High-temperature-tolerable superconducting Nb-alloy and its application to Pb- and Cd-free superconducting joints between NbTi and Nb₃Sn wires

Nobuya Banno^{1,*} , Kensuke Kobayashi¹, Akira Uchida¹, and Hitoshi Kitaguchi¹

¹ National Institute for Materials Science, Tsukuba, Japan

Received: 2 July 2021

Accepted: 28 September 2021

Published online:

13 October 2021

© The Author(s) 2021

ABSTRACT

For more than 30 years, Pb–Bi alloy and Wood’s metal (50% Bi, 26.7% Pb, 13.3% Sn, and 10% Cd) have been used as representative superconducting solder intermedia to establish superconducting joints between NbTi and Nb₃Sn wires in high-field nuclear magnetic resonance magnet systems. However, the use of Pb and Cd has been severely restricted by environmental regulations, such as the Restriction of Hazardous Substances Directive. Herein, a novel method of forming a superconducting joint between NbTi and Nb₃Sn wires without Pb and Cd has been proposed. This approach is based on metallurgical bonding processes using a superconducting Nb-alloy intermedium, whose fine microstructure is maintained even after exposure to temperatures higher than 650 °C. Further, fine crystal defects become sources of magnetic flux pinning centers. Among transition elements close to Nb, Hf is considered the most suitable additive for realizing high-temperature-tolerable (HTT) superconducting Nb-alloy intermedia. Utilizing the HTT characteristic of Nb–Hf, a superconducting joint between Nb₃Sn filaments and one end of the Nb–Hf alloy core was created by forming a superconducting Nb₃Sn layer at the interface through a chemical reaction. The other end of the Nb–Hf alloy core was cold-pressed with NbTi filaments, to connect their active new surfaces to each other in order to create a superconducting joint. Ultimately, a superconducting joint between NbTi and Nb₃Sn wires was realized with a high critical magnetic field (B_{c2}) of more than 1 T. The formation of the superconducting joint was confirmed by current decay measurements. This method of forming a superconducting joint is promising for application in environmentally friendly nuclear magnetic resonance magnet systems.

Handling Editor: Catalin Croitoru.

Address correspondence to E-mail: banno.nobuya@nims.go.jp

GRAPHICAL ABSTRACT

High temperature tolerable (HTT) Nb-alloy

800 °C x 3 h

SC joint between NbTi and Nb₃Sn

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is an essential analytical tool in biology, chemistry, and materials science and requires *operation in persistent current mode* for temporal field stability and a high signal-to-noise ratio. To date, Pb–Bi and Wood’s metal (50% Bi, 26.7% Pb, 13.3% Sn, and 10% Cd) have served as superconducting intermedia to join separated superconducting wires to each other in NMR magnets [1, 2]. Pb–Bi and Wood’s metal have relatively high critical magnetic fields (B_{c2}) of more than 1.5 [3–5] and 1.0 T [6] at the liquid helium temperature, respectively. These superconducting solders are now indispensable materials, especially for achieving superconducting joints between NbTi and Nb₃Sn wires in high-field NMR magnet systems [1, 2].

However, Pb and Cd are toxic. Their use has been severely restricted by environmental regulations, such as the restriction of hazardous substances (RoHS) directive. The utilization of these materials is permitted only after an approval of exemption, and the preparation for this procedure is costly. Furthermore, the use of these materials may be entirely prohibited in future. Therefore, there is an urgent need to develop new methods for realizing Pb- and Cd-free superconducting joints in industry.

Two possible solutions are considered to overcome the aforementioned challenges. The first is the development of new Pb- and Cd-free superconducting solders. Based on this approach, InSn-based alloy was developed. [7–9]. Although this material was demonstrated to be a promising candidate, it only showed a maximum B_{c2} of approximately 0.2 T. Moreover, to date, there has been no report on the successful formation of a superconducting joint between NbTi and Nb₃Sn wires using this material.

The second solution is the utilization of a metallurgical reaction process for bonding without a solder. However, this approach remains largely unexplored. Metallurgical processing without a solder for establishing superconducting joints between NbTi and Nb₃Sn wires becomes difficult to achieve due to two main reasons. The first is the mechanical problem of Nb₃Sn. NbTi is a body-centered cubic alloy in which Ti dissolves in Nb. Solid solution NbTi is ductile, which enables superconducting joints to be established by connecting their active new surfaces to each other through mechanical pressing [10–12]. In contrast, Nb₃Sn is an intermetallic compound with an A15-type lattice structure [13, 14], which is so brittle that mechanical pressing cannot be applied.

