Growth rate of YBCO-Ag superconducting single grains

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Growth rate of YBCO-Ag superconducting single grains

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Abstract
The large scale use of (RE)Ba2Cu3Ox bulk superconductors, where RE=Y, Gd, Sm, is, in part, limited by the relatively poor mechanical properties of these inherently brittle ceramic materials. It is reported that alloying of (RE)Ba2Cu3Ox with silver enables a significant improvement in the mechanical strength of bulk, single grain samples without any detrimental effect on their superconducting properties. However, due to the complexity and number of inter-related variables involved in the top seeded melt growth (TSMG) process, the growth of large single grains is difficult and the addition of silver makes it even more difficult to achieve successful growth reliably. The key processing variables in the TSMG process include the times and temperatures of the stages within the heating profile, which can be derived from the growth rate during the growth process. To date, the growth rate of the YBa2Cu3O7−Ag system has not been reported in detail and it is this lacuna that we have sought to address. In this work we measure the growth rate of the YBCO-Ag system using a method based on continuous cooling and isothermal holding (CCIH). We have determined the growth rate by measuring the side length of the crystallised region for a number of samples for specified isothermal hold temperatures and periods. This has enabled the growth rate to be modelled and from this an optimized heating profile for the successful growth of YBCO-Ag single grains to be derived.

1. Introduction

Single grain (RE)Ba2Cu3Ox bulk high temperature superconductors (HTS), where RE=Y, Gd or Sm, have the ability to trap large magnetic fields, typically of more than an order of magnitude larger than those generated by conventional permanent magnets [1, 2]. This potentially enables a wide range of applications including Maglev trains, energy storage flywheels, rotating electrical machines and trapped flux devices [3-5]. However these ceramic materials are inherently brittle [6, 7] and in many practical cases, the mechanical, rather than superconducting, properties limit their potential for application. Numerous authors have reported that the addition of silver is able to significantly improve the mechanical properties [8, 9] of single-grain bulk YBCO by increasing the fracture toughness [10] and bending strength [9, 11] of the samples without degrading their superconducting properties [8, 12, 13].

Practical applications require bulk (RE)BCO to be fabricated in the form of large single grains, since the presence of high-angle grain boundaries in (RE)Ba2Cu3Ox superconductors prevent the flow of current. The presence of high angle grain boundaries within the bulk results in a significant reduction in the magnitude of the trapped field generated by the sample [14-17]. It is important to ensure the manufacturing process is reliable as the cost of the raw materials are high and the fabrication process takes a relatively long period of time. A carefully considered heating profile is crucial to the successful growth of single grain bulk superconductors for the top seeded melt growth (TSMG) processing technique, in particular [18, 19].

The fabrication of large, single grain bulk samples by batch processing has been achieved successfully for YBa2Cu3Ox (Y-123) and both the GdBa2Cu3Ox−Ag (GdBCO-Ag) and SmBa2Cu3Ox−Ag (SmBCO-Ag) systems [20] although successful, reliable batch processing of YBa2Cu3Ox−Ag (YBCO-Ag) has yet to be achieved due to the greater complexity of the YBCO-Ag system. The addition of greater than 5 wt% Ag to the melt causes a reduction in the peritectic temperature [7] of the YBCO system by approximately 30 °C [21]. This narrows considerably the temperature window available for successful single-grain growth and so a substantially different heating profile is required to that used to melt process YBCO without silver. The reduction in maximum temperature affects many aspects of the growth process, including initial decomposition [22], solute diffusion and interface kinetics and thus reduces the growth rate of YBCO-Ag
in comparison to Ag-free Y-123. [7] There is also an increase in the likelihood of spontaneous nucleation of secondary grains due to the reduction in processing temperature [7], and further complications arise due to the low solubility of silver within the melt. [21] In addition, the diffusion of Y to the growth front is much slower than that of Gd or Sm, so further reduction in the diffusion speed due to the decrease in processing temperature reduces the growth rate yet further and makes it much more difficult to fabricate single grains of YBCO-Ag compared to single grains of GdBCO-Ag or SmBCO-Ag.

