

Superconducting properties of GdBCO coated conductors with high-pressure oxygenation

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Abstract. Signs of overdoping were observed on the superconducting $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (GdBCO) layers of commercially produced coated conductors (CC) after a re-oxygenation through the thin (2 μm) silver layer at oxygen pressures of 100-160 bar, and 600-800 °C. An increase in the charge carrier density $n_{\text{H}}(100 \text{ K})$ up to $7.86 \times 10^{21} \text{ cm}^{-3}$, a decrease in the c -lattice parameters of GdBCO down to 1.1715(5) nm, a peak in the normalized resistivity close to the transition temperature are compatible with an increase of oxygen doping level up to $p=0.1740$. Consequently, the self-field critical current density (J_{c}) at 77 K increased by 21.5% to $J_{\text{c}} = 2.7 \text{ MA/cm}^2$ after reoxygenation at 160 bar oxygen at 800 °C for 3 h. At 5 K in the self-field, J_{c} of this sample reached 30.2 MA/cm^2 . Its superconducting GdBCO layer was characterized by the parameter $c=1.1727(1) \text{ nm}$, the superconducting transition temperature $T_{\text{c}}=92.63 \text{ K}$, the charge carrier density $n_{\text{H}}(100 \text{ K})=7.3 \times 10^{21} \text{ cm}^{-3}$, and the oxygen doping of its CuO planes was $p=0.1727$.

1. Introduction

Several authors have shown in the past that the critical currents can be enhanced through oxygenation at high oxygen pressure PO_2 [1, 2]. Specifically, it has been shown that through a post oxygenation process at a pressure of 100 bar for 12 h at 450 °C in MT-YBCO (melt textured YBCO) ceramics with 30 wt.% of the Y_2BaCuO_5 secondary phase, and previously saturated with oxygen at a pressure of 1 bar at 450 °C for 120 h, the critical current density of the material could be increased from 0.6×10^5 to $1.2 \times 10^5 \text{ A/cm}^2$ at 77 K in the self-field. The authors explained the increase in the critical current density by an increase in the density of dislocations and stacking faults.

Other authors also investigated the high PO_2 annealing process of melt-textured-grown



YBCO (MTG-YBCO) [3 – 6] and established the conditions of oxygenation of MTG-YBCO at PO_2 values as high as 160 bar and 800 °C. A key result was that the twin boundary density is enhanced and the microcrack density decreased when oxygenation is performed at such high PO_2 values due to a "smoother or less stressful" penetration of oxygen into the Y123 structure. As a consequence, the critical current density and its anisotropy may be modified.

Besides the modification of the microstructure, post-annealing with oxygen the YBCO materials has the potential to strongly modify the critical currents because the overdoped state can be reached [7, 8]. This is particularly true in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y123) thin films and coated conductors where it has been shown that the oxygenation process is quite complex [9, 10]. For instance, it has been shown that when Y123 films are heated under oxygen partial pressure of 1 bar via a Ag surface decoration layer at 280-550 °C, its structure is more easily overdoped, even if the efficiency of this process depends on the microstructure of the films when they are grown through different methodologies [7]. The key point of reaching the overdoped state, which can be quantified by measuring the carrier concentration at the normal state by means of Hall effect, is that the vortex pinning energy is enhanced at the quantum critical point p^* and so record values of critical current densities may be reached [7, 8].

It is worth to note that the overdoping efficiency in enhancing the pinning energy is even reinforced when artificial pinning centers are included [8, 11].

Oxygen non-stoichiometry behavior of $\text{REBa}_2\text{Cu}_3\text{O}_y$ (RE123: RE= Nd, Sm, Eu, Gd, Dy, Ho and Y) compounds have been precisely determined by thermogravimetric measurements [12]. It was shown that thermodynamic quantities of oxygen varied with RE element, as well as relationship between T_c and oxygen content is strongly dependent on the RE species. The authors consider that critical current properties of RE123 can be optimized by precise control of oxygen content as well as selection of suitable RE elements. [12].

