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Development of Oxide Superconductor -Recent Progress in Materials and Applied Technologies-

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Abstract

The authors are developing a new bulk oxide superconductor of the $REBa_2Cu_3O_x$ (RE: Y or a rare earth element) system (trade name QMG) and, in parallel, its application technologies for accelerating its market creation. In this paper, several topics concerning the material development and its applications are reported. In the material development, following a 100-mm in diameter crystal of the RE = Y system, a new process has been developed for a new composition material, the RE = Sm system. This new process ensures the stability of a low oxygen concentration during the whole process time and consequently leads to the fabrication of an excellent crystal up to a diameter of 65 mm even in the RE = Sm system. In the application technology development, a kA class meander-shaped superconducting current limiting device was developed, which is expected to have a rated current of 1 kA and a current-limiting current of 2 kA when commercially applied. High temperature superconducting bearings made of the new material showed a high levitation force exceeding 0.2 MPa and stable levitation at high rotation speeds. Its applications to current leads and ultra strong magnets are also attracting attention.

1. Introduction

An oxide high temperature superconductor was first discovered in 1986[1]. 2 years later, Nippon Steel succeeded in developing a unique bulk superconductor wherein fine grains of a non-superconducting phase (RE_2BaCuO_5) are dispersed in a superconducting phase ($REBa_2Cu_3O_x$: RE = Y or a rare earth element). The material then obtained, however, was only several millimeters in size and several grams in weight, and thus far from being usable for widely varied applications proposed one after another amidst the high temperature superconductivity fever. The company thereafter concentrated efforts on development of a method to stably produce the material in the characteristics and sizes suitable for expected applications, and established a series of technologies such as a seeding method, a production method that applies a temperature gradient and a compositional gradient to the crystallization process[2]. As a result, Nippon Steel is now capable of producing homogeneous pseudo single crystal of high temperature bulk superconductor exceeding 100 mm in diameter and 1 kg in weight.

The high temperature superconductivity fever eventually subsided, but expectations on the superconductor technologies have increased on the basis of growing concern over the environment and energy issues. Applications of the superconductors in the form of bulk, however, have not been so actively studied as the applications in the forms of wires and thin films. One of the reasons for this is

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that the application of the bulk superconductor became conceivable only when the high temperature superconductor was discovered and, therefore, the concept has but a short history. On the other hand, it may also be the case that potential users of the bulk superconductor do not know its use and characteristics sufficiently well, because of absence of high performance bulk superconductor available in the market. In this situation, for the purpose of demonstrating that bulk superconducting materials applicable to practical uses have been developed and for creating the market of the materials, the authors have proceeded with R&D activities covering application technologies, too. The development of the very material is, of course, carried on in parallel to offer materials having enhanced performance and, in addition to the past development centered on the RE = yttrium system (Y system), a system where yttrium is substituted with another rare earth element is also being developed.

This paper reports wide aspects of our latest activities of material and application development in the field.

2. Material Development –Development of Sm System Material–

Nippon Steel's high temperature bulk superconductor (trade name QMG) is an RE-Ba-Cu-O system oxide superconductor having a 90K-class critical temperature (T_c). Our material development was focused mainly on the RE = Y system but our superconducting material lineup has been expanded recently in terms of function and size thanks to development of a new material system wherein RE sites are substituted with a rare earth element other than yttrium. Our recent material development results are delineated in this section focusing mainly on the RE = Sm system.

First, the characteristics of Nippon Steel's QMG is outlined. The material has two distinct features for obtaining an excellent superconducting property. One is elimination of large tilt grain boundaries, which drastically lower superconducting current, by realizing single crystal-like orientation of an entire bulk through use of a seed crystal. The other is that its material structure is so controlled that fine grains of a non-superconducting phase (RE_2BaCuO_5) are dispersed virtually evenly in a superconducting phase ($REBa_2Cu_3O_x$). The introduction of the non-superconducting phase enhanced the pinning force of magnetic flux lines and realized a high critical current density (J_c) of 10^8 A/m^2 or higher at the liquid nitrogen temperature (77 K) and 1 T of magnetic field. In the early stages of the development for size expansion, there was a problem of bulk inhomogeneity caused by the large tilt grain boundaries and other factors, but it was solved through optimization of crystal growing temperature etc., and production of a high temperature bulk superconductor of the RE = Y system exceeding 100 mm in diameter was made possible[3]. Samples obtained had homogeneous superconducting property as seen in the concentric distribution of trapped flux density shown in **Fig. 1**.

