

React-Wind-Sinter Processing of High Superconductor Fraction $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x/\text{AgMg}$ Round Wire

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Abstract— $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (Bi2212) conductor technology has advanced significantly but the development of magnets is still hampered by difficulties associated with the partial-melt process (for wind&react magnets) and strain limitations (for react& wind magnets). To avoid these problems, the React-Wind-Sinter (RWS) approach has been proposed. Here we report on experiments that investigate three split processes that are based on the conventional partial-melt process within the RWS concept. The partial-melt process was interrupted at T_1 , $T_1 - 10^\circ\text{C}$ and T_S . After cooling to room temperature, the conductor is bent to a series of diameters (40 mm–100 mm), replicating magnet construction. The heat treatment process is then resumed on the bent samples from the split point and the heat treatment completed. The critical current is measured at 4.2 K in self-field using the four-probe method and the microstructure and phase composition of the Bi2212/AgMg wire are examined with scanning electron microscopy. For the split processes, the critical current after full heat treatment is as high as those from conventionally processed short samples, and in at least one case it is increased by 40% relative to conventional processing. These results show that a split process is a promising approach to improved Bi2212 conductors and magnets, and more broadly shows that conventional Bi2212 partial-melt processing is far from optimized.

Index Terms—Bismuth compound, superconducting filaments and wires, superconducting magnets.

I. INTRODUCTION

AMONG high- T_c superconductors, silver-alloy sheathed $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ (Bi2212) superconductor is one of the most promising materials for high field magnet applications because of its high J_c up to at least 45 T at low temperature, its rapid phase formation and good phase stability. Moreover, Bi2212 is the only high temperature superconductor that can be fabricated into round and rectangular wire as well as tape. Bi2212 round wire has the highest J_c and no anisotropy [1]. Conventional magnet and cable technology has long favored round wire due to ease in winding and cabling into a wide variety of configurations. For these reasons, there is growing

interest from the high energy physics community and widespread interest for high field magnets for research, particularly NMR magnets [2]–[4].

Traditionally, there are two approaches for manufacturing high field Bi2212 magnets: React-&Wind (R&W) and Wind-&React (W&R). The development of magnets, however, remains limited by difficulties associated with the leakage from the oxide filaments through the Ag-alloy sheath, thermal and oxygen diffusion, and compatibility with insulation and reinforcement material options (W&R) and severe strain limitations (R&W) [5]. Recently a novel approach to manufacturing Bi2212 magnets, React-Wind-Sinter (RWS), has been proposed and preliminary results are promising [6], [7]. The RWS approach is aimed at avoiding the primary issues that limit W&R and R&W manufacturing. In the RWS approach, the conductor is heat treated through the partial-melt step, as if R&W was intended, and then cooled to room temperature. The conductor is then wound into final shape and the heat treatment process is resumed, emulating W&R. Insulation can be incorporated either before or after the “react” step. Thus, the highly temperature sensitive partial melt is completed without the large thermal mass and poor oxygen diffusivity of a tightly wound coil, and the mechanical damage to the conductor from winding is minimized by annealing after winding.

In this paper, we focus on three variations of the RWS split process. In these studies, the conventional partial melt heat treatment is interrupted at different stages and the conductor is bent to various diameters after cooling to room temperature. The heat treatment process is then resumed on the bent conductors and the heat treatment completed. The effects of the split process on the electrical properties, superconductive transition and microstructure are investigated.

II. EXPERIMENTAL DETAILS

Two multifilamentary Bi2212/AgMg round wires (0.78 mm and 0.4 mm in diameter) with 555 filaments and a 42% filling factor were fabricated by the powder-in-tube (PIT) method with a single restack by Supercon Inc. The composition, in terms of atomic ratio of the metallic elements, was $\text{Bi} : \text{Sr} : \text{Ca} : \text{Cu} = 2.19 : 1.95 : 0.88 : 1.98$. The 0.78 mm and 0.4 mm wires are from the same initial billet; the only difference is that the 0.4 mm wires were drawn through additional reductions. Fig. 1 shows the cross section of the 0.78 mm wire before heat treatment.

