J Therm Anal Calorim (2012) 108:597–603
DOI 10.1007/s10973-011-2044-1

Non-isothermal model-free predictions

Application to the formation of yttria from yttrium trifluoroacetate

Hichem Eloussifi · Jordi Farjas · Pere Roura · Mohamed Dammak

MEDICTA2011 Conference Special Chapter

Abstract Suitable thermal treatment of metal organic precursors is a key process to obtain oxide films. To this purpose, non-isothermal model-free predictions are specially suited. In this article we will explore the ability of these methods to provide an accurate prediction of the evolution of the decomposition of yttrium trifluoroacetate, a precursor used in the synthesis of YBaCuO superconducting thin-films. A good agreement has been obtained between the predicted and the measured reaction courses.

Keywords Isoconversional methods · Activation energy · Thermal analysis · Solid-state transformations · Kinetic predictions

Introduction

Chemical solution deposition (CSD) methods are low-cost, flexible, and scalable routes for the synthesis of advanced functional oxide thin-films [1–4]. CSD methods involve solution preparation, solution deposition, and thermal treatment to remove the organic species and to crystallize the material. Thermal treatment can be optimized by setting up a temperature program that involves isothermal stages to slow down the reaction at the critical steps and non-isothermal stages to reduce the duration of the whole process, thus improving the thin-film production. To this purpose, "model-free prediction methods" are especially suited [5] because they allow the 'prediction' of the evolution of a solid state transformation for a particular temperature program. This prediction is based on the kinetic parameters of the solid state transformation that can be determined from thermal analysis data using kinetic methods. Kinetic methods can be classified as model-fitting or model-free. While the first methods are based on the assumption that the transformation is ruled by a particular reaction mechanism, the second methods allow the kinetic parameters to be determined independently of the particular mechanism governing the transformation. Isoconversional model-free methods analyze the evolution of a given parameter at a given degree of transformation, α. The main advantages of using kinetic data from the isoconversional methods is twofold: (a) there is common agreement that isoconversional methods are among the most reliable kinetic methods [6, 7], and (b) they allow the prediction of the evolution to be done independently of the particular mechanism governing the transformation [8–10].

In this article, we will apply model-free prediction methods to the thermal decomposition of yttrium trifluoroacetate (Y-TFA). Y-TFA is a precursor used to synthesize yttria thin-films [11]. In addition, it has been mixed with other metal TFAs to fabricate high-performance YBaCuO superconducting films [2, 12]. Two main processes take place during thermal treatment of metal TFAs: calcination and firing [2]. During the calcination stage the precursor decomposes entirely and the organic part is completely removed. The firing stage, on the other hand, involves the decomposition of the metal fluorides to obtain the metal oxide. The calcination step is the process that limit the overall YBaCuO thin-film production [13, 14]. For instance, to obtain YBaCuO superconducting thin-film

---

H. Eloussifi · J. Farjas (✉) · P. Roura
GRMT, Department of Physics, University of Girona,
Campus Montilivi, E17071 Girona, Catalonia, Spain
e-mail: jordi.farjas@udg.cat

H. Eloussifi · M. Dammak
Faculté des Sciences de Sfax, Laboratoire de Chimie
Inorganique, Route de Soukra Km 3.5, BP 1171,
3000 Sfax, Tunisia

the decomposition step can be as long as 66 h [2]. During precursor pyrolysis, the precursor shrinks and a large amount of gases evolve. The gas escape rate during decomposition plays an important role in the formation of pores. Lowering the decomposition rate reduces porosity and improves film homogeneity which in turn enhances the material performance. For instance, it has been observed that porosity diminishes about 15% in samples pyrolized at 275 °C instead of 310 °C [12].

In the case of Y-TFA, its decomposition is a fast process that involves the highest mass loss and results in the formation of YF_3. But the formation of yttria from YF_3 is a slow process that involves two intermediate compounds (non-stoichiometric and stoichiometric yttrium oxyfluoride) [15, 16]. Predicting the reaction course for this two-step transformation represents a challenge for prediction methods.

Thermogravimetry (TG) is used to monitor the decomposition process. Scanning electron microscopy and X-ray diffraction are used to characterize the products at different stages of the transformation.

In the following, we will show that non-isothermal model-free prediction methods allow accurate enough predictions for both the calcination and the firing process. Therefore, they can be used to design more efficient thermal treatments for the fabrication of thin-films via CSD.

