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Isothermal growth of large YBaCuO single domains through an artificial array of holes

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Abstract

For various applications, single domains (centimetric crystals with defects) of the $YBa_2Cu_3O_x$ superconductor oxide are grown using the top seeding melt growth (TSMG) method. During the oxygen annealing inducing superconductivity, cracks open at the surface layer and propagate into the bulk. Since the cracking can be reduced on thin samples, we proposed to grow single domains with thin wall geometry prior to oxygenation.

Holes of 1 mm in diameter and distant of 2.4 mm are drilled parallel to the *c*-axis in $YBa_2Cu_3O_x$ sintered pellets to produce a geometry with walls having a thickness below 1.5 mm. The single domain is then grown from a $SmBa_2Cu_3O_x$ seed placed on the pellet prior to the process. Pictures of the sample surface are regularly taken to allow an in situ monitoring of the growth. The growth front is slightly distorted by the holes, but reaches the edges. Neutron quantitative texture analysis demonstrates a unique crystallographic orientation in the bulk. The growth of a single domain is confirmed by microscopic observation and by flux mapping of trapped field in the superconducting state. The porosity usually trapped within a plain single domain disappears thanks to reduced diffusion paths.

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1. Introduction

The superconducting properties of $YBa_2Cu_3O_x$ (hereafter Y123) have been very attractive for applications since its discovery. This material offers the possibility to transport large currents

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without dissipation at the temperature of a nitrogen bath provided that it is free of grain boundaries. Therefore, the elaboration of single domains in Y123 bulk pellets has been developed. Single domains can be seen as large single crystals having a lot of defects such as secondary phase particles (the Y_2BaCuO_5 phase, a.k.a. Y211), pores, cracks, and slight disorientations (mosaic) due to perturbation at the growth front. Compared to crystals which have a mosaic (defined by a FWHM on characteristic peaks) less than 0.1°, the spread of angles is about 1° in small single domains ($\varnothing < 20$ mm) and can reach 2°–3° or more in large ones (20 mm $< \varnothing <$ 100 mm) [1,2]. Routinely produced nowadays by the top seeding melt texturing technique (TSMG) up to 3–4 cm [3], growth of larger single domains up to 10 cm has already been conducted for demonstration purpose [2,4]. They are used in application where they provide functionality difficult to obtain with conventional technologies: auto-stable levitation in magnetic bearings [5], high trapped field in superconducting permanent magnets [4,6] or self triggering transition to normal state as a threshold current is reached in fault current limiters [7].

Despite their excellent superconducting performances, single domains remain mechanically brittle. Mechanical stresses due to thermal expansion mismatch between the matrix Y123 and the secondary phase Y211 [8] or to thermal gradient during cooling (worse as the sample size increases) are source of cracks in the bulk and contribute to the poor mechanical properties. A particularity of the Y123 material is the necessity to perform an annealing treatment under flowing oxygen at low temperature (around 420 °C) after crystal growth to achieve superconducting properties. To some extent, cracks were found beneficial for accelerating the oxygenation since the oxygen diffusion rate in single domain becomes a mixture of solid diffusion in the bulk (very slow) and oxygen diffusion along the cracks (fast). The oxygenation process itself is known to be a source of large mechanical stresses and eventually of cracks because of the tetragonal to orthorhombic phase transformation. Most of the cracks formed in Y123 are found in the *ab* plane, i.e. (0 0 1) plane, since this plane is the first cleavage plane.

Since most applications are based on the circulation of currents in the *ab* planes, i.e. parallel to the eventual cracks, little attention has been paid to the oxygenation cracks, nearly seen as intrinsic to the material. But *c*-axis elements were shown recently to be very performing for current limitation [9], provided the cracks are suppressed, since the current is flowing in that case perpendicular to the cracks. By a progressive oxygenation process (details can be found in [10]), the oxygen gradients can be maintained below the limit where they induce cracks. But this strategy is limited by the oxygen diffusion: only thin samples, i.e. samples cut in the single domains with thickness below 1.5–2 mm, can be processed in a reasonable time. The dimensions of such small samples are not satisfying for applications. A solution is to shape the bulk sample in order to transform them into a structure with thin walls compatible with the above oxygenation strategy. We report in this paper the successful growth of single domains on sintered pellets being already machined with an array of holes parallel to the intended *c*-direction of the domains.

