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Zone refining of sintered, microwave derived YBCO superconductors

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Post-sintering treatments, such as zone melting under a thermal gradient, have 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 the relatively high speed of $\sim 30\ \mathrm{mm\,h^{-1}}$. A microstructure having uniformly orientated 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.

1. Introduction

Of the various ceramic superconductors having a critical temperature above that of liquid nitrogen, 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 critical current density, J_c, many methods, such as the 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 favourable 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 (50–100 h) [6]. Further, depending on the method, the physical properties of the powders have shown considerable variation and hence have 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 have been devised with considerable advantages in 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. The presence of microcracks causes considerable reduction in J_c values. Other major problems that lead to very low J_c values in YBCO superconductors are the presence of weak links and the lack of adequate flux pinning centres in the sintered samples. Hence, the two major problems in YBCO processing centre on a fast and simple preparation method for powders and an *a–b* plane orientated high density microstructure containing uniformly distributed flux pinning centres [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 above the peritectic melting point, followed by slow cooling. However, because all these methods require very long cooling schedules, cooling rates as low as $1\ ^{\circ}\mathrm{C\,h^{-1}}$ are required. Melt texturing and quenching methods are usually associated with deformation of the original shape. Another method attempted [12–14] is zone melting, where a sample of YBCO is partially melted under a gradient and moved slowly in the heating zones. This technique has 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 overcome some of the above problems in YBCO processing through the use of 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 a mixture of nitrate of yttrium, barium and copper in

123 stoichiometry. The zone movement can be as fast as 30 mm h^{-1} for the sintered pellets made using the microwave derived powders.

2. Experimental procedure

2.1. Preparation of $YBa_2Cu_3O_{7-\delta}$ powders

Appropriate amounts of nitrates of yttrium, barium and copper in 123 stoichiometry were mixed in an agate mortar, in the 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 the tape casting method.

2.2. Tape casting and zone refining

The above powder was ball milled for 12 h in a xylene–butanol solvent medium containing plasticizer, binder and wetting agents [15]. The tape casting was done by spreading the above slurry over a Teflon- coated glass plate using a doctor blade setup. The dried green sheets were cut into strips of ~60 × 10 × 0.5 mm and heated at 30 °C h^{-1} up to 300 °C and sintered at 940 °C for 5 h. Sintered strips kept on an alumina substrate were 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^{-1}. In the present experiment, the initial and final zones were kept at 940 °C and the centre zone at 1050 °C.

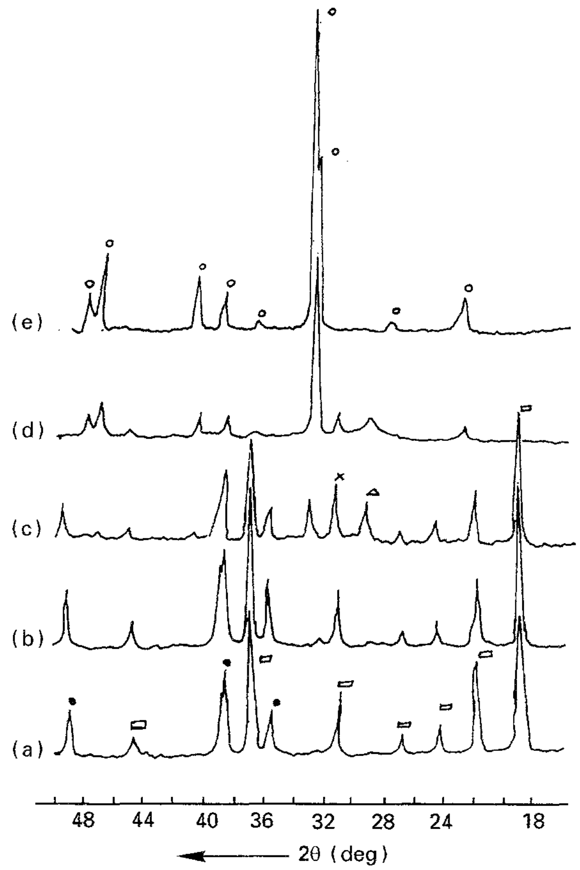

Figure 1 XRD pattern of mixture of nitrates of Y, Ba and Cu after exposing to microwave energy for (a) 1 min, (b) 2 min, (c) 3 min, (d) 4 min, and (e) after heating sample d at 940 °C for 5 h: (○) $YBa_2Cu_3O_{7-\delta}$, (×) Y_2BaCuO_5, (△) $BaCuO_2$, (●) CuO, (□) $Ba(NO_3)_2$.

