High-pressure oxygenation of thin-wall YBCO single-domain samples

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Abstract. The oxygen annealing of ReBCO bulk material, necessary to achieve superconducting properties, usually induces micro- and macro-cracks. This leads to a crack-assisted oxygenation process that allows oxygenating large bulk samples faster than single crystals. But excellent superconducting properties are cancelled by the poor mechanical ones. More progressive oxygenation strategy has been shown to reduce drastically the oxygenation cracks. The problem then arises to keep a reasonable annealing time. The concept of bulk Y123 single-domain samples with thin-wall geometry has been introduced to bypass the inherent limitation due to a slow oxygen diffusion rate. But it is not enough. The use of a high oxygen pressure (16 MPa) enables to speed up further the process. It introduces a displacement in the equilibrium phase diagram towards higher temperatures, i.e., higher diffusion rates, to achieve a given oxygen content in the material. Remarkable results were obtained by applying such a high pressure oxygen annealing process on thin-wall single-domain samples. The trapped field of 16 mm diameter Y123 thin-wall single-domain samples was doubled (0.6T vs 0.3T at 77K) using an annealing time twice shorter (about 3 days). The initial development was made on thin bars. The advantage of thin-wall geometry is that such an annealing can be applied directly to a much larger sample.

1. Introduction

ReBa₂Cu₃O₇₋ₓ (Re123) single domains have practical applications at 77K where no equivalent can be found in a conventional technology, such as auto stable superconducting bearings, fault current limiters, superconducting trapped field magnet. ReBCO bulk material as superconducting permanent magnet can provide much larger field than classical NdFeB permanent magnets, with the restriction of a required cryogenic environment. They can lead to very compact and efficient cryogenic motors and generators [1]. A peculiarity is the necessity to perform an oxygen annealing treatment in order to achieve superconducting properties. This step usually induces micro- and macro-cracks [2]. Excellent superconducting properties are cancelled by the poor mechanical ones.

A progressive oxygenation, i.e., by progressively adjusting the oxygen partial pressure during annealing in accordance to the temperature and to the oxygen content of the surface layer, has been reported to reduce drastically the number of cracks [3]. But the experiment was carried out on small samples presenting a diffusion length below 1.5 mm. With a very reduced cracking, the oxygen
The process becomes very long as illustrated by the oxygen time required for single crystals. Moreover, the annealing time increases as the square of the diffusion length. The concept of bulk Y123 single-domain samples with thin-wall geometry has been introduced to bypass the inherent limitation due to a slow oxygen diffusion rate [4,5]. Single domains are grown on pellets already shaped with an array of holes. They stand in one piece but benefit from reduced diffusion paths.

An improvement in the trapped field has already been noticed comparing plain and drilled samples after a conventional oxygen annealing treatment [1,6]. In that case, the samples were annealed under flowing oxygen in two steps at 420 °C for 144 hours and at 380 °C for 288 hours.

The development of thin-wall geometry for oxygenation aims at applying a more progressive oxygenation strategy to reduce cracks while keeping a reasonable annealing and preferably directly to a much larger sample. The diameter of the sample does not matter anymore; the annealing time only depends on the distance between holes. Note that only diffusion in ab-plane is considered, the diffusion along c-axis being neglected since it is four to six orders of magnitude lower [7].

Whatsoever, the progressive oxygenation mentioned in [3] does not yield a reasonable annealing time considering a full oxygenation to reach a Tc of 92 K. The use of a high oxygen pressure (16 MPa) enables to speed up the process. A higher oxygen pressure does not yield a higher diffusion rate [7], but a higher temperature does, and applying an oxygen pressure introduces a displacement in the equilibrium phase diagram towards higher temperatures. That means the oxygen content achieved at 400°C under flowing oxygen can be achieved faster at a higher temperature if an oxygen pressure is applied [8]. We roughly estimate from literature data [8] that working at 16 MPa and 600°C would give the same result than working at ambient pressure and 400°C in term of oxygen content. The diffusion rate dependence in temperature follows an Arrhenius law. We estimate the diffusion times for a length of 1 mm in ab-plane to be in the order of 300 h, 10 h and 0.5 h at 420°C, 575°C and 720°C respectively. This is just an indication to show how beneficial working at a higher temperature can be.

Tests of such high-pressure progressive oxygenation annealing were performed on thin bars of 1-1.5 mm thickness in ab-plane. Preliminary results have shown that a full oxygenation can be achieved at a temperature as high as 750°C with a 16 MPa oxygen pressure. A decrease of the amounts of microcracks in the structure and an increase of the critical current in the ab-plane as well as of the twin density have been observed [9].

In this paper, we report on this 16 MPa oxygen annealing process successfully applied to thin-wall single-domain samples.

