Kinetics characterization of YBCO thin films growth on LAO (100) single crystals by the TFA-MOD reaction.

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Abstract.
We have studied in detail the kinetics parameters of the YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) thin films growth on LaAlO$_3$ (100) single crystals by the TFA-MOD method, using an i.n-situ fluoride selective electrode. We have considered: temperature, flow carrier gas rates and water partial pressure dependences in the reaction. Kinetics curves show that it exist an intermediate step before the YBCO formation. This step, which starts during the heating ramp (~400ºC) consists in a partial elimination of F from the BaF$_2$ precursor to forms an oxyfluoride intermediate compound. The total YBCO formation appears at temperatures as higher as 700ºC. We have found that at low flow carrier gas rates, the reaction is controlled by diffusion mechanisms and the apparent order of YBCO formation is n = 1 respect to the stirring rate, but at higher flow rates the YBCO formation is controlled chemically, then the apparent order is zero. The apparent reaction order of YBCO formation respect to the water pressure also has been studied.

1. Introduction

Non vacuum techniques such TFA-MOD are relatively simple and inexpensive. Nevertheless, the coexistence of barium and organic compounds during the pyrolysis process could form barium carbonate, which blocks the formation of the YBCO phase and decreases superconducting properties dramatically. For this reason, A. Gupta et al. [1] developed the commonly called TFA-MOD method, which requires employing trifluoroacetates salts as a fluor source to form barium fluoride that is more stable and easier to decompose than barium carbonate. To date, several studies to unfold the kinetics mechanism of the BaF$_2$ decomposition have been made [2 - 5] and all of them propose the following mechanism:

\[
\text{BaF}_2 + \text{H}_2\text{O} \rightarrow \text{BaO} + 2\text{HF} \quad (1)
\]

\[
2\text{BaO} + \frac{1}{2} \text{Y}_2\text{Cu}_2\text{O}_5 + 2\text{CuO} + x\text{O}_2 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_x \quad (2)
\]

Where, Y$_2$Cu$_2$O$_5$ is produced during heating from precursor oxides accoring the following reaction:

\[
\text{Y}_2\text{O}_3 + 2 \text{CuO} \rightarrow \text{Y}_2\text{Cu}_2\text{O}_5
\]

Nevertheless, we have shown in a precedent work [7] that at 575 ºC the precursor films need about 3-4 hours for to arrive at the equilibrium ratio F/Ba = 1, which probably corresponds to the formation of an intermediate amorphous oxyfluoride phase with stoichiometry Ba$_{0.5}$F$_{1.5}$, without the formation of detectable YBCO. In this work we assume that after an optimal pyrolysis process the organic compounds decompose mainly in a mix of CuO, Y$_2$O$_3$, BaF$_2$ and probably some traces of Ba$_{1-x}$Y$_x$F$_{2+y}$ as observed by M.Yoshizumi et al. [6].

In this work, we discuss some experimental data that assigns two different steps for the YBCO formation by TFA-MOD. The first step may be attributed to the formation of an oxyfluoride compound and the second step is attributed to the tetragonal YBa$_2$Cu$_3$O$_{6+x}$ thin film growth, following the reactions:

\[
\text{BaF}_2 + (1-x)\text{H}_2\text{O} \rightarrow \text{BaO}_x\text{F}_{2-x} + (2-2x)\text{HF} \quad \text{with } x \sim 0.5 \quad (1')
\]

\[
2\text{BaO}_x\text{F}_{2-x} + \frac{1}{2} \text{Y}_2\text{Cu}_2\text{O}_5 + 2\text{CuO} + x\text{H}_2\text{O} + y\text{O}_2 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{x+y} + 4x\text{HF} \quad (2')
\]

Where the YBCO formation is controlled by the second step, which corresponds to the elimination of the second fluoride atom from the BaF$_2$ molecule.

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2. Experimental details

A ready precursor film was obtained for the study of the BaF$_2$ decomposition and tetragonal YBCO formation mechanisms as is described in a precedent work [7]. It was held in a tubular furnace with a quartz tube under the following variable conditions: temperature, total gas flow rate and water partial pressure. Oxygen concentration was fixed at 200 ppm and the carrier gas was nitrogen at ~ 1 bar of total pressure. Heating ramp was set at 1500ºC/h.