Samples (8–10 cm in length) were cut and processed in 100% O_2 according to the heat treatment profiles showed in

Manuscript received August 29, 2007. This work was supported by the National Institutes for Health through a Phase II STTR, subcontracted from Supercon, Inc.

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Digital Object Identifier 10.1109/TASC.2008.922258

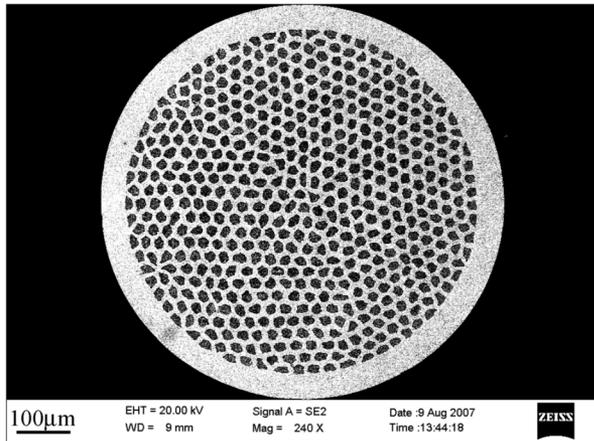


Fig. 1. Cross section of 0.78 mm diameter Bi2212/AgMg wire before heat treatment.

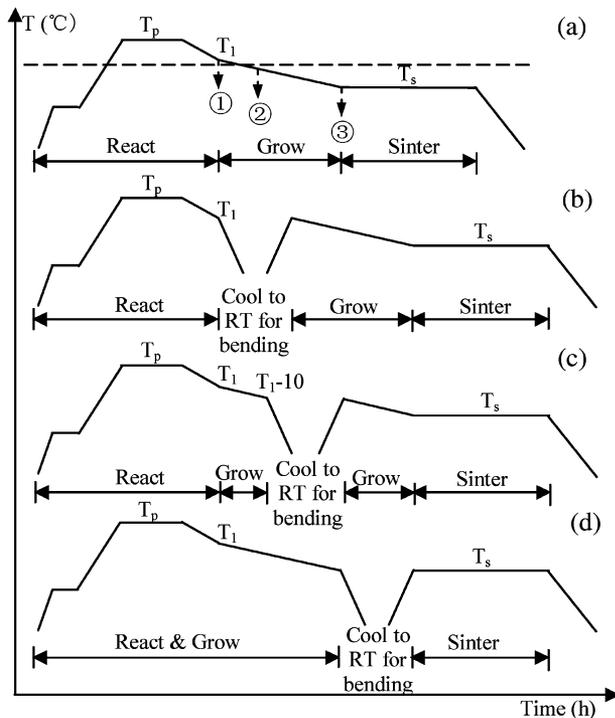


Fig. 2. Schematic for conventional partial melt process and split processes: (a) conventional heat treatment, (b) RCGS, (c) $RG_{10}CGS$, and (d) RGCS.

Figs. 2(a)–(d). Fig. 2(a) represents the conventional heat treatment traditionally used for partial melt-processing of Bi2212 superconductors. The conventional treatment (Cht) includes three regions: the react “R”, grow “G”, and sinter “S” steps.

It is well known that the peak temperature (T_p) during the react step is critical for optimizing the critical current density, so before proceeding with the heat treatment studies, the conventional process is used to determine the optimum peak temperature. For the split processes, optimized conventional heat treatment was interrupted at $T_1 = T_p - 7^\circ\text{C}$, $T_1 - 10^\circ\text{C}$ and $T_s = T_1 - 48^\circ\text{C}$, corresponding to points 1, 2 and 3 in Fig. 2(a). Here we name these three split processes as RCGS, $RG_{10}CGS$ and RGCS as shown in Figs. 2(b)–(d). “C” refers to cooling

