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High-Field A-15 Superconductors Prepared from Intermediate Compound

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A15 Nb₃(Al,Ge) and Nb₃Sn have been easily synthesized starting from Nb₂(Al,Ge) and Nb₆Sn₅ intermediate compound powder, respectively. The intermediate compound powder was mixed with Nb powder by a ball mill in Ar atmosphere. The mixed powder was encased in a Nb or Ta tube, and then fabricated into a tape without intermediate annealing. The mechanical mixing of powders promotes the formation of A15 phase in subsequent reaction treatment. The bulk sintered specimens show higher onset T_c but broader T_c transition than tape specimens. In the Nb₃(Al,Ge) tape reacted at 1300°C, a J_c of over 2.7 × 10⁴ A/cm² has been obtained at 4.2K and 23T. The addition of MgO powder enhances J_c and reduces the peak effect in the Nb₃(Al,Ge) tape. The T_c of Nb₃Sn tape prepared by present process is appreciably higher than that of bronze - processed Nb₃Sn. Even pure Nb₃Sn tape shows B_{c2} of nearly 25T at 4.2K after the reaction at 900°C. The present A15 Nb₃(Al,Ge) and Nb₃Sn tapes seem to be promising for generating 20T at 4.2K.

KEYWORDS : High-field superconductor, Nb₃(Al,Ge), Nb₃Sn, Intermediate compound, Mechanical alloying

1. Introduction

The bronze-processed Nb₃Sn wire with small amount of Ti addition to the matrix has been used for generating high magnetic fields¹⁾. The Ti-doped bronze-processed Nb₃Sn so far generated 18.5T at 4.2K. The technical problems in bronze process are the limitation of Sn concentration in the matrix, and the necessity of frequent intermediate annealings due to the work hardening of bronze, which raises the cost of the wire.

Meanwhile, Nb₃Al and Nb₃(Al,Ge) are considered to be promising alternatives for Nb₃Sn since they have higher upper critical field B_{c2} and better strain tolerance than Nb₃Sn. However, in the formation of Nb₃Al through the diffusion between Nb and Al, Al should be turned into a very thin layer to avoid the formation of intermediate compounds richer in Al, i.e. Nb₃Al and σ -phase Nb₂Al^{2,3)}. Moreover, the stoichiometric A15 Nb₃Al is stable at elevated temperatures above ~ 1800°C ; the diffusion reaction between Nb and Al at ordinary temperatures yields Nb₃Al with a composition poorer in Al. Nb₃Al wires prepared by the diffusion between Nb and Al show lower B_{c2} than that of (Nb,Ti)₃Sn. Quenching from high temperature produces excellent high-field performance through the retention of more stoichiometric A15 phase⁴⁾. However, quenching process seems to be inconvenient for large-scale production of wire.

A new fabrication process for Nb₃(Al,Ge) and Nb₃Sn in which the intermediate compound powder reacts with Nb powder has been recently studied^{5,6)}. In this process, we have easily synthesized a single A15 phase. In the present paper, structures and superconducting properties of the Nb₃(Al,Ge) and Nb₃Sn tapes prepared through this new process will be described. The effect of powder preparation conditions and that of element addition on high-field performance will be also reported.

2. Experimental procedures

2.1 Specimen preparation

Figure 1 illustrates the fabrication procedure of the present Nb₃(Al,Ge) and Nb₃Sn specimens. The starting material for Nb₃(Al,Ge), i.e. σ -phase Nb₂(Al_{0.8}Ge_{0.2}), was prepared by a conventional plasma-arc melting in an argon atmosphere. The purities of constituent elements were 99.8% for Nb, 99.99% for Al, and 99.999% for Ge. The obtained σ -phase buttons (usually 20 gr in weight) were crushed into powders in an alumina pestle bowl with hand, and passed through a 325 mesh sieve. Meanwhile, Nb₃Sn specimens were prepared from Nb₆Sn₅ intermediate compound powder synthesized by the melt diffusion process. A mixed powder of Nb and Sn was heated in vacuum using alumina crucible in which molten Sn reacted with Nb. The purity and the size of Nb powder were 99.8% and under 325 mesh, respectively, while those of Sn powder were 99.9% and under 350 mesh, respectively.

