Oxygenation of bulk and thin-walled MT-YBCO under controllable oxygen pressure

T A Prikhna1, X Chaud2, W Gawalek3, A. Joulain4, Ya M Savchuk1, N V Sergienko1, V E Moshchil1, T Habiserether3, J Rabier4, S N Dub1, V S Melnikov1, D. Litzkendorf3, P A Nagorny1, J. Bierlich3, V B Sverdun1, I Vajda5, J Kósa5
1Institute for Superhard Materials of the National Academy of Sciences of Ukraine, 2, Avtozavodskaya Str., Kiev, 07074, Ukraine
2CNRS/CRETA, 25, Avenue des Martyrs BP 166, 38042 Grenoble CEDEX 9, France
3Institut für Photonische Technologien, Albert-Einstein-Strasse 9, Jena, D-07745, Germany
4Université de Poitiers, CNRS/Lab. de Metallurgie Physique, UMR 6630 CNRS-Université de Poitiers SP2MI, BP 30179, F-86962 Chasseneuil Futuroscope Cedex, France
5Budapest University of Technology and Economics, Budapest, Hungary
1111 Budapest, Egyr József u. 18. Hungary
E-mail: prikhna@iptelecom.net.ua, prikhna@mail.ru

Abstract. The possibility to saturate MT-YBCO with oxygen up to about 7 oxygen atoms per one unit cell of YBa2Cu3O7-δ at 800 °C under controllable oxygen pressure (from 0.5 kPa to 16 MPa) has been established. On condition that the material heating to high temperatures occurs in the nitrogen atmosphere with gradual substitution of it for oxygen and further increase of the oxygen pressure, the saturation of MT-YBCO by oxygen takes place practically without the macrocrack formation and results in the decrease of microcrack density parallel to ab-planes, that leads to the increase of critical current density and mechanical characteristics. It has been shown that in the case of a higher twin density, the material demonstrates higher critical currents, jc. Bulk and thin-walled MT-YBCO oxygenated at high controllable pressure and 800 °C contained a large amount of twins (4-11 and 20-22 µm -1, respectively) and were practically free from dislocations and stacking faults, but demonstrated very high values of jc at 77 K: je higher than 10 kA/cm 2 was observed in the fields up to 5T in ab-planes and up to 2 T in the direction of the c-axis. Specially detwinned MT-YBCO containing a large amount of dislocations (up to 10^12 cm^-2) demonstrated critical currents lower by about one order of magnitude, which gives us ground to conclude that the presence of twins is extremely important for attaining high critical currents in MT-YBCO. The high-pressure oxygenation allows one to essentially reduce the duration of the oxygenation process as compared to that under atmospheric pressure.

1. Introduction
Due to high superconductive characteristics the top-seed melt-textured grown YBCO ceramic (MT-YBCO) is very promising for applications in the devices working on the levitation principles. There are two main stages in the ceramic preparation: (1) the formation using seed crystal the pseudo-single-
domain YBa2Cu3Ox (Y123) structure with fine-dispersed Y2BaCuO5 (Y211) inclusions (up to 30 wt% of the Y211 phase); (2) and the oxygenation for transformation of non-superconductive tetragonal YBa2Cu3O7-δ (Y123) structure to the orthorhombic one due to the increase of oxygen content up to 6.8-7 oxygen atoms per one unit cell. The latest investigations have shown that the presence of fine and homogeneously distributed Y211 grains in the structure, as well as dislocations and stacking faults are of great importance for attaining high critical currents in MT-YBCO. In [1] two contributions to the critical current density (the so-called, weak pinning associated with the in-plane dislocation and correlated disordered pinning that comes from 123/211 interfaces) were identified and it was demonstrated that the dislocation pinning can be counterbalanced by wide stacking faults inducing a downward shift of the irreversibility line. The mechanical stresses, which arise in the sample during its fabrication, are the cause of cracking in this material. The different thermal expansion coefficients of 123 and 211 phases and the dependence of 123 phase lattice parameters on the oxygen stoichiometry are responsible for the formation of three basic types of cracks in MT-YBCO [2]: the \( \frac{a}{b} \)-microcracks (parallel to the \( \frac{a}{b} \) plane) and so-called \( \frac{a}{b} \)- and \( c \)-macrocracks. A new method of the MT-YBCO preparation (the so-called thin-walled MT-YBCO) that allowed avoiding the macrocrack formation during the first stage of the MT-YBCO preparation, increasing the material density and reducing the necessary depth of the oxygen penetration into the MT-YBCO structure at the stage of oxygenation was proposed in [3]. As distinct from the traditional top-seed melt-textured growth, before texturing the set of holes about 1 mm in diameter are formed or drilled perpendicular to the future \( ab \)-planes of Y123 matrix so that the maximum thickness of the wall between the holes is about 3 mm. Then the seed crystal is put on the top surface of a sample with holes, the melt-texturing is performed, and the result can be seen in Figure 1. To avoid the macrocracks, the thin-walled ceramic just after texturing that is performed in air and usually is finished at about 980 °C, the material is cooled to room temperature in a nitrogen atmosphere [3].