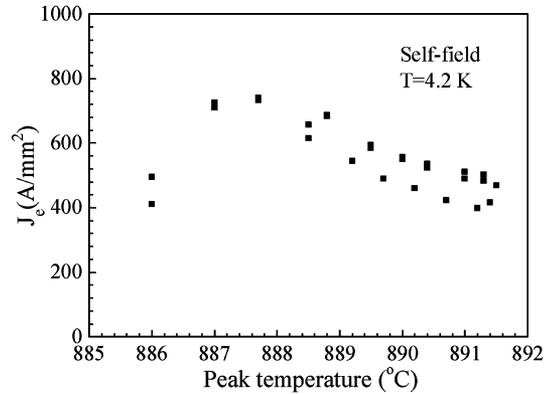


Fig. 3. J_c as a function of peak temperature in the conventional partial melt-process.

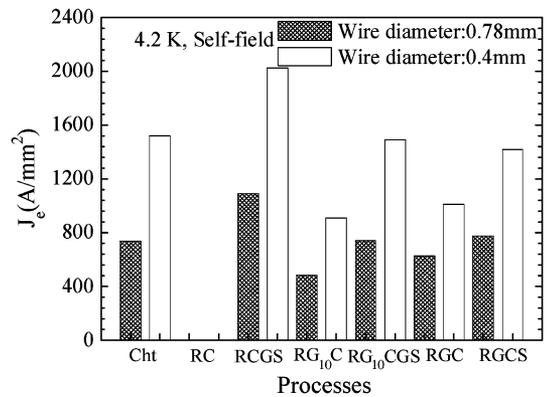


Fig. 4. J_c at 4.2 K, self-field for Bi2212 wires processed using the heat treatments in Fig. 2 and subsets thereof.

to room temperature at a cooling rate of $160^\circ\text{C}/\text{h}$ and then bending to series of diameters (40–100 mm) in a macor sample holder. Some straight samples were also heat treated to determine the effectiveness of the second heat treatment for healing any damage associated with bending. In addition, some samples were heat treated for only part of the entire heat treatment to facilitate understanding of the different stages of the process.

The critical current (I_c) at 4.2 K was measured in self-field using the four point method with an electric field criterion of $1 \mu\text{V}/\text{cm}$. The total sample length and voltage tap spacing were 40 mm and 18 mm, respectively. The engineering critical current density (J_c) was determined by dividing I_c by the total cross-sectional area of the wires. Microanalysis and the superconductive transition measurements were performed on the 0.78 mm wire. The microstructure and phase composition were examined by Scanning Electron Microscopy (SEM) on a Zeiss 1540 XB microscope. The melting temperature was determined by differential thermal analysis (DTA). Magnetization T_c was measured as a function of temperature in a SQUID magnetometer with a magnetic field of 100 G.

III. RESULTS AND DISCUSSION

Fig. 3 shows J_c as a function of peak temperature during the conventional heat treatment. The highest J_c was obtained in the temperature range of 887–888 $^\circ\text{C}$.

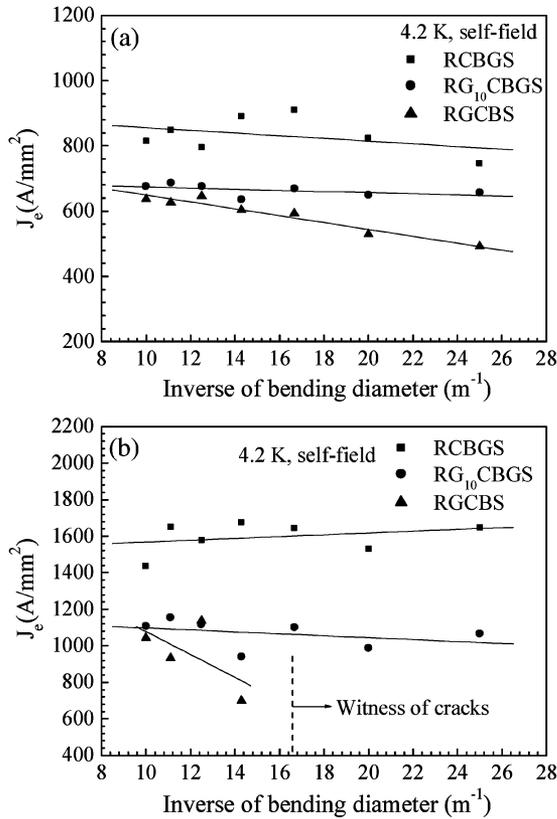


Fig. 5. J_e versus bending diameter for split processes: (a) 0.78 mm wire; (b) 0.4 mm wire.

