History and recent progress of QMG™ and QMG bulk magnets

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Abstract. The microstructure of QMG consists of a single crystal REBa$_2$Cu$_3$O$_x$ phase and fine RE$_2$BaCuO$_5$ particles. Y-based QMG was first produced in 1988 by the Quench and Melt Growth method. A bulk magnet made from QMG was proposed in 1989. QMG bulk magnets were realized by enlargement technology using RE substitute seed crystals. Based on these technological innovations, the development of NMR and MDDS, which are product-based applications of bulk magnets, has recently been reported from the research institutes of applied development. The history of the initial development of these QMG materials and QMG bulk magnets was reviewed. In addition, as progress of the recent QMG bulk magnet development, a new reinforcement method for large ring bulk magnets that can trap 10 T class strong magnetic field magnetization has been reported. For high field magnetization, the reinforcement of bulk magnets is essential to prevent cracking due to large hoop force. Compared to the conventional reinforcement method using only the outer metal ring, the new reinforcement method has been developed using thin QMG rings and metal ring sheets as the composite material with the inner and outer metal rings. In the case of the QMG ring reinforced by the conventional method, cracking occurred at 10T magnetization. Whereas the QMG ring created by the new reinforcement method successfully trapped approximately 10 T.

1. History of QMG and QMG bulk magnets

QMG is a bulk superconductor that has high Jc properties even in the high field. It consists of an RE (Rare Earth)-based oxide superconductor. Figure 1 shows the microstructure of QMG. Figure 2 shows the appearance of QMG. The main technologies characterizing QMG are indicated below.

1) Microstructure: RE$_2$BaCuO$_5$ (211) particles about 1 μm in size are finely dispersed in the single crystal REBa$_2$Cu$_3$O$_x$ (123) phase obtained by Pt or Ce addition for fine 211 particles.

2) Overall structure: QMG appears as a single crystalline structure obtained by the RE substituted seeding technique.

3) RE composition gradient method: This production method is mainly used to produce large QMG materials larger than φ 100 mm.

In this paper, only the origin of the microstructure was mainly reviewed as the history of QMG.

4) QMG bulk magnets: Figure 3 shows an example of the state of the generated magnetic field and superconducting current of the bulk magnet after magnetization.

QMG bulk magnets can generate a high magnetic field stronger than 10T by magnetization using field cooling.
Then the origin of the QMG bulk magnets was reviewed as the history of QMG bulk magnets. A material in which 211 particles 1μm in size are dispersed in a single crystalline 123 phase was manufactured for the first time using a Quench and Melt growth technique in 1988. First of all, the situation before 1988 will be described below.

In 1986 Bednorz & Müller reported the 30K class superconducting phenomenon with LaBaCuO-based material [1]. In 1987, M. K. Wu et al. reported a 90K class superconducting phenomenon with a YBaCuO-based material with $T_c$ exceeding the liquid nitrogen temperature (77 K) [2]. Regarding $J_c$, improvement of the YBaCuO-based material, initially, it was mainly studied using a sintered body. The sintered body is an assembly of crystal grains and contains many grain boundaries. Despite many kinds of investigations, $J_c$ properties of the sintered body could not be improved especially in the presence of the magnetic field. Thus, the cause of the low $J_c$ of the sintered body was explained in view of the weak link between grains at grain boundaries. Experimental evidence of weak link behavior has been demonstrated by Ekin et al. [3]. These weak link phenomena suggest that polycrystalline material such as the sintered body is unsuitable and that single crystals or sharply oriented materials are indispensable for high $J_c$.

On the other hand, magnetization measurements of single crystals prepared by the flux method revealed that $J_c$ in the single crystal is relatively high even in a high magnetic field as shown by Dinger et al. [4]. High $J_c$ values of oriented polycrystalline bulk material were reported by Jin et al. [5]. They used a type of directional solidification called the MTG (Melt – Texture Growth) process. The microstructure is comprised of the alignment of plate-shaped 123 grains grown in the a-b direction. $J_c$ as high as 17000 A/cm² in zero magnetic field and 4000 A/cm² in a field of 1T were reported. This paper asserts that the $J_c$ property can be improved by eliminating the second phase such as coarse 211 particles and the CuO phase [6].

The motivation for the development of QMG was the improvement of $J_c$ by single-crystallization in order to circumvent the weak-link problem. A single crystal was prepared by a self-flux method using a Pt crucible on the surface of a solidified sample. A single crystalline structure of the 123 phase having 211 grains about 10 μm in size was confirmed in the solidified sample also.

