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A SHORT REVIEW ON THE INFLUENCE OF ANTIMONY ADDITION TO THE MICROSTRUCTURE AND THERMAL PROPERTIES OF LEAD-FREE SOLDER ALLOY

For long time, Sn-Pb solder alloys have been used extensively as the main interconnection materials in the soldering. It is no doubt that Sn-Pb offers many advantages including good electrical conductivity, mechanical properties as well as low melting temperature. However, Pb is very toxic and Pb usage poses risk to human health and environments. Owing to this, the usage of Pb in the electronic industry was banned and restricted by the legislation. These factors accelerate the efforts in finding suitable replacement for solder alloy and thus lead-free solder was introduced. The major problems associated with lead-free solder is the formation of large and brittle intermetallic compound which have given a rise to the reliability issues. Micro alloying with Sb seems to be advantageous in improving the properties of existing lead-free solder alloy. Thus, this paper reviews the influence of Sb addition to the lead-free solder alloy in terms of microstructure formations and thermal properties.

Keyword: Lead-free solder; antimony; microstructure; melting temperature

1. Introduction

Solder alloys plays a significant role in the reliability, workability and integrity of the electronic package. For decades, tin-lead (Sn-Pb) solder alloys was widely used in the electronics products to join all the electronic components with the substrate. This was due to the unique properties of SnPb solder alloys which having a low melting temperature of 183°C, good wettability and mechanical properties as well as low expense [1-4]. However, the lead content in solder alloys was very toxic and long-term usage of lead could give negative effects to human health and environment [4,5]. Moreover, many countries have implemented a law in prohibiting the use of lead in the solder alloys [5]. Therefore, the development and research in finding the alternative to replace lead solder alloys took place worldwide.

The lead-free solders which are either binary or ternary alloys such as Sn-Bi, Sn-Ag, Sn-Zn, Sn-Cu, Sn-Ag-Cu were widely investigated and used to replace the traditional Sn-Pb solder alloys [4], [6]. However, there are some drawbacks which come along with these solder alloys. As an example, Sn-Ag has a good creep resistance but the cost of Ag is expensive as well as the high melting point of Ag [4]. Besides, Sn-Zn has a low melting point of 199°C which is near to melting point of Sn-Pb solder alloys [5]. However, Zn is prone to oxidize and contains poor wettability [5]. Besides, Sn-Ag-Cu has been widely used to replace the existing SnPb solder alloys due to the good solderability and mechanical properties [7]. However, the drawbacks of Sn-Ag-Cu solder alloy is the formation of large intermetallics of Cu_6Sn_5 and Ag_3Sn. These large intermetallics could reduce the mechanical strength of solder especially under stressed condition during the service. Therefore, the improvement in the existing lead-free solder alloys was necessary as well as to keep pace with the current advancement in the electronic products. Recent research has investigated on the addition of alloying elements in the solder alloys such as bismuth (Bi), phosphorus (P), gallium (Ga) and so on [8-10].The presence of these alloying elements has proven to improve the properties and performance of existing lead-free solder alloys [2,11].

Antimony (Sb) is one of the metallic elements that can be used as the alloying elements in the solder alloys. It is known that, antimony (Sb) is soluble in tin and could increase the strengths of the solder alloys [12]. Research has reported that the improvement of the mechanical strength of the solder alloys with an addition of Sb was due to the solid solution strengthening [13]. The solid solution strengthening occurred as the Sb substituted Sn and distorted the crystal lattice of the solder

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alloys [14]. Besides, in terms of the liquidus temperature, the temperature will be increased by changing the amounts of Sb [14]. Therefore, this paper provides a review on the effects of adding Sb as the alloying elements in Sn-based solder alloys in terms of microstructure formations and thermal properties of solder alloys. The findings in this review on the effects of Sb addition to the microstructure formations and thermal properties in Sn-based solder alloys will be useful in developing reliable lead-free solder alloys.