Fig. 4 shows J_e at 4.2 K in self-field after conventional treatment and split processes. The results for 0.4 mm and 0.78 mm wires show the same tendency; after the conventional full treatment, RG_{10}CGS and RGCS processing, J_e is on the order of $750 \text{ A/mm}^2 \pm 5\%$ for 0.78 mm wire and $1450 \text{ A/mm}^2 \pm 5\%$ for 0.4 mm wire. The RCGS processed wires show an increase in J_e of at least 40% for both wire geometries; J_e of 0.78 mm wire is greater than 1 kA/mm^2 and that of 0.4 mm is greater than 2 kA/mm^2 . Samples that have experienced only part of the heat treatment show broad differences in J_e . The RC samples are resistive. J_e of RG_{10}C samples are 60–65% of J_e of the RG_{10}CGS samples and J_e of the RGC samples are 70–80% that of RGCS samples. While it has been shown previously that the presence of the partial-melt step (the “R” step) is essential for high J_e [8], these results illustrate that the solid state processing after partial melting plays an essential role in determining electrical behavior.

Fig. 5 shows J_e at 4.2 K, self-field versus bending diameter for the various heat treatments for (a) 0.78 mm and (b) 0.4 mm wires. Note that the inverse of the bending diameter is proportional to strain. J_e of RCBGS and $\text{RG}_{10}\text{CBGS}$ samples are independent of the bending, while those of RGCBS are strongly affected by bending for both wire sizes. For 0.78 mm wire, $J_e(40 \text{ mm bend}) \sim 26\% J_e(100 \text{ mm bend})$. For 0.4 mm wire, the critical current is zero for samples with bending diameters $\leq 60 \text{ mm}$ and cracking is seen on the samples. The cracking in the 0.4 mm wire at small bend diameter may be related to the

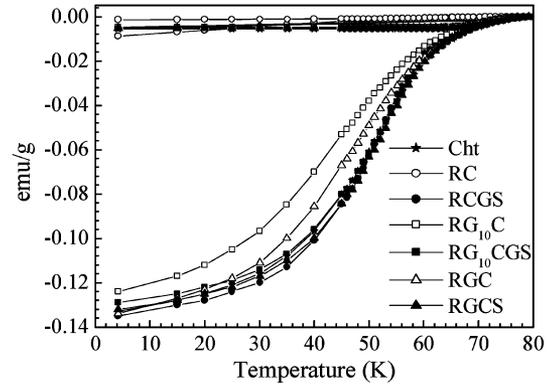


Fig. 6. Superconductive transition as measured by magnetization in a SQUID magnetometer as a function of heat treatment process.

thinner outer sheath that results from the additional deformation, but may also be an artifact of the heat treatment in a macro sample holder designed for larger diameter wires. The results do imply, however, that the sintering alone is insufficient for healing the damage caused by bending, and that at least a partial growth step is necessary.

Fig. 6 shows the superconducting transitions measured magnetically in a SQUID magnetometer as a function of the heat treatment process. From these measurements, it is found that all fully treated samples have nearly the same onset temperature and transition sharpness, indicating that there are no significant differences in the Bi2212 grain composition or oxygenation. The RC sample, however, has a low transition temperature and a very shallow transition. The onset temperature of the superconducting transition of RG_{10}C and RGC samples are comparable to those of the fully processed samples but the transition is much broader. These results we reproduced for a number of samples.

