Oxygenation mechanism of TSMG YBCO Bulk Superconductor

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Abstract: For the first time isothermal thermogravimetric (TG) measurements of oxygen diffusion in to melt processed YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{y}/Y\textsubscript{2}BaCuO\textsubscript{5} (Y123/Y211 or YBCO) bulk samples were conducted in the temperature range 350 – 800 °C. It is shown that the real time to a full sample oxygenation is much shorter than the calculated one assuming the bulk oxygen diffusion along the a/b-planes. It means that the diffusion distances in the oxygenated samples were much shorter at all temperatures of oxygenation then the halve sample size along the a/b-plane (0.1 cm). Estimated diffusion distances correspondent well with the spacing of the cracks formed during oxygenation. The kinetic law of virgin oxygenation at 350 and 400 °C is changed during oxygenation and observed deviation from the typical parabolic dependence of the sample weight on time of isothermal oxygenation was related to oxygenation cracking during the sample oxygenation. The performed microstructural analysis of the samples studied confirmed that the change of oxygenation kinetics is accompanied with cracking. Developed oxygenation cracks along the \{100\} (c-cracks) and \{001\} (a/b-cracks) type planes play a crucial role in shortening the oxygenation time of single-grain TSMG YBCO bulk superconductors.

1. Introduction

The Top-Seeded Melt-Growth (TSMG) process is now applied as a basic technology for production of single-grain YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{y}/Y\textsubscript{2}BaCuO\textsubscript{5} (further Y123/211 or YBCO) bulk superconductors for practical applications [1-4]. Their superconducting and mechanical properties can be improved by applying knowledge about the relationship between their microstructure and properties. Mainly the refinement of pinning centers to nanoscale size, the homogeneity of secondary phase particle distribution in the superconductor as well as the control of cracking associated with oxygenation are now under investigation [5-9]. The presence of oxygenation related cracks has been confirmed by microstructural observations and mechanisms of their formation were proposed [10, 11]. So far, only very few experiments of oxygen diffusion kinetics into Y123/211 bulks were performed [12]. In this paper we present thermogravimetric (TG) measurements of oxygen diffusion in to melt processed bulk samples and we relate the measured TG data with the supposed oxygenation mechanisms.
2. Experimental

Prismatic samples of bulk superconductors were cut out, with the prism walls parallel to the \{100\} planes and cross sections 2 x 2 mm with a typical mass of 2 mg, from non-oxygenated as grown TSMG YBCO pellets and used for oxygenation experiments. The samples were extracted from the inner part of the selected pellets in order to warranty the minimum oxygen content. Thermogravimetric measurements were conducted on SETARAM thermogravimeter with a sensitivity of 0.01 mg, just a 0.2% of the maximum expected mass increasing. The weighted samples were hanged on scales and treated in pure oxygen. Heating and cooling rate was 20 °C per minute. Changes of the sample weight were recorded along the whole isothermal dwell. The microstructure of the sample was studied by polarized light microscope after polishing or etching in the solution of 1 wt % HCl in ethylalkohol.

3. Results and discussion

The thermogravimetric records of an isothermal oxygenation at different temperatures performed on the samples of similar weight (table 1) are in figure 1. At higher temperatures of oxygenation, it was possible to determine the time to full oxygenation and the increase of the sample weight (weight gain) to the full oxygenation (table 1). The theoretical time of oxygenation can be calculated from the known data of oxygen diffusion in Y123 phase. As the diffusion rate in the c-direction is very small [13] practically only oxygen diffusion in the a/b-plane contributes to the sample weight gain. Neglecting the in-plane anisotropy effect, it is reasonable to consider the diffusion as a two-dimensional process. However, simplification to a one-dimensional diffusion is a good way to obtain
the order of magnitude of the timing. The continuity equation for the oxygen deficiency at a constant temperature is, so, given by the

Table 1. $T$ - oxygenation temperature, $G$ - starting weight of the measured samples, $SGFO$ – measured sample weight gain to full oxygenation, $tTGFO$ – measured time to full oxygenation, $D$ - oxygen diffusion coefficient, $\delta$ - equilibrium oxygen stoichiometry in YBa$_2$Cu$_3$O$_{\delta}$ at oxygenation temperature, $C_s$ - equilibrium oxygen atomic fraction, $\delta_x$ - expected oxygen stoichiometry and atomic fraction in the middle of the sample, $C_o$ - atomic fraction of oxygen in the as grown sample ($\delta_o$ = 6.1, $C_o$ = 0.5041), $t$ - time of oxygenation in the Fick’s equation, $tcFO$ - calculated time to full oxygenation, $x_{TG}$ - diffusion distance calculated from the time to full oxygenation measured by TG experiment.