The second reason is the rapid deterioration of the superconducting properties of NbTi after exposure to high temperatures. Figure 1 shows critical current (I_c)– B characteristics before and after heat treatment

Figure 1 Critical current versus magnetic field of standard Nb-62.8 at%Ti wire (SRM 1457) before and after heat treatment at 100 h/685 °C.

at 100 h/685 °C, where the wire employed is standard reference material (SRM) 1457 of the National Bureau of Standards using Nb-46.5wt%Ti (Nb-62.8%Ti). A superconducting joint between NbTi and Nb₃Sn can be achieved via a chemical reaction process. In fact, we confirmed that the Nb₃Sn layer can be formed at the interface as a superconducting pathway between the NbTi and Nb₃Sn filaments through a Sn diffusion heat treatment process. However, the transport properties of the joint sample were unsatisfactory because of the degradation of the NbTi properties. Thus, there was no alternative to incorporating superconducting solders that turn into liquid at low temperatures, between the NbTi and the brittle Nb₃Sn superconducting filaments without damage.

In view of this, a novel method utilizing a Nb-based ductile superconducting alloy as an inter-medium was introduced in this study. The I_c of this superconducting alloy does not deteriorate even after exposure to the Nb₃Sn layer formation temperature, which is typically higher than 650 °C. Utilizing this material, superconducting joints were established with NbTi through mechanical pressing and with Nb₃Sn through a chemical reaction process to form a Nb₃Sn superconducting layer at the interface; ultimately, a superconducting joint was realized between the NbTi and Nb₃Sn wires.

The Nb alloy follows the Ginzburg-Landau-Abrikosov-Gorkov (GLAG) theory [15, 16]. This theory has motivated many microstructural studies of Nb

alloys related to their superconducting properties, dating back to the 1960s [17–22]. The GLAG theory predicts the upper critical field (B_{c2}) at 0 K to be given by $B_{c2}(0) = 3.11 \times 10^3 \rho_n \gamma T_c$, where ρ_n , γ , and T_c are the normal state resistivity, electronic specific heat coefficient, and critical temperature, respectively [15, 16]. The severe deformation of the Nb-alloy solid solution phase leads to the development of a dense dislocation cell structure in the polycrystalline Nb alloy grain morphology following the formation of a preferred orientation or texture. This fine nanoscale microstructure increases ρ_n , thereby increasing B_{c2} . In the case of NbTi, B_{c2} reaches 11 T from a bulk value of approximately 1.5 T. The fine microstructure also contributes to the improvement of the flux pinning property, which is essentially related to the critical current density (J_c) [23–25]. Furthermore, in the Nb-Ti system, precipitation of dense nanoscale α -Ti ribbons can also provide a large additional pinning force [26–29]. However, the fine microstructure becomes coarse after heat treatment at temperatures higher than 650 °C.

Thus, it can be inferred that the key to developing such high-temperature-tolerable (HTT) superconducting Nb-alloys is to create a nanoscale fine microstructure in the alloy and maintain the microstructure even at high temperatures. Recently, Balachandran et al. [30] reported an interesting finding in their Nb₃Sn work that the fine microstructure of the unreacted Nb-Ta-Hf core was maintained after Nb₃Sn layer formation annealing. Following this, a group of researchers, which included the author of this paper, confirmed that Nb with a small addition of Hf has a high recovery temperature of more than 700 °C through a Nb₃Sn layer formation study [31]. This Nb alloy maintains a fine microstructure even after annealing at 800 °C for 3 h. Figure 2 shows an electron backscatter diffraction (EBSD) inverse pole figure (IPF) map and image quality (IQ) map of the microstructure of Nb-4 at%Ta-1 at%Hf bulk tape with severe deformation, before and after annealing. Inspired by these findings, the author of this paper considered this material to be a promising candidate for HTT Nb alloys.

In this work, we explored promising HTT Nb alloys that can be used for establishing superconducting joints between NbTi and Nb₃Sn wires, and successfully developed a Pb- and Cd-free superconducting joint between NbTi and Nb₃Sn wires using the HTT Nb alloy. The realization of the

Figure 2 EBSD IPF and IQ maps of the microstructure of Nb–4at%Ta–1at%Hf bulk tape with severe deformation, before and after annealing at 3 h/800 °C.

superconducting joint was confirmed by ultra-low resistance measurements using a current decay measurement system [32].

Materials and methods

Materials

HTT superconducting Nb-alloys were synthesized with transition metals of Groups 4B–6B, which comprise a ductile body-center-cubic (BCC) superconducting Nb alloy. In particular, Ti and Zr are known to be effective additive elements to improve the superconductivity of Nb substantially after deformation [17, 20]. Bulk alloys consisting of two or three elements were first formed by arc-melting. The as-cast bulks were cold-drawn by grooved-rolling. Subsequently, the bulks were re-arc-melted for homogenization.