Furthermore, 123 melted in a Pt crucible was rapidly cooled by two Cu plates, the obtained melted and quenched body having a thickness of several mm was placed on a Pt net, and placed in a furnace heated to 1100°C. The crystal was grown by slowly cooling to around 1000°C. As a result, QMG (a material in which 211 particles about 1 μm in size are finely dispersed in a single crystal 123 phase) was obtained for the first time in January 1988 [7-9]. This was just before discovery of Bi-based superconducting material by Dr. Maeda et al. [10]. Later on, it was revealed that a small amount of Pt resulted in fine 211 particles about 1μm in size [11-13].

As described above, QMG was created from the single crystal production technology in order to circumvent the weak link problem. As the inventor of QMG, I assert that this invention was not created from the extension of the MTG method that is the process used to make the unidirectional solidified polycrystalline material. The technical concept of the production of single crystal was inherited by the invention of RE substituted seeding technology developed as the manufacturing method for large QMG [14]. By this seeding, large size QMG became manufacturable. As a result, various developments of QMG applications started.

QMG bulk magnets function as a permanent magnet was invented in 1989 [15]. The concept of the QMG bulk magnet was formed during the magnetization measurements for $J_c$ evaluation of QMG of several mm³ using a vibration sample magnetometer (VSM). The result of magnetic susceptibility measurement of the small QMG sample shows that if large QMG are obtained, high magnetic fields greater than 2T can be obtained [16]. At the same time as developing large QMG using seeding technology, the basic form of QMG and QMG bulk magnets was established.

In 1991, the generation of a magnetic field of 1.3 T in liquid nitrogen and the suppression of flux creep by additional cooling (to 63 K) after magnetization of 77 K were reported [17]. In 1998, by precision machining of the outer circumference of QMG and fitting a metal reinforcing ring, maximum flux density of 7.17 T at 40 K was obtained using a refrigerator for sample cooling and a
liquid-He free 10T superconducting magnet [18-19]. Regarding the history of QMG and QMG bulk magnets, the progress that occurred in the first 10 years has been reviewed.

Figure 1. Microstructure of QMG.

Figure 2. Appearance of QMG.

Figure 3. QMG bulk magnet

2. The recent progress of QMG bulk magnets for reinforcement
Recently, the development of NMR and MDDS applications using ring bulk magnets has progressed significantly [20, 21]. In these applications, the generation of a strong magnetic field is necessary. In order to achieve higher performance, it is an important task to prevent cracks due to electromagnetic force. Meanwhile, there have been few reports on the mechanism responsible for material cracking, and the strain behavior of materials that causes fracturing is not well understood [22]. In this part of the paper, the progress in the reinforcement technology to prevent the QMG ring from fracturing is described.

2.1. Trapped flux density and strain behavior of ring-shaped QMG bulk magnets in the magnetization process. [23-24]
Figure 4 shows the temperature and field change profile in the magnetization process. Figure 5 shows the change of distribution on the induced superconducting current in the cross-section of the QMG ring in the magnetization process. The green area represents the induced current. When magnetization was performed at a relatively high temperature (in other words, low $J_c$) in a sufficient applied field, the superconducting current passage was observed on the entire cross-section of the ring, completely magnetizing the ring in phase ④. Conversely, when magnetization was performed at a relatively low temperature (in other words, high $J_c$), the ring was not completely magnetized. The magnetization was terminated leaving areas where no superconducting current flows as in ② and ③.

Stress (F) applied to the QMG ring is divided into the circumferential and radial directions. The stress causing cracking is the circumferential stress (hoop stress). Figure 6 shows the concept of the circumferential stress. The stress can be considered basically proportional to the product of the induced superconducting current (I) multiplied by magnetic field (B); and magnetic field (B) can be considered the sum of the external applied field ($B_e$) and trapped field ($B_t$) by the induced superconductivity current. As shown in Figure 6, a metal ring has been conventionally used for reinforcement. After fitting a QMG ring onto the metal ring with resin in the gap and then cooling, compressive force is obtained from the metal ring, thereby preventing the QMG ring from cracking.

Next, Figure 7 shows examples of the sample preparation for the measurement of the trapped flux density and the change of strain on the QMG ring in the magnetization process. A QMG ring sample with an outside diameter of 60 mm, inside diameter of 28 mm, and thickness of 20 mm was used for the test. It was fitted in a 10-mm thick stainless steel ring. Strain gauges were attached to locations near the inner and outer circumferences of the sample, so that change in the strain in the circumferential direction could be measured. Furthermore, a Hall effect sensor was placed in the center of the ring to measure changes in the trapped flux density. Figure 8 shows the change of the trapped flux density and strain in the magnetization process at 70 K and 4.5 T. Since the external field constituted the x-axis, in this figure, the start point of magnetization is 4.5 T. The magnetization process progressed toward the origin. For the change of strain, the increase of the elongation strain
from the amount of strain immediately before the magnetization was indicated as positive values. For the trapped flux density, values obtained by subtracting the externally applied magnetic field from the values indicated by the Hall effect sensor at the center of the sample were used.

