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CHARACTERISATION OF Bi-Pb-Sr-Ca-Cu-O RODS SUBJECT TO DIRECT CURRENT ZONING (DCZ) AND DIRECT CURRENT ANNEALING (DCA)

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Bulk samples with a nominal composition of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12}$ were prepared as rods by a melt casting process. A dc field was applied to these rods and this produced a well-defined hot zone which travelled along the rod from positive to negative and disappeared at the negative end (DCZ). A further zone could be initiated at the positive electrode by a small increase in the applied field. Direct current zoned rods were then uniformly heated by applying a field just below that required to produce a zone (DCA) and resulted in the production of an 80K superconducting phase. The rods were characterised by means of microstructural and physical property studies.

1. Introduction

In a previous paper [1] we reported that when a dc current is passed through a cast BSCCO rod under certain conditions it produced a well-defined hot zone which travelled along the rod from positive to 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. This paper describes this behaviour and the microstructural and superconducting properties of cast rods treated in this way.

2. Experimental procedure

The rods used in this work were prepared by melt-casting as described in reference [2]. 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 which was preheated to avoid cracking in the rods. The cast rod 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 dc power supply (60 V, 50 A) while the rod was held in air. An experiment has also been carried out in an argon environment.

The microstructures of the rods were studied by optical and scanning electron microscopy. Phase analyses were carried out by EDX and XRD. The crystallisation temperature of the rod was determined by differential thermal analysis (DTA) and %length changes of the rod were measured by a dilatometer. DC susceptibility measurements (Faraday balance) were performed on the rods before and after DCZ treatment. The superconducting transition temperatures were determined by a.c susceptibility and resistivity measurements.

3. Results and discussion

Initial application of the maximum voltage (60 V) resulted in a current of ≈0.3 A passing through the rod shown in figure 1a. This caused the resistance of the rod to fall and after 1 to 2 minutes a steady state was established and the voltage required to maintain this current fell to 20 V. It was found that after around 2 minutes of passing the initial current, the rod was heated up to temperature between 400°C and 450°C. On increasing the current to ≈2.5 A, a well defined hot zone (840(±20) °C) formed at the positive electrode (figure 1b). This zone travelled along the rod and eventually disappeared on reaching the negative electrode leaving a corrugated surface on the rod (figure 1c-1e).

The speed of this first zone could be increased to ≈2 mm/s 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 can be clearly seen from figure 2 that the leading edge of the zone is particularly sharp, indicating an abrupt change at this zone/matrix interface. Reversing the current caused the zone to travel in the opposite direction. The zoning behaviour observed in this work has been referred to as Direct Current Zoning (DCZ) [1].

A small increase in the applied current (0.2 A) when the first zone approached the negative electrode produced another zone at the positive electrode which then exhibited similar behaviour to that of the first (figure 1f-1i).

As reported in the previous paper [2], the cast rod of 2234 contains three major phases: Bi-rich matrix which is glassy, Sr-Ca-Cu-O containing needle-shaped phase, and CaO precipitates. The glass transition and crystallisation temperatures of the rod were determined by DTA analysis to be respectively 420°C and 465°C as shown in figure 3. The crystallisation temperature was also confirmed by X-ray diffraction analysis. This behaviour is similar to that reported for the 2212 composition [3].

The microstructural changes associated with the passage of the zone are revealed in the quenched longitudinal section through the region of the zone shown in figure 2 obtained by switching off the current. The sharp interface and the zone region immediately behind it consist of a fine mixture of phases and is interspersed with rounded particles of free Cu. The presence of free Cu in the quenched zone region has also been indicated by magnetic susceptibility measurements.

