COMMISSARIAT A L'ENERGIE ATOMIQUE
CENTRE D'ETUDES DE SACLAY
M I S T
Service des Bases de Données Spécialisées
F91191 GIF SUR YVETTE CEDEX

CEA-CONF- -10852

ELECTRICAL AND MICROSTRUCTURAL CHARACTERIZATION OF SILVER SHEATHED HIGH Tc SUPERCONDUCTORS WIRES AND RIBBONS

CHAFFRON L.; REGNIER P.; SCHMIRGELD L.; MAURICE F.
CEA Centre d'Etudes de Saclay, 91 - Gif-sur-Yvette (FR). Dept. de Technologie des Materiaux

AGUILLON C.; SENOUSSI S.
Paris-11 Univ., 91 - Orsay (FR). Lab. de Physique des Solides

Communication présentée à : International Conference on Modern Aspects of Superconductivity

Paris (FR)
7-8 Oct 1991

COMMISSARIAT A L'ENERGIE ATOMIQUE

CEREM

Centre d'Etudes et de Recherches sur les Matériaux

CE SACLAY DTA
DEPARTEMENT DE TECHNOLOGIE DES MATERIAUX
SECTION DE RECHERCHES DE METALLURGIE PHYSIQUE

SRMP/91.8307/19

CARACTERISATION ELECTRIQUE ET MICROSTRUCTURALE DE FILS ET RUBANS SUPRACONDUCTEURS A HAUTE T_c GAINES ARGENT

L. Chaffron, P. Régnier, L. Schmirgeld, F. Maurice
C. Aguillon,* S. Senoussi*

SRMP - DTM - CEREM, Centre d'Etudes de Saclay
91191 Gif sur Yvette Cedex FRANCE

* Laboratoire de Physique des Solides, Université Paris-Sud
91405 Orsay Cedex, FRANCE

RESUME

On a préparé des fils et des rubans supraconducteurs à haute T_c selon la méthode de la poudre dans le tube. On montre que les performances électriques des supraconducteurs ainsi préparés peuvent être considérablement améliorées, d'abord en augmentant autant que faire se peut la densité du produit cru avant frittage, puis en texturant par fusion le conducteur fritté. On présente ensuite quelques mesures de la densité critique de courant de transport que l'on compare aux valeurs indirectes obtenues par la méthode de Bean. Les plus fortes valeurs du J_c de transport mesurées dans la présente étude, avant texturation par fusion, sont: : 2 250 et 5 100 A/cm^2 à 77 et 63 K respectivement, pour un ruban gainé argent de 50 µm d'épaisseur. Ces chiffres sont en bon accord avec les valeurs de la densité critique de courant intergranulaire déterminées à partir de mesures magnétiques, et qui sont : 2 100 et 5 000 A/cm^2 aux mêmes températures, et 40 000 A/cm^2 à 4.2 K. Des valeurs intergranulaires beaucoup plus fortes, dans la gamme des 10^5 A/cm^2 ont été obtenues après texturation par fusion des fils. Finalement, on présente et discute les caractérisations effectuées par diffraction de rayons X, analyse à la microsonde et observation en microscopie électronique en transmission.

Pour publication dans les comptes-rendus de :

International Conference on Modern Aspects of Superconductivity

PARIS les 7 et 8 Octobre 1991

ELECTRICAL AND MICROSTRUCTURAL CHARACTERIZATION OF SILVER SHEATHED HIGH Tc SUPERCONDUCTORS WIRES AND RIBBONS

L. Chaffron, P. Régnier, L. Schmirgeld, F. Maurice
C. Aguillon,* S. Senoussi*

SRMP - DTM - CEREM, Centre d'Etudes de Saclay
91191 Gif sur Yvette Cedex FRANCE

* Laboratoire de Physique des Solides, Université Paris-Sud
91405 Orsay Cedex, FRANCE