We have recently started to investigate high oxygen pressure treatments of GdBCO and EuBCO-BaHfO₃ Coated Conductors (GdBCO_CC and EuBCO_CC), previously oxygenated with standard treatments, in order to learn how to reach the overdoped state in these materials [13]. Variation of critical current density, superconducting transition temperature, charge carrier densities, c -lattice parameter and Auger spectroscopy studies indicate that under high oxygen pressures of 100 - 160 bar at 600 - 800 °C their structures can be overdoped and in some cases J_c has been increased [13] while strict correlations between amount of charge carrier density, c -axis lattice parameter variation and T_c were still not clearly established. In the present paper we report new measurements which strictly witness that high-pressure re-oxygenation of commercial GdBCO coated conductors (GdBCO_CC) can lead to an increase in the critical current density, a decrease of c -axis parameter of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ due to overdoping, and increase of charge carrier density. We demonstrate that the control of the oxygenation kinetics is essential to maximize the superconducting performance of the coated conductors.

2. Experimental

2.1 Initial samples preparation, high pressure equipment and regimes of oxygenation

The copper layer of commercially produced GdBCO_CC by Fuijkura Ltd (model number FYSC-S12) was chemically etched for 10 s in $\text{HCl}:\text{H}_2\text{O}_2=1:1$. Then 4×4 mm samples were cut with care from the same tape with architecture (from top to bottom): Ag (2 μm)/GdBCO (1.8 μm)/CeO₂ (700 nm)/MgO/Y₂O₃/Al₂O₃/Hastelloy (75 μm). The critical current density at 77 K was measured for each sample after this process to determine if the samples deteriorated during the etching process or not.

A specially designed high-pressure oxygenation tubular furnace was used for this study. The gas oxygen pressure was increased up to 100 bar or 160 bar before heating and samples were then heated up to 600 or 800 °C with the rate 5 °C/min at the specified pressure and then held under the high pressure and temperature for 3 - 12 h. After the holding time was completed, the heater was switched off. During the cooling of the furnace to room temperature, the oxygen pressure either decreased spontaneously due to the decrease in the temperature in the furnace (Mode of oxygenation 1) or was maintained at the same specified pressure level (Mode of oxygenation 2).

2.2 Characterisation of the materials

The critical current density, J_c , at 77 and 5 K before and after high-pressure high-temperature oxygenation was determined by SQUID magnetometer (Quantum Design) by measuring the $m(H)$ hysteresis loop with the magnetic field applied perpendicular to the sample surface. Afterwards, the substrate residual magnetic moment was subtracted from the measurement by measuring the substrate without the superconducting layer and renormalizing this value to the area of the sample. Finally, the Bean critical state model was used to obtain the critical current density at each applied magnetic field. Transition temperatures, T_c , were estimated using transport measurements (by Van der Pauw technique). Charge carrier density, n_H , was estimated from the Hall effect measurements, also using the Van der Pauw technique at 100 K by Quantum Design PPMS. Before the Hall effect measurements, the Ag layer was etched away from the surfaces of the small samples by immersing them in $\text{NH}_3:\text{H}_2\text{O}_2:\text{MeOH}=1:1:5$ solution. The degree of oxygen doping, p , of the CuO_2 planes was estimated from the relationship $1 - T_c/T_{c, \text{max}} = 82.6(p - 0.16)^2$ with $T_{c, \text{max}} \approx 94$ [7]. Charge carrier density n_H , was used to determine whether the sample is underdoped or overdoped, according to which p value was assigned. The resistivity curve and transition temperatures, T_c , were also determined by the PPMS Quantum Design system using the Van der Pauw technique.

X-ray diffraction patterns obtained using Bruker-AXS, model A25 D8 Advance high resolution diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) were used to estimate the c -parameters of superconducting $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ layer. The range of investigated angles was $2\theta = 20\text{--}120^\circ$, the scanning step was 0.02° , and the acquisition time at one point was 2 s. The obtained diffractograms were refined by the Rietveld method [14].

