FUNDAMENTAL ISSUES FOR COATED CONDUCTORS

OAK RIDGE NATIONAL LABORATORY

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Our Team

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Funding

- **FY 2000 EE/RE Funding: $1,750K**
  - 7 FTE Staff, 4.0 FTE Post-Doctoral Fellows, 1.5 FTE Student

This project is collaborative with the Office of Basic Energy Sciences.

- **FY 2000 BES Funding: $250K**
  - 1.0 FTE Staff, 0.5 FTE Student

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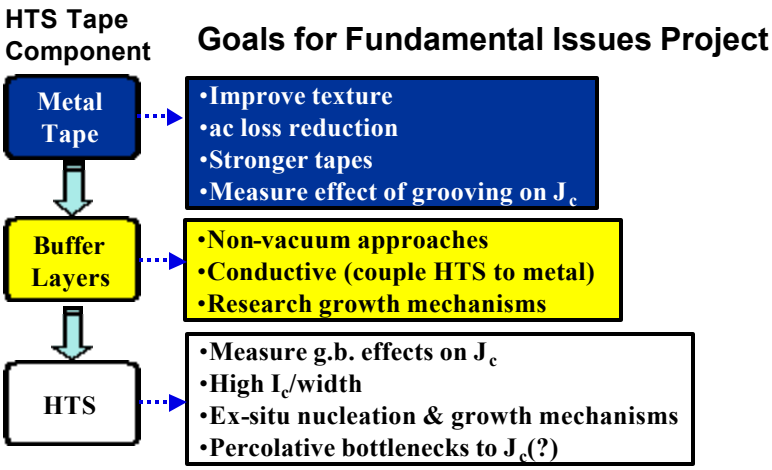
Industrial Licensees/Partners

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

- **GOAL:** To develop a basic understanding of fundamental issues related to coated conductor development for high-temperature and high-field applications.

- **APPROACH:** Address issues related to each of the three important steps of the RABiTS™ process - biaxially textured metal fabrication, buffer layer deposition and superconductor deposition.

Fabrication of YBCO on RABiTS: ORNL Research Framework



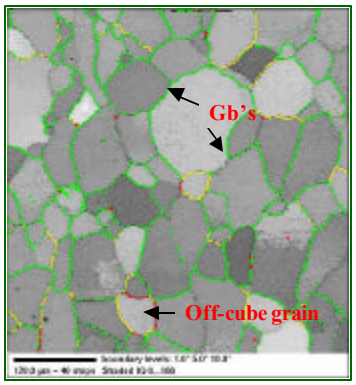
OUTLINE

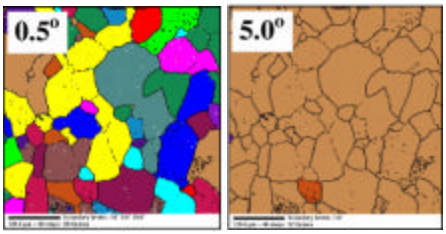
- **FY 2000 Results:**
  - Texture and percolation in long length RABiTS (Amit Goyal)
  - Effects of grain boundary grooving in Ni on J_c
  - New results on effects of GB misorientation angle on J_c
  - Further development of non-magnetic, strengthened alloys
  - All solution buffer layers on Ni (M. Paranthaman)
  - YBCO using TFA on RABiTS
  - Industrial Highlight: American Superconductor (M. Rupich)
  - All conductive oxide buffer layers on Ni (D. Christen)
  - Thick YBCO films on RABiTS
  - Nucleation & growth of YBCO in the ex-situ BaF_2 process
- **FY 2000 Performance and Plans for FY 2001**
- **Technology Integration**

Possible Fundamental Limitations to J_c in Long Length Epitaxial Conductors on RABiTS

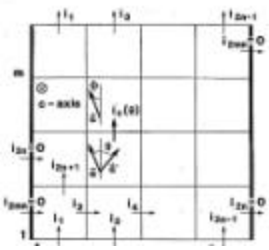
- **Secondary texture components, i.e. non-cube orientations**
- **Full-width-half-maximum (FWHM) of the in-plane and out-of-plane textures in cube oriented material**
- **Texture in-homogeneity in long lengths of RABiTS**
- **Percolation in long lengths due to physical size of the conductor, i.e. grain size in conductor relative to width of conductor**
- **Grain boundary grooving in metal substrate**

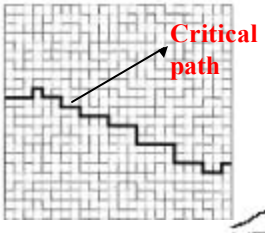
Scaling of Percolative Current Flow to Long Lengths





Limiting Path Model of the Critical Current in a textured Y-123 Film, Phys. Rev.B, 40 (1989) 829.





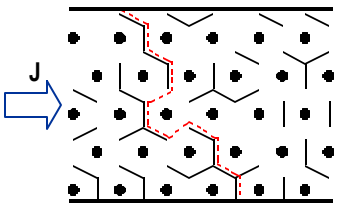
Limiting Path Calculations of Current Flow as a function of the width and length of conductor

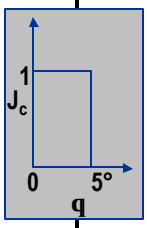
Single Cube Texture Case

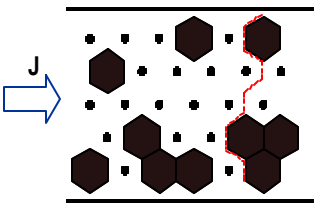
For a uniaxial texture with a FWHM of ϕ, GBMD is also a guassian with a FWHM of $\sqrt{2}\phi$.

When Secondary Texture components are Present

Non-cube orientations are assumed bad regions or grains





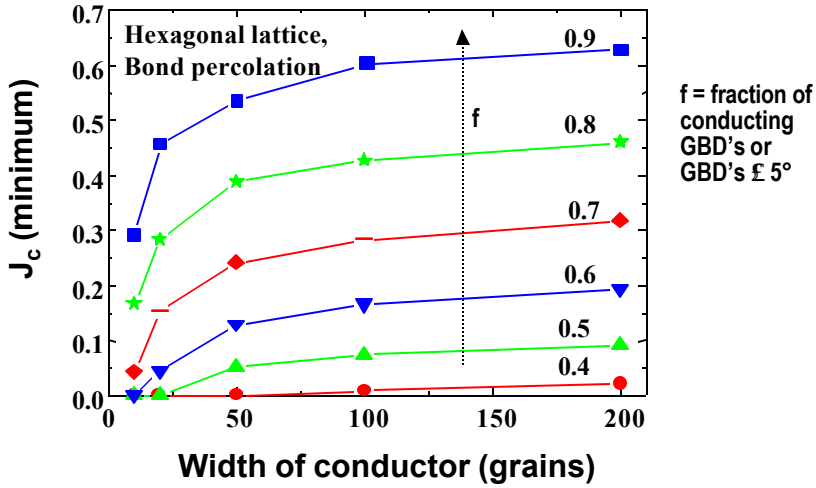


Limiting path, hexagonal bond (f_c = 0.35)

Limiting path, hexagonal site (f_c = 0.50)

To find J_c for a range of samples, J_c for 20,000 samples each 1000 grains long was calculated. Thus the total length sampled is 2 x 10^7grains (1Km for 50 mm grains).

Minimum J_c in a 1km wire as a function of the width of the wire and fraction of good Gbd's



Ref.: E. D.Specht, A. Goyal & D. M. Kroeger, Super. Sci & Tech., 13 (2000) 592.

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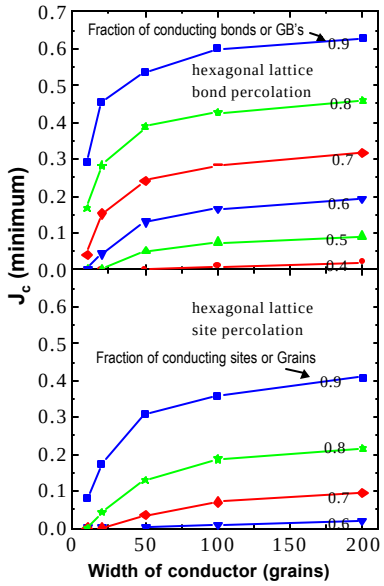
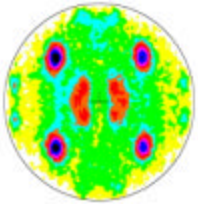
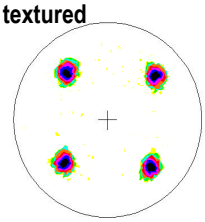
Non-cube texture components more strongly suppress current percolation



Non-cube texture components in Ni (111) pole figure



- **A good substrate should be > 99.5% cube textured**



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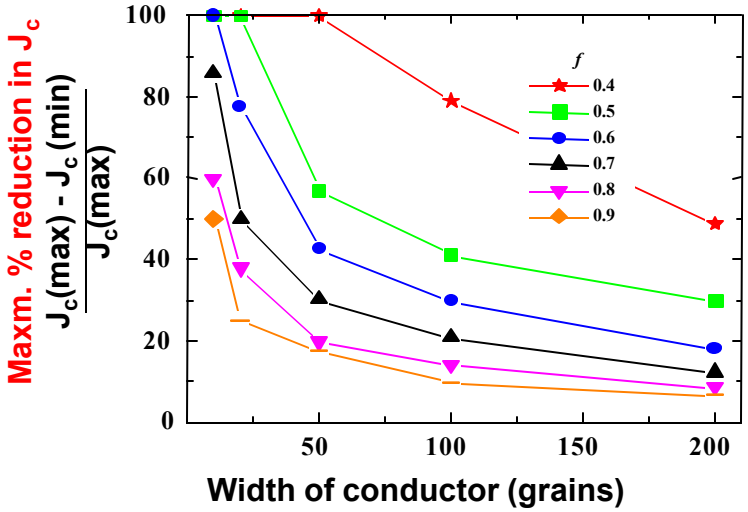
Reduction in J_c in going from a small sample to a kilometer is only 10%



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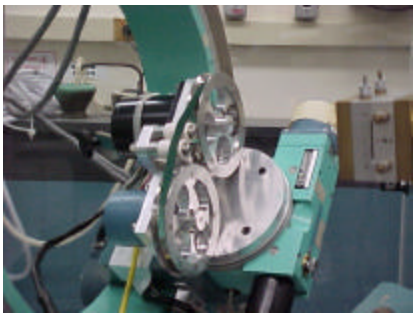
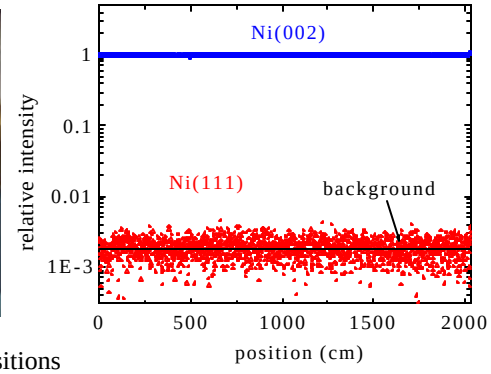
A 20-m-long Ni tape has 99.9% cube-texture and outstanding homogeneity

