Nb_3Sn Wire Technology for High-field Superconducting Magnet

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Nb_3Sn superconducting wires are widely used for high-field superconducting magnets, and the NMR magnet is one of the most successful applications. In order to realize a large Jc (critical current density), which is essential to high-field superconducting magnets, several different types of production methods have been developed, such as the bronze-route method, the powder-in-tube method and the internal tin method. This article first reviews those wire production methods and the technique for Jc value enhancement. After that, current developments in the large Jc Nb_3Sn superconducting wire of Kobe Steel and Japan Superconductor Technology are described. The magnetic field dependence of Jc values in each manufacturing method is presented and the strong and weak points for the industrial usage of each manufacturing method are also described. An effective guideline for achieving the best superconducting magnet performance is discussed, optimizing the placement of Nb_3Sn wire manufactured by each method. The proposed design concept uses PIT method wire for winding the innermost layer and IT method wire for winding the outer layer. This idea could realize an NMR magnet with a high magnetic field and superior cost performance.

Introduction

Superconductivity is a phenomenon that allows electric current to flow with zero resistance under certain conditions. This enables a large electric current to flow in small wires. A general low-voltage wire, for example, has an allowable current density of 4 A/mm^2 due to the generation of Joule heat associated with electrical resistance. A superconducting wire, on the other hand, allows a current of as much as 100 to 200 A/mm^2.[1)] Superconducting phenomena were originally discovered from the fact that mercury exhibits zero resistance when cooled to a temperature of approximately 4 K (-269 degrees Celsius.) Since then, much effort has been devoted to research and development aiming at industrial applications.

Although superconductivity requires cryogenic cooling, it can generate high magnetic fields that otherwise cannot be achieved. Hence, superconducting magnets are widely used for nuclear magnetic resonance (NMR), magnetic resonance imaging (MRI) and linear motor cars, a high-speed train system to be inaugurated in 2027 in Japan.

Japan Superconductor Technology, Inc. (JASTEC), a company in the Kobe Steel group, is the only manufacturer in Japan specializing in superconducting technologies, producing and selling both superconducting wires and superconducting magnets.

There are two types of superconducting wires manufactured and sold by JASTEC, namely, NbTi wires and Nb_3Sn wires. The wires of NbTi are mainly used for apparatuses generating magnetic fields up to 10 T (e.g., MRI and linear motor cars), while the wires of Nb_3Sn are used for applications requiring even higher magnetic fields, such as high-field NMRs.[2)]

The first half of this paper describes typical manufacturing methods and features of value-added Nb_3Sn wires, which require highly sophisticated production technology, and the latter half describes the Nb_3Sn wires being developed by Kobe Steel and JASTEC.

1. Methods for producing Nb_3Sn wires and their features

Nb_3Sn is an intermetallic compound that is hard and brittle. The compound is difficult to deform plastically, which prevents the application of the production methods (e.g., wire drawing) developed for NbTi wires.[3)] In order to resolve the issues of workability and to enable industrial manufacturing, proposals have been made for the use of composite processes, such as the bronze-routed process,[4)] powder-in-tube process,[5)] and internal tin process.[6)] **Fig. 1** schematically illustrates the cross sections

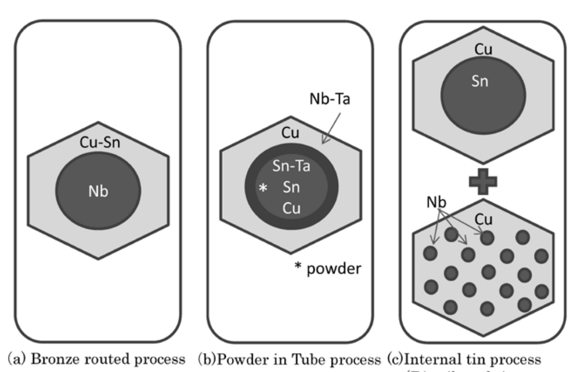

Fig. 1 Schematic cross section of Nb_3Sn single cores in different processes

of the materials made by different production processes, the details of which will be described later.

The characteristics required of superconducting wires depend on the apparatuses and applications, including among others factors, the critical electric current density (hereinafter, Jc), residual resistance ratio (hereinafter, RRR), mechanical strength and alternate current loss. This paper focuses on Jc, which is the most important characteristic of superconducting wires used for high-magnetic-field superconducting magnets, and provides improvement guidelines for each manufacturing process.