The proposed method of the oxygenation under controllable (from 0.5 kPa to 16 MPa) oxygen pressure at 800 °C gives the possibility to reduce the time of oxygenation, to avoid the macrocrack formation and to decrease the microcrack density and increase the critical current density. The improvements in microhardness and fracture toughness as compared to the material oxygenated at 440 °C under the ambient pressure have been attained for both bulk and thin-walled ceramics and the maximal trapped field of the block of thin-walled ceramic oxygenated at 900–800 °C and up to 16 MPa was doubled.

2. Experimental
For comparison, the bulk and thin-walled MT-YBCO (Figure 1) have been oxygenated at ambient oxygen pressure for 270 and 80 h at 440 °C and under controllable oxygen-nitrogen atmosphere (the oxygen pressure was varied from 0.5 kPa to 16 MPa and the nitrogen pressure from 0.1 MPa to 0.5 kPa) for 80 h at 800 °C. In the case of oxygenation under pressure the heating started in flowing nitrogen (0.1 MPa), then, on heating from 700° to 900 °C oxygen gradually replaces nitrogen so that at 900 °C the samples are in flowing oxygen at 0.1 MPa and kept under these conditions for 0.5 h; then the temperature has been reduced to 800 °C at a rate of 10 K/h; on reaching 800 °C, the oxygen pressure was gradually increased (according to the exponential law) to 16 MPa, and at 16 MPa and 800 °C samples were kept for 48 h, after which the temperature was decreased at a constant rate to the room one. The bulk MT-YBCO was produced from a mixture of a commercial YBa2Cu3O7-5 powder (Solvay) with Y2O3 and CeO2 powders taken in the standard ratio of Y1.3Ba2Cu3O7-5+1%CeO2, the texturing process being performed in air [4]. The thin-walled MT-YBCO (with drilled holes, the walls between them of about 3 mm) has been manufactured [3] from the mixture of 70 wt% of YBa2Cu3O7-5, 30 wt% of Y2BaCuO5 and 0.15 wt% of PtO2. The cooling of thin-walled MT-YBCO after the formation of the Y123 texture starts from 980 °C in a low oxygen atmosphere (below 0.5 kPa) in 0.1 MPa nitrogen atmosphere instead of in air. The thin-walled MT-YBCO blocks were cut into rectangular parallelepipeds of about 2.5×3×2.5×3×5.8 mm3 in order they could be inserted into magnetometer as a unit without precutting; the longer side of the
parallelepiped was approximately parallel to the c-axis of the Y123 domain. A block of thin-walled MT-YBCO 16 mm in diameter and 10 mm in thickness (shown in Figures 1a,b) was oxygenated under the high controllable oxygen pressure in the same experiment together with the small cut blocks as well.