Reel-to-Reel X-ray Diffraction Capability

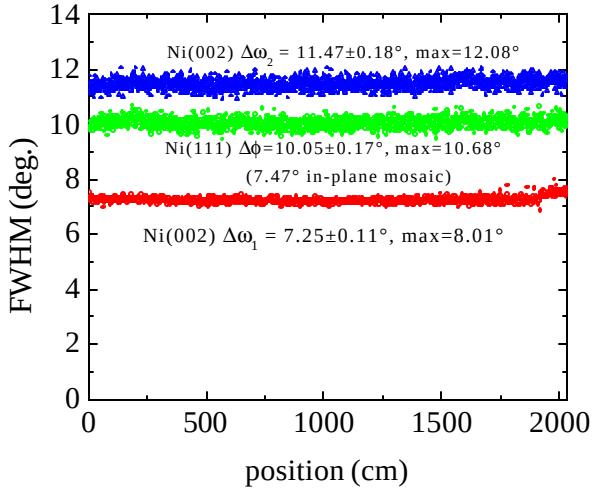




- Tape is scanned with fixed detector positions
- Scan speed = 5 cm/second for a fixed Bragg angle

- Tape obtained from 3M

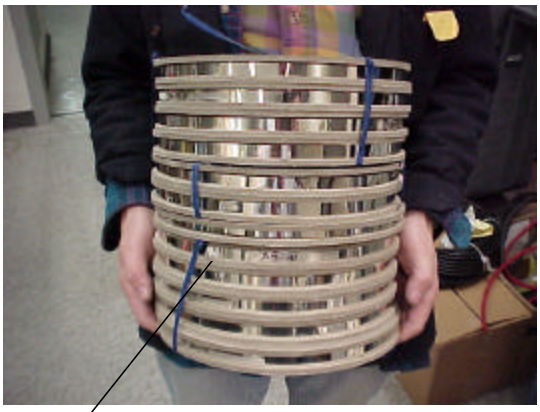
20 m Ni tape shows negligible variation in FWHM implying similar expected GB distributions along the length



• 2000 sets of rocking curves and ϕ scans at fixed sample positions

- Tape obtained from 3M

We have successfully specified rolling conditions and obtained homogeneous, well-textured Ni from an outside commercial source



~2 kilometers of rolled Ni, 1 cm wide and 2 mils thick

Summary

- On scaling to long lengths, J_c is not significantly affected by the width of the conductor if the conductor is at least 100 grains wide.
- For kilometer long conductors with fraction of good GB's (£ 5°) equal to 0.8 the J_c is 50% of that obtained for a single crystal film.
- The maximum reduction in going from short to long lengths (1km) or the maximum fluctuation in J_c is less than 10%,
  i.e. J_c (1km sample) = 90% J_c (short sample)
- Continuous reel-to-reel texture measurements on a 20m long Ni tape show excellent homogeneity of texture along the length with 99.9% cube texture!
- In-plane and out-of-plane texture in 20m long Ni tape were found to be constant implying similar expected GB distributions throughout the length of the conductor.
- Well textured substrates have been fabricated in lengths of ~ 2 km.

Understanding Effects of Grain Boundary Orientations in Coated Conductors

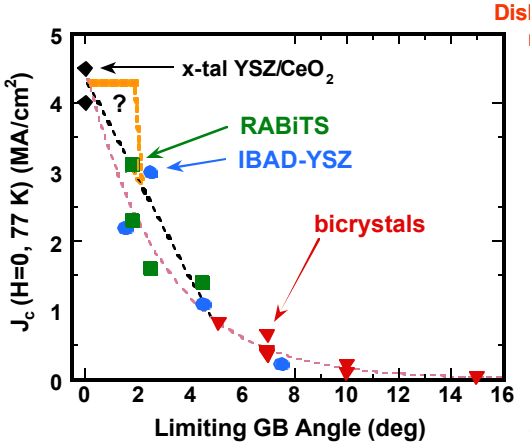
- **Studies of YBCO bicrystals show J_c decreases ~exponentially with gb angle for angles greater than ~4°**
  - *Several signatures of tunneling-limited currents in high-angle regime*
  - *Typical transport measurements inconclusive in low-angle range (cannot resolve grain from grain-boundary limitations)*

  GOAL: *Use high-resolution measurements to determine effects of low-angle grain boundaries on J_c*

- **Measured orientation maps of grain-to-grain angles indicate predominantly low-angle distributions in CC**

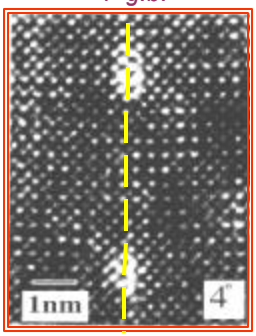
For Coated Conductors, J_c Depends on Observed Grain-to-Grain Connectivity

- ***Systematic, similar behavior for RABiTS and IBAD***



Dislocations cores separate ~undisturbed material, according to *2Dsin(q/2)=b*

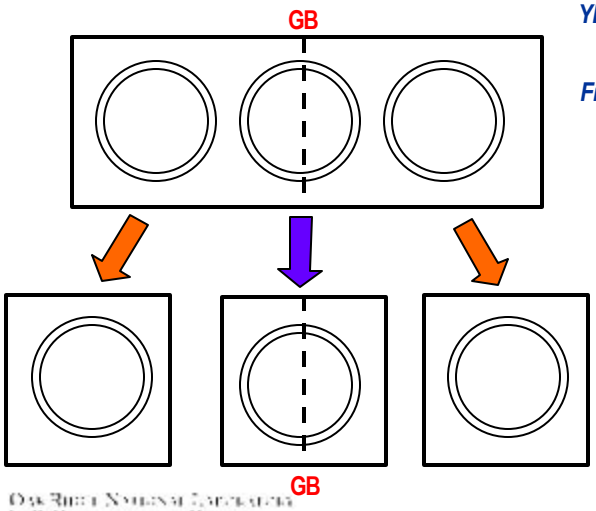
4° g.b.



Wen, *et al*., IEEE Trans. Appl. Supercond. **9** (1999)

Persistent Current Approach

Ring experiment compares GB to Grains by inducing maximum persistent current



YBCO films deposited by PLD on Bicrystal $SrTiO_3$ substrates

Films patterned to 3mm diameter rings by photolithography

Current induced in rings

1. Cool to Low Temp
2. Apply saturation field
3. Remove applied field
4. Measure persistent moment vs. T for each

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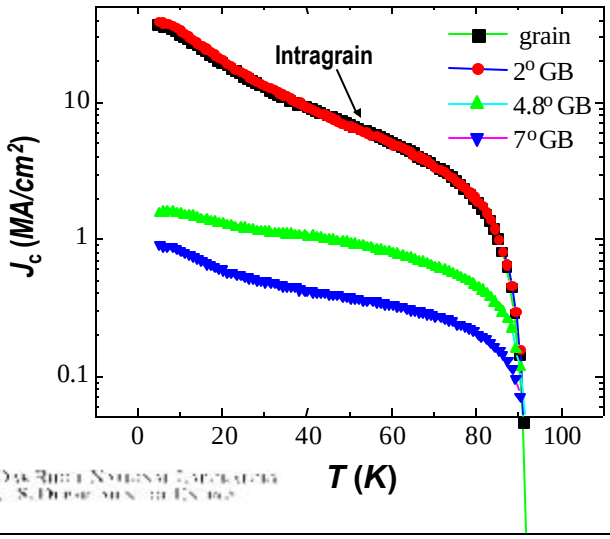
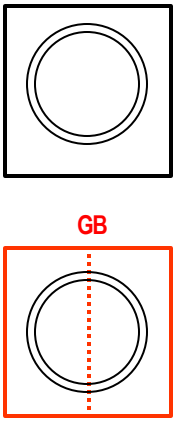
J_c for 2° GB Ring is same as that for bulk

Compare Temperature Dependence of Grain vs. Grain Boundary





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Conclusions

- **High-resolution, self-organized magnetic measurements show:**
  - ***Clear grain-boundary limiting of J_c by 4.8° and 7° gb's, including magnetic hysteresis signature***
  - ***Virtually no limitation by 2° gb***
  - ***Measurements of gb in crossover, 3° range is in progress***

- **For coated conductors with limiting grain boundary angle <3°, expect J_c is predominantly limited by intra-grain properties**
- **It will be desirable to minimize presence of grain boundaries over 4°.**

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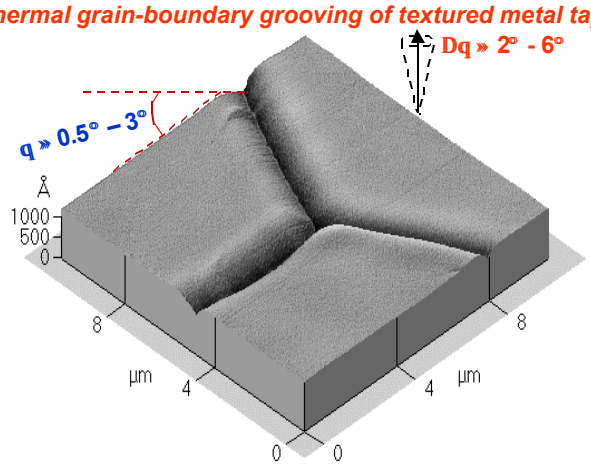
Significance of Vicinal Substrate Surfaces in Coated Conductors

- ***Coated conductor substrates have vicinal surfaces from:***
  - ***Out-of-plane texture, typically 2 - 6°, of textured metal (RABiTS) or buffer layer (IBAD or ISD)***
  - ***Thermal grain-boundary grooving of textured metal tape (RABiTS)***



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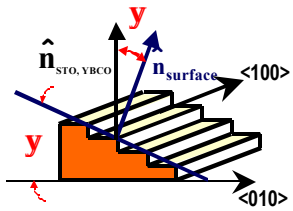
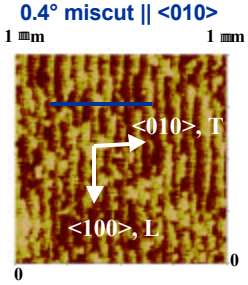
Growth and superconducting properties of YBCO films on vicinal STO (001)

