Superconducting Lead-free Solder Joint: A Short Review

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Abstract. Superconducting solders are widely used as joining material to connect superconducting wires such as Niobium-titanium (NbTi) and Niobium–tin (Nb3Sn) wires in commercial superconducting magnet applications. The physical and superconducting properties of the solder materials are very important since it influence the overall performance of the joint during service. Pb-Bi solder alloy widely used due to their good properties suitable for the superconducting application, however, the restriction on the use of Pb in industry lead to the development of new Pb-free solder material. This paper reviews the superconducting Pb-free solder alternatives, including In-Sn based solder. Besides that, the effect of bismuth (Bi) and antimony (Sb) addition to the binary In-Sn solder alloy were also discussed.

1 Introduction

Solders known as fusible metal or material that become an important element since it will ensure the continuity for the production of electrical and mechanical in the electronic packaging. Previously, Tin-Lead (Sn-Pb) solders have been used for many years due to their good in chemical, physical, thermal and mechanical properties [1]. However, Pb-containing solder has been banned by legislation due to the toxic element of Pb that can cause negative effects on the human health also the environment [2, 3]. Many researches have been done to developed new Pb-free solder to replace the Pb containing solder. Generally, Tin (Sn)-based materials such as Sn-Ag-Cu [4], Sn-Cu-Ni [5], Sn-Ag [6] and Sn-Cu-Bi [7] have been recognized as important alloys for the development of Pb-free solder materials used for the electronics industry.

Eutectic lead-bismuth (Pb-Bi) solder is widely used as a connecting material between the NbTi wire and Nb3Sn conductors in the superconducting applications such as large engineering research projects for examples poloidal field coils in ITER and in the medical sector (MRI) [8]. These Pb-Bi alloy has low melting point (124 °C for the eutectic 55.5 %

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Bi composition), relatively high critical temperature, $T_c$ (~8.3 K at about 40 % Bi) and high critical field values [2]. In the future, the legislation may restrict the use of Pb-Bi solder in the superconducting application. Thus, there is also a need to explore the new solder material with suitable superconducting properties to replace the Pb-Bi solder.

The Pb-free superconducting solder candidate should fulfill several requirements such as low in melting point, satisfactory wettability, good thermal, and mechanical properties in addition, the microstructure of the solder materials also crucial due to the fact that overall performance of the solder joint will influence by the microstructure [9-11]. In this short review, the microstructure and also superconducting properties of Pb-free solder that commonly used in the electronics industry were being discussed.

2 Superconducting Joint

Superconducting joining is known as a technique used to connect the superconducting wire. This technique is requirement for the superconducting magnets operated in the persistent current mode, which are usually used in applications such as magnetic resonating imaging (MRI) systems and nuclear magnetic resonance (NMR) spectrometers [12]. NbTi wire has a critical temperature ($T_c$) of 9.2 K and it is ideal used to fabricate superconducting magnet. There are various technique used for producing the superconducting joints, including solder matrix replacement, ultrasonic welding, diffusion welding, cold-pressing, and spot welding. Among all these techniques, the solder matrix replacement method with lead-bismuth (Pb-Bi) solder become the commonly used technique in industrial [13].

Fig. 1 depicted the fabrication of a superconducting joint using the solder matrix replacing method. This joint was involve in several steps; firstly, the end of the wire was removed using abrasive paper as shown in Fig. 3a. The wires were next immersed in the molten Sn bath (Fig. 3b). After that, the Sn coated wires were then immersed in the Pb-Bi bath can be seen in Fig. 3c. The Pb-Bi solder coated the wires were then being removed from the bath and allowed to cool. Afterwards, the insulated ends of the Pb-Bi coated Nb-Ti wires were cut off. The two wires were aligned, twisted, and tightened with fine Cu wire in open air to enhance their electrical and mechanical properties, as shown in Fig. 3d. Finally, the twisted wires were again immersed in a Cu tube filled with molten Pb-Bi (Fig. 3e) [13].

