Multiple seeding for the growth of bulk GdBCO–Ag superconductors with single grain behaviour

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Abstract
Rare earth–barium–copper oxide bulk superconductors fabricated in large or complicated geometries are required for a variety of engineering applications. Initiating crystal growth from multiple seeds reduces the time taken to melt-process individual samples and can reduce the problem of poor crystal texture away from the seed. Grain boundaries between regions of independent crystal growth can reduce significantly the flow of current due to crystallographic misalignment and the agglomeration of impurity phases. Enhanced supercurrent flow at such boundaries has been achieved by minimising the depth of the boundary between A growth sectors generated during the melt growth process by reducing second phase agglomerations and by a new technique for initiating crystal growth that minimises the misalignment between different growth regions. The trapped magnetic fields measured for the resulting samples exhibit a single trapped field peak indicating they are equivalent to conventional single grains.

Keywords: multi-seeding, single grain, alignment of seeds, grain boundaries, buffer-aided-bridge-seeding

(Some figures may appear in colour only in the online journal)

Introduction

High temperature superconductors based on the RE–Ba–Cu–O system [(RE)BCO], where RE is a rare earth element, have been studied extensively since their discovery in 1986 [1]. Single grain, bulk (RE)BCO superconductors are able to generate magnetic fields that are considerably higher than those produced by conventional ferromagnets, which makes them potentially useful for use as superconducting ‘permanent magnets’. The present authors have recently demonstrated a world record trapped field of 17.6 T at 26 K [2] in a two sample stack of bulk, single grain GdBCO–Ag superconductors.

Bulk samples of melt processed (RE)BCO are referred to as single grains, rather than single crystals, because, although they exhibit one overall crystallographic orientation, they contain a high density of defects, second phases and inclusions that makes it difficult to define the long range order that technically qualifies a single crystal. The growth of single grains involves placing a seed crystal of similar lattice parameter to the target superconducting REBa2Cu3O7-δ (RE-123) phase on the top surface of a pressed powder pellet. This assembly is then melt-processed at a temperature of around 1000 °C followed by slow cooling into an under-cooled region at about 0.3 °C/h, during which, in a peritectic reaction nucleating at the seed, the RE2Ba1Cu1O5 (RE-211) phase reacts with liquid Ba3Cu5O8 to form the desired RE-123 phase. In this way a polycrystalline material is converted into a single grain with the superconducting matrix adopting the crystallographic orientation of the seed. The resulting single grain has five growth sectors; four α-axis growth sectors (A-
GSs) grow outwards from the seed crystal in the $a$–$b$ plane direction and a $c$-axis growth sector (C-GS), which extends downwards from directly beneath the seed, ultimately spreading out laterally to form a square pyramid shape as it grows. A YBCO single grain of diameter 20 mm typically grows. A YBCO single grain of diameter 20 mm typically takes five days to grow by this process.

Multi-seeding was developed initially by Kim [3] et al in 1996 to fabricate larger samples and to reduce the time taken for the melt growth process. However, non-superconducting residue accumulates at the grain boundaries formed where the growth fronts impinge from different seeds [3–11] during this process. This region of contamination at the grain boundary was found to be up to 50 $\mu$m in width [8, 12] and to extend through the entire thickness of the sample. When the trapped magnetic field of such a sample is mapped it is seen typically to exhibit multiple peaks, suggesting that it contains multiple current loops due to a low inter-grain critical current density ($J_c$). The aim of this study is overcome this key obstacle and, hence, to further the commercialisation potential of these technologically important materials.

We first describe the nature of the grain boundaries in multi-seeded samples and identify how to limit the through thickness extent of contaminated grain boundaries. We then describe a technique to obtain growth from multiple, well-aligned seeds via a buffer-aided-bridge-seeding process for the growth of multi-seeded single grain (RE)BCO superconductors. Finally, we present trapped magnetic field data and assess the quality of these samples.

**Development of buffer-aided-bridge-seeding**

The accumulation of non-superconducting phases at grain boundaries in multiply seeded (RE)BCO bulk superconductors has been reported widely [3–5, 9, 12–18]. This effect is observed even when the crystallographic axes of the multiple seed are well-aligned. We have previously reported that a poorly conducting grain boundary is sometimes only seen between $a$-axis growth sections, whereas in the grain boundary between C-GSs is generally imperceptible, which we have attributed to good grain alignment and the absence of second phases. Evidence for this has been seen in the bulk sample microstructure, such as that shown in figure 1(a) [12], and in magnetic property measurements along the length of $c$ direction [15] through the bulk sample and has been depicted schematically by a number of authors [15, 19]. We have recently established that this substantial deleterious grain boundary effect is unrelated to the classical variation of critical current with misorientation angle observed at low-angle grain boundaries in YBCO, which occurs when the crystallographic orientations of individual seeds are not well aligned with one another [20, 21]. Instead, it is the pushing of particles of second phases at the growth front that leads to the accumulation of non-superconducting material at the grain boundary. We refer to such grain boundaries as being ‘contaminated’ in this paper. In other words, we believe strongly that the dominant factor that affects the trapped field at the position of the grain boundary in multi-seeded bulk (RE)BCO is the ‘contamination’ that occurs when the seeds are aligned. The dominant factor affecting trapped field when the seeds are not aligned, on the other hand, is crystallographic mis-orientation between the seeds [20–22].