The detwinned oxygenated superconductive MT-YBCO samples (the density of twins being 0 – 1 µm\(^{-1}\)) were prepared by high pressure-high temperature (HP-HT) treatment at 2GPa and 800 °C, 0.5 h from MT-YBCO bulk ceramics that was previously oxygenated at 430-450 °C for 25 days at ambient pressure. The oxygen content of the detwinned MT-YBCO material was optimal from the point of view of SC properties (about 6.9 oxygen atoms per unit cell; \(a=0.3821\) nm, \(b=0.3895\) nm, \(c=1.1687\) nm), the dislocation density was about 10\(^{12}\) cm\(^{-1}\).

The structures of materials were studied using a polarized optical microscope, TEM, X-ray structural and phase analyses. The amount of oxygen in the Y123 structure of MT-YBCO has been determined by estimating the c-parameter and using its correlation with the amount of oxygen [5, 6]. The \(j_c\) was estimated from magnetization hysteresis loops obtained using an Oxford Instrument 3001 vibrating sample magnetometer (VSM) and Bean’s model. The field map (FM) of a field-cooled thin-walled block has been obtained using scanning by a Hall probe (the distance between the Hall probe and the sample surface was 0.2 mm), in more than 20 minutes after magnetization. The hardness was measured employing a Matsuzawa microhardness tester, Mod. MXT-70, for \(H_v\) (using a Vickers indenter), and a Nano Indenter II for \(H_B\) (using a Berkovich indenter). The fracture toughness was estimated from the length of the radial cracks emanating from the corners of an indent.

**Figure 1.** General view of a MT-YBCO thin-walled (16 mm in diameter and 10 mm in height) with a seed crystal on its top (a) and bulk (45x45x17 mm\(^3\)) ceramic blocks (c); the enlarged structures before oxygenation of thin-walled MT-YBCO (near the wall of a hole a few short (less than 200 µm) macrocracks were formed) (b) and of bulk MT-YBCO (d).

3. Results and discussions.

A comparison between critical currents of different materials give us ground to conclude that the oxygenation of the Y123 structure at 800 °C is possible under comparatively low pressure (16 MPa) in contrary to the predicted in [7]. The field of irreversibility as well as the critical current density under high magnetic fields in ab-plane of MT-YBCO prepared from Y123 and Y211 thin-walled MT-YBCO were usually higher than that of bulk MT-YBCO prepared from Y123 and Y\(_2\)O\(_3\). The oxygenation for 80 h under the atmospheric oxygen pressure even of such small MT-YBCO samples gave lower \(j_c\), especially in the c-direction (Figures 2c, d). It is well seen in Figure 3 that the structure of MT-YBCO prepared from Y123 and Y211 contained coarse Y211 grains that are more homogeneously distributed in the Y123 matrix than in the case of MT-YBCO prepared from Y123 and Y\(_2\)O\(_3\). The twin density in these two materials are different too. In MT-YBCO prepared from Y123 and Y\(_2\)O\(_3\) the twin densities were 4-11 µm\(^{-1}\) and 0.5-1.7 µm\(^{-1}\) in the cases of oxygenation under high controllable oxygen pressure (16 MPa, 800 °C, 80 h) and under atmospheric pressure (0.1 MPa, 440 °C, 270 h), respectively, while after oxygenation at the same conditions MT-YBCO prepared from Y123 and Y211 demonstrated the twin density of 20-22 µm\(^{-1}\) and 12-16 µm\(^{-1}\), respectively. It cannot be the result of the holes formation in MT-YBCO, because, for example, in bulk MT-YBCO, prepared from Y123 and Y211 after
oxygenation at 16 MPa, 700 °C, 72 h the twin density was about 30 μm⁻¹. The fields of irreversibility were higher for the samples with higher twin density. The oxygenation under high oxygen pressure leads to an increase in the twin density of both materials prepared from Y123 with Y₂O₃ and Y123 with Y211. In the samples oxygenated at 800 °C (16 MPa, 80 h), the dislocations and stacking faults were practically absent in both types of the studied ceramics, but both materials demonstrated extremely high critical currents and irreversibility fields. But critical currents in detwinned samples (Figures 2, 4) were lower by about one order of magnitude despite the very high dislocation density. All this gives us grounds to conclude that twins play an extremely important role as pinning centers and promote attaining high current densities in MT-YBCO. The high pressure-high temperature oxygenation at 800 °C decreases the microcrack formation (from 890 to 200 mm⁻¹ for bulk and from 1050 to 280 for thin-walled MT-YBCO), and allows one to practically avoid macrocracking. The decrease of microcrack density may be the main reason for an increase of $j_c$ in the $c$-axis direction. Figure 5 shows the field mapping at 77 K of a thin-walled MT-YBCO block after oxygenation under controllable 16 MPa pressure at 800 °C the maximal trapped-field was 541 mT, while the block of the same size oxygenated under atmospheric oxygen pressure for 144 h at 420 °C and 288 h at 388°C demonstrated maximal trapped field of about 240 mT.

