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Research and Development of Oxide Superconductor —QMG-Processed Bulk Superconducting material with High Critical Current Density—

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Abstract:

A bulk superconducting material with a high critical current density (J_c) *for practical use was developed by using an oxide superconductor of the* $REBa_2Cu_3O_{7-X}$ *system where RE is a rare earth element. A large bulk superconducting material with the non-superconducting phase finely dispersed in the single-crystal superconducting phase was produced by a modified quench and melt growth (QMG) process. The QMG-processed superconducting material has a high* J_c *exceeding* 10^4 A/cm^2 *at the liquid nitrogen temperature of 77 K in a magnetic field of 1 tesla (T), and is expected to find use in many applications. For example, such a large bulk superconducting material proved successful in generating a magnetic field of more than 1 T at 77 K when used as a bulk magnet.*

1. Introduction

Superconductivity is a phenomenon that a certain material (superconducting material) exhibits absolutely zero electric resistance. The zero electric resistance allows the superconductor to generate a powerful magnetic field and transmit electric energy without a loss. Because of this extremely special property, superconductivity-using technologies are expected to bring about technological innovations in various industrial fields.

The phenomenon of superconductivity was discovered by Kamerlingh Onnes in 1911. He succeeded in the liquefaction of helium and discovered that mercury becomes superconductive when cooled to about 4.2 K by using liquid helium as cryogen. Search was then initiated for materials that become superconductive at a higher temperature (critical temperature T_c). The search progressed to the point of discovering Nb_3Ge with the T_c of 23 K, but then stagnated, and led some people to deduct a theory that about 30 K would be the limit of T_c at which superconductivity is generated.

The discovery of a new oxide superconductor [$(La,Ba)_2CuO_4$ with the T_c of 32 K] by Bednorz and Müller in 1986 surpassed a 20-year-old record by a wide margin[1]. This discovery triggered a superconductivity fever for higher-T_c materials the world over. $REBa_2Cu_3O_{7-X}$ (where RE is for rare earth element) with the T_c of 92 K was discovered in 1987, which was followed in succession the next year by $Bi_2Sr_2Ca_2Cu_3O_x$ with the T_c of 110 K and $Tl_2(Ba,Sr)_2Ca_2O_x$ with the T_c of 125 K.

When a superconductor is to be used as a practical material,

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there are other important properties to be taken into consideration in addition to the critical temperature T_c. They are the critical current density (J_c) and upper critical field (B_{c2}). The superconducting state is destroyed by applying a magnetic field intensity of higher than the B_{c2} or passing an electric current higher than the J_c, such as when a temperature above the T_c destroys the superconducting state and returns the superconductor to the normal state. These three critical parameters of temperature, magnetic field intensity, and current density are interrelated, as shown in **Fig. 1**. The superconductor is used as cooled by such cryogens as liquid helium and liquid nitrogen in general. From a practical point of view, a high-J_c material at the cryogen temperature is more advantageous than a high-T_c material.

Take for example the magnet that constitutes a major field of superconductor application. When cooled by the cryogen, the superconductor is placed in a magnetic field created by the supercurrent and can carry the current up to the J_c value that depends on the temperature and magnetic field intensity. If the number of turns is equal, the magnetic field intensity generated by the magnet virtually depends on the current density, the J_c, that can be passed in the superconducting state. The development of high-J_c materials is therefore a key to the fabrication of magnets that can produce high magnetic field intensities.

While the T_c and B_{c2} are intrinsic to a specific superconductor, the J_c is known to vary by two to four orders of magnitude according to such microstructural features as grain boundaries, defects, and precipitates. This means that whether or not a particular superconductor can be practically used depends on whether its microstructure can be controlled.

Niobium titanium alloys (NbTi) are the only metallic superconductor in widespread use, although there are other metallic superconductors that have higher T_c. This is because about 20 years of technology development efforts have made it possible to control the microstructure of NbTi having a T_c of 9.8 K with relative ease and to fabricate it into a high-J_c wire.