A number of studies have been carried out on the growth rate of the YBCO system fabricated without silver [2, 23]. It has been established that the relationship between growth rate and undercooling can be modelled by:

\[ R_a = 4.5 \times 10^{-7} \Delta T^{1.9} \]  
\[ R_c = 2.8 \times 10^{-6} \Delta T^{1.3} \]

where \( R_a \) is the growth rate of the \( ac \)-plane in \( \text{mm/second} \), \( R_c \) is the growth rate of the \( ab \)-plane in \( \text{mm/second} \) and \( \Delta T \) is the undercooling. Experimental results have been found to be in good agreement with these relationships [23].

No growth rate data has yet been reported in detail for the YBCO-Ag system. The measurement of the growth rate for (RE)BCO systems investigated to date have involved a single period of simple isothermal growth [2, 23, 24] and are based on assuming that the growth length of a single grain is proportional to the holding time. However, for the YBCO-Ag system isothermal growth is unreliable and it has proven difficult to grow single grains in this way.

Here, we report measurements of the growth rate using a new, two-stage method, based on continuous cooling and isothermal hold (CCIH), in which a period of slow cooling is followed by a holding period at constant temperature. The slow-cooling stage enables seeding and initialization of the growth for the next stage, which is particularly important in the YBCO-Ag system, since it is difficult to incorporate silver into the lattice, which must take place to ensure that a single grain results. Previous studies involving a single isothermal hold period have shown the growth rate can be modelled by the expression:

\[ R = \alpha(\Delta T)^\beta \]  

where \( R \) is the growth rate in \( \text{mm/hour} \), \( \Delta T \) is the undercooling and \( \alpha \) and \( \beta \) are constants that vary with composition of the precursor powder. In the diffusion limited crystal growth model, \( \beta \) can be approximated to two for the YBCO system, assuming that YBCO crystal growth is controlled by the diffusion rate of the Y element in the liquid phase.

The growth rate in the thermal profile used in CCIH is not fully defined by the growth rate model for an isothermal growth process. In this case, the expression required to model the growth rate in the YBCO-Ag system becomes more complex because the additional slow cooled period must also be considered. The definition of growth rate must be considered in order to calculate the parameter \( \alpha \) from these data:

\[ R = \frac{dL}{dt}; \]

where \( L \) is the growth length and \( t \) is the time over which growth occurs. The CCIH growth process is divided into two parts: the continuous cooling period and the isothermal hold period so that the growth length, \( L \), can be related to the growth rate by:

\[ L = \int_{t_s}^{t} R_c \, dt + R_{ih} t_{ih} \]

Using equation 3 and noting in the continuously cooled region:

\[ \Delta T = -0.5t \]

\[ L = \int_{t_s}^{t} \alpha(-0.5t)^\beta \, dt + \alpha(\Delta T)^\beta t_{ih}; \]

where \( t_s \) is the time at the start of the continuous cooling period, \( t \) is the time at the end of the continuous cooling period, \( R_c \) is the growth rate during continuous cooling, \( R_{ih} \) is the growth rate during the isothermal hold period, \( t_{ih} \) is the time period of isothermal hold, \( \Delta T \) is the undercooling below 970°C, \( L \) is the side
length of the single grain in \( mm \), \( \alpha \) and \( \beta \) are growth parameters to be calculated and \( t \) is the time period in \( seconds \).

The parameters \( \alpha \) and \( \beta \) can be found for each growth condition. When the undercooling is small a significant proportion of the slow cooling and isothermal hold time will be taken up by the seeding and growth initiation period, whereas for large undercooling the majority of this time period will be taken up by growth.

