Journal of Alloys and Compounds, *185* (1992) 311–320
JALCOM 239

Direct current zoning (DCZ) and direct current annealing (DCA) of melt-cast Bi–Pb–Sr–Ca–Cu–O rods

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(Received January 14, 1992)

Abstract

A novel method of processing melt-cast BSCCO rods to produce superconductivity with an onset temperature of 80 K is described. Bulk samples with a nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ were prepared as rods by a melt-casting process. The application of an electrical field to these rods under certain conditions produced a well-defined hot zone which travelled along the rod from the positive to the negative electrode. On reaching the negative electrode, the zone disappeared and a further zone could be initiated at the positive electrode by a small increase in applied current. Reversing the polarity caused the zone to travel in the opposite direction. Observations of the physical and microstructural properties of material treated in this way suggest a possible alternative processing route for producing superconducting BSCCO materials.

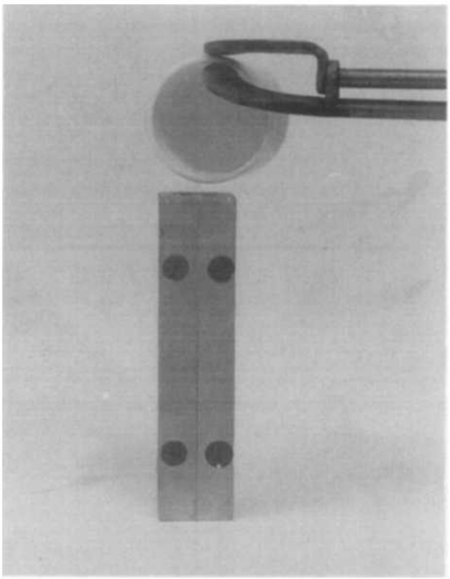
1. Introduction

Since the discovery of superconductivity in the YBCO and BSCCO systems, there have been many studies on the preparation and structural identification of the superconducting phases. In particular, various methods of melt processing have been reported [1–4] which have been designed to produce textured grain alignment and associated microstructural modifications in order to enhance flux pinning and thus increase current-carrying capacities. Among these techniques, melt textured growth (MTG) [1], quench melt growth (QMG) [2], melt–powder melt growth (MPMG) [3] and zone melting [4] have been applied, principally to YBCO. The melt-quenching and melt-casting procedures have been applied successfully to the BSCCO system by several authors [5–8]. Glassy material was produced which was expected to be in a homogeneous state prior to the subsequent crystallization reaction [7]. The most successful approach for BSCCO has been based on mechanical or melt-assisted alignment using a "powder-in-tube" technique [8].

In previous work [9, 10] we have reported melt-casting methods to produce high density, uniform geometry precursor rods of both YBCO and BSCCO which on subsequent heat treatment have developed superconducting properties. In particular, BSCCO rods with a high proportion of the 2223 phase and $T_c = 105$ K, $J_c = 113$ A cm^{-2} have been produced in this way [10]. In an attempt to increase J_c by inducing grain alignment, we have investigated

0925-8388/92/$5.00

the application of controlled solidification to these rods and as a precursor to this work we examined the effect of the application of direct current to cast rods of various compositions. As a result we have discovered a new behaviour in the BSCCO system. This paper describes this behaviour and the microstructural and superconducting properties of cast rods treated in this way. We believe that these observations could form the basis of a novel processing route for superconducting BSCCO materials.



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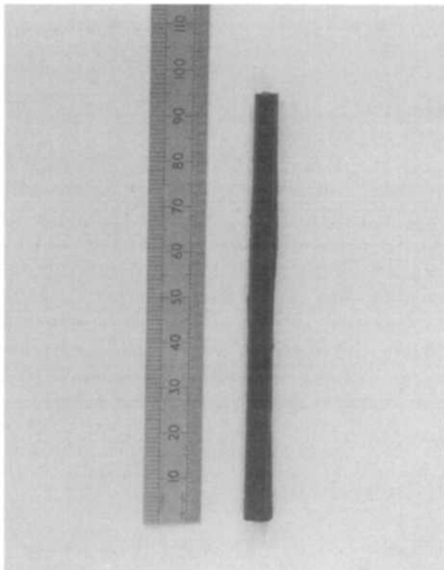