Test wires to assess the superconducting properties of Nb alloys

A fine nanoscale microstructure, which is important for improving the superconducting properties, is created in the alloy by fabricating single-core composite thin tapes. The superconducting properties such as B_{c2} and I_c of the tape wires are checked before and after heat treatment at 685 °C for 100 h, which is a typical Nb₃Sn layer formation condition. The NbTi SRM wire was used as is in a round wire shape.

The arc-melted Nb-alloy bar was swaged down to Ø5.5 mm and annealed at 900 °C for 5 h in a vacuum. The bar was inserted into a Cu tube with outer and inner diameters of 8 and 6 mm, respectively, and cold-drawn to a wire Ø1–1.34 mm. Then, single-core composite thin tapes were fabricated by flat-rolling the single-core Cu/Nb-alloy wire: the tape had a thickness of 0.16–0.33 mm and a width of 2.5–4.2 mm. The rolling reduction ratio was approximately 400–550%.

I_c was measured at 4.2 K using a standard four-probe method with a tap distance of 1 cm and defined with a criterion of 1 μV/cm. The magnetic field was applied perpendicular to the tape axis and parallel to the tape surface. B_{c2} was determined as a magnetic field at which I_c becomes almost zero. The n -values ($V \propto I^n$, where V and I are the transition voltage and transport current, respectively) were obtained by fitting the V – I curve in the range of approximately 0.1–1.0 μV. Cryogenic measurements were performed at the Tsukuba Magnet Laboratory, National Institute for Materials Science (NIMS), Japan.

Joining process

Figure 3 shows a schematic illustration of the developed joining process and a fabricated joint sample. The process basically consists of two steps: in step 1, the Nb₃Sn filaments and HTT Nb alloy are connected via a metallurgical chemical reaction, and in step 2, the HTT Nb alloy and NbTi filaments are joined via mechanical bonding.

In step 1, at first, one end of the Nb₃Sn precursor wire, which is to serve as one end of the Nb₃Sn coil, is chemically etched via HNO₃ to remove the outer Cu sheath. Subsequently, the diffusion barrier inside the Nb₃Sn precursor wire is mechanically polished to expose the Nb filaments. Typical practical Nb₃Sn

Figure 3 Schematic illustration of the developed joining process and picture of a fabricated joint sample.

precursor wires have Cu stabilizers and diffusion reaction barriers of Nb or Ta around the multifilamentary region consisting of Nb filaments and a Cu–Sn matrix. The wire tested in this study was a typical internal-Sn Nb_3Sn wire with a diameter of 0.8 mm, consisting of 1045 Nb filaments, which was fabricated in our laboratory. A detailed description of the wire configuration can be found in the literature [33].

Second, one end of the HTT Nb alloy is chemically etched via HNO_3 to remove the outer Cu sheath. Then, the end of the Nb_3Sn precursor wire is wrapped spirally by the end of the HTT Nb-alloy tape, followed by pressing it with a supporting metal tube to connect the active new surfaces of the filaments and the tape core. In this study, a Nb tube with outer and inner diameters of 6 and 5 mm, respectively, and a length of 15 mm was used. The pressed length of all the joint parts was almost 1 cm, and the pressure was set approximately 120 kN.

Finally, the Nb_3Sn layer formation heat treatment is performed at 685 °C for 100 h in a vacuum. In the final stage, Sn diffuses from the Cu–Sn phase into not only the Nb filaments of the Nb_3Sn precursor wire, but also the surface of the HTT Nb-alloy core and the interface between the Nb filaments and the HTT Nb alloy core, where it subsequently forms the Nb_3Sn superconducting layer.

In step 2, at first, one end of the NbTi wire, which is to serve as one end of the NbTi coil, is chemically etched to remove the Cu matrix and expose the NbTi filaments. In typical NbTi wires, NbTi filaments are

embedded into the Cu matrix and twisted. The exposed bundle of NbTi filaments is untwisted back before being connected with the HTT Nb-alloy by cold-pressing to avoid filament crossing as much as possible during pressing. The Cu sheath of the other end of the HTT Nb-alloy tape is chemically etched as well. The end of the NbTi wire is wrapped spirally by the end of the HTT Nb-alloy tape and pressed with a supporting metal tube to interconnect the active new surfaces of the filaments and tape core. In this study, a Nb tube with outer and inner diameters of 6 and 5 mm, respectively, and a length of 15 mm was used. The pressed length of all the joint parts was almost 1 cm, and the pressure was approximately 120 kN.

Nb has a fairly high O affinity, easily forming a stable thin oxide layer on the NbTi filaments and HTT Nb alloy surface. The existence of an oxide layer suppresses the connection area between new surfaces. Such poor physical connectivity could be improved through additional annealing at a moderate temperature of approximately 450 °C. This additional annealing does not affect the properties of the Nb_3Sn wire and the Nb_3Sn layer formed at the joint interface, because this temperature range is much lower than the Nb_3Sn layer formation temperature.

