

Shaping of $\text{YBa}_2\text{Cu}_3\text{O}_7\text{--Y}_2\text{BaCuO}_5$ Bulk Superconducting Composites

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Abstract

Bulk $\text{YBa}_2\text{Cu}_3\text{O}_7\text{--Y}_2\text{BaCuO}_5$ textured ceramic composites of different shapes and sizes have been prepared through a directional solidification process. Green ceramic preforms for the directional solidification process have been obtained by using uniaxial pressures for the fabrication of pellets, ceramic moulds at low pressures for bars, cylinders and rings, and wet extrusion for the fabrication of fibres. We have studied different ratios of both phases, particle sizes, CeO_2 additions and temperature dependence. The directional solidification process allows to obtain quasi-single crystal superconductors with critical currents above 10^5 A/cm^2 at 77 K and zero field. © 1996 Elsevier Science Limited.

Introduction

Power applications of high-temperature superconducting materials is a very promising field growing day by day. The great development of melt-textured ceramics has made it possible to obtain bulk $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples with critical currents well above 10^5 A/cm^2 at 77 K and zero field, very appealing for immediate applications. Bars of this material may be a straightforward valuable alternative to constructing hybrid metallic-superconductor current leads.¹

Nevertheless, in other promising cases, such as cryomagnetic applications, the fabrication of pieces with different sizes and shapes is required. These requirements are harder to fulfil since the texturing of pieces of complex shapes is not an easy task.

Another immediate practical application of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics may be the fabrication of rings or hollow cylinders for inductive current fault limiters.² On the other hand, superconducting pellets of $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been shown to be very useful materials for the construction of levitating flywheels for energy storage.³ Finally, the fabrication of filaments of $\text{YBa}_2\text{Cu}_3\text{O}_7$ through a plastic extrusion methodology can be considered as a good alternative for the development of superconducting wires.⁴

In this work we will show that directional solidification techniques may be very useful to prepare good quality superconducting samples with different shapes and sizes ready to be used for some of the above practical applications.

Experimental

Green ceramics for the fabrication of high T_c textured superconducting bars, pellets, cylinders, rings and fibres were prepared from commercial powders (99.9% purity) obtained by the spray pyrolysis process (Fig. 1). We used powders of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) mixed with different concentrations of Y_2BaCuO_5 (211) (between 0% and 40%wt) and with small additions of CeO_2 (up to 1.5%wt). Commercial particle sizes were between 2 and 6 μm for the (123) phase and up to 5 μm for CeO_2 , while the (211) phase has fine agglomerates formed by particles between 0.3 and 2 μm . The powders were intimately mixed in an agate mortar and ground for several hours, depending on the quantity of the mixture. The final particle sizes were observed by SEM and by a laser scattering

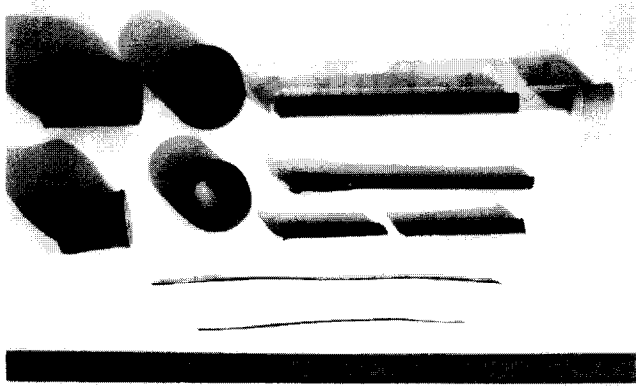


Fig. 1. Picture showing different shapes of green ceramics and textured superconductors of $\text{YBa}_2\text{Cu}_3\text{O}_7$ system.

particle size analyser to be less than $5\ \mu\text{m}$ for the (123) phase and between $0.2\ \mu\text{m}$ and up to $1\ \mu\text{m}$ for the (211) phase.

Three different techniques have been used for shaping green ceramics. Pellets were prepared by uniaxial pressing techniques using pressures up to $10\ \text{Tm}/\text{cm}^2$. Bars, cylinders and rings were obtained introducing the mixture in alumina moulds at low pressures and presintered several times in order to increase the density of the samples. The fabrication of fibres was carried out by the wet extrusion of a compacted slurry prepared by mixing finely divided ceramic powder with a reactive solution of a poly(cyanoacrylic ester) in a volatile organic solvent. The ceramic material, (123) or (123)/(211)/ CeO_2 , was previously annealed at 300°C for 1 h and then ground to obtain an homogeneous and completely dry powder. The viscous mixture was stirred to obtain an homogeneous slurry that was charged into the specially designed extruder. The slurry was then compacted and deaired under vacuum and slight loading ($\approx 10\ \text{MPa}$) (see Fig 2).

