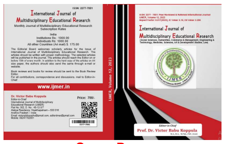
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STUDY OF HIGH TEMPERATURE SUPERCONDUCTORS, ITS RARE EARTH NANOCOMPOSITES AND THEIR BULK TECHNOLOGY

Mohit Kumar Dubey
Assistant Professor
Government Graduate College
Aron, District Guna, Madhya Pradesh, India

Abstract

This paper describes the current status of large single-grained RE-Ba-Cu-O (where RE: Y or rare earth elements) bulk superconductors with excellent superconducting properties in the technological field. The lossless transmission of direct electrical currents in superconductors is very often regarded as an “energy superhighway” with greatly enhanced efficiency. With the discovery of high temperature superconductors (HTS) in the late nineteenth, the prospect of using these materials in efficient and advanced technological applications became very prominent. The impact of superconductor technology on the economy and energy sectors is predicted to be huge if these are utilized on a large scale. The elevated operating temperatures as compared to low temperature superconductors (LTS), relaxing cooling requirements, and the gradual development of facile synthesis processes raised hopes for a broad breakthrough of superconductor technology. In this review, the development of the materials engineering aspect that has been conducted over the last two decades to improve the current carrying capability of HTS thin films is presented. Intensive research on REBa-Cu-O revealed that the optimal RE element is different for application requirements. While Gd-Ba-Cu-O bulk superconductors are greatly attractive for almost all bulk applications, Eu-Ba-Cu-O is suitable for compact NMR/MRI and Dy-Ba-Cu-O for current leads. Furthermore, progress of machining technology enables to obtain various complicated shapes of bulk superconductors.

Keyword: High Temperature Superconductivity**,** Superhighway**,** Gd-Ba-Cu-O, REBa-Cu-O.

Introduction

Superconductivity is the phenomena which was discovered by Kamerlingh Onnes in 1911. For one century the superconductivity has been a great challenge in the field of theoretical physics. Superconductors are those materials which have exactly zero electrical resistance, and magnetic flux lines are expulsed out. They are Diamagnetic materials. Considering the Bardeen–Cooper–Schrieffer theory (BCS theory) to be valid and it is defining the Transition temperature as the temperature at which the electrical resistivity of the material drops to be zero, we are review the development of HTS and its applications. The ordinary superconductors require very low temperatures such as 30-40 K which are very difficult to achieve for all commercial purposes. The discovery of High Temperature superconductors by Georg Bednorz and K. Alex Müller in 1986 at IBM which can go as high as 250K robust its way for commercial applications. Superconductors definitely have at an advantage with extremely low losses and high current carrying capability they offer high efficiency and high power density. HTS has been proven to enable novel devices like Magnetic Energy Storage (SMES), magnetic bearings, fault current limiters and switches. High Temperature superconductors have large number of applications in Power Electronics with established prototypes of power cables, [5] transformers, motors, and Super-Conducting Fault Current Limiters (SCFCL).

High temperature superconductors require liquid Nitrogen at 77K for cooling as compare of the costlier liquid Helium at 4.2K. Generally Liquid Nitrogen has proved to be a cheap alternative and it is found in abundant quantity. It acts as a coolant and facilitates lower temperatures at which superconductivity to be observed. Recently attempts to take this cooling temperature at room temperature have been successfully demonstrated that it could be achieved using high pressure which is not yet useful for most of the practical applications. Another problem with HTS is that presently known semiconductors are ceramics materials, and a major obstacle to make wires. To make it very difficult to convert them into desired shapes and forces limited usability.