This investigation is based on the observation that the grain boundaries in multi-seeded bulk (RE)BCO samples are only contaminated significantly in the growth sector indicated by the white dashed lines in figures 1(b) and (c) when the seeds are aligned and the growth fronts from two seeds
process forward from position O in the C-GS as a single growth front. It can be seen from figure 1 that supercurrent can flow within the \( ab \) planes of the sample, which are usually parallel to the top and bottom surfaces of the single grain, apart from the ‘trough’ region (the A-GSs) at the top centre of the sample where the grain boundaries between the growth regions are contaminated. The grain boundaries are aligned and uncontaminated at the bottom of such a multi-seeded bulk sample and therefore present no barrier to current flow. This results in the formation of a more or less a single peak profile in trapped field, as would be expected from a single grain sample in which the thickness of the grain is comparable to its radius, for which the trapped field saturates [23].

As a result, it is possible to design and grow multi-seeded bulk (RE)BCO superconductors that resemble a single grain, but with shallow, contaminated grain boundaries at the top surface and, in effect, a complete single grain at the bottom where the grain boundaries are uncontaminated and well aligned. The key issue for a multi-seeded growth, therefore, is the alignment of the seeds whilst simultaneously reducing the depth of the contaminated grain boundaries formed at the sample surface.

A bridge seeding technique [9, 13] can be employed to ensure that seeded grains represented by the two legs of a bridge seed are fully aligned [12, 15, 16]. However, the fabrication of bridge-shaped seeds is challenging and typically involves fabricating large, single SmBCO grains up to 20 mm in diameter by a conventional top seeded melt growth (TSMG) process and then further cutting and grinding the brittle single grains into a bridge-shaped geometry. Then the two legs of the bridge with the desired orientation are used as the two seeds. A four seed bridge (a bridge with four legs in the corners of a square) would be extremely difficult to fabricate, which is a real limitation of the bridge-seed technique.

A buffer seeding technique [24–26] has been developed recently by the present authors. This process involves placing a small, \( \sim 0.3 \) g and \( \sim 3–5 \) mm in diameter (RE)BCO pellet between the seed and a (RE)BCO–(Ag) precursor pellet as a buffer to prevent the diffusion of undesirable and growth-affecting elements such as Sm, Nd or Mg from the seed into the pellet at elevated temperature. Simultaneously, the buffer pellet also inhibits diffusion of Ag from the main pellet into the seed crystal during processing and thereby prevents the melting of the seed [27–30]. The buffer layer or layers act essentially as large (compared to the size of the conventional single crystal seed) ‘pseudo hot seeds’ in this process, resulting in a decrease of the extent of the A-GSs in the single grain microstructure [27].

A buffer-aided-bridge-seeding technique, which combines bridge seeding and the newly developed buffering seeding technique, has been used in the present study to fabricate a set of 3, multi-seeded GdBSCO–Ag bulk samples using four seeds. Two layers of buffer pellets (each in the shape of a disc) consisting of one buffer pellet supported by four others to effectively form a cascade seed composed of sintered, thin GdBSCO (without silver) pellets, allow the multiseeds align to a maximum extent and to reduce the depth of the contaminated grain boundaries. Trapped fields, which are an effective measure of the depth of the grain boundary in the fully melt processed sample, were examined at the top and bottom surfaces of the fully processed samples in this study. Furthermore, the levitation forces at 77 K of single-seeded and multi-seeded samples were measured and compared to enable the effectiveness of the multi-seeding technique to be evaluated further.