From this viewpoint, the authors have concentrated on the practical application of the $REBa_2Cu_3C_{7-x}$ superconductor (where RE is Y, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, or Lu) by improving its J_c at 77 K through microstructural control and increasing its available size.

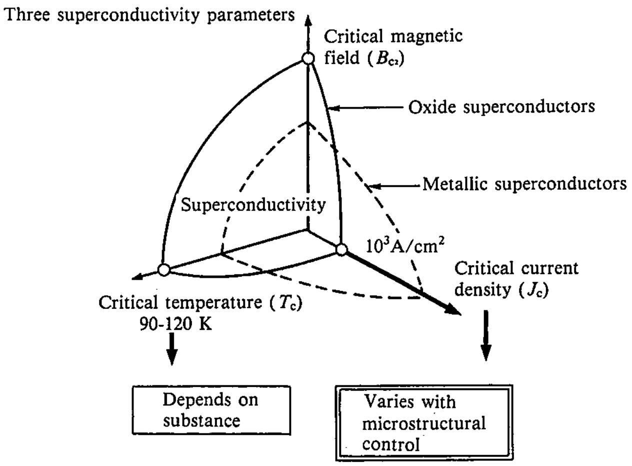


Fig. 1 Relations among temperature, magnetic field, current density, and superconductivity
Dotted line indicates properties of metallic superconductors. T_c and B_{c2} are low, but high J_c is achieved by microstructural control. Solid line indicates properties of initial oxide superconductors. T_c and B_{c2} were high, but J_c was low at that time.

This report discusses the research and development of the high-J_c bulk superconductor produced by the quench and melt growth (QMG) process, a type of melting process originally developed by the authors.

2. High-J_c Oxide Superconductor

In those days when high-T_c superconductors were discovered, many oxide superconducting materials were produced by sintering, the common preparing process for ceramics. Each sintered body is an assembly of fine crystal grains and contains many grain boundaries. When compared with metallic superconductors, one striking feature of oxide superconductors is that grain boundaries are in weak linkage from the viewpoint of superconductivity. That is, grain boundaries are strongly linked mechanically, but the superconductivity is almost broken, resulting in the J_c being drastically lowered. This was mainly responsible for the sharply reduced J_c of sintered bodies. As the sintered bodies are polycrystalline, they are unsuitable for obtaining high-J_c oxide superconductors. Instead, sharply oriented or single-crystal materials are indispensable for generating the high-J_c.

2.1 QMG-processed superconductor

Photo 1 shows the microstructure of a QMG-processed superconductor. A second phase, about 1 μm in particle size, is visible in the matrix. The matrix has a superconducting $REBa_2Cu_3O_{7-x}$ phase (123 phase), contains no grain boundaries, and exhibits a single-crystal microstructure. The second phase, on the other hand, is RE_2BaCuO_5 with non-superconducting phase. As is clear from this, the QMG-processed superconductor is characteristic in that the 123 phase is of single-crystal, and has a fine 211 phase dispersed in the matrix. Such QMG-processed superconductor has a high J_c value exceeding of 10^4 A/cm^2 at the temperature of 77 K in a magnetic field of 1 T.

Superconductors with this type of microstructure were produced for the first time by the QMG process[2,3]. However, a modified QMG process can now produce larger bulk superconducting crystals as shown in **Photo 2**.

2.2 Modified QMG process

Fig. 2 shows the phase diagram of a yttrium-base superconductor produced by the modified QMG process. Above the 123 phase formation temperature (T_f), the precursor consists of the liquid phase (L) of a Ba-Cu oxide compound and 211 solid phase.

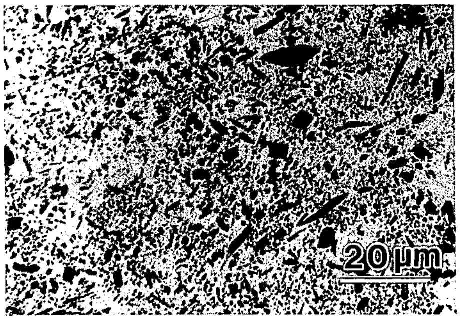


Photo 1 Microstructure of QMG-processed material
Insulating phase (211 phase) is finely dispersed in the matrix of single-crystalline superconducting phase (123 phase).