Meissner effect

Meissner effect is an important property observing in superconductors. It refers to the expulsion of a magnetic field from the interior of a material when a transition occurs from normal phase to a superconducting phase. This is a direct consequence of the fact that magnetic field dies out after small penetration depth (commonly known as skin depth in Electromagnetics).

$$\nabla^2 H = \gamma^2 H$$

Where H= magnetic field
γ= Skin depth

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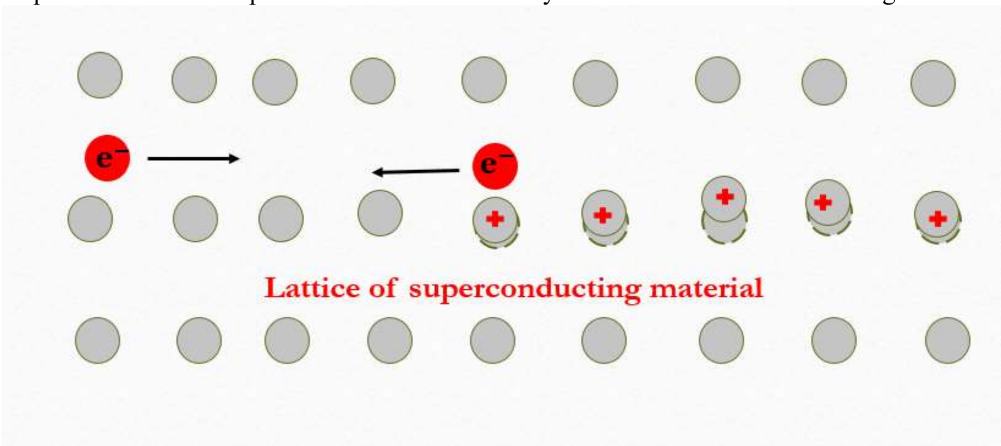
BCS Theory successfully explained the Meissner effect in superconductors and Bardeen, Cooper, and Schrieffer achieved Nobel Prize in 1957 for explaining this theory.

BCS Theory and Cooper Pairs

To explain it we recall fermions, that are pair of fundamental particles like electrons which obeys Pauli's Exclusion principle and have half-integer multiples spins. There is another class of particles known as bosons with spins in integer multiples. They do not obey Pauli's Exclusion principle and can condense into same energy level. BCS theory proposed that electrons near the Fermi level pair up together to give Cooper Pairs. These coupled electrons are essentially bosons and condense into the ground state.



A passing electron attracts the lattice, causing a slight ripple toward its path.
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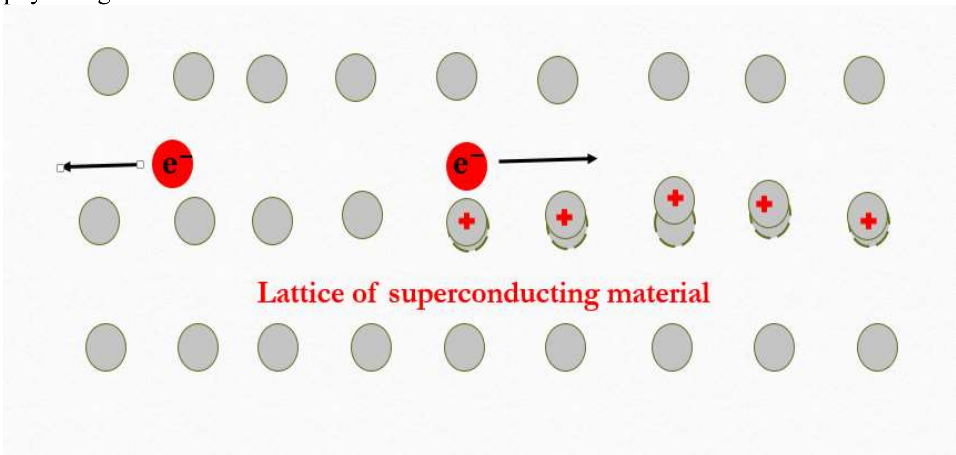

Another electron passing in the opposite direction is attracted to that displacement.
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History of Superconductors