| $T$ [$^\circ$C] | 350   | 400   | 500   | 600   | 700   | 800   |
|----------------|-------|-------|-------|-------|-------|-------|
| $G$ [g]        | 0.1936| 0.2314| 0.2140| 0.2242| 0.231 | 0.2368|
| $SGFO$ [mg]    | -     | -     | >10x10$^4$ | $>7x10^4$ | 2x10$^4$ | 1.5x10$^4$ |
| $tTGFO$ [s]    | -     | -     | $>10x10^4$ | $>7x10^4$ | 2x10$^4$ | 1.5x10$^4$ |
| $D$ [cm$^2$s$^{-1}$] | 3.076 x 10$^{-12}$ | 1.711 x 10$^{-11}$ | 2.720 x 10$^{-10}$ | 2.29 x 10$^{-9}$ | 7.502 x 10$^{-9}$ | 4.95 x 10$^{-8}$ |
| $\delta$       | 7     | 7     | 6.8   | 6.45  | 6.28  | 6.16  |
| $C_s$          | 0.5385| 0.5385| 0.5312| 0.5181| 0.5114| 0.5066|
| $\delta_x$     | 6.91  | 6.91  | 6.73  | 6.415 | 6.262 | 6.154 |
| $C_x$          | 0.5352| 0.5352| 0.5287| 0.5167| 0.5107| 0.5063|
| $(C_sC_o)/C_sC_o$ | 0.09593 | 0.09593 | 0.09225 | 0.10000 | 0.09589 | 0.12000 |
| $x/2\sqrt{Dt}$ | ~0.1  | ~0.1  | ~0.1  | ~0.1  | ~0.1  | ~0.1  |
| $tcFO$ [s]     | 8 x 10$^{10}$ | 1.5 x 10$^{10}$ | 9.2 x 10$^8$ | 1.0 x 10$^8$ | 3.3 x 10$^7$ | 5.0 x 10$^6$ |
| $x_{TG}$ [\mu m] | -     | -     | 10.4  | 25.3  | 24.5  | 54.5  |

Fick’s second law

$$\frac{\partial N_A}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial N_A}{\partial x} \right]$$  \hspace{1cm} (1)

where $N_A$ is the mole fraction of atom A, $x$ is the distance, $t$ is time and the diffusion coefficient $D$ is related to the activation energy $Q$ by the formula

$$D = D_0 e^{\frac{-Q}{k_BT}}$$  \hspace{1cm} (2)

where $D_0$ is a pre-exponential factor, $k_B$ is Boltzman’s constant and $T$ is absolute temperature.

Even though it is known that $D$ varies with composition, it is useful to obtain quick but approximate solution to Fick’s second law. Such a solution assumes that $D$ is constant at a given temperature and does not vary with composition. Grube’s solution is as follows:

$$\frac{C_s - C_x}{C_s - C_o} = \text{erf} \left[ \frac{x}{2\sqrt{Dt}} \right]$$ \hspace{1cm} (3)

where $C_s$ is the surface concentration, $C_x$ is the concentration at the some distance $x$ from the surface, $C_o$ is the initial concentration, $x$ is the distance in centimeters from the surface at which $C_x$ is measured, $D$ is the diffusion coefficient in square centimeters per second and $t$ is the time in seconds.
of the diffusion treatment; “erf” means the error function, where \( \text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_{0}^{y} e^{-\xi^2} d\xi \). Because the concentration appears in a ratio, it is possible to use mole fraction, atomic fraction, or even weight percent. We took \( C_i \), as oxygen atomic fraction in \( \text{YBa}_2\text{Cu}_3\text{O}_\delta \) corresponding to the equilibrium oxygen concentration at given temperature (table 1), \( C_o \) as the oxygen atomic fraction in the inner part of the as grown sample (taken \( x = 6.1 \)) and we calculated the time of oxygen diffusion, which is necessary to increase the oxygen concentration in the middle of the sample (\( x = 0.1 \text{ cm} \)) to the 90 % of the surface oxygen stoichiometry \( \delta \) corresponding to the equilibrium values for the working temperature. The diffusion coefficients were calculated using equation (2) with \( D_o = 0.033 \text{ cm}^2\text{s}^{-1} \) and \( Q = 1.24 \text{ eV} \) from \[14\]. The measured times to full oxygenation were compared with those predicted. The estimated times, \( t_{\text{CF0}} \) in table I, are higher than the measured ones in about 3 or 4 orders of magnitude (table 1). It means that the diffusion distances in the oxygenated samples were much lower at all temperatures of oxygenation than the halve sample size along the a/b-plane (0.1 cm). The discrepancy between measured and calculated oxygenation behavior can be explained by the oxygenation induced cracking. This cracking is associated with tensile stresses in the oxygenated layer caused by shortening of the lattice parameters with increasing oxygen content in the \( \text{YBa}_2\text{Cu}_3\text{O}_\delta \) phase (Fig. 3.) \[15,16\]. The strain \( \varepsilon \) caused by the difference in the c- and (a+b)/2 lattice parameters between the core tetragonal material and the oxygenated layer is directly proportional to the tensile stress induced in the oxygenated layer and is responsible for formation of parallel array of cracks in the oxygenated layer with spacing \( \lambda \)