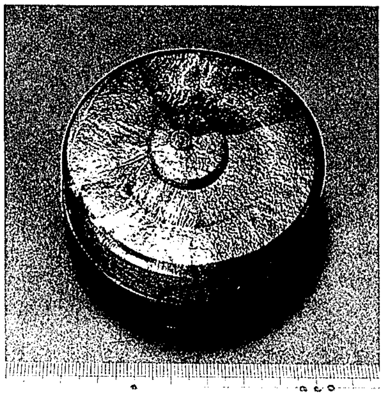


Photo 2 QMG crystal produced by modified QMG process
Single-crystalline grain growth is evident from traces of seeding crystal at the center and facet growth emanating from the center.

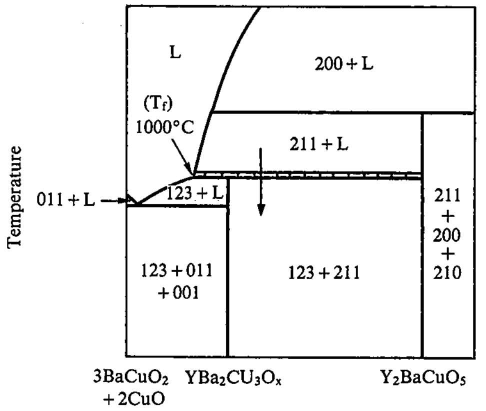


Fig. 2 Phase diagram of yttrium-base superconductor
QMG crystal grain grow by peritectic reaction in which 123 phase is formed from liquid phase (L) and 211 phase at T_f (peritectic temperature).

At temperatures below the T_f, both 123 and 211 phases are stable. The QMG process is a sort of crystal growing process, and the peritectic reaction of the liquid phase and 211 phase at the T_f causes the grains of the 123 phase to grow while forming square facets. At this time, the QMG crystal grows with unreacted 211 phase being incorporated into the 123 phase.

The modified QMG production process is illustrated in **Fig. 3**. There are two main steps: precursor formation and heat treatment for crystal growth.

The starting constituent powders RE_2O_3, CuO, and BaO_2 are mixed in approximate proportions of RE:Ba:Cu = 13:17:24, which are designed to obtain the final 123:211 composition ratio of approximately 7:3. The resultant powder is mixed with about 0.5 wt% of platinum and die pressed into a precursor. When producing a large QMG superconductor, the RE composition may be changed and formed in layers in the pressing process.

The precursor thus prepared is heated from room temperature to about 1,150°C into a semimolten state composed of the 211 phase and liquid phase. It is then cooled to about 1,040°C and seeding is made using seed crystals, followed by slow cooling to allow the QMG crystal to grow.

The important points of the process are as under lined above, which will be explained in detail below.

2.2.1 Fine dispersion of 211 phase by adding platinum

In order to achieve a high critical current density, the absence of grain boundaries, or the single-crystalline state of the 123 phase, is not satisfactory enough. Many fine pinning centers must be created in the superconductor to realize high J_c. When a direct current is caused to flow through a superconductor in a magnetic field, a magnetic flux quantized in the superconductor tends to move under the influence of the Lorentz force. If the magnetic flux is moved by the Lorentz force, it means that work has been performed. This is not superconductivity in substance. To obtain a high J_c, there must be pinning centers that overcome the Lorentz force and stop the magnetic flux motion. Generally, microstructural heterogeneities in the superconductor can all make pinning centers. In the case of QMG-processed superconductor, the finely dispersed 211 phase is considered the main site of pinning centers that brings about the high J_c.

The fine dispersion of the 211 phase was first reported in connection with the QMG process. It was later made clear that trace amounts of platinum from the platinum crucible used in the melting and quenching steps of the QMG process inhibit coarsening of the 211 phase$^{4)}$.