2. The effects of Sb on the properties of lead-free solder

2.1. Microstructure

It has been reported that the Sn-based solder alloys consists of several phases [15]. Fig. 1 shows the as-solidified microstructure in SAC305 solder alloys with an addition of Sb (0.5-3.0 wt.%Sb). As reported by Sungkhaphaitoon et al. [16],

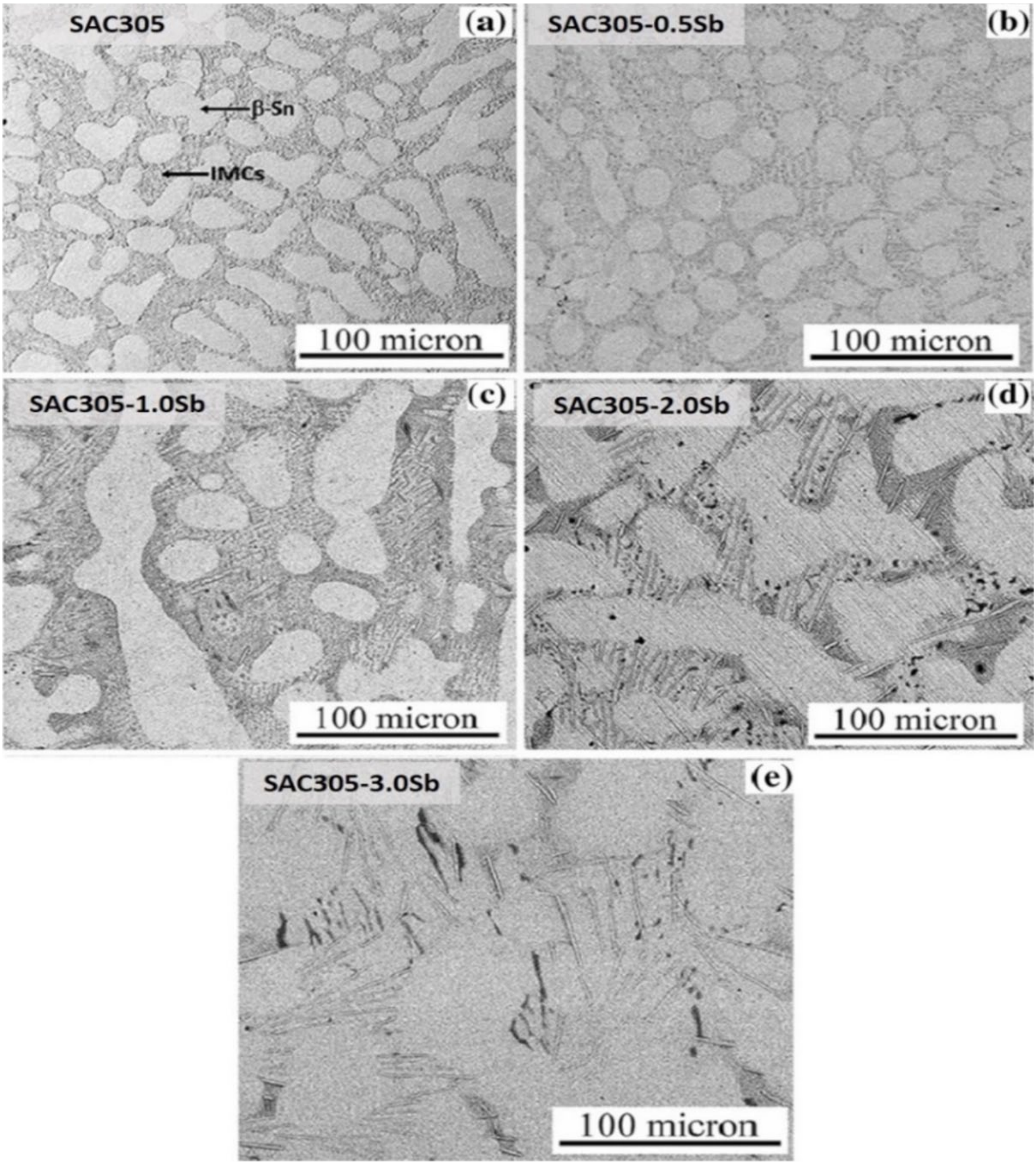

Fig. 1. As-solidified microstructure of SAC305 solder alloys with additions of Sb (0-3.0wt.% Sb) [16]