1.1 Bronze-routed process

The bronze-routed process (the "bronze" means a Cu-Sn alloy in this article) is a production method comprising the following: making a bundle of a multiplicity of hexagonal Cu-Sn alloy rods, each having a Nb filament core (Fig. 1(a)); inserting the bundle into a sheath of oxygen-free copper to create a composite; wire-drawing the composite; and heat-treating the wire-drawn composite at 650-750℃, thereby producing Nb_3Sn compound on the surface of the Nb filament by diffusion reaction.[4] This process involves no as-is use of Sn, which has a low melting point, and thus enables the extrusion of the billets at high temperatures, each billet having a large size and weight. Hence, the bronze-routed process has the advantage of mass productivity. Although, historically speaking, this is the earliest process to have become industrially feasible, issues remain with regards to the cost and Jc characteristic. The Cu-Sn alloy used as raw material is more expensive than pure metal Sn and Cu. Also, the alloy exhibits significant work hardening during the wire-drawing step, requiring frequent annealing to soften it. In addition, the supply of Sn to the diffusion reaction is limited by the solid solubility limit of Sn in the alloy (15.8%). This limits the amount of Nb_3Sn produced, making it difficult to improve the Jc characteristic.

1.2 Powder-in-tube process

The powder-in-tube process for making Nb_3Sn wires comprises the following: filling a tube of Nb alloy with powder containing Sn (e.g., Sn, Sn alloy, Sn compounds) and Cu; placing the tube in a sheath of copper, and bundling a hexagonal column (Fig. 1 (b); forming the Cu sheathed composite (no figure). Nb_3Sn is formed by Sn contained in the Nb alloy tube diffusing into Nb. This method results in the formation of Cu-Sn alloy during the Nb_3Sn-making step, which minimizes the adverse effect of the work hardening that occurs during the wire drawing. A direct reaction occurs between Nb and Sn without involving any Cu matrix, resulting in a high rate of Nb-Sn diffusion. Hence, the powder-in-tube process has the advantage that the volume fraction of Nb_3Sn can be increased and a high critical current density (Jc) can be obtained.

The use of Nb alloy tube, however, results in a Nb_3Sn core that is larger than that produced by the bronze-routed process, or by the internal tin process, which increases the hysteresis loss when used for AC applications.

1.3 Internal tin process

The internal tin process was devised based on the bronze-routed process to resolve the limitation of Sn concentration required for increasing Jc.[7] The resulting wire has a cross-section with multiple Nb cores and Sn alloy embedded in a Cu matrix. Various types of internal tin processes have hitherto been devised, and they all commonly use the three materials, Sn, Nb and Cu. One of the several wire making methods includes assembling modules, each integrating Cu, Nb core and Sn alloy, in advance. Another method involves assembling together a module combining a Cu and Nb core and another module combining Cu and Sn alloy (Fig. 1 (c)). As in the case of the bronze-routed process, heat treatment is applied such that Nb_3Sn is formed on the surfaces of Nb cores by diffusion reaction. The solid-solubility limit of Cu-Sn alloy places no limitation on the supply of Sn, which enables the amount of Nb_3Sn formation to be increased in order to achieve high Jc. Moreover, this production method processes the Cu, Nb core and Sn alloy independently without involving any material, such as Cu-Sn alloy, that would cause a rapid increase in work hardening and thus eliminates the need for frequent intermediate annealing, which is the factor increasing the cost of the bronze-routed process. It should be noted, however, that hot extrusion cannot be applied due to the low melting point of Sn; hence the process requires a newly devised technology for volume production.

2. Improvement of critical current density (Jc)

Various Nb_3Sn wires have been developed for apparatuses applying superconductivity, each having improved characteristics, such as Jc, mechanical properties and alternate-current loss, depending on the intended purpose. The critical current density (Jc) is the most basic characteristic of high-magnetic-field superconductor magnets, since it determines the magnetic field generated by superconducting magnets.

There are three aspects involved in improving Jc: namely, i) the amount of the Nb_3Sn compound formed, ii) grain size (grain boundary) and iii) stoichiometric composition. Among them, increasing the amount (area ratio) of Nb_3Sn occupying the cross section of a wire is the most basic approach for improving Jc. In the case of the bronze-routed process, for example, the amount of Nb_3Sn generated can be increased by increasing the concentration of Sn in the Cu-Sn alloy and adjusting the area ratio of the Nb core. **Fig. 2** shows the relationship between the concentration of Sn in the bronze and Jc. It is revealed that increasing the Sn concentration increases Jc.