2. Experimental procedure

Commercial powders are mixed with a ratio of 70 wt% of Y123, 30 wt% of Y211 and 0.15 wt% in excess of PtO_2. Addition of Y211 helps to keep the sample shape by increasing the melt viscosity and participates to the flux pinning. Addition of PtO_2 prevents the coarsening of the Y211 particles. Cylindrical pellets, typically 25 mm in diameter and 16 mm in height, are pressed under an 80 MPa uniaxial load. Although machining is possible at this stage, the pellets are very crumbly. After a sintering step at 910 °C during 6 h for a slight consolidation, a triangular array of 1 mm diameter holes distant of 2.4 mm is drilled parallel to the pellets axis. Each hole has six equidistant neighbours as can be seen on Fig. 1. The wall thickness of the obtained geometry is less than 1.5 mm.

The elaboration of single domains through the drilled pellets is then conducted similarly to plain pellets. The same equipment and the same heat treatment are used. Details can be found in

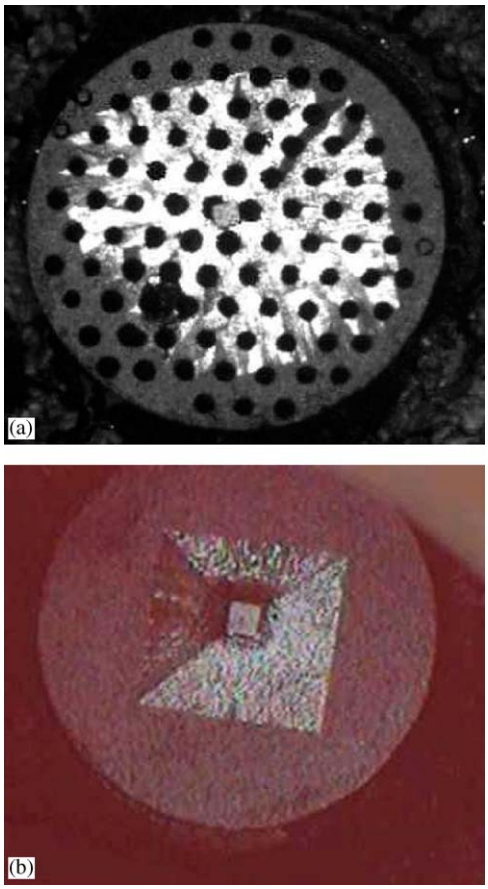

Fig. 1. Pictures of the surface of a drilled (top) and a plain (bottom) pellet taken at an intermediate stage during the growth process. The bright square is the growing domain with a seed at its centre. Steps and streaks result from the interaction of the holes with the growth front (top).

Ref. [2]. A $SmBa_2Cu_3O_x$ seed is placed on top of the pellet between the holes close to the centre. The seed orientation is chosen to induce a growth with the *c*-axis parallel to the pellet axis. The pellet is put on an alumina plate with an intermediate buffer layer to limit reactions. The process is performed in a box furnace with reduced thermal gradient. The pellet is overheated at 1050 °C in air. The peritectic temperatures of $YBa_2Cu_3O_x$ and $SmBa_2Cu_3O_x$, respectively 1015 °C and 1080 °C, differ enough to let the pellet melt while the seed is preserved. Then the pellet is cooled down to the solidification range around 1000 °C and slowly cooled at 0.16°/h until the single domain reaches the edge of the pellet. The ramping down to room temperature is performed under nitrogen atmosphere to prevent oxygenation cracks.