3. Results and discussion

The details of preparation of the YBCO composition through the use of microwave energy were reported recently [16]. Copper nitrate is extremely sensitive to microwaves and raises the local temperature to ~900 °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 a 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 X-ray diffraction (XRD) data of the precursor powder exposed to microwaves for 1, 2, 3 and 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 microwaves (Fig. 1, curves a–d), which may be the

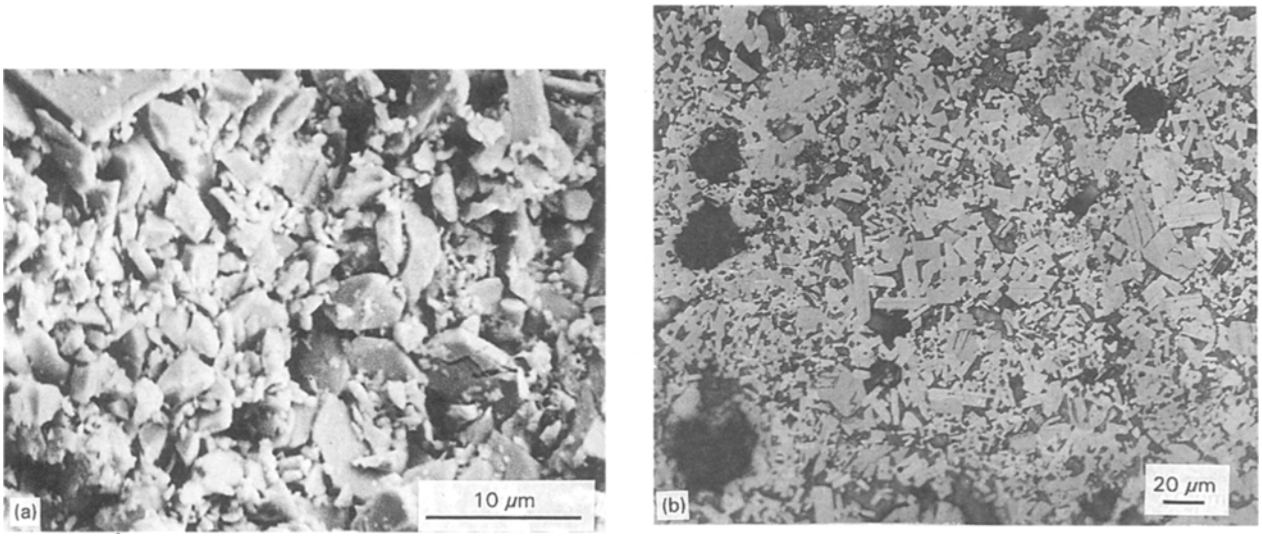

Figure 2 Micrographs of (a) as-derived YBCO powder, and (b) sintered surface of tape cast sample.

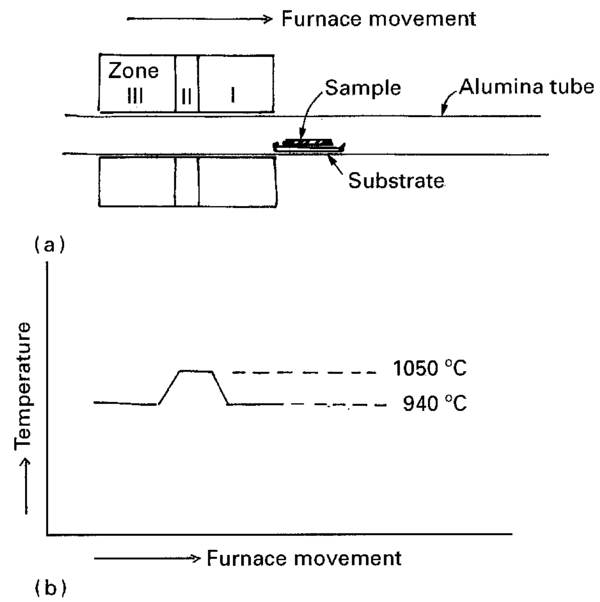

Figure 3 (a) Zone refining setup, and (b) temperature profile in the zone refining furnace.

reason for formation of phase-pure YBCO in a very short time at 940 °C (Fig. 1, curve e). The powder thus prepared has a tap density of 2 $\mathrm{g\,cm^{-3}}$, compaction density of 3.6 $\mathrm{g\,cm^{-3}}$ and average particle size of 2 μm.

The YBCO powders were mixed with a solvent, binder, deflocculant and plasticizer and cast into thin sheets over a Teflon coated glass plate using a doctor blade technique. The tape cast samples were heated at 30 $\mathrm{°C\,h^{-1}}$ up to 300 °C in order to aid the binder burnout and later sintered at 940 °C for ~5 h and annealed in oxygen at ~500 °C for 10 h. For convenience, samples of size 60 × 10 × 0.5 mm were made. The morphology of the starting powder, as well as the sintered microstructure of the tape cast samples, is shown in Fig. 2a, 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 ~10 μm and the grains were randomly orientated.

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 $\mathrm{mm\,h^{-1}}$ to make it many times faster than those reported earlier. The temperature profile obtained after repeated experiments is presented in Fig. 3b. The schedule of heat treatment followed in the experiment was 940 °C for the preheating, 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 $\mathrm{mm\,h^{-1}}$ 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 three times and each time a part of the sample was observed under the microscope for the extent of refinement.

