ISSUES FOR CONTINUOUS PROCESSING OF COATED CONDUCTORS.

OAK RIDGE NATIONAL LABORATORY

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Funding

- **FY 2000 EE/RE Funding: $1200K**
  - 3 FTE Staff, 2 FTE Post-Doctoral Fellows
- **FY 2000 LTR Funding: $125K**
  - 0.5 FTE Staff

National Laboratory Collaborators

- Los Alamos National Laboratory
  - P. Arendt, E. Peterson , S. Foltyn

University Collaborator

- Stanford University
  - R. H. Hammond

Industrial Collaborators

- 3M Company (3M)
  - Myles Brostrom, Dick Ericson, Arnie Funkenbusch, Dave O'Neill, Bill Robbins, Jonathan Storer, Ed Yu
- American Superconductor Corporation (ASC)
  - S. Annavarapu, Les Fritzemeier, Q. Li, Marty Rupich, Bart Riley, C. Thieme, Z. Zhang
- EURUS
  - Y. Hascicek, J. Romans, J. Schwartz, Mike Tomsic
- MicroCoating Technologies (MCT)
  - Adam King, Totd Polley, Shara S. Shoup, Marvis White
- Oxford Superconducting Technology
  - Ken Marken
- Southwire Company
  - R. L. Hughey

FY 2000 Plans

- To design and demonstrate an integrated set of laboratory scale equipment that is capable of handling moving tape throughout the conductor fabrication process.
- To develop laboratory scale processes for conductor fabrication using the new equipment.
- To demonstrate lengths of YBCO coated conductor produced by these processes and equipment.

OUTLINE

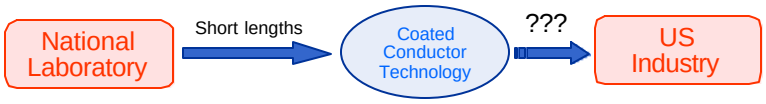
(Issues for Continuous Processing of Coated Conductors)

- FY 2000 Results:
  - New reel-to-reel systems for continuous fabrication of RABiTS coated conductor -- Fred List (ORNL) Ū
  - Progress toward lengths at 3M -- David O'Neill (3M)
  - Reel-to-reel conversion of BaF_2 precursor -- Dominic Lee (ORNL)
- Summary of FY 2000 Results / FY 2001 Plans
- Technology Integration

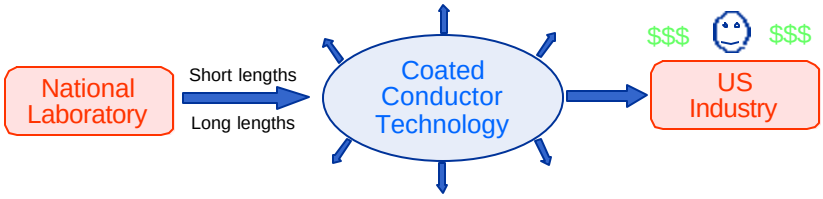
What have we attempted to do?

- **Goal: To develop <u>laboratory scale</u> equipment and processes for fabrication of <u>moving lengths</u> of coated conductor.**
- **Key Features:**
  - **Design is of a laboratory scale (~1-3 m lengths; ~1 m/hr rate)**
    - **Scale is sufficient to address many issues of scale-up.**
  - **Reel-to-reel tape handling is included throughout (11 systems)**
    - **Complete integration is necessary to avoid "bottle necks".**

Why have we attempted this development?



- Short length studies <u>alone</u> may not be sufficient to transfer the coated conductor technology (too different / complex?)

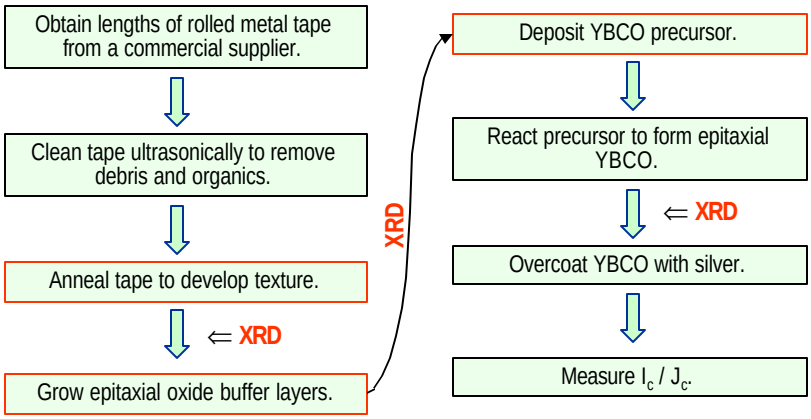


- Long length studies contribute to the technology base and enable successful transfer.

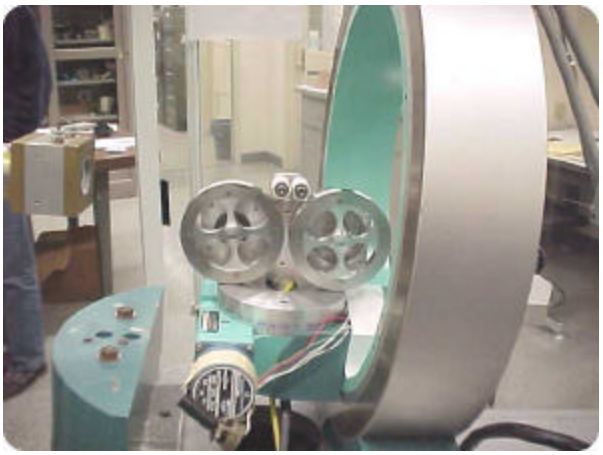
What new issues may be addressed using laboratory scale continuous processing?

- **Short, stationary length studies have demonstrated "proof of principle".**
- **Long, moving length studies may help address issues of:**
  - **Tape handling (*e.g.,* yield strength, minimum bend radius)**
  - **Importance of spatial gradients (*e.g.,* temperature, pressure, flux)**
  - **Process optimization (critical parameters, limits for scale-up)**
  - **Process stability (throughput, yield)**

At ORNL, all steps for processing lengths of YBCO/RABiTS have been equipped with reels.



A system for XRD texture determinations has been used to characterize **> 500 meters** of tape.



