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ZONE REFINING OF SINTERED, MICROWAVE-DERIVED YBCO
SUPERCONDUCTORS*

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ABSTRACT

Post-sintering treatments such as zone melting under thermal gradient has been conducted on sintered YBCO tape cast films. YBCO precursor powder was derived through decomposition of a mixture of nitrates of cations in a microwave oven for ≈ 4 min. The resulting powder was characterized and made into thin sheets by tape casting and then sintered at 945°C for 5 h. The sintered tapes were subjected to repeated zone refining operations at relatively high speeds of ≈ 30 mm/h. A microstructure having uniformly oriented grains in the a-b plane throughout

the bulk of the sample was obtained by three repeated zone refining operations. Details of precursor preparation, microwave processing and its advantages, zone refining conditions, and microstructural features are presented in this paper.

INTRODUCTION

Out of the various ceramic superconductors having critical temperature above liquid nitrogen, the yttrium-barium-copper-oxide (YBCO) has attracted considerable attention with respect to applications in the form of thin and thick films. For preparation of stoichiometric YBCO having superior properties of critical current density (J_c), many methods such as conventional ceramic route [1] precipitation-decomposition [2], sol-gel-decomposition [3] and solid state combustion synthesis [4] have been attempted. All these methods have ultimately resulted in superconducting YBCO composition. However, one of the major problems encountered in all these processes is the preferential formation of barium carbonate (BaCO_3) because of thermodynamically favorable reactions between barium and carbonate ions [5]. Hence the YBCO phase is formed only above 800°C and the heat treatment requires temperatures above 900°C over long periods of time (50–100h) [6]. Further, depending on the method, the physical properties of the powders have shown considerable variation and hence has resulted in different sintered densities and microstructures. In view of this, methods for preparation of YBCO phase without the formation of intermediate BaCO_3 phase has been devised with considerable advantage in case of phase formation and also in the lowering of heat treatment time. Heat treatment of YBCO precursors under controlled partial pressure has

been reported to be very successful in forming YBCO at low temperature [7]. YBCO has an anisotropic expansion and this leads to microcracks in the sintered superconductor. Presence of microcracks causes considerable reduction in J_c values. Other major problems that lead to very low J_c value in YBCO superconductors are the presence of weak links and the lack of adequate flux pinning centers in the sintered samples. Hence the two major problems in YBCO processing centers around a fast and simple preparation method for powders, and to arrive at an a-b plane oriented high density microstructure containing uniformly distributed flux pinning centers [8].

For increasing the J_c values, various versions of melt techniques [9-11] have been reported for sintered YBCO, all based on heating of YBCO samples to above the peritectic melting point, followed by slow cooling. However, all these methods require very long cooling schedules, cooling rate as low as 1°C/h are required. Melt texturing and quenching methods are usually associated with deformation of the original shape. Another method attempted [12-14] is zone melting technique where a sample of YBCO is partially melted under a gradient, and moved slowly in the heating zones. However, zone melting technique has found advantages since it can handle low melt viscosities and liquid phases. The very slow rate of zone movement can be enhanced if a repeated zone refining operation is followed.

Hence this work was undertaken to attempt on some of the above problems in YBCO processing: the microwave technique for fast reaction kinetics for the formation of YBCO and a repeated zone refining technique to solve the existing slow post sintering treatments. YBCO precursor powders can be formed within 4 min. of microwave exposure on mixture of nitrate of

yttrium, barium and copper in 123 stoichiometry. The zone movement can be as fast as 30 mm/h for the sintered pellets made using the microwave derived powders.

EXPERIMENTAL

(a) Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders

Appropriate amounts of nitrates of yttrium, barium and copper in 123 stoichiometry were mixed in an agate mortar in presence of n-hexane to a thick paste. This mixture was transferred to an alumina crucible and was introduced into a microwave oven having a frequency of 2.45 GHz and 600 W power. The mixture turned into black powder within ≈ 4 min. This powder was fabricated into thin sheets by tape casting method.

(b) Tape casting and zone refining

The above powder was ball milled in xylene-butanol solvent medium containing plasticizer, binder and wetting agents for 12 h [15]. The tape casting was done by spreading the above slurry over a teflon coated glass plate using a doctor blade set up. The dried green sheets were cut into strips of ≈ 60 mm x 10 mm x 0.5 mm and heated at $30^\circ\text{C}/\text{h}$ up to 300°C and sintered at 940°C for 5 h. Sintered strips kept on an alumina substrate was introduced into the alumina tube of a three zone furnace. The furnace was moved over the alumina tube at a speed of 30 mm/h. In the present experiment, the initial and final zones were kept at 940°C and the center zone at 1050°C .

