Recent Developments in melt processed Gd-123 and MgB₂ materials at RTRI

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Abstract

In this contribution we will report on the current status, recent developments in $\text{GdBa}_2\text{Cu}_3\text{O}_y$ “Gd-123” and MgB_2 material processing, characterization, and applications at the Railway Technical Research Institute (RTRI). Batch-processing of Gd-123 bulk material grown in air was performed using novel thin film Nd-123 seeds grown on MgO crystals. In this way, we are able to fabricate materials with good quality, and uniform performance. We examined the technology of the uniform performance of the large 45 mm diameter, single grain Gd-123 bulks for use in application of NMR. For this purpose, four 5 mm thick pieces are cut vertically from a single grain Gd-123 material and the magnetic field distribution is measured using a scanning hall sensor. We found that all four pieces are single domain and exhibit a quite uniform field distribution. Furthermore, the batch-processed bulk materials are used for the construction of a chilled maglev vehicle. On the other hand, to optimize the trapped field performance of bulk MgB_2 material, several samples were prepared by solid state reaction at different temperatures ranging from 750 to 950 °C in pure argon atmosphere. X-ray diffraction results indicated that single phase and homogenous MgB_2 bulks are produced when sintering them around 775 °C. Further, atomic force microscopy (AFM) and scanning electron microscopy (SEM) indicated that an uniform grain size results by controlling the processing temperature. So, higher trapped fields can be achieved in sintered MgB_2 material.

Keywords: Gd-123; MgB_2 ; trapped magnetic field; microstructure analysis

Article:

1. Introduction

For industrial application of any material performance and cost are main issues. The same applies to the melt-processed $\text{LREBa}_2\text{Cu}_3\text{O}_y$ “LRE-123” (LRE: Nd, Sm, Gd etc.,) or MgB_2 bulks. In the laboratory stage they constitute a new generation of magnetic substances suitable as super-magnets for variety of industrial applications, including MRI, NMR, drug-delivery systems in medical applications, water cleaning, space or naval transport systems [1-7]. We believe that in the near future, bulk superconducting magnets will enter the market as basic parts of various devices. In all these cases, a large number of pieces with equally high quality and large grain are required. Batch-processing of LRE-123 materials with uniform properties is the necessary step in this process. The seed crystal represents a key issue in this respect. Large single or batch production of melt-processed $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples with single grains can be obtained in the cold seeding process using Sm-123 or Nd-123 as a seed crystal [8]. In this case, the seed crystal is placed on the precursor pellet at room temperature. In the case of LRE-123 fabrication, the peritectic temperature is higher and this kind of seed is partially melted, which reduces the superconducting performance of the samples. To overcome this problem, many researchers have used a technique called hot seeding. However, this method is not practical for production of LRE-123 materials especially in the industrial scale. Furthermore, the Cambridge group [9] introduced Mg-doped LRE-123 crystals as a seed material. These crystals possess a higher melting temperature than pure LRE-123 ones and single as well as batch processing of Gd-123 material could be carried out successfully [10]. On the other hand, Oda et al. [11] reported the use of Sm-123 thin film

seeds grown on MgO crystals for growing Sm-123 blocks in the cold seeding process with a reduced oxygen atmosphere. Recently, we demonstrated that an ample quantity of single-domain Sm-123, Gd-123 and (NdEuGd)-123 bulks of a reasonable quality can be fabricated in air or in Ar-1% O₂ atmosphere using in a single batch process employing a cold seeding method with novel Nd-123/MgO film seeds. The SEM and XRD results confirmed that the quality and orientation of the seed crystals are excellent. The trapped field measurements on the bulks showed that the samples were single-domain and exhibited good pinning performance. The new seeds can withstand temperatures around 1100 °C, and as a result, the cold seeding process was applied even to grow Sm-123 material in air [12].

In this paper, we report the use of high-temperature-melting large-size 10 × 10 mm² Nd-123 thin films grown on MgO single crystals as seeds in the development of large size (67 mm in diameter) Gd-123 pellets in air. The emphasis was focused on application of batch processed Gd-123 samples to develop NMR rings, a child levitation disk, a child Maglev vehicle, etc. Finally, the MgB₂ bulk performance as well as trapped magnetic field measurements at 20 K are reported and compared to LRE-123 material.