the microstructure in as-solidified SAC solder alloys consists of β-Sn phases and IMC phases (Cu_6Sn_5 and Ag_3Sn) as depicted in Fig. 1(a). The addition of Sb elements would result in the formations of new phases of Ag_3(Sn,Sb) and $Cu_6(Sn,Sb)_5$ as in Fig. 1(b,c,d and e). Moreover, the addition of higher 3.0 wt.% Sb has resulted in the formation of SnSb phase and increasing in the amount of small particles of Ag_3(Sn,Sb) [16]. In addition, in the study done by Basaty et al. [17], the addition of Sb has given a significant impact to the microstructure of Sn-9Zn-0.5Al. In a typical Sn-9Zn-0.5Al, there are an existence of three phases which are gray region of β-Sn rich, large dark needle-like α-Zn rich phase and small precipitated of Al_6Zn_3Sn IMC phase as illustrated in Fig. 2. It was reported that addition of 0.5 and 1.0 wt.% Sb could refine the α-Zn rich phase with relatively small spacing as in Fig. 2(b and d). Meanwhile, the addition of 1.5 wt.% Sb has resulted in the deformation in the shape of α-Zn rich phase which are rounded in comparison with a needle-like shape in a sample without Sb addition as in Fig. 2(d). The reduction in the precipitation of needle-like α-Zn shape in β-Sn with the addition of Sb was advantageous since it could inhibit the formation of cracks and the propagation of dislocations.

Then, Lee et al. [18] has reported on the performance of Sn-Ag with an addition of Sb under high temperature storage of 150°C ad 625 h. Fig. 3 displays the microstructure of Sn-Ag with various addition of Sb under as-reflowed condition and isothermal aged. The typical microstructure of Sn-Ag showing large formation of Ag_3Sn surrounded the β-Sn region [18]. However, Sb addition has suppressed the formation of large Ag_3Sn. The addition of 10 wt.% Sb has resulted in Ag_3(Sn,Sb) and SnSb instead. In addition, Ag_3Sn is hard and brittle. The existence of coarsened Ag_3Sn was detrimental since the ductility and creep resistance will be reduced [19]. In addition, under the isothermal ageing conditions, Sb was able to reduce the coarsening of Ag_3Sn region which could improve the shear strength of Sn-Ag solder as well [15,18].