The room temperature magnetic susceptibility

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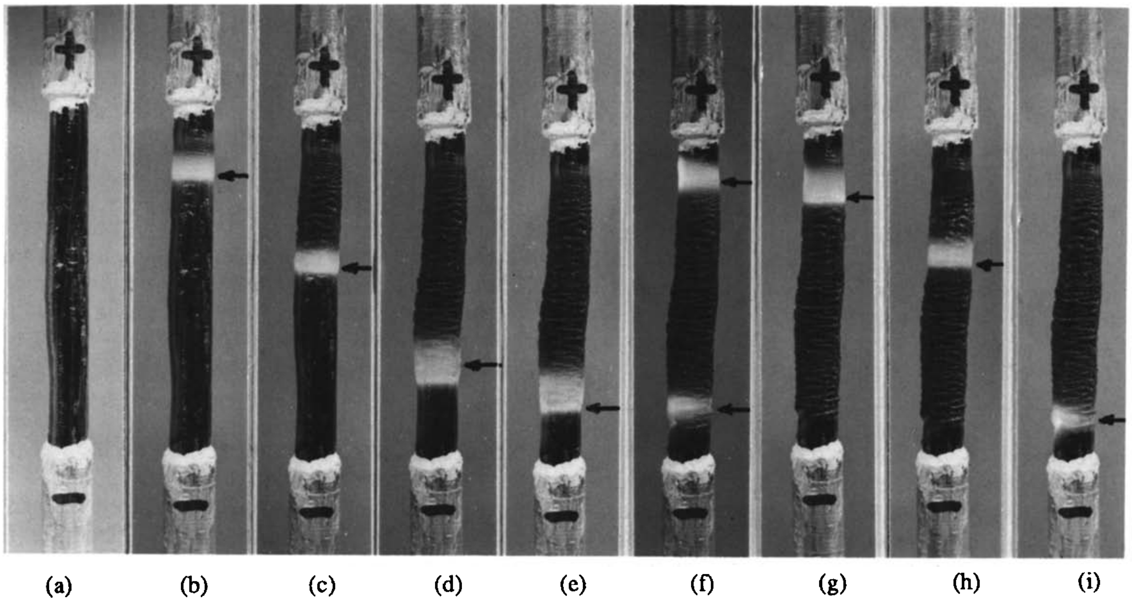

Figure 1. The position of the hot zone (indicated by arrows) in the melt-cast BSCCO rods: (a) the as-cast rod; (b) creation of a hot zone at the positive electrode; (c)-(e) movement of the zone along the rod; (f) creation of another hot zone at the positive electrode before the disappearance of the first zone; (g)-(i) movement of second zone along the rod.

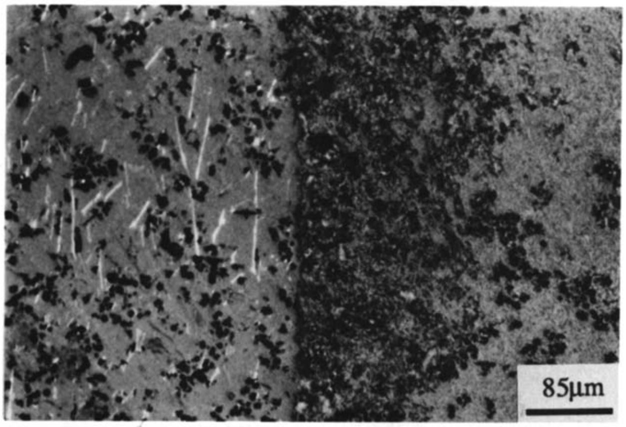

Figure 2. Optical image of the longitudinal section of the rod showing the quenched zone region right and the original cast material on the left. The sharply defined zone interface is clearly evident. The zone region has a fine microstructure. A higher magnification examination of the zone region indicated the presence of globules of free Cu.

measurements on as-cast, half zoned and three times zoned rods were performed using a Faraday balance. The magnetic susceptibility results as a function of position along the rod are given in figure 4. In the case of cast rod (figure 4a), it can be seen that susceptibility values for all data points are very close to each other and this suggests that the cast rod has an almost uniform phase distribution. However, the first data point, which corresponds to the top of the rod, has a slightly higher value. It is thought that the solidification rate between top and bottom of the rod during casting could be slightly different, and this may result in some differences in the magnetic susceptibility.

In the case of the half zoned rod shown in figure 4b, the magnetic susceptibility signal in the different parts of the rod was found to be very different. The susceptibility in the zone region (position 7) exhibited a negative signal which corresponds to diamagnetic behaviour and this is consistent with the metallographic evidence of the presence of free-Cu in the zone region. It was also noted that the susceptibility signal at the +ve electrode exhibited the highest value (position 1) and it was thought that the time spent by the zone at this point is longer and this resulted in some differences in the magnetic behaviour.

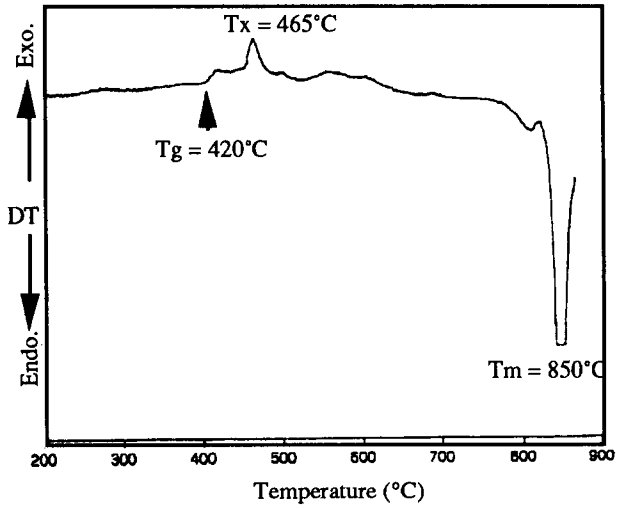

Figure 3. DTA shows the glass transition and crystallisation temperature for the 2234 BSCCO rod.