While production of large high performance samples of the RE = Y system bulk superconductor was brought into reality, materials having yet better functions are looked for in the fields of application to utilize intensive magnetic fields. The bulk superconductor wherein the RE sites are substituted with a rare earth element other than yttrium has superconducting characteristics not seen in the RE = Y system. The materials wherein the RE sites are substituted with a light rare earth element such as Sm and the like, among others, are known to be superior in the T_c value over the Y system and excellent in the J_c value in an intensive magnetic field. For this reason, there are strong demands for this type of large size, high performance bulk

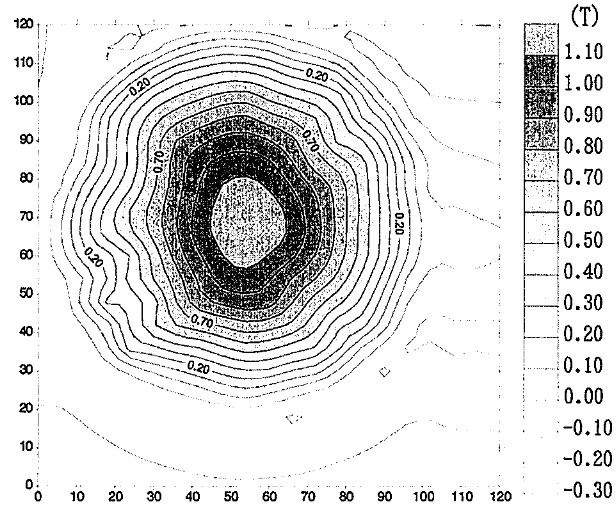

Fig. 1 Example of trapped flux density distribution of 100-mm diameter RE = Y system bulk material

superconductor. The problem, however, is that the T_c value of the Sm system is lowered when it is produced in normal air atmosphere, where the Y system is produced, and, for preventing this from occurring, it is necessary to produce it under a low oxygen partial pressure. Since this inevitably means that the production process of the Sm system is more complex than the Y system, only a limited quantity of large size, high performance bulk superconductor of the Sm system has been available in the market. In view of this situation, we started to develop the large size, high performance bulk superconductor of the Sm system.

While various element process technologies accumulated during the development of the Y system bulk superconductor were applicable to the production of the Sm system bulk material, new element process technologies had to be developed to cope with the constraint of the low oxygen partial pressure and the difference in material properties between the two systems. For example, the seeding method is basically the same for the two systems but, since the melting point of the Sm system is higher than the Y system by about 60K, the seed crystal used for the Y system is not applicable as it is to the Sm system. A new seed crystal suitable for the Sm system grown under a low oxygen partial pressure atmosphere was chosen and optimization of its seeding temperature was pursued. Whereas the difference in melting point between the seed crystal and a precursor is about 60K in the Y system, the difference is as small as 20K or less in the Sm system and, therefore, a more precise control of the seeding temperature is required. With regard to the control of the crystal growing temperature, basic techniques are nearly the same, but poly-crystal is likely to form when the heat treatment pattern of the Y system is applied to the Sm system without modification. At this, the relationship between the supercooling temperature and crystal growth rate of the Sm system were reexamined to find an appropriate super-cooling temperature. The temperature range for a good crystal growth of the Sm system is narrower than that of the Y system, which fact requires a more precise temperature control during the crystal growth. As stated above, the production processes of the Sm system bulk superconductor is significantly different from the Y system in the factors to influence crystal growth stability such as the seeding temperature, crystal growth temperature, super-cooling temperature, etc.

The most important factor to influence the crystal growth stability of the Sm system bulk superconductor is the stability of the low oxygen atmosphere. The element process technologies relating to this, therefore, become very important. Since the crystal growth commencement temperature fluctuates depending on the oxygen partial pressure, it is necessary to precisely control not only the temperature but also the atmosphere during the crystal growth. The atmosphere control requires a space-wise control to make the oxygen partial pressure homogeneous throughout the whole electric furnace interior as well as a time-wise control to maintain the same at a prescribed level during the whole course of the crystal growth. And the task of keeping the low oxygen partial pressure has to be done in as simple a manner as possible in consideration of commercial application of the product.

