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YBa₂Cu₃O_{7-δ} : in pursuit of the ideal microstructure

D. S. Smith ⁽¹⁾, S. Suasmoro ⁽¹⁾, M. Lejeune ⁽¹⁾, J. Rabier ⁽²⁾, M. F. Denanot ⁽²⁾,
J. M. Heintz ⁽³⁾, C. Magro ⁽³⁾ and J. P. Bonnet ⁽³⁾

⁽¹⁾ Ecole Nationale Supérieure de Céramique Industrielle (URA 320 CNRS), 47 à 73 avenue
Albert Thomas, 87065 Limoges, France

⁽²⁾ Laboratoire de Métallurgie Physique (URA 131 CNRS), Faculté des Sciences, 86022 Poitiers,
France

⁽³⁾ Laboratoire de Chimie du Solide du CNRS, 351 cours de la Libération, 33405 Talence,
France

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Résumé. — Dans cet article, nous examinons d'une part la réponse électrique de céramiques supraconductrices massives de type YBa₂Cu₃O_{7-δ} et d'autre part sa relation avec la microstructure. Nous présenterons successivement : 1. L'incidence de modifications microstructurales sur les valeurs de j_c et ρ_{300} , 2. les mesures expérimentales de j_c , 3. la présence de phases minoritaires et de carbonates, 4. la reprise d'oxygène et la microfissuration, 5. la déformation plastique et les défauts structuraux associés.

Abstract. — This paper examines the role of different factors in the microstructure of ceramic YBa₂Cu₃O_{7-δ} with emphasis on its electrical response. In particular we discuss : 1. the effect of microstructural variations on j_c and ρ_{300} , 2. measurement of j_c , 3. the presence of minor phases and carbonates, 4. oxygen uptake and microcracks, 5. plastic deformation and related structural defects.

Introduction.

The electrical properties of ceramic superconductors are strongly influenced by the microstructure relating to the method and details of preparation. For YBa₂Cu₃O_{7-δ}, still one of the most promising candidates for applications, a desired practical microstructure in bulk ceramic may be considered with :

- a minimum of minor phases ;
- well oxygenated orthorhombic grains ;
- grain size and orientation which is *either* fine grained to avoid microcracks *or* aligned large grains to promote current flow through the *a-b* planes, reduce the number of grain boundaries, and minimize stresses which damage the material.

These requirements point to three major aims in the processing : removal of insulating minor phases, satisfactory oxygenation, and relaxation of stress. In this paper, we examine the role of different microstructural factors on the electrical response of YBa₂Cu₃O_{7-δ} in

order to address the question why bulk ceramics present critical currents three orders of magnitude smaller than thin films.

1. Polycrystalline aspects in the electrical behaviour.

In common practice, the electrical behaviour of a ceramic superconductor is characterized by the critical current density at 77 K (j_c) and the normal state resistivity (ρ_{300}). From a technological point of view the aim is to achieve the maximum possible value of j_c . This should be associated with a low value of ρ_{300} since the imperfections in the ceramic which limit j_c also yield additional resistance in the normal state. We present a simple argument which treats the relations between j_c in zero field, ρ_{300} and the microstructure.

(a) NORMAL STATE. — Studies of single crystals show that the resistivity in the a - b plane depends linearly on the temperature which can be attributed to scattering of charge carriers by phonons [1]. Similar behaviour is observed for good quality polycrystalline material [2], suggesting that the resistance to charge transfer at the grain boundaries does not influence significantly the overall character of the response in the ceramic and is essentially ohmic (otherwise, if the grain boundaries presented large barriers to charge transfer leading to high resistance compared to the grains an Arrhenius type behaviour would be expected, as in varistors). Further information can be found in the comparison of room temperature resistivities. The a - b plane of a single crystal has a value of 0.15 m Ω cm whereas the best aligned ceramics have achieved 0.4 m Ω cm [3]. This suggests that the dominant contribution is due to the bulk of the grains and the discrepancy can be satisfactorily explained by a small grain boundary resistance, porosity and remaining tortuosity.