The furnace is modified and equipped so that pictures of the sample surface can be taken regularly during the growth. The contrast is created by the surface reflection of halogen lights. The speed of the growth front can be traced, about 0.3 mm/h in the present conditions. The growth onset from the seed and the growth limit can be determined accurately. The working range for growth is no more than 10 °C and may vary with the powder quality, so the derived information is essential to tune the process. Larger pellet can be processed by adjusting the time spent in the solidification window since the growth is almost isothermal [2].

3. Results

The mechanism underlying the cracking during oxygen uptake has been shown to be related to the combination of a continuous shrinkage of the crystal cell with oxygen uptake along the *c*-axis with a very low diffusion rate [10]. A thin oxygenated layer forms, which is put into tension by the bulk because of the layer shrinkage along the *c*-axis. Only surfaces parallel to the *c*-axis, i.e., the lateral surfaces of the pellets, are considered since the diffusion in the *c*-direction is negligible. Crack opening is induced along the *ab*-planes at the oxygenated surface layer as the stresses reach the threshold strength of the material. Cracks then propagate into the bulk because the oxygen diffusion is enhanced along the cracks: the stress build up of the surface is reproduced at the crack tips. The thin wall geometry obtained by drilling the pellet with an array of holes is part of the solution to reduce this cracking.

The ability of a growth front to proceed through an array of holes or a complex geometry is not evident a priori and is worth studying since it is very hard to machine single domains for applications purpose once they are grown. In situ video monitoring of the surface growth confirms that the growth proceeds as for a plain pellet. The growth starts from the seed. A square pattern typical of

the growth front of the tetragonal Y123 phase in *a*- and *b*-directions appears below the seed and increases homothetically until it reaches the edges of the sample. Intermediate pictures of the growth are shown in Fig. 1 for a drilled pellet (top) and for a plain pellet (bottom). The square pattern is distinguishable in both cases with the seed at its centre. The seeds were cut with edges parallel to the *a*- or *b*-direction which is why they coincide with the growing domain borders.

The comparison, however, points out steps along the growth front for the drilled pellet (Fig. 1). Obviously, they occur as the growth front goes around a hole in the diagonal region of the square pattern. The hole forces the growth front to be divided into *a*- and *b*-directions. Defects seem also to appear in the region where the growth proceeds along only one direction, i.e., the middle of the square pattern sides: streaks appear behind the holes like the one left by the recombination of a flow behind a cylindrical obstacle. Fig. 2 presents a side view of fully processed pellets, drilled (top) and plain (bottom). Because of its composition, the pellet keeps its shape through the entire process. The holes remain open and the regular array is preserved (Fig. 1). The grown domains occupy the entire volume of the pellets. The vertical dark traces on the side of the pellets in Fig. 2 show that the domains have grown down to the pellet bottom. They are the trace of the vertical edges of the domains. The multiple traces on the drilled pellet side (Fig. 2a) are the counterpart in the vertical plane of the above mentioned steps in the horizontal plane and confirmed the subdivision of the growth front.

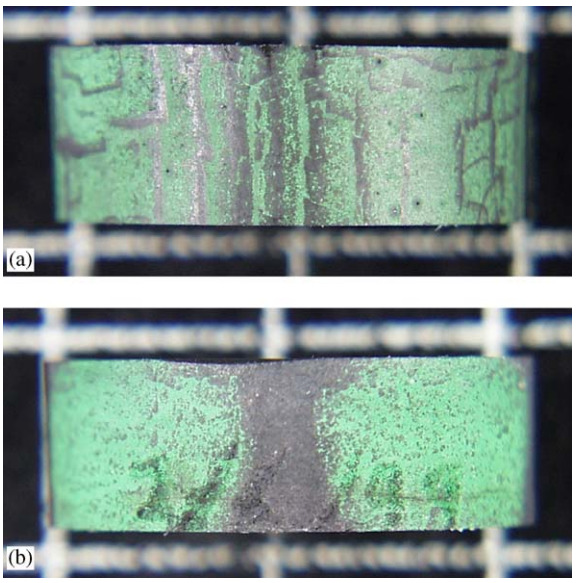

Fig. 2. Comparison of the side surface of a drilled (top) and a plain (bottom) fully processed domain. The vertical traces show that the growth went down to the bottom pellets. The multiple vertical traces on the drilled pellet (top) are related to the growth front steps noticed in Fig. 1.