- Controlled studies of YBCO on vicinal $SrTiO_3$ were conducted to explore effects of growth defects on J_c



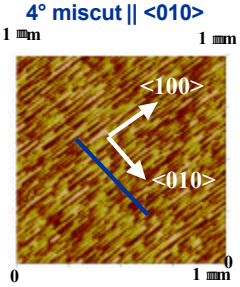
0.4° miscut || <010>



step height = a_{STO}

step width = 550 Å

4° miscut || <010>

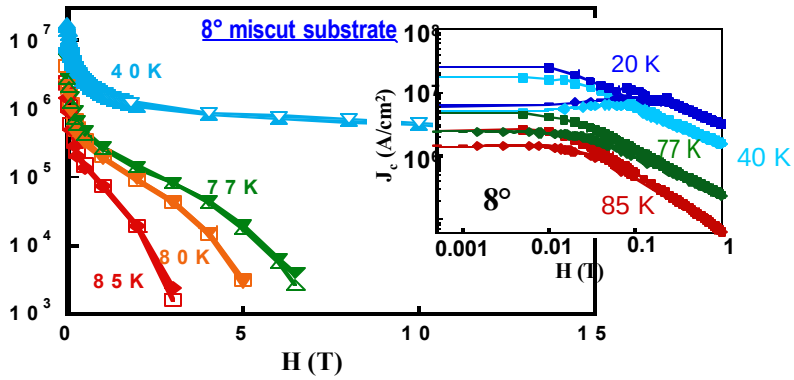


step height = 2-3*(a_{STO})

step width = 110-160 Å

Anisotropy of transport J_c

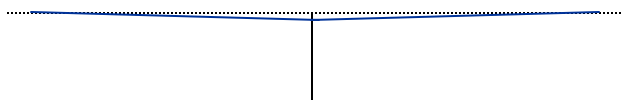
- For all films J_c along L and J_c along T differ only in a small field range (J_{cL}>J_{cT} only for H < ~ 0.2 T)
  - J_c is hardly degraded
- H_{irr} is not higher than in a typical YBCO film on well oriented STO
  - antiphase boundaries do not appear to be strong pinning sites



Grain boundary groove characteristics in textured Ni

AFM measurements on 300 GB grooves in samples annealed at 800°C between 10-120 mins show that the average dimensions of GB grooves are:

- **Width = 1.25-1.7 mm; Depth = 175-290 Angstroms**
- **Dihedral Angle = 175-179°**
- **Slight linear increase of groove depth with GB misorientation.**



- at 800°C for 2 hrs, grooves are completely developed and quite exaggerated

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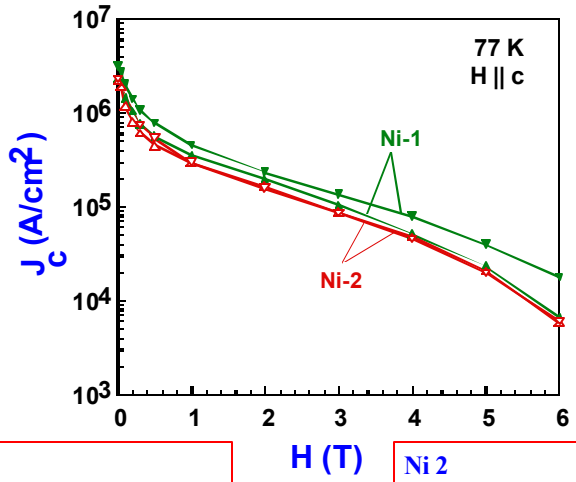
High J_c is observed even with exaggerated grooves!



Ni 1
Sample 1: 2.3 MA/cm^2
Sample 2: 2.2 MA/cm^2

Ni 2
Sample 1: 3.3 MA/cm^2 (0.4 mm)
Sample 2: 2.3 MA/cm^2

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Conclusions

- Miscut substrates do not have a substantial effect on J_c.
- Hence RABiT substrates with various miscuts on different
- Grains do not show a big variation in J_c.
- Grain boundary grooving in Ni does not significantly affect J_c.

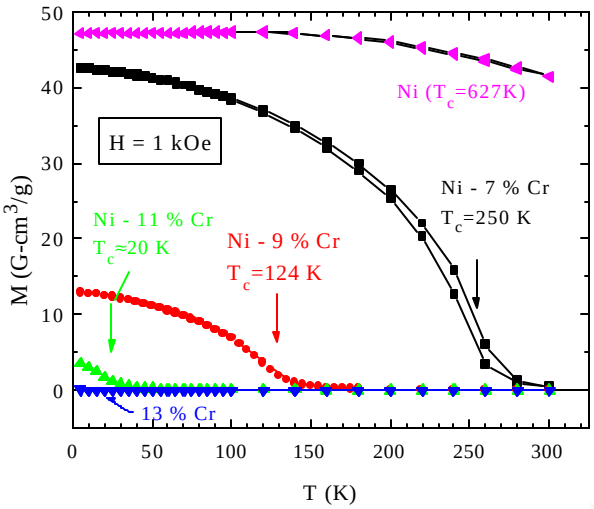
Substrates with reduced magnetism and increased mechanical strength compared to high purity Ni

Objective: To develop a family of ~100% cube textured Ni-based alloys with reduced magnetism and improved mechanical properties compared to Ni

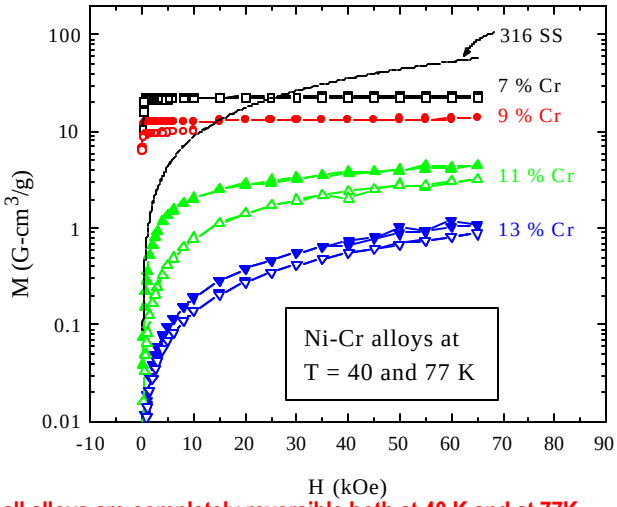
Motivation:

- Various HTS applications have different requirements for the substrate in terms of magnetic and mechanical properties
- Our CRADA partners use different deposition techniques placing different requirements for the substrate to maintain its cube texture as a function of temperature
- It would be desirable to have the minimum alloy content as possible to reduce the complications associated with obtaining high quality oxide buffer layers

Magnetic moment versus temperature for a range of Ni-Cr alloys from 7-13at% Cr

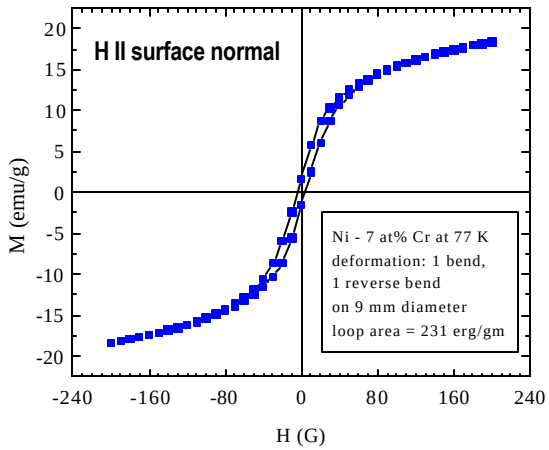


All the Ni-Cr alloys are completely reversible and show no hysteresis in the MH loop



- all alloys are completely reversible both at 40 K and at 77K

Hysteretic AC losses in Ni-7%Cr are estimated to be much lower than that observed for BSCCO



- Eddy current losses are expected to be minimal

For a 1 cm wide tape, with a 1 mm YBCO layer and a J_c of 1 MA/cm^2, the amount of Ni in a 1 kAm conductor is 5 cm^3

Loss per cycle = 231 ergs/gm
~ 2000 ergs/cm^3

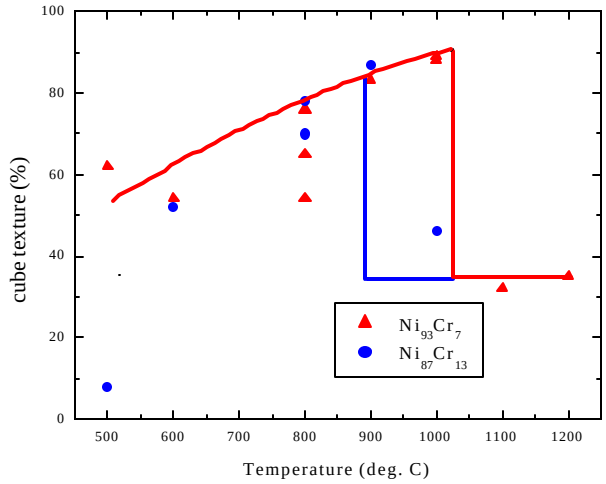
For a 5 cm^3 Ni-7%Cr substrate the AC losses = 60 mW / kAm compared to 1 W / kAm for BSCCO

Mechanical properties of Ni-Cr alloys as a function of Cr content

Substrate	YS (0.2%)	UTS
Ni	34 MPa	221 MPa
Ni-7%Cr	64 MPa	304 MPa
Ni-9%Cr	87 MPa	
Ni-11%Cr	102 MPa	
Ni-13%Cr	164 MPa	525 MPa
Ni-13%Cr -4%Al	228 MPa	657 MPa

- Tensile tests were performed on laser machined dog-bone samples with the stress applied along the [100] direction.

Cube texture in Ni-Cr alloys increases until onset of secondary recrystallization



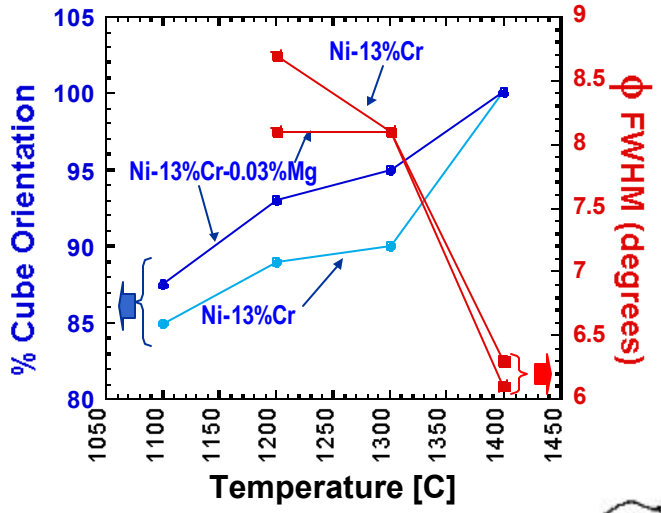
- higher Cr results in lower secondary recrystallization temperature

Texture studies on Ni-13at%Cr Substrates

- Alloys containing 7-13at%Cr can be textured to ~ 100% cube texture.
- Secondary recrystallization temperatures (SRT) have been shifted to higher temperature, however SRT is a function of the composition.
- In-plane and out-of-plane textures are comparable to that obtained in Ni and are typically, Df = 7°.