\[ \lambda = 5.6\{(K_{\text{IC}}^2d/(E\varepsilon)^2)^{1/2} \]  

with the mode I fracture toughness \( K_{\text{IC}} \), thickness \( d \) of the oxygenated layer, Young’s modulus \( E \) and strain \( \varepsilon \) \[9\]. Therefore, we calculated approximate diffusion distances \( x_{\text{TG}} \) using the times to full oxygenation measured by thermogravimetric experiments (table 1). They are in the micrometer range and increasing with the oxygenation temperature. This behavior seems reasonable as the tensile stresses in the oxygenated layer are decreasing with the oxygenation temperature what causes higher crack spacing at higher oxygenation temperatures.

According to analysis of oxygenation cracking done in \[9\] the cracking under the tensile stresses in the oxygenated surface layer starts in the early stages of oxygenation. After some bulk diffusion of oxygen into the sample the first cracks parallel to a/b- and a/c-planes start to form when the thickness of the oxygenated layer is higher than critical. When the cracks are already formed, the mechanism of oxygenation changes from pure bulk diffusion along the a/b-plane to the combination of oxygen flow along the a/b- and a/c-cracks, short distance oxygen diffusion and crack propagation. This change in mechanism can be seen on the TG curves as a sudden increase in the rate of the sample weight gain \[12\]. In our measurements we can evidently detect the deviation from the shape of the curves typical for the parabolic diffusion law only at 350 and 400 °C. TG curves at these temperatures start with concave shape and only later their contour tends to approach a parabolic diffusion law \[17\]. Apparently the behaviour measured in the early stages of oxygenation can be related to bulk oxygen diffusion followed by formation of the first cracks as it was observed in \[9\]. Additional evidence is found in the second or third oxygenation TG curves corresponding to oxygenations realized when the network of cracks is previously developed as shown in reference \[12, 17\]. The TG curves at higher temperatures (800, 700, 600 and 500 °C) do not exhibit great deviation from the one-dimensional parabolic law of diffusion in spite of that they also needed much shorter times to full oxygenation than would relate to the bulk oxygen diffusion and therefore cracks should shorten diffusion distances also in them. We can suppose that cracks in these samples were formed during the heating stage (20 °C per minute in the oxygen atmosphere) and at the isothermal oxygenation, where the weight of the samples was recorded, they were in the stage of oxygenation where the samples were already fragmented into small regions which were oxygenated by bulk oxygen diffusion.
Microstructure observation of the oxygenated samples proved that the samples oxygenated at 350 °C and 400 °C are not fully oxygenated (figure 2.) as well as inhomogeneous oxygenation along the cracks parallel to the a/b- and a/c-planes developed during oxygenation. The samples oxygenated at 400 °C showed cracks along a/b- and a/c-planes in the oxygenated regions (brighter) as can be observed in figure 2.

![Figure 2. Oxygenation at 400 °C. Cracks along a/b- and a/c-planes in the oxygenated regions (brighter) can be observed.](image)

Oxygenation at 700 °C resulted in the formation of macrocracks and microcracks parallel to the a/b-plane. Brighter band along the a/b-macrocrack was created during cooling from 700 °C by further oxygenation.

![Figure 3. Oxygenation at 700 °C. Macrocrack and microcracks parallel to a/b-plane. Brighter band along the a/b-macrocrack was created during cooling from 700 °C by further oxygenation.](image)
higher temperatures were fully oxygenated and contained cracks with higher spacing that at lower oxygenation temperatures and no a/c- cracks in the samples oxygenated at 700 °C and 800 °C (figure 3.).

4. Conclusions

The analysis of conducted thermogravimetric measurements of oxygenation of the samples selected from as grown YBCO TSMG bulk superconductors confirmed that the bulk oxygen diffusion cannot explain very short times to the full sample oxygenation. Change in sample weight gain kinetics was detected and is ascribed to the formation of oxygenation cracks. The formation of oxygenation cracks in the a/b- and a/c-planes was confirmed by microstructural observations. The oxygenation cracks are significantly shortening the oxygen diffusion distances what allows oxygenation of the TSMG YBCO bulk superconductors in reasonable times.

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