The Nb₂(Al,Ge) or Nb₆Sn₅ powder was preliminary mixed with Nb powder in the composition of A15 phase using an alumina bowl by hand. After passing through a sieve of 325 mesh, the mixed powder was mechanically pre-reacted using a planetary-type ball mill under Ar atmosphere for different time. This mechanical pre-reaction in the mixed powder is denoted as MA (mechanical alloying) in this paper. The percentage of O₂ in Ar atmosphere during the MA treatment was kept less than 0.5%. Element addition can be performed either to intermediate compound or to mixed powder. 2 at% Ti was substituted for Nb for the composition of Nb₃Sn at the time of melt diffusion to form Nb₆Sn₅. The addition of 5 and 10 vol% of MgO to the Nb₂(Al,Ge)/Nb mixed powder, and that of 10 wt% of Cu to the Nb₆Sn₅/Nb mixed powder with 2 at% Ti substitution were also performed. The purity and size of MgO powder were 99.9% and ~2 μ m, respectively.

The resulting Nb₂(Al,Ge)/Nb mixed powder and Nb₆Sn₅/Nb mixed powder were encased into Nb and Ta

tube, respectively, both having an outer/inner diameter of 8/5 mm. The composite tubes were groove rolled to 2.5 mm square rods, and then flat rolled to 0.5 mm thick and 5 mm wide tapes without intermediate annealing. The thickness and width of the core were about 0.25 mm and 2.5 mm, respectively. Besides the tape specimens, bulk specimens pressed into 2.5 mm in width, 0.5 mm in thickness and 22 mm in length were also prepared. The tape and bulk specimens were heat treated in vacuum of 1×10^{-5} Torr at different temperatures. Some of the $\text{Nb}_3(\text{Al,Ge})$ specimens were annealed at 700°C for 100h after the reaction.

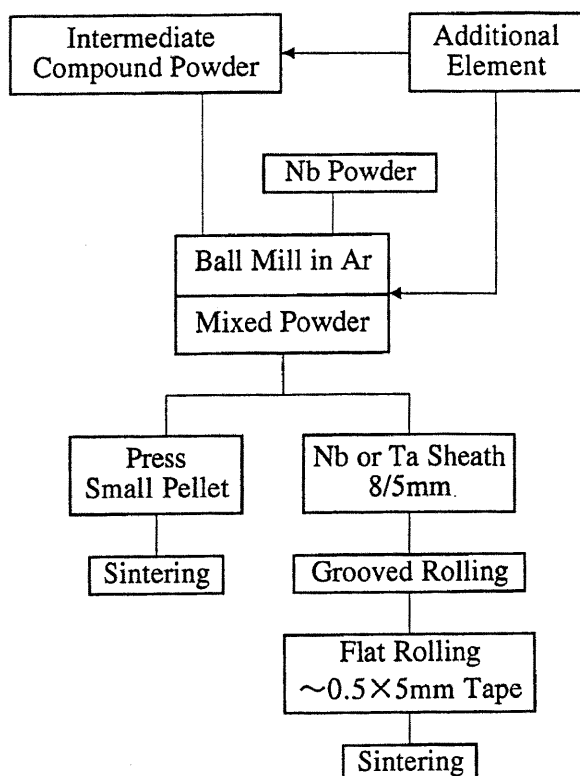


Figure 1 Process for synthesis of A15 compound superconductors starting from intermediate compound powder.

2.2 Characterization

Microstructures of the cross-section of specimens were observed using an optical microscope after an anodic oxidation. The anodizing oxidation was performed using oxalic acid-base solution⁷⁾. X-ray diffraction (XRD) analysis using $\text{Cu K}\alpha$ line was carried out in order to identify phases formed by the heat treatment. Transition temperature, T_c was measured by a four-probe resistive method using calibrated Ge thermometer. Critical current, I_c was measured at 4.2K by a four-probe resistive method, and was defined as the current at which a voltage across the 10 mm length of the specimen reached $1 \mu\text{V/cm}$. I_c at magnetic fields up to 13T was measured by a superconducting magnet at our university, and that at 13-23T was measured by a hybrid magnet at the High Field Laboratory for Superconducting Materials in Tohoku

University. The I_c measurement was limited up to 200A due to the current capacity of both the power source and specimen probe. The magnetic field was applied parallel to the tape surface and perpendicular to the specimen current. Critical current density, J_c was obtained by dividing I_c by a cross-sectional area of the core.

