
Project Title:	Conversion of Oxy-Fluoride Based Coated Conductors
Organization(s):	Massachusetts Institute of Technology, Brookhaven National Laboratory
Presenters:	M.J. Cima, Masaki Suenaga
FY 2004 Funding:	\$200 K

Project Purpose and FY 2004 Objectives: Direct measurements of HF pressure in equilibrium with the film during the BaF₂ process are needed for accurate process design and control. It is the HF partial pressure that governs the rate at which the film composition is changing and is, therefore, an important factor in controlling the composition/time trajectory of the film. Establishing the composition/time trajectory of both MOD-derived and e-beam derived films for a given set of conditions is another goal for the project. These studies will provide a fundamental understanding of the *ex situ* process for producing coated conductors. FY 2004 objectives of our project were:

- 1) Establish modified Knudsen cell technique
- 2) Make modified Knudsen cell measurements on MOD films
- 3) Make modified Knudsen cell measurements on pure BaF₂ films to compare with MOD films

FY 2004 Performance and FY 2005 Plans: Thanks in part to a successful collaboration with BNL, we have completed all the objectives of FY2004. MIT has extensive experience with MOD-derived YBCO coated conductors and BNL has experience with e-beam derived YBCO, so both parties have much to gain from this collaboration and we will continue it into the future. Below is a list of our successes in 2004.

- 1) We have constructed a modified Knudsen cell and measured P_{HF} of MOD derived films using this cell. The measured P_{HF} varies from 0.02 to 0.2 Pa with temperature and extent of reaction. The pressures when YF₃ is still present are 0.028 to 0.17 Pa with temperatures between 525°C and 575°C, respectively. Further reaction gives much lower pressures of 0.02 to 0.06 Pa with temperatures of 575°C and 625°C, respectively. Measured P_{HF} were used to calculate ΔG of the reaction and compared with the literature values. The measured results are different from the estimated values of pure reactants obtained from literature values. This indicates that the literature data for pure reactants is not appropriate and that the actual reaction is more complex.
- 2) P_{HF} of the decomposition of BaF₂ films were also measured. It was hoped that such measurements could be used to judge the accuracy of our method. P_{HF} of the reaction is much smaller than that measured on YBCO films described above and not within our range of sensitivity. Increasing temperature increases the P_{HF}. Ba loss was, however, observed during heat treatment, making measurement difficult. We believe this is the result of reaction with the substrate. The measurement accuracy is not high due to low P_{HF} and Ba loss. Yttrium fluoride decomposition is now being investigated as a control reaction.
- 3) A preliminary F/Ba trajectory of e-beam derived YBCO films from BNL was determined. The F/Ba ratio of the green film is close to 2 and does not show significant change below 700°C. This indicates that BaF₂ in e-beam derived films does not decompose below 700°C even though at those temperatures BaF₂ in MOD derived films can decompose without YBCO formation.
- 4) Given the completion of FY 2004 targets, work was begun on FY 2005 objectives. BaCeO₃ is a known reaction product between YBCO and CeO₂, however, no method for quantifying the extent of the product over the entire film has been demonstrated. We have prepared ~20 nm thick cube-textured CeO₂ films on YSZ substrates using a new nitrate-based MOD process. No off-axis grains were detected in these films and the in-plane texture is similar to that of the YSZ substrate. Critical current measurements will be made on these films to verify they can produce mega-amp current densities, and then the films will be removed to examine the substrate for BaCeO₃ using an x-ray fluorescence method.

5) Publications:

“Reactions of oxyfluoride precursors for the preparation of barium yttrium cuprate films,”
Physica C 403 (2004), 191.

“Determination of HF partial pressure during *ex situ* YBCO formation,” submitted to Physica C.

In summary, our FY 2004 work provided a unique method to measure P_{HF} over the precursor film by using a modified Knudsen cell. It was found that BaF_2 in MOD derived films can decompose without YBCO formation below 700°C, even though BaF_2 in e-beam derived films is stable at those temperatures. Finally, with FY 2004 objectives met, progress was made on the FY 2005 goal of establishing a protocol to quantitatively analyze the reaction between YBCO and a CeO_2 buffer layer.

With appropriate external guidance to maximize our programmatic impact, we propose the following future research and development for FY 2005:

- ◆ More P_{HF} measurements will be performed, especially on e-beam derived film. Precise thermodynamic analysis will give us more information on the reaction path from decomposed film to YBCO coated conductor. The degree of reaction in and out of the partial melt zone will be measured for MOD/e-beam derived films to obtain the reaction path. The amount of melt in the partially reacted film should dictate the extent of reaction with the substrate, which has a negative impact on electrical properties.
- ◆ F/Ba trajectory vs. property relationship will be analyzed for both MOD and e-beam derived films so that the heating profile can be modified effectively. F/Ba ratio is one of the most important factors controlling the amount of the melt and the release of HF gas into the atmosphere. HF gas affects the morphology of YBCO crystals and their electrical properties. The F/Ba trajectory required to obtain the highest performance will be proposed.
- ◆ A protocol will be established for the quantitative measurement of reaction with buffer layers. These measurements will be compared to film performance to determine exactly how substrate reactions affect electrical performance.
- ◆ It is believed the removal of fluorine is the rate-limiting step in the growth of BaF_2 derived YBCO films. To test this theory, the growth rate of the YBCO layer will be compared to the removal rate of fluorine.

Research Integration:

MIT has collaboration with BNL to address the difference between e-beam derived and MOD derived precursor films. This collaboration has consisted of two face-to-face meetings, one video-conference, many exchanged samples, and measurements being performed at each site.