Abstract

High Tc superconductors wires and ribbons were prepared according to the powder in tube method. It is shown that the electrical performances of the so prepared superconductors can be considerably improved, first by increasing as much as possible the density of the green body before sintering, and afterwards by melt texturing the sintered conductors. Some measurements of the transport critical current density of our conductors as a function of their diameter or their thickness are then presented and compared with indirect values obtained via the Bean method. The highest transport Jc measured in the present study, before melt texturing, are : 2 250 and 5 100 A/cm^2 at 77 and 63 K respectively, for a 50 μm thick silver sheathed ribbon. These figures compare nicely with the values of the intergranular critical current densities determined from magnetic measurements which are : 2 100 and 5 000 A/cm^2 at the same temperatures, and 40 000 A/cm^2 at 4.2 K. Much higher intergranular values, in the range of 10^5 A/cm^2 were obtained after melt texturing the wires. Finally, microstructural characterizations carried out by X-ray diffraction, electron microprobe analysis and transmission electron microscopy are reported and discussed.

Keywords

Superconductivity, high Tc superconductors, critical current, ceramics .

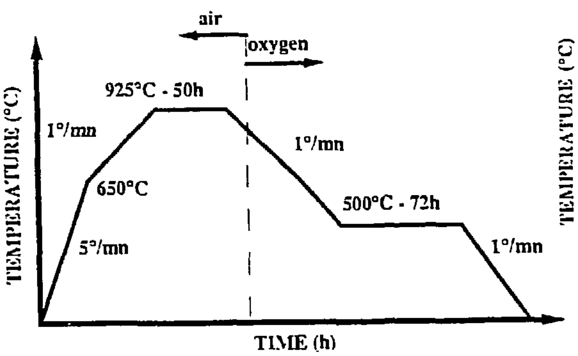
Introduction

With the mid term ambition of demonstrating the feasibility of producing high Tc superconducting wires and ribbons suitable for high Jc applications, we are currently investigating the problems to solve for reaching such a goal. In this paper we reporte on the present state of our research with the powder in tube technique [1, 2].

Experimental procedure

After several trials, previously reported [3-5], the adopted procedure is now as follows : some YBaCuO precursor powder is poured into a latex tube and cold pressed under a pressure of 300 MPa. The rod so obtained, typically $L=60$ mm and $\Phi = 5$ mm, is then sintered for 24h at 920°C in air. After cooling down to room temperature, the ceramic is adjusted in a silver tube and outgassed at 700°C for several hours. The tube is then sealed and swaged down to prepare a 1 mm in diameter wire of about 2 m long. Some sections of this wire are directly sintered at 925°C for 50 h, whereas some others are cold pressed or cold rolled before sintering. Finally the specimens are slowly cooled and maintained at 500°C for 72 h under flowing oxygen to make them superconducting. The temperature run presently used is depicted in figure 1.

After sintering, some of the specimens are melt textured by pulling them at 2mm/h out of a furnace through the temperature profile shown in figure 2.



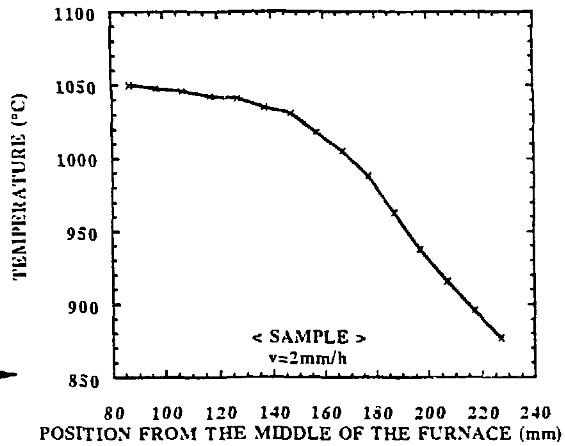
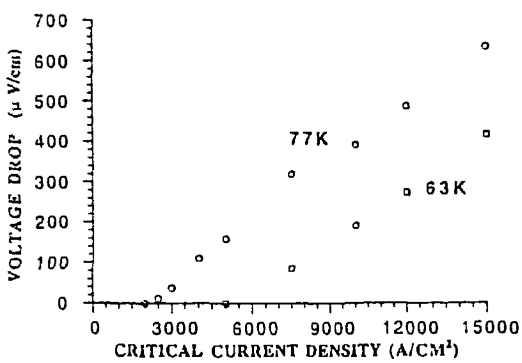


Fig. 1 : Temperature run used to sinter the silver sheathed wires and ribbons

Fig. 2 : Temperature profile of the furnace used to melt texture the sintered wires

