Novel Superconducting Joints for Persistent Mode Magnet Applications

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ABSTRACT

Persistent current joints are a critical component of commercial superconducting magnets.The standard jointing method widely used in the magnet industry for technological low temperature superconducting wires such as NbTi and Nb_3Sn wires uses a superconducting solder (e.g. PbBi). In these joints the physical and superconducting properties of the solder materials inevitably play an important role in the overall performance of the joint. Key requirements for superconducting solders include low melting point to prevent degradation of the superconducting filaments during joining, good wettability of the superconducting filaments, suitable liquid phase viscosity, and finally adequate superconducting properties to enable sufficient supercurrent to pass through the joint under typical operating conditions (typically at 4.2K in a field of 1 T for an MRI magnet). PbBi solder satisfies all these criteria, but restrictions on the use of lead in the magnet industry are expected in the relatively near future, so new lead-free jointing techniques need to be developed.

One approach is the development of superconducting lead-free solder materials. In our work, we have focussed on the In-Sn system and ternary systems involving In and Sn as two of the elements. Thermodynamic modelling has been used to produce ternary phase diagrams of potential alloy systems, and various formulations have been fabricated in order to explore how microstructure and phase chemistry influence the superconducting properties of the solders. Alternative approaches to fabricating lead-free joints, including spot welding and cold-pressing, have also been investigated. These methods have the potential advantage of achieving direct NbTi-NbTi joints with no intermediate, lower performance superconducting material. The spot welding method produced joints with the best superconducting performance, signifiantly better than the currently used PbBi solder, but the lack of reproducibility in this technique may be a problem from an industrial point of view.

INTRODUCTION

Persistent current joints between technological superconductors with operational resistances below ~10^{-12} Ω are essential requirements for the large magnets that are needed for devices such as magnetic resonance imaging (MRI) scanners and nuclear magnetic resonance (NMR) spectrometers. In such applications, soldering is currently employed for making persistent mode joints with extremely low resistances between NbTi wires using Pb-Bi alloys as the superconducting solders [1-3]. However, for environmental reasons it is crucial to develop alternative Pb-free solders which satisfy the basic requirements for superconducting solders in this application, such as low melting temperature (lower than 500ºC to protect the NbTi wires), appropriate thermal and mechanical properties and a high enough critical current density under typical practical operating conditions (4.2 K and 1 T).

The requirement for low melting points means that the superconducting solder systems are usually eutectic alloys in which at least the majority phase must have good superconducting properties [4-5]. Some Pb-free superconducting solders were briefly explored in the literature in the 1960s, containing at least two low melting point elements selected from Sn, Bi, Cd, In, Zn and Sb [5, 6]. No recent research has been done on these Pb-free solders because PbBi alloys shows such excellent superconducting properties and could easily satisfy the needs of magnet manufacturers. Of the Pb-free solders, Sn-In alloys seem to have the most promising superconducting properties according to the limited available reports [6]. We have studied this system in detail to understand the relation between superconducting properties and the microstructure to see if there are opportunities to produce alloys to compete with PbBi by optimising the microstructure [7,8]. It was shown that the superconducting properties of both ß and γ phases improve with increasing solute concentration, and that the In-rich ß phase has better superconducting properties than the Sn-rich γ phase. Moreover, the interphase boundaries are active pinning sites and so refinement of the microstructure results in an enhancement in critical current densities [7]. However, even with optimised performance, the superconducting properties of the binary Sn-In alloys (J_C and B_{C2} values) are much lower than those required in industry and still need to be improved [7, 9]. One approach to improve these properties can be adding a third element to binary Sn-In alloys. This study focuses on the effect of adding Bi, Ta and Sb to the Sn-In system, and discusses how the presence of the third element alters the microstructure and superconducting properties of Sn-In solders.

EXPERIMENT

Different Sn-In-A (A: Sb, Ta, Bi) alloys (listed in Table 1) were fabricated from commercial Sn, In, Ta, Sb and Bi powders (with purities better than 99.9%) by weighing the powders and melting the mixture at temperatures up to 400°C on a hot-plate. The melt was either cast into a Cu-mould or sucked into pre-heated quartz tubes to form convenient cylinders with 2 mm diameter for magnetometry measurements. The superconducting properties were investigated by measuring the magnetization using a Quantum Design SQUID magnetometer. Magnetisation-Temperature curves were obtained in a range of applied magnetic fields.

The microstructure and chemistry of the samples were characterized using scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) analysis respectively in a Jeol 5510 SEM with OI SDD detector and a Zeiss Evo SEM, both operating at 20kV accelerating voltage. The phase maps were generated by the Oxford Instruments Aztec software, and the average composition of each phase and the phase fraction were calculated from reconstructed spectra from each phase in the map.