3. Results on $\text{Nb}_3(\text{Al,Ge})$

Figure 2 illustrates the change in XRD pattern of the σ/Nb tape by the heat treatment. In the XRD pattern taken before the heat treatment, the peaks from σ , Nb and some A15 phases are identified. The XRD pattern of the tape heat treated at 1200°C for 1h is consisted of peaks from major A15 phase and minor σ phase. After the heat treatment at 1300°C for 1h, the XRD pattern is almost completely changed to that of single A15 phase.

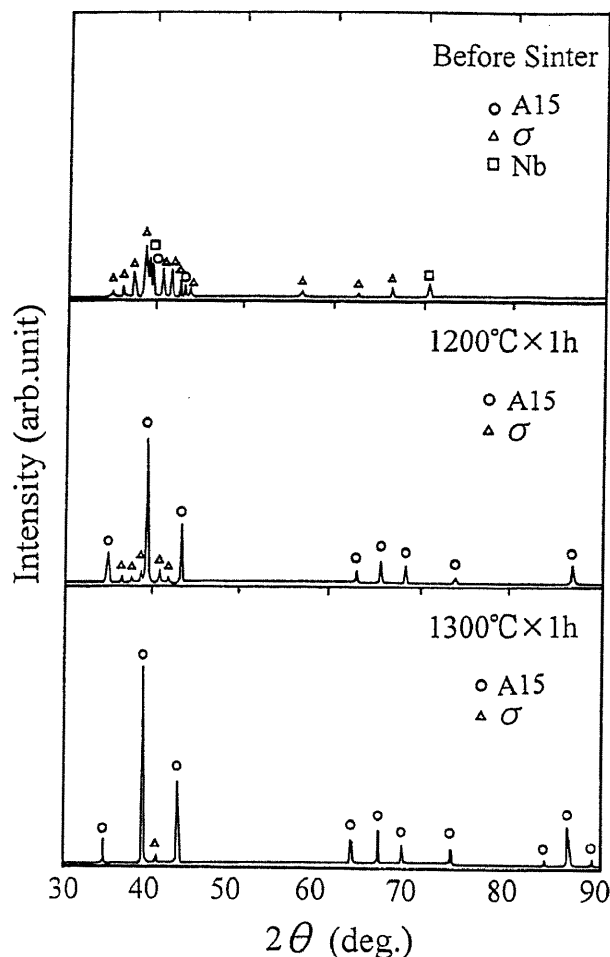


Figure 2 XRD patterns of the $\text{Nb}_3(\text{Al,Ge})$ tape before and after the heat treatment.

Figure 3 is the T_c versus reaction time at 1400°C for the σ/Nb tape and bulk specimens. The σ/Nb bulk specimen shows appreciably higher onset T_c and lower offset T_c than those of the σ/Nb tape specimen. Namely, the tape specimen exhibits much sharper T_c transition than the bulk specimen; the transition width of the tape specimen is less than 0.5K, while that of the bulk specimen exceeds 3.5K. The A15

phase in the bulk specimen may have a much wider composition range than in the tape specimen. The highest onset T_c obtained in the σ /Nb bulk and tape specimens are 19.7K and 18.0K, respectively. MA for 0.5h produces a slightly higher T_c in the tape specimen. The annealing at 700 °C after the reaction enhances the T_c of the specimen by 0.5K-1.0K.

