

Development and Applications of High T_c Superconducting Bulk Materials

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Abstract—This paper summarizes the high T_c superconducting (HTS) bulk materials, with regard to material preparations, characteristics, and practical applications. Consequently it provides the technical base for practical development and applications of the HTS bulk materials to devices.

Keywords—HTS bulk; preparation; HTS applications; superconducting materials

I. INTRODUCTION

The development of technically applicable high temperature superconducting (HTS) materials has been progressed on several routes, e.g., HTS thin films, HTS tapes, HTS bulks, etc. HTS single crystals are not suitable for practical applications due to their small size and low critical current density (J_c) as a consequence of low density of pinning centers. However, the melt-textured HTS bulks show superior flux pinning properties high J_c and have already been applied in various applications, e.g., magnetic bearings, motors, current leads, magnetic separation, etc. The development of the high J_c bulk superconducting materials leads to a promising way to explore the HTS applications in practice.

This paper mainly introduces various preparation methods, unique characteristics and application status of the HTS bulks, with aims to summarize the progresses of the bulk superconducting materials all over the world and discuss the development tendency of HTS bulks in the future.

II. MATERIAL PREPARATIONS

Currently the applicable HTS bulks mainly include Y-123 bulks, LRE-123 bulks, BSCCO bulks and MgB_2 bulks. The preparations and development have been progressed in the world.

As for Y-123 bulk, the HTS bulk growth techniques have experienced four stages: i) solid state sintering (1987) ii) melt-textured-growth (MTG) processing (1989) iii) top-seeded melt-textured growth (TS-MTG) (1993) iv) solute rich liquid crystal pulling (SRLCP) (1996).

As for LRE-123 family, they differ from Y-123 that the replacement of Y by Nd, Sm, Gd, Eu, and some other light rare earth (LRE) results in a particular pinning even in an ideally oxygenated state, namely in the absence of oxygen-deficient clusters.

As for BSCCO bulk, there are two systems for engineering applications: $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) with T_c of 110 K and $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) with T_c of 80 - 90 K. Unlike YBCO or REBCO, flux pinning of BSCCO is extremely weak, mainly due to a strong anisotropy and weak link.

As for MgB_2 bulks, there are a number of preparation methods. They have achieved high-density microstructures with unique advantages making them substantial potentials.

The main preparation methods for HTS bulk materials are summarized as follows:

1) *Melt texture growth (MTG)* [1,2]: The melt-textured growth relates to slow cooling in a temperature gradient which results in directional solidification at a growth front.

2) *Quench melt growth (QMG)* [3]: The quench melt growth process fabricates the bulk by calcining, melting and quenching, grinding into powders and then MTG process is used. A feature of the QMG method is that the second phase Y211 is very fine and homogeneous distribution in the matrix of the materials, so that the flux pinning and J_c are increased.

3) *Liquid phase process (LPP)* [4]: In the liquid phase process method, slow cooling through the peritectic transformation (1030-980 °C) has been shown to control the microstructure of superconductors.

4) *Powder melt process (PMP)* [5]: The process of PMP is as the same as that of MTG method but the using precursor powders of YBaCuO (211) phase and Ba-Cu-O as starting materials instead of Y123 materials in the PMP process.

5) *Melt powder melt growth (MPMG)* [6]: The attractive feature of the MPMG process is that other components such as fine Ag powders can be added during solid-state mixing.

6) *Top-seeded melt-textured growth (TS-MTG)* [7-9]: This preparation technique is described in details in the Fig. 1 – Fig. 3. The standard composition of the starting material is $YBa_2Cu_3O_{7-x}$ (Y-123) with an Y-211 excess of 25 mol%.

7) *Solute rich liquid crystal pulling (SRLCP)* [10-14]: This method uses the high-quality (3N) Y_2O_3 , $BaCO_3$ 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.

8) *Preparations for LRE-123 bulks* [15-17]: 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 a substantial reduction of liquid phase loss.

