RABiTS™ Substrates Research & Development

OAK RIDGE NATIONAL LABORATORY

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FY 2005 Funding: $800K

Objective and Rationale

Objective: To explore *fundamental* issues related to the RABiTS process and to advance the technology to enable commercial fabrication of YBCO/RABiTS

"R&D Needs/Knowledge Gaps" addressed in this project and identified in the DOE Roadmap.

- **To understand microstructural factors affecting J_c**
- **To develop rolling technology and tools to produce long, wide substrates**
- **To understand the interfaces between epitaxial layers**
- **To develop non-Ni substrates**
- **To study grain boundaries**
- **To develop methods to characterize physical properties**

Specific Objectives/Milestones

1. Use ORNL rolling mill facility for fabrication of long and wide NiW substrates for R&D and scale-up at companies. Address any key issues encountered.

2. Develop robust buffers on ORNL Ni-W substrates in reel-to-reel configurations, both internally and assist scale-up activities at companies.

3. Research texture development in substrates with higher tungsten content, particularly the nonmagnetic, Ni-9.3at%W substrate.

4. Work with vendors in developing the powder metallurgy route for starting coils.

5. Research texture development in strengthened and possibly highly conducting Cu-based alloy substrates and deposit previously developed epitaxial buffer layers on them.

Specific Objectives/Milestones

6. Extend percolation calculations in applied magnetic fields to conductors less than 50 grains wide.

7. Develop methods to separate in-plane and out-of-plane misorientations from electron backscatter Kikuchi diffraction (EBKD) measurements in materials with lower-than-cubic crystal symmetry (YBCO) and correlate with J_c.

8. Determine the relative effects of in-plane and out-of-plane misorientations on J_c by fabricating and characterizing YBCO films with the same in-plane but different out-of-plane misorientations.

9. Improve J_c/I_c and pinning in thick REBCO films on RABiTS

10. Fabricate 100-150 nm thick LZO solution based buffer layers on NiW RABiTS substrates. Demonstrate suitability of an all-solution buffer layer process.

Presentation Outline

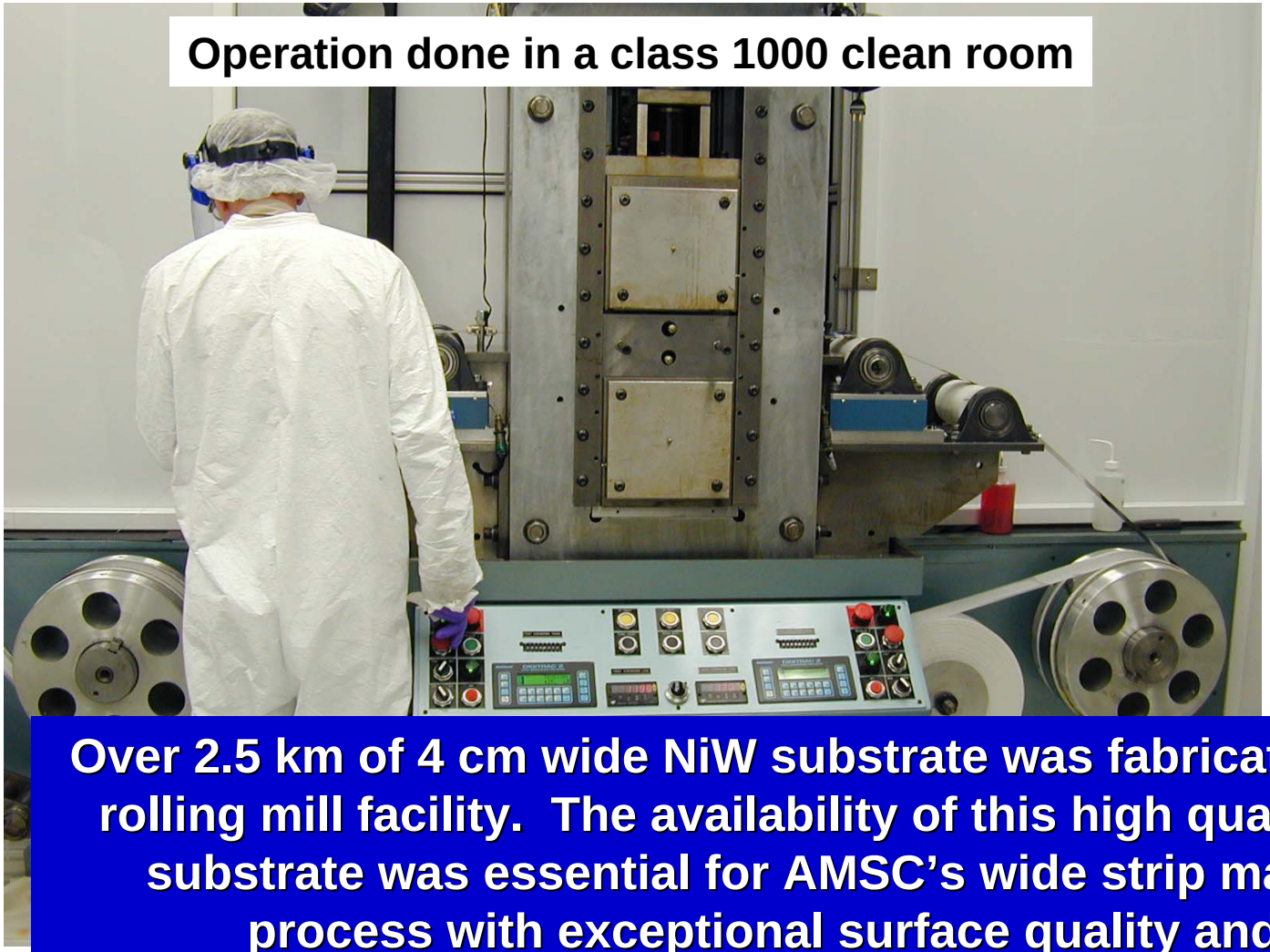
- **FY 2005 Results**

  Rolling of substrates **(Amit)**
  Development of robust buffers
  Development of texture in Cu-based, conductive RABiTS
  Development of texture in Ni-based, non-magnetic RABiTS
  Percolation calculations in applied fields
  Separation of in-plane and out-of plane misorientations in YBCO
  Enhancement of intragranular-J_c