- stationary tape mode

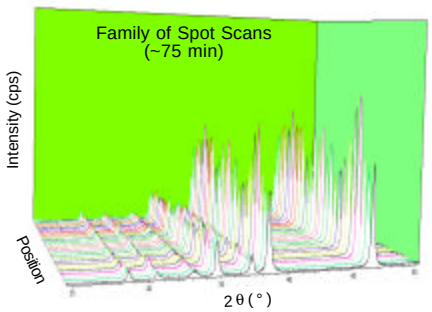
θ-2θ scan	~2 min (20°)
ϕ scan	~2 min (140°)
ω scan	~2 min (30°)
pole figure	~30 min (full)

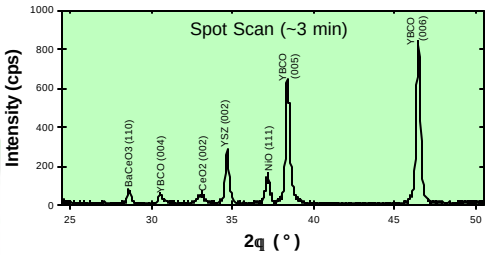
- moving tape mode

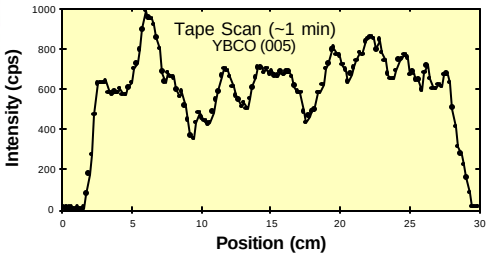
tape scan	**~5 cm/sec**
	~200 m/hr

(operational November 1999)

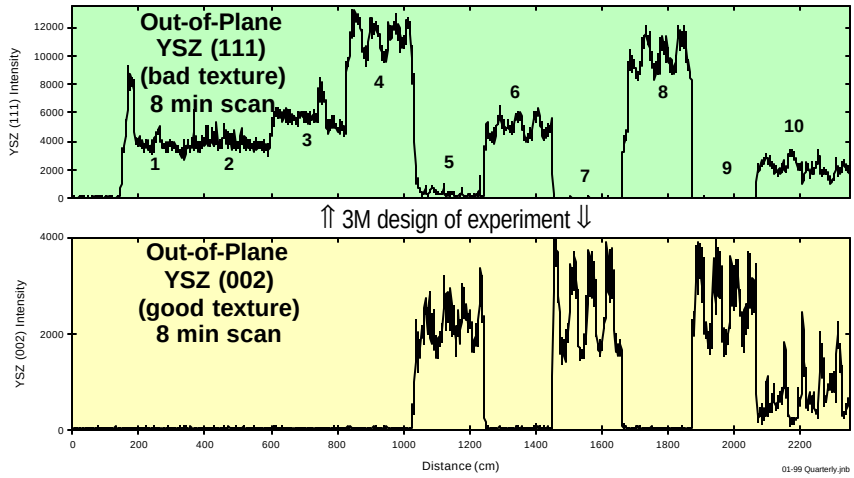
Texture determination is rapid for both stationary and moving tape.



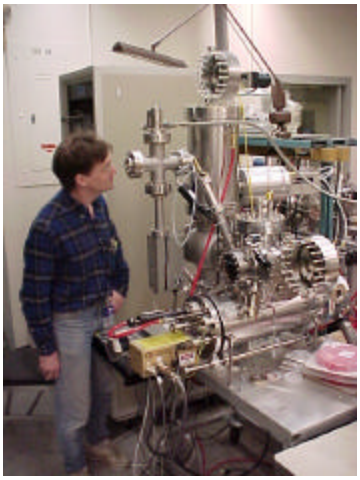




X-ray results can reveal individual experiments and cyclic oscillations.



Annealing of tape and depositing of CeO_2 are accomplished in one reel-to-reel system.



- RF annealing:
  - 6" Ta hot zone
  - 1100°C @ 1m/hr (typ. Ni)
  - T_{max} > 1500°C
- CeO_2 deposition (*in situ*):
  - e-beam Ce + $H_2O \Rightarrow CeO_2$
  - 100Å CeO_2 @ 1 m/hr (typ.)

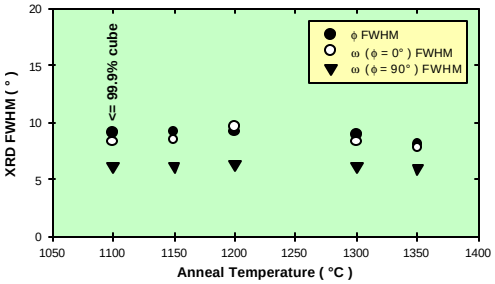
Nickel tape has been successfully annealed for a range of temperature using the RF system.

P_{base} = 5x10^{-8} Torr (P_{O2} <1x10^{-9} Torr)

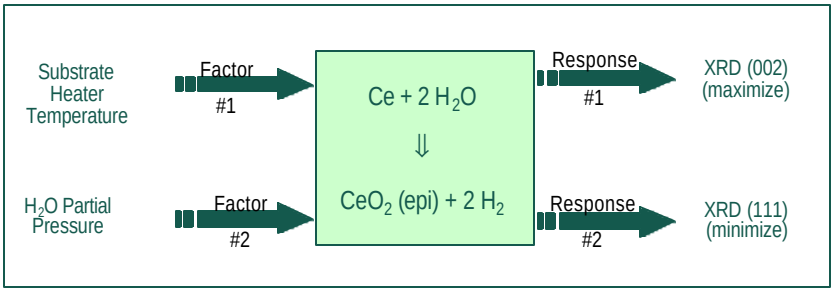
tape travel = 1 m/hr (~10 min anneal)

P_{anneal} = 5x10^{-4} Torr Ar/4%H_2

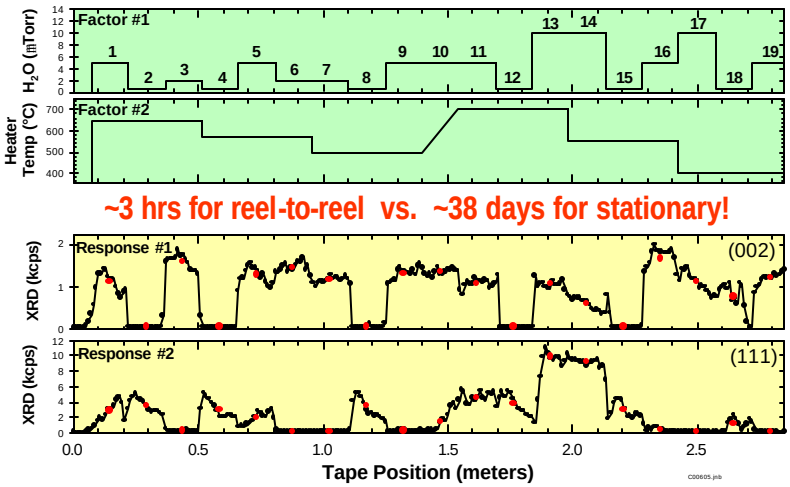
- Good texture for entire range of T ⇓



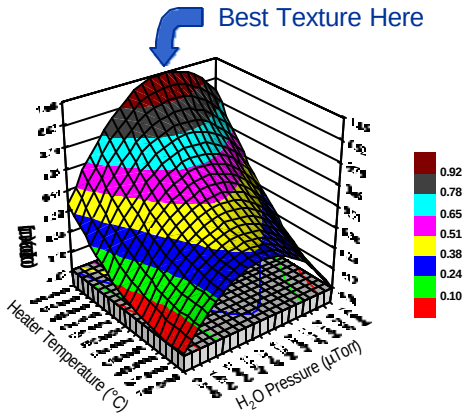
The reel-to-reel approach facilitates <u>systematic</u> optimization of CeO_2 deposition.



