Physica C 471 (2011) 169–178

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Developments in the processing of bulk (RE)BCO superconductors

N. Hari Babu [a,*], Y.-H. Shi [b], S.K. Pathak [b], A.R. Dennis [b], D.A. Cardwell [b]

[a] Brunel Centre for Advanced Solidification Technology (BCAST), Brunel University, West London UB8 3PH, UK
[b] Bulk Superconductivity Group, Engineering Department, University of Cambridge, Cambridge CB2 1PZ, UK

ARTICLE INFO

Article history:
Received 17 September 2010
Accepted 8 December 2010
Available online 24 December 2010

Keywords:
(RE)BCO bulk superconductors
Flux pinning
Multi-seeding
Recycling

ABSTRACT

The development of a practical processing method for the fabrication of high performance large, single grain bulk superconductors is essential for their cost-effective application in a variety of high field engineering devices. We discuss recent developments in the processing of these materials that enable high performance bulk superconductors to be fabricated in a practical way. These include the introduction of nano-scale second phase inclusions to the superconducting phase matrix, the development of a generic seed crystal, the development of practical, batch processing routes for the fabrication of light rare earth superconductors, the processing of complex shaped geometries via controlled multi-seeding and recycling of scrap bulk samples into high performance, single grains.

1. Introduction

The key challenge in the processing of bulk high temperature superconductors (HTS) remains to improve their critical current density, J_c, and to manufacture them in the form of large, single grains using a cost-effective batch process, particularly for light rare earth (LRE) superconductors (LRE)–Ba–Cu–O [(LRE)BCO]. Improved J_c leads directly to grater trapped magnetic field [1]; a two sample arrangement of YBCO single grain superconductors of diameter 2.5 cm inch in diameter has been shown to trap record trapped field of 17 T at 30 K [2]. Typical values of J_c for bulk single grain materials are ~20–40 kA/cm^2 at 77 K and at 0 T external field, which is nearly two orders of magnitude lower than that achieved in thin-films or coated conductors [3]. Defects in the bulk superconducting matrix, which are responsible for flux pinning, should be typically twice the size of the coherence length (a few nano-meters in YBCO) if optimum flux pinning is to be achieved [4]. To date defects in melt textured (RE)–Ba–Cu–O ((RE)BCO) have been engineered partially by refining the size of RE_2BaCuO_5 (RE-211) second phases in the bulk matrix and by increasing their vol ume density [5]. RE-211 particles, however, which are generated as part of the $REBa_2Cu_3O_{7-\delta}$ (RE-123) peritectic decomposition process at high temperature, tend to ripen during the solidification process. As a result, RE-211 particles grow typically to a size of ~1 μm during the large grain growth process, and refining their size on a nano-scale level has proved generally unsuccessful, even if their initial size in the precursor body is as low as 100–200 nm [6]. The addition of U_2O_3 to the YBCO precursor composition is observed to generate U-based second phase inclusions in Y-123 matrix during solidification process [7,8], identified as $Y_2Ba_4CuUO_y$ [9]. However, small, spherical particles of $YBa_2(U,Pt)O_6$ are observed to form [10] when Pt is added to the precursor (note that the U site can be substituted by W and Mo [11]). The $Y_2Ba_4CuUO_y$ single phase compound has been synthesized successfully in a separate process and introduced into single grain YBCO [12]. The remarkable chemical and physical properties of these $Y_2Ba_4CuUO_y$ particles has led to the development of a series of iso-structural single phase compounds of general composition $YBa_2(Cu_xM_{1-x})O_6$ with $x \sim 0.5$, where M is a transition metal element such as Zr, Hf, Nb, Ta, Mo, and W [13]. X-ray diffraction data for the YBa_2MO_y phase, where M belongs to most of d-block transition metals, are available in crystallographic data bases [14]. In this article, we show that the YBa_2MO_6 phase transforms to $YBa_2(Cu_{0.5}M_{0.5})O_y$ when Cu is present. The addition of these novel $Y_2Ba_4CuMO_y$ phases to YBCO precursor powder [where M = U, Zr, Hf, Nb, Ta, Mo, etc.] phases are observed to form nano-scale (10–300 nm) inclusions in the Y-123 matrix during the melt-growth process, without affecting T_c of the superconducting compound and hence compromising its properties.