Microstructural and microchemical analysis

The microstructures were observed using a field-emission scanning electron microscope (FESEM). Compositional analysis was performed by energy-

dispersive X-ray spectroscopy (EDS). Polished samples were prepared with a standard micrographic technique, where a sample was embedded in a conductive phenolic resin and finely polished with a 0.05 μm sol-gel alumina suspension. The grain orientation maps of the microstructure were measured by EBSD analysis.

Current decay measurement

In general, the resistance of a superconducting joint is lower than $10^{-12} \Omega$. The four-probe method is not applicable for such small resistance measurements. Therefore, current decay measurements were carried out here to evaluate the joint resistance, and to confirm the formation of the superconducting joint. The details of the measurement method are described in [32]. The measurements were carried out as follows. First, a single-turn loop consisting of superconducting wires with joints is set in a cryostat, and a current is injected into the loop by magnetic induction. A temporal evolution of the magnetic field around the wire, i.e., current decay, is measured using a Hall sensor. Eventually, the joint resistance can be obtained from the current decay constant ($= L/R$, where L and R are the self-inductance and the joint resistance of the loop, respectively). The loop sample has four joints, i.e., two NbTi wire/HTT Nb-alloy tape joints, and two Nb₃Sn/HTT Nb-alloy tape joints, which is needed to connect one NbTi wire to one Nb₃Sn wire with two HTT Nb-alloy tapes. The self-inductance of the single-turn loop was found to be 0.47 μH in this system.

Results and discussion

Superconducting properties of Nb alloys

Figure 4 summarizes the representative values of B_{c2} , I_c , and n at 4.2 K of the fabricated Nb alloy composite tapes, after heat treatment at 685 °C for 100 h in a vacuum. Figure 5 shows I_c versus the magnetic field (B) of the representative samples. The error bar indicates a measured data range. The I_c values of the tape specimens slightly scattered, which is attributed to nonuniformity caused by the laboratory-scale flat-rolling process. The NbTi SRM wire showed good homogeneity along the wire axis. Notably, 3 at%Hf addition to Nb retains a B_{c2} value of 1.15 T and

	4B	5B	6B
B_{c2}	-62.8Ti 11.5 $\rightarrow$ 1.5 T	V	Cr
I_c	37.4 A@0.5 T		
n	32 @0.5 T		
B_{c2}	-5Zr 2 T (ref.) $\rightarrow$ not measured	Nb 0.41 $\rightarrow$ 0.31 T	Mo
I_c	No data	31 A@0.25 T	
n	No data	46 @0.25 T	
B_{c2}	-3Hf 1.35 $\rightarrow$ 1.15 T	-4Ta-1Hf 0.8 $\rightarrow$ 0.62 T	-2W 0.65 $\rightarrow$ 0.52 T
I_c	65 A@0.95 T	149 A@0.5 T	229 A@0.35 T
n	65 @0.95 T	125 @0.5 T	60 @0.35 T

* B_{c2} : values before and after annealing at 685 °C $\times$ 100 h.

** I_c and n : values after annealing at 685 °C $\times$ 100 h.

Figure 4 Representative values of B_{c2} , I_c and n -value at 4.2 K of the Nb-alloys with addition of transition elements close to Nb, after the heat treatment at 100 h/685 °C. B_{c2} of as-deformed Zr-added Nb-alloy was referred to [34].

Figure 5 I_c versus B of the representative Nb-alloy samples. Nb-3Hf and Nb-2 W are tapes with dimensions of 4.17 mm^w $\times$ 0.33 mm^t and 3.27 mm^w $\times$ 0.186 mm^t, respectively.

maintains a steep I_c - B curve even after heat treatment; I_c and n show values of 65 A and 65 even at 0.95 T, respectively. The Nb-3Hf alloy remained reasonably ductile, which enabled bonding it to NbTi mechanically. The B_{c2} value of 1.15 T is sufficient given the requirements of superconducting joints, because joints can be located in a field of 0.5 T in

magnet systems. Further optimization of B_{c2} and I_c needs to be performed. Presumably, B_{c2} and I_c can be furthermore enhanced by the increase in additive content as well as deformation degree. However, this may worsen drawability owing to the increase in solid-solution hardening.

In contrast, although Nb–62.8%Ti can maintain a B_{c2} value of approximately 1.5 T after heat treatment, the I_c – B curve becomes markedly gentle with rapid I_c degradation; the I_c and n values at 0.5 T decrease to only 37 A and 32, respectively. Figure 6 shows a SEM image and EDS maps of the NbTi filament after heat treatment. As observed, Nb aggregated in the filaments, and Ti and Cu were interdiffused. Presumably, the Nb containing a small amount of Ti determined the B_{c2} of the NbTi wire. Furthermore, the V – I curves of the wire were found to be broadened, which indicates that the microstructure no longer has strong pinning properties. The NbTi wire annealed at 685 °C was not ductile, either.