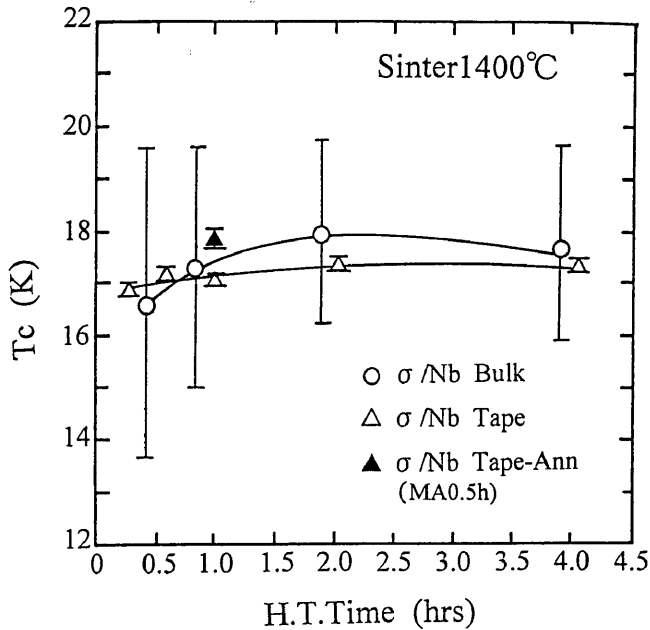


Figure 3 T_c versus reaction time at 1400°C for bulk and tape $Nb_3(Al,Ge)$ specimens.

Figure 4 summarizes J_c -B curves of σ /Nb tape specimens prepared by present process. Tapes prepared from MA mixed powder show enhanced J_c in high-fields than those from manually mixed powder. The tape prepared from MA 10h mixed powder and reacted at 1300 °C for 2h shows a J_c exceeding 2.7×10^4 A/cm² even at 23T and 4.2K.

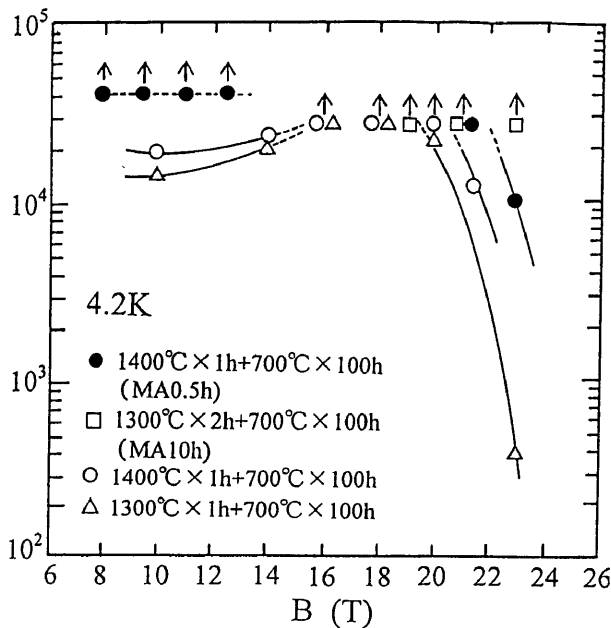


Figure 4 J_c versus magnetic field curves for $Nb_3(Al,Ge)$ tape specimens prepared by quoted conditions.

The peak effect in the J_c -B curve seen in Figure 4 for specimens without MA treatment is considered to be originated from the degradation of J_c at low fields. Then the addition of MgO powder was attempted to introduce artificial pinning centers effective at low fields, and to suppress the peak effect. The EPMA pattern taken on the MgO added tape reveals the fine dispersion of Mg throughout the cross-section of the tape. Figure 5 illustrates J_c -B curves of tape specimens with or without MgO addition, and heat treated at 1400 °C and 1450 °C for 1h. The heat treatment at higher temperatures causes the grain growth of A15 phase enhancing the degradation in J_c at low fields. Specimens without MgO addition show significant peak effect in J_c , although they carry relatively large J_c still at 23T. The MgO addition is effective for enhancing J_c at low fields, e.g. the J_c at 12T is increased by a factor of 2-3 by the MgO addition. Thus the MgO addition seems to be effective for reducing the peak effect; however it slightly decreases T_c , which results a more rapid decrease in J_c at high fields.