  Development of solution buffers **(Parans)**

- **FY 2005 Performance and FY 2006 Plans** **(Parans)**
- **Research Integration**

Objective 1: Use ORNL rolling mill facility for fabrication of long and wide NiW substrates for R&D and scale-up at companies

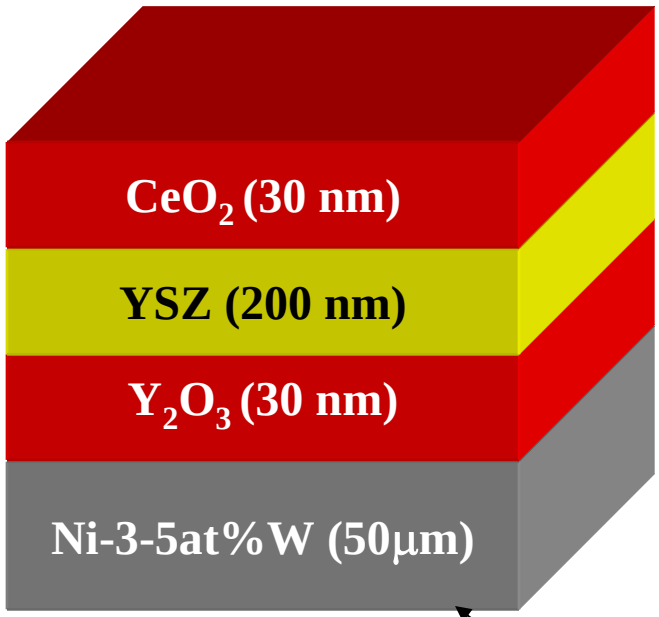


AMSC personnel visited ORNL on a regular basis for rolling of wide NiW substrates for scale-up efforts.

Over 2.5 km of 4 cm wide NiW substrate was fabricated in the ORNL rolling mill facility. The availability of this high quality, 4-cm wide substrate was essential for AMSC's wide strip manufacturing process with exceptional surface quality and texture

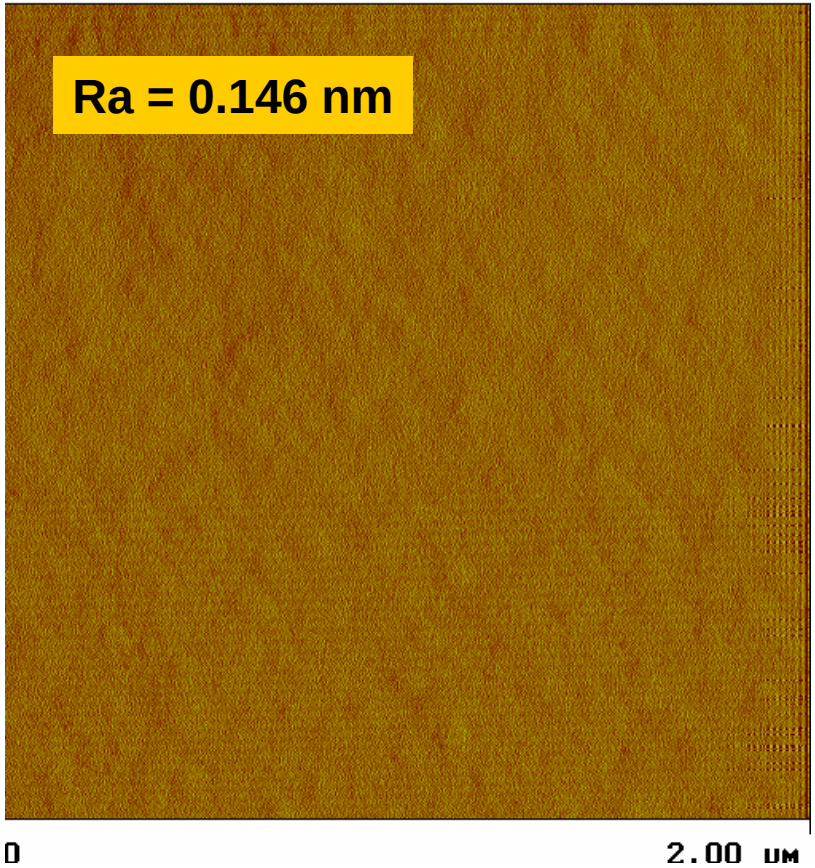
Objective 2: Develop robust buffers on Ni-W substrates in reel-to-reel configurations, and assist scale-up activities at companies.