Figs. 7(a)–(c) show backscattered electron images from the SEM of RC , RG_{10}C and RGC 0.78 mm wires. RC samples seen in Fig. 6(a) consist of non-superconducting phases, Bi2201 , and Bi2212 grains that are beginning to form. EDS analysis showed that the dark phases are 1:1 phases, the dark gray phases are Cu -free phases (bulk shape) and Bi2212 (needle shape) and the light gray phases are Bi2201 . From quench experiments in which the samples are quenched at the same temperature, no Bi2201 or Bi2212 were observed, so these phases likely form during the cooling process from T_1 to room temperature [9]. After RCGS processing, the electrical performance was enhanced greatly, which may be due to re-entering the Bi2212 partial melt during the second heating. DTA results on unreacted and RC samples show that the onset temperature and peak temperatures of RC samples 11°C and 6°C lower than those of the unreacted wires. Thus, although the heat treatment is continued from the same temperature from which it was interrupted, the cooling and reheating process has shifted the partial melt temperature such that some liquid phase is formed. After RG_{10}C and RGC processing the samples are superconducting, indicating that Bi2212 growth and/or the reduction of non-superconducting phases occurs.

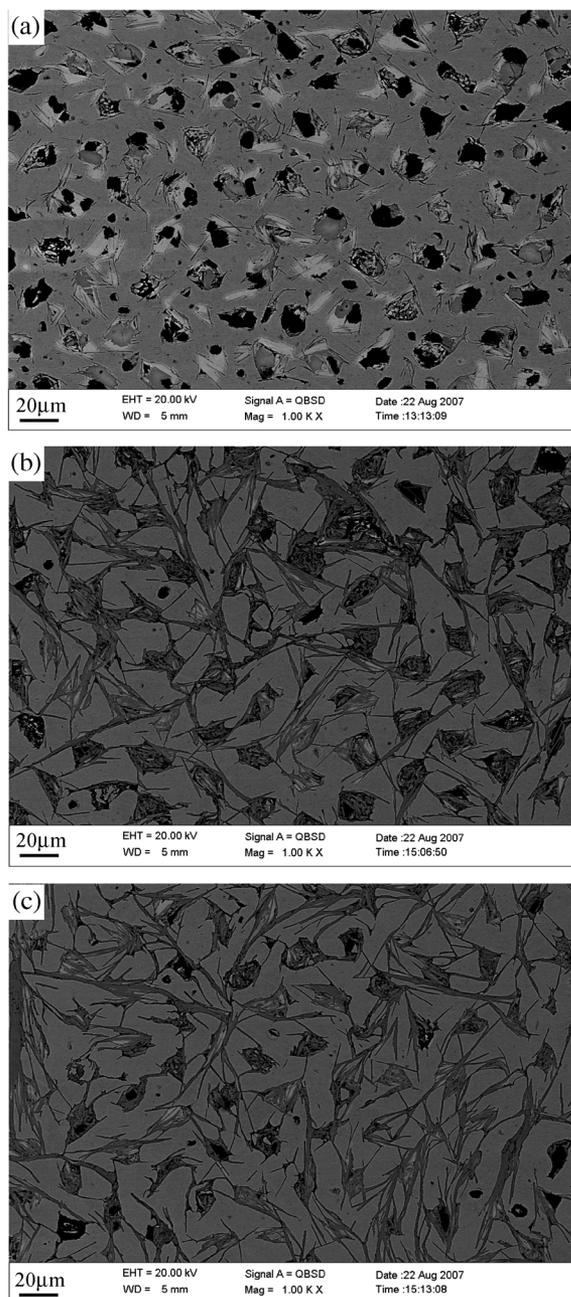


Fig. 7. Backscattered electron images for 0.78 mm wires heat treated with the (a) RC, (b) $RG_{10}C$, and (c) RGC processes.

