Physica C 172 (1990) 361-364
North-Holland

Anomalies in the J_c versus B curves for oxalate route Y–Ba–Cu–O superconductors

E. Altshuler, D. Carrillo, V. Venegas, A.R.R. Papa and C. Curbelo
Superconductivity Laboratory, IMRE, University of Havana, S. Lazaro y L, 10400 Havana, Cuba

Received 19 October 1990

A high-T_c yttrium cuprate superconductor was obtained via oxalate coprecipitation. J_c versus B measurements on the sample showed anomalous behaviour: the curve for increasing B is less steep than is usual at fields above 0.5 mT, while a characteristic different from the typical single maximum shape is obtained for decreasing B. These features might be taken into account for improving the J_c versus B response in Y–Ba–Cu–O superconductors.

1. Introduction

In Y–Ba–Cu–O superconductors produced via solid state reaction, hysteresis behaviour of the critical current density variation with magnetic induction is observed, in such a way that the J_c versus B curve obtained for a generally increasing magnetic field shows an abrupt decrease at low and even very low values of B [1,2] – which is not desirable for some technological uses – while a single-peaked return curve is commonly observed for a gradually decreasing magnetic field [3,4].

An anomalous behaviour of the above type curves will be shown to exist for a Y–Ba–Cu–O superconductor obtained via oxalate coprecipitation. We will discuss the role of the Josephson weak links as well as the percolative paths in the transport phenomena observed, correlating the J_c versus B behaviour with the X-ray diffraction pattern, and the evidences of unstableness of the samples after electrical measurement.

2. Experimental

Superconducting ceramics were obtained via oxalate coprecipitation through a method analogous to that usually followed by other authors [5,6]. Starting from Y_2O_3, a solution of the corresponding nitrate was obtained, and solutions of commercial $Ba(NO_3)_2$ and $Cu(NO_3)_2{\cdot}6H_20$ stoichiometrically calculated were added. An alcohol solution of $C_2H_2O_4$ was used as coprecipitant agent, keeping the pH value of the system about 3 through the addition of KOH solution. The precipitated yttrium, barium and copper oxalates were washed and dried in an oven. A prefiring treatment of 900°C for 8 h was applied to the powders, which were then pressed into pellets and sintered at 950°C for 16 h.

Figure 1 shows a relevant section of the powder X-ray diffraction pattern whose main lines coincide well

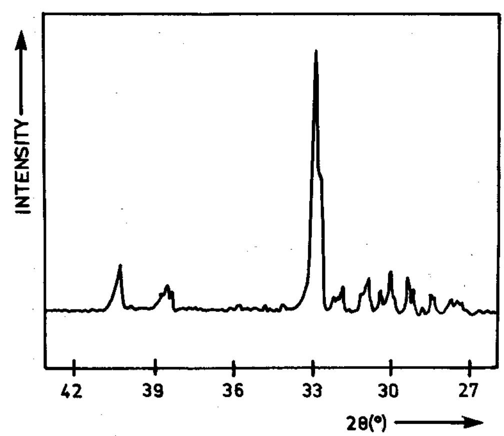

Fig. 1. Powder X-ray diffraction pattern of Y–Ba–Cu–O ceramic via oxalate coprecipitation.

with the ones reported in the literature for Y–Ba–Cu–O via oxalate coprecipitation [5]. Mainly superconducting orthorhombic phase was observed, though some amount of tetragonal material should also exist, as well as other minor phases basically observed in the range 27–32°, which may be related to the lack of stability of our superconductor that will be discussed later.

To obtain the J_c versus B curves, I_c values measured at liquid nitrogen temperature were taken as those corresponding to a magnetic field of approximately 10^{-5} V/cm in the standard four probe method on a sample of dimensions $1 \times 1 \times 12$ mm^2. Firstly, a J_c versus B set of experimental values was obtained by increasing the magnetic field from $B=0$ to a $B=9$ mT, and then, after keeping the sample at this value for a few seconds, the magnetic field was gradually decreased down to $B=0$ and the corresponding I_c values were measured.

