Developments in Superconducting Wires and Magnets

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We have been developing superconducting wires and magnets for over 40 years and decided to focus on the NMR field in the early 1990s. Japan Superconductor Technology Inc., established in 2002, has successfully applied the R&D achievement of Kobe Steel to their production of superconducting wires and magnets. This article describes developments in superconducting wires and magnets with focus on the latest development.

Introduction

We have over 40 years history of developing superconducting technology and started focusing on the NMR (Nuclear Magnetic Resonance) area about 15 years ago. In 2002 we established JASTEC (Japan Superconductor Technology Inc.), the only company in Japan specialized in the manufacturing of superconducting products. We are the top-class manufacturer of the superconducting wires for NMR magnets.

This article introduces the development of superconducting technology and the latest achievements, and also refers to the future direction of the technology.

1. Development history of superconductor technology

We started development of superconducting technology more than 40 years ago. In 1964 Asada Research Laboratory was established to develop technologies beginning with "super" such as superconductor, super-high-pressure, super-high-purity-iron and super-clean water. Since then we have explored superconducting materials, developed cryogenic temperature refrigeration technologies, established cryogenic measurements and developed structural materials for cryogenic applications.

In 1978 we succeeded in producing NbTi based wire and started sales. A ship propelled by superconducting electromagnets (electromagnetic thrust ship) began to be developed in cooperation with Kobe University of Mercantile Marine (currently Kobe University) and Kawasaki Heavy Industries, Ltd. and we supplied a superconducting magnet in 1979[1), which resulted in a successful experimental navigation of a ship in the following year. The basic facilities of our current superconducting wire production were prepared also by 1979 at our Moji Works.

Around 1980 we started developing Nb_3Sn wires which are applied mainly for superconducting magnets generating above 10 T. We succeeded in developing a pulse magnet with stored energy of 1 MJ and ramp rate of 5 T/3 second.[2) The stored energy of 1 MJ was regarded to be a level of a superconducting magnet manufacturer. At the same time, we started developing powder metallurgy processed (PMP) Nb_3Sn wires using Cu-Nb powders in cooperation with Kyushu University.[3) Based on this development, the wire was further developed for use for alternate current under a research association (Super-GM) started in 1988[4), which led to the development of another PMP Nb_3Sn wire described later.

Cryogenic technology was developed in cooperation with our machinery division, which resulted in the development of cryogenic fatigue testing equipment with a liquid helium re-condensing capability in 1979, multi-sample cryogenic fatigue testing equipment in 1984 and helium liquefier for an electromagnetic thrust ship in 1989.

The application oriented developments of wires and magnets were transferred to the New Materials Development Center (later the New Business Division) in 1986 and the basic research was continued at the Corporate Research Laboratories. The New Materials Development Center have developed magnets for research use, magnets for animal MRI (Magnetic Resonance Imaging) and magnet for human body MRI. Although a limited number of magnets were made, we explored business opportunities and decided to start business in the animal MRI magnet. In 1989 we established Japan Magnet Technology (JMT) in alliance with Otsuka Electronics Co. Ltd. and Magnex Scientific Ltd. of the UK and started business after introducing the manufacturing technology of magnet from Magnex Scientific Ltd. In 1991 the business direction was changed from animal MRI to NMR magnet for analysis. A technology called "cold ship" was developed[5) in 1991, which enabled shipment and delivery of magnets in cold condition. Larger scale production was started in

1995 to supply magnets to JEOL Ltd. forming a basis of our current business. In case of NMR for solution analysis, the higher the magnetic field the higher the S/N ratio (the S/N is proportional to the 3/2 power of the field) and higher the resolution become, increasing detectable molecular weight and enabling the analysis of dilute solutions. For this purpose we decided to develop magnets with higher magnetic field.