**Experimental**

GdBa\(_2\)Cu\(_3\)O\(_{7-d}\) (Gd-123) (99.9% Toshima) and Gd\(_2\)BaCuO\(_5\) (Y-211) (99.9% Toshima) powders of average particle size 2 and 1 \( \mu \)m were mixed thoroughly with Pt (99.9%, Alfa Aesar), Ag\(_2\)O\(_3\) (99.9%, Alfa Aesar) and BaO\(_2\) by a tubular mill to form the precursor powder. The precursor powder, of composition (75 wt% Gd-123 + 25 wt% Gd-211) + 0.2 wt% Pt + 10 wt% Ag\(_2\)O\(_3\) + 1 wt% BaO\(_2\) [31] (BaO\(_2\) was used to suppress Gd/Ba substitution in air [32]), was initially pressed uniaxially into pellets and then pressed further using a cold-isostatic press at 1800 bar. Four samples, which were labelled...
as samples 1, 2, 3 and 4, were placed into a box furnace for processing via TSMG in air. The typical arrangement of the seed, the buffer layers and pressed pellet of multi-seeded samples 2–4 is shown in figure 2. The four seeds, which are in close contact with the top surface of the pressed precursor pellet, are actually formed during processing from the top two buffer layers (consisting of one large upper disc and four smaller lower discs), which are located immediately beneath the small single crystal seed, and are therefore perfectly aligned during the initial stages of melt processing. The heating profile for fabricating samples 1–4 is described elsewhere [31].

Trapped fields were measured following a field cooled process, which involved applying a magnetic field of 1.3 T, cooling the sample to 77 K using liquid nitrogen and then removing the magnetic field. The resulting trapped fields at both top and bottom surfaces of the samples were measured after one magnetisation cycle using an array of 19 rotating Hall probes with a distance of about 1.8 mm effective distance between each probe. The distance between the probes and the surface of the sample was approximately 1.0–1.5 mm in each measurement.

The levitation forces for samples 1 and 4 (which was multi-seeded by 4 seeds) were measured at 77 K using a load cell attached to a Nd–Fe–B permanent magnet stack of 30 mm diameter and 20 mm thickness. The load cell approached to and retreated from the sample being measured at a rate of 0.16 mm s\(^{-1}\). The force measured between the magnet and superconducting sample formed the two curves of a hysteresis loop. The Nd–Fe–B permanent magnet stack was removed to a distance of 80 mm from the sample during initial cooling to 77 K to ensure that the sample was effectively zero-field-cooled.

Results and discussion

Multi-seeded samples with good seed alignment

Figure 3 shows photographs of a sample seeded with a single seed (sample 1) and three multi-seeded GdBCO–Ag samples (samples 2–4) and cross sections of the buffer layers, sliced and shown from below for each sample. (a) A photograph of a single seeded GdBCO–Ag single grain 31 mm in diameter and 14 mm in height. (b)–(d) GdBCO–Ag grains of diameter 31 mm seeded using four seeds with increasing separation between seeds. (e)–(g) Photographs of the underneath of the buffer layers used to grow samples 2–4.
side surfaces, which is characteristic of a single grain, singly seeded sample, establishing beyond doubt that the four seeds in samples 2–4 are fully aligned in this growth process.

**Multi-seeded ‘single’ grains**

The maximum value and shape of the trapped field profile indicate the superconducting quality and uniformity of the bulk material. Therefore, measurement of the trapped field profiles can be used to establish whether a bulk sample constitutes a single or a multi-grain sample, as well as indicating the quality of the single grain from its maximum trapped fields at the top and bottom surfaces. Figure 4 shows the trapped field profiles of all four samples measured at 77 K. The maximum observed value of trapped field at both the top and bottom surfaces of each sample is indicated in the figure, along with photographs of the polished top surface in each case. The polished top surfaces of samples 2–4 indicate clearly that these three samples are multi-seeded. The multi-seeds (i.e. the buffer layers placed on the top surface) used for sample 2 are larger than those used for samples 3 and 4, but the distances between the seeds are lager for samples 3 and 4. The maximum trapped field of sample 1 is 1.03 T, which is comparable to the best values observed for batch processed GdBCO-Ag single grains (1.1 ± 0.07 T for 31 mm in diameter samples [31]). The maximum values of trapped field at the top surfaces in figure 3 of the other samples decreases from samples 2–4 with values of 0.90, 0.86 and 0.78 T, as the distance between the seeds increases from 7 mm to 12 mm. (The ‘effective’ distance from the nearest neighbour heterogeneous nucleation locations are <1 mm, <4 mm and <6 mm respectively). The variation of trapped field between the single seeded and multi-seeded is in agreement with a previous observation [16] that the trapped fields of multi-seeded samples decrease when the distance between the seeds increases when bridge seeds were used to fabricate large, single grains.