CeO_2 buffer layer optimization is <u>rapid</u> using the reel-to-reel approach.



Response surface analysis suggests conditions for best CeO_2 texture.

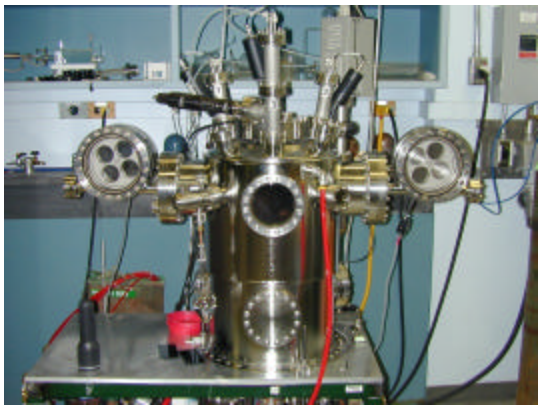


<u>Conditions for best texture</u>:

- $P_{H2O} = 5x10^{-6}$ Torr
- Temperature = 400 °C

- From rolled tape to results, elapsed time = ~3 days.
- Using conditions for best texture, <u>meters</u> of CeO_2/Ni tape have been prepared for subsequent processing.

Reel-to-reel BaF_2 precursor deposition is accomplished on meters of buffered tape.



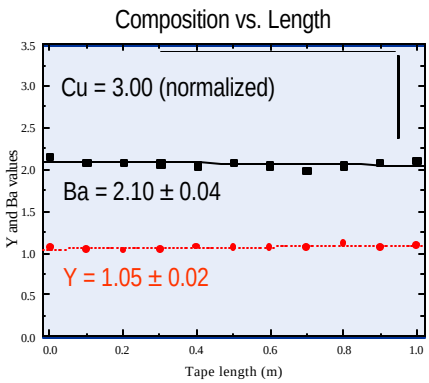
E-beam co-deposition:

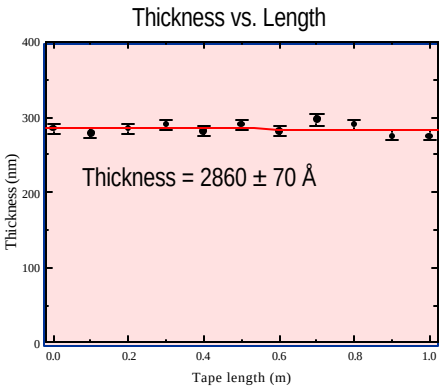
Y, BaF_2, and Cu

Typical Conditions:

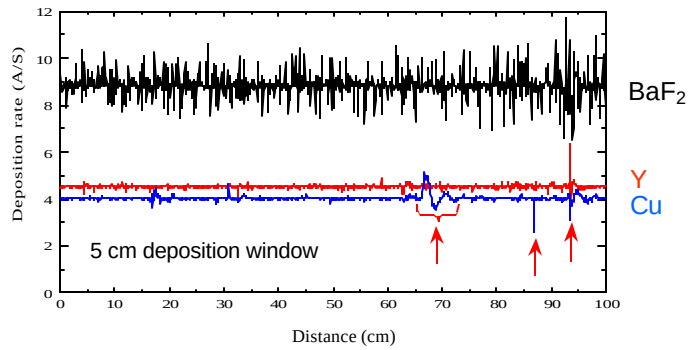
- Length: 1 meter
- Dep. Rate: 12 Å/sec
- Tape Speed: 0.8 m/hr
- Thickness: 3000 Å (<±2.5%)
- Composition: Y:Ba:Cu
  1.05 : 2.10 : 3.00 (±2%)

RBS shows good uniformity of composition and thickness over 1 meter lengths (~±2%).





Quartz crystal flux monitors indicate good <u>average</u> flux control over 1 meter lengths.



- Instantaneous fluxes and discharges <u>may</u> be issues

Reel-to-reel systems for continuous fabrication of RABiTS.
(Summary)

- **Laboratory scale, reel-to-reel tape handling has been implemented throughout the systems for continuous fabrication of RABiTS coated conductor.**
- **Development and optimization of processes is underway exploiting the advantages of the continuous approach.**
- **Designs and use of equipment have been freely shared with our CRADA partners (*e.g.*, 3M, LANL, ASC).**

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OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

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3M Innovation

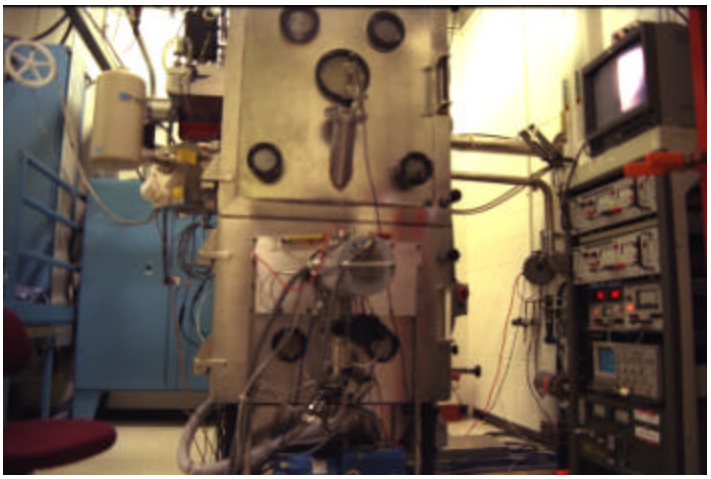
HTSC CRADA

3M, LANL, ORNL, Stanford, Southwire

- RABiTS™ Development ⇒ ORNL & 3M
- IBAD Dev. ⇒ LANL, VIP & 3M
- E-Beam Development ⇒ 3M & VIP
- In-Situ Oxidation ⇒ Stanford & 3M
- Ex-Situ BaF_2 Method ⇒ ORNL & 3M

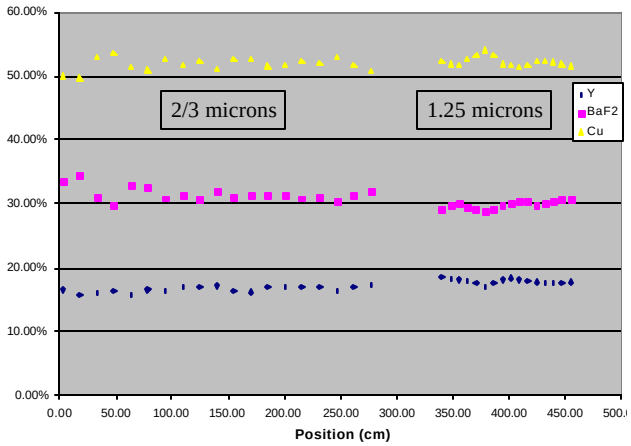
3M Innovation

3M YBCO E-Beam System



Deposited Precursor Composition

~4.5 meter tape



Precursor ⇒ YBCO Conversion Reaction

- Two furnaces at 3M
  - Short, axial flow system similar to ORNL's 1st system
  - Long furnace able to continuously process spool lengths of material, nearly completed