9) *Preparations for BSCCO bulks* [18-27]: Bi-2223 rod is usually prepared by normal sintering, hot forging process, and cold isostatic pressing method. One of the more successful techniques for fabricating Bi-2212 tubes is the melt cast process (MCP) [25].

10) *Preparations for MgB₂ bulks* [28-30]: Among the different sintering routes to highly densify the MgB₂, the main processes available are the hot pressing (HP) [28], the reactive liquid Mg infiltration (RLI) [29], solid phase reaction [29] and diffusion method (PICT) [30].

The top-seeded melt-textured growth is described in details as follows: Raw materials of Y₂O₃, BaCO₃ and CuO with molar ratios of Y : Ba : Cu = 1.8 : 2.4 : 3.4 are mixed as precursor powders. After calcination at 920 °C with intermediate grinding for 60 h, 0.2 wt% Pt powders are added. The precursor pellets are uniaxially pressed with 20 MPa to 30 mm in diameter and 10 mm in thickness [7], as shown in Fig. 1.

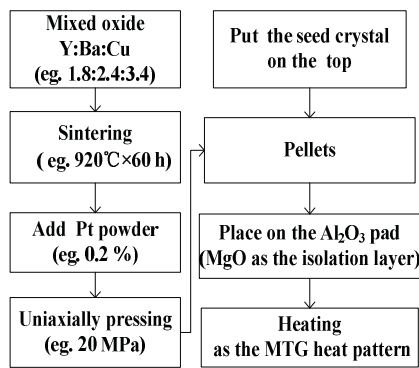


Figure 1. Preparation procedure of the TS-MTG.

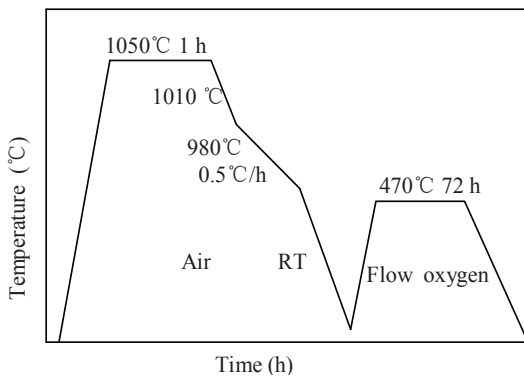


Figure 2. A heat pattern example for melt processing [2].

SmBaCuO seed prepared by MTG method is used to predetermine the orientation of the growing YBCO single grains. One single seed is applied on the top of the cylindrical shaped disks. The c-axis of the seed is parallel to the

symmetrical axis of cylindrical sample. Then the sample is put on the Al₂O₃ pad. The MgO single crystal is used as the isolated layer between the sample and the Al₂O₃ pad. The precursor with seed is placed into the furnace and heated to 1050 °C at about a rate of 300 °C/h. Then hold it for 1 h, cool it down to 1010 °C rapidly, and slowly cool down to 980 °C with a rate of 0.4 - 1 °C/h, and then cool to room temperature in furnace. Finally, the sample is annealed in pure oxygen atmosphere at 470 °C for 72 h [7-9], as shown in Fig. 2 - Fig. 3.

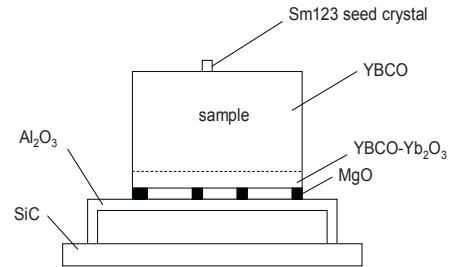


Figure 3. Top-seeded melt-textured growth [14].

III. CHARACTERISTICS

There are two unique characteristics of superconducting materials, i.e., the Meissner effect and flux quantization. The Meissner effect relates to the superconductor's ability to expel the magnetic field, i.e., superconductors are perfect diamagnets; the flux quantization relates to the phenomenon that the magnetic field generated from a current circulating in a superconducting loop is quantized. The characteristics of HTS bulks mainly include: trapped field characteristics, magnetic levitation characteristics, AC losses characteristics and magnetic shielding characteristics.