Next, the crystalline structure of the Nb_3Sn phase, which has a significant effect on Jc, is considered. Nb_3Sn is a type-II superconductor, which, upon the application of an external magnetic field, allows the magnetic field to penetrate into the superconductor. The penetrating magnetic field turns into a quantized state, called magnetic fluxes. When an electric current flows through the superconductor, the Lorentz force is applied to the magnetic fluxes. Any movement of magnetic fluxes in this state generates voltage in the energizing direction, causing energy loss. Hence, practical superconducting wires have mechanisms to suppress the movement of, or to fix, the magnetic flux to avoid the loss. The fixing of magnetic fluxes in a superconductor is called "magnetic flux pinning"; this function is carried out at "pinning centers."[10] The major pinning centers for Nb_3Sn are its grain boundaries, and fine and isotropic crystal grains provide a high Jc characteristic.[11] The grain size changes with the concentration ratio of Nb and Sn, heat treatment, and the like (**Fig. 3**).

Moreover, in the high magnetic-field range exceeding 18 T, the composition of the Nb_3Sn phase affects Jc significantly. To improve the Jc characteristic in the high magnetic-field range, several measures have been taken, including the addition of a third element into the Nb_3Sn phase and the high-temperature heat treatment for making the composition close to stoichiometry.[2]

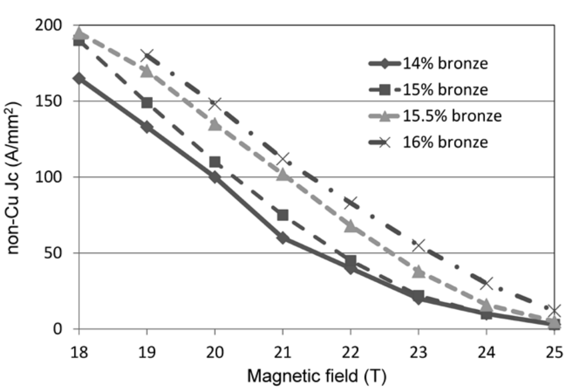

Fig. 2 Non-Cu Jc versus magnetic field curves of Nb_3Sn conductors with shown Sn amount in bronze alloy

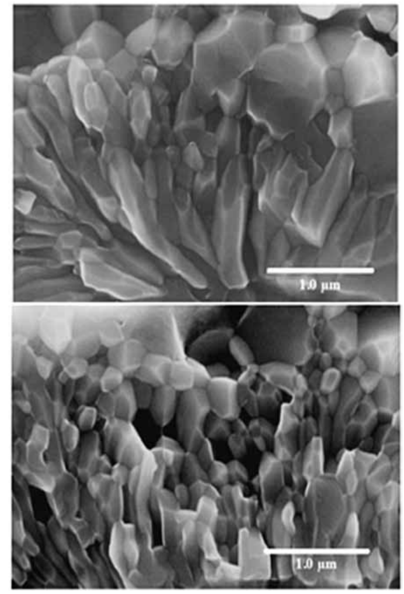

Fig. 3 SEM images of Nb_3Sn crystals using 13 wt% Sn bronze (top) and 15 wt% Sn bronze (bottom)

The next section describes the development of Nb_3Sn wires by the Kobe Steel group.

3. Development of Nb_3Sn wires by Kobe Steel group

As a Kobe Steel group company, JASTEC manufactures, as one of its main products, the superconducting magnets of NMR apparatuses for chemical analysis and focuses also on the business of the Nb_3Sn superconducting wires used for this application. The detection sensitivity of NMR measurement increases proportionally to the 3/2 power of the magnetic field used. The resolution also increases in proportion with the magnetic field.

NMR has been used mainly in the field of chemistry, including the synthesis of organic compounds; however, with the recent development of biotechnology, the demand for it is increasing in the structural analysis of large biomolecules; like proteins. Proteins have complicated structures with large molecular weights; hence, analyzing their structures requires NMR apparatuses with high resolution. As a result, there is a strong demand for magnets with a high magnetic field.[12] Currently, the superconducting magnets most commonly used for NMR have a magnetic field of 9.4 T at median; while the NMR apparatuses for biomolecules use superconducting magnets, each can generate a magnetic field of 14 T or higher. The demand for high-field NMR is strong, and a 1 GHz-class high-field NMR magnet (central magnetic field, 23.5 T) is being developed. The magnetic field to be generated is close to the upper critical magnetic field (Hc2) of Nb_3Sn.[13)]

Against this background and with application to superconducting magnets for high-field NMR as a goal, JASTEC has tested several superconducting wires made by the bronze-routed process, powder-in-tube process (TS-PIT) and internal tin process (DT). **Fig. 4** includes cross-sectional photographs of wires produced by the respective processes, and **Fig. 5** shows their Jc characteristics. Compared with the bronze-routed process, the powder-in-tube process (TS-PIT) resulted in Jc at higher magnetic fields in excess of 18 T, while the internal tin process resulted in higher Jc at magnetic fields up to the vicinity of 18 T. Superconducting magnets designed contemplating the Jc characteristics at these magnetic fields will have an excellent balance of cost and performance. The following describes the details of each process.