The magnetic susceptibility signal of the zone passed region (positions 3 to 5) increased with an increase in the number of zone passes, as shown in figure 4c. This suggests that every zone passage creates a progressive compositional change. It should also be noted that the susceptibility values after three zone passes became negative at the -ve electrode (position 14 in figure 4c). This is consistent with the usual evidence of free Cu at the -ve electrode which is thought to have migrated under the dc field.

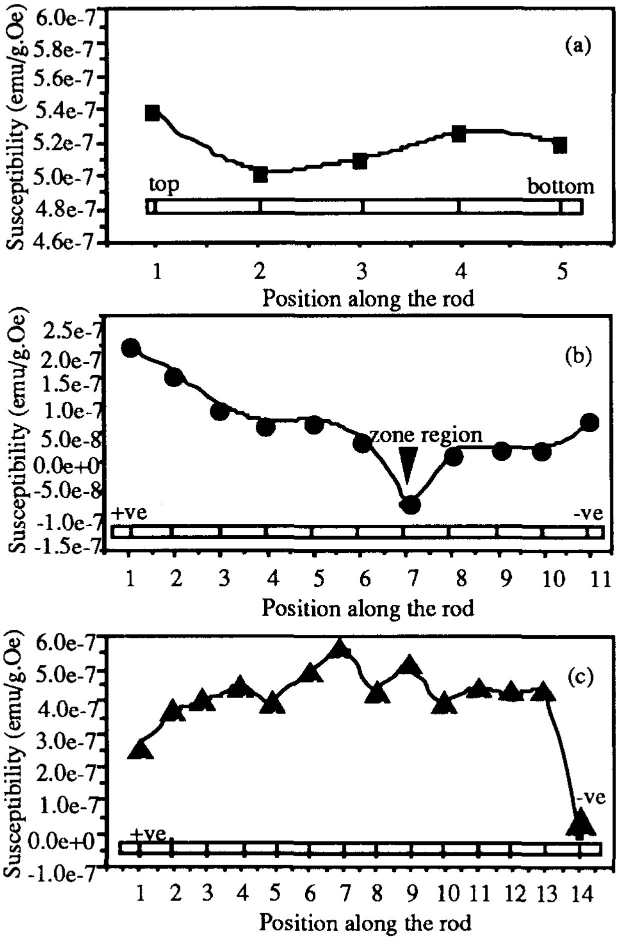

Figure 4. Variation of magnetic susceptibility of (a) a cast rod, (b) half zoned rod and (c) three times zone passed rod.

The volume changes responsible for the surface corrugation were studied by means of dilatometry. Samples of as-cast rod were measured up to 460, 650 and 800°C and their curves superimposed as shown in figure 5. Significant contractions occurred and the changes at 450°C and 650 °C can be attributed respectively to crystallisation and the formation of the low-T_c phase.

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. This process has been referred to as Direct Current Annealing (DCA) [1].

However, it was found that there are very significant changes in the microstructures of the rods on combined DCZ and DCA treatment and after a subsequent annealing in a muffle furnace. SEM/EDX studies on the 75h annealed (DCA) rod revealed the presence of the phases 2212, a phase containing Sr-Ca-Cu-O and CuO.

The temperature dependence of the normalised ac-susceptibility of samples treated by the DCZ/DCA process for the indicated times are shown in figure 6a. The ac-susceptibility measurements show a superconducting transition with an onset temperature of 80 K which becomes progressively sharper with increasing annealing time.

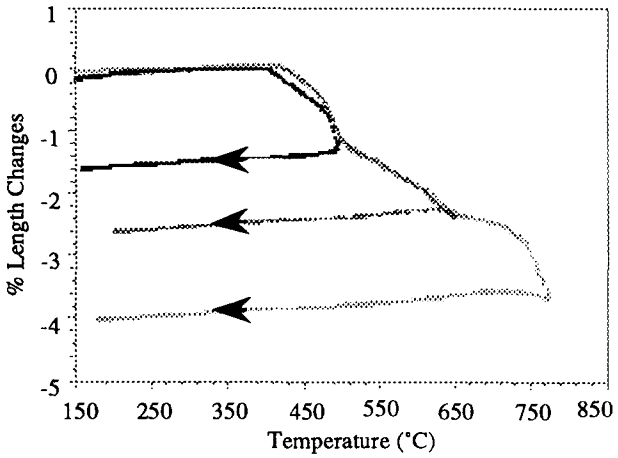

Figure 5. The dilatometry curves of melt-cast 2234 rod in three heating and cooling steps; up to 460°C, 650°C and 800°C.