A more generic phase composition of $(LRE)_2Ba_4CuMO_y$ (the 2411 phase) can be obtained by replacing Y-element with light rare earth elements, such as Sm, Nd and Gd, and their introduction to the $(LRE)Ba_2Cu_3O_y$ single grain can offer significant benefits in obtaining improved trapped magnetic fields due to the higher irreversibility fields that characterize the $(LRE)Ba_2Cu_3O_{7-\delta}$ system compared to $YBa_2Cu_3O_{7-\delta}$ [15–18]. Until recently, unlike Y–Ba–Cu–O, the fabrication of (LRE)–Ba–Cu–O single grains using a top-seeded melt-growth (TSMG) process is not possible practically via a cold-seeding method due to the lack of seed crystal that can

* Corresponding author. Tel.: +44 1895 265466; fax: +44 1895 269758.
E-mail address: mtsthbn@brunel.ac.uk (N.H. Babu).

0921-4534/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physc.2010.12.006

promote heterogeneous nucleation. Shi et al. [19] have developed a novel generic seed crystal of Mg-doped $NdBa_2Cu_3O_{7-\delta}$ that enables the fabrication of all (RE)BCO single grain bulk superconductors using a TSMG process that is similar to that used routinely to fabricate YBCO. Hari Babu et al. [20] have developed a practical processing route for the processing of (LRE)–Ba–Cu–O superconductors using the generic seed crystal and controlling the extent of the formation of RE/Ba solid solution in an air atmosphere, which critically determines T_c. Consequently, we have developed an effective batch process for the manufacture of Sm–Ba–Cu–O and Gd–Ba–Cu–O [21–24] single grain superconductors. The in-plane mis-orientation of grains fabricated using the batch process has been investigated in detail [25] in an attempt to produce bulk superconductors of complex shapes. These studies have established that strongly connected bulk grain boundaries can be manufactured by aligning the orientation of individual seed crystals during the melt process. In this paper, we discuss microstructural variations as a function of inter-seed distance and its influence on the trapped field of a bi-grain sample when the two grains are perfectly aligned. Another significant recent development is the recycling of scrap bulk YBCO superconductors, which is discussed here briefly.

2. Experimental

2.1. The development of novel second phases and their introduction to the single grain microstructure

Oxides in the required molar ratios with initial compositions to form the $YBa_2(Cu_x,U_{1-x})O_6$ and $YBa_2(Cu_x,W_{1-x})O_6$ phases [where $x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5] were mixed thoroughly using a mortar and pestle and calcined at 950 °C, 1000 °C, 1100 °C and 1150 °C progressively with intermediate grinding stages. Various $REBa_2(Cu_{0.5}M_{0.5})O_6$ phases were also synthesized for M = Nb, Bi and Ag and RE = Y, Gd and Sm. X-ray diffraction (XRD) patterns were recorded at each stage of the calcination process using a Cu Kα radiation source. The synthesised powders were mixed with commercially available RE-123 and RE-211 powders in the required molar ratio for the three RE element (Y, Gd, Sm and Nd). A small quantity of Pt powder (0.1 wt.%) was also added to the precursor powders prior to uniaxial pressing. The precursor pellets for RE = Gd and Sm were enriched with 1 wt.% and 2 wt.% BaO_2, respectively, in order to suppress solid solution formation during the melt-growth process under an air atmosphere. Single grain superconductors were melt processed under air by the TSMG [26] technique. An Mg-doped Nd–Ba–Cu–O generic seed crystal was used for the growth of GdBCO and SmBCO single grains, as reported in Ref. [19]. Details of the fabrication of the generic seed processing are given in Refs. [19,27].

