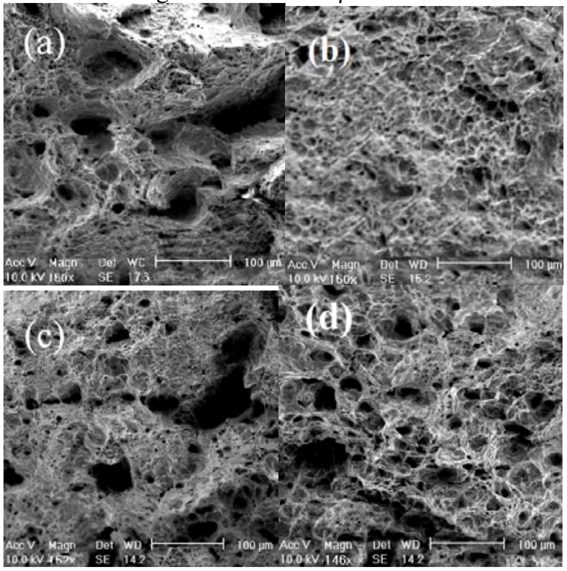

Fig 8. SEM fractrograph in SE mode for (a) Sn-9Zn, (b) Sn-9Zn-0.4Cu, (c) Sn-9Zn-0.7Cu, and (d) Sn-9Zn-1.0Cu alloys.

4. CONCLUSIONS

The melting temperature of Sn-9Zn eutectic solder alloy doesn't alter significantly after small amount of Cu in it, only a 3^{0}C increase is observed up-to 1.0 wt. % Cu addition. The volume fraction of IMCs in Sn-9Zn-xCu ternary alloys increased in contrast to that of the eutectic α-Zn phase, which decreased with Cu addition. At the same time the eutectic α-Zn phase converts into fine needle-like structures rather than thick rod-like lamella. The flower and rod shaped precipitate of Cu_6Sn_5 and Cu_5Zn_8, respectively were observed in the Sn-Zn-Cu ternary alloys. The mechanical properties of Sn-9Zn-0.4Cu are found to be higher compared to the Sn-9Zn eutectic solder alloy. As the amount of Cu further increases, both tensile strength and elongation drops. Sn-9Zn and Sn-9Zn-0.4Cu alloys showed a ductile fracture pattern, while Sn-9Zn-0.7Cu and Sn-9Zn-1.0Cu alloys showed a complex cleavage failure pattern.

Finally, it can be concluded that the addition of a little amount of Cu can improve the mechanical properties of Sn-9Zn eutectic solder alloy. As the Cu content in Sn-9Zn increases, the mechanical properties start to deteriorate.

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