Total flow rate and oxygen partial pressure were stabilized inside the quartz tube using mass flow controllers. Different partial water pressures, were obtained by bubbling the carrier gas through two gas-washers inside a water bath using different temperatures. The in-situ fluoride characterization to monitor fluoride decomposition reactions rate was carried out through a fluoride selective electrode Mettler-Toledo, coupled to the outgoing mixture of gases at the exit of the quartz tube.

3. Results and discussion

3.1. Flow rate influence

Several reactions were carried out with different total flow rates at 795 ºC and for a water vapour pressure of 7 hPa at an oxygen concentration of 200 ppm. Figure 1 show the concentration of fluoride produced by the BaF$_2$ decomposition during reaction for green films prepared with the pyrolysis conditions described above. As we can see, there is an increase of the total fluoride signal at the end of reaction for flow rates below 1.2 $10^{-2}$ m · s$^{-1}$. Nevertheless, total fluoride signal stabilizes at higher flow rates values. So, flow rates of 2.4 and 7.2 $10^{-2}$ m · s$^{-1}$ show apparent fluoride loses, because the initial fluorine mass is about the same for the different precursor films considered. We have attributed these loses to retentions by the YBCO thin films and quartz tube [7]. So, there is a progressive accumulation of HF molecules on the surface of the YBCO films during growing at low total flow rates. HF molecules produce a boundary layer (Nernst layer) that decreases the elimination of fluorine by the low flow rate of the carrier gas. In these experimental conditions (below 1.2 $10^{-2}$ m · s$^{-1}$) the reaction rate is controlled by a diffusive mechanism that may produce additional porosity and/or cavities during the film growth. Moreover, significant not oriented quantities of BaCuO$_2$ and CuO were found by X ray diffraction analysis after reaction, indicating that reaction of precursors is partially obstructed by the HF boundary layer. Detailed critical current properties have been shown in a recent publication [8]. So, the reaction rate is controlled by diffusion of HF molecules through the Nernst layer at low flow rates and the apparent order of YBCO formation is n=1 (see fig 2).

However, no additional fluoride was detected in the quartz tube and thin films at flow rates higher than 1.2 $10^{-2}$ m · s$^{-1}$. The stirring in the quartz tube is enough to eliminate the totality of HF from the interface reaction to the exit of the quartz tube. In these experimental conditions, the YBCO film growth rate does not depend on the total flow rate and the apparent order of YBCO formation versus total flow rate is n = 0. It is fairly likely that reaction have reached chemical control in high flow rate.

3.2. Partial water vapour pressure influence

We have explored the influence of the water pressure at the same constant parameters at 795 ºC in a chemically controlled regime for a total flow rate higher than 1.2 $10^{-2}$ m · s$^{-1}$, which is the limit of the diffusive-chemical control. Figure 3 shows the mass of fluoride detected by the sensor from the precursor film decomposition during reaction at 2.4 $10^{-2}$ m · s$^{-1}$ in function of the partial water pressure from 0.7 to 9 hPa. As we can see, the value of the first slope corresponding to the first steep of the fluoride formation, is constant from 2.7 to 9 hPa of partial water pressure. Then, the apparent
order of the oxifluoride formation respect to the water pressure is \( n=0 \) indicating that the reaction is controlled diffusively. Nevertheless, this first slope of the curves corresponding to the oxifluoride formation decreases substantially at 0.7 hPa, indicating that the oxifluoride formation rate decreases at very low water pressures, probably because the reaction pass to a mixed or chemically controlled regime. On the other wise, the second slope corresponding to the second steep shows a very wide curvature in the 0.7 hPa conditions. This curvature, could be due to a lost of the epitaxic growth quality of the YBCO thin layer as observed by X-ray diffraction pattern, pole figures and \( \mu \)-Raman analysis [8]. Deterioration of the superconducting properties was also observed at very low partial water pressures. Probably, that is due because the fluoride decomposition rate decreases exponentially with time if there are nucleation in the bulk of the films.

In another serie of experiments, we have analysed the curves at high partial water pressures. We have observed that the curves show irreproducible steps at water pressures higher than 19 hPa. The inset of Figure 3 shows three curves corresponding at three different thin films prepared at 23, 24 and 26 hPa of partial water pressure. It is interesting to note that the curves show a lot of small steps, which are irreproducible from an experiment to the other one. This behaviour was observed in partial water pressures from 19 to 26 hPa, which is the highest partial water pressure value obtained in our reactor. The formation of these steps indicates a change in the reaction mechanisms. Probably, there is formation of a water boundary layer (Nernst layer) which blocks the homogeneous fluoride diffusion. Probably, diffusion of HF through this water Nernst layer is very low at the beginning of reaction, but when the quantity of the HF molecules is big enough, the water layer is broken by the stirring rate of the carrier gas. Then, fluoride is desorbed and detected by the sensor giving a curve with steps.