Electrical characterization

The electrical resistivity of the prepared superconductors was systematically measured as a function of temperature with DC current, under a helium atmosphere, using four probes tin soldered on the silver sheath. The raw data were reported to the average area of the ceramic core of the conductors which was determined on several polished cross sections. As reported earlier [3,4] it was observed that the higher the compactness of the green body the narrower the resistive transition. Keeping the same probe arrangement, good specimens were dipped into liquid nitrogen, under atmospheric or reduced presssure, to measure their transport critical current density on the basis of a voltage drop of 1 µV/cm at 77 and 63 K respectively. Figure 3 shows the voltage drop measured on our best silver sheathed ribbon as a function of the current density flowing through its ceramic core at these two temperatures. From these curves it was deduced that the transport critical current density is : 2 250 and 5 100 A/cm^2 at 77 and 63 K respectively . These values are in very good agreement with those of the intergranular critical current density we have determined by magnetic measurements via the Bean method, which are : 2 100 and 5 000 A/cm^2 at 77 and 63 K respectively, and 40 000 A/cm^2 at 4.2 K.



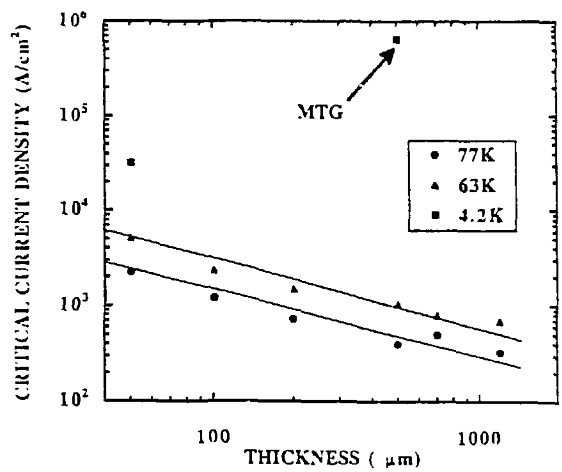


Fig. 3 : Voltage drop versus current density of a 50 µm thick silver sheathed sintered ribbon at 77 and 63 K.

Fig. 4 : Transport critical current density as a function of sample thickness at 77 K, 63 K and 4.2 K

Apart from the values themselves, which are among the highest reported for such a kind of conductor, it is worth noting in figure 3, that, above the critical current density, the resistivity increases more smoothly than observed on unsheathed material. This is probably due to the fact that when the current flowing through the ceramic attains the critical value of the grain boundaries, which constitute the weak junctions of the material, it starts to be locally deviated to the silver sheath. Consequently, what is really measured is not the genuine characteristics of the weak junction, but that of this junction in parallel with a pure resitive element. As for the dependence of the critical current on the sample thickness, which is now well established, (Fig. 4), it is usually interpreted as the evidence that the current is only flowing through a very thin surface layer [6]. According to that idea, it is legitimate to extrapolate the present results down to the thickness of usually prepared thin films, typically 0.1 μm. Now, if that is done, it is found that the critical current of a 0.1 μm thick ribbon should be about $10^5 A/cm^2$ which is a rather high value for a polycristalline untextured thin film ! But even if this optimistic vue was true, it will be probably impossible to prepare such a thin ribbon by cold pressing or cold rolling. As a matter of fact the YBaCuO powder and the silver sheath have very different rheologic properties ; consequently when they are codeformed their flow is generally unstable, which leads to the successive formation of thin and thick sections of the ceramic core. More precisely, for cold pressing these unstabilities of the flow lead to irregular transverse sections of the ceramic, as shown in figure 5, but do not affect the constancy of thickness of longitudinal sections. On the contrary for cold rolled wire, the flow is longitudinal and consequently, the transverse section of the ribbon is now of rather constant thickness, as shown in figure 6, whereas the longitudinal one is irregular. When very pronounced these unstabilities generate cracks which are longitudinal in cold pressed ceramics and transverse in cold rolled ones. The latter are much more detrimental for the transport critical current than the former, and it is probably why Osamura et al [7] have obtained values of critical current ten times smaller with cold rolling than with cold pressing.