3M YBCO via YBCF Efforts: An Abbreviated Summary

- Co-evaporated YBCF (1-2-3)
  - ~4.5 meter long
- 3M RABiTS/3M YBCF/ORNL Converted
  - Jc~350 KA/cm^2 ~10 cm long
- LANL IBAD YSZ/ORNL CeO_2/3M YBCF/ORNL Converted
  - 520 KA/cm^2 (1 cm)

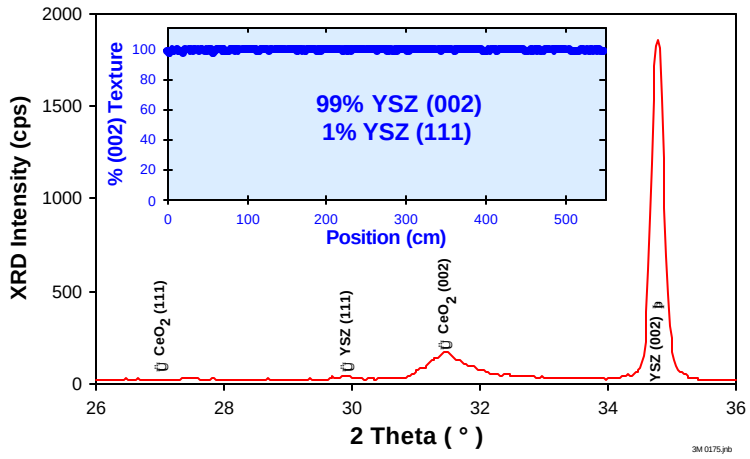
3M RABiTS™

Lengths of highly biaxially textured materials deposited w/ high rate, continuous processing

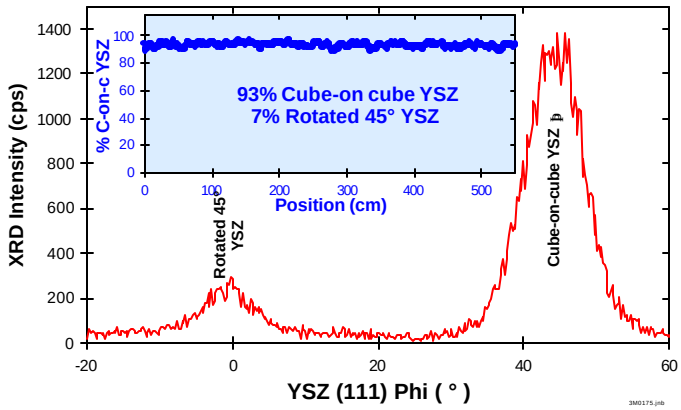
- Ni/CeO_2 30 meters
- $Ni/CeO_2/YSZ$ 5 meters
- $Ni/CeO_2/YSZ/CeO_2$ <1 meters

- Note: Much longer lengths deposited with less well defined texture

Out-of-plane texture of 3M YSZ/CeO_2 buffered tape is excellent over a 5.5 meter length.



In-plane texture of 3M YSZ/CeO_2 buffered tape is uniform over same 5.5 meter length.



- J_c = 860 kA/cm^2 for short length completed at ORNL

3M Innovation

3M RABiTS™
Manufacturing Vision

- Anneal properly rolled nickel
- Slit to YBCO processing width and wind onto spools
- Deposit buffer layers, single pass at >1ft/min (CeO_2, YSZ, CeO_2)
- QC check
- Optional anneal prior to YBCO processing
- YBCO processing...

3M Innovation

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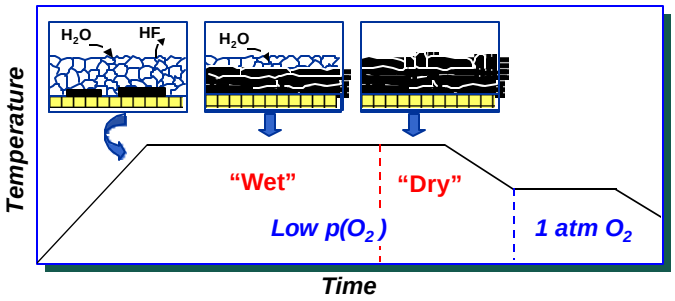
Objective: To Study Issues Related to *Ex-Situ* Processing of Long-Length YBCO on Textured Substrates

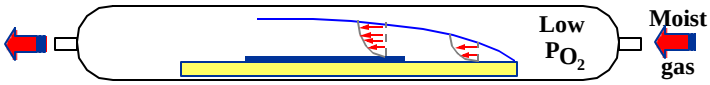
- ***Ex-Situ* Process:**
  - **Separates precursor deposition step from YBCO nucleation and growth.**
  - **Typical precursor à "BaF_2" precursor, TFA, …**
- **After precursor deposition, the sample is processed in a low $p(O)_2$ atmosphere:**



We have Developed Tools that will Enable Technology Advancement Needed for Continuous Processing

- **FY2000 Plans:** To demonstrate lengths of YBCO coated conductor produced by our laboratory-scale equipment:
  - Design and construct a reel-to-reel precursor conversion system for lengths > 1m
  - Initial target J_c = 500 kA/cm^2 (77K)
- Why spend time in designing a conversion system?

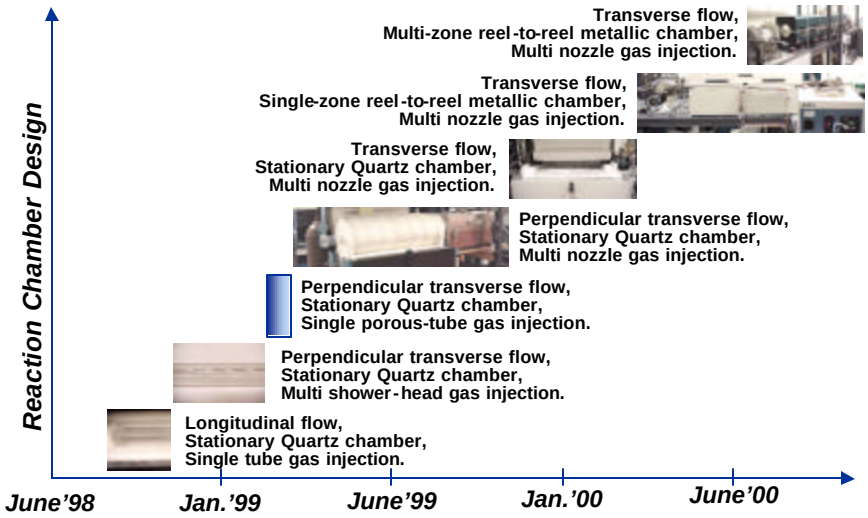
  Typical longitudinal gas injection design …



R. Feenstra et al. 1998.

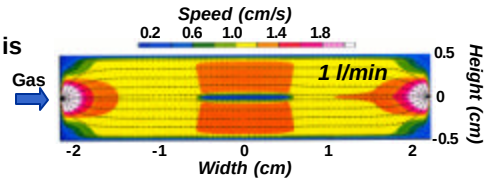
… resulted in non-uniform conversion / decomposition of long-length YBCO!