	7%Cr	9%Cr	11%Cr	13%Cr	13%Cr (0.03%Mg)	Heat Treatment
%Cube	99.4	99.5	99.6	98	(~99%)	1000°C, 30mins Slow heat/cool rates
%Cube	99.9	99.6	99.3	89	98.4	1050°C, 30mins Slow heat/cool rates
%Cube	99.9	98.8	99.9	99.9	Recryst. Completely	1100°C, 30mins Slow heat/cool rates
%Cube	99.8	99.6	100	93	99.5	1100°C, 15mins Fast heat/cool rates
%Cube Int.(002)	99.5 (RE Start)	99.5 (86K)	99.8 (76K)	92 (70K)	96.3 (56K)	1200°C, 15mins Fast heat/cool rates
%Cube Int.(002)	99.5 (56K)	98.3 (85K)	Recryst. Completely (0K)	Recryst. Completely (0K)	Recryst. Completely (0K)	1300°C, 15mins Fast heat/cool rates

100% cube textured Ni-13at%Cr substrates with no secondary recrystallization have been fabricated

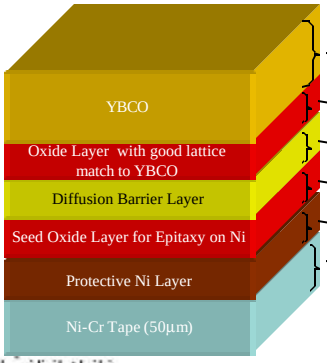


Long lengths of Ni-Cr substrates have been fabricated

Alloy Comp.	Length/thickness	No. of Reels
13%Cr	55 m / 50 mm	6 @ 1cm and 5 @ 0.5 cm
13%Cr-0.03%Mg	55 m / 50 mm	6 @ 1cm and 5 @ 0.5 cm

Method to deposit high quality epitaxial oxide buffer layers on Ni-Cr substrates

- Key is to prevent the formation of chromium oxide.
- Can be easily achieved by depositing a layer of Ni at low temperatures on the substrate before depositing the oxide buffer layers.
- The layer is also transient because it diffuses into the Ni during deposition final oxide layers.



By PLD or *ex-situ* BaF_2 precursor method

CeO_2 (10 nm)

YSZ (400 nm)

CeO_2 (10 nm)

Ni (~5 mm)

Ni-Cr (50 mm)

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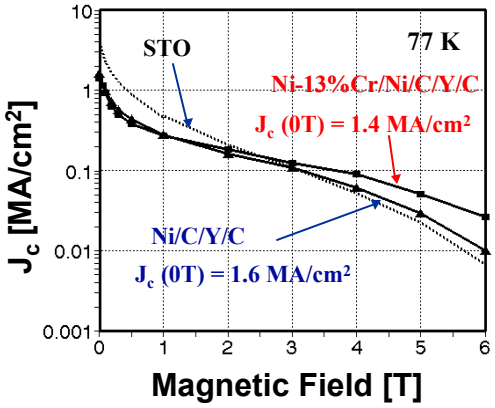
Excellent epitaxy and high-J_c is obtained for YBCO films on Ni-13at%Cr substrates

- In-plane texture for YBCO was same as that for the substrate: Dj = 7.7°
- Out-of-plane texture for YBCO improved significantly from that of Ni-Cr

Rocking curves

In	About
YBCO 3.7°	YBCO 6.9°
YSZ 4.3°	YSZ 7.9°
CeO_2 4.4°	CeO_2 7.0°
Ni-13%Cr 4.7°	Ni-13%Cr 9.2°



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Summary: Ni-Cr alloy substrates

- Highly textured (>99.5% cube) Ni-Cr substrates with Cr contents ranging from 7at% to 13at%, Curie temperatures ranging from 255 K to 0 K and yield stress ranging from 64 MPa to 228 MPa were fabricated, thereby providing CRADA partners with a matrix of alloy compositions and resulting physical properties to choose from.
- SRT temperatures even for 13at%Cr alloy was raised to over 1400°C. Long lengths of such substrates have been fabricated.
- AC losses for 7%Cr alloy were estimated to be a factor of 15 lower than that for BSCCO.
- YBCO films with J_c's over 1 MA/cm^2 have been successfully grown on Ni-13at%Cr substrates using the *protective* Ni layer approach.

OUTLINE

- FY 2000 Results:
  - Texture and percolation in long length RABiTS (Amit Goyal)
  - Effects of grain boundary grooving in Ni on J_c
  - New results on effects of GB misorientation angle on J_c
  - Further development of non-magnetic, strengthened alloys
  - All solution buffer layers on Ni (M. Paranthaman)
  - YBCO using TFA on RABiTS
  - Industrial Highlight: American Superconductor (M. Rupich)
  - All conductive oxide buffer layers on Ni (D. Christen)
  - Thick YBCO films on RABiTS
  - Nucleation & growth of YBCO in the ex-situ BaF_2 process
- FY 2000 Performance and Plans for FY 2001
- Technology Integration

Solution Precursor Approaches to Buffers and YBCO Superconductors

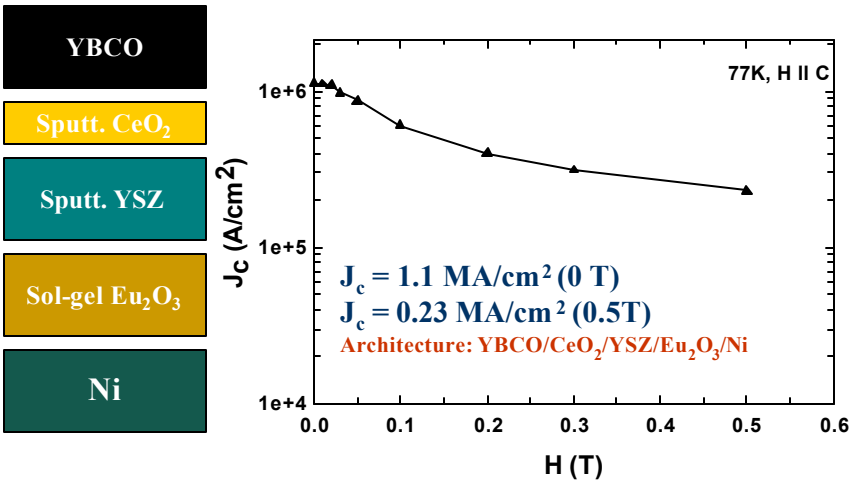
- Buffer layers
  - Sol-gel alkoxides
    - Rare Earth Oxides (RE_2O_3)
    - Rare Earth Zirconium Oxide ($RE_2Zr_2O_7$)
- YBCO
  - Metal-organic decomposition (MOD)
    - Trifluoroacetate (TFA) process
      Y,Ba,Cu trifluoroacetates

- **Advantages of solution process:**
  - Two-step process (coating and annealing)
  - Adjustment of precursor stoichiometry or doping is possible
  - Non-vacuum process
  - High volume deposition process

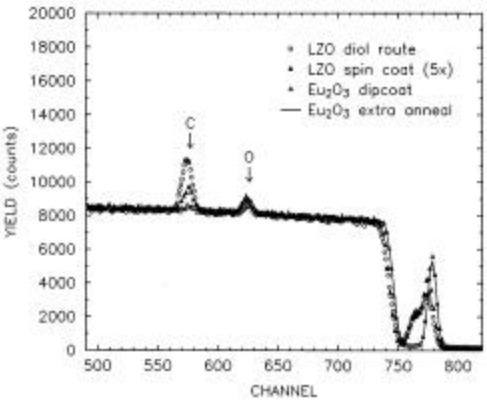
Recent progress towards solution buffers

- **Initial substrate preparation**
  - **sonication**, annealing in Ar/H_2 or high vacuum
- **Solution seed layers**
  - produced 30-50 nm/coat buffers in lengths using alkoxide precursors, single cube texture, crack-free, and continuous
  - demonstrated the growth of YBCO films with a J_c of over 1 MA/cm^2 on solution seed layers; technology transferred to ASC
  - carbon contamination; removed by longer post-annealing
  - multiple coating towards thicker films
- **All solution buffers on textured-Ni**
  - YBCO films with a J_c of 200,000 A/cm^2 at 77 K
- **YBCO TFA process on RABiTS**
  - reduced burn-out process time from reported 10 hours to 2-3 hours

High J_c Ex-situ BaF_2 YBCO films on Eu_2O_3 dip-coated seed layers have been demonstrated – FY 1999



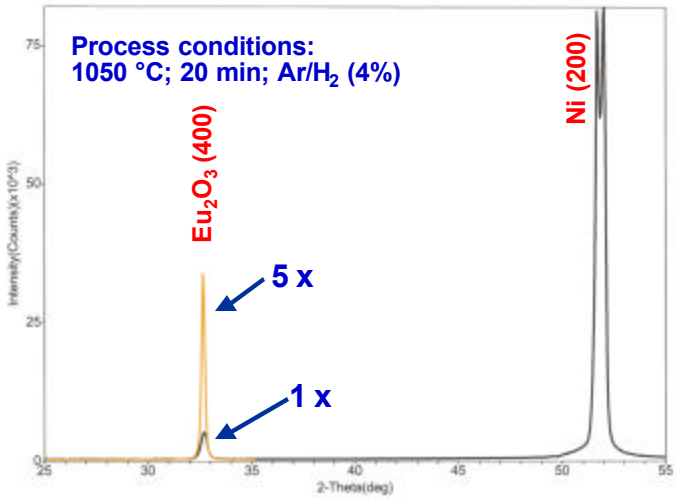
Longer annealing times during processing eliminate the presence of carbon in dip-coated buffers



- Exact amounts of C have been measured before on superconducting oxycarbonates (substitution of Cu atoms by carbon in HTS)
- C conc. has been converted to # of C-atoms per unit cell
  - LZO diol : 374 C-atoms/unit cell area
  - LZO spin: 136 C-atoms/unit cell area
  - Eu_2O_3 dip: 27 C-atoms/unit cell area
  - Eu_2O_3 : 6 C-atoms/unit cell area (extra anneal)
  - STO Xtal : 10 C-atoms/unit cell area (as a standard)