As a result of studies on the atmosphere control method for producing the Sm system bulk material, the method chosen as the most effective and simple to control the atmosphere was a partial modification of an electric furnace for producing the Y system to form a small box for the atmosphere control in the furnace interior and blow a low-oxygen gas into the box. In addition to this, a method to plant a seed crystal on the precursor placed in the box was also established. Introduction of the atmosphere control method in the box inside an electric furnace made it possible to produce good Sm system bulk samples without requiring expensive facilities. The furnace modification was so designed as to allow simultaneous crystal growth of two or more samples. **Fig. 2** is a trapped flux density distribution diagram of an Sm system bulk sample produced by the developed method. The gradient of the peak of the trapped flux density distribution reflects the value of J_c at each magnetic field. The steeper gradient in higher magnetic fields seen in the figure demonstrates high J_c values of the Sm system in high magnetic fields. With regard to the size, a maximum diameter of 65 mm has been achieved with the Sm system.

Nippon Steel is concentrating efforts on establishing technologies for stable production of the Sm system, which is believed to have a potential peak value of the trapped flux density distribution of 2 T or higher. We believe that a diameter exceeding 100 mm can be achieved with the Sm system, like the Y system, through optimization of heat treatment conditions and other related measures. The technologies established during the material development of the Sm system bulk material are applicable to other substitution materials using light rare earth elements other than RE = Sm, such as RE = Gd, Eu, etc. We intend to utilize the technologies for developing different new materials suitable for different fields of bulk superconductor application.

3. Application Development

Large size, high J_c, high temperature bulk superconductors realize stable magnetic levitation and function as a strong magnetic field source besides being capable of large current conduction and, in view of these properties, various new applications are being studied. Such new applications include the uses as conductors such as fault current limiters, current leads, etc., as levitation force generators such as magnetic bearings, flywheel energy storage, etc., and as magnets such as magnetic separators, bulk magnets, etc. In the development of these fields of application, Nippon Steel's efforts are centered not on development of individual application facilities but on clarification of fundamental characteristics of superconductors in different applications and demonstration of their potentials, aiming at accelerating development of actual applications and market creation of high temperature bulk superconductors. Typical examples of our application developments are introduced in this section.

3.1 Application to fault current limiter

A fault current limiter is a protector for power supply systems to suppress overcurrent at occurrence of short circuits, and is expected to allow a remarkable decrease in overcurrent capacity of electric power facilities. The characteristics required of a fault current limiter include the following: (1) quick response (1 ms or less), (2) very low resistance during normal load, and (3) high resistance upon occurrence of a short circuit. The fault current limiter utilizing a quick change called "quench" of a superconductor from the superconducting state to the normal state is considered ideal in view of the above requirements, and development of such current limiters has been vigorously promoted. Fault current limiters using metal superconducting wire, however, have not been brought into actual use because the metal superconductor requires liquid helium (4K). Among these attempts, the development of a thin film type fault current limiter using a film of high temperature oxide superconductor functioning at the liquid nitrogen temperature (77K) has been ahead of the others,