Standard ORNL buffer stack

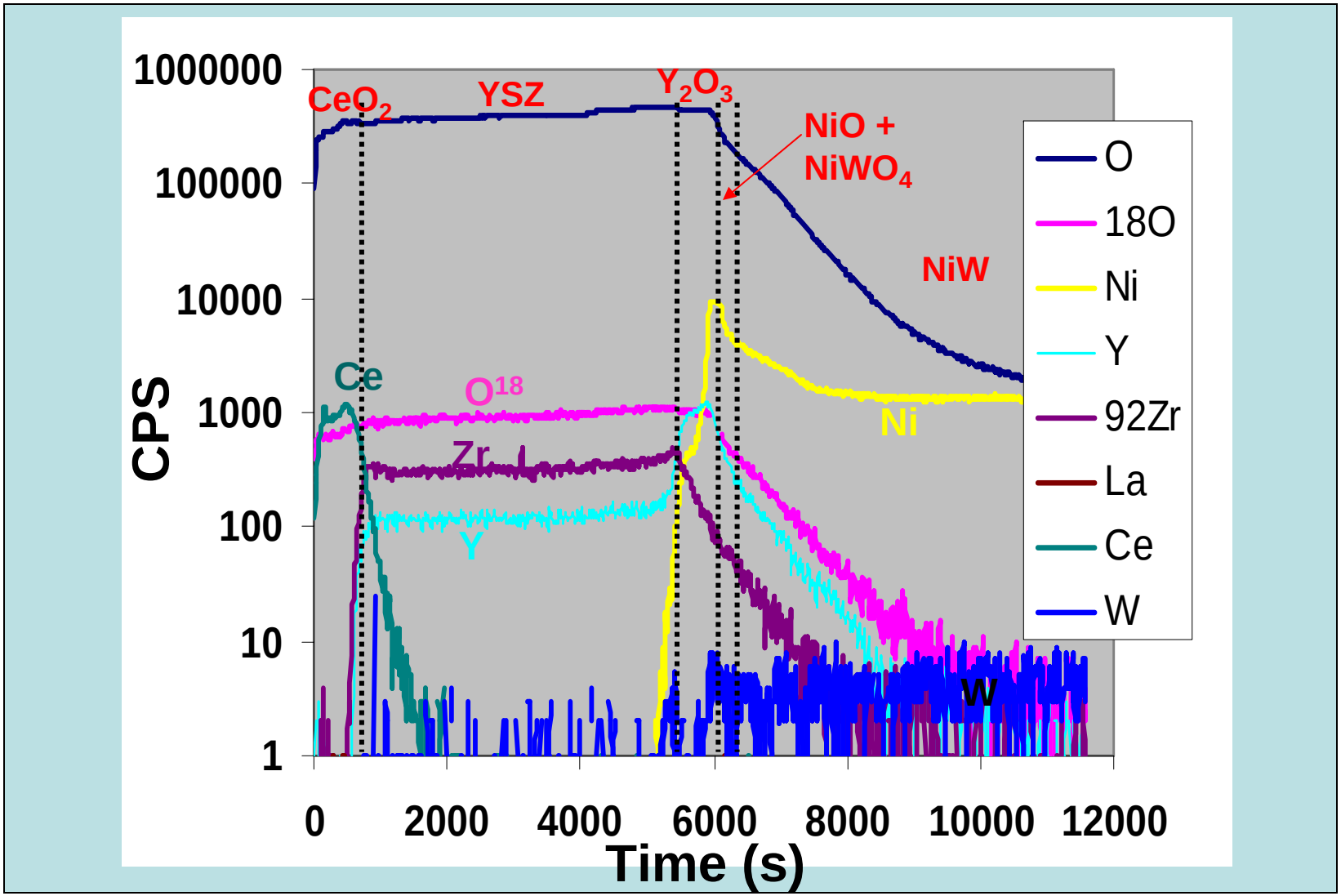


Carbon content reduced to below 50ppm in alloy substrate

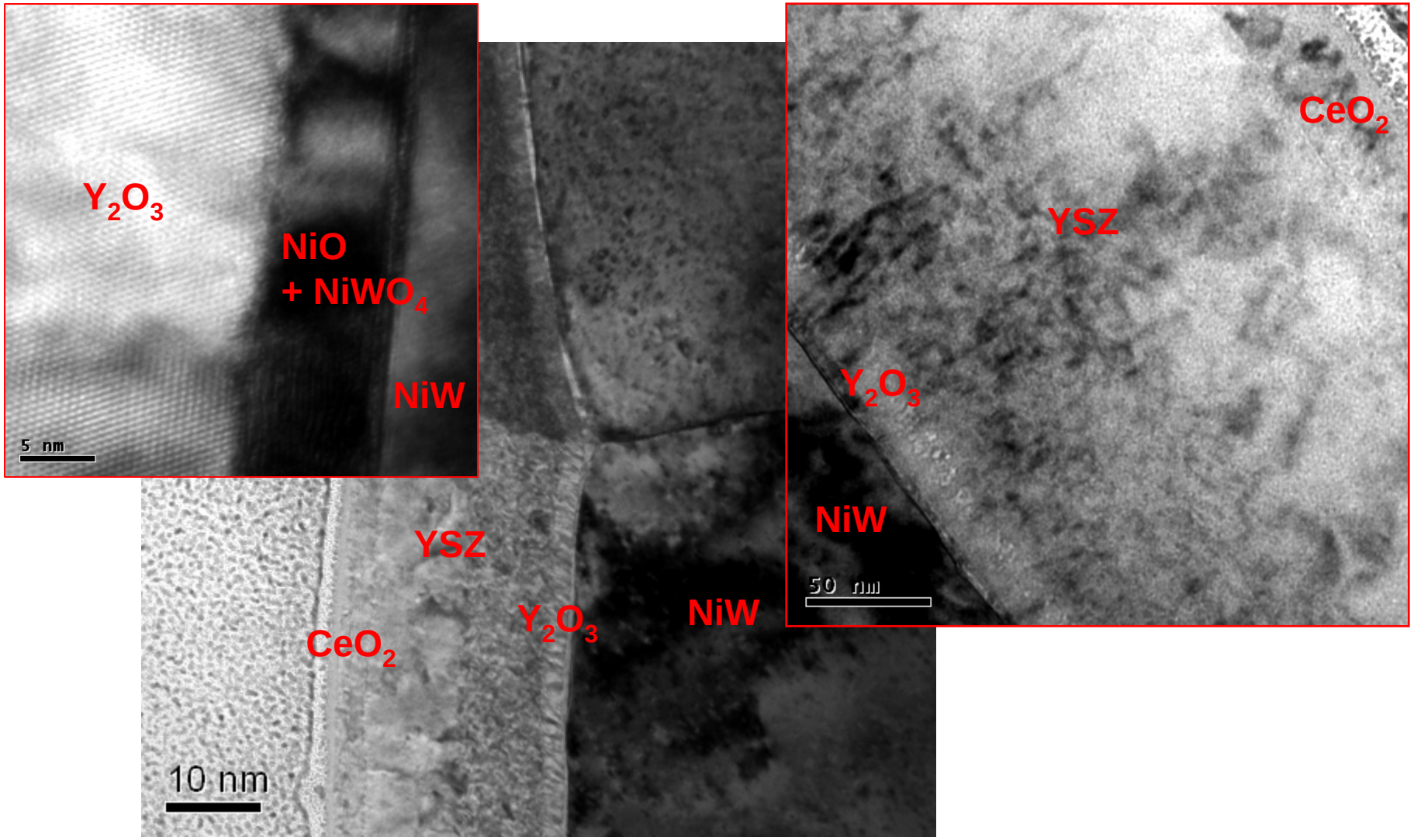
AFM of CeO_2 surface shows that the buffer is very smooth