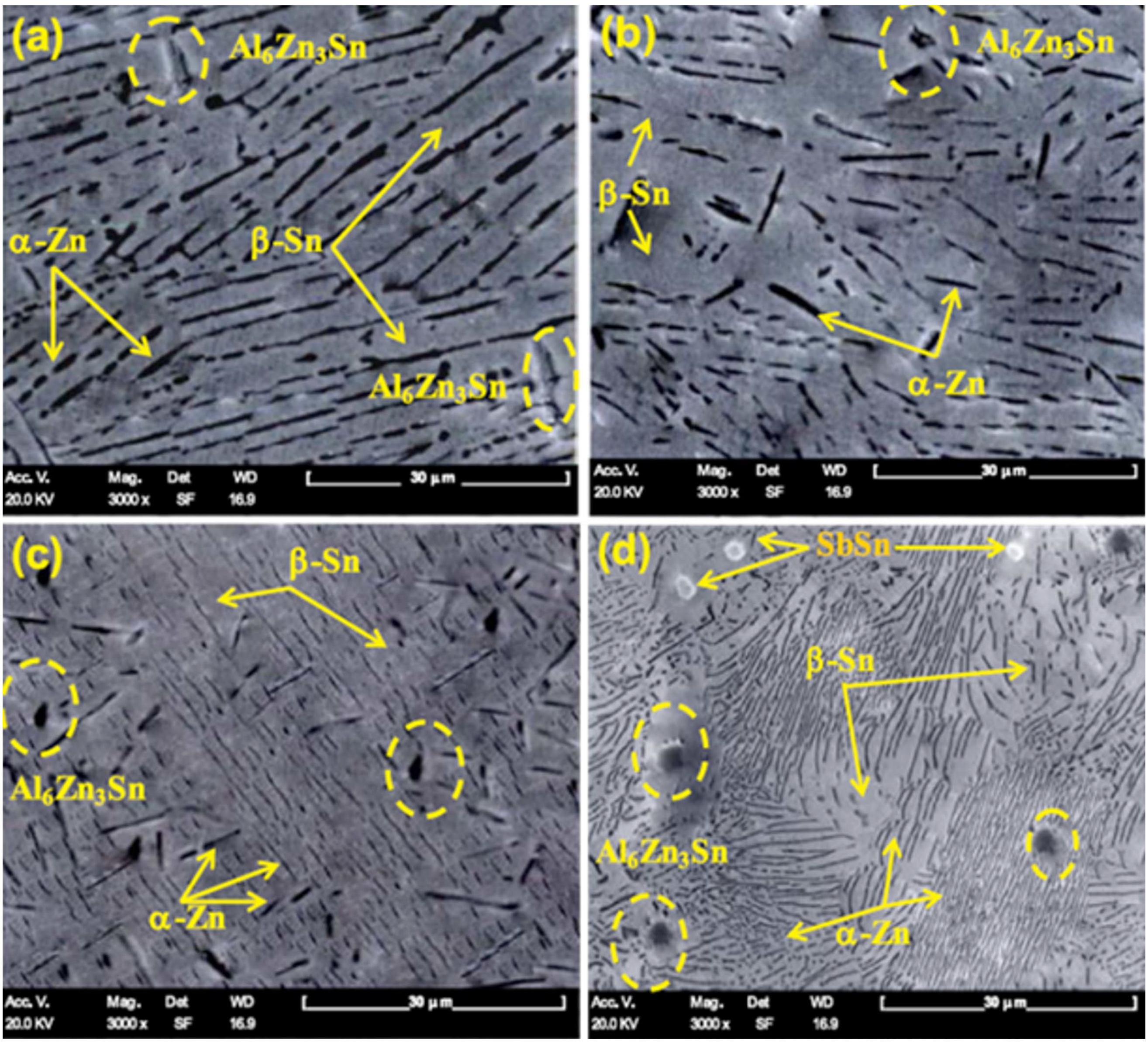

Fig. 2. SEM micrograph of Sn-9.0Zn-0.5Al with various wt.% of Sb (a) 0 wt.% Sb, (b)0.5 wt.% Sb, (c) 1.0 wt.% Sb and (d) 1.5 wt.% Sb [17]