However, once the surface is polished, it appears very homogeneous when examined with an optical microscope under polarized light. At this scale, there is no evident sign of defects around the holes. Further investigations are needed to relate these apparent growth defects with microstructure and properties. Neutron quantitative texture analysis from neutron diffraction data performed on the drilled pellet and obtained using the D1B line at ILL (France) does not demonstrate any significant difference in crystallite orientation between drilled and plain pellet. It clearly indicates only one single domain bulk orientation with mean *c*-axes parallel to the pellet axis and *a*-axes parallel to the main edges of the Sm123 seed. However, since measurements were operated using a 5° angular grid, the crystallite mosaic is not precisely determined, but is lower than 5°.

Fig. 3 shows a 3D representation of the trapped flux mapping performed on the drilled sample. For characterization purpose, the sample has been oxygenated 144 h at 420 °C and then 288 h at 380 °C in flowing oxygen, and is not representing results that can be expected from the progressive oxygenation process mentioned in the introduction. Prior to measurement, the sample is cooled down to 77 K with a permanent magnet (NdFeB with a surface induction of 0.5 T) lying on its surface. Once the magnetization is done, the permanent magnet is removed and the sample surface is scanned with a Hall probe at 0.2 mm of the surface using a 0.5 mm step. This characterization evidences current loops existing on a large sample scale. The current induced by the magnetization cannot flow through defects such as grain boundaries, planar segregation or cracks, which

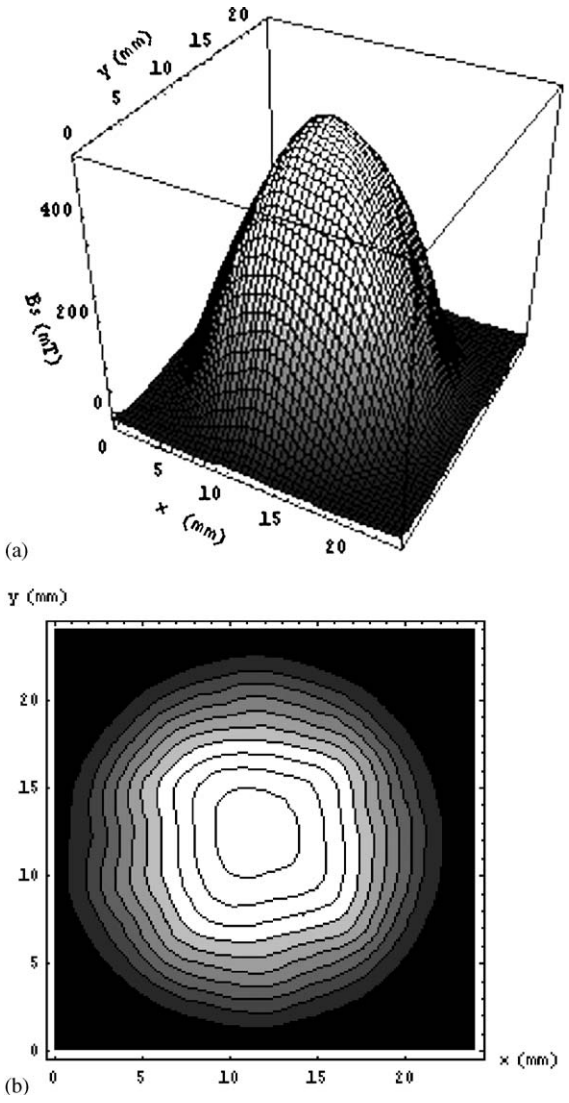

Fig. 3. Flux trapped measurement by a Hall probe scanning on a drilled pellet showing a single magnetization peak typical of a single domain.

affects directly the contour profile. In the present case, the single magnetization peak is the clear signature of a single domain. The array of holes has no significant effect on the current loops at the macroscopic scale.