DISCUSSION

SnInSb-1: Sn-30wt%In-5wt%Sb

Our first attempt to improve the superconducting properties of Sn-In solders was by the addition of Sb. A small amount of Sb (5wt%) was added to the Sn-In solder to investigate how Sb reacts with the Sn-In alloys, and whether it can be dissolved into the β and γ phases and improve

Table 1- The list of samples studied in this work and their compositions.

Sample	Sn (wt%)	In (wt%)	Bi (wt%)	Sb (wt%)	Ta (wt%)
SnTa	80	-	-	-	20
SnInTa	31	59	-	-	10
SnInSb-1	65	30	-	5	-
SnInSb-2	35	50	-	5	-
SnInBi	35	50	15	-	

their superconducting properties. Figure 1 shows the elemental maps of sample SnInSb-1 along with the extracted phase map. As the Sb map shows, Sb is segregated into individual islands where the In content is also high. Apart these In-Sb rich islands, the In and Sn are uniformly distributed across the sample making a uniform matrix. The phase map extracted from this EDX mapping data shows two distinct phases. From the reconstructed EDX spectra, the composition and phase fraction of each phase were obtained (Figure 1e and f). The microstructure is composed of γ-SnIn (with composition Sn-24wt%In-2wt%Sb) as the majority phase forming the matrix, and a small fraction of 10 µm ternary InSbSn islands (approximately 4 vol% of the whole sample) with a composition of In-36wt%Sb-14wt%Sn. This result shows that Sb only has a low solubility in the matrix SnIn-γ phase.

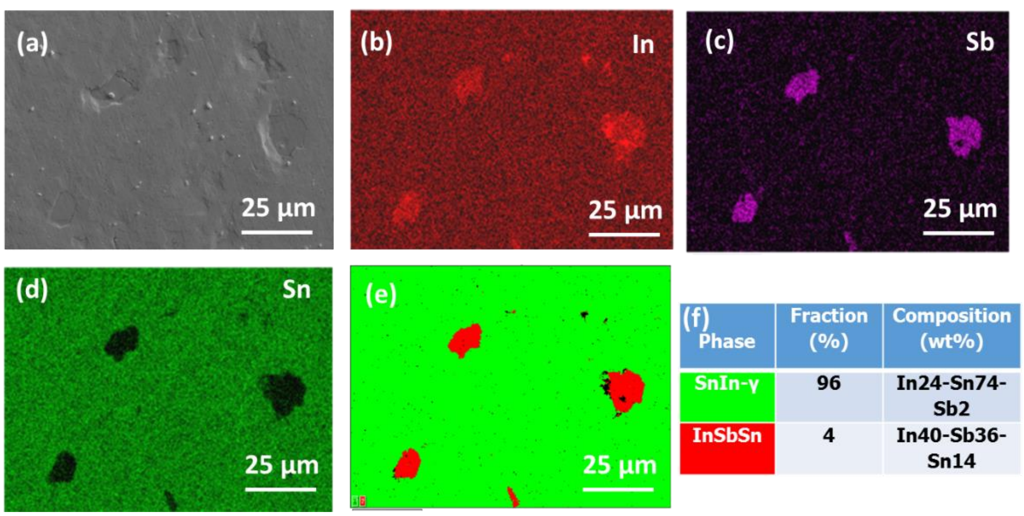

Figure 1: (a) SE image, (b-d) In, Sb and Sn maps, (e) phase map, and (f) table showing phase fraction and the composition of each phase in sample SnInSb-1.

SnInSb-2: Sn-50wt%In-5wt%Bi

In the first alloy, the indium reacted with Sb to form the islands of the ternary InSb-rich phase. This led to a reduction of In content in the matrix resulting in the formation of only the Sn-rich γ phase. However, it has been shown that the In-rich β phase has better superconducting properties than the Sn-rich γ phase [7]. By increasing the In content in the second sample (Sn-50wt%In-5wt%Sb), the aim was to form a substantial volume fraction of the In-rich β phase, and to investigate how Sb reacts with this phase. Typical elemental maps of this alloy are presented in Figure 2. As can be seen, the precipitates of the ternary InSbSn phase still exist at a similar scale, chemistry and volume fraction compared to the previous sample. However, the Sn and In segregate at a scale of 10 microns leading to the formation of two phases in the matrix: Sn-25wt%In (Sn-rich γ phase) and In-40wt%Sn (In-rich β phase). Both of these phases contain only a small amount of Sb (about 2%) showing that Sb has limited solubility in the β as well as the γ superconducting phase.

