Rapid thermal decomposition for YBa$_2$Cu$_3$O$_{7-\delta}$ films derived by DEA-modified TFA-MOD

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Abstract. Thermal decomposition of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) films derived by diethanolamine (DEA)-modified trifluoroacetate acid-metal organic deposition (TFA-MOD) was investigated with respect to the understanding of the correlation between the stress releasing and rapid decomposition. It is revealed that the evaporation of DEA and the decomposition of precursor films occur simultaneously. A pyrolysis time as 20 seconds is optimal to keep the proper amount of DEA which prevents the films from severe stress during the pyrolysis. Then smooth surface of resultant films appears. In case of a pyrolysis time longer than 40 s, cracks emerge in the films accompanied with complete evaporation of DEA and appearance of Cu-rich particles, while films with pyrolysis time shorter than 10s is excessively soft, with large amount of DEA and TFA remaining in the film, implying insufficient pyrolysis.

1. Introduction
It is well known that TFA-MOD process is very promising for the industrial scaling up for YBCO coated conductors due to low cost. One difficulty in TFA-MOD method is the need of a long pyrolysis step to evaporate the solvent and decompose the trifluoroacetates into oxyfluoride precursor, accompanying with great volume shrinkage and out-gassing. During the decomposition process, buckling and cracking generally occur if the film does not maintain sufficient elasticity to endure the strain. The thermal decomposition for conventional TFA-MOD is more than 10h [1], and it is a disadvantage to be applied into commercial-scale production of kilometre-length tapes. In past years, extensive efforts were proposed to reduce the pyrolysis time mainly by three ways, using precursor with low content of fluorine [2~4], additions [5, 6] , or avoiding the appearance of water in the precursor solution [7~9]. Several groups have managed to reduce the pyrolysis time to several hours. As a solution starting method, MOD can be easily modified by additions. Many additives, such as DEA [5], PEG [6], have been demonstrated effective to reduce the pyrolysis time. Of all additives, DEA appears especially effective because of its high boiling- point (268°C). With the addition of DEA in TFA-MOD precursor solution, the pyrolysis time can be reduced as short as 20s [5]. The pyrolysis time greatly affects the development of YBCO phase and morphology of the DEA-YBCO films. Thus, more detailed information regarding DEA-modified pyrolysis process is required to give insight in the possible reasons. In the present work, a series of precursor films quenched at different pyrolysis time are investigated with respect to the morphology and residual particles, to give more understanding of pyrolysis process in the DEA-modified TFA-MOD.
2. Experimental details

In our TFA-MOD process, Y-acetate, Ba-acetate, Cu-acetate are dissolved in TFA with the molar ratios of Y: Ba: Cu =1: 2: 3.15 to prepare the precursor. Diethanolamine (DEA) and methanol are used as solvents, with the ratio of Cu: DEA=1: 2. The molar concentration of the metal ions is 1.5mol/L. Precursor solutions are deposited onto LaMnO$_3$/Epi–MgO/IBAD-MgO /Y$_2$O$_3$/Al$_2$O$_3$/Hastelloy substrates by dip coating. The coated substrates are then placed at 125$^\circ$C in a dry N$_2$/O$_2$ gas mixture for 10 minutes to get dried. Then they are placed directly to pyrolysis process at 325$^\circ$C [5] for different times from 6 to 120 sec in air. The following crystallization carried out at 770$^\circ$C for 60min at a heating rate of 20$^\circ$C/min from 310$^\circ$C to 770$^\circ$C under 150ppm O$_2$/bal. N$_2$ atmosphere, and the dry gas is changed to wet gas at 400$^\circ$C (Tw). Finally the crystallized films are annealed at 450$^\circ$C for 60min in dry O$_2$ for full oxidation. In this work, we focus on the process of pyrolysis. The Metalloscopy and Scanning Electron Microscopy (SEM) test is used for the morphology observation and Fourier Transform Infrared Spectroscopy (FTIR) is used for the characterization of the component of the films.

3. Results and discussion

In order to further understand the pyrolysis process, the samples quenched after different pyrolysis time (tp) are studied. The pyrolysis process is as the following: The coated films are placed directly to 325$^\circ$C for different time in air to pyrolysis, then pulled out of the tube furnace and placed at room temperature. In figure 2, both Metalloscopy and SEM images (after gilded) of samples quenched after different pyrolysis time are obtained.