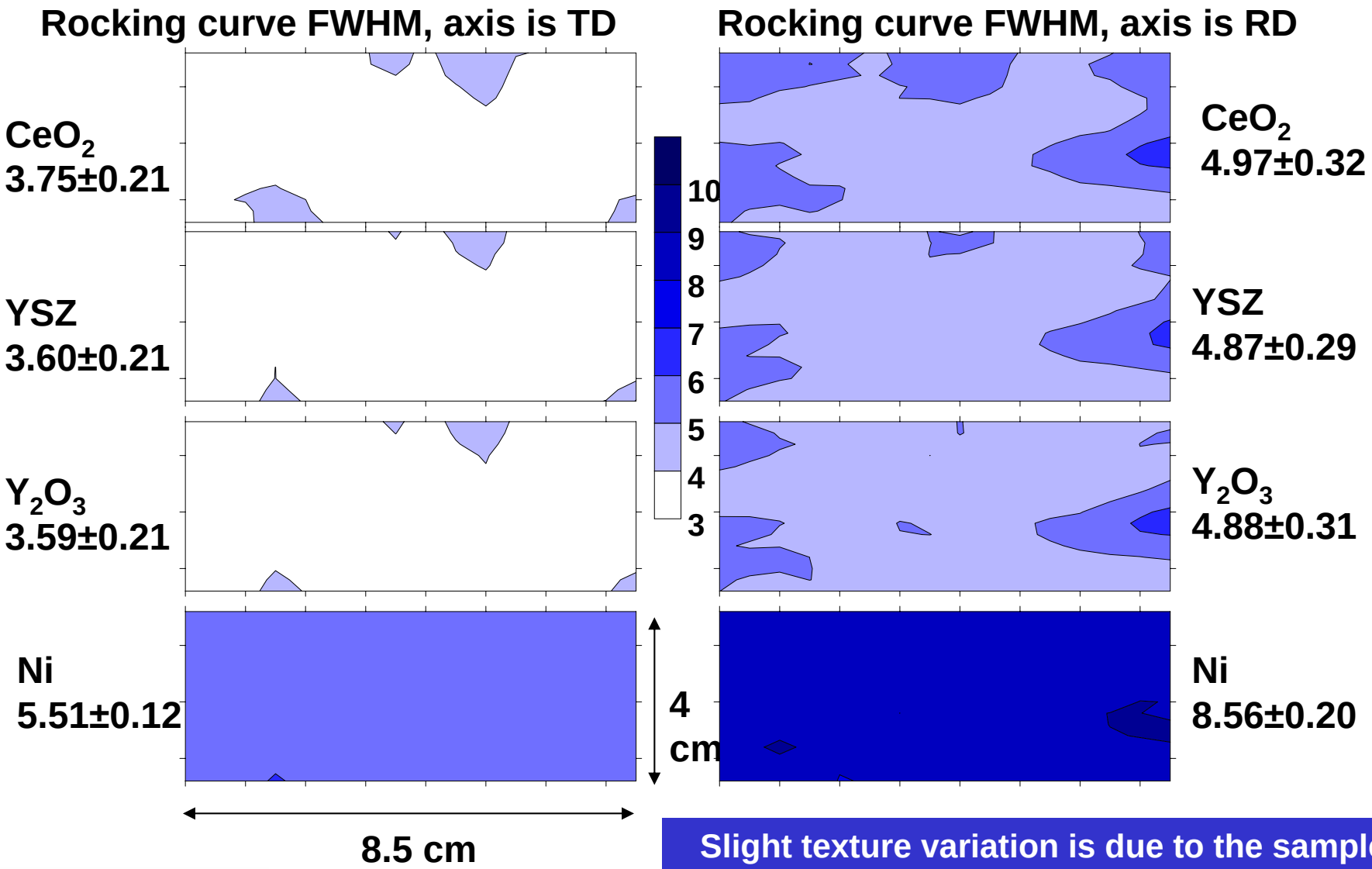
SIMS depth profiling after a simulated anneal in O^{18} shows that Ni is contained at Y_2O_3/YSZ interface in the buffer stack



TEM shows excellent correlation with the SIMS depth profile and shows the formation of a continuous as opposed to discontinuous NiO + $NiWO_4$ layer



AMSC-ORNL CRADA: Good texture is also obtained for the full buffer stack (CeO_2/YSZ/Y_2O_3/NiW) made in long lengths in a reel-to-reel process



Slight texture variation is due to the sample not remaining completely flat on the stage