The addition of 4 at%Ta–1 at%Hf to Nb enhanced B_{c2} and I_c . These enhancements could be attributed to the addition of Hf, which contributes to maintaining the fine microstructure, as shown in Fig. 2. Previous reports show that the addition of Ta to Nb does not increase but rather depresses the B_{c2} of Nb [18, 20]. The recovery temperature of Nb–4Ta is almost the same as that of Nb, which explains that the addition

Figure 6 SEM image plus energy dispersive X-ray spectroscopy (EDS) Nb, Ti, and Cu maps of the NbTi filament after heat treatment at 100 h/685 °C. Nb aggregates in the filaments, and Ti and Cu interdiffuse.

of Ta has little effect on the superconducting properties of Nb.

Nb–5 at%Zr has poor composite deformability with Cu, and therefore wire could not be cold-drawn and there were no transport properties. According to previous studies, the addition of 5 at%Zr to Nb increases B_{c2} to approximately 2 T [34, 35]. However, as the recovery temperature of the Nb–Zr alloy seems to be below 700 °C [35], the steep I_c – B curve of Nb–Zr should not be maintained after annealing. In the case of W addition, although a steep I_c – B curve was obtained, B_{c2} was approximately 0.5 T after annealing. Hence, based on the above observations, Hf seems to be the most effective additive element for Nb to realize a HTT Nb alloy with a relatively high B_{c2} .

Microstructure at the interface of the joints

Figure 7a–d shows the SEM and EDS maps of Nb, Sn and Hf, respectively, at the joint of the Nb₃Sn and Nb–3 at%Hf core. Apparently, the Nb₃Sn layer forms

Figure 7 Joint interface microstructure: a–d SEM image and EDS maps at a joint area of Nb₃Sn and Nb–3 at%Hf core, and e and f SEM images of the interface microstructure between the NbTi filament and Nb–3 at%Hf core without and with annealing at 2 h/450 °C, respectively.

a superconducting pathway between them. Furthermore, Hf appeared to diffuse into Nb filaments in the Nb₃Sn precursor wire from the Nb–Hf core. Figure 7e, f shows the SEM images of the interface microstructure between the NbTi filament and Nb–3 at%Hf core without and with annealing at 450 °C for 2 h in a vacuum, respectively. Notably, there are some small gaps visible at the interface without annealing, whereas the bonding appears to be improved after annealing. This additional annealing may be performed as needed.

Superconducting properties of the joints

Figure 8 shows I_c of the joint samples as a function of magnetic field, where I_c is defined with a dimensionless criterion of 1 μ V. The voltage taps were soldered at a position of approximately 5 mm above the supporting tube surrounding the joint part. The joint configurations were (A) Nb₃Sn wire/Nb–3Hf tape, (B) NbTi wire/Nb–3Hf tape, and (C) Nb₃Sn wire/Nb–3Hf tape/NbTi wire. The Nb–3Hf tapes for joint B were annealed at 685 °C before joining. Joint C was a completed form of the joints of NbTi and Nb₃Sn wires using an HTT Nb alloy intermedium. The magnetic field was applied parallel to the pressed joint surface. The error bar indicates a measured data range. All the joint parts were not stabilized with superior electrical conductors such as Cu. Therefore,

Figure 8 Critical current properties of the developed Nb₃Sn/Nb–3Hf (Joint A), NbTi/Nb–3Hf (Joint B), and NbTi/Nb–3Hf/Nb₃Sn (Joint C) superconducting joints.

the quench phenomenon at more than 100 A, which is a peculiar phenomenon to superconductors, easily damaged the wire. Prevention of the quench phenomenon is expected to be an active area of research in future.

Joint A exhibits a steep I_c – B curve from 1.15 T with decreasing magnetic field, and I_c at 0.8 T surpasses 150 A. Importantly, the yield rate of the successful superconducting joints between Nb₃Sn wire/Nb–3Hf tape was 100%, and the scattering of the I_c data of the joints was found to be extremely small. Even if some filament damage occurred in the Nb₃Sn precursor wire during the severe cold-pressing, the damage could be repaired as the Nb₃Sn layer formed at more than 650 °C. These findings indicate that superior metallurgical bonding was achieved between the Nb₃Sn filaments and Nb–3Hf alloy core.