A. Trapped Field Characteristics

The strong flux pinning in HTS allows the trapping of high magnetic fields. In single domain cylinders YBCO bulk with a diameter of 30 mm, an induction of 1.3 T can thus be fixed at 77 K [31], 16 T magnetic field has been achieved at 24 K in-between two cylindrical samples [32], very recently even 17.24 T at 29 K in-between two $d = 2.65$ cm / $h = 1.5$ cm samples without fracturing [33].

Compounding the RE-123 [34,35] with several rare-earth ions was found to dramatically enhance flux pinning, e.g., (Nd, Eu, Gd)-Ba-Cu-O exhibits an extremely high irreversibility parallel magnetic field of 15 T at 77 K with a critical current value exceeding 10^4 A/cm² at 10 T [36,37].

B. Magnetic Levitation Characteristics

In the levitation system using HTS bulk, the restoring force from the pinning effect works on the bulk against the displacement due to external mechanical disturbances. The combination of melt-textured YBCO with permanent magnets leads to levitation properties. The strong levitation forces (e.g., > 80 N for zero field cooled $d = 3$ cm YBCO pellets at 77 K at a distance of 0.5 mm from a 0.4 T / $d = 2.5$ cm SmCo magnet [38]) with force densities of > 10 N/cm² and the stiffness are

already limited by the magnetic field strength of the permanent magnet [39-41].

C. AC Losses Characteristics

HTS bulks are exposed to magnetic field perturbations which cause alternating current (ac) losses in the bulks. A disk-shaped $\text{SmBa}_2\text{Cu}_3\text{O}_y$ bulk with the diameter of 62.0 mm and thickness of 15.5 mm was tested to study its characteristics of ac loss in the conditions of $T = 65 - 100$ K, $B_m = 1.7 - 80$ mT, and $f = 17.3 - 62.2$ Hz. It was experimentally verified that the ac loss was not dependent on frequency (f) and was approximately proportional to B_m^3 when $T < 85$ K. There was slight increase of ac loss at higher frequency with higher B_m value. AC loss was linearly dependent on f for a certain B_m and proportional to B_m^2 for a certain f [42].

D. Magnetic Shielding Characteristics

HTS bulks have a frequency-independent magnetic shielding ability because of its shielding mechanism, i.e., the Meissner effect [43]. Shielding occurs because magnetic flux through a circuit is constant when the resistance of the circuit is zero and because superconducting materials exhibit diamagnetism with B_0 well inside the superconductor. Usually the shielding factor is defined as the ratio of the magnetic field inside the shield at its center to the applied field.

A high-degree shielding is achieved up to a critical external field which is determined by the critical current density of the material [44]. Typically the critical field is 23 Oe at 77 K extending up to 105 Oe at 4 K. Effective shielding using high T_c superconducting shields can be achieved up to critical magnetic fields of 10 - 100 Oe. In order to shield higher magnetic fields, the current density has to be raised by lowering the temperature below 17 K, or by improving the quality of the HTS bulks.

IV. APPLICATIONS

The typical applications of HTS bulks in strong current applications mainly include high current leads, resistive / inductive fault current limiters, levitators, friction-free flywheel, flywheel energy storage, transportation, superconducting magnets, motors, magnetic separation, magnetron sputter, detector and accelerator in high energy physics, magnetic window and gyroscope in aviation. Laboratory prototypes for these devices have been designed, constructed and tested, and in some cases the devices have been tested in practical systems.

A. Current Leads

HTS current leads (CLs) have become suitable for practical HTS applications. Both HTS tapes and HTS bulks can be applied for HTS CLs. The advantages of the CLs with HTS bulks compared to the CLs with HTS tapes include low thermal conductivity, single lead handling large current, auto quench protection, low manufacturing cost, etc. The Bi-2223 bulk is suitable to be a current leads for cryogenic devices [48]. In Japan, a pair of 1 kA current leads using Bi-2223 bulks was developed for LTS magnet systems [45]. Then current leads with the available current being more than 2.5 kA were fabricated by YBCO bulks and investigated the transport properties in LN_2 at an applied magnetic field of 0.5

T in 2003 [46]. Two types of the current leads, i.e., “1 K-type” and “B-type”, were fabricated and tested using DyBaCuO bulks, as shown in Fig. 4 [47].