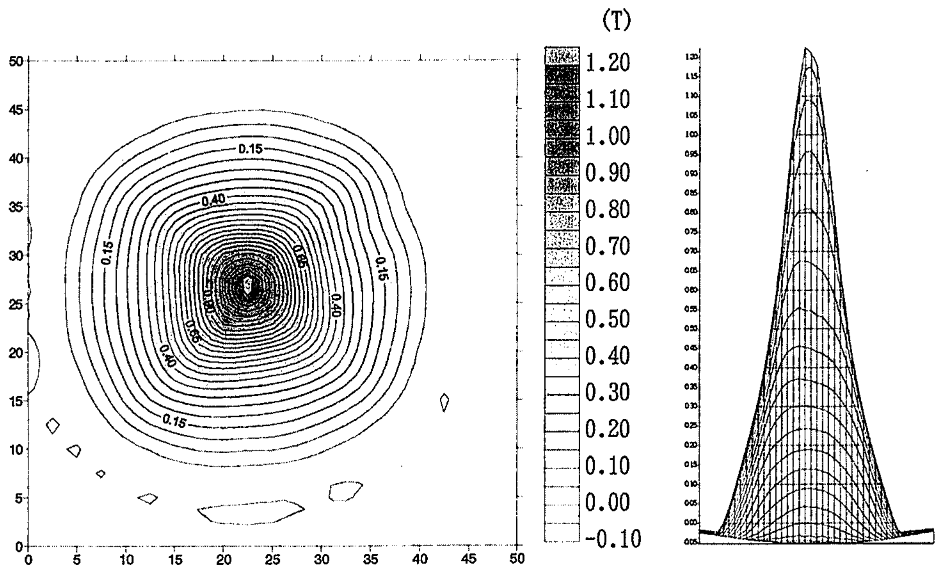

Fig. 2 Example of trapped flux density distribution of RE = Sm system bulk material

but this type of current limiter has a problem in dealing with heavy current.

There is a good possibility of realizing a fault current limiter capable of working at the liquid nitrogen temperature and withstanding heavy current by applying the high temperature bulk superconductor since Nippon Steel's high temperature bulk superconductor, QMG, has a value of J_c as high as 10^8 A/m^2 or above at the liquid nitrogen temperature (77K), a kA-class current capacity is obtained with a sectional area of several mm^2. Thus, a current capacity of 1 to 2 kA, generally used in common power supply systems, can be easily achieved.

A series of simplified current loading tests using thin bar-shaped specimens revealed, however, that a homogeneous quench property and a high speed current limiting action were indispensable, and development of element technologies therefor were required for actual use of high temperature bulk superconductors for the fault current limiters. For example, since the quench occurs locally at an initial stage and the conductor device may be burnt out by the heat generated in the process, it is necessary to disperse the occurrence of the quench as evenly as possible in the entire element. At this finding, it was decided to apply a silver coating on the whole device surface so that the coating might disperse the heat locally generated by the initial quench quickly to the entire device and act as a by-pass of the loaded current. The coating layer thickness and contact resistance between the silver coating and the superconductor body are essential in the design of the quench homogenization method using the silver coating layer.

Another finding was that, although the current limiting response of the superconducting fault current limiter was theoretically rapid because the quench used therein is a physical phenomenon, it was necessary to quicken the response yet more by intentionally inducing the quench. For coping with this, we applied a field assist mechanism to the current limiter so as to impose a magnetic field on the device upon detection of an abnormal current to lower the value of J_c in the entire device. The key technology in the higher-speed current limiting response with the magnetic field assist is the design of the intensity and orientation of the imposed magnetic field. As a result of the quench homogenization with the silver coating and the higher-speed response with the magnetic field assist, fundamental current limiting action has been confirmed with the high temperature bulk superconductor.

In the element technologies related to the fault current limiter, however, what is most different between the superconducting wire and the high temperature bulk superconductor is the significance of the technologies to obtain long devices. A resistance of several Ω is required for obtaining an effective current limiting function. Since the resistivity of the QMG at the normal state is approximately 1.5×10^{-6} Ωm, an effective length of 1 to several m is required to obtain the desired level of resistance with a sectional area of several mm^2. We decided to pursue the possibility of obtaining a long device through the following two development steps: (1) forming of the elements into a meander shape; and (2) connection of element units.

Fig. 3 shows a unit of a meander-shaped QMG current limiting device. The device was manufactured from a cylindrical high temperature bulk superconductor by slicing it into a thickness of 0.5 mm and cutting the ends and the slits. It has a silver surface coating about 1 μm in thickness covering the whole surface, a sectional area of 0.5 mm × 1.5 mm and an effective length of 170 mm. **Fig. 4** shows the result of preliminary current limiting tests of the device immersed in a liquid argon bath (87K). Whereas a current of 800 A flowed when

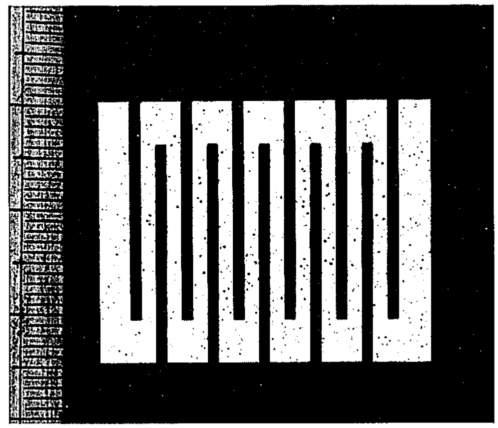

Fig. 3 Meander-shaped current limiting device of QMG superconductor (for 87K)
(25 mm × 32 mm, conductor section: 1.5 mm × 0.5 mm)