Directional solidification techniques have been used to prepare textured superconductors. Two different procedures were followed depending on the size and shape of the samples. In the first configuration, used for bars and fibres, the sample was suspended in a vertical tubular furnace and melted. Directional solidification was achieved pulling out the sample at a constant rate through an axial temperature gradient zone until the full length of the sample was solidified. In the second configuration, used in pellets, cylinders and rings, the sample was placed on a ceramic substrate and then slowly cooled in a tubular furnace with a vertical temperature gradient. Finally, superconductivity was achieved by a thermal treatment in pure O_2 at 450°C during several days, depending on diameter of the samples. The structure of the

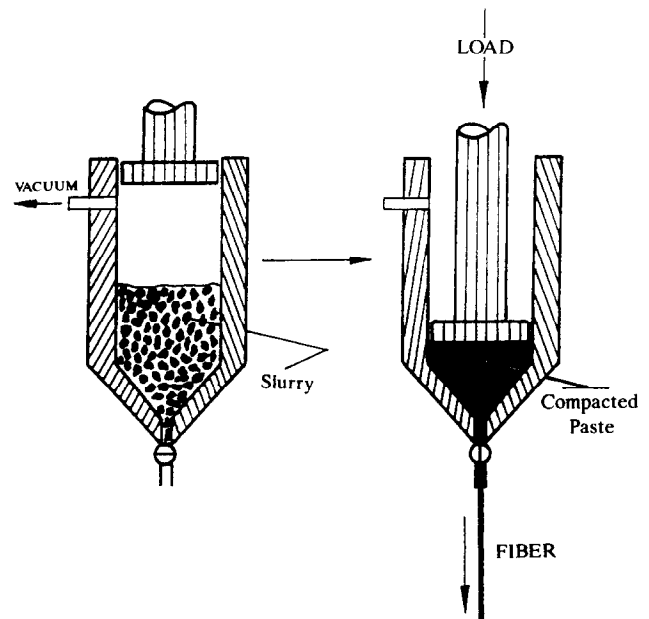


Fig. 2. Equipment for the extrusion of wet wires of YBCO-poly(cyanocrylic ester) composites. The fabrication of the fibres was carried out by the wet extrusion of a compacted slurry prepared by mixing finely divided $\text{YBa}_2\text{Cu}_3\text{O}_7$ powders with a reactive solution of a poly(cyanocrylic ester) in a volatile organic solvent.

matrix (123) changed from tetragonal to orthorhombic during the oxygenation process which produced microcracks parallel to the ab planes.

Results and Discussion

Fabrication of bars

Cylindrical and semicylindrical bars have been obtained with lengths up to 12 cm and with cross-sections from 3 to $100\ \text{mm}^2$ using commercial sintered tubes and moulds of alumina of 99.7% purity. The samples were sintered for 15 h at a temperature between 900°C and 940°C , depending on composition.

The decrease of volume of the bar during the sintering process permits easy extraction of the sample from the alumina mould. The optimum sintering temperature depends on the concentration of (211) phase. So, while 900°C was enough for 0% (211) compositions, temperatures up to 940°C were required for 40% (211). This effect can be understood by the obstruction of the (211) particles, with an incongruent melting point (1200°C) higher than the (123) phase (1020°C), in the sintering process between the (123) particles. The density obtained in this process is slightly higher than obtained by slow pressing, close to 50% of the theoretical density for the (123) structure ($6.4\ \text{g}/\text{cm}^3$).