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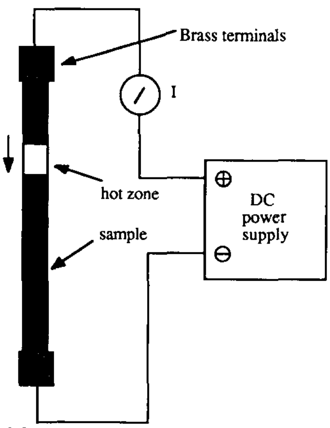


(c)

Fig. 1. (a) Copper mould, (b) the as-cast rod and (c) a schematic representation of the experimental set-up.

2. Experimental procedure

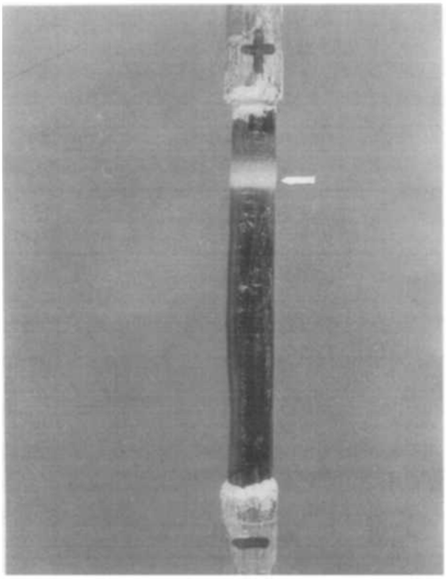
The rods used in this work were prepared by melt casting as described in ref. 10. A mixture of Bi_2O_3, PbO, $SrCO_3$, CaO and CuO in the ratio 1.6:0.4:2:3:4 was heated in a covered alumina crucible to 1150 °C until fully molten. This charge was then poured into a copper mould as shown in Fig. 1(a), which was preheated to avoid cracking in the rods. The cast rod (Fig. 1(b)) was removed from the split mould and mounted between two brass terminals using silver conductive paint to reduce the contact resistance. A current was then applied from a d.c. power supply (60 V, 50 A) while the rod was held in air. The experimental arrangement is shown schematically in Fig. 1(c). Some experiments have also been carried out in an argon environment.

The microstructures of the rods were studied by optical microscopy and scanning electron microscopy (SEM). Phase analyses were carried out by energy-dispersive X-ray (EDX) analysis and X-ray diffraction (XRD). The superconducting transition temperatures were determined by a.c. susceptibility measurements (0.5 G, 200 Hz).

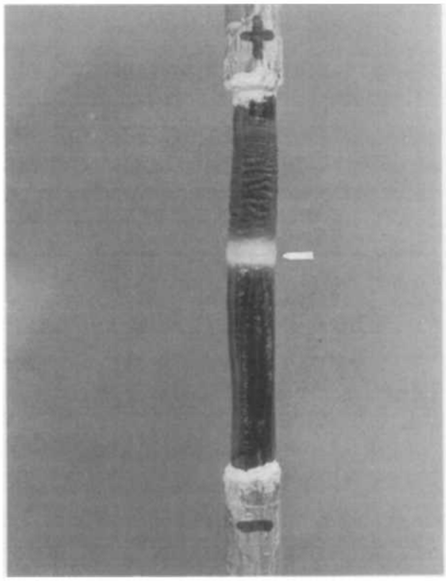
3. Results and discussion

Initial application of the maximum voltage (60 V) resulted in a current of about 0.3 A passing through the rod. This caused the resistance of the rod to fall and after 1–2 min a steady state was established and the voltage required to maintain this current fell to 20 V. On increasing the current to about 2.5 A, a well-defined hot zone (840 ± 20 °C) formed at the positive electrode (Fig. 2(a)). This zone travelled along the rod (Fig. 2(b)) and eventually disappeared on reaching the negative electrode, leaving a corrugated surface on the rod (Fig. 2(c)). The speed of this first zone could be increased to about 2 mm s^{-1} by increasing the current to a maximum value of approximately 3 A; above this current the sample started to melt in the zone region. The zone could be arrested and then eliminated by reducing the current progressively; on subsequent application of the current the zone reappeared at the position on the rod where it had stopped. It is worth noting from Fig. 2 that the leading edge of the zone is particularly sharp, indicating an abrupt change in the resistive properties of the rod at this zone–matrix interface. Reversing the current caused the zone to travel in the opposite direction. The zoning behaviour observed in this work will hereafter be referred to as direct current zoning (DCZ).

