

ATMOSPHERE CONTROL DURING PREPARATION OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
MAGNET WINDINGS*

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Atmosphere Control During Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Magnet Windings

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ABSTRACT

Large coils of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ can be fired successfully if the furnace atmosphere is carefully controlled. Organics added during processing produce CO_2 during the initial portions of the firing schedule. Transmission electron microscopy of material fired in atmospheres containing various levels of CO_2 clearly shows the extent of grain boundary degradation caused by CO_2 . Coils with acceptable critical current density can be produced if the rate of CO_2 removal is adequate.

KEY WORDS: $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, CO_2 , grain boundary degradation

INTRODUCTION

Since the discovery of high- T_c superconductors, people have envisioned many possible applications, ranging from small-scale items such as electronic components to large-scale devices for generating, storing, and distributing energy. For most of these applications, the required critical current density, J_c , is in the range of 10^4 - 10^6 A/cm². Thin-film techniques can produce superconductors whose performances meet these requirements, with J_c ranging up to $\approx 10^6$ - 10^7 A/cm² [1]. However, these techniques are limited to production of small-scale superconductors, and bulk fabrication processes will be required to produce the long lengths of continuous superconductor necessary for large-scale applications.

In this paper, we describe bulk processes by which multilayer superconductor coils can be fabricated with a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO)/silver composite as the superconductor and $\text{Y}_2\text{BaCuO}_{25}$ (211) as an insulator. In particular, we discuss the importance of carefully controlling the furnace atmosphere during the firing of coils, and demonstrate that even small concentrations of CO_2 lead to degradation of grain boundaries. Firing extruded coils at reduced total pressure allows for close control of the atmosphere, and prevents decomposition of YBCO, whereas firing coils at ambient pressure leads to decomposition of YBCO during removal of organic constituents. With the low-pressure process, large, multilayer coils with acceptable J_c can be produced.

EXPERIMENTAL

Details of the coil fabrication process are given elsewhere [2-4]. To examine the reaction between YBCO and CO_2 , pellets were fired at 900-1000°C for ≈ 5 h in various O_2/CO_2 gas mixtures (0-5% CO_2). J_c was measured by the four-probe technique with a criterion of 1 $\mu\text{V}/\text{cm}$. Other details are given in Refs. 5 and 6.

RESULTS AND DISCUSSION

Table 1 shows the firing conditions for coils made by extrusion, their J_c 's, and the magnetic fields generated when they operated just below their critical currents. Although the J_c 's are well below those necessary for many large-scale applications, an important accomplishment is that the length of continuous superconductor in these coils ranges up to ≈ 12 m. Moreover, the measurements were made in magnetic fields as high as 73 Gauss, and fringing effects at the coil ends probably increase the field even further at the extreme end turns. Considering that just a few years ago it was not possible to consistently obtain such performance on even short lengths of superconductor in zero field, these results represent significant improvement in the fabrication of bulk superconductors. In the green state, superconducting coils contain ≈ 10 wt.% organics, which must be completely removed in a way that does not damage the superconductor. Incomplete removal of the organics can cause decomposition of the superconductor or leave carbon-rich material at the grain boundaries, either of which will degrade superconducting properties. Organics can be easily removed by thermal decomposition at 240-350°C, but if the decomposition proceeds too rapidly, the

Table 1. Description and Properties of Three Superconductor Coils

Coil Description	Firing Conditions	J_c (A/cm ²)	B^a (Gauss)	B (Fe Core) (Gauss)
1 Uncoated 21 Turns	2 mm Hg 875°C	225	36	---
2 Coated 211 2 Layers 42 Turns	10 mm Hg 875°C	150	42	160 @ 77 K
3 Coated 211 5 Layers 75 Turns	10 mm Hg 875°C	150	73	330 @ 77 K 420 @ 73 K

^aMagnetic field.

coils can become severely bloated and, in some cases, even explode. Also, decomposition of the organics produces significant concentrations of CO₂ and H₂O, two species that are known to react with YBCO [7,8]; therefore, the rate at which organics are removed must be carefully controlled.

