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Development of Oxide Superconductors
– High-T_c Bulk Superconductor, QMG, and Its Magnetic Applications –

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Recent progress in processing and applications has been reported for the oxide bulk superconductor (QMG) developed by NSC. QMG comprising an RE (rear earth element) based oxide superconducting phase with high performance can be enlarged by processing modification using the RE substitution effect. With the developments in processing, the number of applications has increased, for instance bulk magnets, which can generate a five times stronger magnetic field in comparison with conventional permanent magnets. Small and strong electromagnets made of QMG are also underdevelopment now by the investing the precision fabrication method of QMG.

1. Introduction

Superconductivity, a phenomenon in which electrical resistance becomes zero, was discovered in 1911 by Kammerlingh Onnes et al. when they measured the electrical resistance of Hg at low temperatures using liquid helium (4.2 K) as the cooling medium[1)]. Ever since, researchers have developed applications of the attractive characteristic of superconductors of zero electrical resistance and searched for substances that exhibit superconductivity at higher temperatures for nearly a century. As a result of such R&D activities, now there are various technologies using the superconductivity around us such as the magnetic resonance imaging (MRI) using superconducting coil magnets formed by winding wire of a superconductor. With regard to the search for substances that exhibit superconductivity at higher temperatures, Bednorz and Müller found in 1986 that an oxide material showed superconductivity at 30 K. This discovery triggered a boom of research called a superconductivity fever: within a period of a few years after it, other materials that showed superconductivity at comparatively higher temperatures of liquid nitrogen (77 K) were discovered one after another[2,3)].

Nippon Steel Corporation began researches into the superconductivity nearly two years earlier, and during the superconductivity fever, successfully developed, for the first time, a bulk superconductor (named QMG) that exhibited markedly good properties of critical current density (J_c, the maximum current applicable to a superconductor while retaining its superconductivity), which is one of the most important parameters in the application of a superconducting material[4,5)]. The developed bulk material had a critical temperature (T_c, the temperature at which superconductivity is attained) of approximately 90 K and consisted of complex oxide of Ba, Cu and rare earth elements (RE) such as Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb: its main component was a superconducting substance expressed as $REBa_2Cu_3O_{7-x}$.

The microstructure of QMG is characterized by the fact that, as seen in **Fig. 1**, fine particles approximately 1 μm in size of an insulating substance expressed as RE_2BaCuO_5 (211) are dispersed in the single crystal of the 123 phase of $REBa_2Cu_3O_{7-x}$. **Fig. 2** shows a bulk of QMG; an entire bulk is composed of a single crystal of the 123 phase having grown from a seed crystal. Because the crystal of QMG is made to grow typically by positioning a seed crystal so that its c axis is in parallel to the normal of the upper surface of a product crystal, crystal habit lines stretching from the seed crystal in a fourfold axisymmetric pattern are seen on the upper surface of an as-

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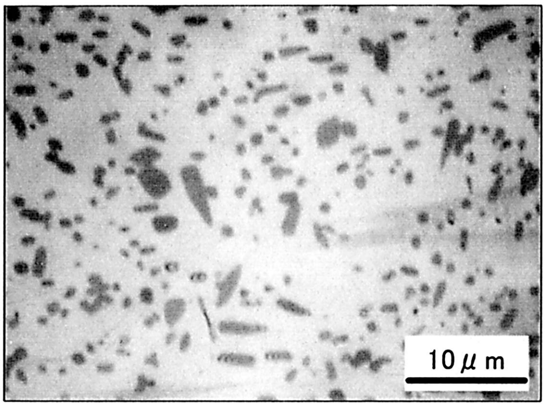