3. Results and discussion

While the absolute values of J_c were lower than some of those reported in the literature using coprecipitation techniques (see for example ref. [6]), the J_c versus B behaviour of our samples showed some interesting anomalies.

The increasing field measurements showed an abrupt change in the decreasing rate of the critical current around $B=0.5$ mT as seen in fig. 2(a). Making use of an averaging formula developed by two of us [7] based on the Josephson junction assembly model of the granular superconductor, the experimental points below 0.5 mT were fitted to the theoretical curve shown in the same figure, which closely coincides with the common steep curves reported for yttrium cuprate ceramics. A single maximum statistical distribution of Josephson critical fields of the intergrain material at 0.3 mT was selected for the fit, as normally done for the usual ceramics [8]. The clear discrepancy between the theoretical curve and the experimental points displays the anomalous behaviour of our sample.

The only way found to achieve a reasonable fit of the whole set of points was to select not a single, but a double-maximum statistical distribution of the "critical fields" for the intergrain material with the second maximum localised at 4.5 mT (which is quite a high value indeed). This suggests that our sample was made of materials with different stoichiometries in a certain range near that corresponding to the ideal superconducting phase, in which two stoichiometries seem to predominate.

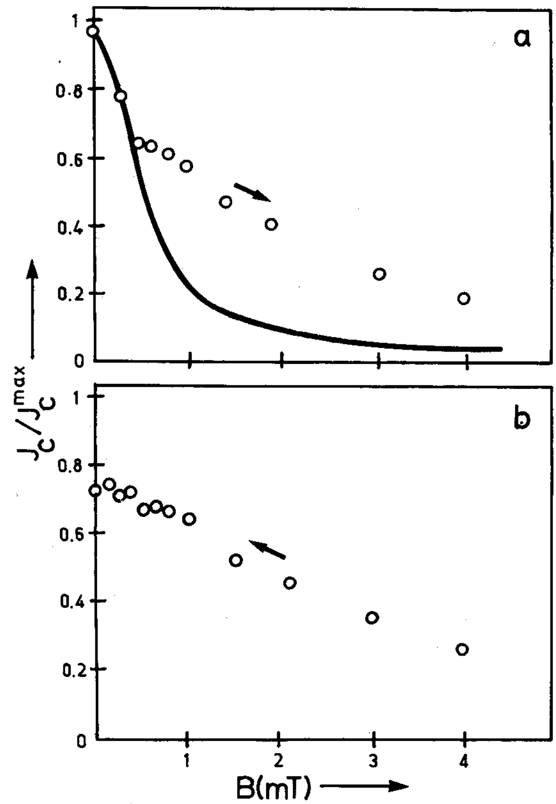

Fig. 2. Relative values of the critical current density of a typical Y–Ba–Cu–O ceramic obtained via oxalate coprecipitation for increasing the external field (a) and decreasing the external field (b). The curve in (a) is the theoretical fit for the experimental points below $B=0.5$ mT. The critical current density has been normalised to J_c^{max} for increasing field measurements.

Such a model does not contradict our X-ray diffraction results, but it does contradict the detailed work of Hampshire et al. [9], who have pointed out that when the sample has a sharp distribution of T_c, the J_c versus B characteristic is flat, but becomes strongly field-dependent when a broader distribution of T_c (i.e. more than a single phase) is present. The above stated view on stoichiometricity suggests that the latter applies to our samples, where J_c versus

B curve is, however, weakly field-dependent.

An alternative explanation for our results would be to consider that the superconducting percolative (or not weak-linked) paths predominate over Josephson junction paths at fields above 0.5 mT thus showing a weaker field dependence of the critical current density in that region. This speculation has been stated by Küpfer et al. [10] for explaining a quite analogous flattening in their J_c versus B curves obtained above fields as high as 0.3 T for solid state reaction pellets of $YBa_2Cu_3O_{7-x}$ and by Ekin et al. [11] for explaining a similar phenomenon above 10 mT. More recently, the latter author has demonstrated the validity of that hypothesis through experiments with grain aligned samples of fine grain size [12]. Following his approach, we conclude that there is an important enhancement in the volume fraction of not weak-linked material in our samples as compared with conventional ones obtained through solid state reaction. At the moment, available data do not suffice to explain what specific features of our coprecipitation technique are responsible for this phenomenon.