We have explored the influence of different partial water pressures in the YBCO formation rate for the determination of the reaction order respect to the water pressure. As we have explained above, we have obtained curves within two different regimes in the YBCO formation, depending on partial water pressure values, for a constant total flow flux rate of the carrier gas of \( 2.4 \times 10^{-2} \) m \( \cdot \) s\(^{-1}\). In the first regime corresponding at low partial water pressures, the kinetics curves are continuous (Figure 1, 3). But the curves show a lot of irreproducible steps at higher water pressures (inset Figure 3). In these conditions, the reaction is partially controlled diffusively at high water pressure conditions (mixed control). Nevertheless, we have obtained curves without any steps for thin films growth at high partial water pressure, when we have increased the flow rate from \( 2.4 \times 10^{-2} \) m \( \cdot \) s\(^{-1}\) to \( 4.8 \times 10^{-2} \) m \( \cdot \) s\(^{-1}\). Increasing the stirring rate, probably the Nernst layer of water is eliminated by the carrier gas and the reaction is again totally controlled chemically.
In figure 4 we have plotted the logarithm of the reaction rate corresponding to the YBCO formation during the second steep, in front of the logarithm of the partial water pressure. We can observe that the reaction order of YBCO formation is $n=0.5$ for partial water pressures lower than 20 hPa. But, the apparent order of the YBCO formation is zero or negative for higher water pressure values. This result indicates that the YBCO formation is controlled chemically during water pressures lower than 20 hPa at a stirring rates of $2.4 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$. Nevertheless, when we increase the flow rate until $4.8 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$, keeping the same experimental conditions, the reaction rate increases and the value of the logarithm of the YBCO formation rate attains the extrapolated value expected in the curve obtained at $2.4 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$ of stirring rate with order $n=0.5$ (see open cercle in Fig. 4). So, the reaction appears in a diffusive or mixed control at partial water pressure higher than 20 hPa, but the YBCO formation attains again a chemical control when we increase the total flow rates.

4. Conclusions

There is another process prior to epitaxic formation of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ on LAO (100) single crystals, which can be associated to the loss of the first fluorine atom of BaF$_2$ to form an intermediate oxyfluoride compound with stoichiometry BaO$_{1-x}$F$_{2x}$. Moreover, this work also evidences the formation of a water boundary layer (Nernst layer) at high partial water pressures and low flow flux rates, i.e. at 795 °C, $2.4 \times 10^{-2} \text{ m} \cdot \text{s}^{-1}$ of total flux rate and a partial water pressures higher than 20 hPa. This water boundary layer could be eliminated by increasing the stirring rate of the carrier gas.

References

[1] Gupta A, Jagannathan R, Cooper E I, Giess E A, Landman J I, and Hussey B W 1988 Appl. Phys. Lett. 52 2077
[2] Araki T, Takahashi Y, Yamagiwa K, Iijima Y, Takeda K, Yamada Y, Shibata J, Hirayama T and Hirabayashi I 2001 Physica C 357-360 991
[3] Honjo T, Nakamura Y, Teranishi R, Tokunaga Y, Fuji H, Shibata J, Asada S, Izumi T, Shiohara Y, Iijima Y, Saitoh T, Kaneko A. and Murata K. 2003 Physica C 392-396 873
[4] Solovyov V F, Wiesmann H J, Wu L, Zhu Y, Suenaga M 2001 IEEE Trans. Appl. Supercond. 11 2939
[5] Solovyov V F, Wiesmann H J, Li-Jun Wu, Suenaga M and Feenstra R 1999 IEEE Trans. Appl. Supercond. 9 2 1467
[6] Yoshizumi M, Seleznev I, Cima M J 2004 Physica C 403 191
[7] Oscar Castaño and Salvador Piñol 2004 Supercond. Sci. Technol. 17 1415
[8] Puig T, Gonzalez J C, Pomar A, Mestres N, Castaño O, Coll M, Gázquez J, Sandiumenge F, Piñol S and Obradors X 2005 Supercond. Sci. Technol. 18 1141