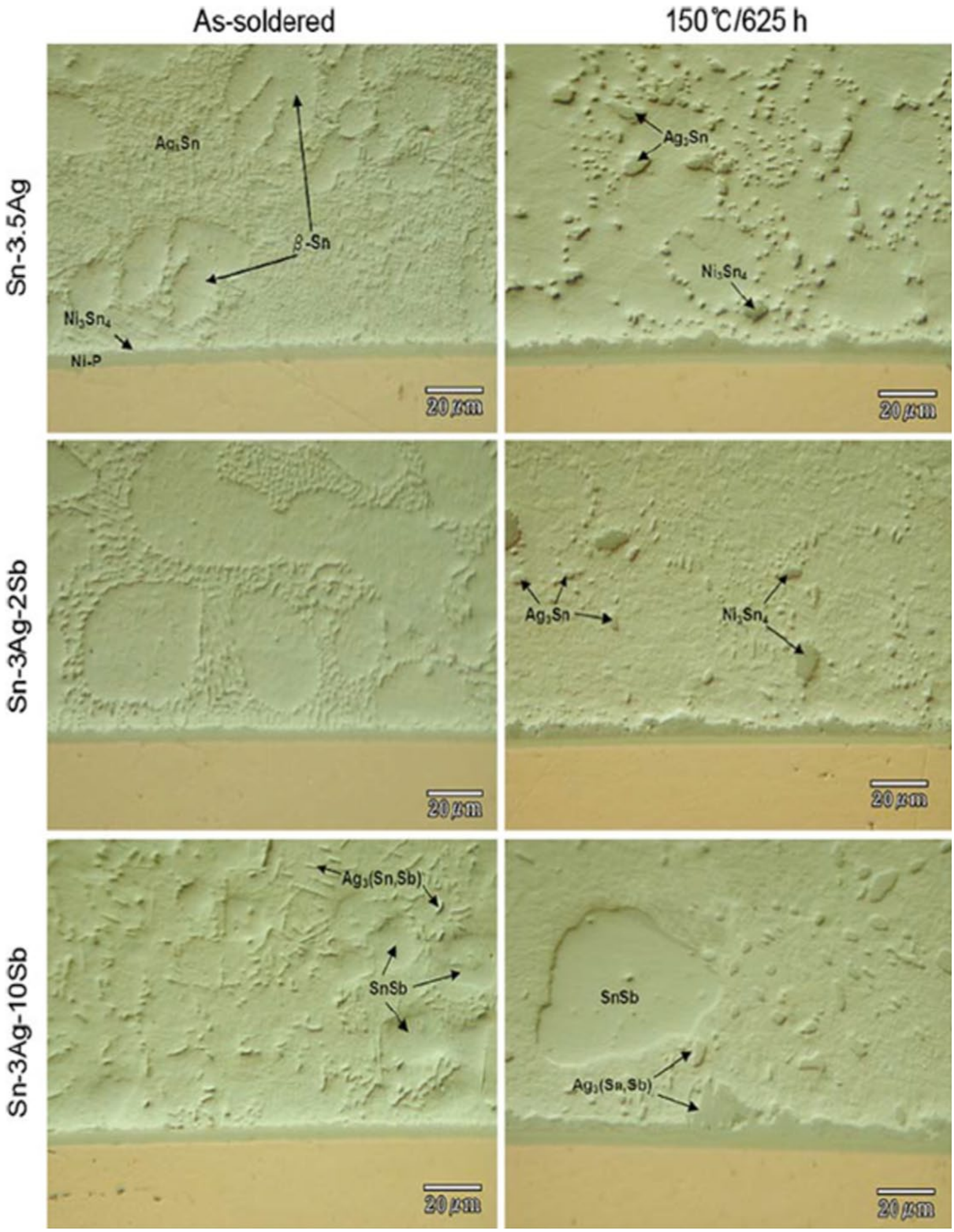

Fig. 3. Microstructure of solidified soldered under as-reflowed and isothermal ageing conditions [18]

2.2. Thermal properties

The melting temperature of solder alloy is one of the most important parameters in soldering process. Fig. 4 shows the DSC curves of SAC305 with different wt.% of Sb addition. Based on the DSC curves, there is an existence of an endothermic peak at the eutectic point [16]. The melting temperature of SAC305 with various addition of Sb was summarized in TABLE 1. According to TABLE 1, the addition of Sb increases the melting temperature of SAC305 solder. The increment in the melting temperature of SAC305 was due to the formation of new eutectic phase of $Ag_3(Sn,Sb)$ and $Cu_6(Sn,Sb)_5$. Moreover, Li et al. [20], has investigated the thermal properties with higher addition of wt.% of Sb (25, 28 and 31 wt.%Sb) in SAC305 solder alloy. The results ascertained that; the melting temperature was increased significantly as depicted in TABLE 2. Li. et al. [20] reported that, the increment in the melting temperature was associated with the formation of bulk SnSb phase. For the pasty range, the Sb addition has increased the pasty range as presented in TABLE 2. For a good solder alloy, the pasty range should be small. However, according to the National Center for Manufacturing Sciences (NCMS), the pasty range for the lead-free solder should not exceed 30°C [20]. Therefore, solder alloy of SAC305 with 25 wt.% Sb addition can still be used even though the pasty range and melting temperature are higher than the plain SAC305 solder alloy [20].