A small increase in the applied current (approximately 0.2 A) when the first zone approached the negative electrode produced another zone at the positive electrode which then exhibited similar behaviour to the first. The coexistence of the two zones is shown in Fig. 2(c). In the present work we have propagated consecutive single zones through the same bar, up to six times, each subsequent operation requiring a slight increase in the applied



(a)



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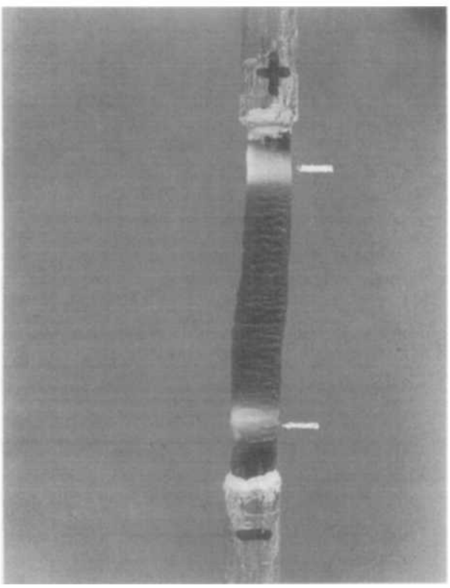

(c)

Fig. 2. The position of the hot zone (indicated by arrows) in melt-cast BSCCO rods: (a) creation of a hot zone; (b) movement of the zone along the bar; (c) creation of another zone at the positive electrode before the disappearance of the first zone. The white areas at the electrodes are silver dag.

current. We saw no evidence that these operations could not be continued by further incremental steps in the current and the number was only limited to six by time constraints in the present work.

It is also possible to heat the whole rod uniformly by applying a current just below that required to produce a zone. This situation is quite stable and may be maintained for several tens of hours (any limits have not yet been established). This process will hereafter be referred to as direct current annealing (DCA). Table 1 gives a list of samples treated in this way as a function of treatment time.

An SEM image of a cross-section of the melt-cast rod is shown in Fig. 3(a). The micrograph indicates three different phases, namely matrix (I), needle-shaped (II) and rounded (III) phases. These phases were determined [10] by EDX analysis to be a bismuth-rich phase, a copper-rich phase and CaO respectively.

In order to investigate the effects of DCZ on the microstructure of the rod, a hot zone was arrested in the middle of the rod on a first pass by switching off the current. The microstructure of a longitudinal section of the quenched zone region is shown in Figs. 3(b) and 3(c). These micrographs show that there is a sharp interface between the zoned and unzoned material which is consistent with the observation of the zone in Fig. 2 and suggests a recrystallization and/or constitutional transformation front moving through the rod. It can also be seen that after zoning, the microstructure of the rod has changed radically from that of the initial cast state. The interface and the zone region immediately behind it consist of a fine mixture of phases and are interspersed with rounded particles of free copper. The presence of free copper in the quenched zone region has also been indicated by magnetic susceptibility measurements [11].

There are further very significant changes in the microstructures of the rods on combined DCZ–DCA treatment (sample D) and after DCZ–DCA treatment and subsequent annealing in a muffle furnace (sample E). The microstructures of these rods are shown in Figs. 3(d) and 3(e) and a common feature is the presence of a needle-like phase. SEM–EDX studies on these

TABLE 1

Samples prepared by direct current processing. All samples have been zoned six times and then annealed by passing a current of 2 A through them (DCA) for the periods indicated. Sample E was removed from the zoning rig after a 3 h anneal and further annealed in a muffle furnace in air for 50 h at 850 °C