Model-free prediction methods

Model-free prediction methods rely on the kinetic parameters retrieved from thermal analysis [17]. Isoconversional methods allow the kinetic parameters to be determined without assuming any particular reaction mechanism, i.e., they are model-free. They are based on the determination of one or more of the system parameters (temperature, transformation rate,…) at which the same degree of transformation, α, has been reached for measurements performed at different constant temperatures (isothermal) or different heating rates (non-isothermal). In general, non-isothermal experiments are preferred [18] because they are easier and faster to perform and can explore a wider temperature range.

Isoconversional methods rely on the hypothesis that at a given α, the transformation rate is only a function of temperature [17, 19],

$$\left[\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}T^{-1}}\right]_{\alpha} = -\frac{E_{\alpha}}{R}, \tag{1}$$

where the subscript α indicates the degree of transformation, R is the gas constant, and E_{α} is the activation energy. Integration of Eq. 1 results in a transformation governed by a single mechanism where the rate constant, $k_{\alpha}(T) = A_{\alpha}\exp(-E_{\alpha}/\mathrm{RT})$, depends on α [5]. A variation of E_{α} with α corresponds to a thermally activated process whose energy barrier depends on the degree of transformation. Although, the solid state transformations that can be described by this model are scarce, it has been shown that the isoconversional hypothesis provides an accurate description for complex transformations (such as heterogeneous transformations, multi-step reactions, or transformations depending on parameters other than α and T) [18, 20–22]. In this context, Eq. 1 is an approximate relationship and E_{α} must be interpreted in terms of an apparent activation energy.

To design thermal treatments that combine isothermal and non-isothermal stages, we need to use prediction methods that can deal with an arbitrary temperature program $T(t)$. Two methods have been developed that are derived directly from Eq. 1 without any approximation: Roduit's method [9, 23, 24] and our own method [5]. Our method determines the time necessary to reach a degree of transformation α_j:

$$t_j = t_{j-1} + \frac{E_j}{R\beta_i}\left[p\left(\frac{E_j}{\mathrm{RT}_{j,i}}\right) - p\left(\frac{E_j}{\mathrm{RT}_{j-1,i}}\right)\right] \cdot \left[\int_{t_{j-1}}^{t_{j-1}} \exp\left(-\frac{E_j}{\mathrm{RT}(t)}\right)\mathrm{d}t\right]^{-1}, \tag{2}$$

where E_j is E_{α} when $\alpha = \alpha_j$, β_i is the constant heating rate of one of the experiments used in the isoconversional determination of the kinetic parameters, $T_{j,i}$ is the temperature at which a degree of transformation α_j is reached when the sample is heated at the heating rate β_i, and $p(x) \equiv \int_x^{\infty} \frac{\exp(-u)}{u^2}\mathrm{d}u$ is the temperature integral [10, 25]. Conversely, Roduit's method delivers the degree of transformation once a time interval Δt has elapsed:

$$\alpha(t+\Delta t) = \alpha(t) + A_{\alpha}f(\alpha)\exp\left(-\frac{E_{\alpha}}{\mathrm{RT}(t)}\right)\Delta t. \tag{3}$$

To apply Eq. 3 we need an isoconversional method that calculates $A_{\alpha}f(\alpha)$. We have used Friedman's method [26] because, in addition, it is exact within the framework of the isoconversional hypothesis, Eq. 1.

Experimental

Commercial high purity (Aldrich, 99.99%) yttrium trifluoroacetate $Y(CF_3COO)_3$, were analyzed by TG (Mettler Toledo model TGA851eLF thermobalance). Samples were placed inside uncovered alumina crucibles. The mass accuracy is 2 µg. High purity nitrogen, oxygen, and synthetic air were used. Humid atmospheres were obtained by bubbling the carrier gas in water at standard temperature and pressure (25 °C, 1 atm). XRD experiments were done in a D8 ADVANCE and SMART APEX diffractometers from Bruker AXS. SEM observations were performed in a

Zeiss DSM 960A scanning electron microscope operated at 20 kV. Samples were coated with a thin-film of gold to remove electrostatic charges.

Calcination

First, we will analyze the thermal decomposition of Y-TFA into YF_3 [15, 16]:

$$Y(OOCCF_3)_3 \rightarrow \; YF_3 + (CF_3CO)_2O + CO + CO_2. \qquad (4)$$

This process is a fast exothermic process that is responsible for the complete decomposition of the organic matter.