The liquid-phase enrichment technique [25] has been used in the present work to enable successful fabrication of single grains of YBCO-Ag. The growth rate was measured by a new method in which thermal processing, comprising continual cooling and isothermal holding, was followed by measurement of the side lengths of the crystal. The time periods of continuous cooling and isothermal hold and the isothermal hold temperature have been varied for a series of YBCO-Ag samples. Measurement of the growth rate of small samples has provided a large amount of information on the growth process at a low relative cost, because the samples used in the study are small, the time required for growth is short. These data have enabled the growth rate for each condition to be calculated based upon the diffusion-limited growth model and have subsequently enabled a suitable temperature profile to be determined for the successful growth of 20 \( mm \) as-pressed diameter YBCO-Ag single grains.

2. Method

Nine samples were prepared by the TSMG [14, 26] process with liquid-phase enrichment [25]. Precursor powder was prepared from 99.9 % purity powders in the weight ratio \( Y-123 : Y-211 : CeO_2 : Ag_2O \) of 50 : 150 : 1 : 22.2 in order that excess 10 wt% \( Ag_2O \) was added to each sample. Additional liquid-phase rich powder was prepared with the composition \( Yb_2O_3 : BaCuO_2 : BaO \) in a molar ratio of 5.0 : 5.6 : 1.0, which was subsequently calcined once at 850°C for 5 hours.

Green compacts were pressed uniaxially in a 20 \( mm \) diameter cylindrical die with 1.5 g of liquid-phase-rich powder below 10 g of precursor powder. A layer of \( Yb_2O_3 \) paste was painted onto the base of each compact to avoid sub-grain formation at the base. Each compact was assembled on \( ZrO_2 \) rods above a ceramic plate. A buffer pellet [27-31] of mass 0.15 g was pressed uniaxially from the standard precursor powder without \( Ag_2O \) to a cylinder of diameter 5 \( mm \) and placed centrally above the precursor powder pellet. A generic seed [32] was placed at the center of the buffer pellet prior to melt processing.

Samples were heated above the peritectic temperature in a box furnace. The peritectic temperature was measured to be 989 °C by differential thermal analysis (DTA) for the precursor composition with 10 wt% \( Ag_2O \). The samples were held above this temperature to enable complete decomposition to occur. This was followed by rapid cooling to 970 °C, then slower cooling at 0.5 °C/hour, to enable seeding and growth initiation to take place, and then to the isothermal hold temperature \( (T) \) in the range 970 °C and 952 °C. The sample was then held isothermally for a given time period \( (t) \) of between 45 minutes and 10 hours. The isothermal hold time was varied to ensure the side length of the partially grown single grain could be measured. Each sample was quenched to ambient temperature at the end of the isothermal hold period. It was assumed that heat dissipation at the growth front is large in comparison to the growth rate, so quenching will enable the growth dimensions and microstructure at the end of the isothermal hold period to be preserved. A schematic of the heating profile can be seen in Fig. 1, which represents the heating profile used conventionally to measure growth rate with a single isothermal hold period superimposed onto the figure.
The side length of the square single grain was measured on the top surface of each sample and the average of the two perpendicular side lengths recorded as grain growth in the $a/b$-axis direction. Each sample was then cut in half to enable the extent of growth in the $c$-axis direction to be measured as the vertical distance from the top of the buffer pellet to the edge of the single grained region observed in the rectangular central cross section at the center of the sample. The positions of the measurements taken on each sample cross-section are illustrated in Fig. 2.

3. Results and Discussion

All nine samples were partially grown successfully, with their top surfaces and cross sections shown in Fig. 3, the edge of the single grained region is marked by the yellow dotted line. Measurements of the size of the single grain region enabled the growth rate parameters, $\alpha$ and $\beta$, to be calculated to give the following models for growth of the YBCO-Ag system:

$$R_{a/b} = 1.4 \times 10^{-3} (\Delta T)^{1.76} + 0.035$$

$$R_{c} = 4.5 \times 10^{-3} (\Delta T)^{1.42} + 0.035$$

where $R_{a/b}$ is the growth rate in the $a/b$-axis direction in mm/hour, $R_{c}$ is the growth rate in the $c$-axis direction and $\Delta T$ is the undercooling below 970 °C.