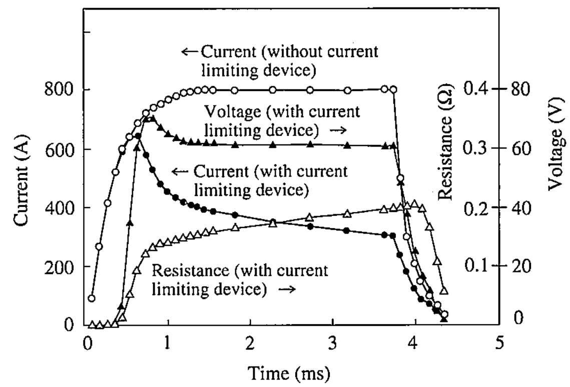

Fig. 4 Action measurements of meander-shaped current limiting device of QMG superconductor
(Temperature: liquid argon temperature 87K)

the current limiting device was absent as shown with blank circles, resistance showed at about 500 A when the device was present and the current was limited to 400 A or so within 1 ms of the loading of the current. A sufficiently quick response speed was obtained in the tests by applying the magnetic field assist[4)], and a good repeatability was also confirmed in repeat loading tests of the device.

Thereafter, we manufactured another device reinforced with resin and glass fiber-reinforced plastic so that it withstood the shock of a several kA loading, which corresponds to a normal loading level of actual power systems. **Fig. 5** shows its outlook. The device has a sectional area of 0.8 mm × 2.2 mm, an effective length of 180 mm and a silver coating on the entire surface, too. It was tested in a liquid nitrogen bath (77K) using a power supply unit having a capacity for several kA equipped with an LC resonance circuit, and a good current limiting effect was confirmed against single pulse sine currents. Further, heat shock resistance of the device was enhanced through an improvement of a coil for the magnetic field assist and optimization of by-pass resistance. This led to a successful development of a kA-class current limiting element having a rated current of approximately 1 kA and a current-limiting current of about 2 kA[5)].

We will concentrate our efforts hereafter on the serial connection of the devices and homogenization of the quench property, aiming at establishing device connecting technologies for actual application of the developed devices. Since the normal voltage of the power

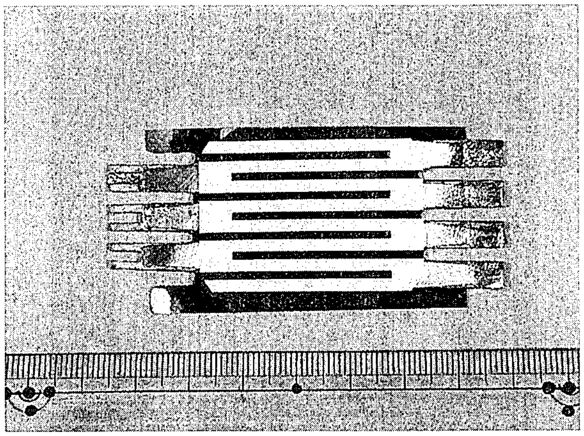

Fig. 5 kA-class current limiting device of QMG superconductor (reinforced with resin and glass fiber-reinforced plastic after meander-shaping and silver coating)

supply systems to which the fault current limiters are applied is as high as 6.6 kV or more, enhancement of voltage resistance of the devices will also be tackled.

3.2 High temperature superconducting bearing

A high temperature superconducting bearing is a new non-contact type bearing utilizing a non-contact positioning force owing to the pinning effect working between a high temperature bulk superconductor and a permanent magnet. In view of a remarkable reduction of bearing losses expected of this type of bearing, flywheel energy storage systems using high temperature superconducting bearings are being energetically developed. Its application is also studied in the fields of bearings used in high rotation speeds, low temperatures, vacuum, space, clean room ambient, etc. However, for effective application of this type of bearing, (1) large levitation force and (2) good rotation stability are essential.