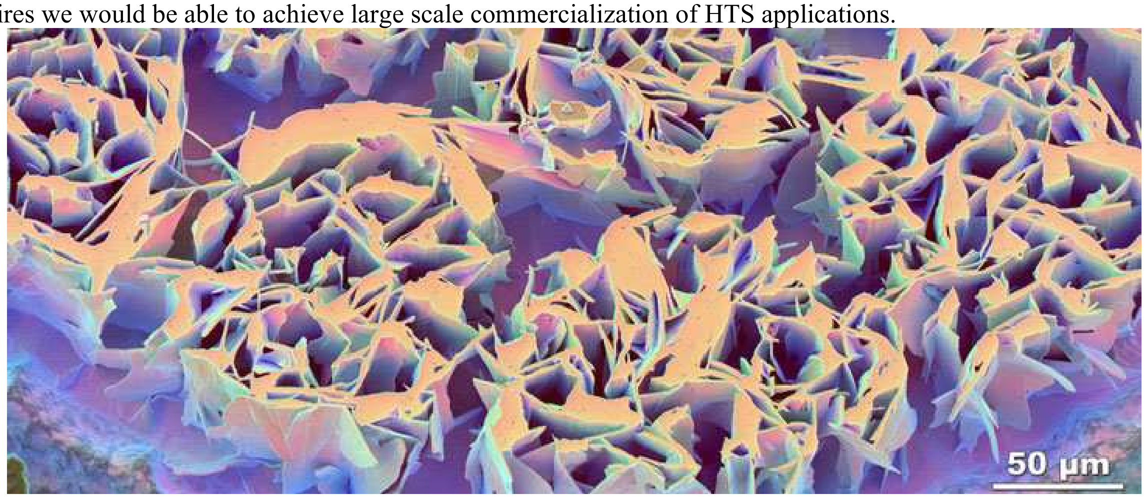
Superconductors, are that materials which have no resistance to the flow of electricity, it is one of the last great limit of achievement of scientific discovery. Not only have the limits of superconductivity not yet been reached, but the theories that explain superconductor behavior seem to be constantly under review. In 1911 superconductivity was first observed in mercury by Dutch physicist Heike Kamerlingh Onnes of Leiden University. When he cooled it to the temperature of liquid helium, 4 degrees Kelvin (-452F, -269C).

Although the BCS Theory does not have any constraint at critical temperature (Tc), physicists are used to believe that 30K is the upper limit for Tc, which is probably false. Such low temperatures were reached using liquid Helium as a coolant which has boiling temperature as low as 4K. Until recently in 1986, Bednorz and Müller observed superconductivity in lanthanum-based cuprate perovskite material which increased the Tc to 35K. This rise in the assumed limit of Tc _ 30 led to aboundance research in finding superconductors with high Tc. It was later found by Bednorz and Müller that by replacing Lanthanum with Yttrium raised critical temperature to Tc = 92K for which both are awarded by Nobel Prize in 1987. This rise in critical temperature allowed N2 as a coolant which is abundant in the atmosphere and readily available.

High Temperature Superconductors

To obtain supconductors at room temperature several attempts have been done by scientist. Eremets et al., (2018) assert that they have attained Tc as high as 250K in H2S which is a leap forward to room temperature superconductivity. But the alert here is that such high critical temperatures require very high pressure of the order of 170 GPa's and this makes it practically unusable for commercial applications. But still, Eremets idea promote new methods of superconductivity in which high oscillations are traced at high temperature in light materials and pressure keeps it intact. Like most of the other work in High Temperature superconductivity this work remains unproven. Further Eremets et al. was not able to show Meissner effect which is important to superconductors. Room temperature superconductors are not far away from now. Gauging their new applications and commercializing them is underway.

Another advantage of High Temperature superconductors is that they have high critical field and therefore high critical current density. This leads to their high current carrying capability and low resistivity allows high energy density and negligible energy losses. High Temperature Superconductors can revolutionize the world provided we can discover materials which can be easily transformed into wires/rods and desired shapes instead of current brittle ceramics which are costly and difficult to manufacture. It has been shown that the cost involved in maintaining HTS is lesser than the performance and efficiency achieved from them. Once we can form desired shapes and wires we would be able to achieve large scale commercialization of HTS applications.