(b) SUPERCONDUCTING STATE. — At 77 K the grains in a hypothetical polycrystalline material, in a first approximation, have zero resistance and do not present internal weak links. But the grain boundaries which gave negligible resistance to charge transfer in the normal state, become relatively significant barriers through which the charge must tunnel and now dominate the electrical response by acting as weak links. In reality further weak link contributions may result from structural defects and local chemical inhomogeneity (example : presence of a carbon containing layer).

Two types of microstructural change can be envisaged. The first type involves a change in the effective current carrying cross section due to microcracks, porosity, or presence of insulating second phases. This will be revealed by both j_c and ρ_{300} . The second type involves alteration of the weak links at the grain boundaries or elsewhere without necessarily modifying ρ_{300} very much. As an example, non aligned bulk ceramics are typically reported with $\rho_{300} = 1$ m Ω cm and $j_c = 500$ A.cm $^{-2}$ whereas thin film exhibits similar values $\rho_{300} = 1$ m Ω cm but $j_c > 10^5$ A.cm $^{-2}$.

2. Measurement of transport j_c .

The fabrication of high quality ceramic which passes large amounts of current leads to experimental difficulty. Typically bar samples are prepared with silver electrodes yielding a contact resistance of approximately 0.5 Ω . The sample is then immersed in liquid nitrogen for measurement. At low $j_c < 100$ A.cm $^{-2}$, $j_c = \text{constant}$ as a function of cross section implying that this parameter represents the material response.

At higher $j_c \sim 500$ A.cm $^{-2}$, j_c decreases for larger cross sections while the room temperature resistivity remains constant. In addition non contact magnetic susceptibility measurements on a bar which was successively polished down showed little change in the estimates of j_c (600 A.cm $^{-2}$).

Possible explanations include self induced magnetic fields or heating from the electrodes which decrease the transport j_c from its true value. Though we do not exclude magnetic effects, we have found some direct evidence concerning thermal effects. In essence during a current pulse several watts can be dissipated at the ends of the bar transforming them into the normal state. Further information is required on the extent of these normal regions compared to the superconducting middle in order to assess the influence on transport j_c . However we may assume that the measured values represent lower limits.

3. Minor phases - carbon.

SECOND PHASE. — Early work showed that elimination of minor phases by improved calcination and use of accurately stoichiometric powder yielded lower ρ_{300} and higher j_c [4]. However the low value of j_c measured for bulk ceramics cannot be explained by the presence of second phases (such as CuO, BaCuO₂, Y₂BaCuO₅). Polycrystalline YBa₂Cu₃O_{7-δ} has yielded j_c values as low as 100 A.cm⁻² at 77 K for ceramic (density = 5.4 g.cm⁻³) without any detectable second phase, even with oxygenation treatment in favourable conditions [5].

The following deductions were made after study on a highly reactive chemically prepared powder (*via* nitrates, specific surface area 7 m² g⁻¹), but are of general concern.

ELIMINATION OF CARBONATES. — When the sintering temperature is less than 920 °C, the decomposition of carbonates appears to be difficult. For example, pure BaCO₃ is thermodynamically stable till 1 015 °C in an atmosphere with $P_{CO_2} = 0.01$ atm. Thermogravimetric analysis (Fig. 1) shows, at 920 °C under flowing oxygen for ceramic (density = 5.5 g.cm⁻³) pretreated at 800 °C under different partial pressure of CO₂, that 2 h is the minimum time to obtain an undetectable departure of CO₂ after pretreatment with 2 % CO₂. For higher CO₂ a longer time is necessary.

Fig. 1. — Thermogravimetric curves under flowing oxygen at 920 °C for two carbonated samples (2 % CO₂: sample heated previously in Ar-CO₂ with $P(CO_2) = 0.02$ atm.) (5 % CO₂: sample heated previously in Ar-CO₂ with $P(CO_2) = 0.05$ atm.).