RESULTS AND DISCUSSION

The details of preparation of the YBCO composition through the use of microwave energy are reported recently [16]. Copper nitrate is extremely sensitive to microwaves and raises the local temperature to $\approx 900^{\circ}\text{C}$ within 2 min. of exposure. Other nitrates also absorb microwave energies to some extent. The internal temperature of the mixture when exposed to the microwave is sufficient to form tetragonal YBCO phase. The nitrates are completely decomposed within ≈ 4 min. of exposure. However, it takes about 4 h of further heating at 940°C to convert the powder to phase-pure YBCO. The XRD data of the precursor powder exposed to microwaves for 1, 2, 3, 4 min. and after 940°C heat treatment are presented in Fig. 1 (curves a-e). There are no detectable levels of BaCO_3 found in the powders exposed to microwave (Fig. 1, curves a-d), which may be the reason for formation of phase-pure YBCO in very short time at 940°C (Fig. 1, curve e). The powder thus prepared has a tap density of 2 g/cm^3 , compaction density of 3.6 g/cm^3 and an average particle size of $2\text{ }\mu\text{m}$.

The YBCO powders were mixed with a solvent, binder, deflocculant, and plasticizer and cast into thin sheets over a teflon coated glass plate using doctor blade technique. The tape cast samples were heated at 30°C/h up to 300°C in order to aid the binder burn out and later sintered at 940°C for ≈ 5 h and annealed in oxygen at $\approx 500^{\circ}\text{C}$ for 10 h. For convenience, samples of size $60\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$ were made. The morphology of the starting powder as well as the sintered microstructure of the tape cast samples are shown in Fig. 2 (a,b). Generally, these particles are rod-like with a rectangular cross section and they retain a similar cross section in

the sintered samples. The average grain size in the sintered sample was $\approx 10\text{ }\mu\text{m}$ and the grains were randomly oriented.

The sintered sample was subjected to zone melting and refining by the use of a horizontal three- zone furnace (Fig. 3a). The rate of zone movement is fixed at 30 mm/h to make it many times faster than those reported earlier. The temperature profile obtained after repeated experiments is presented in Fig. 3(b). The schedule of heat treatment followed in the experiment was 940°C for the pre-heating, 1050°C for the central melting zone and 940°C for the cooling zone. The first zone is important in order to reduce thermal shock, and the third zone is important in order to avoid fast cooling. Thermal shock and fast cooling induces microcracks in YBCO superconductors. During the first step of the experiment, the furnace is moved over the sample. The sample is preheated at the rate of 30 mm/h and then subjected to partial melting in the second zone and cooled to 940°C in the third zone. The zone refining process was repeated up to 3 times and each time a part of the sample was observed under the microscope for the extent of refinement. Figure 4 (a-c) show the changes in the orientation introduced during this zone refining operations. It can be seen that the random orientation in Fig.2 has undergone considerable rearrangement under the thermal drag introduced by the different zones and the zone movement. Elongated grains having a-b plane alignment and random precipitates of the Y_2BaCuO_5 (211) can be seen in Fig. 4. The grains in various domains possess fewer intergranular cracks along the a-b plane. The zone refined sample, after annealing in oxygen, shows an attractive levitation characteristics at 77 K that is normally obtained only in melt textured samples. The starting sintered samples (solid state sintered) do

not exhibit attractive levitation phenomena. The XRD patterns of YBCO before and after zone refining is compared in Fig. 5 (curves a and b). The a-b plane orientation obtained by repeated zone refining is clearly seen from Fig. 5 (curve b). By suitably selecting an appropriately sintered starting microstructure and density, and also by adjusting the various zone temperatures, it may be possible to obtain desired refined microstructure even under faster zone movements. Our results indicate that the melt texturing technique can still be modified to achieve shorter processing times and make it a technologically viable route to fabricate YBCO superconductors for practical applications.

CONCLUSION

YBCO high T_c superconductors have been made by a fast and simple microwave decomposition technique. In order to improve the microstructural features, the powders were tape cast to strips and sintered to density as high as 93%. Such tapes were further zone refined by a fast moving zone, about 10 times faster than that has been reported previously, using an adjustable three-zone furnace set up. It was possible to obtain a-b oriented long YBCO grains starting from the random oriented microwave derived YBCO by the repeated zone refining method.

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FIGURE CAPTIONS

- Fig. 1: XRD pattern of the mixture of nitrates of Y, Ba, and Cu after exposing to microwave energy for (a) 1 min., (b) 2 min., (c) 3 min., (d) 4 min., and (e) after heating the sample d at 940°C for 5 h.
- Fig. 2: Micrographs of (a) as derived YBCO powder and (b) the sintered surface of the tape cast sample.
- Fig. 3: (a) Zone-refining set up and (b) temperature profile in the zone-refining furnace.
- Fig. 4: Optical micrographs of samples after subjecting to zone refining operations: (a) one (b) two, and (c) three times.
- Fig. 5: XRD patterns of surface of (a) sintered sample and (b) sample after zone refining operation.

Figure 1

(a)

(b)

Figure 2

Figure 3

(a)

(b)

(c)

Figure 4

Figure 5