Sample	Specification
A	six zone passes +10 h annealing at a constant current (2 A)
B	six zone passes +25 h annealing at a constant current (2 A)
C	six zone passes +50 h annealing at a constant current (2 A)
D	six zone passes +75 h annealing at a constant current (2 A)
E	six zone passes + 3 h annealing at a constant current (2 A) +50 h at 850 °C annealing in a muffle furnace

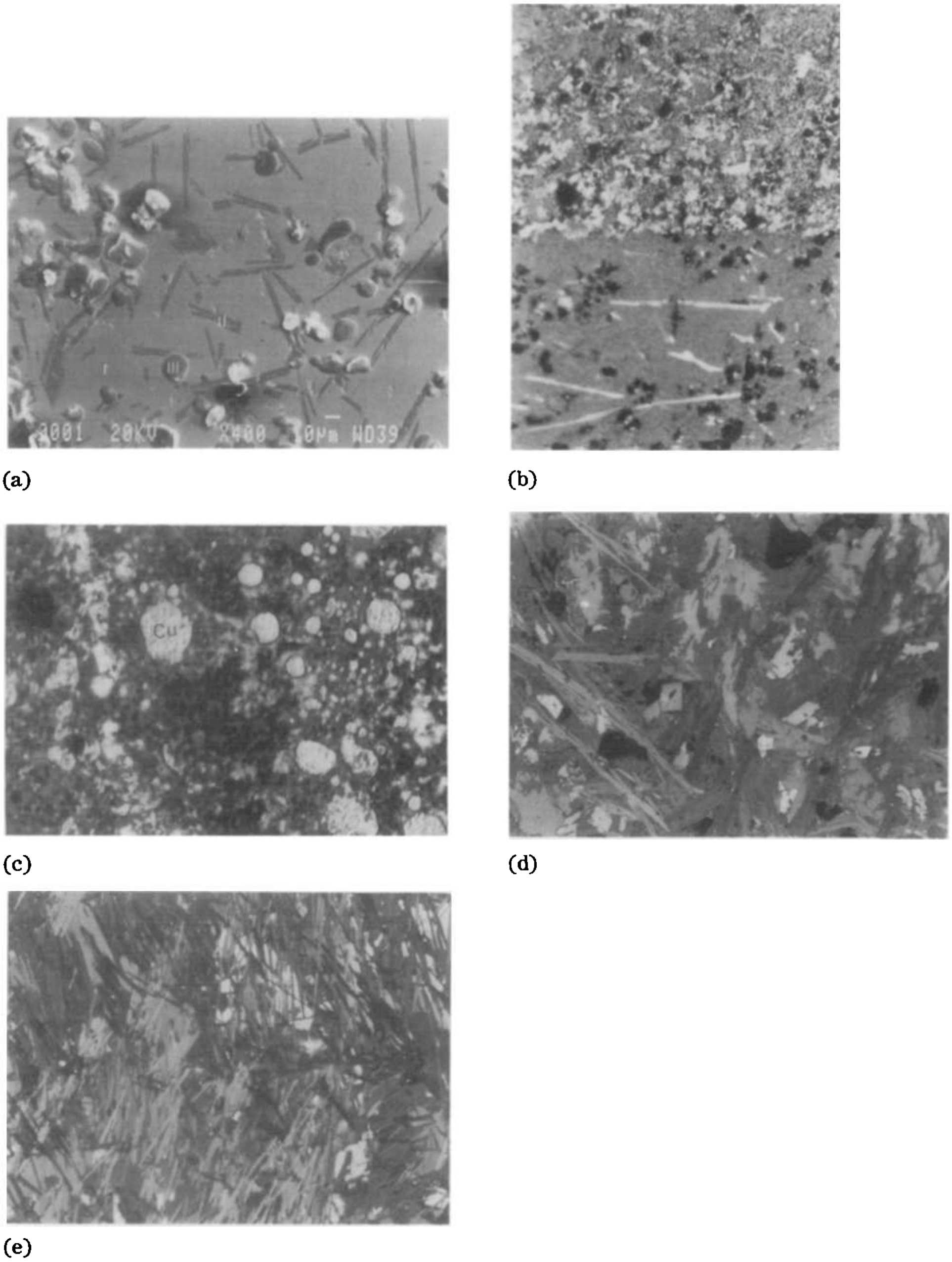

Fig. 3. (a) SEM (secondary electron) image of the as-cast rod: I, matrix bismuth-rich phase; II, copper-rich needle-like phase; III, globular CaO. (b) Optical image of the longitudinal section of the rod showing the quenched zone region on the top and the original cast material on the bottom. The sharply defined zone interface is clearly evident. The zone region has a fine microstructure. (c) Optical image of (b) at a higher magnification showing a fine distribution of phases and relatively course globules of copper. (d) Optical image of transverse section of sample D. (e) Optical image of transverse section of sample E.

materials indicate the presence of the phases 2212, Ca_2CuO_3 and CuO in sample D and of 2223, 2212 and Ca_2CuO_3 in sample E.

Powders obtained from the various rods have been examined by X-ray diffraction (Cu Kα) and some of the patterns are presented in Fig. 4. The significant features of these patterns are as follows.