To perform Friedman's kinetic analysis, we have measured the evolution of the mass (TG) with temperature for six different heating rates ($1 \leq \beta \leq 40$ K/min). A flow rate of 40 mL/min of humid synthetic air was set. The mass of the samples was between 2.4 and 17 mg (the larger masses were used for experiments carried out at low heating rates). The degree of transformation extracted from the thermograms is plotted in Fig. 1. The result of the kinetic analysis is shown in Fig. 2, where the activation energy is seen to be fairly constant (variations below 10%). Consequently, the process can be approximately described as a single-step process with constant activation energy [27]. Note that this decomposition step takes place in a relatively short-time interval; therefore, the results are quite sensitive to experimental artifacts such as apparatus time response and inaccuracies of temperature related to the thermal lag [28]. These artifacts are especially relevant for the experiments performed at high-heating rates.

To check the self-consistency of our approach (Eqs. 1, 2, and 3), we have calculated the predicted evolution for the experiments used to determine E_α. The result is plotted as symbols in Fig. 1. The agreement between experimental data and the calculated evolution is quite good. Moreover, the small discrepancies between both predictions, Eqs. 2 and 3, are related to the decomposition of Y-TFA following an "acceleratory" or a "sigmoidal" reaction [5, 29, 30].

The goal is to slow down the decomposition. The duration of the decomposition, and therefore the transformation rate, can be controlled by heating the sample to a given isothermal step. The lower the temperature, the longer the duration of the decomposition. To this purpose, we can use a temperature program that consists of a heating ramp followed by an isothermal period. The prediction methods allow us to determine the temperature that will fit the desired duration for the whole decomposition stage.

As a test, we have calculated the predicted reaction course when the sample is heated at a constant heating rate of 10 K/min up to 250 and 280 °C and compare it to the experimental reaction course for this temperature program (Fig. 3). Actually, the non-isothermal predictions has been obtained using as temperature program, $T(t)$, the measured evolution of the temperature (dashed line in Fig. 3). From Fig. 3 one can state that both non-isothermal predictions correctly predict the time required for the transformation to reach completion. Notice that, for a temperature difference of 30 °C, the duration of the isothermal step to complete the transformation varies by a factor of nearly 6: from 1 h at 250 °C to 11 min at 280 °C. So, despite the strong dependence of the duration of the decomposition on the temperature, the non-isothermal prediction methods are able to provide an accurate result.

We have analyzed the XRD pattern of the solid residue (Fig. 4) after heating the sample up to 360 °C at a constant rate of 20 K/min, and after the thermal treatments ended with an isothermal step at 250 and 280 °C. From Fig. 4, we

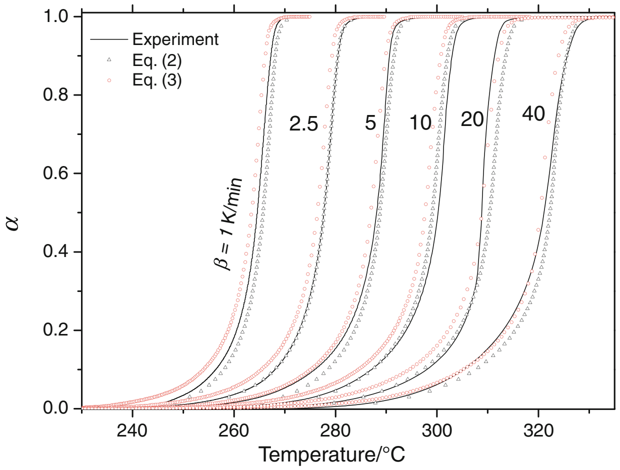

Fig. 1 *Solid line* evolution of the transformed fraction for the thermal decomposition of Y-TFA measured by TG at several heating rates, β. *Symbols* non-isothermal predictions (for the sake of clarity not all the calculated points have been plotted)

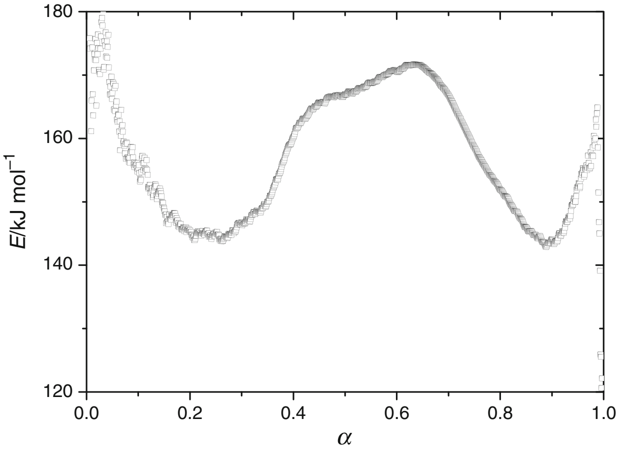

Fig. 2 Evolution of the activation energy with the degree of transformation derived from Friedman's isoconversional analysis of the thermal decomposition of Y-TFA (see Fig. 1)

have confirmed that the solid residue in all cases is YF_3, the expected solid product of reaction 4. Moreover, we have not observed significant differences between peaks widths, i.e., the grain (single crystalline domains) sizes are similar.