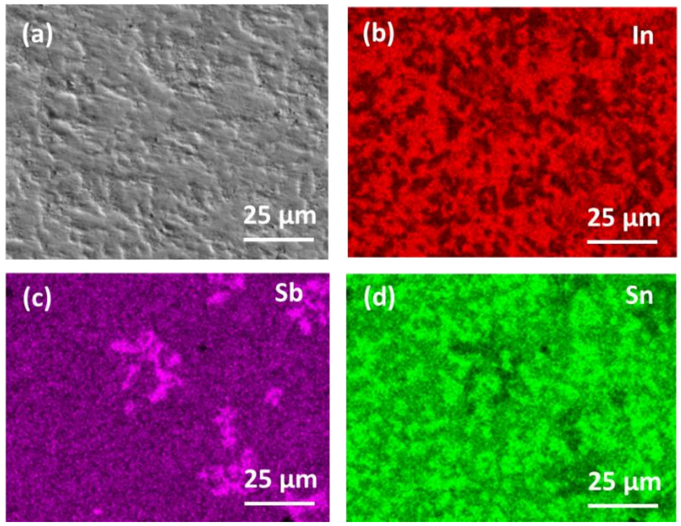

Figure 2: (a) SE image, (b-d) In, Sb and Sn maps of sample SnInSb-2.

Sn-In-Ta system

It has been reported that $SnTa_3$ has T_C and B_{C2} values of about 8K and 6080 Oe respectively [9], higher than the typical values in Sn-In alloys. If this phase is formed in a low melting-temperature matrix (eg. Sn or SnIn), the mixture might have the advantages of both low-melting temperature and good superconducting properties, and so may perform as a good superconducting solder. To investigate this, samples of binary Sn-Ta and ternary Sn-In-Ta were made by adding Ta powder (3-5 µm) into a Sn bath and Sn-65wt%In bath respectively at about 400ºC (the practical temperature for soldering superconducting wires). The mixtures were held for 2 hours at this temperature. Unfortunately, SEM analysis of these samples shows that no reaction occurs between the solid Ta and liquid Sn at this temperature. As can be seen in Figure 3, pure metallic Ta particles are present in the matrix with no reaction with Sn. Similar results were found for the SnInTa sample (ie. no reaction between Ta and In) showing that such reactions need higher temperatures which will be far from the practical temperature for soldering of superconducting wires.

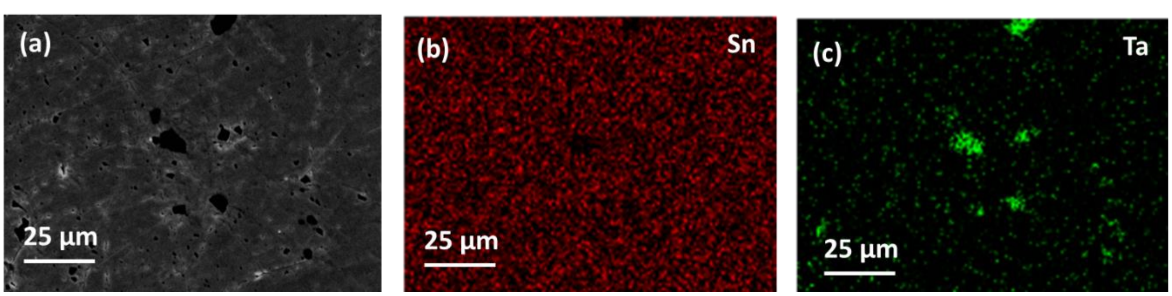

Figure 3: (a) SE image, (b) Sn map and (c) Ta map of sample Sn-Ta.