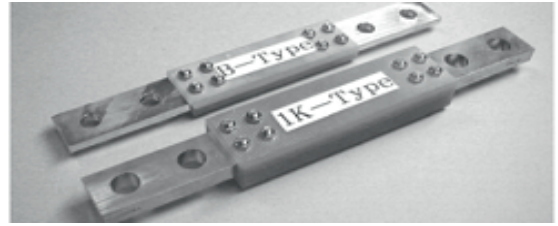


Figure 4. Photograph of the two types of power current leads fabricated by use of the ab-plane DyBaCuO bulk [47].

B. Resistive/Inductive Fault Current Limiters

Fault current limiters (FCLs) are one of the most promising applications of HTS bulk. The bulk Bi-2223 samples are suitable to be the key element for the development of an electrical fault current limiter [48]. In France, a FCL prototype was developed at 1080 A under 1100 V with Bi-2223 bulks in 1998 [49]. A 100 kVA class inductive prototype of SFCL using Bi-2212 bulks was developed within the joint collaboration between Hydro-Québec, Canada and Siemens, in Germany [50]. In Japan, a kA class resistive SFCL device for 6 kV distribution networks was developed by YBCO bulks in 1998 [51]. A 3-phase 6.25 kVA (275 / 105 V) high temperature superconducting fault current limiting transformer ($\text{HT}_c\text{-SFCLT}$) with functions of both superconducting transformer in normal operating condition and superconducting fault current limiter in fault condition was developed with its secondary coil consisting of MCP-BSCCO 2212 / CuNi composited bulk monofilar coils in Japan [52]. A three-phase resistive current limiter based on bifilar coils of MCP-BSCCO 2212 bulk material was developed and successfully tested up to the nominal voltage and power (10 kV, 10 MVA) within the German project CURL 10, as shown in Fig. 5 [53,54].

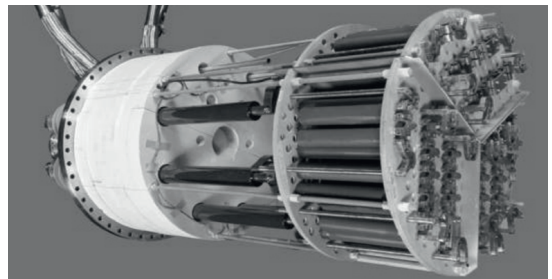


Figure 5. A three-phase resistive current limiter [53,54].

C. Transportation

The superconducting YBaCuO bulk materials can trap higher magnetic fields than both Bi-based and Ti-based superconductors at liquid nitrogen temperature. Therefore, much research has been done for maglev systems using bulk superconductors as a flux source [55-61]. Several types of magnetic levitation have been studied, such as electromagnetic suspension (EMS), electro-dynamic suspension (EDS) and high temperature superconductor suspension (HTS).

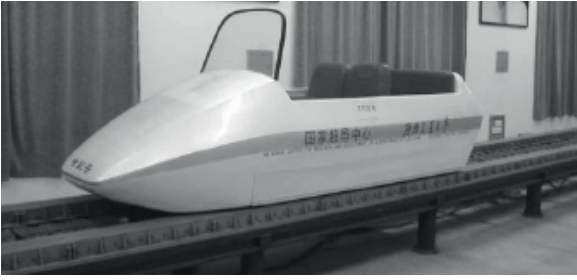


Figure 6. The man-loading high-temperature superconducting maglev test vehicle [63,64].

In China, the Qingchengshan maglev vehicle test line was proposed using high T_c SCPMs to replace the normal electromagnets as the suspension magnets of the maglev vehicles [62]. Demo HTS maglev test vehicle was built to study the integrated performance of HTS maglev system, such as shown in Fig. 6 [63,64]. The YBCO bulks are cylinders with 30 mm in diameter and 18 mm in thickness. A permanent magnet (PM) linear synchronous motor was developed for driving a small-scale prototype vehicle with PM-HTS bulks used for the levitation in the University of Electronic Science and Technology of China [65-67].