Fig. 1 Microstructure of QMG

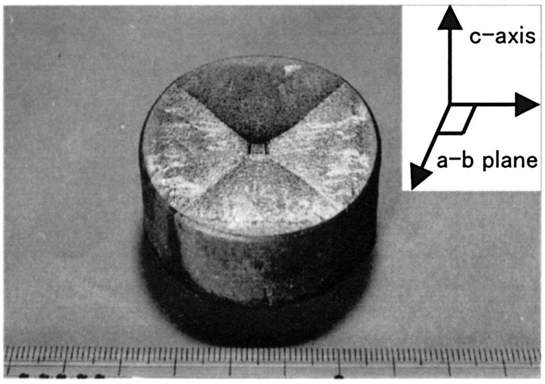

Fig. 2 Appearance of QMG bulk

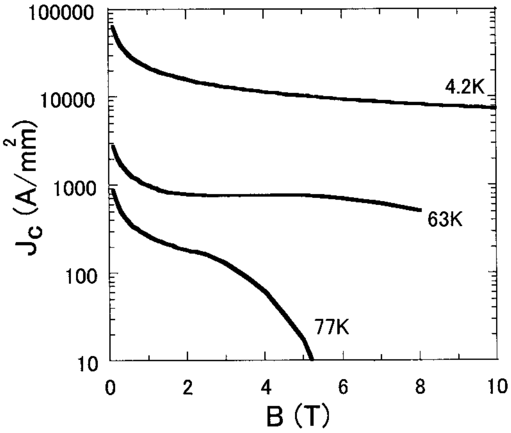

Fig. 3 Field dependence of J_c at each temperature

grown product crystal.

Since QMG is composed of a single crystal as described above, it is characterized, in terms of macrostructure, by the fact that there are no crystal grain boundaries, which interfere with the flow of superconducting current, and in terms of microstructure, by the fact that fine 211 particles having a magnetic-flux-pinning effect are dispersed in the matrix of the 123 phase to markedly enhance the critical current density J_c. **Fig. 3** shows the magnetic-field dependence of J_c of QMG at 77 K (the boiling point of nitrogen), 63 K (the melting point of nitrogen) and 4.2 K (the boiling point of helium). One can see in the graph that the critical current density of QMG exceeds 1×10^2 A/mm^2 under a flux density of 1 T at 77 K. This means that the superconductor is applicable to practical purposes. Considering the fact that the values of J_c of conventional sintered bulk superconductors are somewhere around 10 A/mm^2 under a flux density of 0 T at 77 K, it is clear that the J_c properties of QMG are far superior to those of conventional bulk superconductors.

Usually, a cylindrical bulk of QMG has the crystal orientations shown in Fig. 2, and is used by applying a magnetic field in the direction of the c axis and having the current flow in the a-b plane. Accordingly, what Fig. 3 shows is the temperature dependence of J_c in the a-b plane under a magnetic field applied in the direction of the c axis. By the way, QMG having these excellent characteristics was so named because it was manufactured for the first time by a method called a Quench and Melt Growth method[5]. Its basic manufacturing method was established later when a modified QMG method using a seed crystal was developed[6].

More recently, modified QMG materials having improved mechanical properties were developed by adding Ag by approximately 10 wt % and dispersing its particles several hundreds of micrometers in size in the matrix, and also a manufacturing method (the OCMG method) for improving the T_c and J_c properties was developed by using light rare earth elements (La, Nd, Sm, Eu and Gd), which have relatively large ionic radiuses, and growing the crystal in an atmosphere of a low partial pressure of oxygen[7,8]. As a result of these improvements, the diversity of bulk materials of QMG has been expanded, and their properties improved. Application technologies are being developed in various fields using these bulk superconductors.

QMG can be applied in the following three fields:

1) Levitation: Applications of QMG to the non-contact bearings of a flywheel for storing electric power, non-contact transfer facilities, etc. are being studied taking advantage of its capability to enable stable magnetic levitation when used in combination with a permanent magnet[9,10].
2) Bulk magnet: QMG functions as a permanent magnet by cooling it to below the critical temperature in a magnetic field, then reducing the external magnetic field to zero, and applying a permanent current to it to trap magnetic flux. Studies of applications of a bulk magnet thus produced to a magnetic separator, motor, sputtering facility or the like are under way[11-13].
3) Current carrying: This is an application of QMG by providing it with power terminals and applying electric current from an external power source. Applications of QMG to a current lead, coil magnet, current limiter or the like are being studied[14-16].