The modified QMG process thus retards the grain growth of the 211 phase by adding a trace platinum to the precursor. **Photo 3** compares the microstructures of QMG-processed superconduc-

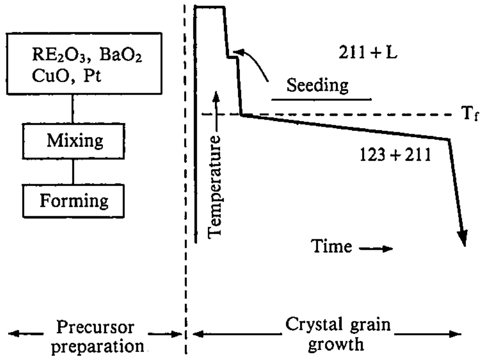
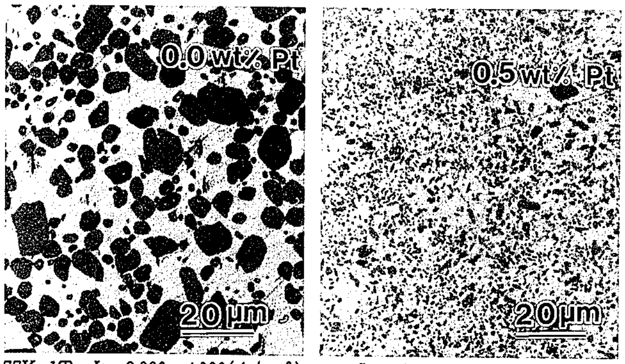


Fig. 3 Modified QMG process
Modified QMG process involves precursor preraration step where the precursor with platinum added in trace amount and RE constituents in a stratified arrangement is prepared and crystal grain growth step where the grain growth is controlled by seeding.



77K, 1T J_c=2 000 − 4 000(A/cm²) J_c=10 000 − 30 000(A/cm²)

Photo 3 Effect of platinum addition on fine dispersion of 211 phase
When no platinum is added, 211 phase is about 10 μm in grain size. Addition of about 0.5 wt% of platinum disperses 211 phase in fine grain size of about 1 μm and markedly improves J_c.

tors with a 0.5 wt% platinum addition and with no platinum additions. The latter shows many 211 phase particles, several tens of micrometers in size. Its J_c is a matter several thousand amperes per cm^2 in 1 T magnetic field, where as the former exhibits a fine dispersion of 211 phase particles, about 1 μm in size, and its J_c is more than one order of magnitude higher. The rhodium addition is reported to have an effect similar to that of the platinum addition[5)].

2.2.2 RE constitution gradient

The temperature T_f for the formation of the 123 phase from the 211 phase and liquid phase varies with the type of RE element used. The RE elements develop a lanthanide shrinkage as its atomic number increases, resulting in decreasing the ionic radius. Among the RE elements, those trivalent RE elements listed in **Table 1** exhibits phase diagrams that are practically the same as that of **Fig. 2**. These trivalent RE elements can form the 211 phase and 123 phase to make QMG crystals. Their 123 phase formation temperature T_f linearly changes like the ionic radius as shown in **Table 1**.

Taking advantage of this phenomenon, QMG grains can be uni-orientedly grown while suppressing their polycrystallization, even under a uniform temperature instead of using a temperature gradient, namely, by stratifying the RE constituents in the precursor according to T_f and slowly cooling the precursor.

2.2.3 Control of nucleation and crystal orientation by seeding

Control of nucleation and crystal orientation by seeding is important in producing a large single-crystalline QMG-processed superconductor. When the QMG-processed superconductor is of the same RE composition as the precursor is, however, its seed crystal is partly melted during seeding. Therefore, a QMG crystal of such RE constitution that the T_f of each RE element is higher than that in the precursor was used, utilizing the T_f difference between RE elements. Seeding at a temperature lower than the decomposition temperature of the seed crystal facilitated the production of QMG superconductors with controlled grain orientation. **Photo 4** shows a growing QMG crystal grain after seeding.

