
Project Title:	Processing and Nucleation Kinetics for YBCO Films by the BaF₂ Process
Organization(s):	Brookhaven National Laboratory
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Project Purpose and FY 2003 Objectives: The purpose of this project is 1) to develop synthesis methods/protocols which are suitable for the fabrication of YBCO coated conductors, and 2) to develop an understanding of the mechanisms, kinetics, and thermodynamics of a- and c-axis nucleation in the BaF₂ process for YBCO thick films. 3) Another purpose of this project is to perform small-scale ac loss measurements which assist in the development of understanding of the currently known or expected ac losses in electric utility devices using HTS conductors. [Note that this latter portion of the work is reported jointly with S. Ashworth of Los Alamos National Laboratory, (LANL), in the "Systems session".] Our objectives for FY 2003 were to continue the study of the nucleation mechanisms in thick films and to investigate the effects of variations in the precursor deposition conditions on the c-axis nucleation in thick films of YBCO. We also planned to extend our nucleation study on films which were deposited on buffered metallic substrates. These were provided by different groups through inter-laboratory and industrial collaborations. Also, we began a component of this program devoted to the theory and modeling of the thermodynamics and kinetics of nucleation and growth in the BaF₂ process, focusing especially on factors which control a- and c-axis nucleation and the evolution of defects and nanoscale structure.

FY 2003 Performance and FY 2004 Plans: YBCO thick film processing: a) Thermal spray pyrolysis for precursor deposition. We have been investigating the use of thermal spray pyrolysis for deposition of the precursor films for YBCO thick film synthesis. Although we could grow thick c-axis oriented YBCO films, critical current densities of these films could not exceed ~ 0.5 MA/cm². Since it was not clear how this situation could be overcome, we terminated this work for the time being. b) In situ extraction of HF by BaO (SrO): We have demonstrated that HF, which is a reaction product in the process of converting the precursor to YBCO, can be absorbed by having BaO powder in proximity of the precursor films. Hence, one can conceptually consider the YBCO conversion being accomplished without a flowing process gas in a batch process. c) YBCO formation on buffered substrates. Buffered metallic substrates from LANL, American Superconductor Corp., (AMSC), and Microcoating Technology, (MCT), are used to grow thick YBCO layers. At the present, the highest result was achieved for a 2.2 μm thick film on a AMSC tape with a CeO₂ cap layer. The critical current was 30 A at 1.0 T and 77 K for a 3 mm wide tape. d) Theory and modeling efforts were focused on the use of semi-empirical atomistic and statistical thermodynamic methods to estimate thermophysical properties of the (Y,Ba)(O,F)₂ precursor phase pertinent to the kinetics of the epitaxial nucleation of YBCO.

In FY2004: 1) The in situ HF extraction method will be further investigated including the subatmospheric conversion of the precursor films to YBCO films. 2) The growth of thick (> 3 μm) YBCO films on buffered metallic substrates will be continued emphasizing the control of the precursor conditions to achieve the consistency of the properties of the films. 3) Theory and modeling will be focused on delineating processing conditions which result in appreciable a-axis nucleation or in high levels of cation site-exchange disorder in thick films. A collaboration will also be initiated with Prof. Cima at MIT on the modeling of nucleation and growth kinetics and nanoscale structure evolution in the case of MOD-derived precursors for comparison with the behavior for e-beam or other physical precursor deposition methods used at BNL.

FY 2003 Results: Key results from the FY 2003 program are summarized below.

1)YBCO thick-film processing

a) Thermal spray pyrolysis: In FY 2003, we continued to investigate methods to enhance the diffusion rates of the gaseous species in the YBCO precursor films during the conversion of the precursor to

YBCO films. We believe that the insufficient diffusion rates for HF and/or H₂O in thick films present the major difficulty in growing c-axis-oriented thick (> 2–3 μm) YBCO films. The precursor films by this deposition method appeared to have better properties for diffusion of these gases since it was easy to grow thick (~ 7 μm) YBCO films with c-axis orientation on SrTiO₃. However, critical current densities of the films were only ~ 0.5 MA/cm² and could not be improved. Since the compositions of the films were essentially at stoichiometric values, as determined by the ICP (Inductively Coupled Plasma) technique, this is unlikely to be the problem. In collaboration with V. Maroni, ANL, it was shown using Raman spectroscopy that there was a significant amount of the atomic site exchange between Y and Ba in the YBCO structure in these films. This is consistent with our observation of the high values of the extrapolated resistivity at 0 K in these films. Thus, this is a source of low J_c's in these films, and we have terminated this work for the time being since we do not know how to alleviate this problem.

- b) In situ extraction of HF: We believe that in general the simplification of the production process leads to the reduction of the cost of the products. In the case of the BaF₂ process, the growth rate of YBCO is very slow (~ 0.1-0.3 nm/s). Thus, a reel-to-reel process for the formation of YBCO in making ~ 1 km tapes would be very time consuming and expensive. A batch process for the YBCO formation without gas-flow or dynamic pumping would be much more desirable. One possible way to accomplish this is to extract HF, a reaction product, in situ in the reaction chamber. It was shown that placing BaO powder coated plate above the YBCO precursor film in a confined space could convert the precursor to a c-axis orient YBCO without a flowing gas. The conversion rate was nearly the same as that for the film grown in a flowing process gas. Thus, we believe that this constitutes as a proof-of-principle test for a batch process applicable to the production of long YBCO coated conductors.
- c) YBCO formation on buffered substrates: Buffered metallic substrates from AMSC, LANL, and MCT are used to grow thick YBCO layers. At the present, the best result was achieved for a 2.2 μm thick film on a AMSC tape with a CeO₂ cap layer. The critical current was 30 A at 1.0 T and 77 K for a 3 mm wide tape. Currently, we are testing the consistency and the robustness of the process which led to this encouraging result.

2) Theory and modeling

Modeling of Nucleation and Growth, Thermodynamics and Kinetics: The need to better understand processing conditions which lead to nanostructural degradation such as a-axis grains, porosity, cation disorder, etc., and to help in the optimization of the BaF₂ process led us to initiate a new program component in FY2003 of theoretical studies of the thermodynamics, mechanics, and kinetics of nanoscale structure formation. This year the effort was focused on semi-empirical methods for estimating properties of the precursor (Y,Ba)(O,F)₂ which control the thermodynamic driving forces and interfacial energies of importance in nucleation kinetics.

Research Integration: Our studies were performed as informal collaborations with the staffs at ANL, LANL, OST/MCT and AMSC. We would like to point out that the results of the work in this program can take some “incubation period” before their value becomes apparent to industry. For example, the concept of subatmospheric pressure processing in the BaF₂ process, which we introduced 2-3 years ago, is now an indispensable modification in the fabrication of YBCO coated conductors by this process.