The levitation force is one of the most fundamental characteristics of the high temperature superconducting bearing, and its enhancement is an important task for actual use of the bearing, since this not only enables supporting of heavy objects but also downsizing and cost reduction of the bearing. The levitation force increases in proportion to the value of J_c and the size of the area where superconducting current flows through. Nippon Steel pursued enhancement of the J_c vale and size expansion in consideration of the above, and succeeded in producing the 100-mm diameter Y system material as stated before. **Fig. 6** shows measurements of the levitation force of superconducting materials of different sizes. The measurement was made using a 90-mm diameter Nd-Fe-B magnet and the following sets of specimens: 1 piece of 100-mm diameter sample, 3 pieces of 46-mm diameter samples, and 7 pieces of 33-mm diameter samples. The levitation force when the distance between the superconductor(s) and the permanent magnet was 0 mm was 1,676, 711 and 519 N for each set of the above samples. This means that the levitation force per unit area of the superconductors, namely their levitation force density, is 0.21, 0.14 and 0.09 MPa, respectively. As is clear from the above, a significant improvement in the levitation performance was obtained through the size expansion.

Besides the J_c vale and size of the superconducting material, many other factors are considered to affect the levitation force. We examined influences of crystal orientation, material thickness, shape, sample division, etc. on the levitation force in both the bearing types proposed for the high temperature superconducting bearing, namely axial bearing and radial bearing, and accumulated fundamental data valuable for the bearing design.

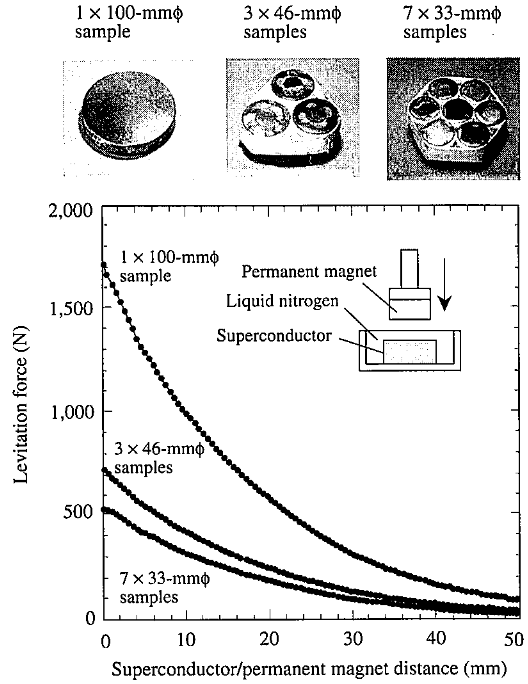

Fig. 6 Levitation force measurement of different sample sizes (Temperature: liquid nitrogen temperature 77K, permanent magnet: 90-mmϕ Nd-Fe-B)

Rotation stability is another important requirement, besides the high levitation force, for actual application of the high temperature superconducting bearing. The most significant characteristic of the high temperature superconducting bearing is stable levitation, but a rotating body in the real world inevitably is not always balanced (deviation of the center of gravity from the center of a bearing) and this causes various modes of vibration. Unless this is accounted for in the bearing design, stable levitation rotation is not realized. At this challenge, levitation rotation models were worked out and the models through tests using miniature bearings were verified. As a result, it was clarified that suppression of the vibration modes to tilt the rotation axis was important for maintaining high rotation stability, and that forming a rotating body to have a short axle (ring or disc shape) was effective as one of specific measures to achieve stable rotation.

Fig. 7 is an example of rotation vibration measurement of a high temperature superconducting bearing. Here, a short-axled rotating permanent magnet 60 mm in diameter and 16 mm in height levitating above a superconducting material 60 mm in diameter was used and its vibration was measured using a laser displacement sensor. In the figure is seen an abnormal increase in amplitude caused by resonance of a horizontal vibration mode near 700 rpm, but the rotation is stabilized in the range above the resonant frequency, since the rotating body spins about its center of gravity in the range. It was also confirmed with the high temperature superconducting bearing that the vibration amplitude could be decreased by properly adjusting the dynamic balance of the rotating body. We therefore consider that it is possible to contain the vibration amplitude within a tolerable range by the dynamic balancing if the amplitude in either the resonant frequency or the stable rotation range constitutes a problem in the bearing design.