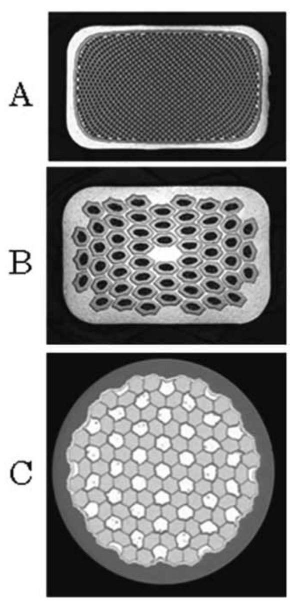

Fig. 4 SEM images of Nb_3Sn conductors developed by Kobe Steel A: bronze routed process, B: power in tube process, C: internal tin process (distributed tin process)

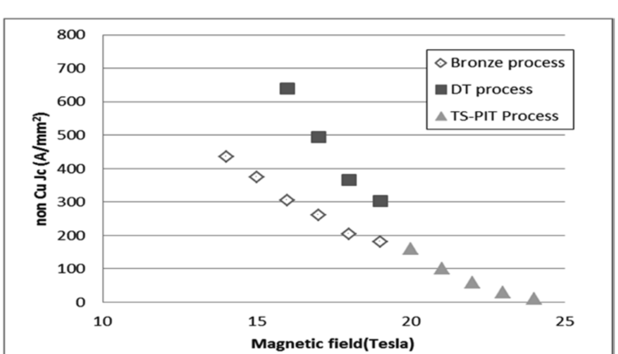

Fig. 5 Non-Cu Jc versus magnetic field curves of Nb_3Sn conductors with three types of manufacturing processes

3.1 Bronze-routed process; Development of Nb_3Sn wire based on high Sn bronze

The first industrial Nb_3Sn wire was produced by the bronze-routed process. Kobe Steel group adapted this process first and continued its development. As a means for increasing Jc, the company aimed at increasing the amount of Nb_3Sn generated in wires and conducted development based on Cu-Sn alloy (bronze) with a high Sn concentration. As described above, increasing the Sn concentration in the Cu-Sn alloy results in a large amount of intermetallic compound, rendering the processing difficult. To this end, the Kobe Steel group focused on the design of cross-sections that are less susceptible to working and on the optimization of the process steps, including the wire drawing and heat treatment. As a result, the company successfully developed a Nb_3Sn wire on the basis of a Cu-Sn alloy containing 16%Sn and achieved a Jc of 194 A/mm^2 at 18.5 T, 4.2 K. The superconducting magnet based on this wire succeeded in generating a high magnetic field of 22 T in 2000. This magnet was used for NMR measurement at 930 MHz, and the NMR apparatus achieved the highest central magnetic field at the time.[8)]

3.2 Powder-in-tube process; Nb_3Sn wire made by TS-PIT process.

In order to achieve a high magnetic field for an NMR apparatus, it is particularly important to improve Jc at high magnetic fields. JASTEC conducted development adapting a type of powder-in-tube process, called TS-PIT.[9)] In the TS-PIT process, powders of Ta and Sn are heat-treated for molten diffusion to produce a Ta-Sn compound, which is ground to powder. The powder is used to fill a sheath of Nb-Ta alloy to be wire-drawn. The idea behind this was that the addition of Ta would increase the diffusion rate of Sn in Nb, which would increase the amount of Nb_3Sn that would be formed. As seen above, the powder-in-tube process is characterized by the fact that elemental addition is relatively easy. Moreover, this process is not limited by the supply of Sn, as in the case of the bronze-routed process, which enables the Nb_3Sn phase to be formed in a large amount, resulting in an excellent Jc characteristic at a magnetic field of 20 T or higher. It should be noted, however, that this process involves the handling of powder, which requires dedicated facilities. Also required are technologies that are different from the wire drawing of ordinary composite wires.

In order to demonstrate that the excellent magnetic field characteristics of Nb_3Sn wires made by the TS-PIT process can be realized on a practical scale, a prototype 50 kg wire was produced, which verified a significant improvement of Jc in the high-magnetic-field region.