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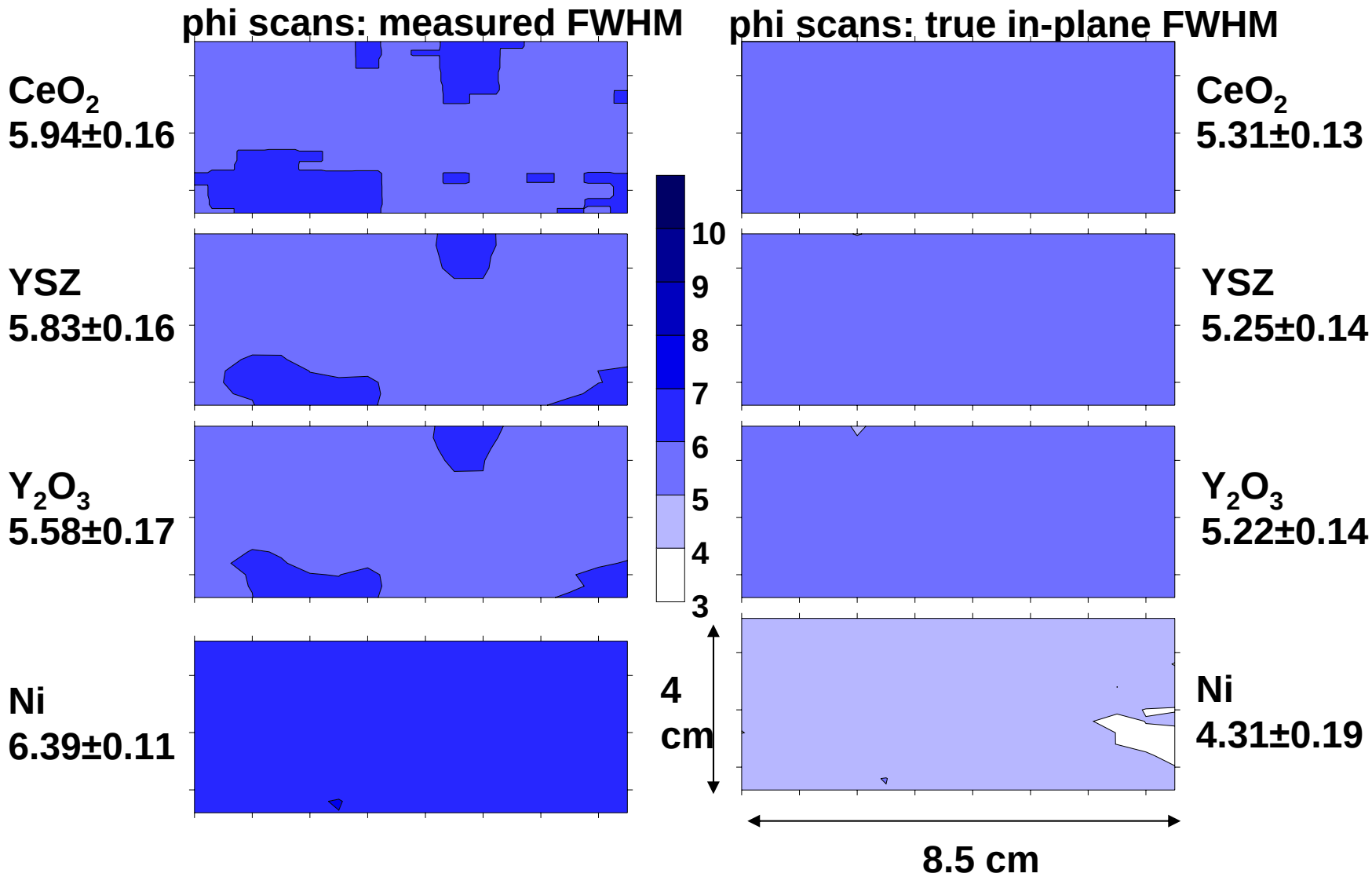
Good in-plane texture is also obtained for the full buffer stack (CeO_2/YSZ/Y_2O_3/NiW) made in long lengths in a reel-to-reel process



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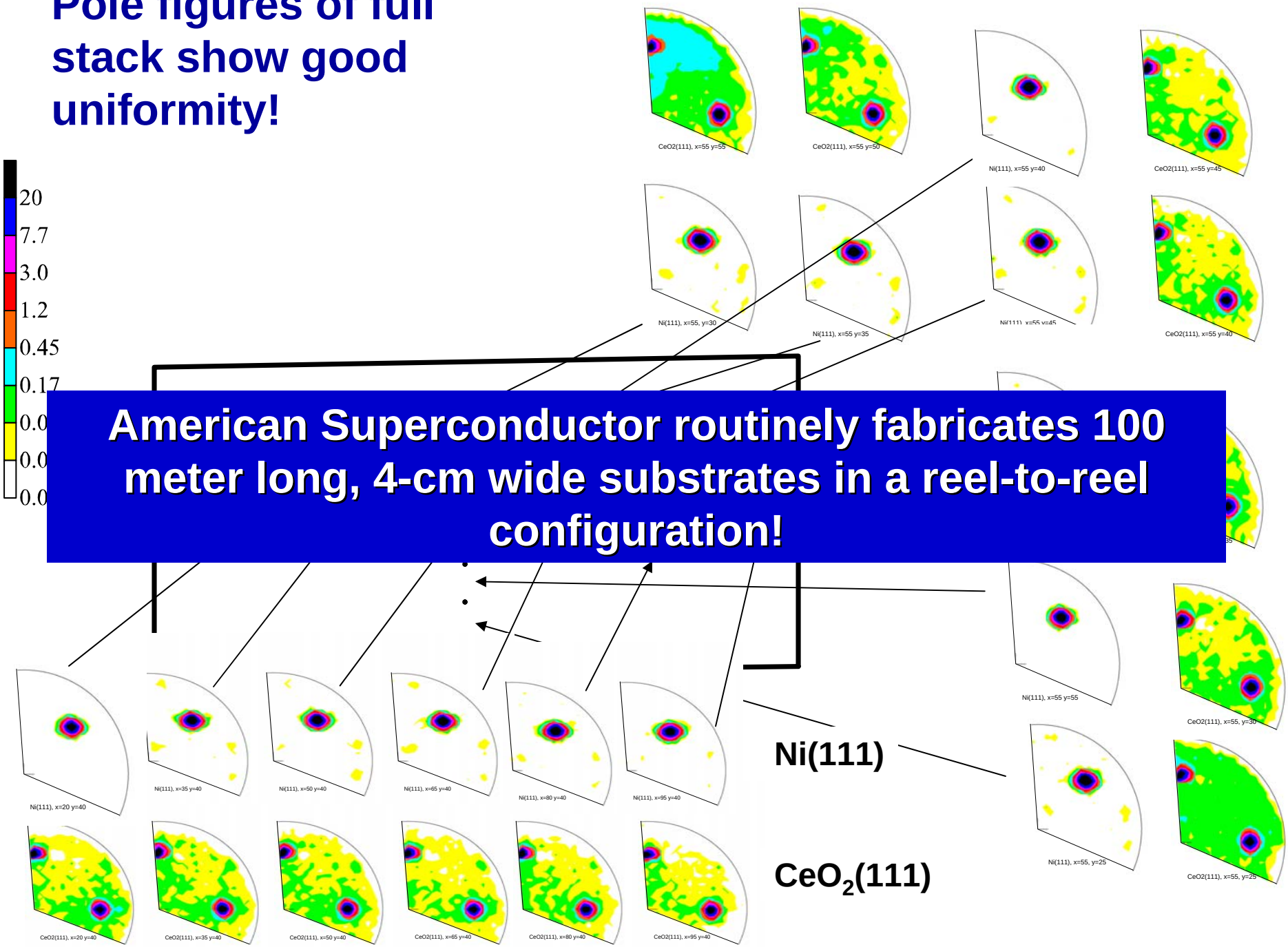
Pole figures of full stack show good uniformity!