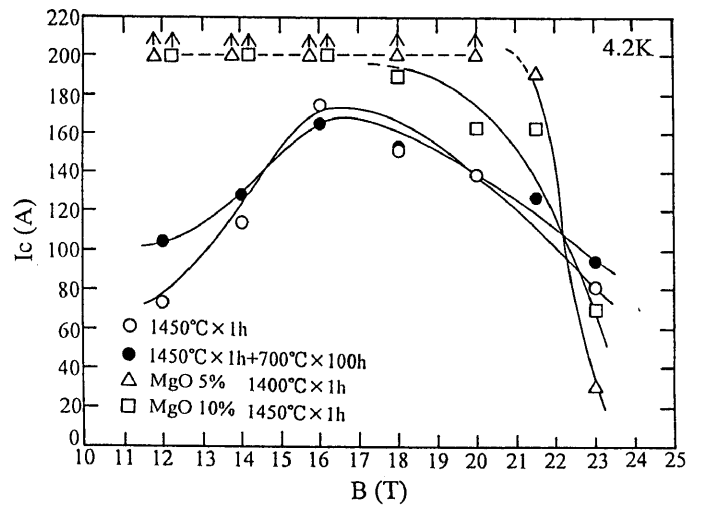


Figure 5 J_c -B curves of tape specimens with or without MgO addition.

4. Results on Nb_3Sn

After the melt diffusion between Nb and Sn powders, Nb_6Sn_5 compound is synthesized into a fine powder form as illustrated in Figure 6. Enough Nb_6Sn_5 powder can be

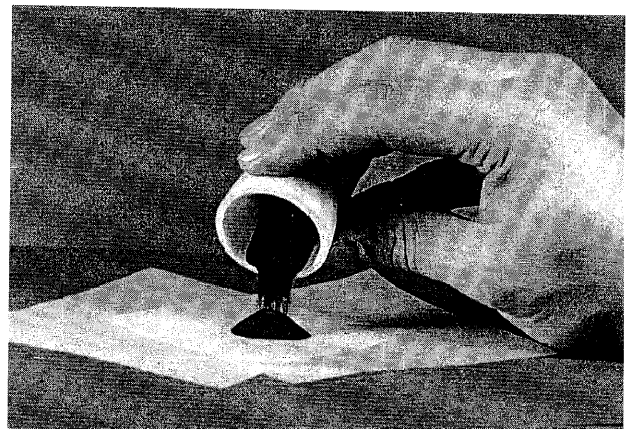


Figure 6 Nb_6Sn_5 powder prepared by melt diffusion process.

obtained by this process, the most appropriate reaction temperature to form Nb₆Sn₅ being around 900°C. The σ-phase Nb₂(Al,Ge) compound can be also synthesized by a similar melt diffusion process. However, σ-phase powder prepared by melt diffusion process produces no difference in high-field performance of Nb₃(Al,Ge) compared with that using σ-phase powder prepared by arc-melting.

Figure 7a is the XRD pattern of the Nb₆Sn₅/Nb powder mixed by hand in an alumina bowl, while Figure 7b is that of the mixed powder after MA for 3h, where the XRD peaks become broad, and those of Nb₆Sn₅ and Nb are difficult to separate. This implies that a pre-reaction between Nb₆Sn₅ and Nb may take place during the mechanical mixing.

In the tape and bulk specimens reacted at 800°C for 10h, appreciable amount of residual Nb₆Sn₅ and Nb are observed in the XRD pattern and in the optical microstructure, while in those reacted at 900°C for 10h only a very small amount of Nb₆Sn₅ and Nb are observed. The MA treatment apparently reduces the amount of residual Nb₆Sn₅ and Nb in the specimens reacted at 800°C for 10h⁶⁾. The pre-reaction between Nb₆Sn₅ and Nb caused by the MA treatment mentioned above is effective for promoting the formation of A15 phase.