2.2. A practical processing route

Generic seed crystals were placed at room temperature on the top surfaces of pressed, Gd–Ba–Cu–O and Sm–Ba–Cu–O green bodies enriched with excess BaO_2 and melt processed in an air atmosphere [20]. The overall melt processing procedure is similar to that of YBCO, except that Mg-doped NdBCO crystal [19] is used as a seed and (LRE)–Ba–Cu–O precursors are enriched with BaO_2. The temperature profiles for Gd–Ba–Cu–O and Sm–Ba–Cu–O are adjusted based on the peritectic temperature of the system.

2.3. Development of batch processing route

A special furnace was designed specifically for the batch processing of large (RE)BCO single grains. The hot zone in the furnace is (H) 20 cm × (D) 60 cm × (W) 60 cm, which includes an active zone of uniform temperature of dimensions (H) 10 cm × (D) 40 cm × (W) 40 cm. The processing atmosphere was not controlled in any way during the batch TSMG process. Large area heating coils are placed on four sides of the chamber to maintain a homogeneous lateral thermal distribution within the hot zone, and the temperature is sampled at various positions to ensure the homogeneity. Twenty five YBCO precursor pellets of initial diameter 32 mm were pressed uniaxially and an Nd–Ba–Cu–O seed was placed on the surface of each sample. A ceramic plate was used as a tray to support an assembly of several precursor pellets in the furnace. All the samples were transformed into single grains after melt processing [28]. A similar procedure was adopted for the batch processing of Gd–Ba–Cu–O single grains [29]. In this case, the precursors of all the pellets were enriched with 1 wt.% BaO_2 and the recently developed generic seed crystals were used to seed the single grain formation. Five GdBCO samples were fabricated in each batch process.

2.4. Development of multi-seeding process with strongly-coupled grain boundaries

YBCO precursor pellets of diameter 25 mm and thickness 15 mm were used to investigate the multi-seeding process in this study. TSMG was used to fabricate YBCO multi-grains using a bridge-shaped Sm–Ba–Cu–O seed crystal in an attempt to achieve perfectly aligned grains. This technique was extended to produce a cavity structure using a multi-seeding process.

2.5. Annealing, microstructure and superconducting properties

The as-processed single grain superconductors were annealed in an O_2 atmosphere between 450 and 350 °C for 100 h, depending on type of rare earth system. The annealed samples were polished with diamond paste and their microstructure examined by optical microscopy and scanning electron microscopy. Particular attention was applied to the size of the Y-211 and $RE_2Ba_4CuMO_y$ phase inclusions. A scanning Hall probe was used to measure the trapped magnetic fields of the samples at 77 K in a field cooled process. The superconducting transition temperature, T_c, and critical current density, J_c, of the fully-processed samples were determined by measuring the magnetic moment as a function of temperature under an external field of 2 mT and magnetic hysteresis loops as a function of applied field using SQUID magnetometry, respectively.

3. Results

3.1. Introduction of nano-scale second phase inclusions

XRD patterns for solid state reacted powders with starting composition $YBa_2(Cu_xW_{1-x})O_6$ for $x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5 are shown in Fig. 1. It is important to note that the existence of the iso-structural YBa_2MO_y phase ($x = 0$) is well known for M = U, W Zr, Hf, Nb, Ta, Mo, W etc. The oxygen content in the synthesized powders is unknown and is referred to simply as "y". Clear evidence for the evolution of an additional phase can be seen in the XRD data for $x > 0$. The peak at 52.9°, for a starting composition of $x = 0.1$, for example, corresponds to the (4 2 2) reflection of a second phase, suggesting that the synthesised powder is a mixture of two different phases. The existence of two different, distinct phases can be seen more clearly for $x = 0.2$. The (4 2 2) reflection peak corresponding to the YBa_2WO_y phase disappears completely when the Cu concentration is increased to 0.5, suggesting that the YBa_2WO_y phase transforms to $YBa_2Cu_{0.5}W_{0.5}O_y$ in the presence of Cu. This