Finally, it has been shown that this decomposition is independent of the partial pressure of O_2 and H_2O [15]. The kinetic analysis has been carried out in humid air while the experiments represented in Fig. 3 have been done in dry air (Fig. 3a) and in dry N_2 (Fig. 3b). Despite the atmosphere differences, the prediction is still valid. This result confirms the independence of the decomposition kinetics on the atmosphere.

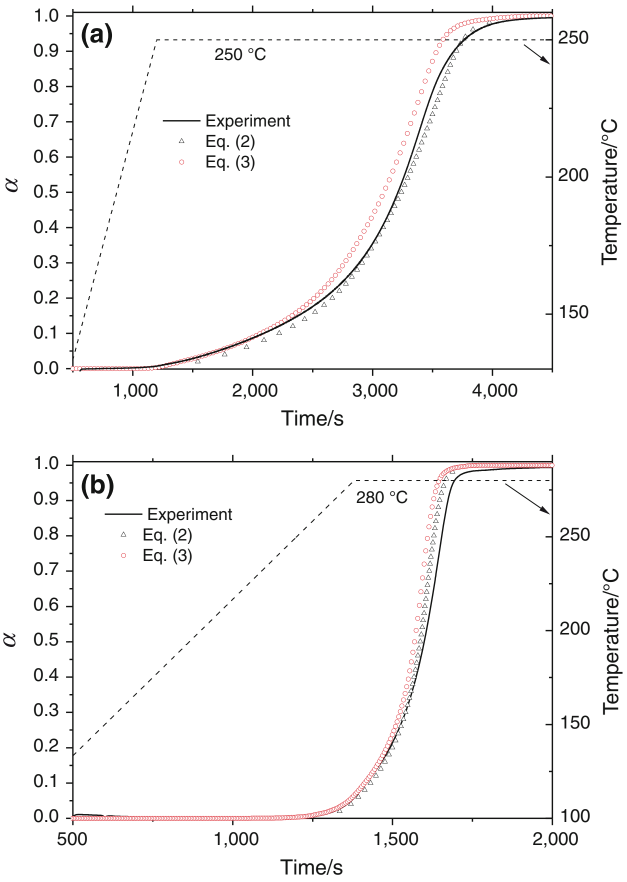

Fig. 3 *Solid line* evolution of the transformed fraction when the temperature is raised at a constant heating rate of 10 K/min up to a constant temperature of 250 °C (**a**) and 280 °C (**b**). *Dashed line* temperature evolution. Dry air (N_2) has been used in the experiment performed at 250 °C (280 °C)

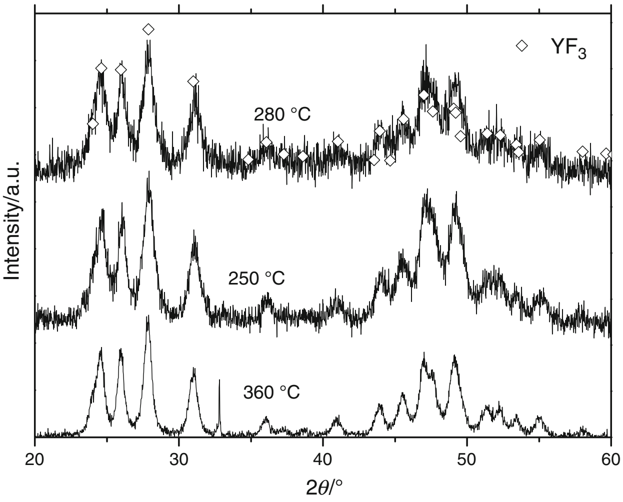

Fig. 4 X-ray powder diffractograms of solid residues after heating the Y-TFA up to a 360 °C at 20 K/min in dry N_2 and after the heat treatments plotted in Fig. 3. The final temperature of the treatment is indicated. *Symbols* orthorhombic YF_3 [31]