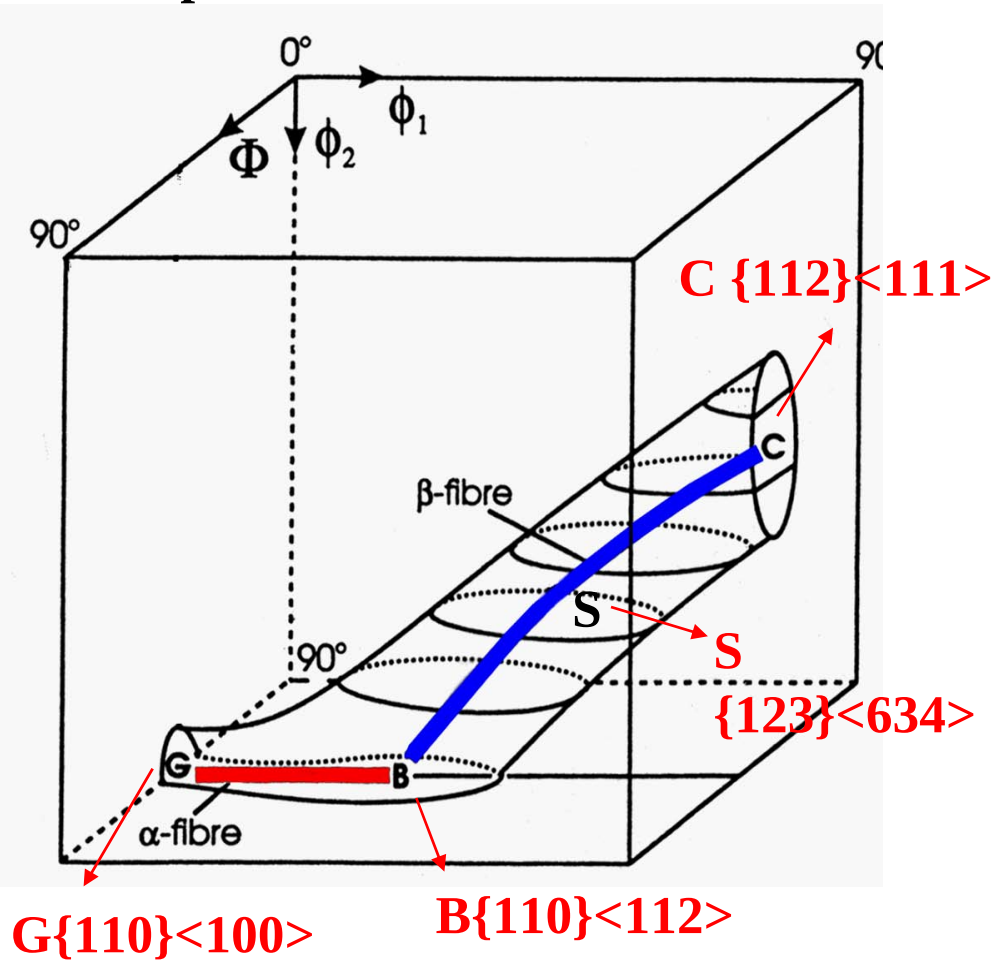
American Superconductor routinely fabricates 100 meter long, 4-cm wide substrates in a reel-to-reel configuration!

Objective 3: Research texture development in substrates with higher W content, particularly, the non-magnetic, Ni-9.3at%W