Moreover, the trapped value (454 mT) for this drilled pellet is even 37% better than the one measured on plain pellets (330 mT), which strongly underlines an increase of the material quality. This

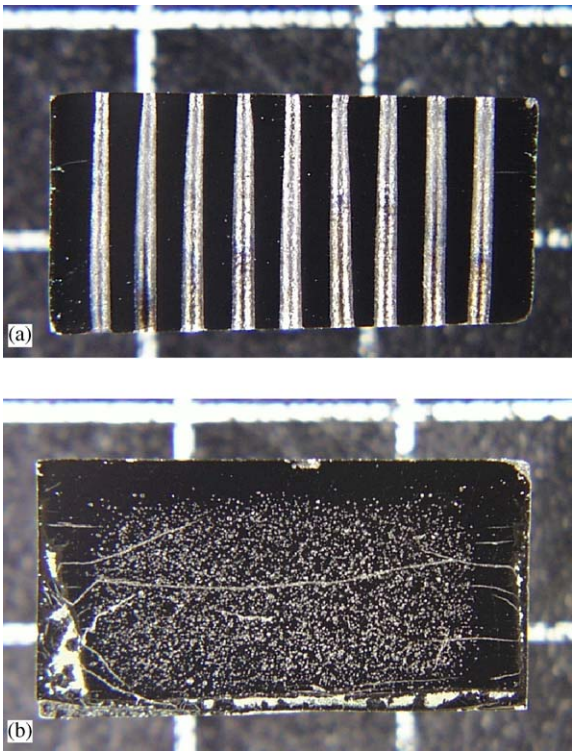

Fig. 4. Comparison of a vertical section in a drilled (top) and a plain (bottom) pellet. Note a drastic reduction of the porosity in the drilled pellet.

is supported by the comparison of transversal sections for drilled and plain pellets as seen in Fig. 4. A large porosity region is noticeable within the plain single domain, whereas the surface layer is almost exempt from pores on 3–4 mm. On the contrary, the porosity is drastically reduced in the bulk of the drilled pellet. This can be related to the fact that the typical wall thickness in such sample is far below the 3–4 mm of the dense crust observed in the plain pellet. This dense surface layer can be assumed acting as a barrier which maintains the porosity trapped inside the bulk. That is not the case anymore for thin wall geometry.

4. Conclusion

The growth of Y123 single domains on pellet already machined with a regular array of holes was

successfully conducted to produce bulk samples with thin wall geometry. This thin wall geometry appears as a way to optimize diffusion path in samples while keeping the bulk properties that make those samples so suitable for applications. Growth on drilled samples is shown to proceed as for plain samples, although perturbations of the growth front are observed when passing holes, with appearance of steps or streaks on surface. Nevertheless, no significant effect of these perturbations is clearly evidenced on a microscopic or macroscopic scale. The single domain nature of the growth result has been confirmed by neutron diffraction and trapped flux mapping. Although this thin wall geometry was first intended to reduce diffusion paths for oxygen annealing purpose, it also appears to be beneficial to evacuate porosity from the bulk. The 37% enhancement of the value of the trapped field measured on drilled pellets whereas the material volume is decreased by 20% evidences an improvement of the material quality and is a clear encouragement to pursue this study. Further investigations are underway to fully characterize this new material. It opens exciting perspectives: reduced diffusion paths can be exploited for better processing and doping control as well as for improved thermal exchange, whereas this peculiar geometry offers new opportunities in terms of mechanical reinforcement.

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