We started developing, in cooperation with MIT, a superconducting magnet having 750 MHz (17.6 T) which exceeded 600 MHz (14.1 T)[Note)], the world's highest field NMR magnet of the time. The superconducting magnet at the time used round wires, however, we decided to use rectangular wires to downsize magnets and increase the turn densities. In general, rectangular Nb_3Sn wires tend to deteriorate the superconducting properties. We optimized parameters of fabrication, established a technology to produce wires without sacrificing the superconducting properties and succeeded in the development of a 750 MHz magnet.[6)] Quench simulation technology developed in cooperation with MIT contributed to the successful development. We also succeeded in the development of a 800 MHz magnet in 1998.

Discoveries of oxide superconductor in 1986 brought "superconductivity fever". We participated in ISTEC (International Superconductivity Technology Center) in 1986 and in 1989 established Superconductor and Cryogenic Technology Center which developed not only oxide systems but also metallic wires and magnets. Oxide superconductor have zero resistivity and low thermal conductivity. These properties, when used in electrical leads, allow a large current to flow in the leads without head leak from outside. In 1995 we developed a cryogen-free magnet, which does not use any cryogen such as liquid helium and liquid nitrogen, by utilizing both an oxide superconductor and a small 4KGM refrigerator using the Gifford-McMahon cycle. This magnet has been used in a variety of applications with its ease of generating strong magnetic field without use of any coolant and has grown to the second basis of our business.

The wire business, on the other hand, has been supplying to world class NMR magnet manufacturers continuously since 1994. In 2002 the electronics materials division, which was in charge of superconducting wire production at that time, was merged with JMT and has become our current JASTEC.

2. Recent development of Nb_3Sn superconducting wires for practical applications

We supply Nb_3Sn wire produced by bronze process. In bronze process, a number of Nb filaments are placed in the matrix of Cu-Sn alloy (bronze), which forms Nb_3Sn on the surface of the Nb filaments during a heat treatment after drawing. The following section describes recent development of Nb_3Sn superconducting wires for practical applications.

NMR magnets operate under persistent current mode. The reasons for the magnetic field decay of a superconducting magnet in persistent current mode are the resistance of the wire itself and the resistance at the joints between wires. The former is expressed in the following equation in relation to the electric field E generated by the current in the superconducting wire;

$$E = E_c\,(J/J_c)^n \quad \cdots\cdots \quad \textbf{(1)}$$

Where, J and J_c are current density in the wire and critical current density respectively, E_c is the critical electric field which defines J_c, and n-value is as exponent. The resistivity is proportional to E.

Thus J_c and n-value are important indices for wires of NMR magnet. Mechanical strength is also an important factor to protect the magnet. We have been focusing on those three parameters in developing Nb_3Sn wires for NMR magnets.

2.1 High critical current density

In a bronze processed Nb_3Sn wire, a high Sn content in bronze increases the amount of Nb_3Sn, refines the grain-size of Nb_3Sn and makes the composition of Nb_3Sn close to stoichiometric, improving the J_c. However the solubility limit of Sn is 15.8mass% and, as the Sn content approaches this limit, the manufacturing of wire becomes difficult due to increase of undesirable precipitates. This had limited the Sn concentration to 13mass% and had limited the value of J_c.

We have worked for over ten years on utilization of bronze with higher Sn concentrations. In cooperation with a bronze manufacturer, we developed a high Sn content bronze alloy with a uniform microstructure without segregation and developed a technology to draw wires. As a result the Sn content of Nb_3Sn wire was successfully increased from 13mass% to 16mass% on a

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Note)

In NMR, capacities of magnets and equipment are generally denoted by resonance frequencies of hydrogen corresponding to the strength of generated fields, because resonance frequencies are directly proportional to the strength of fields. 23.5 T corresponds to 1,000 MHz.

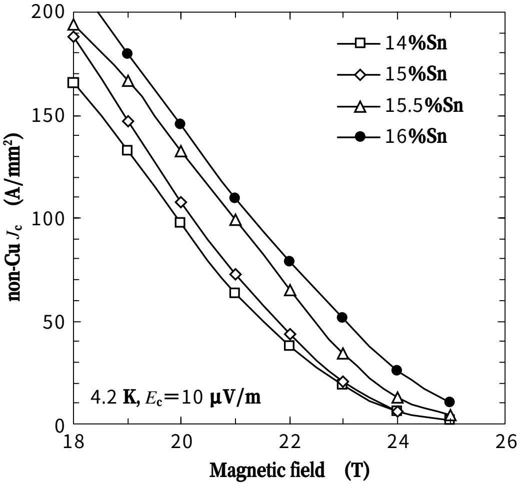

Fig. 1 Magnetic field dependence of non-Cu critical current density for bronze processed Nb_3Sn superconductors with different Sn content

commercial basis.