The temperature dependence of the normalised resistivity of samples used for ac. susceptibility measurement are shown in figure 6b. The 10h and 50h annealed samples show a semiconducting behaviour prior to the superconducting transition whilst the 75h annealed sample and the sample indicated by a " * " ,which was annealed for 3h by DCA and 50h in a muffle furnace, show metallic-like behaviour. The zero resistance transition temperature($T_{c,\ zero}$) increases with increasing annealing time and the transition temperatures for these samples were found to be respectively 30K, 72K and 102K. The behaviour of sample indicated by a " * " shows the presence of the 2223 phase with an onset temperature of 105 K and also the presence of the 2212 phase.

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 the formation of a high proportion of the 2212 phase with a sharp T_c at 80K.

The 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.

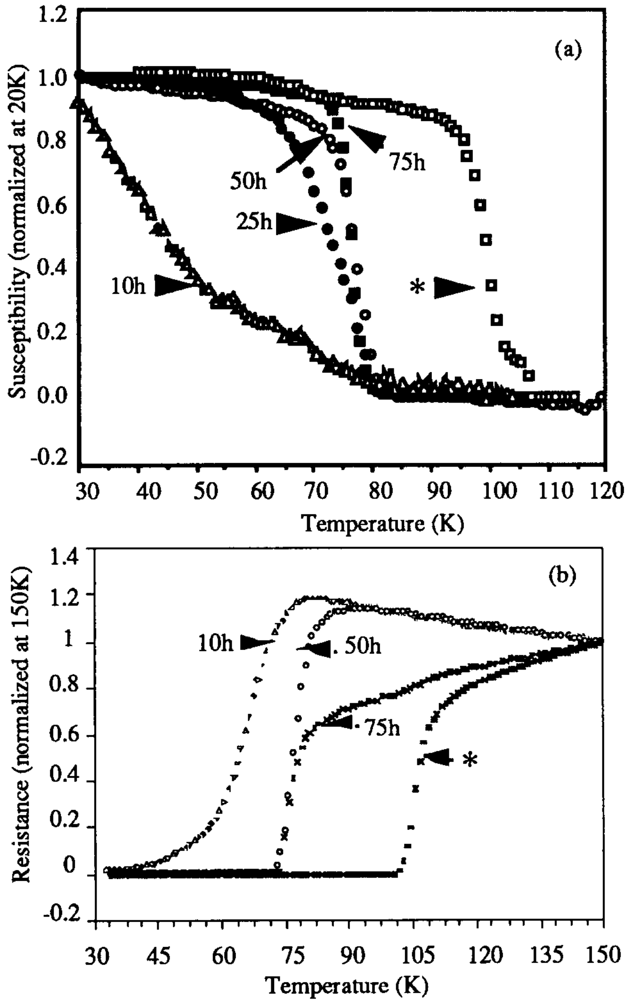

Figure 6. Temperature dependencies of normalised ac. susceptibility and resistivity results for samples prepared by a combination of DCZ and DCA processing. All samples have been zoned six times and then annealed by passing a current of 2A through them for the periods indicated. Sample * was removed from the zoning rig after a three hour anneal and then further annealed in a muffle furnace in air for 50h at 850°C.

We have been unable to find any reference in the literature to the application of this process to melt-cast BSCCO rods; Osip'yan et al. [4] have applied a dc current only to isostatically pressed and sintered YBCO rods. They observed the formation of a hot zone upon passing a dc current through the rod and this zone was observed drifting towards the negative pole. These researchers associated the zoning behaviour to 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.

Recently, Nefedov et al [5] have reported the DC treatment on the YBCO superconducting ceramics at 77K and this work indicates that light impurities (Na, K, Cl) and oxygen migrate towards the appropriate electrode, results the changes in properties.

It is not clear at this stage whether 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 because very different behaviours are observed in air and in argon. The DCZ phenomenon could be due to solid state electrolysis whereby O^- ions migrate initially under an electric field gradient from the -ve to the +ve electrode. Thus, there is an increase in the O^- ion concentration at the +ve electrode with a consequent increase in the electrical resistance. This results in a "hot spot" and the creation of a hot zone due to resistance heating. Because the material becomes hot, oxygen is lost, the resistance falls and the zone then moves to another high resistance region. This way the zone moves down the bar and lowers the oxygen content as it moves. Once it gets to the end then the process begins again. Crystallisation of the bar will lower the overall resistance and hence the current condition will change on subsequent runs until a stabilised microstructure is attained. Reversing the polarity of the rod should reverse the direction of the zone movement and this is in fact observed. An additional observation is the presence of the free Cu in the quenched zone region and the Cu enrichment at the -ve electrode. These effects could be field induced or could be the result of constitutional changes induced by the zoning action. Clearly further experiments are required to resolve these outstanding questions.

Acknowledgements

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