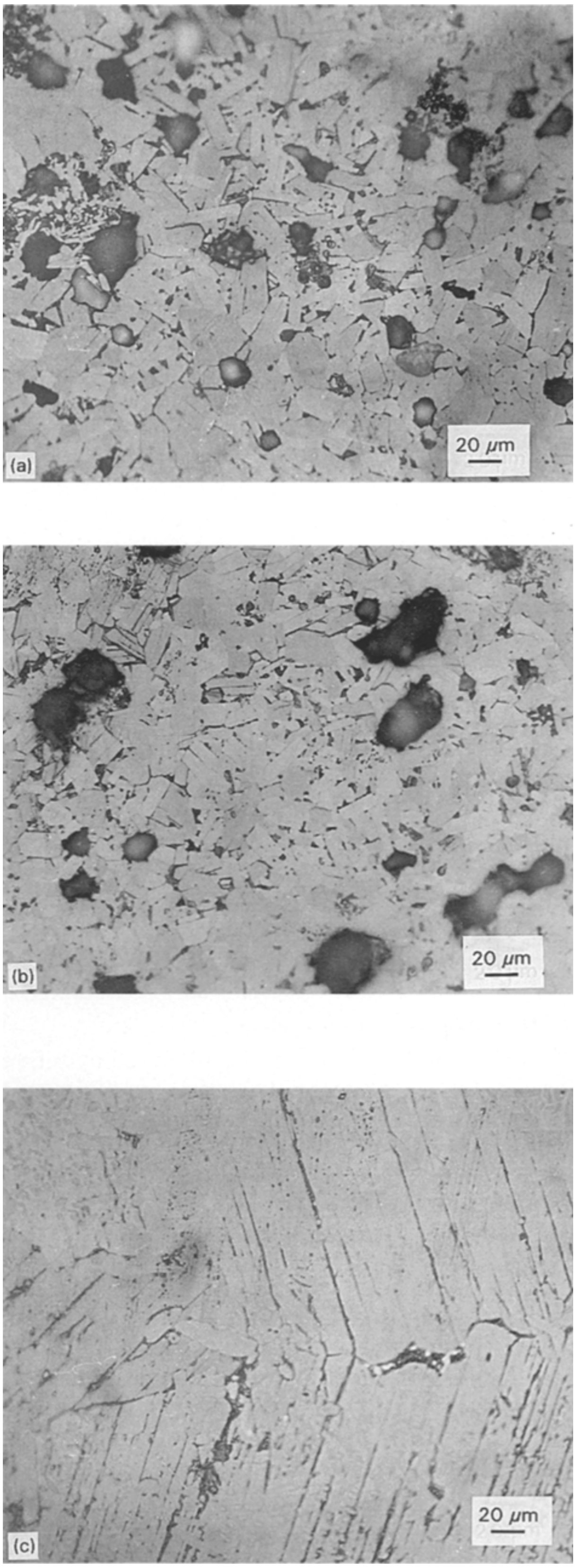

Figure 4 Optical micrographs of samples after subjecting to zone refining operations: (a) one (b) two and (c) three times.

Fig. 4a–c shows the changes in the orientation introduced during the 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

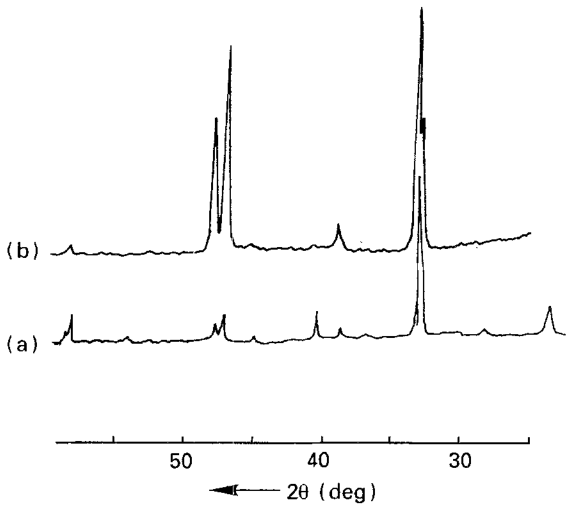

Figure 5 XRD patterns of surface of (a) sintered sample, and (b) sample after zone refining operation.

alignment and random precipitates of the Y_2BaCuO_5 (2 1 1) 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 attractive levitation 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 are 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 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.

The magnetic-hysteresis measurements were performed on the zone refined samples at 77 K on a commercial d.c. SQUID magnetometer. By applying a simplified Bean model ($J_c = 30\ \Delta M/d$, where ΔM is the hysteresis difference and d is the sample diameter), J_c has been calculated. At 77 K and 1 T, J_c of $\sim 3 \times 10^4$ A cm^{-2} was obtained in the zone refined samples. McGinn *et al.* [17] have reported magnetization J_c of $\sim 2 \times 10^4$ A cm^{-2} at 1 T in YBCO wires zone melted at a rate of ~ 3 mm h^{-1}. The authors' 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.

4. Conclusions

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 a density as high as 93%. Such tapes were further zone refined by a fast-moving zone, about ten times faster than has been reported previously, using an adjustable three-zone furnace setup. It was possible to obtain *a–b* orientated long YBCO grains starting from the random orientated microwave derived YBCO by the repeated zone refining method. Magnetization measurements at 77 K indicated a J_c of $\sim 3 \times 10^4$ A cm^{-2} at 1 T.

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