When superconducting coils are fired at a reduced total pressure, CO₂ and H₂O are removed as they are produced, thereby minimizing their concentrations and preventing decomposition of YBCO. But when coils are fired at ambient pressure, the harmful gaseous products accumulate and lead to the decomposition of YBCO. To demonstrate this, mixtures were made from YBCO powder and the same organics that are used in extrusion: they were fired in flowing oxygen at either ambient or reduced pressure (\approx 2 mm Hg). Two different powders were used: powder produced by solid-state reaction at reduced pressure, and powder produced by a liquid mix technique. Samples were taken from the mixtures at 240, 300, and 350°C, and their X-ray patterns were obtained. Figures 1 and 2 are schematic illustrations of the major peaks in these patterns. Figure 1 shows that, when the YBCO/organic mixtures were fired at ambient pressure, both samples of YBCO decomposed, the liquid-mix powder at 240°C, the solid-state powder at 300°C. Figure 2 shows, however, that gross decomposition of YBCO did not occur when the mixtures were fired at reduced total pressure, even though the relative intensities of peaks varied as a result of changing oxygen content.

Figure 2 shows that gross decomposition of YBCO is avoided by firing coils at reduced total pressure; however, small concentrations of impurities (<5 wt.%) would not be apparent in X-ray diffraction results. It was possible, therefore, that coils fired at reduced total pressure could still be degraded by small, residual concentrations of CO₂ in the furnace atmosphere. Therefore, it was important to investigate the effect of small concentrations of CO₂ on the properties of YBCO.

It has been shown [5] that, as the CO₂ partial pressure in the firing atmosphere increased, J_c (zero field/77 K) of sintered pellets decreased and finally became zero. Resistivity measurements showed that the materials with $J_c = 0$ were semiconductive. On the basis of such measurements, the stability region for superconducting YBCO was derived with respect to the partial pressure of CO₂ at the four firing temperatures, 910, 940, 970, and 1000°C. (Fig. 3). Magnetization measurements indicated that major portions of the semiconductive samples were still superconducting, and that the onset temperature of superconductivity (\approx 90 K) was almost the same for all of the samples. These results suggest that CO₂ reacts with YBCO to form a thin layer of nonsuperconducting second phase at grain boundaries, but does not degrade the superconducting grain interior. When enough of the grain boundaries become coated with second phases, as in the semiconductive samples, the passage of superconducting current is effectively blocked; however, because of the superconducting-grain interiors, a sharp change in magnetization is still evident.

These arguments are supported by TEM observations [6], which show the presence of secondary phases at some grain boundaries. An example of one such grain boundary is shown in Fig. 4 for a sample fired at 970°C in a 0.5% CO₂/O₂ gas mixture. The second phase was determined to be BaCuO₂ and BaCO₃ by X-ray energy-dispersive spectroscopy. The width of this grain boundary phase is much larger than the coherence length in YBCO, so that the phase can completely obstruct the superconducting current and reduce the overall J_c . However, this type of grain boundary accounts for only \approx 10% of the observed grain boundaries; the majority appear quite sharp, with no obvious evidence of a second phase. Because of the multitude of possible percolation paths, the value of J_c would not become zero if only 10% of the grain boundaries are coated with a second phase. For the superconducting current to be completely blocked, as in the case of

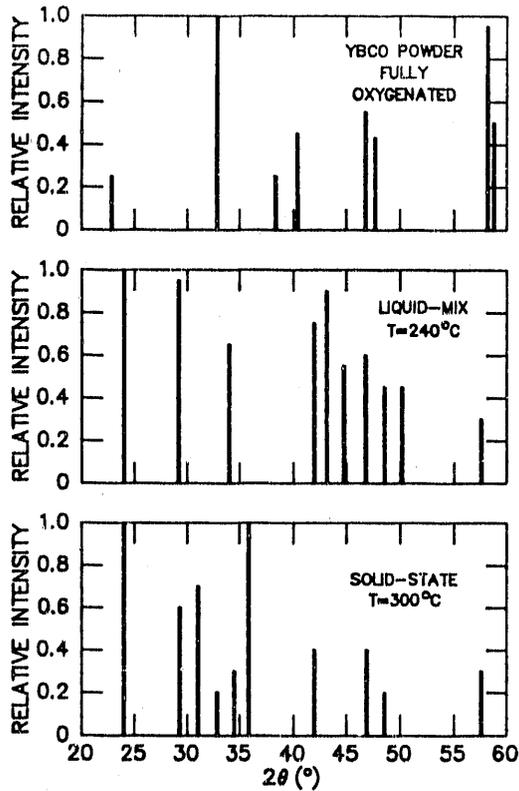


Fig. 1. Schematic X-ray patterns of fully oxygenated YBCO powder (as reference) and two YBCO powders that were first mixed with organics used in extrusion, then fired at ambient pressure. The patterns show that both powders completely decomposed during firing.