Carbon conc. in solution buffers have been determined using proton resonance (E_H = 1.73 MeV) from RBS

Sol-gel 200-nm-thick Eu_2O_3 buffer layers were grown epitaxially on textured-Ni substrates



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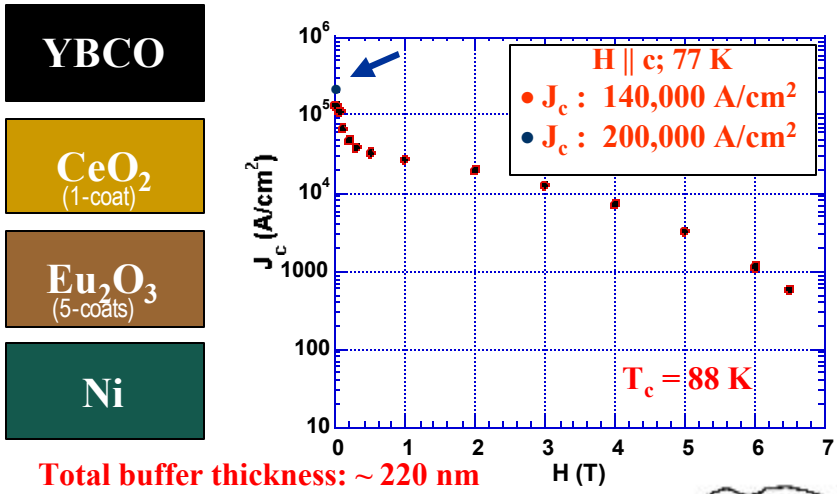
Demonstration of the growth of PLD YBCO films with a J_c of 200,000 A/cm² on all solution buffers



Total buffer thickness: ~ 220 nm

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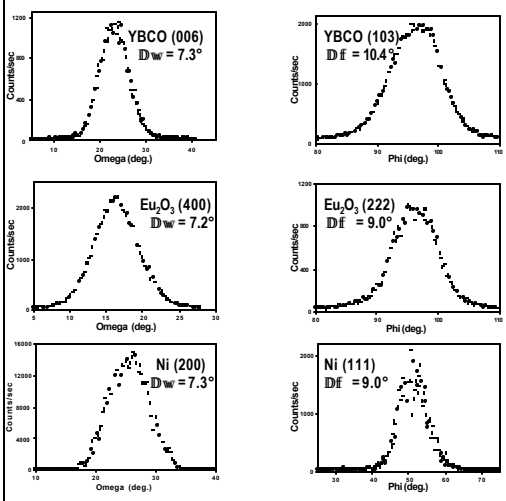
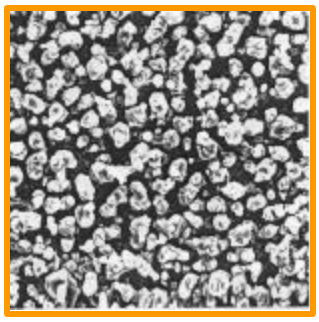
X-ray and Microstructure of PLD YBCO on all solution buffers

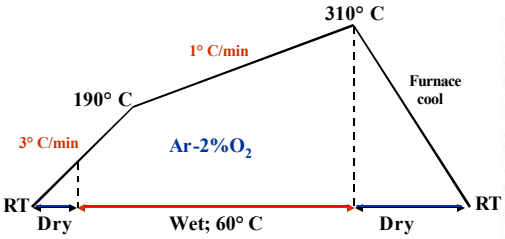




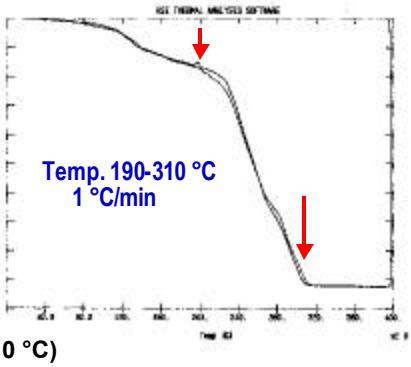
20 KX

- Porous microstructure
- NiO still present
- single cube texture
- improvements are possible

Progress on YBCO TFA precursors

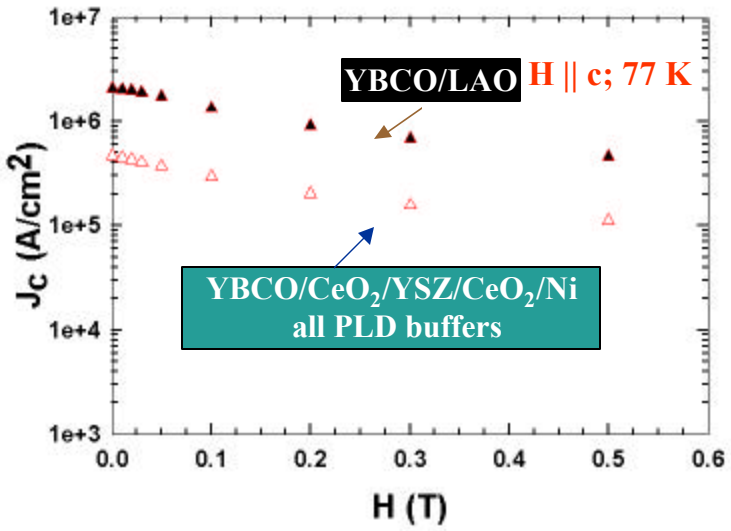


TGA data on TFA precursors



- Burn-out step has been shortened
  - 3 hours in Ar-2%O_2; 60 °C wet (RT to 310 °C)
  - in a stationary mode, produced 40 cm long crack-free TFA precursors on RABiTS
  - in a continuous mode,produced 10 cm long crack-free TFA precursors on RABiTS (coating speed: 20-30 m/h)

TFA derived YBCO films on RABiTS



Summary

- Solution seed layers provide a good template for producing YBCO films with a J_c of over 1 MA/cm^2
- Carbon free dip-coated buffers were produced
- Demonstrated the growth of YBCO films with a J_c of 200,000 A/cm^2 on all solution buffers using PLD
- Developed a short burn-out step for YBCO TFA precursors

Outline

- **FY 2000 Results:**
  - Texture and percolation in long length RABiTS (Amit Goyal)
  - Effects of grain boundary grooving in Ni on J_c
  - New results on effects of GB misorientation angle on J_c
  - Further development of non-magnetic, strengthened alloys
  - All solution buffer layers on Ni (M. Paranthaman)
  - YBCO using TFA on RABiTS
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  - All conductive oxide buffer layers on Ni (D. Christen)
  - Thick YBCO films on RABiTS
  - Nucleation & growth of YBCO in the ex-situ BaF_2 process
- **FY 2000 Performance and Plans for FY 2001**
- **Technology Integration**

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Current and Future Status of HTS Conductor Manufacturing at ASC

- Current capacity of Bi-2223 HTS conductor is 400 km/yr at ~$300/kA-m (77K, sf)
- Capacity is projected to increase to 2,000 km/yr by the year 2002
- Price of the Bi-2223 is projected to reach ~$50/kA-m by 2004
- Second Generation HTS conductors must be <$50/kA-m to compete with the Bi-2223 technology
- ASC Second Generation HTS conductor program focus:
  - low cost materials and processing
  - electrical performance and mechanical properties meeting or exceeding Bi-2223 conductors
- ASC partnering with many key Coated Conductor players

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ASC-ORNL Program Objectives

- Development of a YBCO HTS conductor technology based on low-cost, high rate manufacturing processes
  - Target conductor price of $10/kA-meter using RABiTS™ technology pioneered at ORNL
  - ASC-ORNL program directed to:
    - Reel-to-reel deposition of epitaxial buffer layers by low-cost, non-vacuum and/or vacuum technologies on deformation textured substrates
    - High J_c YBCO films on RABiTS™ substrates from metal trifluoroacetate (TFA) precursors

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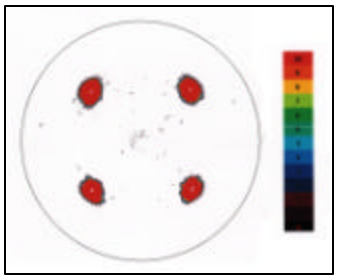
Deformation Textured Substrate Production

- Deformation textured Ni (1 cm x 50 mm) produced in lengths up to 140 meters
- Texture anneal performed in a reel-to-reel system
- Typical FWHM: ~ 7° w-scan; ~ 6.5° f-scan
- Average surface roughness (R_a) of ~ 15 nm
- 99.5% cube texture

Substrate bar stock



Ni (111) Pole Figure

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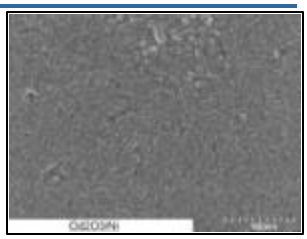
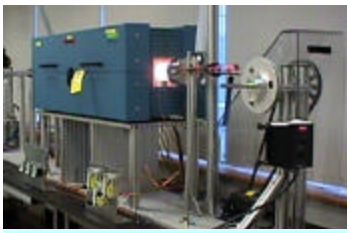
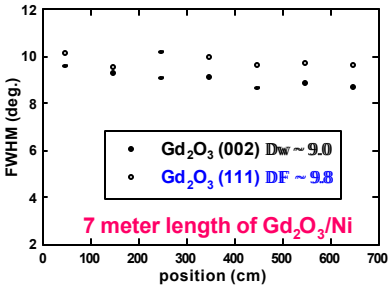
Reel-to-Reel Deposition of Oxide Seed Layers from Sol Gel Precursors

- Reel-to-reel laboratory web coating line developed at ASC for depositing and annealing of RE_2O_3 oxide layers on metal substrates
  - process based on ORNL technology
- Deposition rates of >0.5 meter/min
- Epitaxial texture and uniform coverage
- Gd_2O_3/Ni tapes used at ASC and ORNL for deposition of YSZ and CeO_2 buffers





Laboratory coating/annealing line



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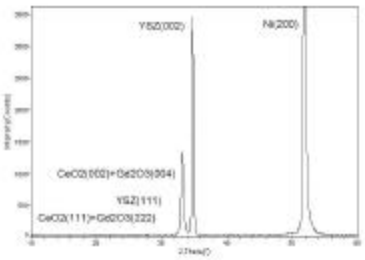
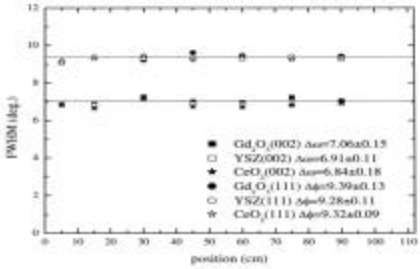
Reel-to-Reel Deposition of YSZ and CeO_2 Buffer Layers