In the early phases of the magnetization process (① to ②), since the superconducting current is induced in proportion to the amount of demagnetization in a high applied field, the change of strain and trapped flux density are increased almost proportionally. In the phase near the end of the magnetization process (④), the induced superconducting current is almost saturated. For this reason, the trapped magnetic flux density is almost constant as well. The change of strain is linearly decreased along with the reduction of the external field. However, the change of strain for the trapped field (B_t) remained in the end. The results described above indicate that depending on the circumstances, the change of strain would reach a peak in the magnetization process. In particular, when a sample is in the shape of a ring, it is easier to be magnetized completely, and the change in strain is considered to have a peak more frequently than in the case of a cylindrical sample. Furthermore, these results show that the change in strain near the inner circumference is larger than that near the outer circumference.

![Figure 4. Temperature and field change in the magnetization.](image)

![Figure 5. Distribution change of superconducting current in the cross section QMG ring.](image)

![Figure 6. Hoop stress of magnetized bulk magnet with outer metal ring.](image)

![Figure 7. Reinforced sample with a metal ring and placement of sensors.](image)

![Figure 8. Change of stress and trapped field in the magnetization process.](image)

Figures 9(a) and 9(b) compare the change in strain when a crack was caused in the magnetization process and that with no cracking during the magnetization. Figure 9(c) shows the sample used for the magnetization and the positions in which strain gauges were attached. As these figures show, while the change in strain near the inner circumference on the top face increased faster than that on the inner circumferential face, it reached a peak and took a downward turn quicker as well; and the value of the change in strain on the inner circumferential face rose higher at the end of magnetization.

In the case of magnetization at 55 K and 10 T, the increase of the strain amount was sharper than that at 60 K and 9 T due to the larger stress. When the strain near the inner circumferential face on the
top face reached approx. 800 με, a crack occurred. This confirms that cracking started in the vicinity of the inner circumference in the magnetization process of a ring-shaped QMG bulk magnet.

Figure 9 Change of strain in the magnetization on the piled reinforced rings (a) 9T at 60K magnetization, (b) 10T at 55K magnetization, (c) Sample and placement of sensors.

2.2. Concept of the new reinforcement method
These results indicate that the compression stress from the outer circumference alone would not be sufficient to reinforce the inner circumference to which a large amount of stress is applied. For a QMG bulk in the ring shape, as the largest strain works in the vicinity of the inner circumference, reinforcements of both the material itself and the inner periphery were considered to be effective. For this reason, a new reinforcement method of ring QMG bulk magnets was devised.

The method involved laminating QMG sheets and high-strength metal sheets into a high-strength composite material, as well as using an inner circumferential metal ring for reinforcing the inner circumference of the laminated QMG ring. The following describes an example of sample structures used for the new reinforcement.

Figure 10(a) shows a cross-sectional view of a ring-shaped QMG bulk magnet reinforced using the new reinforcement method. Figures 10(b) and 10(c) show an enlarged view of the center of the ring cross-section and that of the vicinity of the inner circumferential metal ring, respectively. First, I examined the method for making the composite material shown in Figure 10(b), and studied a method that involved making thinly-sliced QMG sheets and high-strength metal sheets into a composite material by laminating them. In order to improve the mechanical bonding between the metal rings and ring-shaped QMG sheets, Ag coating was applied to the QMG sheets before they were combined with the metal rings by soldering. Figure 10(c) shows the inner circumferential reinforcement. Due to the rate of thermal shrinkage of ordinary metals larger than that of QMG, an inner ring cannot be fixed by the compression force from cooling contrary to the outer circumferential metal ring. When the inner circumferential metal ring alone is attached as-is, it will shrink due to cooling and detach from the QMG rings. In view of this, the inner circumferential metal ring and metal sheets used to combine
with the QMG rings were firmly soldered to maintain metallic bonding. This was performed to elicit the reinforcement effect of the inner circumferential metal ring work to prevent the QMG rings from deforming.

2.3. **Production of a QMG bulk magnet reinforced by the new method and evaluation of the reinforcement effect**

A ring-shaped QMG bulk magnet with the new reinforcement method was actually created based on the concept described above. The strain and the trapped flux density were measured. Furthermore, the prototype was compared with a bulk magnet produced using the conventional reinforcement method. The following describes the details of the test production and evaluation.