The bars were suspended in the tubular furnace working in air at 1050 – 1150°C , depending on composition. A hole in the top of the bar allows it to be held by means of a platinum hook made of

0.5 mm wire. The bar is then pulled out at a fixed rate (≈ 1 mm/h). The sample crosses an axial temperature gradient zone ($\approx 20^\circ/\text{cm}$) in which solidification occurs. The process continues until the full length of the bars is cooled down to 900°C . The solid/liquid interface was situated at about 1 cm down from the platinum contact. The tops of the textured samples were polycrystalline due to an initial multinucleation of crystallites in the liquid/solid interface (Fig. 3). This region is about 2 to 10 mm in length depending on composition. After this initial stage, a single domain is obtained consisting of a well-oriented matrix of (123) phase containing small precipitates of (211) phase (Fig. 4). The actual size of this precipitate depends on composition and varies from 50 nm to 5–10 μm . The crystallographic orientation of the matrix seems to depend on the section of the bar. The angle α formed between the ab plane of the orthorhombic structure and the longitudinal axis of the bar grows with cross-section (between 3 mm^2 at $\alpha \approx 45^\circ$ and $>40\text{ mm}^2$ where $\alpha \approx 90^\circ$).

The final size of the (211) precipitate depends on the homogeneity and size of the initial particles.



Fig. 3. Picture of a melt-textured sample showing the (211) phase precipitations, twins and microcracks formed during the tetragonal-orthorhombic transition ($G=5000$).

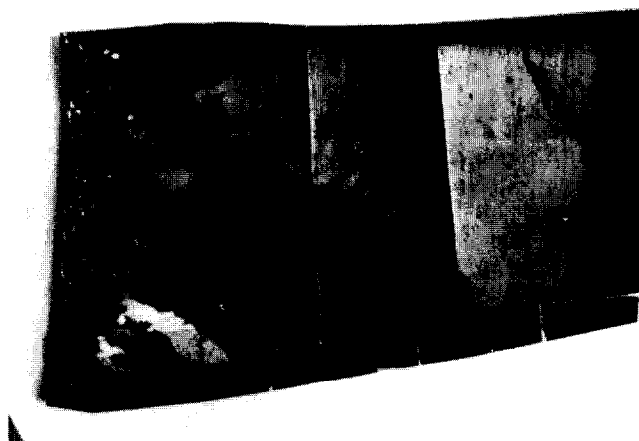


Fig. 4. Picture of the start of a melt-textured bar of 3 mm diameter showing the competition between different grains.

The (123) phase melts incongruently producing new (211) phase which mainly nucleates and grows on the initial (211) particles. During the slowly directional solidification, the (211) phase reacts with the surrounding liquid forming a solid (123) phase. This peritectic reaction is not complete due to the difficult diffusion of the liquid to the nucleus of the (211) solid particles. As a result, the final concentration of (211) phase is greater than the initial one. The presence of (211) particles in the semi-solid compound increases the solid structure into the liquid proving the mechanical stability of the system which enables us to suspend longer bars. Nevertheless, high concentrations of (211) precipitates can produce new nucleations decreasing the size of the single domains. This effect can be minimized by lowering the solidification rate.

CeO_2 additions increase the surface tension of the liquid and also allows to increase the weight and the length of the suspended bars. The presence of CeO_2 produces the decomposition of some (211) particles leading to the formation of Y_2O_3 and BaCeO_3 .⁶ The Y_2O_3 particles act as new nucleation centres for the (211) phase as has been observed by TEM.⁷ As a direct consequence of this decomposition-nucleation mechanism, the number of the nucleation centres grows which leads to a notable increase of the number of (211) particles and a decrease of their mean size.

Fabrication of cylinders and rings

We have prepared cylinders and rings up to 5 cm diameter and up to 4 cm long with the same mixtures (123)/(211)/ CeO_2 used in the fabrication of bars. The homogenized powders were introduced at low pressures and sintered in crucibles of alumina. Cylindrical crucibles have been employed to obtain cylindrical green ceramics, while hollow concentric cylinders have been used for the fabrication of rings. After the first sintering at relatively low temperature (900 – 920°C), the samples were taken out from moulds and sintered again progressively at 940°C and 960°C in order to increase the density and decrease the porosity of the material before the melting process. The final density obtained with this process was about 90% of theoretical. Then the samples were placed on a ceramic CeO_2 substrate, in order to decrease liquid lost during the melting process, and slowly cooled in a vertical tubular furnace at $1^\circ\text{C}/\text{h}$ in a temperature gradient of about $5^\circ\text{C}/\text{cm}$. We have studied the solidification from the top and from the bottom of the cylinders. In both cases, samples smaller than 1 or 2 cm diameter were typically single domain, but bigger samples were usually composed by few grains of several cm^3 . The ab plane of the grains mainly grows parallel to the bases of cylinders.