Table 1 Superconducting phase (123 phase) formation temperature T_f for superconductor contained rare earth elements
Rare earth elements decrease in ionic radius with increasing atomic number, which in turn decreases 123 phase formation temperature T_f. Y is located between Dy and Ho.

Element	Y	Sm	Eu	Gd	Dy	Ho	Er	Yb
T_f (°C)	1000	1060	1050	1030	1010	990	970	900

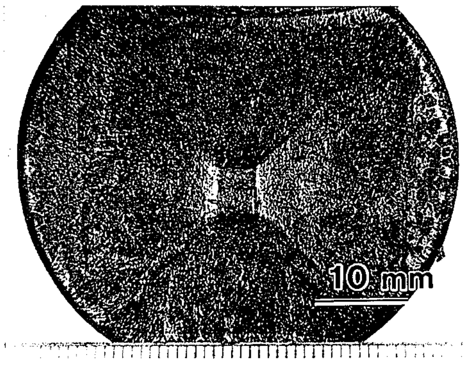


Photo 4 Growing QMG crystal grain
QMG crystal grain is growing while forming square facets from central seed crystal.

3. Application of QMG-Processed Superconductor

Traditional metallic superconductors have been used in the form of wire for coils to produce strong magnetic fields. Now that bulk oxide-base superconductors with high J_c can be produced by the above-mentioned process, they are being put to applications special to bulk use. They include bulk magnets, magnetic bearings, noncontacting magnetic transportation, magnetic shields, current leads, current limiters, and so forth. Some typical applications introduced below.

3.1 Bulk magnets

Metallic superconductors were mainly fabricated into wire, coiled, and used as magnets to produce strong magnetic fields of a few teslas. In contrast, the 123 superconductor is such a brittle crystal itself that it cannot be easily formed into wire for subsequent fabrication into coils. The QMG-processed superconductors, however, can make magnets in the bulk form itself in a permanent current mode if their excitation method is proper.

More specifically, the QMG-processed superconductor in the normal state before cooling is placed in an external magnetic field and is cooled by liquid nitrogen or the like into the superconducting state. The external magnetic field is then removed. The superconductor tends to maintain the initial magnetic flux distribution by inducing a permanent current in itself. As a result, it becomes a bulk magnet having the surface magnetic flux distribution shown in **Fig. 4**.

Fig. 4 shows the distribution of magnetic fields generated when a 50 mm-diameter and 24 mm-thick QMG-processed superconductor was excited by the above-mentioned method at each temperature. As shown, magnetic fields of up to 1.27 and 1.72 T are produced at 77 and 63 K, respectively[6)]. These magnetic field intensities cannot be achieved with permanent magnets and suggest a new application for the QMG-processed superconductor.

3.2 Magnetic levitation

When a permanent magnet is brought close to a superconductor, it carries supercurrent and magnetizes itself to prevent the intrusion of the magnetic field. As a result, repulsive force acts between the superconductor and the permanent magnet. **Fig. 5** shows the relationship between the repulsive force and distance

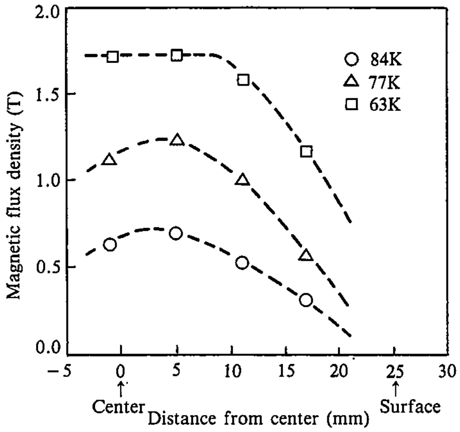


Fig. 4 Magnetic flux distributions at 84, 77, and 63 K
77 K is the boiling point of nitrogen, and 63 K is the triple point of nitrogen. Single-crystalline QMG superconductor was cooled in a magnetic field, and its surface magnetic flux density was then measured. The magnetic flux density is distributed in a convex form at each temperature. The center portion is flat at 63 K, because trapped magnetic field was 1.74 T. It would have reached nearly 2 T if a high enough magnetic field was applied.