Firing

During this stage YF_3 is transformed into yttria. This is a slow process controlled by the out-diffusion of fluorine and involves the formation of two intermediate phases: $Y_6O_5F_8$ and YOF [15, 16]. The evolution of the decomposition does not depend on the partial pressure of water or oxygen provided that the oxygen and water partial pressure are above 0.02 and 0.002%, respectively [15]. For this stage, we have measured the evolution of the mass with temperature for five different heating rates under a flow rate of 40 mL/min of humid high purity N_2. The initial mass of the samples varied between 7.4 and 46 mg. In Fig. 5 we have plotted the evolution of the degree of transformation and in Fig. 6 we have plotted the activation energy calculated with Friedman's method.

The presence of several inflection points in the evolution of the transformed fraction (Fig. 5) and the strong dependence of the activation energy on α (Fig. 6) evidences the

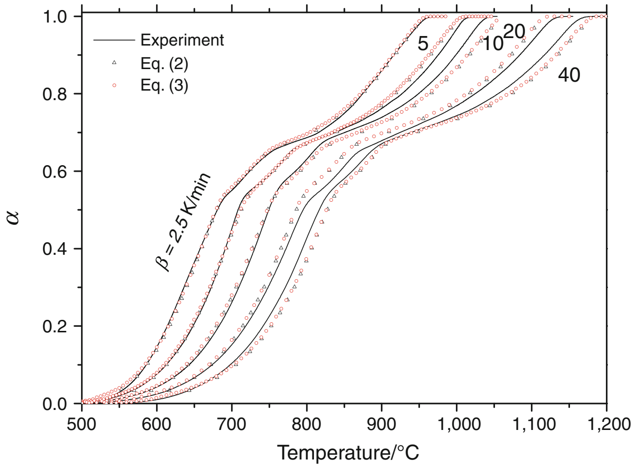

Fig. 5 *Solid line* evolution of the transformed fraction for the firing stage measured by TG at several heating rates, β. *Symbols* non-isothermal predictions (for the sake of clarity not all the calculated points have been plotted)

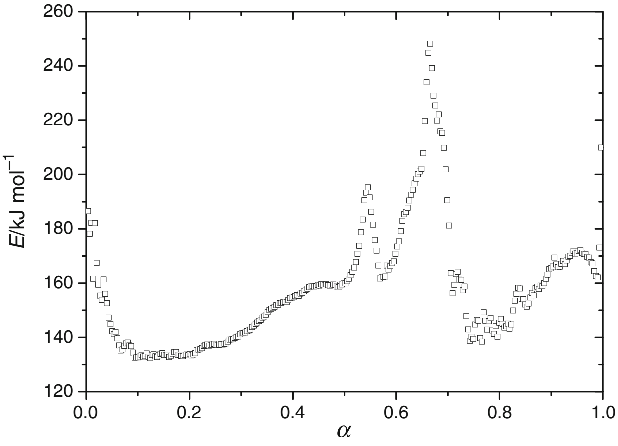

Fig. 6 Evolution of the activation energy with the degree of transformation derived from Friedman's isoconversional analysis of the firing stage (see Fig. 5)

complex nature of this transformation, which includes different reactions, as expected for a transformation that involves two intermediate compounds. Therefore, in this case, the isoconversional hypothesis, Eq. 1, is an empirical approximation.

Similarly to the previous case, we have tested the self-consistency of our approach. From Fig. 5 one can verify that there is a nice agreement between the experimental data and the prediction provided by Eqs. 2 and 3. Therefore, the isoconversional hypothesis provides an accurate description of the actual kinetics. Contrary to the previous case, both methods deliver a nearly identical prediction. This coincidence is expected for "deceleratory" reactions [5], and agrees with the fact that this transformation is governed by gas diffusion [15] because diffusion-controlled reactions exhibit deceleratory behavior.

For the firing process, the goal is to control the final temperature, e.g., to prevent the decomposition of the oxide, to prevent the degradation of the substrate, or to control the crystallization kinetics to achieve the desired texture. To do so, one can use the same scheme as that used for the calcination stage: a heating ramp from the calcination temperature to the final temperature followed by an isothermal step. In this case, the prediction methods are useful to calculate the duration of this isothermal step.