3. Results and discussions

Table 1 shows the regimes of re-oxygenation, the results of c -parameter of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ layers and their superconducting characteristics. Sample "A" in Table 1 is a typical reference sample to characterise c -parameter, transport T_c , and charge carrier density n_H of the GdBCO_CC before re-oxygenation. For each small GdBCO_CC sample, before the re-oxygenation J_c at 77 K was determined. Figures 1a, b demonstrate variation of normalized J_c in self field at 77 K and 5 K after re-oxygenation under 100 bar at 600 °C and 160 bar at 800 °C vs. dwell time relative to baseline values for each sample before re-oxygenation. The behaviour of temperature dependence of the resistivity and the normalized resistivity estimated by transport measurements is shown in Fig. 2, where the overdoped state corresponds to values higher than "1", and the underdoped state corresponds to values lower than "1" [15]. An increase in normalized resistance before the superconducting transition is considered evidence of overdoping.

Table 1. Regimes of oxygenation (oxygen pressure, p , maximal heating temperature, T_s , holding time at maximal temperature, τ) and J_c in 0 T field at 77 and 5 K before and after re-oxygenation; transport T_c , $n_H(100\text{ K})$, and c -parameter after re-oxygenation.

No	$p(\text{O}_2)$, bar	T_s , °C	τ , h	Mode of oxyge- nation 1 or 2	J_c (0 T)*, MA/cm ²				c -para- meter, nm	n_{H} (100 K), ×10 ²¹ cm ⁻³	T_c , K
					at 77 K		at 5 K				
					Before	After	Before	After			
A	Reference sample for c , T_c and n_{H}				2.57	-	-	-	1.1735(1)	6.55	92.58
1	100	600	3	1	2.04	2.22	24.79	26.19	1.1715(5)	6.50	92.72
2	100	600	6	2	2.14	2.49	24.98	28.26	1.1718(8)	7.86	92.79
3	100	600	12	1	2.10	2.42	-	28.25	1.1720(6)	7.73	-
4	160	800	3	1	2.12	2.70	-	30.22	1.1727(1)	7.30	92.63
5	160	800	6	1	1.87	2.29	23.14	26.06	1.1725(3)	6.74	92.35
6	160	800	12	1	1.79	1.11	22.73	11.95	1.1724(8)	3.25	92.63

*The J_c at 5 K for Samples 3 and 4 before re-oxygenation was not determined because of the SQUID

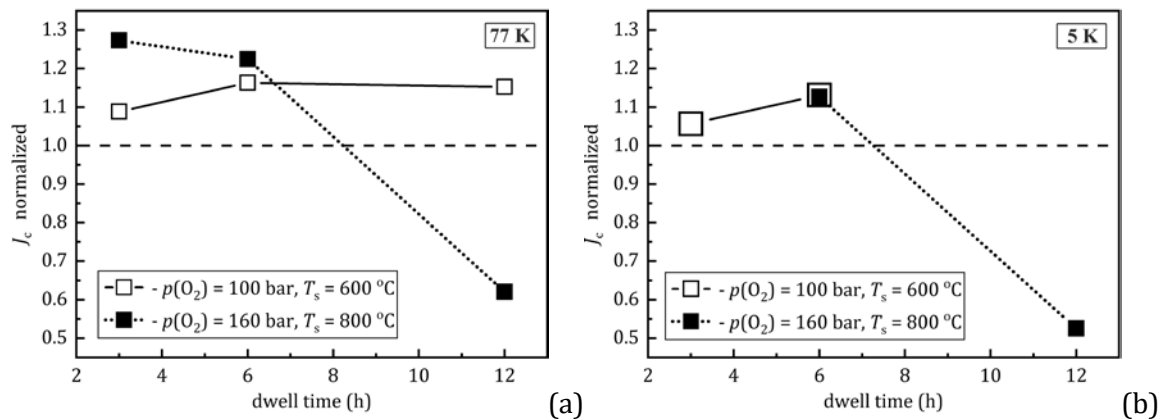


Figure 1. Normalized critical current density J_c in 0 T field after re-oxygenation under 100 bar at 600 °C and 160 bar at 800 °C vs. dwell time at 77 K (a) and 5 K (b) relative to baseline values for each sample before re-oxygenation.

