A short review: Properties of superconducting solder

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Abstract. Development of electronic devices were moving towards miniaturization, multifunction and increasingly specific service environment of solder interconnects, where this drive to the higher requirements on the solder properties. Without solder, it would be impossible to produce the infinite electronic devices that define the 21st century. Hence, solder is important in the design and engineering process. This review paper was summarized on the literature of the low-temperature solder systems for superconducting solder materials, which provide further theoretical basis for the study of superconducting solder of electronic and aerospace applications. Pb-Bi system is the most satisfactory solder as a superconducting solder, but due to the restrictions of the lead usage, so new Pb-free superconducting solder need to be invented. Of those Pb-free superconducting materials had been studied, the Sn-In-Bi ternary solder system show the greatest superconducting properties as compared to other Pb-free superconducting solder where \( T_c = 6.9 \) K, \( H_{c2} (4.2 \) K) = 0.18 T and \( J_c (4.2 \) K, 0.01 T) = \( 1.3 \times 10^8 \) A/m\(^2\) respectively.

1 Introduction

In the electronic assemblies, solder plays an important role to hold the electronic components together while permitted various components to expand and contract, to transfer heat [1], and to conduct electrical signals [2]. Superconducting solder is crucial in the industry as standard joints between superconductors. The overall behavior of the solder interconnects are highly dependent on the performances of the solder materials and the microstructure such as residual strains, precipitates, and imperfect sintering [3]. Superconducting solders should have the properties of low melting temperature to avoid degradation of the superconducting filaments when interconnecting, good wetting properties, suitable liquid phase viscosity, and sufficient superconductivity to allow sufficient current to penetrate through the joint [4].

It has been reported that most of the superconducting solders systems are binary or ternary eutectic alloys. The dominant phase of the eutectic superconducting solder alloy act as continuous matrix holding the other disconnected phases, while the secondary phase work as the flux pinning sites to improve the magnetic irreversibility and critical current

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densities in the magnetic field [5]. Besides, at least one phase of the solder alloy must being superconducting element such as In (T_c = 3.4 K), Pb (T_c = 7.2 K), Bi (T_c = 8.7 K) or Sn (T_c = 3.7 K) [4]. In addition, Levy et al [3] also conclude the concept of flux pinning in the solder system where solder alloys with combination of superconducting and non-superconducting phase (e.g: Pb-Bi) have greater structure sensitivity compared to the solder alloys with two superconducting phases because of the interphase boundary separating a area of radically distinct electronic properties would be expected to impede the motion of flux lines.

Nevertheless, in certain condition, solute contents [5], values of critical temperature (T_c), critical field (H_c), and critical currents (J_c) of the constituent phases in the eutectic alloys will be influenced by the composition, thermal and mechanical history of the material [3, 5, 6]. For instance, Levy et al [3] reported that Sn-Zn and Sn-Cd eutectics solder alloys have H_c of ~0.1 T, but other researchers discovered much inferior values for these materials [7]. This paper reviews the research progress of the different compositions of Pb-free superconducting solder system. The effect of the solder composition to the solder properties such as T_c, H_c, and J_c of the solder system were discussed.

2 Lead-based binary superconducting solders.

The lead-bismuth alloys (Pb-Bi) is the typical superconducting solder has been practiced for many decades as a metallic superconductor. These solder interconnects were able to carry 1000 A current at 4.2 K and 1 T [8]. Fig. 1 shows the Pb-Bi phase diagram, which indicated there are ε-Pb-rich and α-Pb-rich superconducting phases in this system, but there is an extensive doubt in the ε-phase composition at the Bi-rich region due to the solidus steep gradient. These alloys have low melting temperature of 124°C (eutectic Pb_{44.5}Bi_{55.5}), high T_c = 8.4 K (Pb_{60}Bi_{40}), H_{c2} (4.2 K) = 1.77 T (Pb_{60}Bi_{40}) [6, 8], and J_c = 2.0 \times 10^8 A/m^2 [9].