2. Experimental

2.1. Samples

The initial precursor is a mixture of commercial powders in the following ratio: 70wt% of Y123, 30wt% of Y211 and 0.15wt% of PtO2 in excess. The thin-wall geometry is obtained by compacting pellets with embedded needles. A 20 mm diameter die has been modified to insert 0.7 mm diameter and 7 cm long stainless steel needles. The needles are maintained by the bottom and top pressing plates to form a triangular array of 0.7 mm holes distant of 2.5 mm. To ease the release of the needles and of the pellet from the die, all surfaces are covered with a lubricant film made of stearic acid diluted into acetone. When the acetone is fully evaporated, 25g of the mixed precursor is poured into the die and uniaxially pressed at a moderate pressure of 50 MPa. The needles are removed from the die before release of the pellet.

The thin-wall bulk single-domain samples are then prepared as classical plain single-domain samples by the TSMG method as already fully described elsewhere [4,5]. Note that at the end of the process the samples are cooled down under a nitrogen atmosphere from about 940°C to avoid oxygen uptake and limit cracking due to oxygenation. After processing, the pellet has a 16 mm diameter and the holes have reduced to about 0.6 mm in diameter. Top and bottom parts are cut and polished. The final height is about 10 mm.
Figure 1. Picture of single-domain samples after TSMG process: a plain sample (right) and a thin-wall sample (left). The diameter of the pellets and of the holes reduced to 16 mm and 0.6 mm respectively.

2.2. Oxygenation
The oxygenation is performed in a long vessel made of Haynes 230 steel, a refractory steel able to sustain oxidizing atmosphere at high temperature. The vessel has been designed for a maximum oxygen pressure of 16 MPa at 760-800°C, higher temperature being admissible at lower pressure. The inner diameter of the vessel is 25 mm, so that only that the diameter of the samples to be oxygenated is limited to about 20 mm. One end of the vessel is welded and inserted in a tubular furnace. The samples are placed close to this end in an alumina boat and surrounded by alumina wool. The other end of the vessel, out of the furnace, is closed by a screwed cap and sealed by a reinforced O ring. The cap is water cooled and equipped with in and out gas tubes.

In a first stage, the samples are brought to 900°C at 60°/h under a flowing atmosphere (1 bar) which is changed from 100% nitrogen at room temperature to 100% oxygen at 900°C. The change is made to abide by the equilibrium line in the oxygen partial pressure-temperature diagram [8] corresponding to x=6.3. The samples are then cooled at 10°/hrs down to 800°C for a 2 hrs dwells, then at 4°/hrs down to 750°C. From 800°C, the vessel is directly connected to an oxygen bottle (200 bars). A first circuit with a 24 bars low pressure manometer is used to slowly raise the oxygen pressure up to 24 bars by 4 bars every hour. Then a second circuit equipped with a 160 bars high-pressure manometer enables to reach 160 bars by 10-20 bars every hour. This progressive increase is necessary to limit the oxygen gradient between the surface and the bulk and to avoid the intensive cracking that would result from a direct increase to 160 bars. Contrary to previous attempt [5], no subsequent dwells are performed at lower temperature. Once the 16 MPa oxygen pressure is reached, the sample is kept at 750°C for 24 hrs. The sample is then assumed to be fully oxygenated and is cooled down to room temperature at about 60-120 °/hrs (furnace cooling). Oxygen pressure is then released to ambient pressure.

The total annealing time is about 3 days, and may be surely reduced by an optimization of the process and an automatisation of the pressure increase which was done by hand up to now.

2.3. Trapped flux
The trapped field of the samples is measured by mapping the remnant surface induction with a Toshiba Hall probe. The samples are first magnetized in a superconducting coil at 2T following a field cooled procedure. Then the sample holder is transferred to a 3-axis moving table. By taking into account the time needed to ramp the field down and to place the sample onto the scanning setup, the measure is done more than 20 minutes after magnetization, so that relaxation phenomenon can be neglected during the experiment. Liquid nitrogen is poured regularly in the sample holder to maintain
its level above the surface sample. The scan is performed at a distance of 0.2 mm of the surface with a grid step of 0.5 mm. This experimental setup yields results which are within a few percent to those obtained in other European laboratories (round Robin test led by Cardwell et al. [10]). Our setup allows scanning a 20 mm by 20 mm area with a 0.5 mm step in about 5 minutes.

3. Results-discussion

Previous results were already showing an improvement about 40% of the properties of drilled pellets compared to plain one following a classical oxygenation annealing [4,5]. Then, in different attempts, we reproducibly obtained drilled pellets oxygenated under high-pressure with the highest trapped field we never get with our precursors, i.e., above 500 mT for a diameter of 16 mm. It has been shown on thin bars that the result of high-pressure oxygen annealing differs depending on initial microstructure (classical MTG with Y211 or Y2O3, or bars cut out thin-wall geometry samples) [9]. We have postulated that the high-pressure oxygen annealing can be optimal only for the thin-wall geometry because of the reduced diffusion length. A plain and a thin-wall geometry samples were prepared for comparison purpose. They were fabricated together at the same time, so that the precursors, the TSMG process and the oxygenation annealing under high pressure are exactly the same. They also have the same diameter and height.