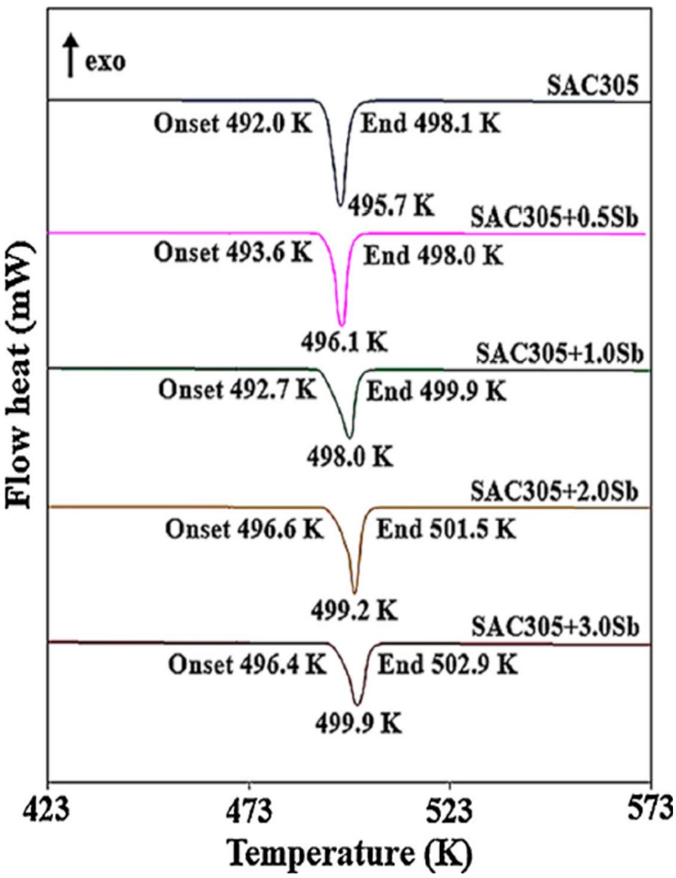

Fig. 4. DSC curves of SAC305 with various addition of Sb [16]

TABLE 1

Melting temperature of SAC305 with addition of Sb (0.5-3.0 wt.%Sb) [16]

Solder alloy	Melting temperature (°C)
SAC305	222.7
SAC305 + 0.5Sb	223.1
SAC305 + 1.0Sb	225.0
SAC305 + 2.0Sb	226.2
SAC305 + 3.0Sb	226.9

TABLE 2

Melting temperature of SAC305 with higher addition of Sb (25, 28 and 31 wt.%Sb) [20]

Solder alloy	Melting temperature (°C)	Pasty range (°C)
SAC305	218.90	5.19
SAC305 + 25Sb	332.91	28.74
SAC305 + 28Sb	342.53	38.67
SAC305 + 31Sb	354.68	47.78

3. Conclusions

The investigations and research on the addition of Sb in lead-free solder alloys was reviewed in this paper. It was proven that an addition of antimony as an alloying element in lead-free solder alloys was beneficial to the microstructure formations and thermal properties of solder alloys. Based on the literature reported, Sb can be incorporated into Cu-Sn and Ag-Sn intermetallic compound by substituting Sn atoms by forming $Cu_6(Sn,Sb)_5$ and $Ag_3(Sn,Sb)$. However, the solubility of Sb in the intermetallic compounds are not well understood. Therefore, the future research needs to pay a particular attention on the solubility of Sb in the intermetallic compounds which would be useful in providing the insight knowledge on the enhancement of solder alloys properties with the addition of Sb element. In addition, a suitable amount of antimony additions in solder alloys need to be taken into consideration in the future research as to avoid the degradation of the solder's thermal properties and performance.

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