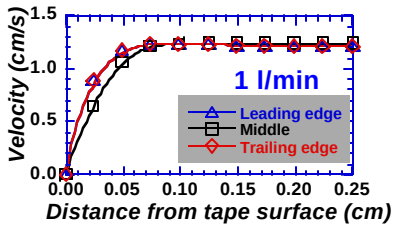
Refinement in Transverse-Flow Multi-Port Injection Design Based on Parameter-Microstructure-Properties Feedback

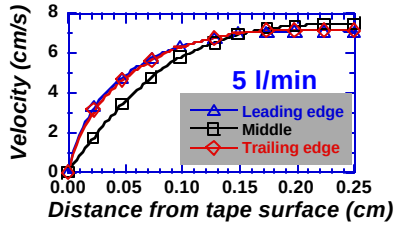


Computational Fluid Dynamic Simulations were Utilized to Analyze Potential Reactor Designs

- Simulations showed that gas flow is uniform and no stagnant regions around sample.
- Decomposition of BaF_2:
  $BaF_2 + H_2O$ à $BaO + 2HF$



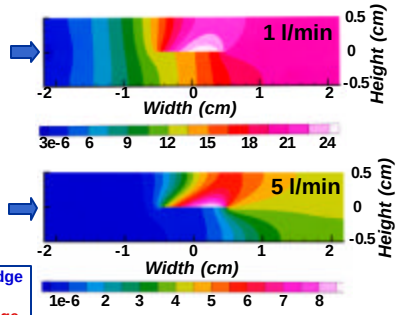


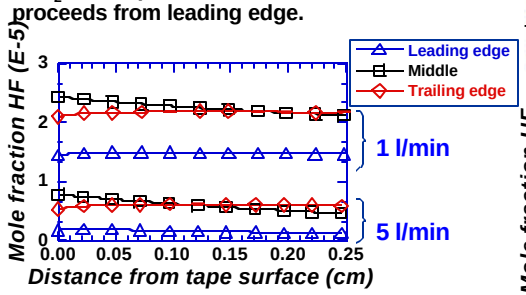


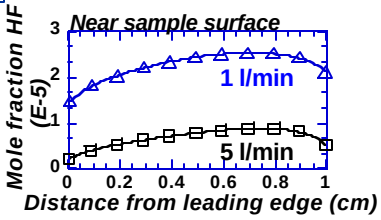
- Gas velocity increases with flow rate à at 50 mm from surface, velocity is three times higher at 5 l/min than at 1 l/min.

Higher Concentration of HF is Located Downstream

- Simulations showed that HF concentration is significantly affected by gas flow rate:
  - HF is concentrated toward the trailing edge of the sample.
  - Lower overall HF concentration at higher flows.
  - HF concentration at the surface of the sample decreases with increasing flow rate.
- BaF_2 decomposition / YBCO formation proceeds from leading edge.

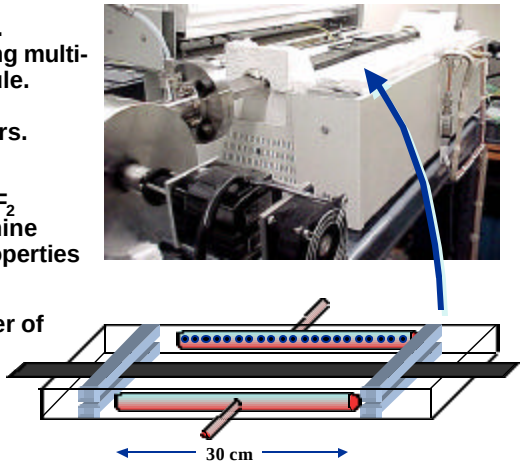






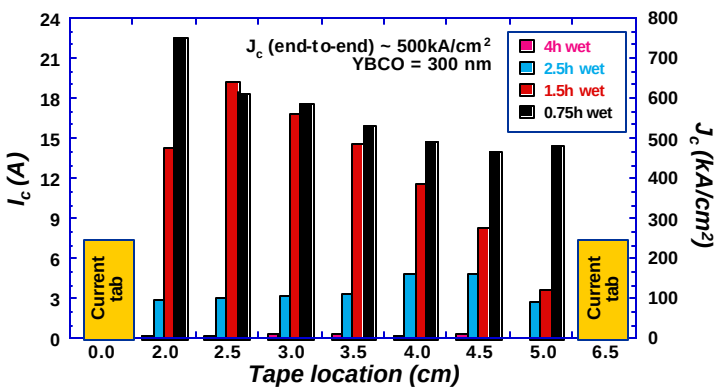
A Single Flow-Module Reel-to-Reel Metallic Reaction Chamber was Constructed to Verify the Design Concept

- **Furnace:** Single 60 cm zone.
  Chamber material: Inconel 601.
  Gas injection: Single 30 cm-long multi-nozzle transverse flow-module.
  Sensors: Multiple pressure, oxygen, and humidity sensors.
  Operation: "Stationary"
- 1 cm x 6.5 cm RABiTS with BaF_2 precursor were used to determine processing-microstructure-properties relationship.
- Sample was translated to center of flow-module before temperature ramp-up. Sample was oscillated within flow-module during processing.



Ability of Transverse Flow Design to Convert YBCO was Verified by Initial Runs

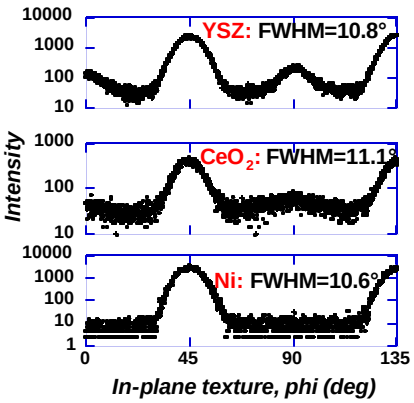
- **Samples:** Ni / CeO_2 / YSZ / CeO_2 / BaF_2 à YBCO
  ORNL(s) / ORNL(s) / ORNL(s) / ORNL(s) / ORNL(m) ORNL(s)



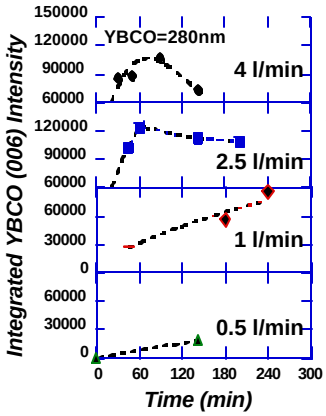
- **Higher** J_c values and **shorter** conversion time compared to previous versions.