High density Bi-2212 filament macrostructure produced by the over-pressure (OP) technique developed at the Applied Superconductivity Center.
Image: Peter Lee Courtesy: https://nationalmaglab.org

1.1 Manufacturing methods for HTS materials

Mostly HTS materials were first synthesized in bulk form. Blocks or pucks of BSCCO and YBCO are widely made by grinding mixed oxide precursors followed by powder pressing and sintering. However, due to fundamental anisotropy in these materials polycrystalline material with randomly oriented grains has very low J_c . Melt texturing could be used to achieve grain alignment. Aligned polycrystalline, BSCCO-2212 in particular, was made early on, and continues to be made, by melt casting precursor powder mixtures into near-final shape bars, rods or tubes.

Melt textured growth of aligned polycrystalline YBCO bulk samples was demonstrated in 1988, followed by several variants over the years. However, the best bulk YBCO has been obtained by adding a single crystal seed to the surface of a pressed pellet followed by a melt process, which nucleates and grows YBCO with the orientation of the seed. This method and variants on it first appeared in the early 1990s in several groups, and an excellent review of the thermodynamics, processing details and properties can be found in Krabbes et al. (2006).Referred to generically as large-grain (RE)BCO superconducting materials, the large values of trapped field obtained in these materials have enabled interesting applications including magnetic bearings, take wing flywheels and trains, and trapped flux magnets that are 'permanent' as long as they are kept cold.

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1.11 BSCCO (2223) tapes

BSCCO (2223) tapes found much more interest compared to the BSCCO (2212) system, since extraordinary transport currents could be reached at 77 K due to the high critical temperature of 110 K. The low irreversibility field, however, limits applications at 77 K to fields below 1T. Conductors were developed with several options, with an Ag/AgMg composite sheath for improved mechanical strength and with AgAu alloy sheath for enough reduced thermal conductivity and application in current leads.

until, commercial conductor lengths over and above 2000 m are offered by three companies: Bruker HTS, Innost and Sumitomo. A typical tape cross-section dimension is 4 × 0.25 mm. Innost (Bejing, China) is able to deliver 37 filamentary BSCCO (2223)/Ag/AgMg tapes in up to 1000 m lengths and critical currents of >110 A (77 K, self fi eld). Bruker HTS is able to produce up to 2500 m lengths of 121 filamentary tapes with Ag/AgMg sheathing and a critical current of about 120 A (77 K, self field). BSCCO (2223) tapes from Sumitomo can be ordered with up to 180 A critical current (77 K, self field) in lengths of up to 1500 m, with Ag or reinforced Ag/AgMg sheaths. All companies offer the option of insulated wires, made by coextrusion (Bruker HTS), laquer impregnation or tin clad (Innost) or wrapped with polyimide tape (Sumitomo).

1.12 (RE) BCO tapes (CC)

(RE)BCO coated conductors (CCs) are prepared by a most variety of methods and conductor architectures. Commercially available long length conductors are offered by two manufacturers, AMSC and Super Power, made by using two completely different approaches.

The method adopted by AMSC is based on the use of textured cube recrystallized Ni-W-substrates transferring the texture to the $CeO_2/YSZ/Y_2O_3$ buffer/superconductor architecture. The (RE)BCO layer is applied by slot-dye chemical solution deposition (metal-organic deposition with the TFA-method) with Dy-doping of the superconducting phase. The typical length of a sample piece is 300 m, with the potential to produce 1000 m lengths. The sample width is typically 40 mm for the coating procedure and final splicing leads to 10 samples of 4 mm-wide tapes. The current carrying capacity on a 100 m length of 4.4 mm wide (344 superconductor) was given as at minimum 262.5 A/cm width. The installed capacity for this conductor performance at AMSC is claimed to be 500 km per year.