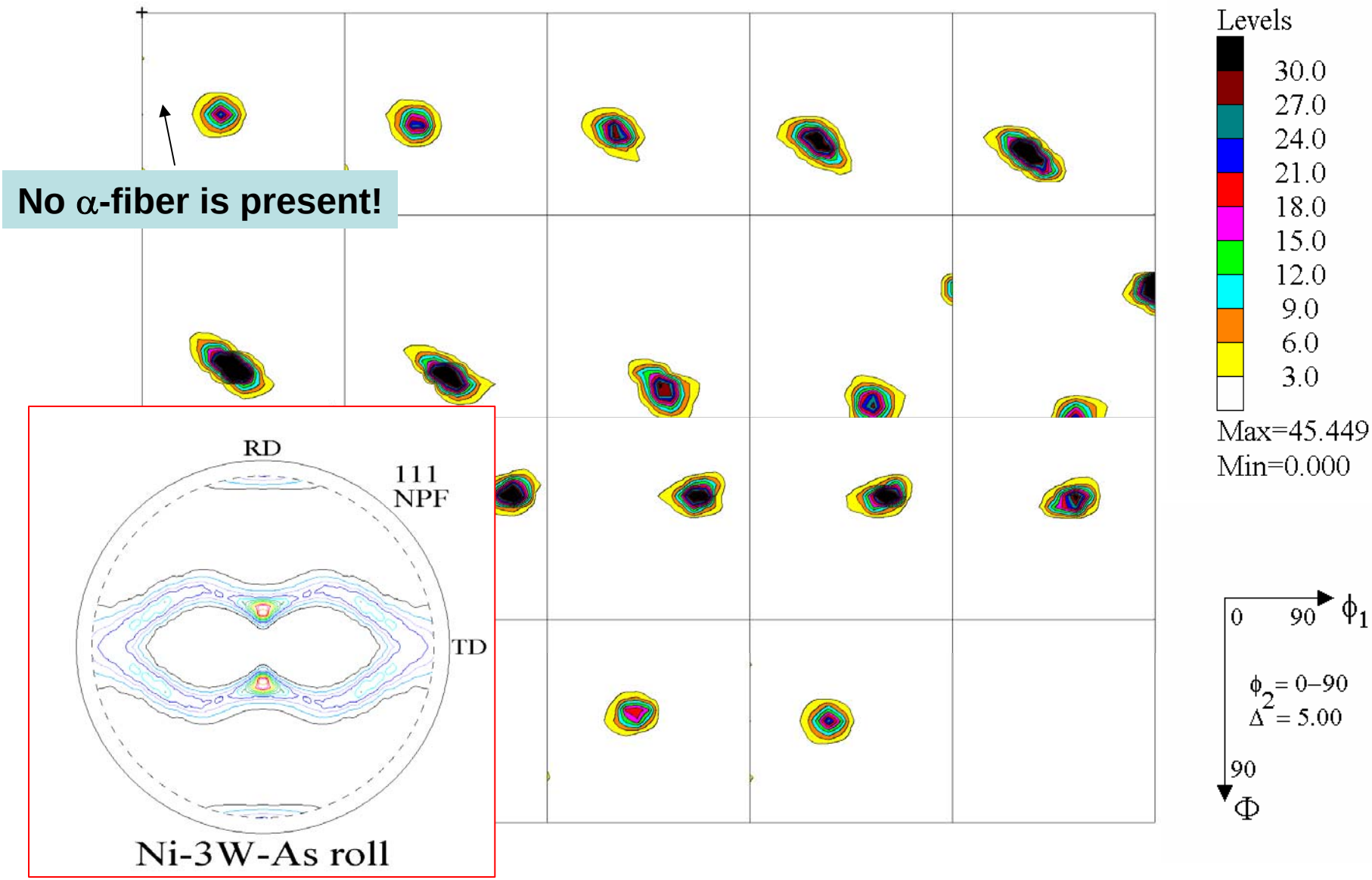
Requirements for good cube texture development

- Must have the correct rolling texture, i.e. Cu-type rolling texture
- Annealing conditions should allow primary recrystallization to be complete. No pinning at GB's to result in retained rolling texture is desirable. Also, the onset of abnormal growth needs to be avoided