To check the ability to provide an accurate prediction, we have calculated and measured the evolution when the heating rate is 10 K/min and the final temperature is 860 and 950 °C. The results are plotted in Fig. 7a, b, respectively. There is good agreement between the experimental and the predicted reaction course. The major discrepancies, which take place near completion of the transformation, are probably related to the complex nature of the decomposition. Note that, in this case, isothermal prediction methods would fail because the major part of the reaction takes

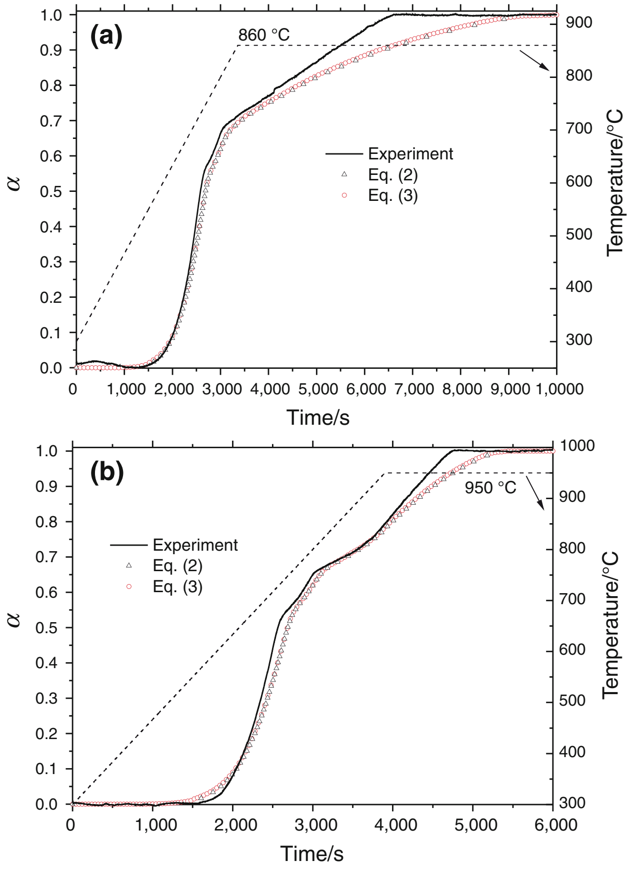

Fig. 7 *Solid line* evolution of the transformed fraction when the temperature is raised at a constant heating rate of 10 K/min up to a constant temperature of 860 °C (**a**) and 950 °C (**b**). *Dashed line* temperature evolution. Humid N_2 has been used in all the experiments

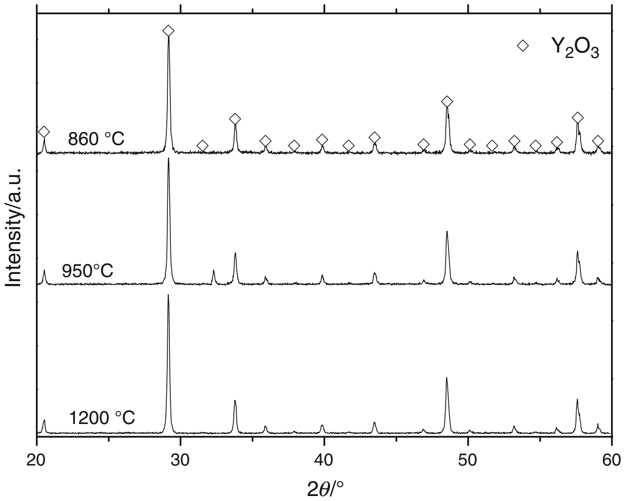

Fig. 8 X-ray powder diffractograms of solid residues after heating the Y-TFA up to a 1,200 °C at 20 K/min in humid N_2 and after the heat treatments plotted in Fig. 7. The final temperature of the treatment is indicated. *Symbols* body-centered yttria phase [32]

