Optimization of growth parameters for fabricating single grain (Gd, Dy)BCO bulk superconductors in top-seeded infiltration growth process

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Abstract. Fabrication of single grain bulk REBa$_2$Cu$_3$O$_{7-δ}$ (REBCO) superconductors with superior performance along with shape retaining is a recent topic. Mixed REBCO superconductors produced in melt growth (MG) technique had showed enhanced superconducting performance. However, this process offers many disadvantages such as macro-porosity, shrinkage in final products, inhomogeneous distribution of 211 secondary phase particles etc., which limit many practical applications. Infiltration growth (IG) process is advanced and superior to MG technique in several aspects. Recently, we fabricated (Gd, Dy)Ba$_2$Cu$_3$O$_{7-δ}$ ((Gd, Dy)BCO) bulk superconductors through systematic addition of Dy$_2$BaCuO$_5$ (Dy-211) content. The addition of 20 wt.% of Dy-211 in GdBCO was found to be optimum which resulted in enhanced superconducting performance. In the present work, in order to determine a suitable temperature window for fabrication of large single grain (Gd, Dy)BCO bulk superconductors, isothermal experiments were carried out at several constant temperatures in top-seeded IG process in air atmosphere. Systematic microstructural and magnetic properties were assessed and analysed. The 211 secondary phase particles are enlarged to as high as ~ 25 µm when the sample assembly is dwelled at high temperatures and reduced to ~ 2 µm – 4 µm in the samples dwelled at lower temperatures. Main emphasis will be given on the growth rate progress and difficulties involved in IG processing of mixed REBCO superconductors.

1. Introduction
The high temperature REBa$_2$Cu$_3$O$_{7-δ}$ (REBCO or RE-123, RE refers rare earth elements such as Nd, Sm, Gd, etc.) are potential for many practical applications due to their superior flux pinning abilities compared to YBCO superconductors. Among all REBCO composites, GdBCO superconductors are interested due to the ease of preparation. GdBCO materials can be synthesized in air atmosphere with very small fraction of solid solutions of type Gd$_{1-x}$Ba$_{2-x}$Cu$_3$O$_y$, which are lower superconducting critical temperature ($T_c$) phases [1-4]. In addition, it is reported that the GdBCO materials produce very small sized Gd$_2$BaCuO$_5$ (Gd-211) phase particles, which are very essential for improving the critical current densities ($J_c$) especially at lower fields [4-6].

The mixed REBCO superconductors with binary and ternary RE elements are well-studied [1-5]. The results show that the mixed REBCO bulks are superior and promising candidates for many high field applications. The mixed REBCO materials produced in conventional melt growth (MG) technique are well established in literature. However, MG process offers the final products with many
unwanted large shrinkage, macro-defects such as pores etc., [7]. Infiltration Growth (IG) process was developed to overcome the problems associated with MG process and is superior. The IG process offer to fabricate the bulk samples with negligible shrinkage and microstructure in which homogeneously distribute fine sized 211 phase particles without addition of any costly grain refiners such as Pt and CeO$_2$ [8-10]. Still, mixed REBCO materials processed in IG process are not studied well and very few reports are available in the literature [11-14]. Recently, we optimized the Dy- content in bulk GdBCO bulk superconductors and the addition of 20 wt.% of Dy-211 in GdBCO (GdDy-20) was found to be optimal composition which exhibited superior superconducting properties [15]. In this report, we study the growth, microstructural and superconducting properties of GdDy-20 samples, which were under-cooled at various constant temperatures.

2. Experimental details

The synthesis procedure followed for preparing the precursor powders of Gd-211, Dy-211 and liquid phases detailed in our previous works [15-17]. The preform pellets of GdDy-20-211 (mixture of 80 wt.% of Gd-211 and 20 wt.% of Dy-211) and liquid phase sources were pressed at an uni-axial pressure of 420 MPa. It is well-known fact that, the peritectic temperature ($T_p$) of a mixed REBCO system will be modified depending on the RE elements present in the mixture. To have the knowledge on the peritectic temperature of the GdDy)-20 composite, a simultaneous TG-DTA measurement was performed and the $T_p$ was found to be 1027 °C ±3 °C [16]. The GdDy-20 sample assembly was heat treated to a maximum temperature ($T_{\text{max}}$) of 1060 °C and dwelled at various constant temperatures ($T_{\text{iso}}$) from 1032 °C to 1012 °C for 20 h for top-seeded IG (TS-IG) processing in air atmosphere. The heat treatment schedule followed for fabricating undercooling samples is shown in figure 1. A sub-specimen of size ~0.5x1.5x2 mm$^3$ was collected from the as processed bulk samples below ~ 1.5 mm of the seed and were oxygenated in flow of oxygen for 175 h at 450 °C to 400 °C. The final isothermal samples were referred as GdDy-1032, GdDy-1030 etc.