Design of Experiment : To Explore Processing Parameter – Properties Relationship

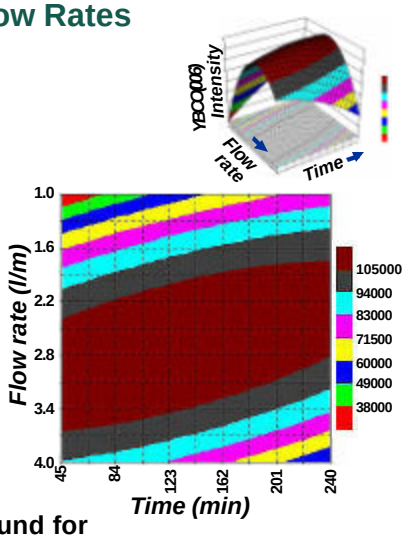
- **Samples:** A one meter long BaF_2 coated RABiTS was cut into 6.5 cm sections - Ni / CeO_2 / YSZ / CeO_2 / BaF_2 à YBCO
  3M(m) / 3M(m) /ORNL(m) / ORNL(m) / ORNL(m) ORNL(s)
- Flow rate and conversion time were varied (all others fixed).
- As received seed-layer contains:
  - ~ 1% (111) out-of-plane component
  - ~ 10% 45° in-plane rotation.
- Short samples converted in longitudinal flow furnace:
  - J_c = 860 kA/cm² (77K)
    YBCO = 280nm
    à Expected best value based on texture.



YBCO Intensity Increases at a Reduced Rate at Very Low Flow Rates

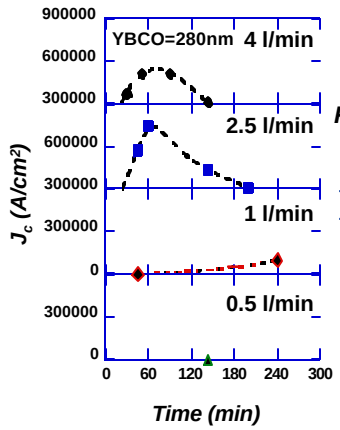


Response Surface Analysis

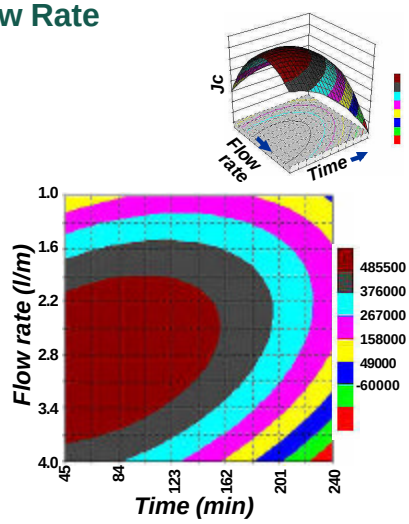


- Maximum YBCO intensity was found for intermediate to high flow rates.

Maximum Value of J_c was Attained at a Moderate Flow Rate



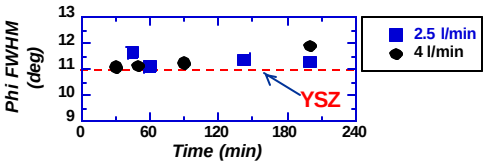
Response Surface Analysis

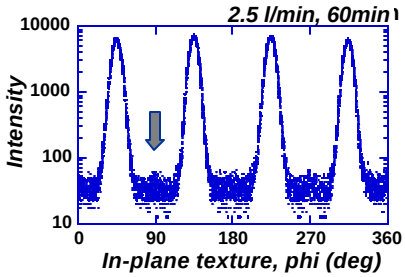


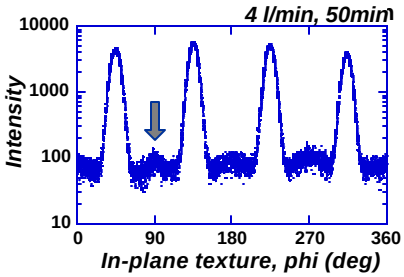
- Max J_c = 750 kA/cm^2.
- J_c response corresponds remarkably well with that of YBCO intensity.

Texture Analyses of These Sample Revealed Some Interesting Features

- In-plane textures of samples from 2 flow rates are similar, and agree well with buffer.
- Little or no 45° in-plane rotation in YBCO!

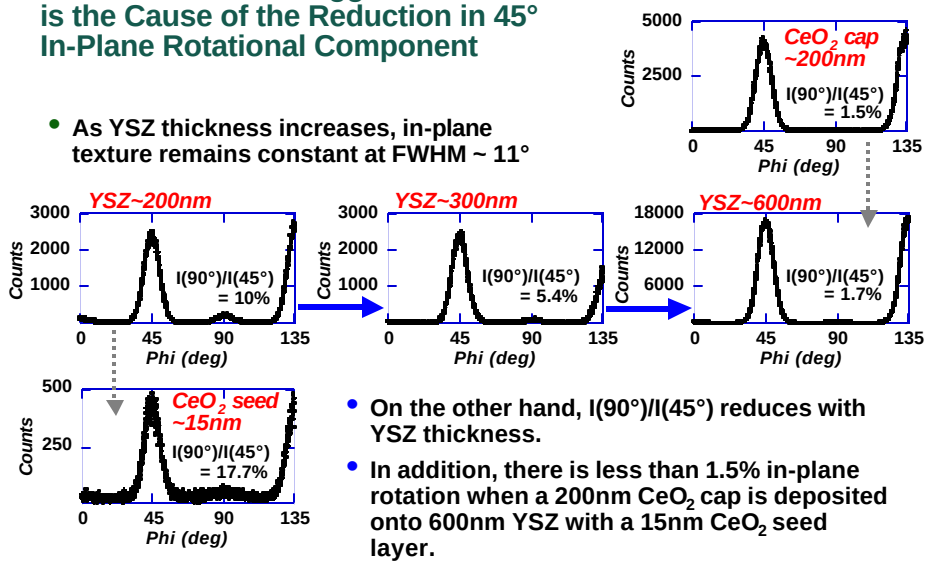






Indirect Evidence Suggests that YSZ is the Cause of the Reduction in 45° In-Plane Rotational Component

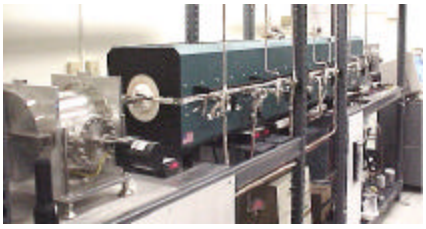
- As YSZ thickness increases, in-plane texture remains constant at FWHM ~ 11°

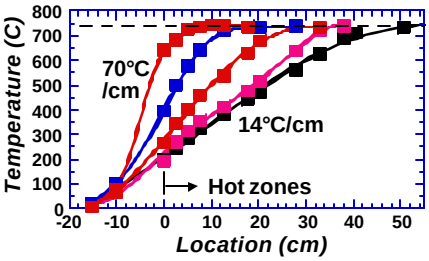


- On the other hand, I(90°)/I(45°) reduces with YSZ thickness.
- In addition, there is less than 1.5% in-plane rotation when a 200nm CeO_2 cap is deposited onto 600nm YSZ with a 15nm CeO_2 seed layer.