Figure 1 shows magnetic field dependence of non-Cu critical current density (J_c) on Sn content for bronze processed Nb_3Sn superconductors.[7),8)] The J_c is improved significantly with the increase of Sn concentration. The wire with higher Sn concentration enabled development of superconducting magnets having higher magnetic fields including the 930 MHz (21.9 T) NMR magnet.

2.2 High *n*-value

It has been pointed out that the localized critical current (J_c) distribution in a wire determines the *n*-value. If superconducting filaments have uniform diameters and narrow J_c distribution among each other, the superconducting transition of the current (I) - voltage (V) curve becomes steep, which results in a high *n*-value. On the other hand, filaments with non-uniform diameters along the length, having a broad J_c distribution, result in a wide superconducting transition width making the *n*-value low.

We have optimized the wire drawing and annealing conditions to obtain filaments having uniformity along the whole length of the filaments. The average *n*-values of our Nb_3Sn wires, though they vary depending on wire structure, fall in the range of 50 to 70 for 12 T, 40 to 60 for 15 T and 30 to 50 for 18 T.

2.3 High strength

As the magnet size becomes larger, the electromagnetic force exerted on wires during quenching becomes significantly larger. In the case of 1GHz class magnets, the largest force is exerted on wires used around 12 T magnetic field and the force is estimated to be as large as 300 MPa. This makes it difficult to produce a 1GHz class magnet using conventional Nb_3Sn wires, since the 0.2% yield strength of the wires are typically in the range of 150 to 170 MPa and are not high enough.

Photo 1 Cross-section of Ta reinforced Nb_3Sn superconductor

A high strength Nb_3Sn wire (**Photo 1**) was developed using Ta as a reinforcement material based on our observations that Ta (1) has good workability in cold forming, (2) has high strengths at cryogenic temperatures due to its bcc structure and (3) has a high melting point (3,263K) which retains strength after the heat treatment to form Nb_3Sn.[9)]

The wire with 11volume% of Ta has 0.2% yield strength of 305 MPa at 4.2 K which is almost twice as high as that of conventional Nb_3Sn wires. Utilization of this wire enabled the development of a 1GHz class large size magnet which does not suffer from unexpected quench. The wire has become indispensable in the production of NMR magnets with ultra high magnetic field.

3. Latest development in the NMR magnet

3.1 Ultra high field NMR magnet

In 1995 we started development of a 1GHz class NMR magnet entrusted by the Independent Administrative Institution National Institute for Materials Science, Tsukuba Magnet Laboratory (NIMS/TML).[10)] The following developments were made in addition to the development of wire described above. The stored energy of the magnet is approx. 33 MJ which is more than 4 times the maximum stored energy of conventional magnets. The quench simulation technology was established first, in order to design a protective circuit to ensure the safety of the magnet even when the energy is discharged due to breakage of superconducting condition. To maximize the potential of the wires and magnet, technologies for ultra-low temperature generation and control were developed to lower the operating temperature of the magnet from 4.2 K to 1.6 K. Those technologies led to a successful generation of a 900 MHz (21.1 T) magnetic field in persistant current mode for the first time in the world in 1999. The magnet, after partial modification, reproduced 900 MHz in autumn of the following year and generated 920 MHz (21.6 T) in April, 2001. The magnet was transferred, reassembled and energized at the NIMS/TML[11)-13)] and is used for solution analysis related to the Protein 3000 Project.[14), 15)] In March 2004 a 930 MHz (21.9 T) magnetic field was generated successfully using a 16mass% Sn bronze wire.[16)] This is the highest field of NMR magnets at date and a record of high magnetic field produced by a persistent current mode magnet having a room temperature bore. **Photo 2** shows the outside view of the magnet and **Figure 2** shows advances in magnetic field generation.[17), 18)]