2. Experiment

High-purity commercial powders of Gd₂O₃, BaCO₃ and CuO were mixed in a nominal composition GdBa₂Cu₃O_y “Gd-123”. The starting powders were thoroughly ground and calcined at 880 °C and 900 °C for 20 h and then pressed into pellets. Sintering was performed at 925° C for 15 h. This process was repeated twice in air. In parallel, the powders of Gd₂O₃, BaO₂, and CuO were mixed in the nominal composition of

Gd₂BaCuO₅ “Gd-211” and calcined three times at 840 °C, 870 °C and 900 °C for 10 h. The average particle size of the Gd-211 powders was less than 1 µm as determined by the BET specific area measurements. For the batch process Gd-123 and Gd-211 powders were mixed in the molar ratio of Gd123:Gd211 = 10:5. In order to suppress the coarsening of the Gd-211 particles during the melt process, 0.1 wt% Pt and 1 mol% CeO₂ were added. To improve the mechanical performance of the bulk, 20 wt% of Ag₂O was also added. The powder mixture was pressed into pellets of 50 mm diameter and subjected to a cold isostatic pressing under 200 MPa. Finally, commercial 700 nm thin Nd-123 films evaporated on 0.2 mm MgO <100> substrates were used as seed crystals. We used a special box furnace with the utility volume of 20 × 50 × 25 cm³, in which a vertical temperature gradient could be created. Six 50 mm high Gd-123 pellets were placed on 2 mm high Gd-211 rods inside the furnace. The MgO crystals covered by Nd-123 thin film were placed at the top center of each pellet, which were then melt-grown in Ar-1% O₂. The heat treatment profile used in the present experiment was as follows: The sample was heated in 5 h to a temperature 80 °C above the peritectic temperature (T_p) and held there for 50 min. Then, the temperature was reduced during 30 min to 2 °C above T_p , and slowly decreased by 25 °C with a cooling rate of 0.1 – 0.5 °C/h. Finally, the temperature was reduced with a cooling rate of 20 °C/h to 100 °C and then the furnace was left to cool down to room temperature. The melt textured samples were annealed at 400 – 450 °C for 350 h in flowing pure O₂ gas. Further, to develop the large grain batch processed Gd-123, Gd123-Gd211 powders are pressed in to pellets of 80 mm in diameter and subjected to a cold isostatic pressing under 200 MPa. Moreover, the composition is same as described above. However, 1wt% of BaO₂ was also added to suppress the Gd/Ba

solid state substitution in the superconducting phase composition, since the large size samples are melt-grown in air. For the melt growth, $10 \times 10 \text{ mm}^2$ commercial MgO crystals covered by 700 nm thin Nd-123 films are used as nucleation seeds and samples were grown isothermally at 985 °C for 150 h in air.

The measurements of trapped magnetic field were carried out by magnetizing the ring bulk samples in a 10 T superconducting magnet. The ring bulk samples were cooled to liquid nitrogen temperature in a magnetic field of 2 T applied parallel to the *c*-axis and kept 15 min constant. After switching off the external field, the profile of the trapped magnetic flux density was measured by a scanning Hall probe sensor. The total gap between the top surface of the sample and the active area of the Hall sensor was 1.2 mm, including the sensor mould thickness of 0.7 mm.

3. Results and Discussion

3. 1. Production of Gd-123 material by cold seeding process

The Nd-123/MgO seeds are the most suitable ones for the development of large grain LRE-123 material. They have a melting point higher than that of all LRE-123 and very similar unit cell parameters. Further, one can make large size seeds. We have recently succeeded in fabricating single domain Gd-123 bulks by batch process using the Nd-123 thin film as a seed [13]. The maximum trapped field of 0.9 to 1.35 T was routinely obtained for the sample size varying from 24 mm to 45 mm in the batch. Further, batch production of Sm-123 and NEG-123 materials in air and Ar-1% O₂ atmosphere was also reported [12,13]. Figure 1 (a) presents an example of Gd-123 bulk material in various sizes produced using the cold seeding method with Nd/MgO seed crystals. Figure 1(b)

presents the result – the photograph of as grown samples after the melt-growth in Ar-1% O₂ atmosphere. 6 pieces of samples with the final diameter of 42 mm per one batch have been repeatedly produced (see Fig. 1(b)). The four-fold growth facet lines are clearly visible on the top surface of all pellets which indicates that the crystal growth was perfectly controlled in all positions within the furnace. These results motivated us to proceed with batch production of samples with a diameter more than 50 mm using the Gd-123 using cold seed process. For this, two 80 mm in size Gd-123 pellets were placed on Gd-211 rods inside the furnace. The $10 \times 10 \text{ mm}^2$ MgO crystals covered by Nd-123 thin film were placed at the top center and corner of each pellet, which were then melt-grown in air. Samples were grown isothermally for 150 h at 985 °C in air. The results are presented in Fig. 2. The final diameter of the bulk superconductor after melt growth was 67 mm and the sample is fully textured as the seed was placed in the center of the sample surface. Further experiments are under the way to optimize and produce the batch production of 67 mm large size single grain Gd-123 material in a single run. The preliminary results indicate that larger size more than 67 mm Gd-123 materials can processed batch production using new class of Nd/MgO seed crystals. We checked the uniformity of the large 45 mm in size Gd-123 material use in NMR applications. And the results are given below.