D. Magnetic Separation

The magnetic separation system consisting of superconducting magnets enlarges applicable fields of magnetic separation and efficiently separates the paramagnetic or diamagnetic materials. In general, HTS bulk magnets can be easier to generate the stronger magnetic field than that of permanent and electro magnets.

In Japan, a membrane-magnetic separator using YBCO bulks was developed for water treatment with a water-treatment capacity of 100 m³/day [68]. A high gradient magnetic separation system (HGMS) formed by face-to-face type YBCO bulk magnets was developed to separate the slurry mixed α -hematite (Fe_2O_3) particles. Its separation ratios of over 99 % and 90 % were achieved at the flow rate of 0.5 /min and 2.0l /min, respectively [69]. A high gradient magnetic separation system (HGMS) using GdBaCuO bulks was developed for purification of wastewater from paper factory in Japan, as shown in Fig. 7 [70-73]. The developed system can treat wastewater with the amount of 2000 t/day and continuously operated without changing magnetic filters.

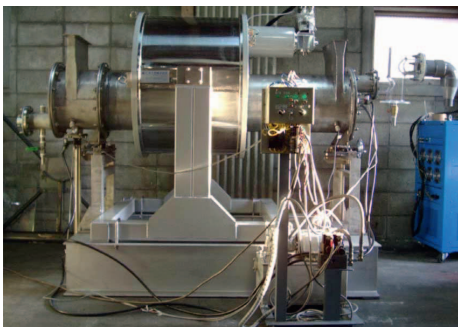


Figure 7. The developed HGMS by Japan [73].

E. Flywheel Energy Storage

The flywheel system is very attractive for the energy storage system because of its relatively high stored energy density. The flywheel systems are, however, now used mainly for short time usage such as load averaging or peak load energy supply because of the energy loss during rotation. One of the main losses of the flywheel system is the loss of bearings. Recently the superconducting bearing using the high temperature superconductor and the permanent magnet is being developed, which causes only a little loss [74].

In Japan, radial type superconducting magnetic bearings formed by an inner-cylindrical stator of YBCO bulks and an outer-rotor of permanent magnets were developed for a 10 kWh-class flywheel energy storage system in New Energy and Industrial Technology Development Organization (NEDO) project [75-77]. In Korea, a double-evaporator thermosiphon for cooling YBCO bulks in the 100 kWh SFES system was designed [77,78]. In USA, a 5 kWh / 100 kW flywheel energy-storage system (FESS) using a HTS bearing suspension / damping system was developed by the Boeing team in USA, as shown in Fig. 8 [79,80].

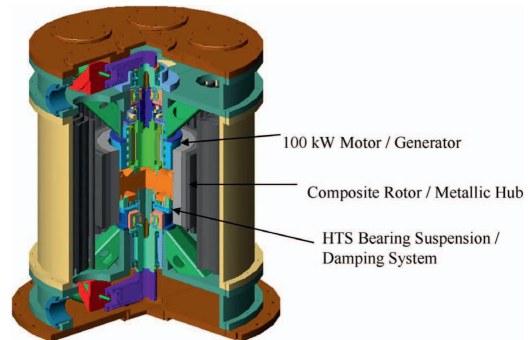


Figure 8. The Boeing 5 kWh, 100 kW FESS in USA [79].

V. CONCLUSION

Before the discovery of HTSs, applications of superconducting bulks were generally deemed not practical. A practical application in the levitation of a permanent magnet (PM) over a HTS bulk had started researchers thinking about their potential for applications [81]. During the past years, researchers have investigated and studied various practical applications of HTS bulks.

A common figure of merits for HTS bulks is about \$15 /kAm, which can compete with the conventional copper conductor. The cost of HTS bulks is expected to reach the improvements in the materials properties for even more applications in the future.

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