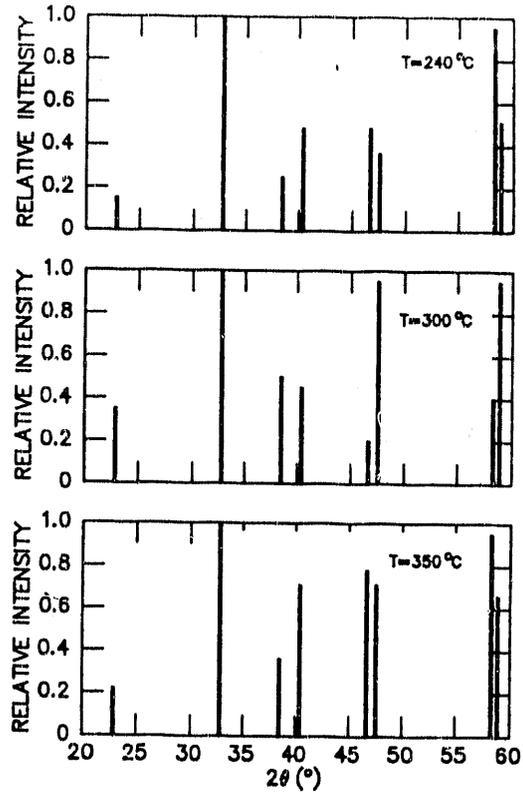


Fig. 2. Schematic X-ray patterns of YBCO powder as a function of temperature. The powder was mixed with organics used in extrusion, then fired at reduced total pressure. The patterns show no signs of decomposition of YBCO.

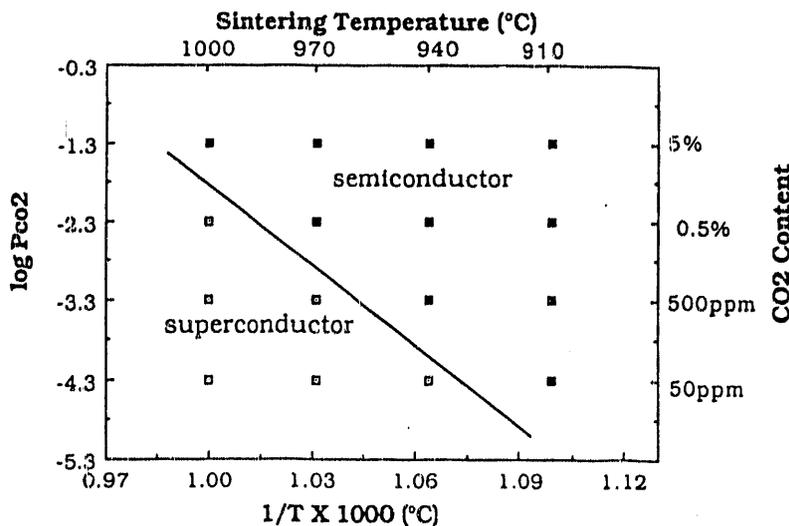


Fig. 3. Plot showing stability of YBCO with respect to partial pressure of CO₂ at various temperatures.

semiconductive samples, a majority of the grain boundaries must be nonsuperconducting. High-resolution electron microscopy (HREM) images of the grain boundaries suggested that, in fact, the majority of grain boundaries probably are nonsuperconducting.