The decrease in c -parameters of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and the increase in charge carrier density depending on dwell time shown in Fig. 3a witness about the oxygen doping conditions of the $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure by the high-pressure oxygenation. Figure 3b presents transition temperature, $T_c(\text{K})$, charge carrier density at 100 K, $n_H/10^{21}(\text{cm}^{-3})$, and estimated doping, p , after re-oxygenation under 100 bar and under 160 bar O_2 .

Increase in critical current density (Table 1 and Fig. 1) was observed for all samples except the one sample oxygenated under 160 bar, at 800 °C for 12 h. For the sample oxygenated for 12 h additional peaks in the x-ray pattern were observed thus witnessing of the $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure partial decomposition. This can be the explanation of the critical current and charge

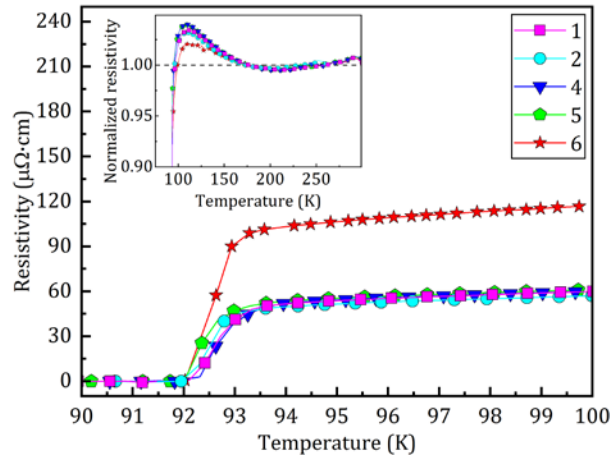


Figure 2. Resistivity, ρ , as a function of temperature for re-oxygenated GdBCO_CC samples with numbering according to Table 1. Inset shows the normalized resistivity estimated according the procedure described in [15]: $[\rho(T) - \rho(0)]/bT$, as a function of temperature for each sample where b is the slope and $\rho(0)$ is the intercept of the linear fit of each $\rho(T)$ for $T > 180$ K. The normalization is done for each temperature from 180 K upwards, meaning that from 180 K upwards all points should be 1 if the resistivity curve is linear in that region.

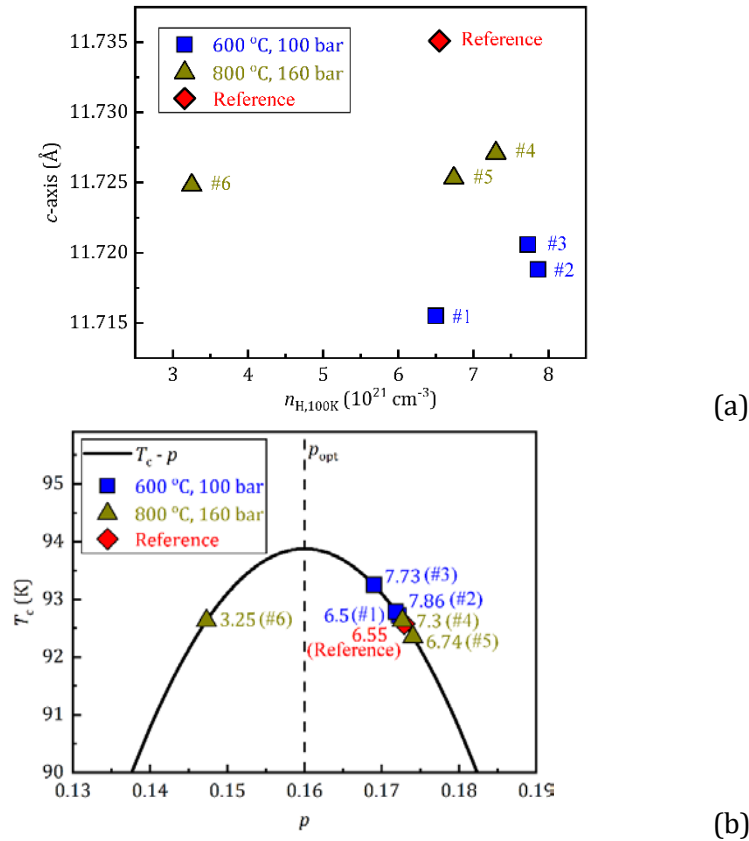


Figure 3. (a) – c -lattice parameters of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ after re-oxygenation vs. charge carrier density n_H estimated at 100 K; (b) – Transition temperature, T_c (K), charge carrier density at 100 K, $n_H/10^{21}$ (cm^{-3}) (values next to the data points), and estimated doping, p , for GdBCO_CC after re-oxygenation under 100 bar at 600 °C and under 160 bar O_2 at 800 °C. The c -parameter, T_c , n_H and p of the reference sample A are as well presented.