(a) The cast rod (Fig. 3(a)) exhibits a large halo (Fig. 4(a)) which is typical of amorphous material.

(b) The disappearance of the halo after one zone pass (Fig. 4(b)) indicates clearly that crystallization of the rod has occurred after this treatment. The volume change associated with this effect probably accounts for the corrugated surface of the rods after the passage of one zone (Fig. 2(c)).

(c) The radical change in the diffraction pattern in Fig. 4(c) now indicates a majority of the 2212 phase.

(d) The appearance of the 2223 phase in Fig. 4(d) is in agreement with SEM–EDX studies and with the microstructure shown in Fig. 3(e).

The temperature dependence of the normalised a.c. susceptibility of samples A–E is shown in Fig. 5. The a.c. susceptibility measurements indicate a superconducting transition with an onset temperature of about 80 K which

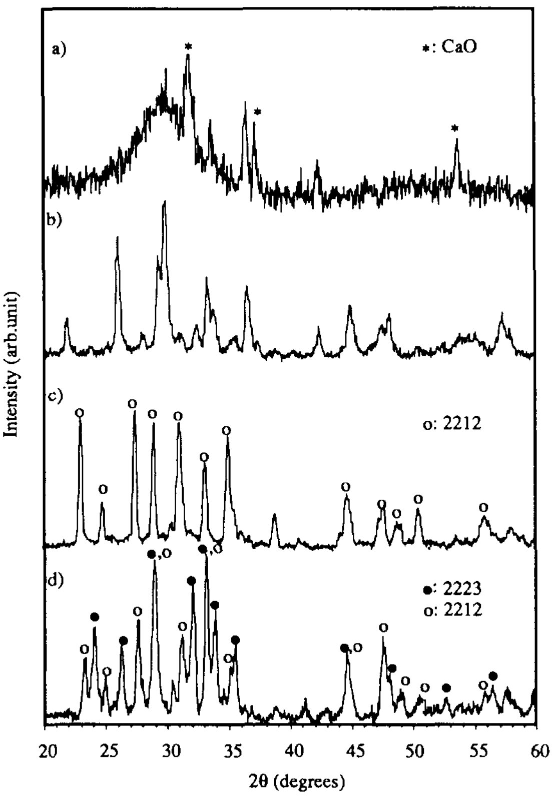

Fig. 4. Room temperature XRD patterns for (a) melt-cast sample, (b) same sample after one zone pass, (c) sample D (see Table 1) and (d) sample E (see Table 1).

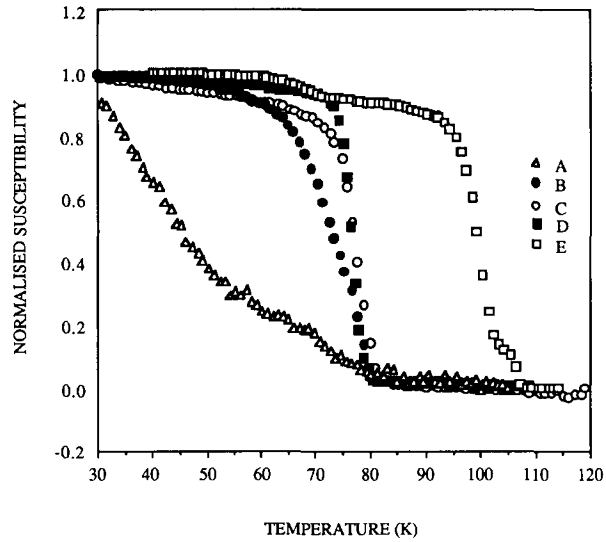

Fig. 5. Temperature dependence of the normalized a.c. susceptibility of samples A–E.