Coated conductors from Super Power are prepared on Hastelloy substrates and the texture is introduced via the MgO/LMO based buffer architecture. This approach is using metal-organic chemical vapour deposition (MOCVD) for (RE) BCO and the application of additional Zr flux pinning centres. Tape thickness can be customized and is usually 100 μm including a 20 μm surrounding Cu-stabilizer. Commercial tape performance is well exceeding 300 A/cm width depending on piece length. This company's CC material is available in lengths greater than 1000 m with minimum 282 A/cm width and can be ordered in 4 and12 mm widths. The mechanical performance of SuperPower CC is outstanding with >800 MPa tensile stress tolerance and bending tolerance <11 mm bending radius.

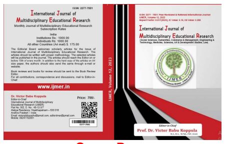
2. Design of bulk high temperature superconductor (HTS) materials

The commonly accepted method of preparing bulk superconductors is the melt powder melt growth (MPMG) method. In this technique precursor powders are pressed into a puck and a seed placed on top of the puck. The temperature of the puck is then raised to the melting point of the powders and from there is slowly lowered. The seed, which does not melt, acts as a nucleation site and when correctly managed the material solifies and grows from this single point. Even though the genuine material was YBCO this has expanded to include a whole family of cuprates known as (RE) BCO where Re can be a range of rare earth elements such as neodymium, samarium, gadolinium or indeed yttrium itself.

All accordingly, a range of different seeds have been tried. Until recently the seeds were firstly crystals but recent developments have included thin film seeds. Pinning centres are important if we are going to obtain a high J c and a high magnetic moment. By far the most common method of including pin down centres is to have so-called 211 inclusions. The superconducting phase is $(Re)Ba_2\,Cu_3O_y$ and an additional (Re) 2 BaCuO 5 211 phase is included, which is non-superconducting. Finely distributed, these non-superconducting particles act as barriers to the movement of flux lines. In this section we present a number of different processing way for some of the most important bulks superconductors.

3 Materials and methods of preparation

To explain it We would take the three main materials which are also in volume form. These are MgB_2 (Magnesium diboride) (RE)BCO (Rare-earth barium copper oxide), and BSCCO (Bismuth strontium calcium copper oxide)



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(RE)BCO - Rare-earth barium copper oxide

The materials which are usually available in the bulk form by far the most studied was YBCO and by extension (RE)BCO. The major steps to developments of YBCO/(RE)BCO are given below:

- melt textured-growth (MTG) processing
- solute rich liquid crystal pulling (SRLCP)
- solid state sintering (SSS)
- top-seeded melt textured growth (TS-MTG)

(RE)BCO – exchange of various rare earths can lead to pinning amplified changes in Tc. The main preparation methods for (RE)BCO bulk materials are abridge as Following

- Melt texture growth (MTG). The melt-textured growth relates to slow cooling in a temperature gradient, which results in directional solidification at growth front.
- Quench melt growth (QMG). The quench melt growth process fabricates the bulk by calcining, melting and extinguish, grinding into powders and then the MTG process is used. A feature of the QMG method is that the second-phase Y211 is very fine and has homogeneous distribution in the matrix of the material, so that the flux pinning and Jc were increased.
- Powder melt process (PMP). The powder melt process of PMP is the same as MTG but uses precursor powders of YBaCuO (211) phase and Ba-Cu-O as start materials instead of Y123 materials in the PMP process.
- Liquid-phase process (LPP). In the liquid-phase process method, slow cools through the peritectic transformation (1030–980 °C) has been shown in control the microstructure of superconductors.
- Top-seeded melt-textured growth (TS-MTG). The standard composition of the top-seeded melt-textured growth method starting material is YBa2Cu3O7 -x (Y-123) with a Y-211 excess of 25 mole%.
- Preparations for LRE-123 bulks. The oxygen-controlled-melt-growth (OCMG) process has been developed to prepare the LRE-123 bulks. MgO seeds prove to be efficient in the growth orientation control of large-grain LRE-123 pellets when a small quantity of ZnO is added, accompanied by an insubstantial reduction of liquid phase loss.
- Melt powder melt growth (MPMG). The attractive feature of the melt powder is melt growth (MPMG) process is that other components such as fine Ag powder can be added during solid-state mixing.
- Solute rich liquid crystal pulling (SRLCP). This method uses high-quality (3N) Y2O3, BaCO3 and CuO powders as the solute and solvent. Natural flow and forced flow dissolve the 211 particles, and Y-123 phase is precipitated to Y-123 crystal.