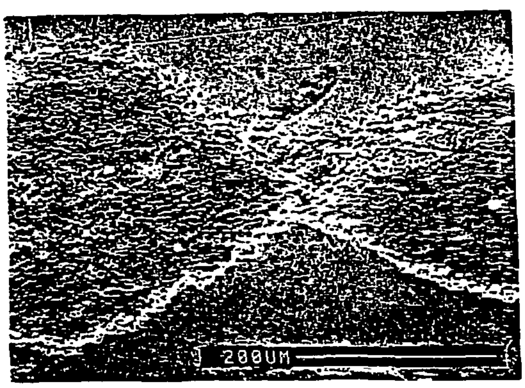


Fig. 5 : High magnification observation of the transverse section of a cold pressed ribbon showing a pronounced constriction

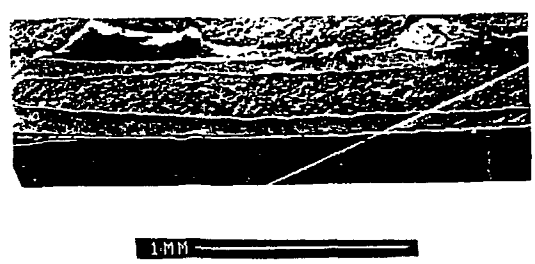


Fig. 6 : Low magnification observation of the transverse section of a cold rolled ribbon showing the absence of constriction

As for the melt textured material, its transport critical current density was so high that it was impossible to measure it with our regular electrical contact technic. To obtain the relevant information, a 4.5 mm long piece of melt textured ceramic was sliced from a 0.45 mm rod and inserted into a vibrating magnetometer system to estimate the intergranular critical current density, J_c, along the rod axis according to the Bean method. From the hysteretic cycles (figure 7 shows the one registered at 4.2 K), the results presented in figure 8 were obtained.

It is worth noting that despite the fact that the field was applied along the rod axis and the CuO planes were about 30 degrees off this same axis, the obtained values are very high, especially in comparison with those estimated for the silver sheathed sintered ribbons. Furthermore, in agreement with these high values of the critical current, it was observed that when dipped into liquid nitrogen, the specimens stayed suspended under a powerfull magnet.

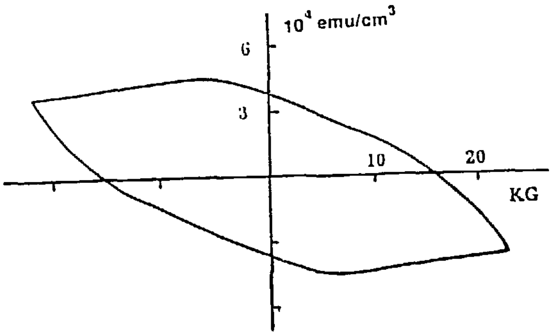


Fig. 7 : Typical hysteretic cycle registered at 4.2 K on a melt textured wire

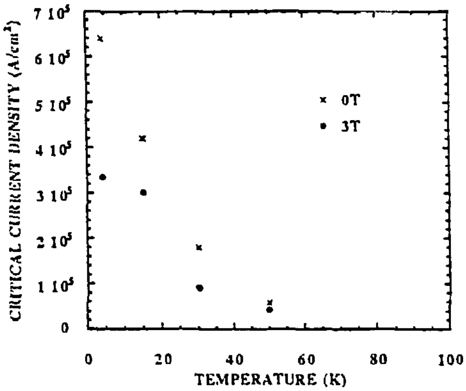


Fig. 8 : Variation of the intergranular critical current density for two different field values

MICROSTRUCTURAL CHARACTERIZATION

Examination of longitudinal and transverse sections of our superconductors in scanning electron microscopy have shown that our thinnest ribbons, those having a green body density of about 95% of the theoretical one, were free of big craks and big pores, and that their grains were rather small with a platelet shape. Figure 9 shows the typical aspect of these grains observed on a cold rolled specimen (the aspect of the cold pressed material was very similar). After melt texturing, the material was very different, it consisted of millimetric and sometime centimetric long grains occupying the whole section of the rod and containing some incorporated silver originating from the melted sheath (Fig. 10).There were also well separated rounded precipitates of the 112 phase dispersed in the 123 matrix with a very irregular density and some thin slabs of amorphous phase parallel to the CuO planes.