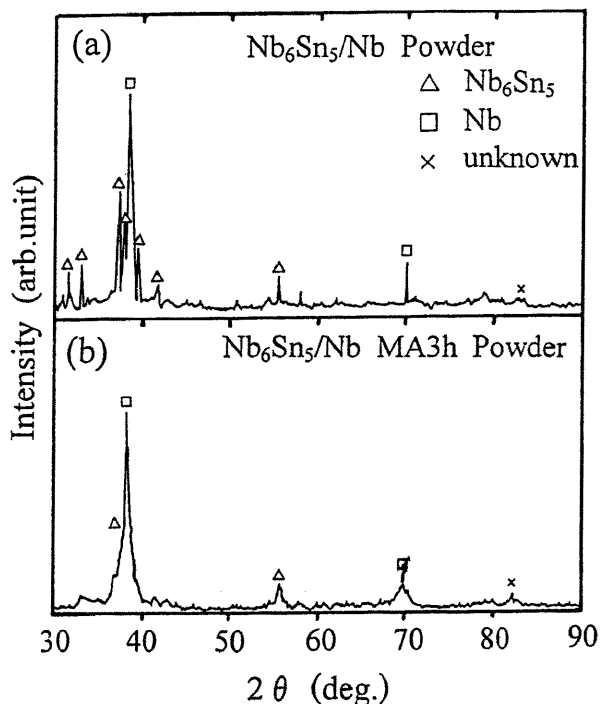


Figure 7 XRD patterns of Nb₆Sn₅/Nb mixed powders: (a) mixed in alumina bowl by hand; (b) mixed in planetary-type ball mill for 3h (MA3h)

Figure 8 is T_c versus reaction temperature curves for Nb₃Sn bulk and tape specimens with 2 at% Ti substitution. Bulk specimens show slightly higher but broader T_c transition than tape specimens. Specimens prepared from mixed powder of MA 3h show appreciably higher T_c than those prepared from mixed powder of MA 1h. The 2 at%

Ti substitution for Nb does not cause an appreciable change in the maximum T_c of Nb₃Sn. T_c of the specimen prepared by present process is higher than that of bronze-processed (Nb,Ti)₃Sn by ~0.5K. Cu addition to the mixed powder decreases optimum reaction temperature from 950°C to 850°C.

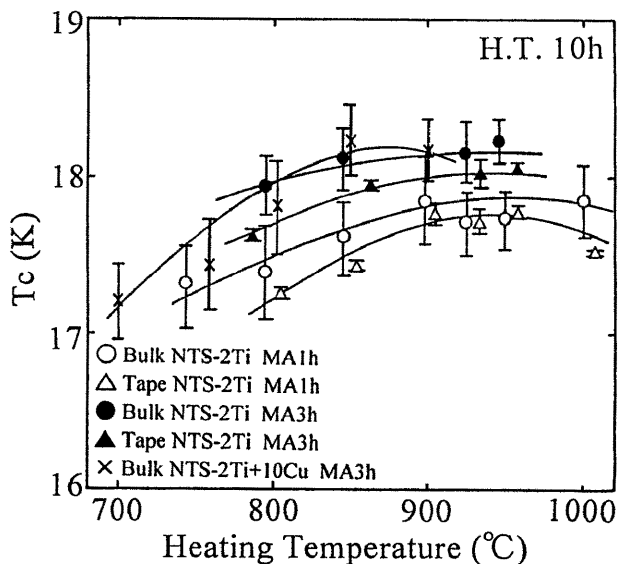


Figure 8 T_c versus reaction temperature for Nb₃Sn bulk and tape specimens with 2 at% Ti substitution for Nb.

Figure 9 is I_c and J_c versus magnetic field curves of different specimens. Even pure Nb₃Sn tape prepared by present process shows B_{c2} of nearly 25T at 4.2K which is about 5T higher than that of bronze-processed Nb₃Sn. Ti addition yields further improvement in B_{c2}. Tape specimen seems to have slightly lower B_{c2} than bulk specimen may be due to the stress effect caused by the sheath in tape specimen. Cu addition decreases optimum reaction temperature with respect to I_c from 900°C to 850°C. Nb₃Sn specimens prepared by present process keep J_c of over 3 × 10⁴ A/cm² at 20T, which is promising for