For sintering temperatures less than 920 °C, even in the absence of CO₂ introduced during the heat treatment, CO₃²⁻ species can be detected in the ceramic by infrared spectroscopy. The vibrational frequency characteristic of carbonate ions remains noticeable even after two sintering cycles under oxygen (heating, 2 h sintering, cooling). Their origin can be related to the formation of barium carbonate in the starting powder during storage.

EXISTENCE OF AN AMORPHOUS LAYER. — At the solid/gas interface a thin layer with 5 to 30 nm thickness (Fig. 2) is often observed by TEM. This layer, which occurs systematically around pores (Fig. 2A, 2B) and sometimes in cracks, does not seem to be the result of ionic etching. The dark field image (Fig. 2A) shows its amorphous nature. The layer is related to the presence of carbon at the grain periphery. This has been established by Auger microscopy analysis, also only at solid pore interfaces [5]. Therefore, it seems reasonable to assume that the layer contains carbonates.

Fig. 2. — Transmission electron micrographs of ceramics sintered 2 h at 920 °C.

ROLE OF THIS AMORPHOUS LAYER. — A low oxygenation rate is observed in ceramics pretreated in Ar/CO₂ mixtures and heated under flowing oxygen (Fig. 3). This result can be explained by the barrier effect of the carbonate rich amorphous layer for oxygen diffusion [6]. A further consequence is that such layers obstruct the superconducting current passing through the grain boundaries hence decreasing j_c [7].

The next section discusses samples prepared from a less reactive mixed powder and therefore less susceptible to the carbon problem.

Fig. 3. — Thermogravimetric curves (heating rate : 60 °C.h⁻¹) in flowing oxygen of ceramics pre-heated at 800 °C under different Ar-CO₂ atmospheres.

4. Oxygen uptake and relaxation of stress.

There are two objects in cooling ceramic YBa₂Cu₃O_{7-δ} after sintering : oxygen uptake and relaxation of stress.

OXYGEN. — By trial and error workers have established that at least 10 % porosity has been found to be necessary for satisfactory oxygenation. Strong drops in j_c occur for values below this [8]. However the solution of a large amount of porosity must be compromised with the penalty of a reduced effective cross section. Variation of the sintering time provides a commonly used method to alter the sample density. By using X-ray measurements to estimate the oxygen content *via* the volume of the unit cell, we have demonstrated the role of density for air cooled samples [9].

In particular there is a decrease in oxygen content at 89 % of theoretical density where the porosity starts to close off. It can also be noted that in larger grained material oxygen can penetrate into the sample through microcracks.

MICROCRACKS. — The sintering time can be used to vary the average grain size for densities which are approximately constant. We observe that ultrasonic velocities v_L , v_T measured at room temperature increase as the porosity is eliminated but exhibit peak values after 10 h sintering [9]. Since the density of the ceramic only slightly increases thereafter and then remains constant with further sintering time, the decrease in v_L and v_T marks the onset of microcracking for larger grained ceramic. In fact after 45 h sintering, the attenuation of the signal was so strong that no echo was observed. Large grains promote microcracks because of anisotropic volume changes on cooling from the sintering temperature. Anisotropic volume changes can occur due to anisotropy in the thermal expansion coefficients and also during the tetragonal to orthorhombic phase transition with the associated oxygen uptake.

More precise information concerning oxygen uptake and microcracking can be obtained from ultrasonic measurements as a function of temperature. For « long bar » samples Young's modulus E is given as

$$E = v_L^2 \times \text{density} .$$

For porous ceramic with a small grain size ($< 5 \mu\text{m}$, density = 5.1 g.cm^{-3}), we observe two regions (Fig. 4 - heating curve).