Fig. 9 · Typical aspect of the grains of a cold rolled sintered ribbon after etching

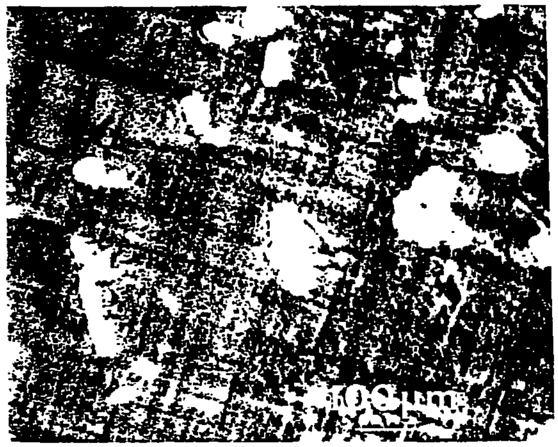


Fig. 10 : Observation in polarized light of a polished section of a melt texture wire

After cutting the edges of the ribbon and opening the ceramic sandwiched between the rest of the silver sheath, X-ray diffraction diagrams were taken. They shew that the material was single phased within the detection limit of the technique, had *a*, *b* and *c* lattice constants corresponding to an oxygen stoichiometry of 6.95 to 7.00 and that it was not very textured.

Both types of specimens were extensively analysed with our CAMECA SX 50 electron microprobe. It was found that the composition of both materials was very homogeneous ; for the sintered ceramic, in the bulk of the grains it was as follows, in weight % : Y : 13.6 , Ba : 40.0, Cu : 28.0, O : 16.9, Ag : 0.3, which makes a total of 98.8. Corresponding values for the melt textured material are : Y : 13.6, Ba : 40.8, Cu : 28.5, 0 : 16.95 which makes a total of 99.85. Considering that the sensibility limit of this equipment is about 0.5 wt %, it can be asserted that the sintered material is slightly deficient in Ba and Cu, and probably polluted by some impurities like carbon for example. The vicinity of the Ag-YBaCuO interface was carefully analysed and it was found that within the accuracy of the technique, the composition of the ceramic was the same in that region and in the bulk. Moreover, no interdiffusion of Y and Ba in the silver sheath was detected, and the Cu concentration profile observed in Ag can be entirely explained by fluorescence effect induced by the continuous radiation distribution in the neighbouring Cu rich ceramic.

Detailed observation of the material was also carried out in transmission electron microscopy. The most stricking feature is that the sintered material is strongly defective. In the bulk of the grains, narrow bands were observed rather frequently, in the high resolution mode (Fig. 11). These bands which are sandwiched between CuO planes were identified as amorphous-like for no trace of atomic plane was clearly seen in them and also because they appear as bright when imaged with the objective aperture positioned on a part of the diffuse ring of the diffraction pattern (Fig. 12). Crystallization is very poor in the surroundings of this band as can be seen from the almost continuous diffuse streaks present in this pattern as well as from the arcing of the diffraction spots. This is confirmed by the images taken in the high resolution mode which show that the atomic planes are often higly distorted. Several scans were performed through that bands to determine their composition using the EDAX facility of the microscope and it was determined that it was not different from that of the rest of the grains, at least for Y, Ba and Cu.

Fig. 11 : Observation in the high resolution mode of an amorphous like band and its neighbouring

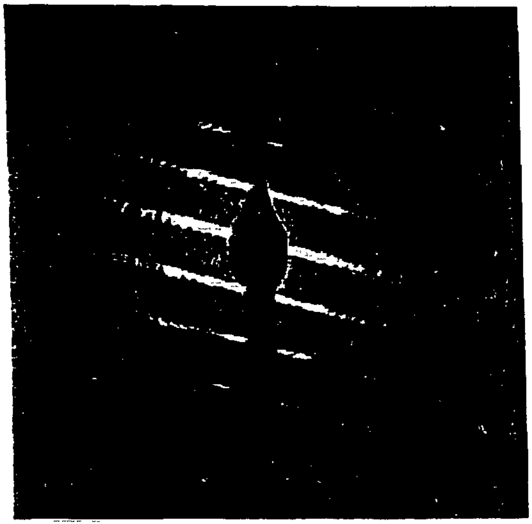


Fig. 12 : Diffraction pattern of a region crossed by an amorphous like band

It is worth noting that these bands when long enough divide the grains into smaller regions which should be taken as the relevant grain size when estimating the intragranular critical current density from magnetic measurement. In addition to these bands numerous stacking faults and dislocations were also observed in the well crystallized regions of the sintered ribbons. Fine microstrutural characterization of the melt textured material is now in progress.