BSCCO

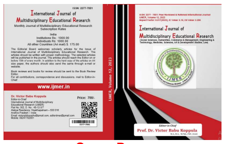
There are a number of preparations for BSCCO bulk. In addition to this, Bi-2223 rod is available, which is usually prepared by normal sintering, hot mold process, and cold hydrostatical pressing methods. One of the most successful method for fabricating Bi-2212 tubes is the melt cast process (MCP). Another method that has been used is the fabrication of cylinders strengthened using MgO side whiskers.

Even though it is important mostly because it is cheap to fabricate and can be made in much bigger sizes than the rare earth bulks. MgB_2 is mainly produced by using a sintering route and the challenge lies in shrinking it. Various preparations for MgB_2 are available, the main ones of which are hot pressing (HP), reactive liquid Mg infiltration (RLI), solid phase reaction and the powder-in closed tube (PICT) diffusion method .

4. Development and application of bulk HTS materials

Today a great deal of effort has gone into the manufactured of HTS bulk materials and a massive process routes have been tried and perfected. Along with there are several applications have been investigated. Although a lot of these applications are relatively mature there has as yet been relatively little take up and there are still challenges to be solved. In no particular order the applications that have received the most attention are

- Bearings/levitation (diamagnetic effect).
- The fact that a superconductor will react to external changes in magnetic field enables us to produce an entirely passive non-contact bearing. This has been demonstrated both as a thrust bearing and a journal bearing.
- Bearings for flywheels (diamagnetic effect).
- In principle the non-contact bearings could be used in a range of different machines. An energy storage flywheel is the most suitable environment for two reasons. The first is that in a very real sense a superconducting bearing provides a quantifiable advantage over a rolling element bearing. The losses are extremely low and a very efficient flywheel can be built as a result. The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second reason is that an energy storage flywheel is a static environment there are no external forces and consequently design of the system is relatively simple.

- Motors/generators (diamagnetic effect/trapped field magnet).
- Many different arrangements have been proposed and considered. These fall into two classes. The first is the ones that use the same property as the bearings. A moving rotor field drags the superconducting rotor around. These are loosely termed reluctance machines. They are of interest but do not offer substantial advantages over conventional machines. Of more importance are designs that use the superconductors as trapped field magnets. Potentially at least a superconducting trapped field magnet is an order of magnitude stronger than a conventional permanent magnet. Consequently, magnets of this type would lead to considerable improvement over conventional machines.
- Magnetic separation (trapped field magnet).
- Magnetic separators could have been built that use trapped field superconducting magnets.
- Magnetrons (trapped field magnet).
- Magnetron sputtering: superconductors could be used as trapped field magnets in a magnetron sputtering device to deposit films. This would yield considerable advantages over conventional machines.
- Current leads (current carrying capability at high temperatures).
- A very practical application of HTS bulks is as current leads. Compared to tapes, bulks have a very low thermal conductivity and this makes them ideal for use as current leads feeding an LTS magnet system. Their use cuts down expensive thermal losses and (potentially) reduces loss of helium. Both BSCCOs and (RE)BCOs have been used as current leads.
- Fault current limiters (current carrying/normal state resistivity).
- A lot of work has gone into the development of fault current limiters, both resistive and inductive. Both BSCCO and (RE)BCO bulks have been used to build demonstrator fault current limiter projects.