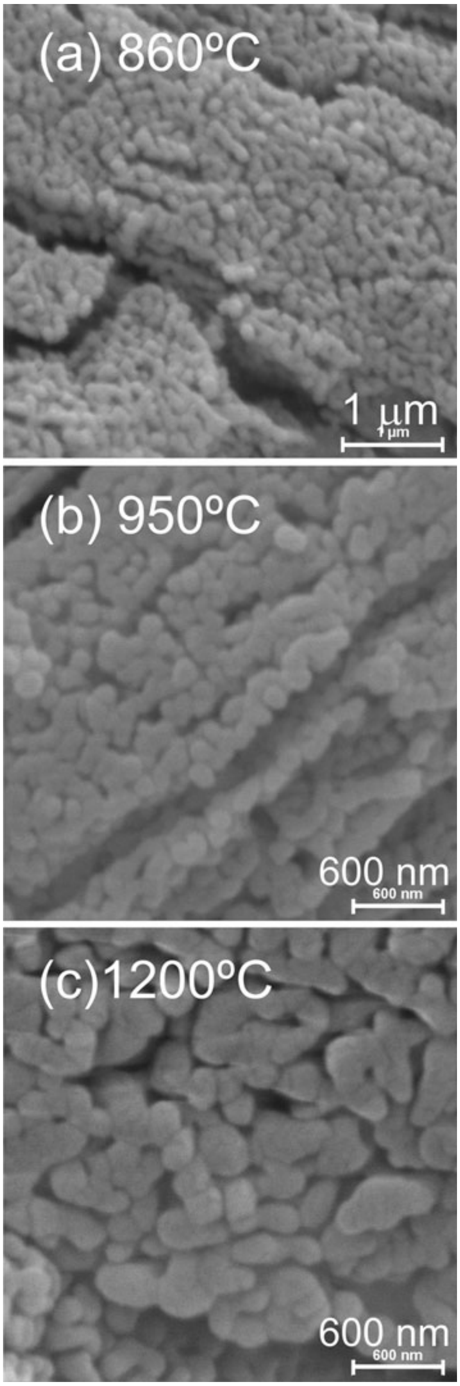

Fig. 9 SEM micrographs of solid residues after heating the Y-TFA up to a 1,200 °C at 20 K/min in humid N_2 and after the heat treatments plotted in Fig. 7. The final temperature of the treatment is indicated

place before the onset of the isothermal step. In general, a slow transformation that takes place in a large temperature interval under continuous heating conditions will be very difficult or impossible to reduce to a single isothermal experiment.

XRD analysis of the solid residues after the heat treatments are plotted in Fig. 7 and after heating at a constant rate of 20 K/min up to 1,200 °C they are plotted in Fig. 8. In all cases, the final product is yttria, as expected when the firing stage is completed. Moreover, there are no significant differences in the peak width. Application of Scherrer's formula gives an approximate grain size of 55 nm in all cases. However, SEM analysis reveals differences in the final structure. The sample is in the form of loose powders. These powders are formed by aggregates of particles. The average sizes of these particles measured from the SEM images (Fig. 9) are 220 nm for 1,200 °C, 140 nm for 950 °C, and 80 nm for 860 °C. Thus, the lower the temperature, the smaller are the particles.

Conclusions

We have applied model-free non-isothermal prediction methods to two different stages involved in the chemical solution deposition of crystalline yttria from Y-TFA: calcination and firing. Both stages have intrinsic properties that make it difficult to use prediction methods. In a constant heating experiment, the calcination stage is a relatively simple transformation that takes places in a short-temperature interval while the firing stage is a complex transformation that takes place in a long-temperature interval.

The objective was to check the ability of kinetic prediction methods to design temperature programs. In both cases we have obtained good agreement between predictions and the measured evolution. Therefore, model-free non-isothermal prediction methods can be considered as adequate tools for the design of thermal treatments like those used in the synthesis of functional oxides from the chemical solution deposition technique.

Acknowledgements This study was partially funded by the Spanish *Programa Nacional de Materiales* through project MAT2009-08385 and by the *Generalitat de Catalunya* contract No. 2009SGR-185.

References

1. Schwartz RW, Schneller T, Waser R. Chemical solution deposition of electronic oxide films. C R Chim. 2004;7:433–61.
2. Araki T, Hirabayashi I. Review of a chemical approach to $YBa_2Cu_3O_{7-x}$-coated superconductors—metalorganic deposition using trifluoroacetates. Supercond Sci Technol. 2003;16:R71–94.
3. Banger KK, Yamashita Y, Mori K, Peterson RL, Leedham T, Rickard J, Sirringhaus H. Low-temperature, high-performance solution-processed metal oxide thin-film transistors formed by a 'sol–gel on chip' process. Nat Mater. 2011;10:45–50.
4. Kim M, Kanatzidis MG, Facchetti A, Marks TJ. Low-temperature fabrication of high-performance metal oxide thin-film electronics via combustion processing. Nat Mater. 2011;10:382–8.