A 22 zone Furnace with a Seven Flow-Module Reel-to-Reel Metallic Reaction Chamber was Built to Study *Ex-Situ* Conversion of Long-Length YBCO

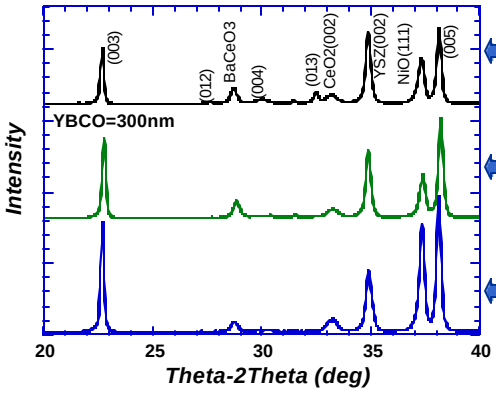
- In operation on June 22, 2000.
- Combines tape movement and temperature profile to mimic heat treatment in stationary conversion.
- Furnace: 2 meter long, 22 hot zones.
  Gas injection: Seven 30 cm-long flow-modules, independent flow rate, wet or dry.
  Tape capacity: 1-3 meters.
  Operation: Single pass.
- Sizable range of temperature gradients possible by manipulating the hot zones.
- Five 6.5cm, one 30cm and four 1 meter samples have been processed.





Randomly Oriented YBCO was Found when a High Ramp-Up Rate was Utilized

- **Samples:** Ni / CeO_2 / YSZ / CeO_2 / BaF_2 à YBCO
  3M(m) / 3M(m) / ORNL(m) / ORNL(m) / ORNL(m) ORNL(m)



Velo=1.73 m/h, I_c = 0.2A ± 0.2:
Conversion time = 45 min,
Ramp-up rate ~ 90°C/min.

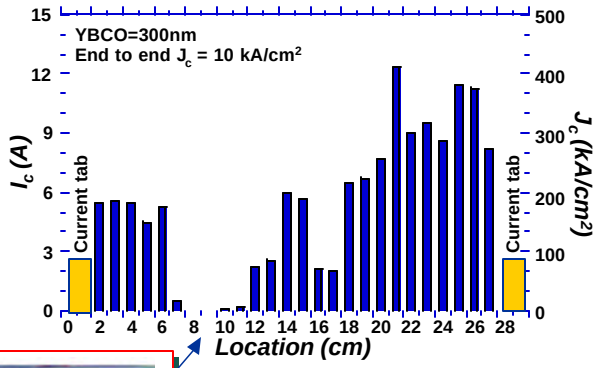
Velo=1.30 m/h, I_c = 7.6A ± 0.4:
Conversion time = 60 min,
Ramp-up rate ~ 68°C/min.

Velo=0.86 m/h I_c = 6.8A ± 0.5:
Conversion time = 90 min,
Ramp-up rate ~ 45°C/min.

First Conversion of "Long-Length" YBCO Gave Encouraging Results

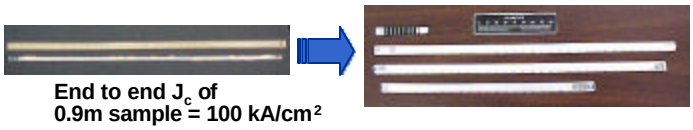
- **30 cm Sample:** Ni / CeO_2 / YSZ / CeO_2 / BaF_2 à YBCO
  3M(m) / 3M(m) / ORNL(m) / ORNL(m) / ORNL(m) ORNL(m)

- Sections with zero or very low J_c correspond exactly to locations where there was a halt in precursor deposition due to discharge.

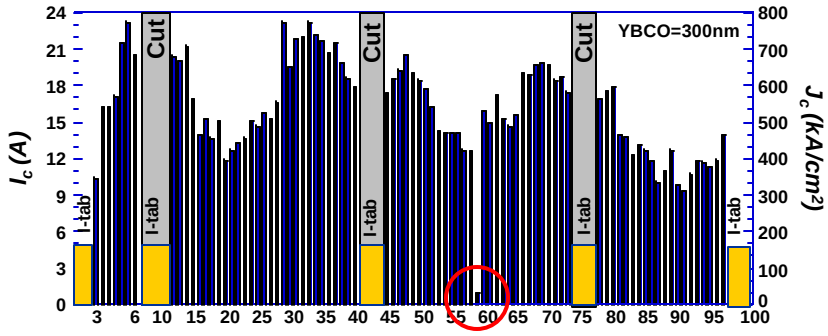


Adjustment in Processing Parameters Enabled Us to Almost Fully Convert the Third 1-meter Tape

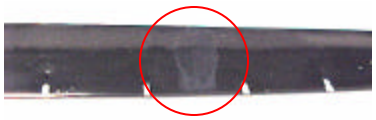
- **1 meter Sample:** Ni / CeO_2 / YSZ / CeO_2 / BaF_2 à YBCO
  3M(m) / 3M(m) / 3M(m) / ORNL(m) / ORNL(m) ORNL(m)
- Ni/CeO_2/YSZ deposited by 3M at a rate of 30 cm/min!!



End to end J_c of 0.9m sample = 100 kA/cm²

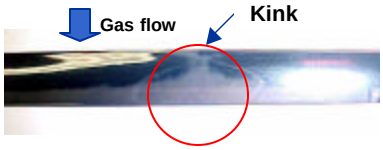


Low 1 Ampere I_c Section Corresponds to a Blemish in the Precursor Before/During Deposition

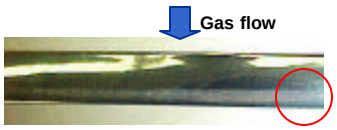


- There are other flaws besides those generated during precursor deposition: e.g. Incomplete conversion due to:

Ø Tape mishandling:

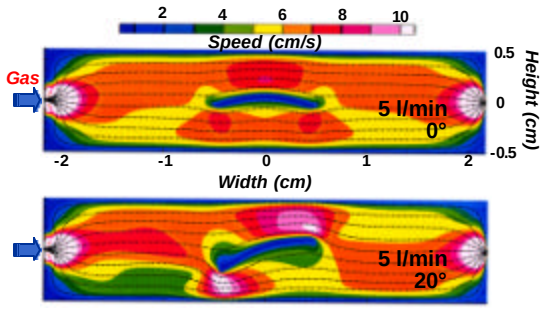


Ø Sample curvature / tilting:

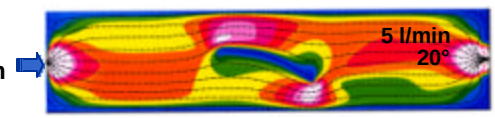


Sample Curvature and Tilting Can Affect the Flow Profile Within the Reaction Chamber