This paper reports the development of a large-size bulk of QMG 85 mm in diameter and that of a bulk magnet using such a bulk material. The latest advance in precision machining technologies has made it possible to produce coils of homogeneous quality from bulk materials, and as a result, the possibility of fabricating superconductive coil magnets that work at the temperature of liquid nitrogen has been increased. This paper also describes the development of such a coil magnet.

2. Development of Large-size Superconductor

Because QMG is a single-crystal material, it can only be produced through crystal growth from a seed crystal. By this production method, however, the single-crystal yield falls at an accelerating pace as the material diameter increases, because the probability of undesirable nucleation at positions other than the seed crystal increases. Nevertheless, because QMG can be produced from systems of different RE elements, it is possible to increase the single-crystal yield by a method called a RE compositional gradient method, which takes advantage of the change in the formation temperature of the 123 phase resulting from substitution of RE sites. **Table 1** shows the formation temperature of QMG crystals of different RE systems in the air. There is a difference of the formation temperature of approximately 150℃ between a Sm system and Yb system, and in consideration of the difference, QMG of a Sm system is used for a seed crystal. The formation temperature of a complex system containing two or more RE elements is known to be the molar average of the formation temperatures of systems each containing one of the RE elements[6]. Additionally, the temperatures shown in Table 1 are known to decrease by approximately 30℃ when Ag is added or the partial pressure of oxygen in the atmosphere is controlled to approximately 1%[7,8].

Fig. 4 schematically shows an example of a QMG material of a three-layer structure produced by the RE compositional gradient method. When the content of Gd in the center portion is set at 100% and that of Dy is increased by 10% from layer to layer, the formation temperature of each layer becomes lower by approximately 2℃. It is possible to obtain a large-size single crystal while minimizing a super-cooled zone, which is prone to become polycrystalline, by having a seed crystal contact the center of a precursor that has such a RE compositional gradient and then slowly cooling them. **Fig. 5** shows the appearance of a grown QMG material 85 mm in outer diameter produced by the said method. The crystal habit lines in a four-fold axisymmetric pattern extending from the seed crystal at the center towards the periphery evidence the fact that the entire material is composed of a single crystal. The quality of a large-size, single-crystal QMG is evaluated by magnetizing it into a bulk magnet. The evaluation criterion is how large a current can be made to pass homogeneously through the material in the state of superconductivity, or how strong a magnet can be obtained.

The development of a bulk magnet using the material 85 mm in outer diameter shown in Fig. 5 is explained below.

Table 1 Formation temperature of each RE based QMG

Large ← Ionic radius → Small

RE element	Sm	Gd	Dy	Y	Ho	Yb
Formation temperature (℃)	1060	1030	1010	1000	990	900