These models with an appropriate off-set are a good fit to the actual data, as seen in Fig. 4, with $R^2$ fit parameters of 0.9984 and 0.9966 for the $a/b$-axis and the $c$-axis direction for an undercooling between 0 and 18 °C. A greater magnitude of undercooling leads to a higher growth rate. However, although a large undercooling enables more rapid growth, the magnitude of undercooling must be limited because the probability of random nucleation of secondary grains increases to a critical level when the undercooling is sufficiently large.
Figure 3: Photographs of the samples grown for the calculation of growth rate. The dashed lines show the edge of the single grained region.

Figure 4: Plot of the actual and modelled growth rates for both the $a/b$-axis and $c$-axis directions of the single grain YBCO-Ag samples.
The requirement for an additional continuous slow cooling stage before the isothermal hold period has led to a requirement to develop a revised method to calculate the growth rate, since some growth will occur during the slow cooling period, of which account must be taken. The need for the slow cooling period is evident both from the structure of the bulk samples and the growth rate models. The buffer is clearly evident in the cross sections of all samples, with a region immediately below this that appears to be deficient in silver compared to the central region, as shown in Fig. 5. In addition to lower silver content, the size of the agglomerates present in the silver-deficient region are much smaller in size relative to those in the adjacent region towards the center of the sample, which appears to be silver-rich. Silver is forced to the growth front during the initial stages of growth, since it cannot be easily incorporated into the lattice. As the growth-front advances, too much silver is present to be pushed with the growth front and it is therefore forced to move into the pores already present within the solidifying single grain structure. This discontinuity can be interpreted as the change from a silver deficient region to a silver-rich region, where the silver agglomerates are much larger and fill some of the regions that were initially pores. In addition, the growth rate model required an offset of 0.035 mm/hour to fit a power law model. This provides further evidence for the importance of the seeding and growth initiation period required for successful nucleation and growth of the YBCO-Ag system. This offset value is the same for both directions within the sample, suggesting that the slow cooling period is critical to 3D growth and affects both directions to the same extent.

The growth rate model can be compared with that derived for isothermal growth for the YBCO system containing Pt in equations 1 and 2 [23] and the isothermal growth of YBCO of composition 75 wt% Y-123, 25 wt% Y-211, 1 wt% CeO:: [2]

\[
R_{a/b} = 1.6 \times 10^{-3} (\Delta T)^{2.12} \text{ (mm/hour)}
\]

\[
R_c = 2.4 \times 10^{-3} (\Delta T)^{2.12} \text{ (mm/hour)}
\]

The differences between the coefficients in these models are due to a combination of factors, including the presence of silver agglomerates, the use of additional liquid-phase and differences in the heating profiles.

![Silver deficient](image1)

**Figure 5:** The locations of the silver deficient and silver-rich regions observed in the YBCO-Ag samples.

The dependence of growth rate at various values of undercooling and peritectic temperature, measured using DTA, have enabled the derivation of a suitable heating profile to enable the successful growth of single-grain 20 mm as-pressed diameter samples. The optimum heating profile derived from this investigation is shown in Fig. 6, with a sample fully grown using this heating profile shown in the inset.
4. Conclusions

The growth rate of single grains in the YBCO-Ag system has been studied in detail using a new method based on continuous cooling and isothermal hold (CCH), which differs from previous studies in that it provides a seeding and growth initiation period prior to the isothermal growth stage. We have developed a model for the growth rate of YBCO-Ag in both the a/b- and c-axis directions based on this technique. In addition to the limitations on successful growth and growth rate due to the diffusion of Y species in the melt, the presence of silver further limits the growth rate of this system. The growth rate model has enabled an optimised heating profile to be derived to successfully grow single grains of 20 mm as-pressed diameter of YBCO-Ag. We are now able to grow large single grains of YBCO-Ag reliably.

5. References

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