Superconducting properties

Figure 4 shows B_{C2} values as a function of temperature for the samples studied in this work. For comparison, the superconducting properties of PbBi ($Pb_{60}Bi_{40}$), the Sn(In)-γ phase, Sn(In)-β phase and ternary SnInBi alloys studied in earlier work [7] have been also added to the graph. By comparing sample SnInSb-1, which mostly contains the γ phase with a low concentration of dissolved Sb, with the pure Sn(In)-γ phase, it can be found that the presence of Sb in γ does improve the superconducting properties, particularly the T_c value which is increased from 4.4 K to 5.5 K. Similarly, by comparing the SnInSb-2 sample, which is mostly composed of the In(Sn)-β phase with dissolved Sb, with the pure In(Sn)-β phase, the dissolved Sb seems to increase both T_C and B_{C2} values. As a result, adding 5wt% Sb to the Sn-In alloys leads to a modest improvement in overall superconducting properties. Similar results have been obtained in the Sn-In-Bi system where the addition of Bi results in solders that show better superconducting properties than the binary Sn-In alloys [7]. According to Figure 4, alloys in the SnInBi system show higher T_C and B_{C2} values than the SnInSb alloys tested here. However, it should be noted that the ternary SnInBi alloy reported in Figure 4 is the best alloy we have have found in this system in terms of superconducting properties based on a systematic study of different ternary alloys, whereas in the Sn-In-Sb system, only two different compositions both containing only 5wt% Sb were studied, and there might be other alloys in this system with better T_C and B_{C2} values. It can be also noticed that the superconducting parameters of all these Pb-free alloys are still considerably lower than those for PbBi, indicating that we have not yet found a suitable replacement for the PbBi solder.

The SnTa sample also shows low T_C and B_{C2} values, similar to those of Sn [10]. This is expected from the microstructure of this alloy which is composed of a pure Sn matrix with no dissolved Ta (Figure 3).

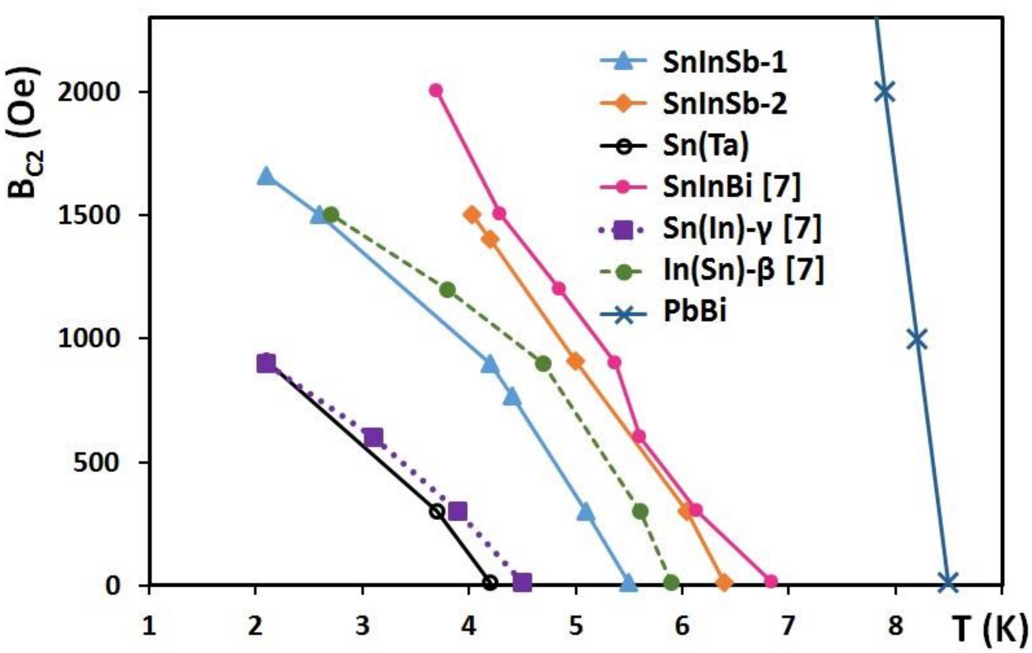

Figure 4: (a) B_{C2} as a function of temperature for the different solder samples studied in this work and some samples from [7]. (Each data point in the graph is the transition temperature obtained from a M/T measurement at the corresponding applied field).

CONCLUSIONS

The superconducting properties of Sn-In binary alloys can be improved by dissolving a third element. By adding either Sb or Bi into the Sn-In phases (Sn-rich γ and In-rich β), the T_C and B_{C2} values can be increased significantly. At the temperatures we have used, Sb shows lower solubility in these phases than Bi. Up to 2-3wt% Sb can be dissolved into the SnIn phases at room temperature, and the excess Sb in the alloy will form the islands of an SbIn-rich phase. Bi has a higher solubility in both γ and β, and has a greater influence on enhancing the superconducting parameters of these Sn-In phases. However, both of these two ternary systems have much lower B_{C2} and T_C values than the currently used PbBi alloys, and cannot be considered as a good replacement for this alloy unless their properties are further improved. In the Sn-In-Ta system, no reaction occurs at the practical temperature of soldering (400ºC) between Ta and Sn-In, and no solubility of Ta in the Sn-In superconducting phases was observed. As a result, the microstructure is composed of a matrix of Sn-In phases with unreacted Ta particles, and T_C and B_{C2} values show no improvement.

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