Moreover, some of the joint B specimens also showed a very good I_c – B curve. The best I_c – B property was superior to that of the annealed Nb–3Hf tape as shown in Fig. 5. Presumably, this I_c – B is determined by the property of the Nb–3Hf tape of the joint sample but not the joint part itself. The superconducting properties of the Nb–3Hf tape of the joint were influenced by the magnetic field direction to the tape. In the transport test for the tape, the field was applied perpendicular to the tape axis, while in the joint sample, the field was applied diagonally to the tape axis. In the diagonal field, the Lorentz force working on magnetic fluxes inside are weakened, which results in an increase in I_c .

However, a few samples of joint B showed low I_c characteristics. Excessive pressure, stress concentration at an edge of the pressing fixture, or filament crossing in the cold-pressing could be the possible reasons, which could cause irreversible severe filament damage. In order to improve the yield rate of the high quality joint, optimization of the cold-pressing method and its pressure and the joint length are required.

Some of Joint C samples also showed good I_c – B properties, where the best I_c value reached more than 150 A at 0.8 T. However, the I_c data scattered well similar to joint B. This scattering could be ascribed to the joint property between the NbTi wire and Nb–3Hf tape, considering the small scattering in the superconducting properties of Nb₃Sn and Nb–3Hf joints.

Figure 9 Decay current and curve fitting at 4.2 K and 0.5 T for a loop sample with NbTi wire/Nb–3Hf tape/Nb₃Sn wire joints.

Joint resistance

Figure 9 shows one of the decay curves and the curve fitting using a decay function ($V_{\text{Hall}} = A + B \exp(-(R_j/L)t$, where V_{Hall} , R_j , L and t are the Hall sensor output, joint resistance and self-inductance of the loop, and A and B are arbitrary constants) at 4.2 K and 0.5 T for a loop sample with NbTi wire/Nb–3Hf tape/Nb₃Sn wire joints. The external magnetic field was applied parallel to the pressed joint surface. The initial induced current was 47 A. The current decreased rapidly at first and became stable after 1000 s. The curve was fitted between 1000 and 3000 s to evaluate R_j . The residual loop current after stabilizing was estimated to be approximately 16 A from the Hall sensor output. The estimated joint resistance was approximately $6.55 \times 10^{-13} \Omega$. The joint resistances at the other magnetic fields were also in the order of 10^{-14} – $10^{-13} \Omega$ in magnetic fields of 0–0.9 T, which further confirms the superconducting state of the joints.

The small residual loop current is ascribed to the quality of the joint. After the current decay measurement, the loop sample was cut and the I_c – B characteristics of each joint part were measured by a four-probe method. Evidently, the I_c of the NbTi/Nb–3Hf joint showed small values, approximately 16 A at 0.5 T, which corresponds to the residual loop current. This indicates that the induced loop current was limited by the NbTi/Nb–3Hf joint. Moreover, we gave additionally a stronger pressure up to 160–230 kN for the NbTi/Nb–3Hf joint parts, and re-measured their I_c . However, I_c characteristics were

further deteriorated. The pressure of 120 kN may have been too strong for joining of NbTi/Nb–3Hf.

Conclusions

The author developed superconducting Nb alloy intermedia whose critical current does not decrease even after exposure to high temperatures. Based on this Nb alloy, a new concept for metallurgically realizing completely Pb- and Cd-free superconducting joints between NbTi and Nb₃Sn wires was proposed and proven experimentally. This superconducting joint method is expected to contribute to the realization of environmentally friendly NMR magnet systems.

Among transition elements close to Nb, Hf is the most suitable additive for realizing an HTT superconducting Nb-alloy intermedium with a relatively high critical magnetic field.

A superconducting joint between Nb₃Sn filaments and one end of a Nb–Hf alloy core was created by forming a superconducting Nb₃Sn layer at the interface through a chemical reaction. The joint between the NbTi filaments and the other end of the Nb–Hf alloy core was formed via cold pressing to connect their active new surfaces to each other. Ultimately, a superconducting joint between NbTi and Nb₃Sn wires was realized. The realization of the superconducting joint was confirmed by ultra-low resistance measurements using a current decay measurement system.

The B_{c2} value of the Nb–3 at%Hf alloy was 1.15 T even after Nb₃Sn layer formation at 685 °C. B_{c2} needs to be further optimized. The I_c value of the NbTi wire/Nb–3Hf tape/Nb₃Sn wire joint with a joint length of 1 cm at 0.8 T reached more than 150 A. The yield rate of the successful superconducting joints between Nb₃Sn wire/Nb–3Hf tape was 100%, and the scattering of the I_c data of the joints was small. In contrast, I_c of the NbTi/HTT Nb-alloy joints shows a relatively larger scattering tendency at the moment. One of the possible reasons for the I_c degradation would be an excessive pressure, causing filament damage. Optimization of the cold-pressing method and its pressure and the joint length are therefore necessary to improve the yield rate of high quality joints, especially for NbTi/HTT Nb-alloy joints.