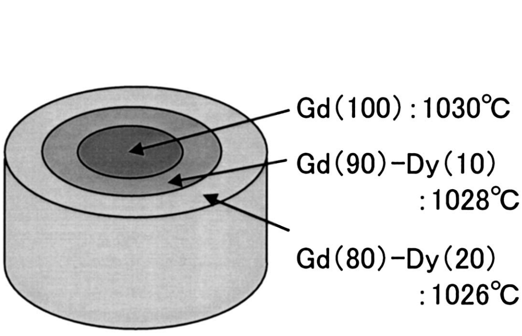

Fig. 4 Example of RE compositional gradient

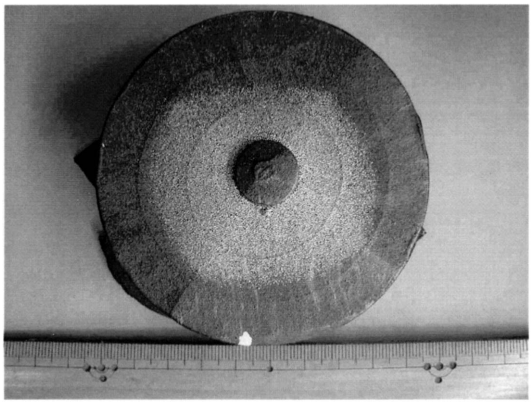

Fig. 5 Appearance of 85mm ϕ QMG bulk

3. Development of Bulk Magnet

A concept of a bulk magnet was established as a form of application of QMG at an early stage of its development[17]. Thereafter, as new superconductive materials were developed, the intensity of magnetic fields that could be trapped in them increased, and recently, flux densities of 3 T at 77 K and 17 T at 29 K have been achieved[18-20].

A bulk material of QMG 85 mm in outer diameter was cut at the upper and lower ends, its outer surface was finished by precision machining to a diameter of 83 mm, and a reinforcing ring of stainless steel 5 mm in wall thickness was fitted to it and fixed with resin as shown in **Fig. 6**. Since the coefficient of thermal expansion of stainless steel is larger than that of QMG, when cooled to 77 K QMG undergoes compressive force of the stainless-steel ring. In addition, since QMG has a strong magnetic field of several T after magnetizing, it is subjected to strong outward force of the magnetic field. Because the mechanical strength of QMG is comparatively low, approximately 70 MPa, reinforcement with a stainless-steel ring or the like is required. The reinforced specimen was then magnetized by placing it in an external magnetic field of 3.5 T, cooling with liquid nitrogen, and reducing the external magnetic field to zero.

Fig. 7 shows the distribution of the magnetic flux trapped in the specimen. The flux density at the center was approximately 2.5 T, and the flux density exhibited a concentric distribution pattern, evi-

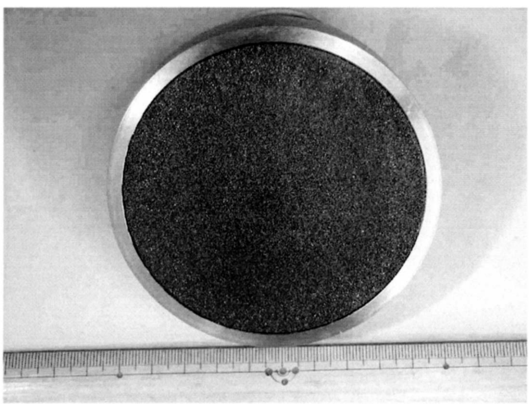

Fig. 6 QMG reinforced by stainless steel ring

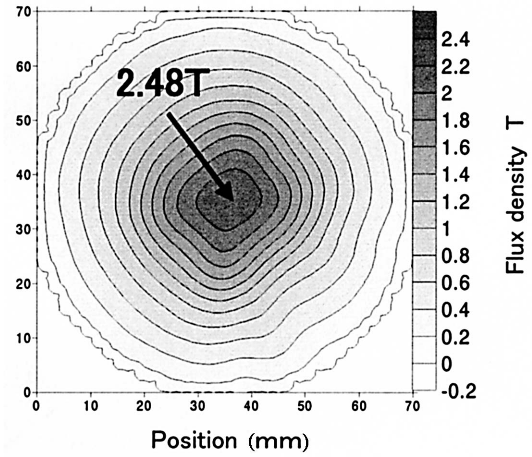

Fig. 7 Distribution of trapped field

dencing substantially homogeneous properties of the material. As seen in **Fig. 8**, the gradient of field distribution is steeper near the center. This indicates that the value of J_c increases as the field strength increases; this phenomenon, seldom seen with common superconductors, is called a peak effect.

As explained above, a bulk magnet of QMG has a flux density approximately five times as strong as that of a permanent magnet. In view of the fact that a compact and strong magnet is effective in reducing the size and enhancing the efficiency of a motor or generator, studies into the use of a bulk magnet of QMG for such applications are under way. Its application to the magnet for a sputtering machine for forming magnetic thin films at high efficiency is also being developed.