5 Technological and commercial barriers to adoption of bulk superconductors

There are many steps for commercialisation of bulk superconductors. The first is the manufacturing process itself. This has been extensively studied and many groups have reported on their ability to make high-quality samples. Initially these were made singly but as the process matured it was found that with a suitably well-controlled furnace a batch process in which 25 samples at a time can be made. The furnace used for this is a laboratory-type box furnace and the limit of 25 samples corresponds to the size of the furnace, not the maximum number of samples that can be made. It is reasonable to assume that the process can be scaled up with the purchase of larger or multiple furnaces. Central to the utilisation of superconductors is the overall cost of manufacture. This cost is dominated at the moment by two things; the first is the purchase of the constituent powders. Bought in small batches the cost of these is currently £600–800 per kilogram. This price, it is felt, would be considerably reduced were the materials to be produced on an industrial scale. The constituent materials are not in themselves rare; yttrium is the 28th most common element in the earth's crust. There are large deposits of barite in various countries of the world. It is not particularly difficult to extract either metal but there are relatively few uses for both, which at least partly explains the current price. The other component in the process of manufacture is the energy required to produce good quality YBCO and (RE)BCO. The process is in two parts. The first is the growth of the grains themselves; this will typically take 5–6 days at temperatures greater than 1000°C.This is followed by oxygenation, which takes two weeks but occurs at a much-reduced temperature, typically 400 °C less. Manufacture is therefore an energy intensive process and for this reason YBCO will never be as cheap gram- for-gram as typical rare earth magnets such as NdFeB and SmCo.

Examples of machined bulks (a) various shapes (b) thin sliced disks (c) a coil shaped sample

However, this is not a bar to the adoption of bulk materials. A YBCO magnet can have a strength of 1–2 orders of magnitude greater than similarly sized rare earth magnets. Thus, machines can be built with specifications far in excess of those made using NdFeB. A motor or a generator (such as one used for wind power) for example that uses 10 T magnets is one-tenth of the size of a machine that uses 1 T magnets. Very high fields make bulks appropriate for use in large accelerator magnets, magnetic resonance imaging (MRI) and

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nuclear magnetic resonance (NMR) machines, as well as facilitating machines that rely on the magneto hydrodynamic effect to produce power, brake space ships and perform magnetic cleansing of, for example, sea water. There are many other high-value machines where the use of high-power compact superconducting permanent magnets would provide a compelling economic argument.

6 Challenges and future trends

Bulk materials could have been, used for current leads. Bulk materials have and are being used for fault current limiters (BSCCO – nexans cylinders etc) and they are being used as the 'active' component in an otherwise passive magnetic bearing. All of these applications are described in detail above. In addition, bulk materials have been used in reluctance machines; a range of these were developed by Oswald and others. Current leads and fault current limiters exploit the very high current carrying capacity of superconductors. Bearings and reluctance machines exploit the diamagnetic properties of HTS machines.

None of the above, however, exploit the most unique property of bulk HTSs and that is their ability to function as very-high-field magnets. Bulk HTS magnets have found their way into water purification systems as was described earlier but apart from this there are no current applications in which HTSs are used purely as magnets. When borne in mind that the maximum trapped field recorded in an HTS magnet was 17.24T and that the maximum realistically available from a permanent magnet is an order of magnitude less than that, it becomes clear that there is enormous potential for devices in which HTSs are used as magnets. To use superconductors as permanent magnets we need to overcome two problems. The first is magnetisation and the second is demagnetisation.

7 Conclusion

In this paper, the recent progress in material technology and performance for large-grained RE-Ba-CuO bulk superconductors with strong pinning force is described. Advance of machining technology enables us to obtain various complicated shapes of bulk superconductors. In bulk applications, as-grown crystals are not utilized as they are, and they are machined into various shapes depending on the application requirements, such as disks, rings, squares, hexagonal shapes and so on. Recently, most complicated shapes are available by machining, such as silicon-wafer-like disks 1 mm in thickness and a coil-shaped bulk. It is expected that a great variety of shapes will expand the possibility of the bulk applications further and further. The research and development of HTS bulk materials have been making a steady progress, in accordance with the advance of application development. HTS bulks can be expected to create a new frontier field in superconducting applications.

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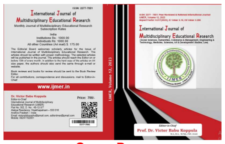
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