carrier density decrease (Table 1, Sample 6) and means that 12 h dwell at 800 °C occurred to be too long. While at lower temperature - 600 °C, dwell for 12 h did not result in decomposition of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and J_c of the superconducting layer was increased as compared to the initial value (Sample 3, Table 1). The best results for high pressure re-oxygenated GdBCO_CC were obtained after 6 h dwell under 100 bar at 600 °C (Sample 2, Table 1 and Fig. 1) and after 3 h dwell under 160 bar at 800 °C (Sample 4, Table 1 and Fig. 1). Consequently, the J_c at 0 T and 77 K, in the first case increased by 18% and in the second by 21.5% (Fig. 1a). The re-oxygenation under 160 bar at 800 °C for 3 h resulted in charge carrier density $n_H = 7.3 \times 10^{21} \text{ cm}^{-3}$ and doping of CuO planes $p=0.1727$; c -parameter decreased to 1.1727(1) nm (Fig. 3a, b and Table 1). The re-oxygenation under 160 bar at 800 °C for 6 h result in $n_H = 6.74 \times 10^{21} \text{ cm}^{-3}$ and $p=0.1741$; c -parameter decreased to 1.1725(3) nm (Fig. 3a, b, Table 1). The re-oxygenation under 100 bar at 600 °C for 6 h result in the highest $n_H = 7.86 \times 10^{21} \text{ cm}^{-3}$. Its $p=0.1719$ and c -parameter decrease down to 1.1718(8) nm, its $J_c(0 \text{ T}, 77 \text{ K})$ increased by 14% and $J_c(0 \text{ T}, 5 \text{ K})$ by 11% (Fig. 3a, b, Table 1). The reference sample was overdoped as well with $p=0.1730$. Analysing the obtained results we can conclude that in the commercial GdBCO_CC with $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ layer of 1.8 μm thick, $J_c(0 \text{ T}, 77 \text{ K})$ varied from 1.79 to 2.57 MA/cm². The 3 h long high pressure re-oxygenation though the silver layer under 160 bar at 800 °C allowed to increase $J_c(0 \text{ T}, 77 \text{ K})$ by 21.5% (up to 2.7 MA/cm²), its J_c at 5 K was 30.22 MA/cm². The maximum doping level of Gd123 it was achieved in this high pressure oxygenation study was $p=0.1741$.

Conclusions

As a result of the present study, for the first time it was convincingly demonstrated that the high pressure-high temperature (HP-HT) oxygenation under 100 and 160 bar pressure at 600 and 800 °C temperature is the way for further essential increase in critical current density of GdBCO coated conductors. It has been shown that the increase in critical current density is due to overdoping by oxygen and thus due to an increase of charge carrier density in superconducting layer (about what the value of Hall effect was witnessed). The increase of the levels of overdoping states of superconducting layers after HP-HT oxygenation were as well confirmed by reduction of their c -parameters and by somewhat increase in normalized resistivity of the samples before sharp superconducting transitions. It was found that the HP-HT oxygenation is possible through the thin silver coating that protects the GdBCO protect GdBCO layer from decomposition when keeping in air.

As a result of HP-HT oxygenation, the maximum achieved doping level for the Gd123 layer was $p=0.1741$ (its J_c increased by 18.3% at 77 K and reached 2.29 MA/cm²) and the largest increase in J_c (by 21.5% at 77 K) was observed for the Gd123 layer with $p=0.1727$, which demonstrated $J_c(0 \text{ T}, 77 \text{ K})=2.70 \text{ MA/cm}^2$ and $J_c(0 \text{ T}, 5 \text{ K})= 30.22 \text{ MA/cm}^2$.

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