Figs. 8(a)–(d) show the microstructures of samples after full heat treatment, including the conventional treatment and split processes. Significant differences in the microstructures are not observed. For both fully heat treated samples some black second phases and Bi2201 exist. The EDS results indicate that the second phases are the 1:1 phase and not the 14:24 phase. Previous studies showed that during Bi2212 partial melt-processing, Bi2212 melts incongruently so that at the maximum processing temperature the melt consist of liquid and non-superconducting phases, including Bi-free and Cu-free phases [10]. The 1:1 phase is not an equilibrium phase below the Bi2212 solidus, and decomposes to the 14:24 phase with the alkaline-earth cuprates breaking up as the temperature decreases [11]–[13]. In our studies, however, only 1:1

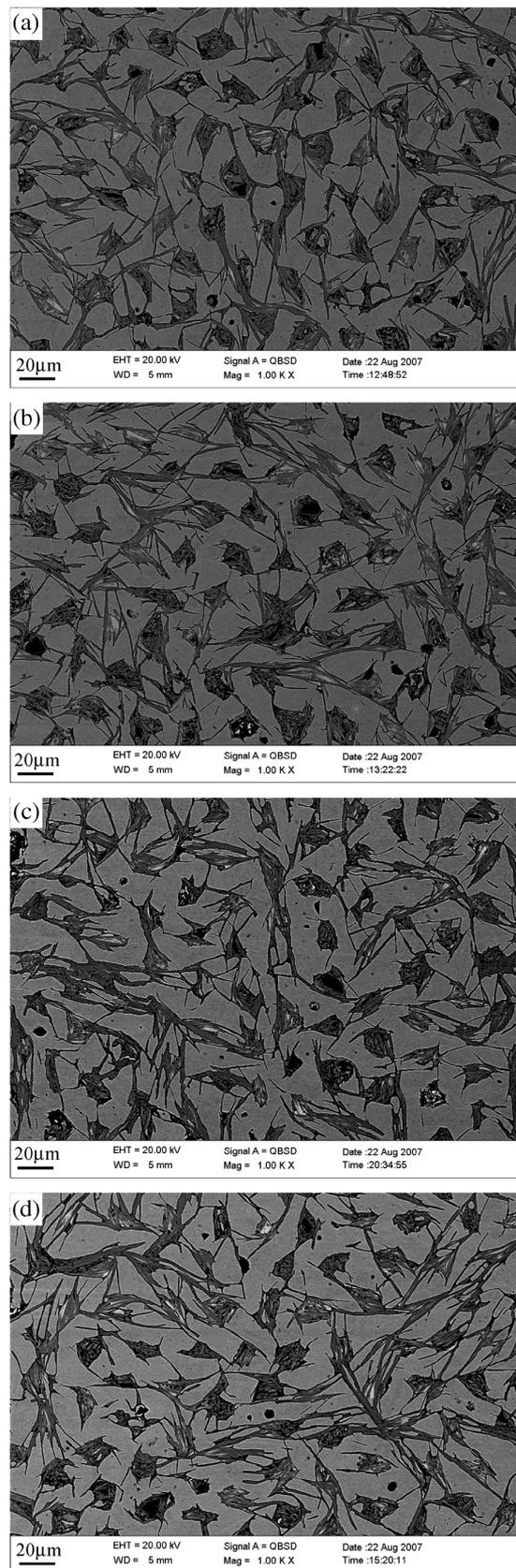


Fig. 8. BSE images of fully treated samples: (a) Cht, (b) RCGS, (c) $RG_{10}CGS$, and (d) RGCS.

alkaline-earth cuprate was found, even after conventional full heat treatment. This difference may be due to the differences in

the precursor powder used in forming the wire, and further work is required to better understand the phase evolution mechanisms affecting the split heat treatments.

IV. CONCLUSIONS

We investigated three split heat treatment processes for magnet manufacture based on the RWS approach. It is shown that the split processes do not adversely affect the J_e and superconducting transition of the conductors and that for the RCGS process, J_e is enhanced greatly. For RCGS and RG_{10}CGS processes, J_e is independent of the bending diameter, while wires processed with RGCS show a clear dependence. Furthermore, microstructural studies show the spectrum of non-superconducting phases that are formed in the RC process, illustrating why those wires are resistive and the importance of the latter stages of partial-melt processing.

ACKNOWLEDGMENT

The authors thank Supercon Inc. for providing conductors, and B. Goddard, Dr. J. Jiang, Dr. B. Cui, and Dr. Y. Xin for their assistance with the microanalysis.

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