3.2. Performance check of 45 mm in size Gd-123

We have recently succeeded in fabricating single domain Gd-123 bulks by batch process using the Nd123 thin film as a seed. The maximum trapped field of 45 mm in diameter samples shown around 1.35 T at 77 K [13]. In general, superconducting properties of large bulks vary from place to place. In particular, properties of the pellet

top usually differ from its bottom, partially due to the bottom surface reaction with the supporting material, but also due to different dominant growth orientations (on the top a -axis sectors prevail, while the bottom lies mostly in the c -axis growth sector. Aiming these materials for NMR-related applications, a ring shape and an uniform field distribution is essential. Therefore, we mapped the properties within the large bulk from the top to the bottom surface. The melt-textured sample (45 mm diameter) was cut vertically into four 5 mm thick slices. Then, a 25 mm diameter hole was made in the bulks by a commercial laser cutting. All four resulting samples are named from top to bottom T1, T2, T3 and T4 bulk rings respectively (see Fig. 3). The measurements of trapped magnetic field were carried out after magnetizing the bulk samples in a 10 T superconducting magnet. For characterization at 77 K, the ring bulk superconductors were field-cooled by liquid nitrogen in 2 T applied magnetic field parallel to the c -axis and the field was maintained for 15 min before reducing it to zero. After reducing the external field to zero, the trapped magnetic flux density at the top surface of all bulk rings were measured 1.2 mm above the sample surface using a scanning Hall sensor. The results are presented in Fig. 3. The maximum trapped fields measured at the top of the ring bulks are 0.26 T, 0.24 T, 0.18 T and 0.22 T for top to bottom rings, respectively. Further, the trapped field contour plots clearly indicate that all rings are of single peak nature (see Fig. 3, bottom). These results demonstrate that a uniform and good quality melt processed Gd-123 material can be made by employing the cold seeding process using the new class of Nd-123 thin film as a seed.

The reproducible quality and quantity of the batch processed Gd-123 bulks allowed us to construct a home-made, chilled levitation disk and a Maglev vehicle. This is an

important milestone on the way to potentially replace superconducting coils of Maglev vehicles by bulk super-magnets cooled by the far more economic liquid nitrogen or even by cryogen-free refrigeration. More details of the chilled levitation set-up are reported elsewhere [14]. Recently, we designed and constructed a home made Maglev vehicle, which is even more attractive than the levitation disk. We made a magnetic rail using NdFeB permanent magnets on a 80 mm wide and 6 meter long iron plate. 25 mm wide, 50 mm long and 5 mm thick permanent magnets were arranged on the iron plate in three rows with the N-S-N configuration. A simple cryostat was constructed using fiber-reinforced plastic (FRP). The cryostat had two walls. A thermal insulating material was inserted between the two FRP plates to minimize the liquid nitrogen losses. Inside the cryostat, 3 batch-processed Gd-123 bulks (42 mm in diameter) were fixed. An aluminium bottom frame supported six Maglev cryostats; from these, two were fixed in the center and one in each corner. Then, the space filled by the thermally insulating material was closed to prevent thermal losses. Eventually, the body of the vehicle was attached (see Fig. 4). The attraction was used during the Open day of RTRI on October 8, 2011. More than 200 children enjoyed the experience of Maglev (Fig. 4). These results prove that the novel seeds have a great potential for batch-processing of large single grain LRE-123 pucks, reducing the production time and cost. We hope that the continuing development of melt-processed LRE-123 materials, their processing and cost control will encourage numerous new industrial applications.

3.3. Recent results on MgB₂ material

Superconducting MgB₂ magnets have a wide variety of commercial and industrial applications around 20 K, especially in the medical field for MRI instruments similar to the LRE-123 material at liquid nitrogen temperature of 77 K. MgB₂ has a high critical temperature (39 K), high critical current densities (10^5 - 10^6 at 4.2 K), and high H_{c2} values as compared to the conventional low temperature superconductors made of Nb₃Sn or NbTi. Furthermore, bulk MgB₂ materials are more attractive because of their low fabrication cost, and these materials can be used at liquid hydrogen temperature (20 K). These two key factors of cost and functionality at 20 K can drive lower the overall cost of medical systems. In the recent years, the superconducting bulk community was attracted to MgB₂ bulk material, since this material does not require a strong texture to reach a high enough critical current density and eventually high trapped field values around 20 K [15-18]. A large size can be produced in an easy way to enable several industrial applications, especially superseding super-magnets. Further, the smaller weight and a higher mechanical strength make this material more competitive for the applications.