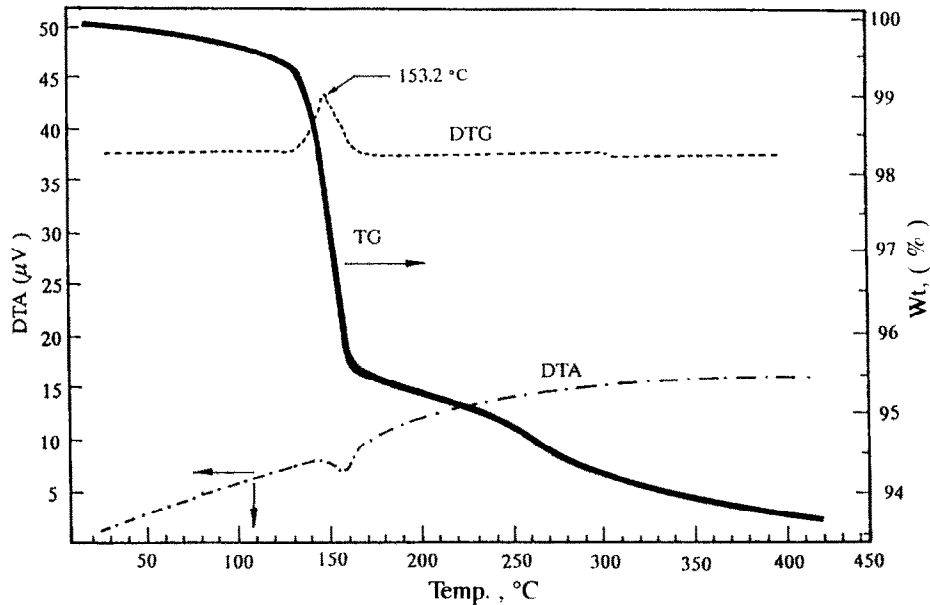


Fig. 5. Thermal behaviour of YBCO-poly(cyanocrylic ester) composites. The most characteristic is the sharp weight loss (≈ 5 wt%) which appears in a narrow interval between 130°C and 160°C whereas the second step is rather smooth and corresponds to a very small fraction (≈ 2.0 wt%) in the interval 160 – 450°C .

The rings were always integrated by different grains smaller than 1 cm^3 . The microstructure of all the samples is similar to that in the preparation of the bars, but the final (211) phase concentration is higher because of the loss of liquid, rich in CuO phase, due to the contact with the substrate.

Fabrication of fibres

Wet wires of diameter from 0.5 to 2 mm and up to 100 mm length were prepared by the extrusion of the compacted paste through a nozzle of the appropriate diameter. The extrusion rate was regulated by a loading of 10 MPa. In these conditions a homogeneous wet wire is produced at a rate about 2 cm/min. After the slow evaporation of the solvent (10–15 min), rigid hollow fibres of the (123) particles bound by a very thin polymer film were obtained.

Thermal studies, TGA and DTA of ceramic-polymeric fibre composites were carried out on a TG-DTA 320 Seiko thermobalance with a heating rate of $5^{\circ}/\text{min}$ in the range 30 – 400°C under a flow of nitrogen of 100 ml/min (Fig. 5).

The thermal treatment corresponds to a temperature interval in which the polymeric component is degraded and eliminated totally by the vaporization of the degradation products in nitrogen atmosphere. The experiment was carried out under dynamic conditions with a relatively low heating rate ($\Delta T=5^{\circ}/\text{min}$). The dry fibres present a loss of about 7 wt% during the thermal treatment in the interval 50 – 450°C , following a thermal degradative process in two steps apparently. The most characteristic is the sharp weight loss (≈ 5 wt%) which appears in a narrow interval between 130°C and

160°C , whereas the second step is rather smooth and corresponds to a very small fraction (≈ 2.0 wt%) in the interval 160 – 450°C . The rate of the thermodegradative process can be regulated by controlling the heating rate, in such a way that the polymeric component is vapourized without any foaming of the extruded fibres. This means that the diameter of the dried fibres does not change significantly by this thermodegradative treatment. In addition, the fibres obtained present enough mechanical stability to be subjected to sintering at higher temperatures. Finally, the fibres were suspended by a fine Pt wire and were textured at the same experimental conditions as the bars. The structure obtained was similar to the other samples, but the *ab* plane of the (123) matrix was found to be parallel to the longitudinal axis of the fibres.

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