For thin-walled MT-YBCO at 77 K, the $j_c$ in $ab$ plane was 85 kA/cm² in 0 T field and higher than 10 kA/cm² in the fields up to 5 T, the field of irreversibility was 9.8 T, and in the $c$- direction $j_c$ was 34 kA/cm² in 0 T and higher than 2.5 kA/cm² in 10 T field; the microhardness, $H_v$, and fracture toughness, $K_{IC}$ at 4.9N-load were $H_v= 8.7±0.3$ and $7.6±0.3$ GPa and $K_{IC}=2.5±0.1$ and $2.8±0.24$ MPa m⁰.⁵, in $ab$-planes and in perpendicular direction, respectively.

Figure 2. The critical current density, $j_c$, vs. magnetic field, $\mu_0H$, at 77 K for oxygenated MT-YBCO, when external field is parallel to the $c$-axis of Y123 (a) and parallel to $ab$-plane (b); comparison between the $jc$ in both directions of the samples of thin-walled MT-YBCO (c) and bulk MT-YBCO oxygenated under controllable high oxygen pressure and atmospheric pressure for 80 h. Curves 1, 2, 6 – thin-walled MT-YBCO and 3, 4, 7 – bulk MT-YBCO; 5 – HP-HT detwinned MTYBCO; curves 1, 3 – oxygenated at 16 MPa, 800 °C, 80 h; 2, 4 – oxygenated at 0.1 MPa, 440 °C, 270 h and 6, 7 – oxygenated at 0.1 MPa, 440 °C, 80 h.
Figure 3. TEM images of the MT-YBCO structure after oxygenation under controllable oxygen pressure at 16 MPa, 800 °C, 80 h of two types of ceramics: bulk MT-YBCO prepared from Y123 and Y2O3 (a, b) and thin-walled MT-YBCO prepared from Y123 and Y211 (c). Structures of MT-YBCO after oxygenation (seen in polarized light) at 16 MPa, 800 °C, 80 h of bulk MT-YBCO (d) and thin-walled MT-YBCO (e) and at 0.1 MPa, 440 °C for 270 h of bulk MT-YBCO (f) and thin-walled MT-YBCO (g).
**Figure 4** TEM images of the MT-YBCO structure after HP-HT detwinning (a) [5] and (b) [6].

**Figure 5** The field-map of the thin-walled MT-YBCO block 16 mm in diameter and 10 mm in height oxygenated under controllable pressure at 16 MPa, 800°C, 80 h.

**Conclusions**

The oxygenation under controllable oxygen pressure up to 16 MPa is possible at such a high temperature as 800 °C. The advantages of this oxygenation method are the most pronounced for thin-walled MT-YBCO ceramics. The proposed method allows us to reduce microcracking, macrocracking (to avoid practically) and the time of oxygenation, to increase critical current density and mechanical characteristics of MT-YBCO materials. The high importance of twins in the Y123 structure of MT-YBCO for attaining high critical currents has been demonstrated. The influence of the starting materials on size and distribution of Y211 phase in MT-YBCO structure, which in turn affects the amount and distribution of microcracks and twins in the Y123 matrix of MT-YBCO has been revealed.

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