2.3.1. **Sample preparation**

Figure 11 shows the parts used for the new reinforcement method. Figure 12 shows the assembling method. As shown in these figures, Ag coated QMG rings were arranged in the Cu ring. A stainless steel ring was arranged in the Ag coated QMG ring. Eight units thus prepared were alternatingly laminated with nine stainless steel sheets ring. The inner stainless steel ring and outer stainless steel ring were attached to the laminate. Each part was bonded by solder, and the QMG bulk magnet was created. Table 1 shows the dimensions of each reinforcement material. Figure 13 shows the appearance of the sample obtained through the assembly process. The sample was fixed in the center of the cold head of a refrigerator with grease. The outer circumferential ring was fixed with screws.

![Figure 11. The QMG ring and reinforcing members used.](image1)

![Figure 12. Assembly drawing](image2)

![Figure 13. A sample prepared by the new reinforcing method.](image3)

| Parts of QMG ring magnet reinforced by new method | Outside diameter (mm) | Inside diameter (mm) | Thickness (mm) |
|--------------------------------------------------|----------------------|---------------------|----------------|
| QMG ring                                         | 60.0                 | 28.0                | 2.0            |
| Stainless steel sheet ring                       | 64.0                 | 24.0                | 0.5            |
| Upper/lower stainless steel sheet ring           | 80.0                 | 24.0                | 0.5            |
| Outer stainless steel ring                       | 80.0                 | 64.0                | 20.0           |
| Cu ring                                          | 64.0                 | 60.0                | 2.0            |
| Inner stainless steel ring                       | 24.0                 | 22.0                | 20.0           |
| Stainless steel ring                             | 28.0                 | 24.0                | 2.0            |

2.3.2. **Measurement method**

The sample was cooled by He gas cooling using the refrigerator to maintain thermal uniformity of the sample. The sample was inserted into a superconducting magnet bore. After cooling the specimen...
from room temperature to 95 K (non-superconducting state), a magnetic field with predetermined strength was applied to the specimen. Then, it was cooled to a predetermined temperature. When the temperature was sufficiently stable, the magnetic field was reduced at the rate of 0.03 T/min for demagnetization. The values of the strain gauges and flux density were recorded.

2.3.3. Results and discussion

Figure 14 shows the trapped flux density and change of strain when the magnetization was performed at 20 K and 10 T. The colors of the data plot lines in the figure correspond to the sensor colors indicated in sensors placement illustration in the figure. In this figure, the QMG bulk magnet is trapping approximately 10T. The slight decrease from 10T can be considered due to the aspect ratio of the sample. In the case of low temperature, that means high $J_c$, the induced superconducting current is concentrated on the outer circumferential face part of the sample. For the change of strain, in comparison with conventional reinforced bulk magnets, the same trend whereby change of strain at the inside is larger than that at the outside is observed.

Figure 15 shows a comparison of the change of strain in the magnetization at the same 60 K. Figure 15(b) shows the result of 9T magnetization for the bulk magnet with conventional reinforcement. Figure 15(a) shows the result of 10T magnetization for the sample with the new reinforcement described above. In the comparison of Figure 15(a) and Figure 15(b), firstly, in the case of the new method, The magnetic field of the peak of each strain curve is almost the same. This trend is thus considered due to the improved uniformity of material strength by the composite material structure.

In a quantitative comparison, in the case of the conventional method, the strain reached a maximum of 700 $\mu e$ on the inner circumferential face. In the case of the new method, the maximum strain value did not exceed 350 $\mu e$. The maximum change of strain under the conventional method would reach 800 $\mu e$, if the bulk magnet reinforced using the conventional method had been magnetized with 10 T not entailing a crack. From this result, the new reinforcement method is considered to have reduced the change of strain to about 40% of that working on the conventionally-reinforced bulk magnet. As seen from the comparison result, the new reinforcement method has an advantage over the conventional method. Moreover, in view of the strain maintained low when magnetizing with 10 T, the sample reinforced with the new method is very likely to endure magnetization using a magnetic field exceeding 10 T.

After these measurements, the distribution of trapped flux density was measured at 77 K. No change was observed in the distribution before and after the 10T magnetizations. For this reason, on
the QMG sample reinforced using the new method, the sample was sufficiently prevented from being damaged from even the stress caused by repeated magnetization.

3. Conclusions

1) The first ten years of the history of QMG and QMG bulk magnets was reviewed.
2) As the recent progress of the ring QMG bulk magnets, a new reinforcement method was reported based on the following two concepts.
   One is to create a composite material of metal sheet and sliced QMG ring. The other is the inner circumference reinforcement by the metal rings to which metal sheets are bonded.
   For example, QMG rings and stainless steel rings were laminated into a composite material; the outer circumferential and inner circumferential metal rings were attached to the laminate by soldering. The obtained ring-shaped QMG bulk magnet trapped 10T without cracking. Compared with the conventional reinforcement method, the new reinforcement method enables significant reduction of the strain of the excited QMG bulk magnet.

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