3 In-Sn Solder

The conventional In-Sn lead (Pb) free solder has become the promising candidate for replacing Pb containing solder in the superconducting joint [8, 14]. The composition of In$_{65}$Sn$_{35}$ solder that contains a matrix of In-rich $\beta$ (In$_3$Sn) containing the Sn-rich $\gamma$-phase (In$_4$Sn) has been explore as potential replacement materials. Mousavi et al. have investigated the influence of chemistry and microstructure on the In-Sn solder on the
superconducting properties. According to their findings, both β and γ phase was stable over a wide range of chemical composition, with improving superconducting properties for each phase as increasing in solute concentration. The best superconducting properties can be achieved when the alloys have a high volume fraction of β phase [14]. Studied by Tsui et al. found that superconducting properties of In₅₂Sn₄₈ solder has low in $B_{c2}(T)$ and critical temperature ($T_c$) than Pb-containing solder as tabulated in Table 1 [15]. Moreover, more effort has been done to improve the In-Sn solder through microalloying with other elements such as bismuth (Bi) [2, 8, 9, 14], tantalum (Ta) and antimony (Sb) [16].

Table 1. The melting point, resistivity, and superconducting properties of the solders [15].

| Solder Alloy         | Melting Point °C | $\rho$ (Room Temp.) $10^{-7}$ Ωm | $\rho$ (77 K) $10^{-7}$ Ωm | $T_c$ K | $B_{c2}$ (0 K) T |
|---------------------|------------------|----------------------------------|----------------------------|--------|------------------|
| Bi₃₀Pb₁₀In₂₀Sn₄₀    | 58               | 9.4                              | 8.1                        | 6.4    | 3.3              |
| Pb₅₀Sn₄₀Bi₂₀        | ~96              | 5.5                              | 2.6                        | 8.4    | 2.3              |
| Pb₅₀Sn₄₀Bi₃₀        | ~170             | 2.6                              | 1.1                        | 8.5    | 2.2              |
| In₅₂Sn₄₈            | 118              | 2.6                              | 1.3                        | 6.4    | 0.34             |
| Pb₂₀Sn₆₂            | 183              | 1.5                              | 0.48                       | 7.3    | 0.30             |
| Pb₃₈Sn₆₂             | 200-230          | 6.1                              | 3.7                        | 8.5    | 2.5              |
| Pb₃₈Bi₅₆Sb₇         |                  |                                  |                            |        |                  |

3.1 In-Sn Solder Microalloyed with Bismuth Addition

The properties of Pb free solder alloy can enhance by adding the third or fourth element. Recently, bismuth (Bi) was added into binary In-Sn solder to improve the performance of the superconducting joint. Mousavi et al. have investigated the influence of the different composition of Sn-In-Bi solder alloy on the properties of the superconducting solder joint. The four ternary alloys that had been studied on the calculated ternary Sn–In–Bi phase diagram as shown in Fig. 2(e). From the finding in Fig. 2 (a-d), ternary Sn-In-Bi solder alloy contains the In-rich β phase, Sn-rich γ phase with more superconducting phases, including BiIn and BiIn₂. Based on the Fig. 3, the Sn₅₂In₃₀Bi₁₅ solder was the best superconducting properties achieved in Sn–In–Bi phase diagram systems. The solder composition consisting of a majority phase β-phase in which fine fibers of γ and BiIn₂ are embedded [14].

![Fig. 2. (a-d) Phase maps of the four studied ternary Sn–In–Bi alloys. Pink colour represents the β phase, blue the γ phase, orange BiIn₂ and red BiIn [14] and (e) In-Sn-Bi phase diagram [17].](image-url)
The interaction of Nb (47wt.%Ti) superconducting filament with liquid ternary (In(In50-Bi15)Sn35(In54.3Sn36.8Bi8.9 at.%) was studied by Santra et al. There are three phases detected, β, γ, and BiIn2 existed as shown in Fig. 4. Interaction of NbTi with ternary (In,Bi)Sn results in a lack of any detectable interaction zone. In addition, morphology and chemical composition of the superconducting joints were influenced by the size of NbTi filament [8].

3.2 In-Sn Solder Microalloyed with Antimony Addition
The microstructure and superconducting properties Sn-In-Sb solder alloy were investigated by Mousavi et al. [16]. As shown in Fig. 5, SnIn-γ is the majority phase with low solubility of Sb in the matrix of γ phase. Moreover, the presence of Sb helps to improve the superconducting properties by increasing the $T_c$ and $B_{c2}$ values.
4 Conclusion

The superconducting properties of Pb-free solder such as In-Sn binary solder alloy can be enhanced by dissolving the third element. The addition of alloying elements such as Bi and Sb into the Sn-In phase (Sn-rich γ and In-rich β) can significantly increase the $T_c$ and $B_{c2}$ values which resulting in an improvement in the superconducting properties of the solder. Further research in developing a reliable Pb-free superconducting solder joint was required to search for the solder replacement of Pb-Bi solder.

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