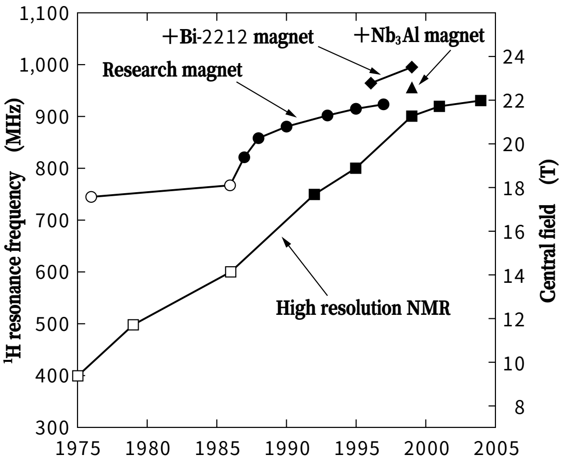

Fig. 2 Advances of magnetic field generated by superconducting magnet

3.2 High field NMR magnet

With the increase of magnetic field a countermeasure was required for the increased stray field. In response to this, a self-shield type 700 MHz magnet with bore diameter of 89 mm was developed in 2003 and a self-shield type 800 MHz magnet with bore diameter of 54 mm was developed in 2004. Both the magnets have approx. 70% smaller volume at 5 Gauss level compared to the non-shield type, lightening up the installation conditions. The latter was the world's first 800 MHz superconducting magnet of self-shield type that operates at 4.2 K. This was made possible by Nb_3Sn wire with higher Sn content made by bronze process, which is applied to the inner most coil.

Photo 2 Outside view of 930 MHz NMR superconducting magnet

3.3 Horizontal magnet

In 2003 we started development of a self-shield type animal MRI magnet with central magnetic field of 7 T and bore diameter of 400 mm entrusted by National Institute of Radiological Sciences. We achieved the "cold ship" of a cold mass of 7 ton under cooled condition by developing a strong support structure with low thermal conductivity. Zero-boil-off condition was achieved by re-condensing vaporized helium through a refrigerator, and self shield technology reduced 5 Gauss area by 70%. **Photo 3** shows the appearance

Photo 3 Outside view of 7T/400SS superconducting magnet for animal MRI

of the magnet. The high magnetic field produced by the magnet improves resolution significantly, allowing the magnet to be used for experiments to elucidate brain function of animals.

3.4 Cryogen-free magnet

A schematic of a cryogen-free magnet is shown in **Figure 3**. There are two stages of cold heads extended from the refrigerator. The first cold stage cools the thermal shield which shuts out thermal radiation from outside and the second stage is connected to a superconducting magnet to be cooled. The elimination of cryogen allows (1) easy handling (2) flexible rotation of field axis (3) operation in clean rooms and (4) easy access to the magnet center. The magnet is being used in a variety of applications. **Photo 4** shows cryogen-free magnets with their fields of applications. Optimization of heat-conduction structure has lowered the temperature of the magnet itself, downsized the magnet and increased the magnetic field. We succeeded in generating 15.5 T field in Feb 2005 to renew the record of field produced by cryogen-free magnets and also completed a 15T magnet having 170 mm room temperature bore.

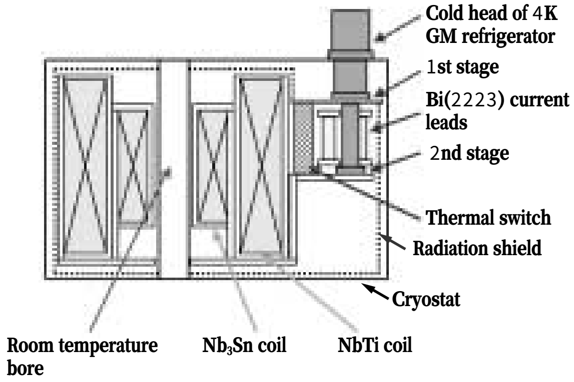

Fig. 3 Schematic cross section of cryogen free superconducting magnet

15**T**/170
(Scientific research)