The Jc characteristic has improved by 52% (Jc : 295 A/mm^2 at 18.5 T and 4.2 K,) compared under the same condition with the wires produced by the bronze-routed process, used for the superconducting magnet for NMR at 930 MHz previously described. Another challenge for practical applications was the uniformity of the characteristics over the entire length of the wires, since this production method employs powder for raw material. For evaluating the uniformity of Jc characteristic, samples were taken at intervals of 50 m from a 500 m long prototype material, and the samples were subjected to Jc measurement. The results are shown in **Fig. 6**. The average value of Jc was 295 A/mm^2, while the standard deviation was 10 A/mm^2. This value is as good as the values for the bronze-routed process used in practical applications, verifying that a uniform Jc was obtained over the entire length. In addition, a Jc of 170 A/mm^2 was achieved in a high-magnetic-field region (21.5 T.) Although this value falls slightly short of 190 A/mm^2, which is required for an NMR superconducting magnet for 1,000 MHz, the results appear promising for the improvement of characteristics by the future optimization of the production process.

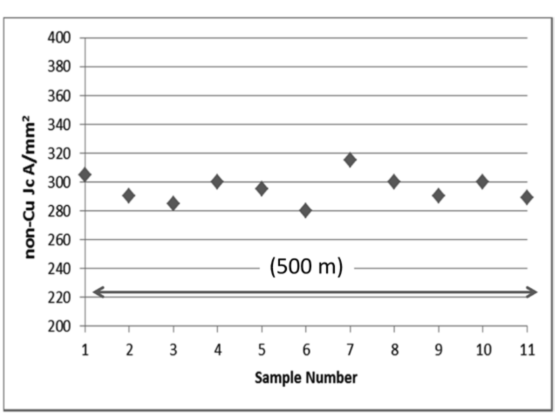

Fig. 6 Jc distribution by PIT process in 500 m long Nb_3Sn conductor

3.3 Internal tin process; Development of Nb_3Sn wire based on dispersed-tin process

In the case of superconducting magnets for super-high magnetic fields, the amount of wire used for an intermediate layer coil (located outside the innermost layer coil) is much greater than that of the innermost layer coil, affecting the cost more significantly. Using a wire based on the powder-in-tube process for these coils is not desirable from the aspect of market competitiveness. The intermediate layer coils require Nb_3Sn wires that cost less than those made by the TS-PIT process and have Jc values higher than that achieved by the bronze-routed process in the high-magnetic-field region of approximately 16-18 T. JASTEC has been conducting technology development based on the concept that the distributed-tin process, a type of internal-tin process, is suitable for this purpose and so far has completed prototype production on a volume production scale. The distributed-tin process is a method involving wire drawing, in which an Nb module (an array of Nb cores disposed in a Cu matrix) and Sn module (Sn alloy embedded in a Cu matrix) are combined. This process allows the amount of Cu matrix to be reduced below that of the conventional process incorporating Nb and Sn into the same module and enables the improvement of Jc. That is, the one module of Nb and Sn requires a Cu matrix that promotes the diffusion reaction of Nb_3Sn, while the distributed-tin process allows Nb and Sn to be distributed, which decreases the amount of Cu matrix, enabling a high Jc to be obtained.

Another prototype 50 kg wire was produced using the distributed-tin process to verify its performance. The resulting Jc was 373 A/mm^2 at 18.5 T and 4.2 K, indicating an improvement in the Jc characteristic of 70% or greater compared with the bronze-routed process.

3.4 Summary

Nb_3Sn wires based on three different processes have been developed for application to magnets with a high magnetic field. As shown in Fig. 6, the relationship between Jc and the magnetic field varies depending on the production processes. Each process has pros and cons, and an optimal one must be selected—with reference to specifications and economy, for example. **Table 1** summarizes the features of these processes. When designing a magnet with a high magnetic field, care is taken to selectively exploit the wire performance for the most economical generation of a high magnetic field.

Table 1 Featured aspects of Nb_3Sn conductors made by different processes and design consideration for NMR magnets

Process	Bronze	Poder in tube (PIT)	Internal tin
Critical current dessity Typical value	Low 180(A/mm^2) @18.5(T)	High up to 24(T) 170(A/mm^2) @21.5(T)	High below 18(T) 270(A/mm^2) @18.5(T)
Material cost	Middle	High	Low
Lead time	Long	Long	Shrot
Heat teatment	Short	Short	Long
Single unit length	Long	Short	Short
Suitable magnetic field and amount usage in NMR magnet	>16(T) Large	18(T)< Small	>18 (T) Middle

Conclusions

In order to develop a superconducting magnet that generates a high magnetic field, it is imperative that the Nb_3Sn wires have a high Jc. The wires must also be made at low cost to increase market competitiveness. With consideration to these two aspects, we will strive to contribute to the superconductivity business of the Kobe Steel group through the development of Nb_3Sn wires.

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