Figure 2. 3D representation of the surface induction at 77 K on a plain (left) and thin-wall geometry (right) samples after field cooling under 2T. The plots are made using LAMP, the Large Array Manipulation Program. http://www.ill.fr/data_treat/lamp/front.html. The X and Y axis are mm, the Z axis represents the surface induction in mT.

Figure 2 shows the 3D representation of the surface induction at 77 K for both samples after field cooling under 2T. The remarkable result is the maximum trapped field value measured on the thin-wall geometry sample being almost twice the one obtained on the plain sample. The nice conical shape of the induction peak indicates one single current loop. The peak is flattened in the case of the plain sample. This usually reveals defects in the sample, although the current seems to flow in the whole sample. It has been shown on thin bars that the high-pressure oxygen annealing increases the Jc in ab-plane, which is associated with an observed higher twin density [9]. The worse performances of the plain sample can be explained either by lower local critical currents (for instance because of too large diffusion path) or by more defects such as cracks. The first hypothesis has not been probe yet, but the second is the most probable and is easily verified by microstructural observations as seen on figure 3. We note on the thin-wall geometry sample the same remarkable microstructural features already observed for conventional oxygenation, i.e., almost no more porosity in the matrix, a decrease of the ab-plane cracks and almost no ac- or bc-cracks [5].
All observed cracks being parallel to the cleavage planes of the Y123 phase, they are formed on the already grown single domain. The most noticeable feature is the a/c-oxygenation crack network seen in the case of the plain sample (figure 3a). Such network is not visible on figure 3c. These cracks will impede the current to flow in ab-planes and so participate directly to the degradation of the trapped field. The ab-plane cracks are also reduced in the thin-wall geometry and we believe it also participates to the general improvement of the trapped field through an improvement of the overall mechanical stability. Whereas ab-plane cracking is not reduced despite thin-wall geometry after a conventional oxygenation, it does when combined with the high-pressure oxygenation annealing. One feature that is worth to notice on the plain sample is the a/c-oxygenation cracks which seem to nucleate on ab-cracks (figure 3b). This feature is also not seen on the thin-wall sample.

Figure 3. Micrographs of the ab-plane (a, c) and of a vertical section along the c-axis (b, d) of the high-pressure oxygenated plain (a, b) and thin-wall geometry (c, d) samples respectively. The thin-wall geometry is almost free of porosity, of ac- or bc-plane cracks, and only few ab-plane cracks are seen (not shown here). It is impossible to find an area on the plain sample free of cracks with the magnetization used. One noticeable feature is that not only ab-plane cracks are seen on b, but also ac- or bc-cracks.

Table 1. Summary of different trapped field results. The best combination appears to be pressed pellets and high-pressure oxygenation.

| Geometry          | Plain     | Drilled (holes Ø 0.8mm) | Pressed (holes Ø 0.6 mm) |
|-------------------|-----------|-------------------------|--------------------------|
| Oxygenation       | Classical | Classical 16 MPa        | Classical 16 MPa         |
| Diameter (mm)     | 22        | 22                      | 16                       |
| Trapped flux (mT) | 240/375   | 454/532                 | 190/223                  |
| Normalized result to 16 mm (mT) | 174/272 | 330/387                 | 190/223                  |
Table 1 summarizes different results at 77 K depending on the geometry and on the annealing process. The thin-wall geometry and the high-pressure oxygen annealing have both a beneficial effect. The combination of both yields the best results.

4. Conclusions
The trapped field of 16 mm diameter Y123 thin-wall single-domain samples oxygenated under the high oxygen pressure of 16 MPa was doubled (0.6T vs 0.3T at 77K) using an annealing time twice shorter (about 3 days) than our conventional oxygenation annealing. This confirms at the scale of a 16 mm diameter pellet the improvement seen on thin bars. Combination of thin-wall geometry and high-pressure yields a sample with general cracking features drastically reduced so that the advantage of high-pressure enhanced can be fully exploited. This combination is shown to be efficient, and moreover to be easily scalable to larger sample size provided the sample has a thin-wall geometry.

A question remains open: can this combination be also applied successfully to initial -compositions with better pinning properties?

Acknowledgement
The authors would like to thank for their exchange support French and Ukrainian foreign ministries (PHC Dnipro program), French and Slovak foreign ministries (PHC Stefanik program). They also would like to acknowledge the role of the EFFORT network in the present collaboration. P. Diko thanks VEGA foundation and NANOSMART for support.

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