- (i) $RT \rightarrow 400^\circ\text{C}$ where a steady decrease in E occurs,
- (ii) a significant departure from this typical behaviour of a solid for $T > 400^\circ\text{C}$ due to oxygen loss and the orthorhombic to tetragonal phase transition. We have deduced a direct

Fig. 4. — Young's modulus *versus* temperature for YBa₂Cu₃O_{7- δ} sintered *in situ* 55 h (oxygen atmosphere). $E_0 = 90 \text{ GPa}$. The insert shows the evolution of E with time at 950°C .

role for oxygen content in the intrinsic behaviour of Young's modulus [10]. The choice of a small grain size in a relatively porous structure minimizes microcracking and permits a rapid oxygen movement to and from the grains.

However the mechanical history of denser larger grained ceramic ($9\text{ }\mu\text{m}$, density = 5.7 g.cm^{-3}) during cooling after sintering (Fig. 4 - cooling curve) is strongly different. The significant drop at 890°C on heating is attributed to a liquid phase. During the thermal treatment at 950°C , E increased asymptotically with time due to elimination of porosity with sintering. On cooling below the transition temperature, the ceramic stiffens with oxygen uptake. However we note that the increase in E is not so steep as compared to the heating curve. This is explained by the greater density of the ceramic which inhibits oxygen uptake. Finally, the strong decrease below 450°C indicates microcracking.

Critical current density measurements show that a well oxygenated non cracked sample yields $6\text{--}700\text{ A.cm}^{-2}$ compared to 300 A.cm^{-2} for the sample in figure 4. The aspect of stress relaxation is explored further in the final section.

5. Plastic deformation mechanisms and related structural defects.

During material processing : sintering, sinter forging at high temperature or oxygen uptake, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ undergoes plastic deformation of grains which result from applied stresses or from relaxation of internal stresses.

A fundamental study of plastic deformation is then of interest in order to elucidate the mechanisms controlling plastic deformation. Two domains of stress and temperature can be roughly distinguished :

- a low stress, high temperature range,
- a high stress, low temperature range.

At high temperature ($T > 700^\circ\text{C}$), corresponding to the stable tetragonal phase, deformation is diffusion controlled. The sensitivity of the strain rate to the partial pressure of oxygen and the activation energy lead to the conclusion that the slowest diffusing species, which controls the deformation, is interstitial Ba or Y cations [11, 12].

In the orthorhombic phase (high stress, low temperature range) the deformation substructure observed at the TEM level gives evidence of the following features : deformation is achieved by dislocations with $\langle 100 \rangle$, and to a smaller extent $\langle 110 \rangle$, Burgers vectors gliding in the (001) plane. No other glide systems are observed [13, 14]. Dislocations with $\langle 100 \rangle$ Burgers vectors interact strongly with transformation twins [14] such that stress pile-ups can be expected at these intersections. Twin boundaries have been seen to be deformed for material exhibiting a high dislocation density [15].

Although mechanical twinning on (110) planes can also be a limited deformation mechanism in the orthorhombic cell (the maximum possible strain with such a deformation mode is $\varepsilon = 1 - a/b$), this analysis shows that plastic deformation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is restricted to the (001) plane. As a consequence, build-up of stresses in these ceramics can be relaxed by plastic deformation only in a highly anisotropic way so that microcracking has to take place in the accomodation of deformation. This latter effect can be limited in textured samples where adjacent grains can have a common deformation mode. Plastic deformation and high dislocation densities are then expected.

Due to the small coherence length of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, dislocations can act as flux pinning sites. We note that high j_c values in the presence of a magnetic field have been obtained for « melt textured growth » samples. In addition to second phases (Ex. : finely dispersed 211) which are thought to provide pinning sites, TEM observations on this type of highly textured

microstructure reveal grains with high dislocation densities [16]. Furthermore shocked samples have also been reported with an increase in flux pinning energy [17].

Conclusions.

Randomly oriented bulk ceramic can be prepared with a room temperature resistivity which is similar to thin films and approaches single crystals. However the critical current density is at least 2 orders of magnitude less than a thin film. Given that the ceramic is satisfactorily decarbonated the difference can not be attributed to factors such as oxygen content, porosity, or microcracking. Consequently further attention is being paid to grain orientation and stress relief mechanisms.

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