Acknowledgements

The authors would like to acknowledge Taro Morita, PhD student at Sophia University, for his assistance with the EBSD analysis. He is a collaborator in research related to Nb₃Sn metallurgy and is currently an intern at NIMS. This study was supported by the National Institute for Materials Science, Japan, and JST-Mirai Program Grant Number JPMJMI17A2, Japan.

Author contributions

NB: Conceptualization, Investigation, Methodology, Project administration, Validation, Writing – original draft, and Funding acquisition. KK: Carrying out current decay measurement, Methodology, Analysis, and Validation. AU: Carrying out current decay measurement, Methodology, Analysis, and Validation. HK: Carrying out current decay measurement, Methodology, and Validation.

Declarations

Conflict of interest The authors declare no possible conflict of interest.

Supplementary Information: The online version contains supplementary material available at <http://doi.org/10.1007/s10853-021-06585-8>.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- [1] Thornton RF (1988) Superconducting joint for superconducting wires and coils and method of forming. US Pat 4744506. <https://patents.google.com/patent/US4744506>
- [2] Swenson CA, Markiewicz WD (1999) Persistent joint development for high field NMR. *IEEE Trans Appl Supercond* 9:185–188. <https://doi.org/10.1109/77.783267>
- [3] Evetts JE, Wade JMA (1970) Superconducting properties and the phase diagrams of the PbBi and PbIn alloy systems. *J Phys Chem Solids* 31:973–982. [https://doi.org/10.1016/0022-3697\(70\)90308-2](https://doi.org/10.1016/0022-3697(70)90308-2)
- [4] Brittles GD, Mousavi T, Grovenor CRM et al (2015) Persistent current joints between technological superconductors. *Supercond Sci Technol* 28:93001. <https://doi.org/10.1088/0953-2048/28/9/093001>
- [5] Patel D, Kim SH, Qiu W et al (2019) Niobium-titanium (Nb-Ti) superconducting joints for persistent-mode operation. *Sci Rep* 9:1–7. <https://doi.org/10.1038/s41598-019-50549-7>
- [6] Okada T, Takahata K, Nishijima S et al (1988) Magnetic shielding with superconducting wires. *IEEE Trans Magn* 24:895–898. <https://doi.org/10.1109/20.11370>
- [7] Levy SA, Kim YB, Kraft RW (1966) Effect of structure on the superconducting properties of eutectic alloys. *J Appl Phys* 37:3659–3665. <https://doi.org/10.1063/1.1707901>
- [8] Mousavi T, Aksoy C, Grovenor CRM, Speller SC (2016) Microstructure and superconducting properties of Sn-In and Sn-In-Bi alloys as Pb-free superconducting solders. *Supercond Sci Technol* 29:015012. <https://doi.org/10.1088/0953-2048/29/1/015012>
- [9] Santra S, Davies T, Matthews G et al (2019) The effect of the size of NbTi filaments on interfacial reactions and the properties of InSn-based superconducting solder joints. *Mater Des* 176:107836. <https://doi.org/10.1016/j.matdes.2019.107836>
- [10] Phillip S, Porto JV, Parpia JM (1995) Two methods of fabricating reliable superconducting joints with multifilamentary Nb-Ti superconducting wire. *J Low Temp Phys* 101:581–585. <https://doi.org/10.1007/BF00753357>
- [11] Liu J, Cheng J, Zhou F et al (2013) Electrical properties of cold-pressing welded NbTi persistent joints. *Cryogenics* 58:62–67. <https://doi.org/10.1016/j.cryogenics.2013.09.011>
- [12] Mizumaki S, Yamamoto A (1997) Experimental study of current sharing and transfer in superconductor joint. *IEEE Trans Appl Supercond* 7:805–807. <https://doi.org/10.1109/77.614625>
- [13] Hardy GF, Hulm JK (1953) Superconducting silicides and germanides. *Phys Rev* 89:884–884. <https://doi.org/10.1103/PhysRev.89.884>