A very special attention was also paid to the observation and analysis of grain boundaries. Some of them are very clean at the atomic level, even when they are of the high angle type, (Fig. 13), which is a bit amazing ; some are cracked which is dramatic for the intergranular critical current, and finally others are jammed with a layer of various amorphous phases which is very bad for the critical current. It was found that there are at least two very different types of amorphous phase : badly crystallised YBaCuO of the same nature as that constituting the bands described above, which may be in fact a complex carbonate, and another one, the composition of which is close to $BaCuO_2$, but with some amount of Y and Ag, the latter coming from grain boundary diffusion (Fig. 14).

Fig. 13 : Clean high angle grain boundary obseved in TEM high resolution mode

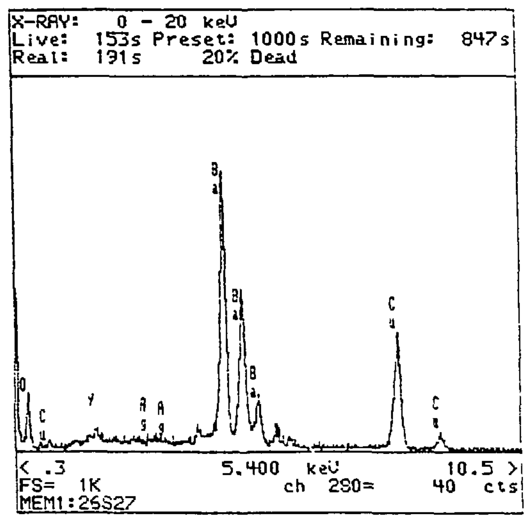


Fig. 14 : EDAX analysis showing the presence of $BaCuO_2$ at a grain boundary

CONCLUSION

The first problem encountered with the powder in tube technique used to prepare silver sheathed superconductors is that the powder shrinks during sintering whereas the sheath does not. To minimize this problem, the density of the green body was increased as much as possible. The main reason why the transport critical current densities of our conductors are modest is that the current is flowing through a thin surface layer at the periphery of the ceramic. Consequently, the most evident route to improve them is to prepare much more thinner material, which is unfortunately difficult. Some progress can also be obtained by improving the processing itself, in particular by reducing the amount of amorphous phase in some of the grain boundaries.

ACKNOWLEDGEMENTS

Many thanks are due to R. Dahlenne for cold pressing, to R. Le Goff for swaging and A. Zemskoff for electron microprobe analysis. The Ministère de la Recherche et de la Technologie is sincerly acknowledged for partial funding of the project, and the Comptoir Lyon Alemand Louyot for the cofinancement of the CIRCEA grant attributed to L. Chaffron.

REFERENCES

[1] S. Jin, R.C. Sherwood, R.B. Van Dover, T.H. Tiefel and D.W. Jonhson, Jr, Appl. phys. Lett. 51-3- (1987) 203-204
[2] R. Flukiger, F. Weiss, W. Goldacker, E. Seibt, T. Wolf and T. Muller, Proc. 1st Europ. Workshop on High T_c Mat. Genova (1987) 131
[3] P. Régnier and L. Chaffron, Supercond. Sci. Technol. 2 (1989) 295-299
[4] P. Régnier, L. Chaffron and L. Schmirgeld, International Conference on Modern Aspects of Superconductivity Grenoble 1990 published by IITT-International
[5] L. Chaffron and P . Régnier, Supercond. Sci. Technol. 4 (1991) S 247-249
[6] S. Senoussi, M . Oussena, C. Aguillon and P. Tremblay, Journal de physique Colloque C8- n° 12 Tome 49 p 2098-2013
[7] K. Osamura, T.Takayama and S. Ochiai, Supercond. Sci. Technol. 2 (1989) 111-114