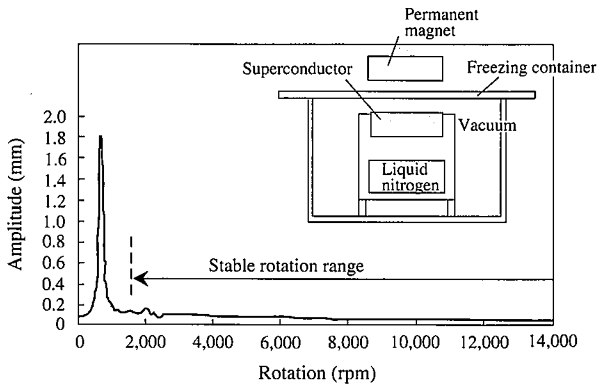

Fig. 7 Example of measured rotation vibration of a high temperature superconducting bearing

In designing a high temperature superconducting bearing, it is essential to examine the arrangement and shapes of the superconductor and the permanent magnet and, in each of the bearing applications, study every factor exerting influence over the levitation force and rotation stability. Through generalization of the levitation rotation models, we hope to be able to propose design guidelines of the bearing materials and structure for different applications.

3.3 Trends of other application technologies

Current lead is one of the fields to which the high temperature superconductor has already been applied actually. The current lead is a conductor to feed power to an ultra low temperature device such as a superconducting magnet. What is required of the current lead is to minimize heat leakage from outside and generation of the Joule heat by current loading. Copper was conventionally used for the current lead but, since copper is a good conductor of heat as well as electricity, there is a limit to the reduction of the heat leakage. The high temperature superconductor, in contrast, is an oxide material and has a smaller thermal conductivity compared with copper. Besides, since its electric resistance is zero, its Joule heat generation can be kept under control. Although a Bi system superconductor has been widely used for the current lead, it has a problem that its J_c value falls drastically in a magnetic field. This problem has been coped with by designing device structure so that a large magnetic field is not imposed on the current lead. However, since it is necessary to arrange the current leads as close to the magnet as possible for making the whole equipment compact, current leads of the Y system superconductor has recently attracted attention thanks to its smaller drop of the J_c value in a magnetic field.

Another application of the high temperature bulk superconductor is the use as a permanent magnet. An ultra strong magnet beyond the capability of any conventional permanent magnets can be produced taking advantage of the pinning effect. While the surface flux density of a conventional permanent magnet is 0.5 T or so, a bulk superconductor magnet has a potential for 2 to 3 T at the liquid nitrogen temperature and, when combined with a refrigerator to lower the temperature yet further, a surface flux density surpassing 10 T can be realized. With enhanced magnetic field intensity, a higher efficiency and further downsizing are viable in the fields of magnetism application such as magnetic separators, motors, etc. When more compact and strong magnetic field sources are thus made easily available, various magnet applications totally new to us will be explored.

4. Summary

A wide variety of superconductor application technologies are being developed in view of its excellent properties, but the present state of technology requires cooling for realizing superconductivity. Actual use of superconductivity, therefore, is presumed to proceed first in the fields where the superconductivity forms an indispensable element technology or the burden of the cooling is tolerable. In fact, the current leads to which the high temperature superconductor has already been applied are used for ultra low temperature facilities and, thus, a refrigerator already provided can serve also the current leads. Besides, the superconductor current leads are indispensable for liquid helium-free superconducting magnets.

The high temperature bulk superconductor is expected to expand its use, besides the current leads, for wide variety of applications such as the fault current limiters, high temperature superconducting bearings, bulk magnets, magnetic separators, motors, and so forth.

References

1) Bednorz, J. G., Muller, K. A.: Z. Phys. B64, 189 (1986)
2) Morita, M. et al.: Shinnittetsu-Giho. (349), 16 (1993)
3) Fujimoto, T., Morita, M., Masahashi, N.: Cryogenic Engineering. 34 (11), 569 (1999)(in Japanese)
4) Morita, M., Miura, O., Ito, D.: Supercond. Sci. Technol. 13, 896 (2000)
5) Morita, M., Miura, D., Ito, D.: Trans. 63rd Autumn Conv. Cryogenic Eng. & Supercond., Kumamoto, Oct., 2000 (in Japanese)