- YSZ and CeO_2 layers deposited on meter length of Gd_2O_3/Ni by magnetron sputtering in reel-to-reel system at ORNL
- Uniform texture of all buffer layers achieved over length of tape
- Quality of meter length CeO_2/YSZ/Gd_2O_3/Ni tapes comparable to short samples prepared by static process





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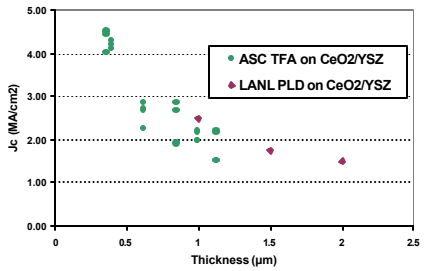
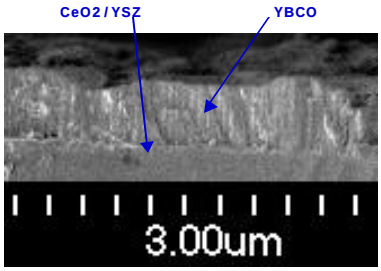
TFA Process Developed for Preparation of High J_c YBCO Films on RABiTS™ Substrates

- Quality of YBCO from TFA process matches that of PVD process for short samples
  - 4.5 MA/cm² for 0.4 mm film on CeO_2/YSZ_{sc} (77K, sf)
  - 2.2 MA/cm² for 1.1 mm film on CeO_2/YSZ_{sc} (77K, sf)
  - 1.9 MA/cm² for 0.37 mm film on $CeO_2/YSZ/CeO_2/Ni$ (77K, sf)





0.8µm, Jc ~ 2MA/cm²

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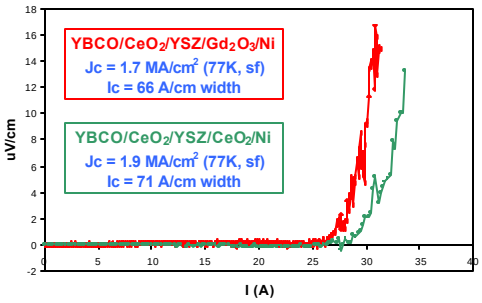
Quality of RABiTS™ Substrates Prepared by Reel-to-Reel Process Approaches Static PVD Deposition

- $CeO_2/YSZ/CeO_2/Ni$ prepared at ORNL by static PVD; TFA YBCO
  - J_c = 1.9 MA/cm² (77K, sf) for 0.37 mm film (spin coat)
  - J_c = 1.1 MA/cm² (77K, sf) for 0.27 mm film (5 cm length; web coat)
- $CeO_2/YSZ/Gd_2O_3/Ni$: *Gd_2O_3 by reel-to-reel sol gel*; YSZ and CeO_2 by static PVD; YBCO by TFA
  - J_c = 1.7 MA/cm² (77K, sf) for 0.37 mm film (spin coat)
- $CeO_2/YSZ/Gd_2O_3/Ni$: *complete reel-to-reel process*; TFA YBCO
  - J_c = 1.1 MA/cm² (77K, sf) for 0.37 mm film (spin coat)



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ASC-ORNL Program Plans

- Continue improvement of low-cost reel-to-reel buffer deposition
- Develop reel-to-reel deposition of YBCO films by TFA process on continuous length of RABiTS™ substrates
- Replace Ni substrates with non-magnetic substrates

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Summary

- Demonstrated reel-to-reel process capability for sol gel seed layers
  - 10 meter length; (002) Dw ~9°, (111) Df ~9.8°
- Demonstrated TFA process capability on RABiTS™ substrates
  - J_c = 1.9 MA/cm² (77K, sf) on CeO_2/YSZ/CeO_2/Ni
  - J_c = 1.7 MA/cm² (77K, sf) on CeO_2/YSZ/Gd_2O_3/Ni
- Demonstrated reel-to-reel process capability for meter length CeO_2/YSZ/Gd_2O_3/Ni tapes
  - J_c of 1.1 MA/cm² (77K, sf) on short sample
  - FWHM of buffer layer of ~ 7° over meter length
- Expanded ASC-ORNL program

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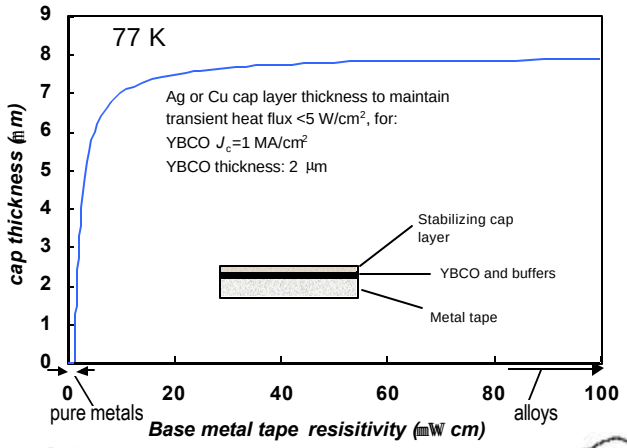
Outline

- **FY 2000 Results:**
  - **Texture and percolation in RABiTS** — **A. Goyal**
  - **Nonmagnetic, strengthened alloys**
  - **Solution buffer layers and HTS** — **M. Paranthaman**
  - **Industrial Highlight: ASC** — **M. Rupich**
  - **All conductive oxide buffer layers on Ni** — **D. Christen**
  - **Nucleation and growth of ex-situ YBCO on RABiTS**
- **FY 2000 Performance and Plans for FY 2001**
- **Technology Integration**

HTS coatings will require electrical stabilizer

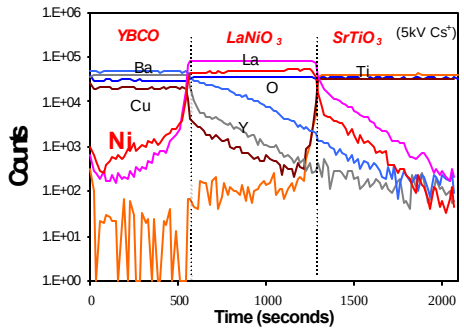
- ***For dissipative occurrence (e.g. microcrack, thermal transient), heat flux should not exceed critical value for boiling LN_2 (10-20 W/cm^2)***
- ***For envisioned operating parameters, cap layer and/or base metal should be electrically connected to HTS coating***

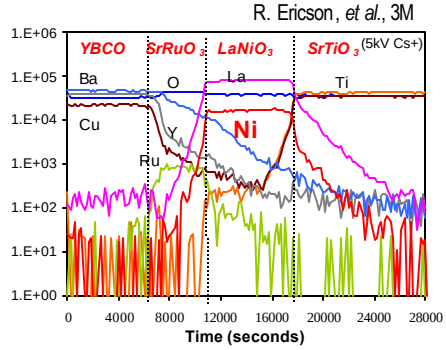


Controlled studies suggest bilayer buffer of conductive oxides $SrRuO_3$ and $LaNiO_3$

- *YBCO on $LaNiO_3$ show suppressed T_c, J_c and high resistivity*
- *SIMS analyses show Ni contamination of YBCO by $LaNiO_3$*
- *$SrRuO_3$ layer provides Ni-diffusion barrier*

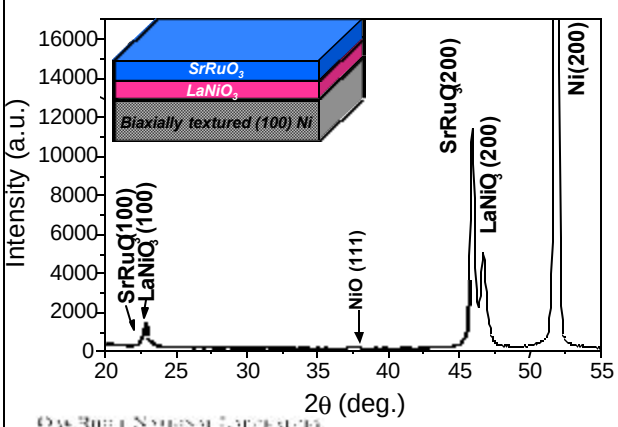
R. Ericson, *et al.*, 3M



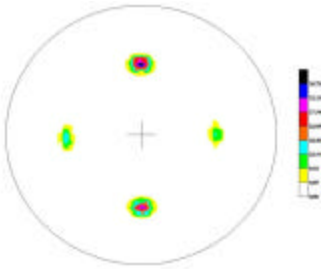


Epitaxial $SrRuO_3$(PLD)/$LaNiO_3$(sputtered) Buffers on Textured Ni

- *Fully conductive structure*
- *Buffer thickness ~0.4 mm*
- *Texture determined by that of Ni*



Cube-on-cube epitaxy
$LaNiO_3$ on Ni



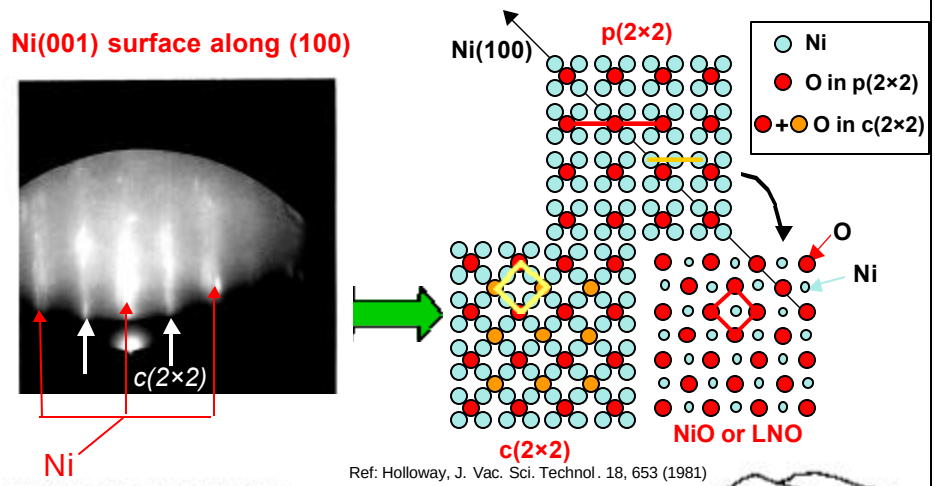
(111) $LaNiO_3$ Pole Figure

$LaNiO_3$: $\Delta\omega$ = 8.2°, $\Delta\phi$ =8.9°

Ni: $\Delta\omega$ = 7.9°, $\Delta\phi$ =8.9°

RHEED study of textured Ni surface and buffer layer growth

- Stable sub-oxide on Ni surface is difficult to remove
- Effect on buffer layer growth is being assessed