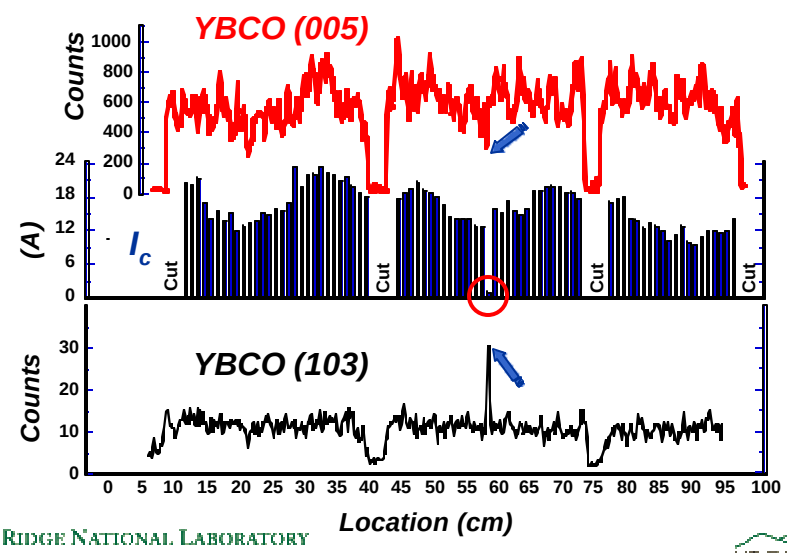
- Sample curvature can perturb the flow profile: slightly reduced gas velocity at leading and trailing edges.
- Sample tilting towards gas inlet leads to reduced velocity at the leading edge and increased velocity at the trailing edge.



- Reverse is true for sample tilting away from inlet à this combines with BaF_2 concentration downstream can strongly reduce the reaction.



Variations in Critical Current Follow Amount of Epitaxial YBCO



FY 2000 Plans and Performance

- **To Design and demonstrate an integrated set of laboratory-scale equipment that is capable of handling moving tape throughout the conductor fabrication process:**
  - Reel-to-reel systems were designed, built, and put into operation.
  - Systems range from tape cleaning to Ni annealing to deposition to YBCO conversion.
- **To develop laboratory-scale processes for conductor fabrication using the new equipment:**
  - Operation of these systems has been verified.
  - Long lengths of textured Ni can be formed at 1 m/h.
  - Continuous x-ray characterization can be conducted in long lengths.
  - Optimization of CeO_2 seed-layer deposition is underway.
  - BaF_2 precursor with good averaged composition was deposited in 1 m lengths.

FY 2000 Plans and Performance (cont.)

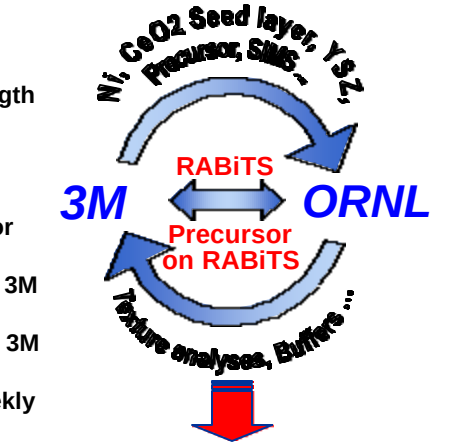
- **To demonstrate lengths of YBCO coated conductor produced by these processes and equipment:**
  - Validity of transverse-flow design was verified.
  - Ability of Inconel 601 to resist corrosion and oxidation was demonstrated.
  - *Ex-situ* YBCO conversion can now be performed in moving lengths.
  - Optimization of processing parameter for flow-module is underway.
  - Meter-length of YBCO was processed: Sectional J_c range from 300 to 750 kA/cm^2.
  - Defects that reduced J_c to zero in long-length samples were located.

FY 2001 Plans

- **Improve the structure, processing and throughput of buffer layers:**
  - Use Design of Experiment in conjunction with reel-to-reel equipment.
  - Develop equipment and procedures to improve tape handling to reduce defects.
- **Further develop *Ex-situ* process to convert YBCO in 1 meter lengths:**
  - Improve homogeneity of precursor and YBCO conversion.
  - Identify and optimize dominant processing parameters.
  - Target J_c of 1 MA/cm^2.
  - Collaborate with LANL to process YBCO on meter-length IBAD.
- **Fabricate meter-length RABiTS using textured alloys:**
  - Modify equipment to handle strengthened alloys if necessary.
  - Optimize processing parameters to produce meter lengths of Alloy RABiTS.
- **Continue to assist collaborators with equipment design and conductor characterization:**
  - Continue technology transfer of equipment design and ideas.

Technology Integration: Strong and Close

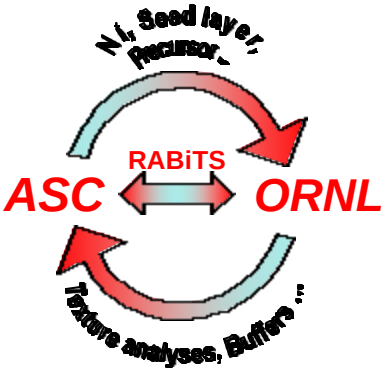
- **3M:**
  - We have fabricated long length RABiTS where both collaborators performed deposition on SAME tape.
  - 2-way exchange of BaF_2 precursor-coated RABiTS for conversion studies.
  - Characterized ~40 spools of 3M buffered tapes (~400 m).
  - Contributed to the design of 3M XRD capabilities.
  - Quarterly meetings and weekly telephone conferences.



First Long Length YBCO Produced by Collaboration Between US Industry and Gov't Lab

Technology Integration (cont.)

- **ASC:**
  - We have fabricated long length RABiTS where both collaborators performed deposition on SAME tape.
  - Received ASC TFA precursor-coated RABiTS for conversion.
  - Characterized ~7m of ASC buffered tapes.
  - Transferred detailed drawings of ORNL deposition and reel-to-reel equipment to ASC.
  - Contributed to the design of ASC XRD capabilities.
  - Received valuable vacuum heater information from ASC.
  - ASC employee temporarily assigned to ORNL.
  - Regular meetings and weekly telephone conferences.



Technology Integration (cont.)

- **MCT/Oxford:**
  - Assisted Oxford in fabricating long length Ni tapes.
  - Characterized long length MCT buffered tape by XRD.
  - Contributed to the design of MCT XRD capabilities.
- **EURUS:**
  - Assisted EURUS in fabricating long length Ni tapes.
  - Characterized meters of EURUS Ni by XRD.
  - Transferred sol-gel technology.
- **Southwire:**
  - Assisted Southwire in demonstrating machine winding of Ni tapes.
- **LANL:**
  - Provided details for design of reel-to-reel equipment.
  - Obtained valuable information from LANL for the design of reel-to-reel J_c equipment at ORNL.
  - Quarterly meetings and weekly telephone conferences via 3M CRADA.
- **Stanford University:**
  - Obtained valuable information and ideas via 3M CRADA.
- **Dissemination of Technical Information:**
  - 40 publications and 15 Presentations.
  - 6 US patents issued.