The Effect of Germanium Addition on the Lead-free Solder Alloys: A Short Review

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Abstract. The Restriction of Hazardous Substances (RoHS) has been enforced a law to restrict the use of hazardous materials in electronic and electrical industries. Hence, it leads to the development of lead-free solder among the electronic industry. SnAg, SnCu, SnAgCu, and SnZnBi solders are found to be alternatives to replace SnPb solder alloys. However, they still have many problems, such as large undercooling and large intermetallic compounds are still present in the solder alloys. Later, researchers come up with the idea of adding alloying elements to lead-free solders to further enhance the properties of lead-free solders. This review paper is aimed to analyze and summaries the effects of germanium (Ge) addition to lead-free solders focusing on its microstructure and thermal properties. The Ge has an almost similar crystal structure as pure tin (Sn), so it is expected that the properties of the lead-free solder could be enhanced by adding an appropriate amount of Ge. Nevertheless, Ge has a unique characteristic as it could act as an antioxidant agent in the lead-free solders.

1 Introduction

The Restriction of Hazardous Substances (RoHS) has enforced the ban on using hazardous materials for electrical and electronic equipment since the year of 2006. Lead is one of the banned substances by the RoHS, yet, it is still used for solder alloy in certain electronic applications [1]. Therefore, electronic industries have raised extensive concerns about the development of environmental friendly lead-free solders. As a result, many Sn-based solders are developed as alternatives to leaded solder alloys. For instance, SnAgCu (SAC), SnAg, SnBi, SnCu, and SnZnBi are the candidates to take over SnPb solder in the current electronic industries [2-4]. The most dominant lead-free solders in current industries are made up of Sn-based materials, this is because most of the properties of Sn-rich solders, such as chemical and mechanical properties are influenced by the properties of pure Sn [5].

Although there are suitable candidates to replace SnPb, they still have many unsolved problems and unknown characteristics of the lead-free solder alloy. For instance, the precise composition of the solder, large intermetallic compounds that still present in the

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microstructure and the problems of large undercooling. Consequently, some researchers have added some metal alloys or rare-earth elements into lead-free solder. For example, silver, copper, nickel, aluminum, and bismuth are added to Sn-based solder to improve the solder properties [6-9]. Based on the literature, the addition of alloying elements can strongly influence the microstructure of Sn-rich eutectic solders. With a small amount of alloying elements can enhance the properties of solder alloys, by reducing the undercooling, refine the grain structure and improve the solderability of the solder alloys [6, 8-10].

Some authors have driven further development of germanium (Ge) addition into lead-free solder. The Ge has a similar crystal structure to Sn element and they are belonging to group 14 elements in the periodic table. Therefore, researchers believe that adding an appropriate amount of Ge into the Sn-rich lead-free solder could enhance effectively the microstructure and leads to improvement in their properties. Furthermore, Ge shows a great property of anti-oxidant and dross reduction during the soldering process. Formation of dross during oxidation will influence the solderability and wetting properties of the solder. Yet, it also adds the cost of the process as maintenance is required to clean the mechanical parts damaged by the dross. Thus, it causes value loss of the solder [11]. Nevertheless, oxidation of high-temperature solder alloy also important as it might give rise to crack propagation. In the previous studies, it is proven that the growth of oxides can be inhibited by adding Ge [12, 13]. Therefore, this paper is aimed to review the effects of Ge addition on the microstructure and thermal properties of lead-free solders.

2 Effect of Ge Addition to Lead-free Solders

2.1 Microstructure

Fig. 1 (a, b) depicts the microstructure of Ge added SnCu and SnCu solder alloys. According to M. Hasnine et al. [7], the microstructure of SnCu solder alloy consists of rich beta-tin phases and Cu6Sn5 particles. It is noted that the Ge rich precipitation was not present in the microstructure. This may due to the content of Ge in the solder alloy was very low, which was only 0.01%. These results were in agreement with T.H. Chuang et al. [14]. The authors further noted that as it can be seen that after the addition of 0.5Ge into Sn-3Ag-0.5Cu-0.5Ce solder alloy, new phases were formed, which are AgSn3 and CeSn3. Furthermore, G. Meng et al. [15] stated that the microstructure of intermetallic compounds, AgSn3 and Cu6Sn5 have been refined and their dispersion tends to be well spread.

![Image of microstructure](image_url)
2.2 Thermal properties

From the results of S.H. Wong et al. [16] and his team, the melting points of Ge added solder is almost similar with and without Ge to the SnZnBi solder alloy. Referring to Fig. 3, it can be seen that the addition of a small amount of Ge does not significantly affect the melting point of the SnZnBi solder. While X.D. Zhang et al. [17] added 0.01-0.10wt% of Ge into Sn0.7Cu and the melting points were found that slightly increase with an increase in the Ge content.

In contrast, the undercooling of Sn0.7CuGe solder alloy decreased as the amount of Ge increase. As explained by M. Hasnine et al. [7] the undercooling of the solder alloy can be described as the difficulties of a solder alloy to be solidified. This is because undercooling is a period when liquid solder turns to solid, thus, the microstructure and mechanical properties can be influenced [18]. Furthermore, a large amount of undercooling can give an impact on the reliability performance of solder joints [20-21]. In view of the fact that stress concentration might occur in an uneven solidified solder and could lead to mechanical failure. Therefore, with the addition of Ge into lead-free solders is expected to enhance the mechanical properties as they have lower undercooling value.

![Fig. 2. Microstructure of (a) SnAgCu-Ce and (b) SnAgCu-CeGe solder alloy [14].](image-url)

![Fig. 3. Differential Thermal Analysis (DTA) curves of SnZnBiXGe; x = 0.1, 0.3, and 0.5 respectively [16].](image-url)

It is well acknowledged that the CTE values decrease with an increase in the amount of Ge [7]. The coefficient of thermal expansion of a solder alloy can be defined as the change in the size of the solder per degree change in temperature at the constant pressure [19]. Based on the results published by S.H. Wong et al. [16] in Fig. 4, the thermal deformation
of (Sn84Zn13Bi3)99.9Ge0.1 is almost the same as Cu, which is 17 ppm/°C. Therefore, 
(Sn84Zn13Bi3)99.9Ge0.1 / Cu joints will have the least CTE mismatch. CTE mismatch will 
cause residual stress and stress concentration to happen in between the solder and Cu 
substrate. Hence, it will lead to crack propagation to happen in the interfacial [17].

![Thermomechanical Analysis (TMA) measurement](image)

**Fig. 4.** Thermomechanical Analysis (TMA) measurement of Ge added into (a) SnZnBi and (b) SnCu 
solder alloys [7, 16].

### 3 Summary

The effects of Ge addition to lead-free solders were reviewed in this paper and be 
summarised as below:

- The dominant microstructure that presents in Ge-added solder alloy is rich beta-Sn 
  phases and Cu6Sn5. However, there are no Ge-rich phases as the amount of Ge added 
  into solder alloys is very little. Also, it would seem that the microstructure of lead-free 
  solder alloy was significantly refined with a proper amount of Ge addition.
- The addition of Ge does not significantly affect the melting points of SnZnBi and 
  SnCu solder alloys. While the degree of undercooling decreased with an increase in 
  Ge content.
- CTE of the Ge-added lead-free solder alloy was found to decrease as an increase in Ge 
  content. In the literature, a small amount of Ge content is sufficient to reduce the 
  difference of CTE of solder and Cu substrate.

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