Ref: Holloway, J. Vac. Sci. Technol. 18, 653 (1981)

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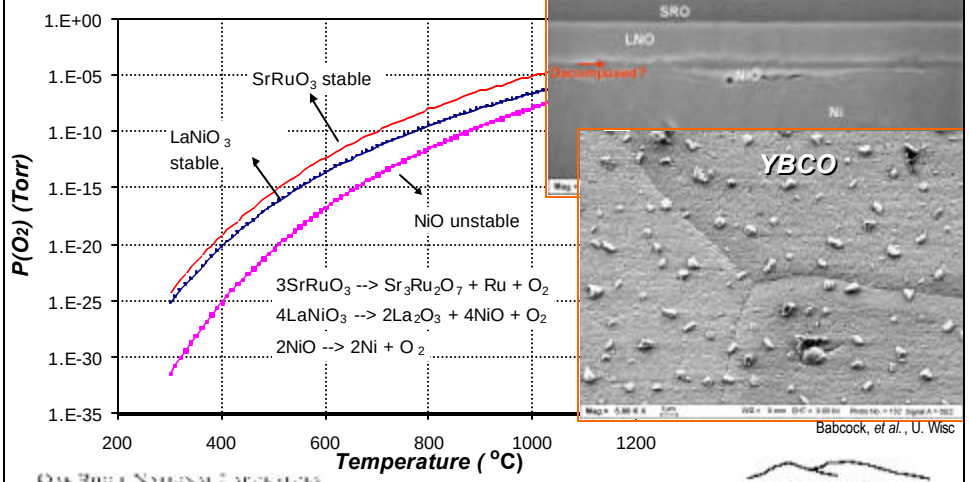
NiO: thin, discontinuous layer during YBCO deposition

- *NiO more stable than SRO or LNO*
- *YBCO not degraded by NiO*
- *Overall tape resistivity is low*



Babcock, *et al.*, U. Wisc

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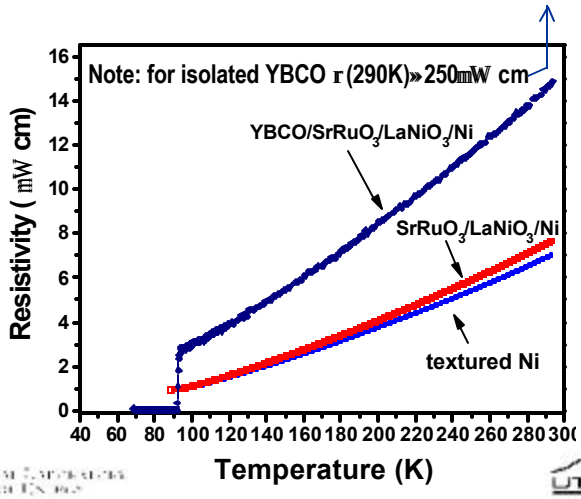
Normal state properties show good electrical coupling through buffers

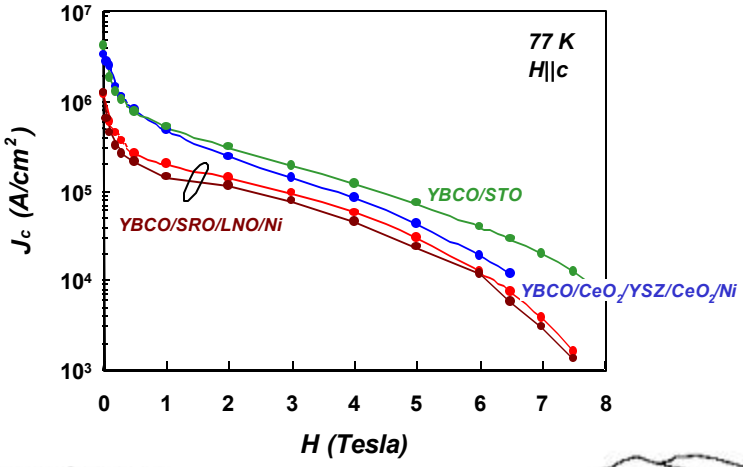
- *Overall net resistivity values are low, but*
- *Four-terminal resistivity indicates some contact barrier*



UT-BATTELLE

YBCO/SRO/LNO/Ni with Good $J_c(H)$

- **Fully conductive structure**
- **Good high-field flux pinning properties, and** *$J_c(H=0)$>1 MA/cm² at 77K*
  3 MA/cm² at 64K



UT-BATTELLE

SUMMARY

- **For pure metal tapes, conductive buffer layers should provide electrical stability**
- **A *RABiTS* architecture was developed with conductive oxide bilayer: $SrRuO_3/LaNiO_3$**
  - **$LaNiO_3$ can be deposited epitaxially on Ni having a native (sub)oxide**
  - **$SrRuO_3$ provides barrier to Ni-diffusion contamination of YBCO**
- **Despite formation of some NiO, coated conductor shows low net electrical resistivity**
- **J_c values of 1.3 MA/cm^2 have been obtained, with robust magnetic field dependence**

Increasing I_c of YBCO coated conductors

BaF_2 *ex situ* process

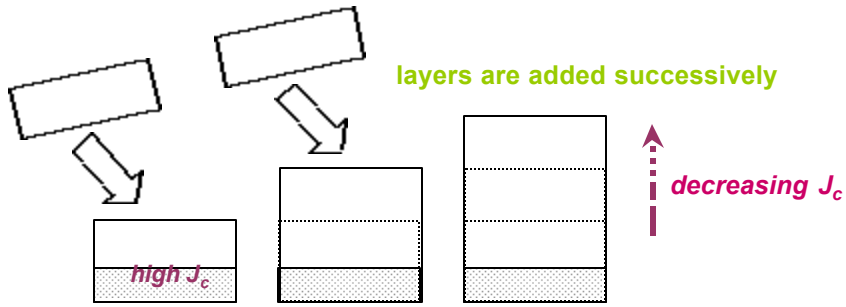
evaporated precursor layers (Y, Cu, BaF_2 sources)
ex situ furnace anneal for chemical conversion, YBCO epitaxial growth

previously demonstrated: high-J_c YBCO on RABiTS and IBAD-YSZ
standard YBCO thickness: 0.3 µm
best results: J_c(77 K)= 3.2 MA/cm^2 (IBAD-YSZ) } $I_c \cong$ 80-90 A/cm width
2.7 MA/cm^2 (RABiTS)

plans for FY2000

- increase YBCO thickness to obtain j_E =40 kA/cm^2 (at 77 K, self field)
  - metal substrate 50 µm: required I_c = 200 A/cm width
  - J_c=1 MA/cm^2: required thickness is 2 µm
- compare trends and results with *in situ* PLD

in situ: growth conditions for initial c ⊥ YBCO are independent of (final) film thickness



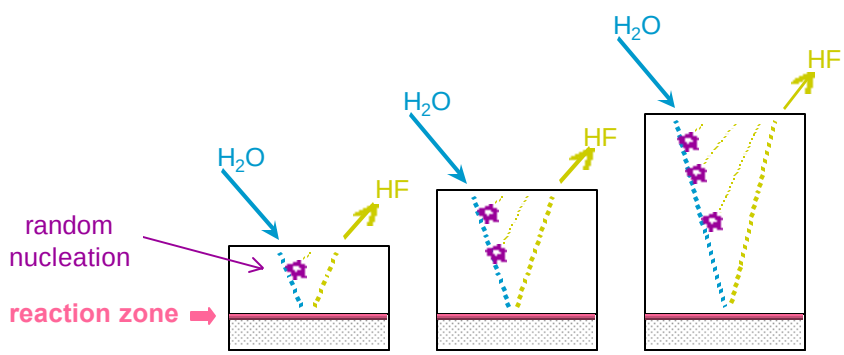
I_c saturates with thickness, possibly due to:

- reduced J_c of added layers

  possible causes: kinetic roughening, fewer substrate-induced defects, substrate temperature drift, intrinsic(?), …
- degradation of high-J_c bottom layer due to slow reaction with buffer layer

ex situ process: formation of initial c ⊥ YBCO layer more difficult to control in thick precursors

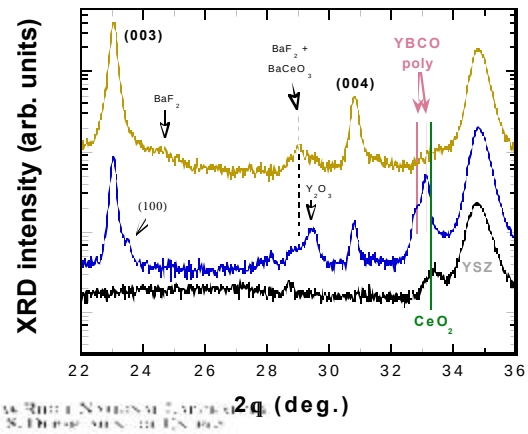
- **longer diffusion paths inside precursor** modify conversion kinetics at substrate interface → *indirect control through H_2O supply, gas flow*
- enhanced probability of **random YBCO nucleation**



$BaF_2 + H_2O$ ® $BaO + HF$

annealing process has been modified to enhance I_c in films converted from thick precursors

- **nucleation step with reduced H_2O supply** provides scalable approach
- similar to Cima (1998) for TFA process *(different in detail)*
- *here*: **nucleation step reduces random YBCO nucleation**