becomes progressively sharper from samples A to D. Taken together with the XRD and SEM–EDX results, this behaviour indicates an increase in the proportion of the 2212 phase and progressively greater intergranular connectivity with DCA processing time. Further enhancement of T_c will require careful environmental control during processing. The behaviour of sample E indicates the presence of the 2223 phase with an onset temperature of 107 K and also the presence of the 2212 phase. This behaviour is in agreement with the SEM–EDX and XRD (Fig. 4(d)) investigations.

The DCZ process for BSCCO rods reported in this paper has been shown to be an effective way of recrystallizing the high density, predominantly glassy phase, melt-cast rods and, combined with a subsequent DCA treatment, has resulted in a high proportion of the 2212 phase with a sharp T_c at 80 K. Neither process has yet been optimized and there seems no reason why, under the right experimental conditions, the DCZ–DCA combination cannot be used to generate the high T_c 2223 phase. Finer control of the power, particularly during DCA, in order to hold the temperature close to 850 °C will be necessary to achieve this on a reasonable time scale. Control of the environment during processing will also be an important consideration in achieving optimum superconducting properties.

Preliminary observations on DCZ behaviour in BSCCO rods in an argon environment indicated that, compared with the same conditions in air, the zone took longer to form and appeared to be immobile. The zone also became progressively hotter with time and eventually melting occurred with the consequent separation of the rod in the region of the zone.

It should be noted that there are similarities between the present observations on cast BSCCO rods and those of Osip'yan *et al.* [12] on sintered YBCO rods. They observed the formation of a hot zone on passing a d.c. current through the rod and this zone was observed to drift towards the negative pole. These workers associated the zoning behaviour with a non-linear temperature dependence of the resistance and with a sharp increase in the resistance during the evolution of oxygen during Joule heating. They pointed out that such a loss would be accompanied by the formation of a high concentration of positively charged oxygen vacancies and they speculated that the mobility of these vacancies could then determine the observed drift of the zone in an electric field. An exchange of oxygen with air was also suggested to play an important role in the process.

It is not clear at this stage what the degree of similarity is between the mechanisms of zone formation and movement in both YBCO and BSCCO. It is not presently known whether a significant loss of oxygen at high temperatures occurs in the case of BSSCO. However, the movement of oxygen ions under the influence of the electric field is thought to be an important factor, as is the exchange of oxygen with the prevailing environment as shown by the very different behaviours observed in air and argon. A comprehensive model to explain the BSSCO DCZ behaviour has to take account of the following observations ((1)–(7) in air, (8) in argon) made in the present work:

(1) the creation of a hot zone at the positive electrode after a short incubation period;

(2) the sharp leading edge of the zone;

(3) the presence of free copper in the quenched zone region;

(4) the movement of the zone is always from positive to negative;

(5) increasing current results in increasing zone velocity;

(6) the zone reappears in the same position on switching the current on and off;

(7) there is a threshold current below which the zone disappears and the whole bar heats up to a steady temperature;

(8) in argon the zone takes longer to form and appears to be immobile.

Work is continuing to provide more information on the various factors controlling DCZ and DCA behaviour in BSSCO rods to develop these techniques as a means of providing high T_c material.

Acknowledgments

Thanks are due to Dr. K. Donnelly and A. J. Twin for useful discussions and to J. C. Clarke for experimental assistance. Thanks are also due to the Karadeniz Technical University, Trabzon, Turkey for the provision of a studentship (E.Y.) and to the SERC and the EC (Twinning Programme) for their support of the research programme in high T_c superconductors.

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