2.2**T**/250
(Plasma research)

1.6**T**/1250
(Polarization control)

8**T**/100/50
(Split type)
(Optical physics)

5.5**T**/400
(Scientific research)

1.2**T**/250
(Split type)
(R&D of semiconductor device)

6.7**T**/140
(Gyrotron)

3**T**/400
(Magnetic separation)

8**T**/45/9
(Split type)
(X-ray diffraction)

1.6**T**/600
(Molecular distribution control)

Photo 4 Several types of cryogen free superconducting magnet

4. Future perspectives of superconducting technology

4.1 Development for next generation wire

It had been generally believed that a superconducting magnet of 1GHz class could not be produced from metallic superconducting wires. Recently several new processes other than bronze process are proposed for Nb_3Sn wire and progresses have been made in property improvements. We have developed the production technology of PMP Nb_3Sn wire using Ta-Sn compound powder developed by Tachikawa et al.[19] under support of Japan Science and Technology Agency .[20)-22)]

Photo 5 shows the cross-section of a multifilamentary PMP Nb_3Sn.[21] The wire comprises 54 filaments made from copper sheathed Nb-Ta alloy tubes filled with Ta-Sn compound powder. We have experimentally manufactured a PMP wire using the actual production process and have confirmed a non-Cu J_c at 21 T to be approx. 1.5 times higher (170 A/mm^2 @4.2 K) than that produced by bronze process.[22] Considering that the operating temperature of over 900 MHz magnets is below 1.8 K, this value corresponds to the J_c of 1GHz level field, implying a possibility of producing a 1GHz class magnet using Nb_3Sn.

Nb_3Sn wires will not be able to produce magnetic fields above 1 GHz and substitution by other materials will be needed at this level. Various data published to date suggest that J_c values of intermetallic compound of Nb_3Al and high T_c oxide superconductors should enable production of magnets up to 1.1 GHz (25.8 T) and over 1 GHz respectively. However, application of new materials in NMR magnets requires not only high J_c-value but also various peripheral technologies including superconducting joint. We will continue development of wires taking those peripheral technologies into account.

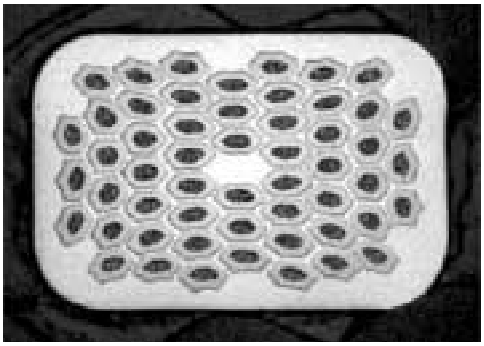

Photo 5 Cross-section of Ta-Sn powder-in-tube processed Nb_3Sn superconductor

4.2 Future development of superconducting magnet

The International Human Genome Consortium announced the successful completion of the Human Genome Project in April 2003 and has been focusing on the mechanism and application of the human genome. The subjects include personalized medicine, genomic drug discovery, regeneration medicine and gene therapy. NMR analysis technologies are becoming more important and there are needs for machines with higher magnetic fields to improve analysis efficiencies.[23]

In the field of solid state NMR analysis, the achievements of high magnetic field machines enabled the structure analysis of materials having quadrupolar nuclei such as oxygen, aluminum and titanium.[24] There also are strong needs for magnets with higher magnetic fields in this area.

Our development aims at a magnet higher than 930 MHz using wires with higher magnetic field and higher properties to meet to those requirements.

Higher magnetic field, downsizing and low stray field are required for horizontal magnets. We continue development of those magnets to make our products more user-friendly.

Similar requirements exist for magnets used in solid state analysis. We will focus on areas such as equipment for heat treatment under magnetic fields and magnetic separator systems, which will expand their market in the near future, and we will develop characteristic products fitting our customer's needs.

Conclusions

Superconductor technologies, not having any alternative technologies and superseding other technologies significantly, have a variety of future applications. We will continue to develop the technologies by addressing the issues to be overcome.

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