![Fig. 1. Pb-Bi binary phase diagram [6].](image)

However, solid state diffusion of the phases in this system happened rapidly even at 300 K, due to the equilibrium solubility with temperature alter the structures and thus superconducting behavior is significantly alter by time at room temperature [6]. For instance, the eutectics Pb_{60.5}Bi_{35.5} H_{c2} values decline notably with room-temperature ageing, apparently due to the precipitation of Bi from the superconducting phase [5]. Moreover, Thornton [10] revealed that increasing of Bi content in the Pb-Bi solders joints in the range 30-55.5 wt% Bi could increase the J_c values due to the flux pinning at finely dispersed Bi
precipitates. The $H_{C2}$ values of Pb-Bi joints also can be reached to function at fields lower than 2 T at 4.2 K [11, 12].

Apart from Pb-Bi, the lead-tin (Pb-Sn) solder is considered most suitable mixture for soldering because it has the eutectic composition of Sn$_{37}$Pb$_{63}$ combination with melting point of 183 °C [13], relatively high $T_C = \sim 7.5$ K, good wettability, strength, and low cost. Pb permitted the solder melted at low temperature and Sn improved the wetting properties of the alloy by lending higher strength joining. The compositions usually used for superconducting solders are Sn$_{30}$Pb$_{70}$ ($T_C = 7.45$ K) [4] and Sn$_{60}$Pb$_{40}$ ($T_C = 7.05$ K) [14]. Among all these solder systems, Sn$_{60}$Pb$_{40}$ solder system is more applicable for the assembly of the superconducting joint which has a deformation range of 5 °C. Moreover, high Sn content can improve the $H_C$ value, wettability consequently reduce the liquidus temperature of the solder alloys [15]. Thus, they account 80-90% of all solders in electronics production.

The Sn equilibrium solubility in Pb is depending on temperature which differ from 29 at.% till ~2 at.% (from eutectic point till room condition). For instance, the microstructures of as-cast Pb-Bi are instable even though at room condition and the Pb phase still consist of adequate Sn in solution for post-solidification sample that aged for over one month in room condition to increase $H_C$ to 0.12 T (at 4.2 K) [5]. Consequent annealing at 170 °C then rapid cooling to cryogenic temperatures could raise both Sn content and $H_C$ to 0.19 T. Yet, room-temperature precipitation of excess Sn happened quickly in rapid cooling sample, and $H_C$ decline quickly to 0.05 T. In the Sn-Pb system, cold work also can diminish $H_C$ value mainly caused by the increasing of precipitation.

In summary, the composition of Pb$_{60}$Bi$_{40}$ is the most compromised leaded superconducting solder used as the joining for the superconducting metallic in terms of the superconducting properties. However, future research on new Pb-free superconducting solder must be invented due to the restrictions of Pb usage in the electronics application.

3 Lead-free binary superconducting solders.

Since the legislation of restriction Pb in industries with a few exceptions, it is important to invent alternative Pb-free solders that meet the elementary properties for superconducting solders [16, 17]. The superconducting solder systems are required to have low melting points, generally eutectic alloys wherein the majority phase is essential to have good superconductivity [3, 6]. Among all the Pb-free binary superconducting solders that has been studied up to date, the tin-indium (Sn-In) systems are a capable replacement for Pb-free superconducting solders according to the limited available reports which has the advantages of low melting point of 120 °C for the eutectic alloy, relatively high $T_C = 5.4 \pm 0.2$ K (Sn$_{48}$In$_{52}$) [9], higher ductility, better wetting properties, and longer fatigue life compared to the other competing Pb-free solder system [15]. Additionally, the In-rich phase in the solder system is desirable for low melting temperature and good ductility which can reduce the coefficient of thermal expansion (CTE) mismatches between component and substrate.

The binary phase diagram of Sn-In as shown in Fig. 2 (a) shows two superconducting phases, $\beta$ and $\gamma$ in this system. The $\beta$-phase has better superconductivity compared to the $\gamma$-phase where the $T_C$, $H_{C2}$ and $J_C$ values of the $\beta$-phase are 5.9 K, 0.066 T and $6.1 \times 10^7$A/m$^2$, and $\gamma$-phase are 4.5 K, 0.025 T and $1.22 \times 10^7$A/m$^2$ respectively [18], whereas Warren Jr and Bader [14] state that $\beta$-phase has $T_C$ of 6.5 K and $\gamma$-phase has $T_C$ of 4.7 K. This shows that the $T_C$ values for the intermetallic phases is highly dependence to the composition of the solder system [19]. Furthermore, Levy et al [3] proposed that strong flux pinning at the interfaces boundary in the Sn-In system by discovered a linear variation among the critical current density and the interphase boundaries density for randomly and highly oriented specimens.
Sn-In rapid cooling from the liquid state samples attain greater transition temperature (~2-3 K) compared to those of annealed samples as shown in Fig. 2 (b). There is an argument arise and state that the raise of transition temperatures is derive from the samples internal strain and not caused by short-range disorder of the structure [19], nevertheless it may cause by the $\beta$-phase variances in the composition thus result in the higher gradient to lower Sn contents of the solvus line among $\beta$ and $\beta + \gamma$ phase region. However, even optimized the binary Sn-In alloys, the superconductivity is still much lower than those required in industry.