- [14] Matthias BT, Geballe TH, Geller S, Corenzwit E (1954) Superconductivity of Nb₃Sn. *Phys Rev* 95:1435–1435. <https://doi.org/10.1103/PhysRev.95.1435>
- [15] Goodman BB (1966) Type II superconductors. *Reports Prog Phys* 29:302. <https://doi.org/10.1088/0034-4885/29/2/302>
- [16] Foner S, Schwartz BB (1981) Superconductor materials science: metallurgy, fabrication, and applications. Springer, US, Boston, MA
- [17] Berlincourt TG, Hake RR (1962) Upper critical fields of transition metal alloy superconductors. *Phys Rev Lett* 9:293–295. <https://doi.org/10.1103/PhysRevLett.9.293>
- [18] Hempstead CF, Kim YB (1964) Resistive transitions and surface effects in type-II superconductors. *Phys Rev Lett* 12:145–148. <https://doi.org/10.1103/PhysRevLett.12.145>
- [19] Ralls KM (1966) Internal surface superconductivity: the relationship between resistive critical field and bulk upper critical field. *Phys Lett* 23:29–31. [https://doi.org/10.1016/0031-9163\(66\)90240-X](https://doi.org/10.1016/0031-9163(66)90240-X)
- [20] Suenaga M, Ralls KM (1969) Some superconducting properties of Ti–Nb–Ta ternary alloys. *J Appl Phys* 40:4457–4463. <https://doi.org/10.1063/1.1657215>
- [21] Bychkova MI, Baron VV, Savitskii EM (1970) Superconducting properties of Nb–Hf alloys and the effect of mechanical and Heat treatment on their structure and properties. *Physics and Metallurgy of Superconductors*. In: *Proceedings of the Second and Third Conferences on Metallurgy, Physical Chemistry, and Metal Physics of Superconductors held at Moscow in May 1965 and May 1966*, pp 74–79. https://doi.org/10.1007/978-1-4684-8220-1_13
- [22] Hill DC, Rose RM (1971) Experimental tests of proposed relations between the critical field and dislocation cell structure of superconducting niobium. *Metall Trans* 2:585–589. <https://doi.org/10.1007/BF02663353>
- [23] Dew-Hughes D (1974) Flux pinning mechanism in type II superconductors. *Philos Mag* 30:293–305. <https://doi.org/10.1080/14786439808206556>
- [24] Kramer EJ (1973) Scaling laws for flux pinning in hard superconductors. *J Appl Phys* 44:1360–1370. <https://doi.org/10.1063/1.1662353>
- [25] Sernetz F (1976) Flux pinning in porous type II superconductors. *J Low Temp Phys* 24:85–103. <https://doi.org/10.1007/BF00659197>
- [26] Larbalestier DC, West AW (1984) New perspectives on flux pinning in niobium-titanium composite superconductors. *Acta Metall* 32:1871–1881. [https://doi.org/10.1016/0001-6160\(84\)90168-8](https://doi.org/10.1016/0001-6160(84)90168-8)
- [27] Meingast C, Lee PJ, Larbalestier DC (1989) Quantitative description of a high J_c Nb–Ti superconductor during its final optimization strain. I. Microstructure, T_c, H_{c2}, and resistivity. *J Appl Phys* 66:5962–5970. <https://doi.org/10.1063/1.343624>
- [28] Lee PJ, Larbalestier DC (1987) Development of nanometer scale structures in composites of Nb–Ti and their effect on the superconducting critical current density. *Acta Metall* 35:2523–2536. [https://doi.org/10.1016/0001-6160\(87\)90149-0](https://doi.org/10.1016/0001-6160(87)90149-0)
- [29] Lee PJ, McKinnell JC, Larbalestier DC (1989) Microstructure control in high Ti NbTi alloys. *IEEE Trans Magn* 25:1918–1921. <https://doi.org/10.1109/20.92681>
- [30] Balachandran S, Tarantini C, Lee PJ et al (2019) Beneficial influence of Hf and Zr additions to Nb4at%Ta on the vortex pinning of Nb₃Sn with and without an O source. *Supercond Sci Technol* 32:044006. <https://doi.org/10.1088/1361-6668/aaff02>
- [31] Banno N, Morita T, Yagai T, Nimori S (2021) Influence of parent Nb-alloy grain morphology on the layer formation of Nb₃Sn and its flux pinning characteristics. *Ser Mater* 199:113822. <https://doi.org/10.1016/j.scriptamat.2021.113822>
- [32] Kobayashi K, Nishijima G, Uchida A et al (2020) Development of a superconducting joint resistance evaluation system. *IEEE Trans Appl Supercond* 30:10–13. <https://doi.org/10.1109/TASC.2020.2967680>
- [33] Banno N, Morita T, Yu Z et al (2019) Effect of Zn addition and Ti doping position on the diffusion reaction of internal tin Nb₃Sn conductors. *Supercond Sci Technol*. <https://doi.org/10.1088/1361-6668/ab4632>
- [34] Doi T, Mitani M, Umezawa T (1966) Superconducting properties of Nb–Zr–Ti ternary alloys (studies of hard superconductor, I). *J Jpn Inst Met* 30:133–138. https://doi.org/10.2320/jinstmet1952.30.2_133
- [35] Nobuki M, Tachikawa K (1970) Fabrication of Nb–Zr superconducting wires. *J Jpn Inst Met* 34:88–94. https://doi.org/10.2320/jinstmet1952.34.1_88

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.