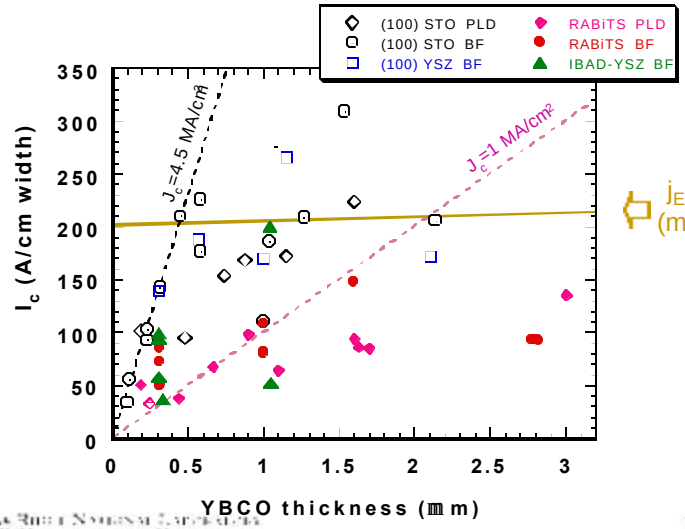
YBCO: 1.0 µm
IBAD-YSZ / CeO_2

reduced H_2O activity
I_c = 200 A/cm width

high H_2O activity
I_c = 3.2 A/cm width

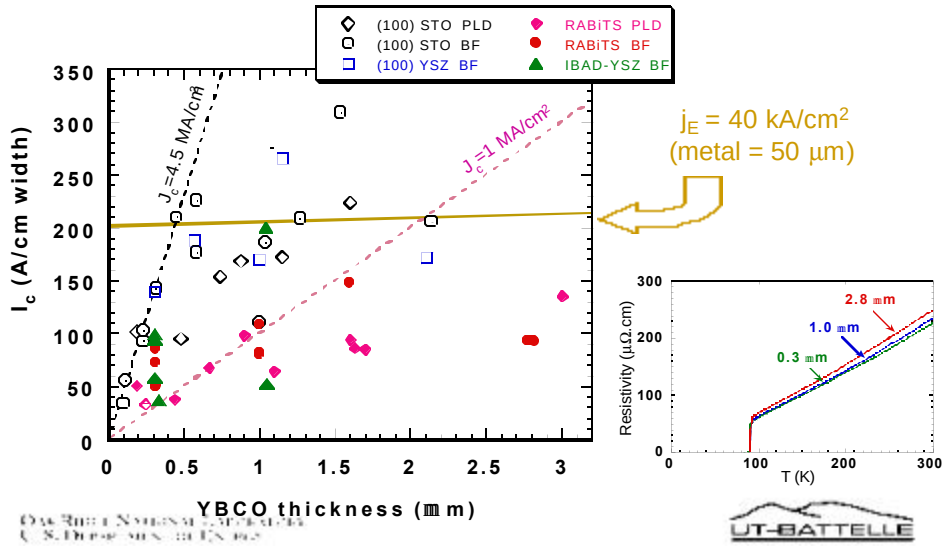
precursor

Similar thickness dependence of I_c is observed for YBCO coated conductors made by *ex situ* BaF_2 process and *in situ* PLD



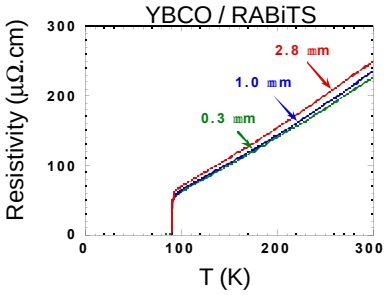
j_E = 40 kA/cm^2
(metal = 50 µm)

Similar dependence of I_c is observed for YBCO coated conductors made by *ex situ* BaF_2 process and *in situ* PLD for thickness to 3 mm



Summary: BaF_2 *ex situ* process, enhancing I_c

- thickness for c⊥ epitaxial growth has increased: 0.3 → 2.8 μm
  - longer processing times are not prohibitive (RABiTS, IBAD-YSZ)
- relation among basic processing parameters has been delineated → low H_2O nucleation step



- I_c (77 K) for coated conductors has been increased from 90 → 200 A/cm
  - YBCO thickness: 1.0 μm; substrate IBAD-YSZ CeO_2
  - potential for $j_{E(}$(77 K) = 40 kA/cm² (metal=50 μm) demonstrated
- J_c decrease for films converted from thicker precursors prevents further enhancement of I_c
  - annealing conditions have not been fine-tuned (duration-H_2O supply)
  - departure from ρ – J_c correlation requires further investigation

FY2000 Performance and FY2001 Plans

FY2000 Plans

- **Continue to develop strengthened, reduced-magnetism textured alloys**
- **Further develop effective buffer layers on textured metals**

FY2000 Performance

- **Ni-Cr alloys developed and refined**
  - *good texture to high temperatures*
  - *fabrication scaled to long lengths*
  - *Minimal low-temperature magnetism*
    - less than stainless steel
    - low hysteresis
  - *High-J_c YBCO coatings demonstrated*
- **Two-layer, conductive buffers**
  - *Electrical stability, High J_c*
- **Solution-based buffer layers**
  - *Long-length fabrication demonstrated*
  - *High J_c YBCO on PVD-capped seed buffers by both ORNL and ASC*
  - *All-solution buffers demonstrated; J_c values over 200 kA/cm^2*

FY2000 Plans (cont'd)

- **Continue studies on nucleation and growth of oxides on metals**
- **Determine dependence of *ex situ* YBCO reaction mechanism on processing parameters**

FY2000 Performance

- ***in situ* RHEED and *ex situ* XRD characterization have shown:**
  - *apparent sub-oxide surface layer on Ni*
    - more stable than NiO
    - may help orient oxide layers
    - NiO-containing buffer forms readily
- **Special nucleation step developed**
  - *Prevents random, polycrystalline mat'l*
  - *Enables processing of thicker coatings*
  - *High I_c obtained*
- **Advances made in TFA solution approach**
  - *Lengths of precursor formed*
  - *Reduced first burnout duration*
  - *High J_c on RABiTS by ASC*

FY2000 Plans (cont'd)

- **Work with LANL to develop *ex situ* YBCO on IBAD MgO seed buffers**
- **Work toward *ex-situ* YBCO coated conductors with J_E(77K)>40 kA/cm^2**

FY2000 Performance

Work in progress to find suitable cap buffer layer

- *Re-focus on further improving ex-situ processing for general compatibility*
- *Adverse reaction with $SrTiO_3$ cap layers*
- *IBAD MgO now available*

- **New method to induce *c*-perp growth in thick precursors has been developed**
  - *c-perp. growth extended beyond 2 mm*
  - *High I_c of 200A/cm-width Þ 40 kA/cm^2 for standard (50 mm thick) tapes*
  - *Positive comparison with in-situ YBCO*

FY2001 Plans

- **Continue fundamental studies of epitaxial oxide growth on metals, including alloys**
- **Collaborate with LANL to develop *ex-situ* YBCO on IBAD-MgO substrates**
- **Increase I_c/width to consistent values >150 A/cm for *ex-situ* processed YBCO coatings**
- **Continue studies of thermo-mechanical processing for texture improvement**
- **Develop solution-based buffer layer deposition on alloy tapes**
- **Perform research on fundamental issues of continuous processing with CRADA partners**

Technology Integration

- **Four CRADA teams working with ORNL staff on diverse approaches to coated conductors**
  3M Company; American Superconductor Corp.; EURUS Technologies; MicroCoating Technologies/Oxford Superconducting Technology

- **Collaborations with universities and other labs**
  U. Wisconsin; U. Kansas; Boston College; U. Houston (TCSUH); Stanford; ANL; BNL; LANL; NIST

- ***Information/expertise transfer:***
  - ***Over 40 publications, 15 presentations, 6 patents issued; WEB posting of Annual Report, etc.***
  - ***Three post-docs hired by industry in past three months***

American Superconductor Partnership Leverages Facilities and Expertise

- **ASC**
  - ***TFA of YBCO precursors***
  - ***Buffer layers by PVD and Sol Gel***
  - ***Textured nickel with excellent properties***

- **ORNL**
  - ***Conversion of TFA precursors to YBCO***
  - ***Short-sample sol-gel buffer layer development***
  - ***Characterization***

Key Achievements:

- ***1.9 MA/cm^2 TFA YBCO on RABiTS short samples***
- ***7 meters of Gd_2O_3/Ni sol-gel buffer: uniform, highly cube textured***

Scaling Combustion Chemical Vapor Deposition (CCVD) to Fabricate Long Lengths of HTS Tape

Substrate - Scaled up to ~100 m nickel tapes with good texture

ORNL - technology transfer of nickel processing

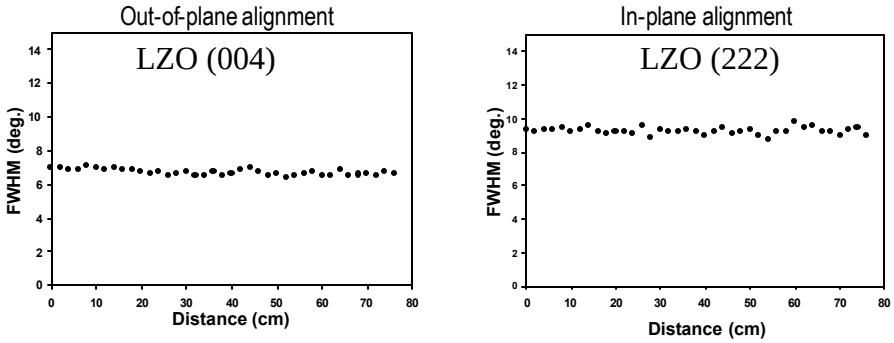
Buffer - 1 and 10 meter lengths of CCVD buffered Ni have been prepared with minor 2nd in-plane orientation

Superconductor - epitaxial, single-phase YBCO has been deposited by CCVD on single crystals with T_c > 89K

ORNL - transferred technology for electrical properties characterization

X-ray data on dip-coated $La_2Zr_2O_7$ on EURUS-Ni

• ORNL LZO by sol gel



Ni (002): 6.8 deg.
Ni (111): 9.2 deg.

Examples: Effective Partnerships with Universities

- **U. Wisconsin**
  - *Magneto-optical imaging of coated conductor micro-homogeneity*
  - *Microstructural studies of YBCO/RABiTS*
- **U. Kansas**
  - *Cation exchange process for Hg1212 on ORNL RABiTS*
  - *J_c > 1 MA/cm^2 @ 92 K*
- **Boston College**
  - *Development of Cr-doped Tl1212 for coatings on alloys*
- **U. Houston**
  - *Development of YBCO coatings by photo-enhanced MOCVD on ORNL RABiTS*

Inter-laboratory Research Areas have Leveraged Special Facilities and Expertise

- **ORNL and LANL collaborated on development of *ex-situ* YBCO coatings on IBAD substrates, with outstanding results (200 A/cm-width) on IBAD YSZ**
- **ORNL supplied buffered Ni to LANL for PLD YBCO**
- **ORNL and ANL collaborated on microscopic properties characterization and materials modification research on coated conductors and related materials**
- **ORNL and NIST collaborated on studies of cryogenic strain tolerance using unique NIST measurement apparatus**
- **NIST Gaithersburg studied *ex situ* YBCO conversions**

FY 2000 Results for Fundamental Issues Project

Tape Component

Results

Metal Tape

- Improved thermomech. process → improved texture
- AC loss in alloys is much lower than Ag/BSCCO
- Developed excellent texture (with high J_c) in non-magnetic, stronger alloys
- Showed that g.b. grooving does not affect J_c

Buffer Layers

- All-solution buffers yield promising J_c
- Conductive buffers → potential for protection, high J_c

HTS

- Percolation theory → J_c (1 km) ~ 0.9 J_c (1-cm)
- TFA YBCO yields 1.9 MA/cm^2 on RABiTS (ASC)
- 200 A/cm width for BaF_2 approach on IBAD-YSZ
- 2 degree g.b. in HTS are single-crystal-like