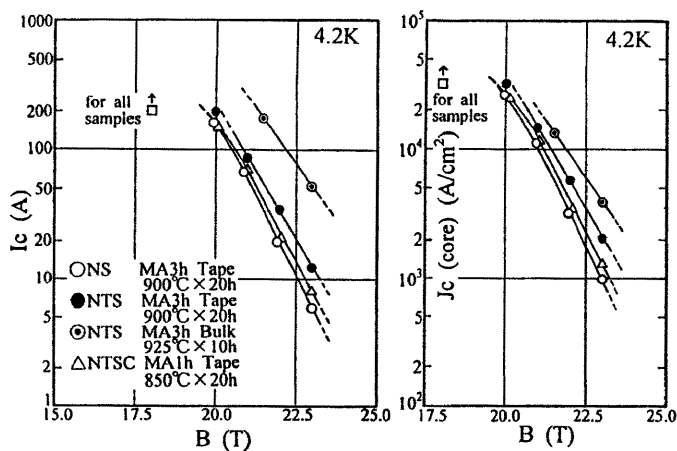


Figure 9 I_c and J_c versus magnetic field curves for different Nb₃Sn specimens. NS: Nb₃Sn, NTS: (Nb,Ti)₃Sn with 2 at% Ti substitution for Nb, NTSC: (Nb,Ti)₃Sn+10 wt% Cu.

generating 20T at 4.2K. The reaction temperature of 850°C-900°C may facilitates to compose Cu stabilizer into the conductor, which is necessary for practical use.

Table 1 indicates the normal state resistivity ρ_n of bulk Nb₃Sn and (Nb,Ti)₃Sn specimens heat treated at 950°C for 20h. XRD patterns of these specimens are composed of sharp A15 diffraction peaks, and do not indicate the presence of the second phase. The ρ_n values reported for bronze-process Nb₃Sn (reference 8) are also listed in Table 1. It should be mentioned that the ρ_n value of present Nb₃Sn specimen is much larger than that of bronze-processed Nb₃Sn. The ρ_n value of present Nb₃Sn is equivalent to that of bronze-processed Nb₃Sn with 1.5 at% Ti substitution. The enhanced Bc₂ obtained in present pure Nb₃Sn specimen seems to be mainly due to its large ρ_n value, since Bc₂ is dependent on ρ_n in type-II superconductors. However, the origin of large ρ_n in present Nb₃Sn specimens is not yet clear. The Ti-doping causes a more significant increase in ρ_n in bronze-processed Nb₃Sn than in present Nb₃Sn specimen. The ρ_n value of present (Nb,Ti)₃Sn specimen with 2 at% Ti substitution is slightly higher that of Ti-doped bronze-processed (Nb,Ti)₃Sn.

Table 1 Normal state resistivity ρ_n just above T_c in different Nb₃Sn specimens. Data of bronze-processed Nb₃Sn are taken from reference 8.

Present Process	$\rho_n (\mu\Omega \cdot m)$
Pure Nb ₃ Sn	0.29
(Nb,Ti) ₃ Sn (2at%Ti)	0.39
Bronze Process	$\rho_n (\mu\Omega \cdot m)$
Pure Nb ₃ Sn	0.08
1.60at%Ti in Nb ₃ Sn	0.33
2.71at%Ti in Nb ₃ Sn	0.41

5. Conclusions

- (1) A15 Nb₃(Al,Ge) and Nb₃Sn tapes capable of generating 20T at 4.2K have been fabricated starting from intermediate compound powder.

- (2) The fabrication of tapes has been performed without intermediate annealing.
- (3) The pre-reaction between intermediate compound and Nb powders caused by mechanical mixing promotes the synthesis of A15 phase.
- (4) The Nb₃(Al,Ge) tape shows a J_c of over 2.7×10^4 A/cm² at 23T and 4.2K after the reaction at 1300°C.
- (5) MgO added to Nb₃(Al,Ge) tape acts like an artificial pinning center to enhance J_c.
- (6) Pure Nb₃Sn Tape prepared by the present process shows Bc₂ of nearly 25T at 4.2K, maybe due to its large ρ_n value. The J_c of the tape exceeds 3×10^4 A/cm² at 20 T and 4.2K.
- (7) Ti substitution for Nb still increases Bc₂, and Cu addition decreases reaction temperature of Nb₃Sn.
- (8) The Nb₃Sn tape prepared by present process seems to be more promising for practical use than the Nb₃(Al,Ge) due to its lower reaction temperature, although the latter keeps larger J_c at high-fields than the former.

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