Recently, we prepared several sets of 20 to 30 mm in size bulk MgB₂ materials by simple solid state reaction route. To optimize the highest trapped field of the bulk MgB₂ material, we fixed the initial composition of Mg/B = 1:2, chose a holding time of 3 h, an annealing step in argon, and a sample size of 20 mm in diameter and a thickness of 7 mm. The synthesis temperature was varied between 700, 725, 750, 800, 825, 850, 875, 900, 925, and 950 °C. X-ray diffraction results indicated that single phase and homogenous MgB₂ bulks are produced around 750 to 825 °C (see Fig. 5). However, the trapped field results are different, and show a dependence on the sintering temperature. Figure 6 shows

the trapped field values obtained at 20 K for varying sintering temperatures. For lower temperatures, the recorded trapped field values are high and decrease upon increasing the sintering temperature. The results clarify that the processing temperature is the key parameter to optimize the highest trapped magnetic field for the MgB_2 material. Samples of 7 mm thickness and of 20 mm diameter prepared at 775 °C exhibited a trapped field of 1.5 T at 20 K. Further, the TF values are increasing dramatically with increasing the size, thickness and flux pinning of the sintered MgB_2 bulks. Finally, we performed a thorough analysis of the resulting micro- resp. nanostructures on varying the preparation temperature using SEM and tapping mode AFM in ambient conditions. Typical results obtained on the sample prepared for 3 h at 775 °C are presented in Fig. 7; the SEM image is shown in Fig. 7 (a), while the AFM topographies and their corresponding 3D representation [19] are given in Figs. 7 (b) – (e). The AFM images reveal a characteristic grain size of the order of 300 – 400 nm. The trapped field results on Gd-123 and MgB_2 materials indicate that both systems are useful for superconducting super-magnets for several industrial applications. The choice between the two materials for a given application are the liquid nitrogen and liquid hydrogen temperatures.

4. Summary

In summary, a new class of large-size thin film Nd-123 seeds grown on MgO crystals can be used to develop a batch production process, allowing the fabrication of single grain Gd-123 pellets with a diameter larger than 67 mm in air by cold seeding. Trapped field experiments indicated that the entire large-sized bulk sample is uniform and consists of a single domain, which is clearly indicated by measuring several bulk rings cut from such a

pellet. Furthermore, batch processed Gd-123 materials are utilized for the construction of a children's Maglev vehicle, which was demonstrated during the open day of the RTRI. On the other hand, MgB₂ bulks can be utilized at around 20 K similarly to the Gd-123 material at 77 K. The present technology opens the way for several reliable industrial applications for both MgB₂ and Gd-123 materials.

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FIGURE CAPTIONS

Fig. 1 (a). Photograph of the as-grown Gd-123 material in various sizes prepared by a cold seeding method using an Nd-123/MgO film as seed. Note that the samples are single-domain and no cracks were observed.

Fig. 1 (b). A photograph of the batch-processed as-grown Gd-123 samples prepared by a cold seeding method using an Nd-123/MgO film as seed crystal (the sample size is 42 mm).

Fig. 2. A photograph of the as-grown Gd-123 samples prepared by a cold seeding method using an Nd-123/MgO film as seed crystal (sample size is 67 mm). The samples are grown isothermally for 150 h at 985 °C in air. Note that samples were grown fully and more than 70%, the seeds are placed centre and corners respectively.

FIG. 3. Gd-123 bulk superconductor rings prepared by cutting the large single grain sample into four slices (T1, T2, T3, T4 from top to bottom). The sample was prepared by a cold seeding method using an Nd-123/MgO film as seed (top picture); and the trapped field distribution at 77 K for the top surface of all rings produced single bulk from top to bottom surface (bottom picture).

FIG. 4. Home-made chilled MAGLEV vehicle used during the open day of RTRI on October 8, 2011. Around 200 children enjoyed the experience of the HTS Maglev.

Fig. 5. X-ray diffraction spectra of bulk MgB_2 samples produced using the sintering process 3h at 775 °C in Ar atmosphere.

Fig. 6. Trapped field values of MgB_2 material measured at 20 K as a function of sintering temperature. All samples are 20 mm in diameter and 7 mm thick, and are prepared in argon atmosphere by a sintering method.

Fig. 7. SEM image of the sample prepared for 3 h at 775 °C (a) and tapping mode AFM images (ambient conditions) of the same sample. Shown are two different magnifications and their corresponding 3D representation.

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