In short, Sn-In is the best Pb-free binary superconducting solder that had been studied up to date. However, the superconductivity of the solder is highly structure sensitive. The cooling rate of the solder system could significantly affect the solder transition temperature, where quenching can improve the transition temperature.

4 Ternary superconducting solders.

Some modification has been done by previous researchers on the Pb-free superconducting solder by incorporated ternary elements into the solder to enhance the properties. Tayebeh Mousavi [18] studied that incorporation of Bi into Sn-In solders have better superconductivity, where the optimum composition for this solder system is Sn$_{35}$In$_{50}$Bi$_{15}$ which show $T_C = 6.9$ K, $H_C2$ (4.2 K) = 0.18 T and $J_C$ (4.2 K, 0.01 T) = 1.3×10^8 A/m$^2$ respectively. The improvement of the superconductivity is due to the system contain superconducting phases such as Bi-In ($T_C = 4.8$ K) and BiIn$_2$ ($T_C = 5.5$K) [21]. The superconductivity of the Sn-In-Bi shows good superconducting properties even the microstructures are relatively coarser, because the $\beta$-phase with best superconductivity is the major phase in this alloy. This can be concluded that the enhancement of $J_C$ of the solder system is mainly attributed by the intrinsically higher values of $T_C$ and $B_C2$ of the phase as compared to the interphase boundaries act as the active flux pinning sites.

Susannah Speller et al [4] discovered the addition of 5 wt% Sb into the Sn-In alloy, can improved the overall Sn-In system superconductivity where the $T_C$ and $H_C2$ values can be greatly improved, primarily the $T_C$ value improved from 4.4 K to 5.5 K. However, the low solubility (2-3wt% Sb) in the Sn-In is due to the excess Sb reacted with In alloy and result in the development of ternary In-Sb-rich phase islands and cause diminish of In content within the matrix and cause the Sn-rich $\gamma$-phase development only [4] which has lower
superconductivity than In-rich β-phase [18]. Additionally, Susannah Speller et al [4] has compared the addition of Bi and 5 wt.% Sb into Sn-In and found that the $T_C$ and $H_{c2}$ values of the Sn-In-Bi is higher than the Sn-In-Sb and conclude that the addition of Bi into the Sn-In alloy is better than Sb where it shows better superconducting properties.

In a word, the addition of ternary elements can enhance the superconducting properties and improve the reliability of the Pb-free superconducting solder. However, the addition have a critical value, where excessive addition can cause negative effect to the characteristics of the solder material. For example, excessive of Sb addition into Sn-In can lower the superconductivity of the solder. Thus, determining the optimum content is very important.

### 5 Conclusion

In spite of Pb-Bi solder satisfied all the criteria as the superconducting solder, but the prohibitions of the Pb usage in the industry has driven towards the exploration of the Pb-free superconducting solder materials. Sn-In is the most promising Pb-free binary solder system. By incorporation of Sb or Bi to the Sn-In phases, the $T_C$ and $B_{c2}$ values can be increased significantly. Sb shows lower solubility (up to 2-3wt% Sb) in the Sn-In phases than Bi, and the excess Sb in the system will cause the formation of Sb-In-rich phase islands. Bi element has greater solubility in β and γ phases, and can enhance higher superconductivity of Sn-In phases. However, even the greatest $T_C$ Sn-In-Bi alloy are still far away under the Pb-Bi alloys (8.4 K) and indicating that the suitable replacement for the Pb-Bi solder have not yet found. The undiscovered ternary Pb-free systems are a fertile field to be explored for the novel of high-performance superconducting solders.

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