The microstructural features of the isothermal (Gd, Dy)BCO samples were investigated employing a scanning electron microscope (SEM). The temperature dependence of DC magnetic susceptibility $\chi(T)$ and MH loops at 77 K for estimating the field dependence of $J_c$ were assessed employing a SQUID (Quantum Design, model MPMS-XL5minSITO). The field dependence of $J_c$ was calculated utilizing the Extended Beans critical state model [18-19].

Fig. 1. The time-temperature schedule employed for under-cooling experiments.
3. Results and discussion

Fig. 2. Top surface photographs of under-cooled (Gd, Dy)BCO samples. Growth has initiated from the Nd-123 seed at 1030 °C and the area of growth increased with lowering the under-cooling temperature.

The images of as processed under-cooled GdDy-1032 – GdDy-1012 samples are shown in figure 2. The sample under-cooled at 1032 °C show no growth indicating the temperature is higher than the peritectic temperature of (Gd, Dy)BCO system. The epitaxial growth has initiated in GdDy-1030 sample from the seed. As the under-cooling temperature decreased from 1030 °C-1022 °C, the area of growth increased. When the temperature is further reduced below 1022 °C, the random nucleation’s (parasitic growth) has increased. Random nucleation’s could occur in bulk REBCO materials due to various reasons such as doping, temperature differences especially at the edges of the sample, inhomogeneity in availability of liquid phases for peritectic reaction etc. From figure 2, it is evident that, as the parasitic growth increased, the epitaxial growth was inhibited largely and when the temperature reduced to 1012 °C, no growth was observed. From all these observations, we can conclude that the effective temperature window for fabricating large (Gd, Dy)BCO single grains is 1030 °C to 1022 °C.

The SEM micrographs of under-cooled GdDy-1030, GdDy-1028, GdDy-1026, GdDy-1024, GdDy-1023, GdDy-1022, GdDy-1021 and GdDy-1020 samples are shown in figure 3 (a)-(h) respectively. From a keen observation of microstructural features, it can be noticed that the 211 grains are refined as the under-cooling temperature reduced. This clearly indicates that, as the under-cooling temperature decreased, the peritectic reaction increased due to which the 211 phase particles consumed largely and becoming smaller sized. Larger sized 211 phase particles (~ 25 µm) were observed in GdDy-1030 – GdDy-1024 samples could be attributed to the Ostwald ripening phenomenon. As the temperature reduced, the 211 grain size are reduced to ~ 10 µm and 2 µm – 4 µm. Therefore, to produce fine sized 211 phase particles in the (Gd, Dy)BCO bulk samples, longer time slow cooling should be given between 1024 °C – 1015 °C.
Fig. 3. The SEM images recorded at a magnification of 500 X for GdDy-1030, GdDy-1028, GdDy-1026, GdDy-1024, GdDy-1023, GdDy-1022, GdDy-1021 and GdDy-1020 are shown in panels (a)-(h) respectively.

The normalized DC magnetic susceptibility curves for under-cooled GdDy-1020, GdDy-1021, GdDy-1022, GdDy-1023, GdDy-1024 and GdDy-1026 samples are displayed in figure 4 panel (a). The onset of critical temperature is varied from 90 K to 92.5 K indicating all samples show superconducting nature. The superconducting transition width ($\Delta T_c$) is varied from 3 K to 25 K. The broad width in $\chi(T)$ curves could be attributable to the compositional deviations occurred in different under-cooled composites. The field dependence of $J_c$ for under-cooled GdDy-1020, GdDy-1021, GdDy-1022, GdDy-1023, GdDy-1024 and GdDy-1026 superconductors are determined at 77 K and the curves are compared in figure 4 (b). The self-field $J_c$ values are of the order of 7.5 kA/cm$^2$ to 11.5 kA/cm$^2$. As the under-cooling temperature decreased, the growth rate was improved due to which the 211 phase was refined largely and supported higher $J_c$'s compared to the samples dwelled at higher temperature.

Fig. 4. (a) The normalized temperature dependence of DC magnetic susceptibility measurements for under-cooled GdDy-1026 to GdDy-1020 samples. Panel (b) shows the field dependence of $J_c$ at 77 K.
4. Conclusions

In summary, isothermal experiments were conducted on optimized composition of 20 wt.% added Dy-content in GdBSCO through top-seeded IG process. The temperature window for fabricating single grain (Gd, Dy)BCO materials was investigated. The non-superconducting 211 grains are grown as large as ~ 25 μm sized in samples dwelled at elevated under-cooling temperatures (i.e., 1030 °C – 1024 °C) due to Ostwald ripening. The decrease in under-cooling temperature (below 1024 °C) resulted in fine sized 211 grains due to increased growth rate. The onset critical temperature for under-cooled samples was varied from 90 K to 92.5 K. The field dependence of \( J_c \) was superior in the samples dwelled at lower under-cooled temperature due to refined 211 phase particles. Utilizing the present results, one can fabricate larger sized single grain (Gd, Dy)BCO bulk superconductors with superior superconducting performance.

Acknowledgements

SPKN would like to acknowledge gratefully Shibaura Institute of Technology, Tokyo, Japan for supporting various facilities and financial support.

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