It was further observed that, if we repeated the measurements on a sample in order to obtain a second increasing field curve, the "Josephson junction region" was flattened, which suggests that an irreversible destruction of the superconductivity of the Josephson junctions had taken place.

The J_c versus B experimental values for a decreasing field are shown in fig. 2(b). Following the model proposed by Evetts and Glowacki [3], the superposition of these points with the ones shown in fig. 2 (a) for fields above 0.5 mT tells us that there is no significant amount of flux trapped by the grains, so perfect reversibility of the curve within the full range of applied field instead of the typical maximum displayed in hysteresis curves could be expected. However, the strong steep region seen in fig. 2(a) was flattened for fields below 0.5 mT in fig. 2(b), which in our view may be taken as additional evidence of the permanent destruction of the superconductivity of the Josephson junctions in the sample.

Both increasing and decreasing field anomalous behaviour were measured for different pellets that had been obtained simultaneously but, as said before, once are made the first measurement for a given sample, it was impossible to obtain repetitive experimental values. The strange lines observed in the range 27–32° in our diffractogram, which do not seem to belong to raw materials or to typical intermediate phases of the reaction, could play some role in the degradation process probably accelerated by the effect of thermal shocks, the application of the transport current or both, which should be related to the irreversible degradation of the Josephson junctions described above.

4. Conclusions

We have obtained a J_c versus B dependence noticeably weaker than the one commonly obtained for yttrium cuprates at very low magnetic fields.

The dominance of the percolative paths over the Josephson junction ways at fields above $B=0.5$ mT seems to be the cause of the phenomenon, whose deeper explanation must lie in the microstructural features of the coprecipitation method.

Taking into account the results presented here, we believe that oxalate coprecipitation might be a way to improve the J_c versus B characteristics of Y–Ba–Cu–O ceramics in the low field region. These characteristics, as well as the J_c absolute values, could be further improved through the optimisation of our coprecipitation technique combined with the obtainment of grain-aligned samples.

Acknowledgement

We would like to thank Professor S. García for helpful discussion, particularly in relation to the interpretation of X-ray diffraction patterns.

References

[1] J.W. Ekin, A.J. Panson, A.I. Braginsky, M.A. Janocko, M. Hong, J. Kwo, H. Lion, D.W. Capone II and B. Flandermeyer, Proc. Symp. on High T_c Superconductors, Vol. 1 EA-11, eds. D.U. Grubser and M. Schluter (Materials Research Society, Pittsburgh, 1987) p. 223.
[2] D.W. Capone II and B. Flandermeyer, in ref. [1], p. 181.
[3] J.E. Evetts and B.A. Glowacki, Cryogenics 28 (1988) 641.
[4] E. Altshuler, S. García and A. Aguilar, submitted for publication to Phys. Status Solidi.

[5] A. Mozhaev, personal communication.
[6] P.Y. Hsiegh, J. Ye and Z. Shi, submitted to Mod. Phys. Lett. B.
[7] X.Z. Wang, M. Henry, J. Livage and I. Roseman, Solid State Commun. 64 (1987) 881.
[8] A.R.R. Papa and E. Altshuler, submitted for publication to Solid State Commun.
[9] D.P. Hampshire, X. Cai, J. Seutjens and D.C. Larbalestier, Supercond. Sci. Technol. 1 (1988) 12.
[10] H. Küpfer, I. Apfelstedt, R. Flukiger, C. Keiler, R. Meier-Hirmer, B. Runtsch, A. Turowski, U. Wiech and T. Wolf, Cryogenics 28 (1988) 650.
[11] J.W. Ekin, T.M. Larson, A.M. Hermann, Z.Z. Sheng, K. Togano and H. Kumakura, Physica C 166 (1989) 489.
[12] J.W. Ekin, H.R. Hart Jr. and A.R. Gaddipatti, to be published in J. Appl. Phys. (Sept. 1990).