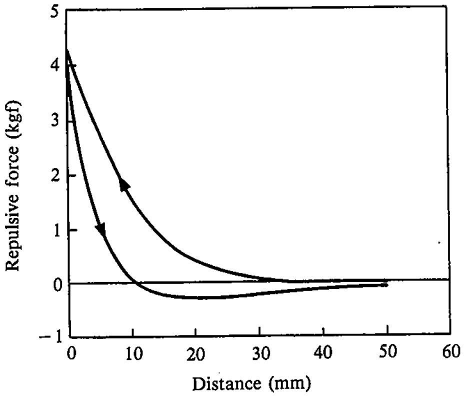


Fig. 5 Repulsive force versus distance
This figure shows change in repulsive force when a superconductor is first brought near a permanent magnet (Sm-Co with a surface magnetic flux density of 0.28 T) and then moved away from the permanent magnet. When the superconductor is moved about 10 mm or more from the permanent magnet, a negative repulsive force (or attractive force) acts between the superconductor and the permanent magnet. This brings about stable magnetic levitation.

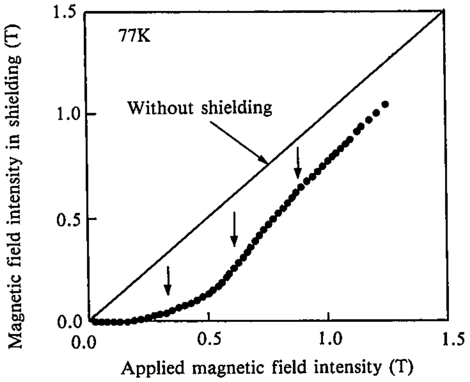


Fig. 6 Magnetic shielding effect of QMG superconductor
Solid line indicates the magnetic field intensity when no magnetic shielding is provided, and dotted line indicates the magnetic field intensity in a magnetic shielding (measured values). Each value measured is located below the dotted line, which means that QMG superconductor provides a magnetic shielding by a difference from each magnetic field intensity.

when a permanent magnet is brought near the QMG-processed superconductor[7]. The better the crystallinity and J_c of the superconductor, the greater becomes the repulsive force. The QMG-processed superconductor is thus suited for such an application.

As compared with the force acting on two permanent magnets placed near each other, the force acting between a permanent magnet and a superconductor is characterized by the existence of a distance at which the magnetism stably balances. When the S pole of one permanent magnet is brought close to that of a second magnet in order to obtain repulsive force, either magnet rotates and the S pole of one magnet and the N pole of the other magnet attract each other. Therefore, the repulsive force cannot be stably obtained with the permanent magnets.

The stable levitation force produced by combining superconductors and permanent magnets is expected to find use in such applications as noncontacting bearings with practically no friction and noncontacting transportation of silicon wafer in a chamber.

3.3 Magnetic shields

Superconductor tends to prevent its internal magnetic conditions from changing, as described above with regard to bulk magnets and magnetic levitation. When a superconductor placed in a zero magnetic field exposed to an external magnetic field, it induces a shielding current (superconducting current) in an attempt to magnetically shield itself and the space around it. **Fig. 6** shows the magnetic shield at the center of a 16 mm outside diameter, 7 mm inside diameter, and 20 mm high QMG crystal at 77 K. Practically complete shielding is attained up to the magnetic field intensity of 0.2 T, and the shielding effect is obtainable even in such a strong magnetic field as to exceed 1 T[8].

Since actual magnetic shields cover a considerably wide space, the possibility of a successful application of the QMG-processed superconductor as the magnetic shielding material will depend on whether or not larger QMG crystals can be commercially produced.

4. Conclusions

As discussed above, QMG-processed bulk superconductor is finding increasing usage in its unique applications among oxide-base superconductors. Magnets capable of generating stronger magnetic fields will come to be by enhancing the J_c, improving the production process, and so forth. A variety of application systems incorporating QMG-processed superconducting materials will also come into light.

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