Careful study of the HREM images showed that the structure near the sharp grain boundaries was not orthorhombic, but some other phase, possibly tetragonal YBCO. By careful measurement of the interplanar spacing, it was found that the spacing, *c*, is =1.19 nm at the region near the grain boundary, while *c* =1.17 nm in the region far from the grain boundary. Neutron diffraction data [9] show that tetragonal YBCO has *c* = 1.19 nm. Another indication of tetragonal material is the termination of twinning near the grain boundaries, which can be taken as the demarcation line between orthorhombic and tetragonal structures,

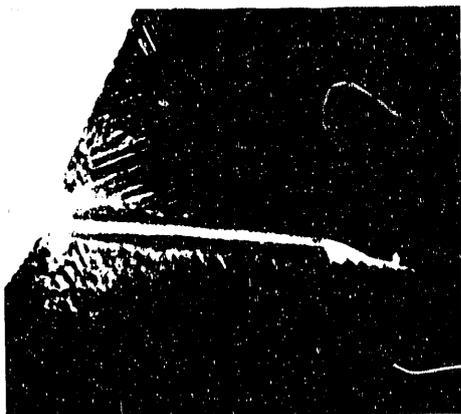


Fig. 4. TEM micrograph of YBCO sample sintered at 970°C in 0.5% CO₂/O₂ atmosphere. The thick grain boundary layer was identified as BaCuO₂.

because the tetragonal structure has no twins. A possible explanation for the phase transformation from orthorhombic to tetragonal structure is the incorporation of carbon into the lattice, due to the presence of CO₂ in the firing atmosphere [5,6]. Segregation of carbon at grain boundaries or in regions near grain boundaries has been confirmed in a previous study [6] by secondary ion mass spectroscopy. Carbon can diffuse into the lattice, and expel oxygen from the orthorhombic structure, thereby forming a nonsuperconducting tetragonal structure that can block the superconducting current.

Large differences in size and geometry make it difficult to compare the J_c results of pellets and coils; nevertheless, comparison suggests that CO₂ had minimal impact on the superconducting properties of coils that were fired at reduced total pressure. Keeping in mind that the J_c of bulk materials drops dramatically with magnetic field, and that the coils were measured in fields up to at least 73 Gauss, it is suggested that the coil results agree most closely with the results for pellets fired in 0% CO₂/100% O₂ (J_c of such a pellet was ≈ 300 A/cm² in zero field). This further suggests that large, multilayer, superconducting coils can be successfully fabricated by firing at reduced total pressure, and that the superconducting properties of these coils are representative of bulk materials.

CONCLUSIONS

It has been shown that very small concentrations of CO₂ in the firing atmosphere can react with YBCO, leaving superconducting grain interiors encased in nonsuperconducting grain boundary phases. In the firing of large, multilayer coils, decomposition of YBCO can be avoided and the concentration of CO₂ can be minimized by firing at reduced total pressure. As a result, superconducting coils can be fabricated that produce magnetic fields up to 73 Gauss with an air core, and 330 Gauss with an iron core.

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REFERENCES

1. T Nakahara (1988) In: World Congress on Superconductivity, C G Burnham and R D Kane (eds.) World Scientific, Singapore, p. 88 1988.
2. U Balachandran, R B Poeppel, J E Emerson, S A Johnson, M T Lanagan, C A Youngdahl, Shi, K C Goretta, N G Eror (1989) Mater. Lett. **8**(11,12): 454.
3. J P Singh, H J Leu, R B Poeppel, E Van Voorhees, G T Goudey, K Winsley, D Shi (1989) J. Appl. Phys. **66**(7): 3154.
4. S E Dorris, J T Dusek, J J Picciolo, R Russell, J P Singh, and R B Poeppel (1990) In: Proceedings of the International Conference on Electrical Machines (ICEM), Cambridge, MA, August, 1990, in press.
5. Y Gao, Y Li, K L Merkle, J N Mundy, C Zhang, U Balachandran, and R B Poeppel (1990) Mater. Lett. **2**: 347.
6. Y Gao, K Merkle, C Zhang, U Balachandran, and R B Poeppel (1990) J Mater. Res. **5**: 1363.
7. M S Jahan, D W Cooke, H Sheinberg, J L Smith, and D P Lianos, (1989) J Mater. Res. **4**: 759.
8. P K Gallagher, G S Grader, and H M O'Bryan (1988) Mat. Res. Bull. **23**: 1491.
9. J D Jorgensen, M A Beno, D G Hinks, L Soderholm, K J Volin, R L Hitterman, J D Grace, I K Schuller, C U Segre, K Zhang, and M S Kleefisch (1987) Phys. Rev. **B36**: 3608.

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