Importantly, the values of peak trapped field at the bottom of all four samples are very similar to each other and are as high as 0.85 T. As the trapped field profiles show, all four samples constitute single grains right down to the bottom of the sample. Indeed, the multi-seeded samples are as good as the single-seeded single grain, confirming the grain boundaries of the multi-seeded samples are shallow and do not extend to the bottom of the sample due to the complete alignment of the seeds, as discussed earlier. It has been reported previously based on trapped field measurements on the top surface of the sample only that well-aligned, multi-seeded samples can support good, well-connected...
supercurrents at the bottom of a sample grown by three seeds [17]. In the present study, however, we report for the first time high trapped field values measured directly at the bottom surface of multi-seeded samples, and demonstrate unequivocally that the bottom surface of these samples both constitute single grains and support large, fully connected currents. It may be concluded, therefore, that the multi-seeds in this research are effective in nucleating single grain growth but do not cause any significant grain boundary issues, as has been the case in previous attempts to multi-seed large (RE) BCO grains.

**Shallow grain boundaries at top surfaces**

The trapped field profiles of all 4 samples measured at their top surface in figure 4 exhibit single peaks, suggesting they constitute quasi-single grains within the range of measurement accuracy, even though the top surfaces of samples 2–4 appear to exhibit multi-grain features. The results displayed in figure 4 indicate only that the grain boundaries are shallow in these three multi-seeded samples (samples 2–4). In other words, they constitute quasi-single grains with shallow grain boundaries.

The trapped fields of the top and bottom surfaces of the single seeded and multi-seeded GdBCO–Ag grains measured after a layer of thickness 0.5 mm had been polished away from the top surface of the as-grown sample, are shown in figure 5. This indicates that the trapped fields of the multi-seeded samples are almost unchanged and are at least as good as that observed for the single-seeded sample after the removal of 0.5 mm from its top surface to enable meaningful comparison. This result indicates further that the grain boundaries in the multi-seeded samples are shallow and constitute quasi single grains. This is a direct effect of using buffers, which resulted in the decrease of the extent of A-sectors in the single grain microstructure [27], which is where the grain boundaries reside. The method, which we refer to as the buffer-aided-bridge-seeding technique, used to produce the multi-seeded samples is a highly effective way of minimising the effects of grain boundaries in large grain (RE) BCO samples, which are generally difficult to avoid using conventional processing techniques.

**Comparison of the levitation force of single-seeded and multi-seeded samples**

The levitation forces of the single-seeded sample 1 and multi-seeded sample 4 were measured and compared at 77 K, as shown as figure 6, and found to exhibit peak values of of 72 N and 82 N cm$^{-2}$ at a magnet-sample separation distance of 1 mm. These correspond to force densities of 9.54 N cm$^{-2}$

![Figure 5](image_url). Photographs of the polished top surfaces of samples 1–4 after removal of the top 0.5 mm layer from the as-grown upper surface of each sample. The trapped field profiles at both the top and bottom surfaces measured at a distance of 1 mm are shown. The maximum trapped field values at the top and bottom surfaces of each sample are indicated in the figure.
and 10.86 N cm$^{-2}$, respectively, illustrating clearly that multi-seeded samples can generate equivalent or even greater levitation forces than single-seeded samples, in agreement with a previous report [33]. Owing to the strong correlation between the local magnetic moments, total flux and levitation force, a possible explanation for the higher levitation force observed for the multi-seeded sample maybe due to a higher total flux when the samples were magnetised under the conditions used (i.e. the samples were almost certainly not fully magnetised in the levitation measurement). For example, the trapped field distribution when the maximum force was measured might exhibit a double peak structure, predicted by the Bean model, that occurs characteristically when a type II bulk superconductor is not fully penetrated initially, as has been observed after the initial pulse in a pulsed field magnetisation process [34]. Results from the levitation force measurements indicate the strong possibility that multi-seeded quasi single grains may even yield materials performance advantages, and therefore offer better impact, in situations where the total amount of flux penetration is more important, such as in levitation applications, including Maglev, superconducting magnetic bearings and in flywheel energy storage system and motors. The ability to grow large quasi-single grains reliably via this buffer aided bridge seeding technique has advanced significantly the processing of large grain bulk (RE)BCO superconductors, and hence the realisation of commercial, large-scale applications of bulk HTS.

Conclusions

The main objective in using multi-seeding to obtain single grains was to reduce the vertical length of the contaminated grain boundaries after achieving complete alignment of the seeds. The practical buffer-aided-bridge-seeding technique developed as part of this study has been able to realise this aim for the first time. As a result, 3 large multi-seeded GdBCO–Ag single grains of diameter 31 mm grown using four seeds have been fabricated successfully. The buffer-aided-bridge-seeding technique effectively enables the growth of a multi-seeded sample in the form of a single grain all the way to the bottom of the sample with only very shallow grain boundary remaining at the top surface of the sample, as evidenced via trapped field measurements. The higher levitation force of the multi-seeded sample compared to the single-seeded sample is attractive for practical applications that are based on levitation, such as flywheel energy storage systems, magnetic bearings and superconducting motors and generators.

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