![Figure 1. Typical thermal profile for our research](image1)

![Figure 2. Series of (a)Metalloscope images (b)SEM images (after Gilded) of pyrolyzed films quenched after different pyrolysis time](image2)

According to Metalloscopy image, the surface of the films with pyrolysis time shorter than 10s is smooth [Figure 2(a)]. Increasing tp to 20s, the whole surface of the sample is bestrewn with pits of almost the same size. The bubbled surface looks like gas rush through the films intensively. During 30–40s, the surface of films are generally flat again except a few large bubbles. Further increase tp to 60–120s, more and more particles and cracks appear on the surface. The decomposition temperature range for Cu-fluroacetate is 240–270$^\circ$C and 320–400$^\circ$C for Y- and Ba-fluroacetates, respectively. The
decomposition is runaway exothermic and out-gassing. The films are pyrolyzed at 325°C, a large amount of gas is expected for the evaporation of DEA and the part products of decomposition of organic salts. According to the phenomenon, it is supposed that tp varies at 1~10s, both evaporation and decomposition are mild due to the short time and the surface remains smooth. As tp increases to 10~20s, DEA evaporates intensively and pits the surface by rushing through the film. All the pits are shallow which may imply that there is enough DEA remaining in the film, thus the film is still elastic. By increasing tp to 30~40s, the amount of DEA and TFA in the film decreases with the long heat treatment time thus the vaporization and decomposition became mild. A few large bubbles appear because of gas accumulation while other places remain flat. Further lengthening tp to 60~120s, there is nearly no DEA left and the film become rigid. Hence, defects and cracks occur. SEM images show the same trends with the change of pyrolysis time. The particles in the surface of samples pyrolyzed for more than 60s are Cu rich according to the EDS analysis. This may be the result of composition inhomogeneity.

Figure 3 shows the dependence of the size and number of Cu-rich particles on pyrolysis time. Data in figure 3 is acquired by capturing images of the same size (3.9 μm * 3.9 μm) by visual counting and vernier caliper respectively. The relative size to the average diameter of the particles (330nm) at 60s and particles number, changes from zero to 1.49 and 23 respectively with the increase of pyrolysis time. This phenomenon indicates that the composition homogeneity degrade when the pyrolysis time is longer than 50s. In both figure 2(a) and 2(b), samples pyrolyzed for tp = 30 s or 40 s are smoother than those with shorter pyrolysis time except for the big bubble. This may suggest that fluoroacetates decomposition reaction has finished or become slow after 30-40 s for the surfaces reveal a very slow rate of emission of gas.

The FTIR patterns of precursor films quenched after different pyrolysis time is measured in figure 4. The strong carbonyl (C=O) absorption appears at 1685 cm⁻¹. Stretching vibrations of C-O absorptions appear at 1209 cm⁻¹, 1145 cm⁻¹, and 1064 cm⁻¹. The absorption appears at 1456cm⁻¹ maybe indicating C-H stretching vibration, which needs more evidence. However, N-H (3300-3500cm⁻¹) peak indicates DEA which appears as a small trough. It is reasonable that the intensity of N-H peak is generally mild, while that of C=O is strong. The C=O and C–O bonds are related to carboxyl absorption, which could be ascribed to the TFA species. With the increasing of tp, the peak intensity of C=O and C-O decreased quickly, but the tiny peak at 80s indicates that TFA is not totally decomposed. Meanwhile, the vibration of N-H cannot be observed after pyrolyzing for 40s. It implies that the evaporation of DEA and the decomposition of TFA proceed simultaneously, and once no more DEA remains in the samples which are pyrolyzed for more than 40s, the decomposition continues slowly.

To summary, the morphology diagram of DEA-modified TFA-MOD pyrolysis is given in figure 5. We divide the pyrolysis process into three stages. In the stage I, we achieve smooth surface with appropriate amount of DEA remaining in the film as the pyrolysis time (tp) is in the range of 0~40s. Then in the stage II, Cu-rich particles appear with few DEA remaining and the decomposition
proceeding as the tp varies in the range 40–60s. In the stage III, with the tp increasing to 60–120s, more and more Cu-rich particles accompanied by cracks emerge with the absence of DEA.

4. Conclusions
In this work, the precursor YBCO films quenched after different pyrolysis time derived by DEA-modified TFA-MOD are investigated to give more understanding of pyrolysis process. These films are studied by Metalloscopy, SEM, FTIR, which reveal that a pyrolysis time as short as 20s is optimal. The short pyrolysis time appears necessary to keep the proper amount of DEA, which prevents the films from severe stress, and assure smooth surface of resultant films. According to FTIR, the clusters of C=O, C-O and N-H correspond to TFA acid radical and DEA respectively, which give the evidences that the evaporation of DEA and the pyrolysis process occur simultaneously. And the pyrolysis continues slowly with the absence of DEA after 60s. A pyrolysis time longer than 60s leads to the appearance of cracks and Cu-rich particles without the protection of DEA. In case of excessively short pyrolysis time, namely shorter than 10s, there would be insufficient pyrolysis leaving the surface extremely soft.

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