5. Farjas J, Roura P. Isoconversional analysis of solid state transformations: a critical review. III isothermal and non isothermal predictions. J Therm Anal Calorim. doi:10.1007/s10973-011-1642-2.
6. Vyazovkin S, Wight CA. Isothermal and nonisothermal reaction kinetics in solids: in search of ways toward consensus. J Phys Chem A. 1997;101:8279–84.
7. Vyazovkin S. Computational aspects of kinetic analysis: part C. The ICTAC kinetics project—The light at the end of the tunnel? Thermochim Acta. 2000;355:155–63.
8. Vyazovkin S. A unified approach to kinetic processing of nonisothermal data. Int J Chem Kinet. 1996;28:95–101.
9. Roduit B, Folly P, Berger B, Mathieu J, Sarbach A, Andres H, Ramin M, Vogelsanger B. Evaluating SADT by advanced kinetics-based simulation approach. J Therm Anal Calorim. 2008; 93:153–61.
10. Farjas J, Roura P. Isoconversional analysis of solid state transformations: a critical review I single step transformations with constant activation energy. J Therm Anal Calorim. 2011;105: 757–66.
11. Fujihara S, Koji S, Kadota Y, Kimura T. Phase-selective pyrolysis and Pr3 + luminescence in a YF3–Y2O3 system from a single-source precursor. J Am Ceram Soc. 2004;87:1659–62.
12. Llordés A, Zalamova K, Ricart S, Palau A, Pomar A, Puig T, Hardy A, Van Bael MK, Obradors X. Evolution of metal-trifluoroacetate precursors in the thermal decomposition toward high-performance $YBa_2Cu_3O_7$ superconducting films. Chem Mater. 2010;22:1686–94.
13. Tokunaga Y et al. High critical current YBCO films using advanced TFA-MOD process. Phys C Supercond. 2004;412–414, Part 2:910–915.
14. Wesolowski DE, Yoshizumi M, Cima MJ. Understanding the MOD process between decomposition and YBCO formation. IEEE Trans Appl Supercond. 2007;17:3351–4.
15. Eloussifi H, Farjas J, Roura P, Camps J, Dammak M, Ricart S, Puig T, Obradors X. Evolution of yttrium trifluoroacetate thermal decomposition. J Therm Anal Calorim. doi:10.1007/s10973-011-1899-5.
16. Mosiadz M, Juda K, Hopkins S, Soloducho J, Glowacki B. An in-depth in situ IR study of the thermal decomposition of yttrium trifluoroacetate hydrate. J Therm Anal Calorim. doi:10.1007/s10973-011-1772-6.
17. Vyazovkin S. Thermal analysis. Anal Chem. 2010;82:4936–49.
18. Vyazovkin S, Wight CA. Kinetics in solids. Annu Rev Phys Chem. 1997;48:125–49.
19. Vyazovkin S. Evaluation of activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature. J Comput Chem. 1997;18:393–402.
20. Vyazovkin S. On the phenomenon of variable activation energy for condensed phase reactions. New J Chem. 2000;24:913–7.
21. Wilburn FW. Kinetics of overlapping reactions. Thermochim Acta. 2000;354:99–105.
22. Farjas J, Roura P. Isoconversional analysis of solid state transformations: a critical review. II complex transformations. J Therm Anal Calorim. 2011;105:767–73.
23. Roduit B, Dermaut W, Lunghi A, Folly P, Berger B, Sarbach A. Advanced kinetics-based simulation of time to maximum rate under adiabatic conditions. J Therm Anal Calorim. 2008;93: 163–73.
24. Roduit B, et al. The simulation of the thermal behavior of energetic materials based on DSC and HFC signals. J Therm Anal Calorim. 2008;93:143–52.
25. Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature. 1964;201:68–9.
26. Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. J Polym Sci C. 1964;6:183–95.
27. Farjas J, Butchosa N, Roura P. A simple kinetic method for the determination of the reaction model from non-isothermal experiments. J Therm Anal Calorim. 2010;102:615–25.
28. Roura P, Farjas J. Analysis of the sensitivity and sample—furnace thermal-lag of a differential thermal analyzer. Thermochim Acta. 2005;430:115–22.
29. Galwey AK, Brown ME. Chapter 3 kinetic background to thermal analysis and calorimetry. In: Brown ME, editor. Handbook of thermal analysis and calorimetry. vol 1. Amsterdam: Elsevier; 1998. p. 147–224.
30. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data. Thermochimica Acta. 2011;520:1–19.
31. JCPDS card no. 70-1935, The International Centre for Diffraction Data, Newton Square, PA.
32. JCPDS card no. 65-3178, The International Centre for Diffraction Data, Newton Square, PA.