Once magnetized, a bulk of QMG works as a magnet practically permanently unless its temperature is raised, but since it has to be magnetized at low temperatures in a magnetic field or by methods such as pulse magnetization, an external field source is indispensable. In many applications of the magnetic field, the magnets are excited by applying electric current from an external power source.

Then, development of a coil magnet that can be excited by applying electric current is explained below.

4. Development of Coil Magnet

QMG is produced in the form of a bulk of a single crystal, so it has been considered difficult to form it into a coil shaped magnet by drawing it into wire and winding it into a coil like the wire of a Nb-Ti superconductor now commercially used. However, the latest advance in machining techniques has made it possible to slice a bulk of QMG to a thickness of 1 mm or less and form a sliced piece into a spirally wound coil. Thus, by piling coils of QMG fabricated through such machining work and connecting them to each other by normal solder, a magnet that could be excited by applying electric current was experimentally produced[15,21].

4.1 Test Method

A cylindrical QMG specimen of a Ag-added Gd system 60 mm in diameter and 20 mm in thickness was produced by the modified QMG method. Then, the specimen was sliced into pieces 1.0 mm in thickness, each of the sliced pieces was machined into a seven-turn spiral coil 55 mm in outer diameter (with a line width of approximately 2.3 mm and a gap between turns of 0.5 mm), Ag was sputtered onto the upper and lower surfaces of the coils to a thickness of approximately 2 μ m, and the coils were annealed in an oxygen atmosphere. **Fig. 9** shows a specimen of the coils thus prepared. Six of such coils were piled in alternately inversed winding directions and connected serially at the ends. To measure the voltages generated inside the superconductive coils and at the connections, measuring terminals were provided. The piled coils were encased in a reinforcing Ni-Cr ring as seen in **Fig. 10**, connected to copper electrodes, and then embedded with Stycast and GFRP as shown in **Fig. 11**. In addition, a Hall sensor was fitted into the hole at the center to measure the magnetic field. The coil magnet thus prepared was cooled to 77 K in liquid nitrogen, a current was applied to it using a constant-current power source, and voltages were measured at various positions. In addition, for measurements at the triple-point temperature (63 K), the pressure of the liquid nitrogen was lowered to 94.6 Torr in a sealed vessel.

4.2 Test Results and Discussion

Fig. 12 shows the voltages generated in each of the coils at 77 K. The application of the current was discontinued at 340 A as a quickly increasing flux-flow voltage was measured in the 6th coil from approximately 275 A and higher. The magnetic flux density at 340 A at the coil center was 0.55 T. The voltages in the 1st and subsequent coils increased gradually in the current range from approximately

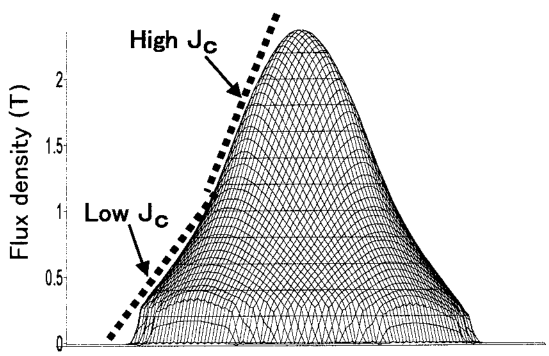

Fig. 8 Gradient of field distribution

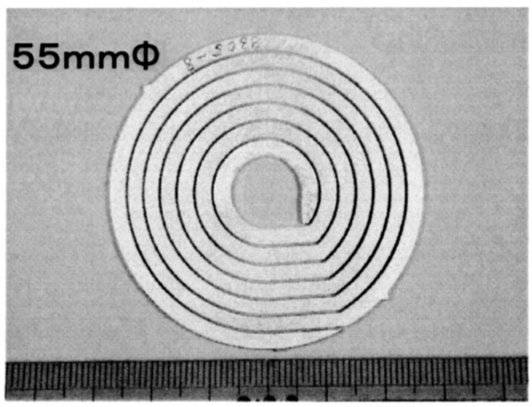

Fig. 9 Appearance of 7 turn coil with 55mm in outside diameter

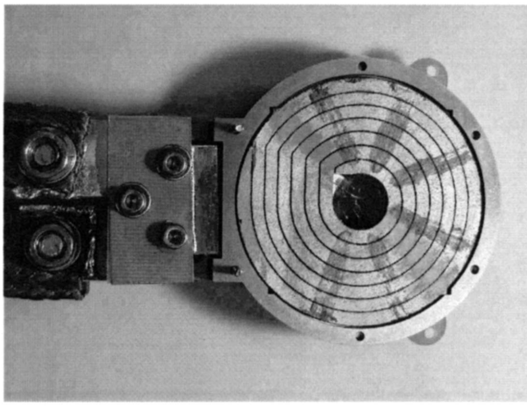

Fig. 10 Six layer coil with Cu electrode and NiCr ring

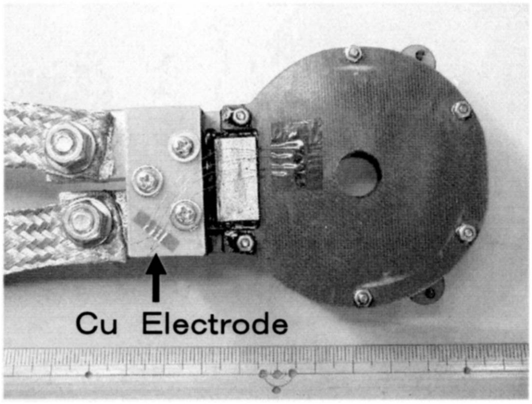

Fig. 11 QMG coil magnet embeded by resin

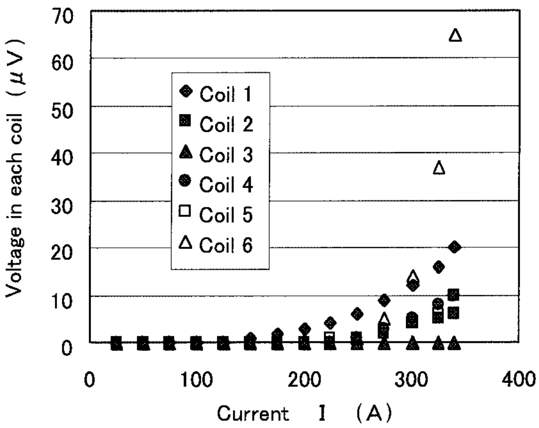

Fig. 12 Voltage - current properties in each coil

200 A and higher, but the increase was moderate up to 340 A. The difference in the generated voltages between coils is presumably due to the difference from coil to coil in the sub-grain structure within the QMG bulk or the difference in the angle between sub-grains and the current applied.

The electrical resistance within the coil magnet, namely the sum of the resistance of the connections between the copper electrodes and the coils and that between the coils, was 3.18 μΩ.

Thereafter, the coil magnet was tested in the same manner in the liquid nitrogen at the triple-point temperature, and a magnetic field of 1.18 T was measured at 700 A. **Fig. 13** shows the relationship between the applied current and the flux density of the magnetic field at the boiling point (77 K) and triple point (63 K) of nitrogen. The flux density looks proportionate to the current applied in the low-current range up to 100 A, but its deviation from the proportionality becomes larger as the current increases. This behavior can be explained by the model shown in **Fig. 14** using the critical state model $J_c(B) = C$ as follows: during the process of the initial magnetization, a zone of positive current (I^+) expands from the inside of a coil and another of negative current (I^-) from the outside as magnetic flux penetrates as shown with (1) to (3), but after all the zones have reached the critical state, the boundary between the positive and negative currents shifts towards the outside as shown with (3) to (12). This is because the current flows in effect in the outside portion of the coil, and the flux density of the magnetic field that results from the cur-

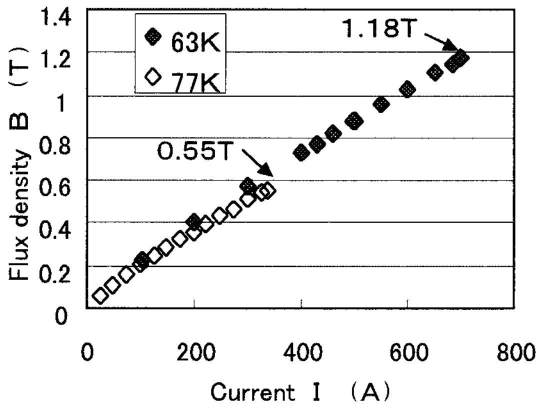

Fig. 13 Flux density - current properties at 77K and 63K

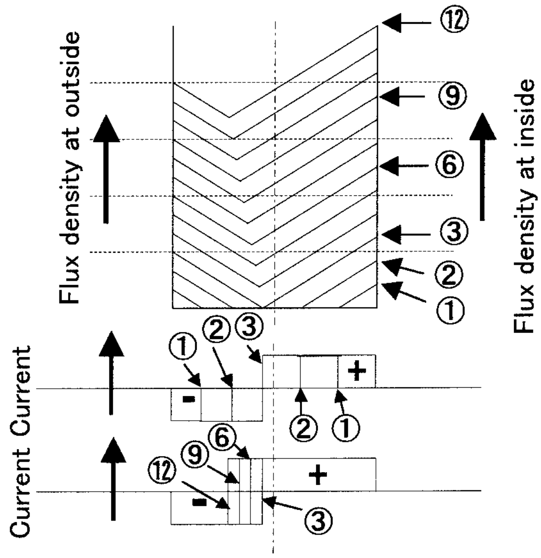

Fig. 14 Model of current and flux distribution in the coil element

rent is reduced accordingly.

The influence of the change in the current distribution within a coil upon the magnetic flux density is presumed to increase, especially when the sectional area of the coil is relatively close to that of its center hole. Fig. 13 also shows that the behavior of the flux density is slightly different at 77 and 63 K. This difference is presumably attributable to the difference in the current distribution within the superconductor due to different values of J_c at different temperatures. The resistance inside the coil at 63 K was 2.73 μΩ, and the connection resistance fell to approximately 85% of that at 77 K after cooling to 63 K. This is presumably because the resistance of the solder decreased as it was cooled to the lower temperature.

As explained above, a novel superconducting magnet was fabricated that is capable of forming magnetic field of 1-T class when cooled with liquid nitrogen. That confirmed that by lowering the temperature of the liquid nitrogen from the boiling point to the triple point, the intensity of the magnetic field could be nearly doubled. Since the J_c(B) properties of QMG at 63 K are little deteriorated even in a magnetic field of approximately 10 T, when a coil magnet of QMG is made larger and used for generating an intensive magnetic field, use of nitrogen at 77 K or lower as the cooling medium is expected to be effective in such an application.

The above results showed that it was possible by precision machining to produce spirally wound coils of homogeneous quality from a bulk material of QMG, and that the coils thus produced would show excellent current application properties. It is intended to produce larger coil magnets by increasing the number of coil layers and their inner and outer diameters; we expect that tests of larger coil magnets will expand the actual applicability of QMG.

5. Closing

This paper has explained the development of large size QMG materials and that of bulk and coil magnets as applications of QMG for forming magnetic field. The development of bulk magnets began from an early stage of the development of QMG, and the properties of the bulk magnets have been improved steadily. Development of a simple magnetizing method will be a key to their practical application. The coil magnet is a new form of application of the superconductor, and the flux density achievable with a simple system for use will determine their practical applicability. The homogeneity of the bulk material and the technology for coil fabrication will be decisive in the actual application.

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