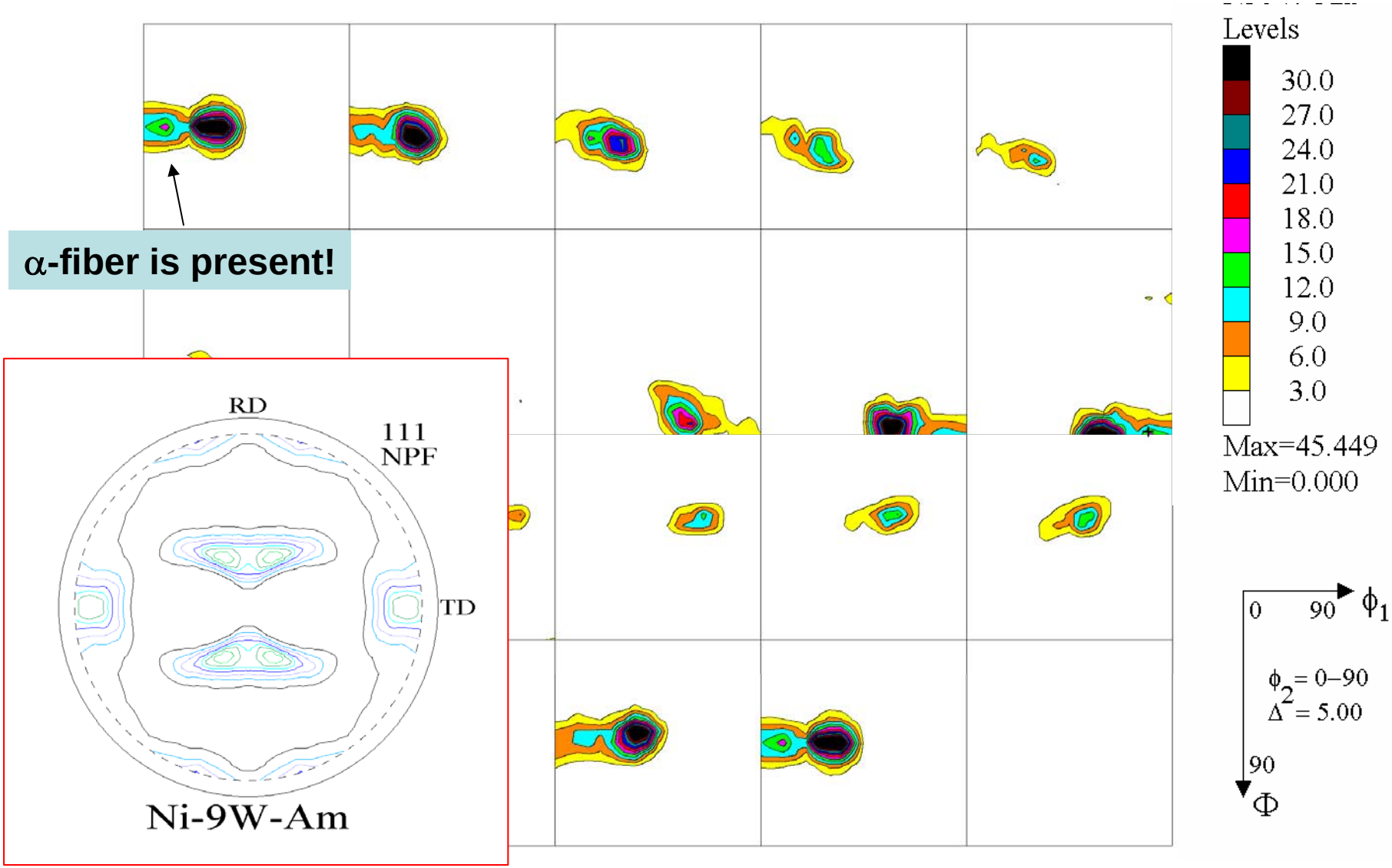
Euler Space



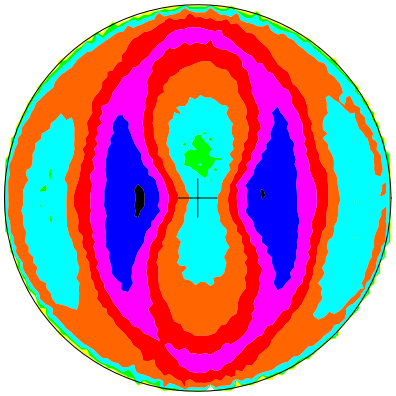
Cu-type rolling texture: ϕ-ϕ_1 slices as a function of ϕ_2 of the orientation distribution function (ODF) for 99.9% deformed Ni-3at%W



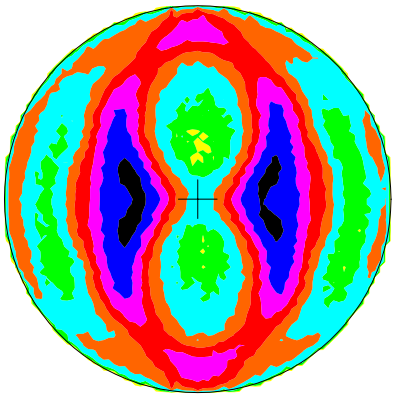
In Ni-W alloys, with W higher than 6.5at%W a texture transition is obtained: ODF for 99.9% deformed Ni-9.3at%W



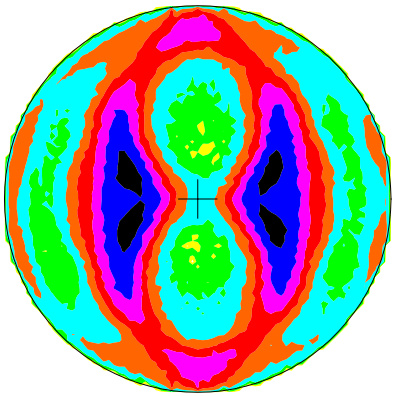
Texture evolution in Ni-9.3at%W



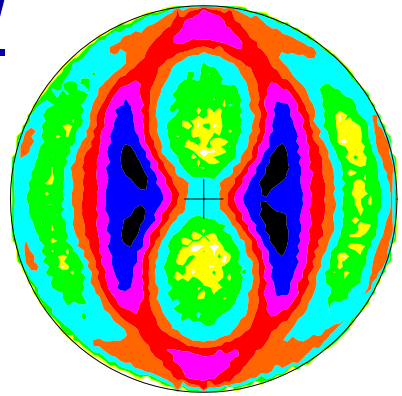
80% deformation



90% deformation



92% deformation



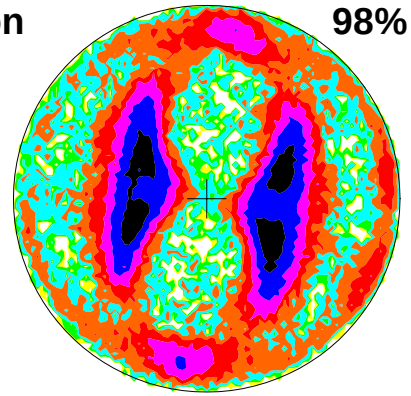
94% deformation

Similar transition is observed for NiW alloys with W content higher than 6.5 at% W. Hence, cube texture formation in <u>NOT</u> possible under standard processing conditions.

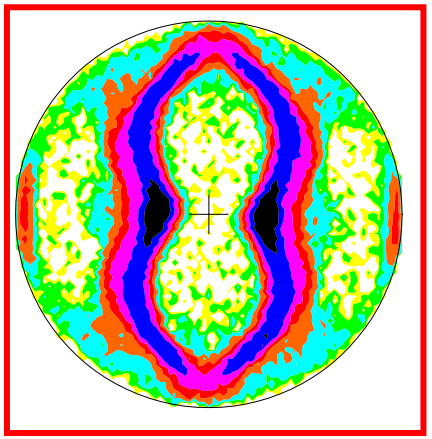
96% deformation

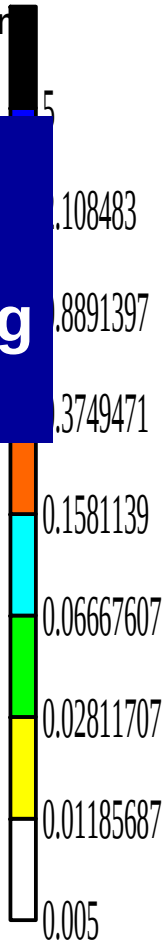
98% deformation

99% deformation

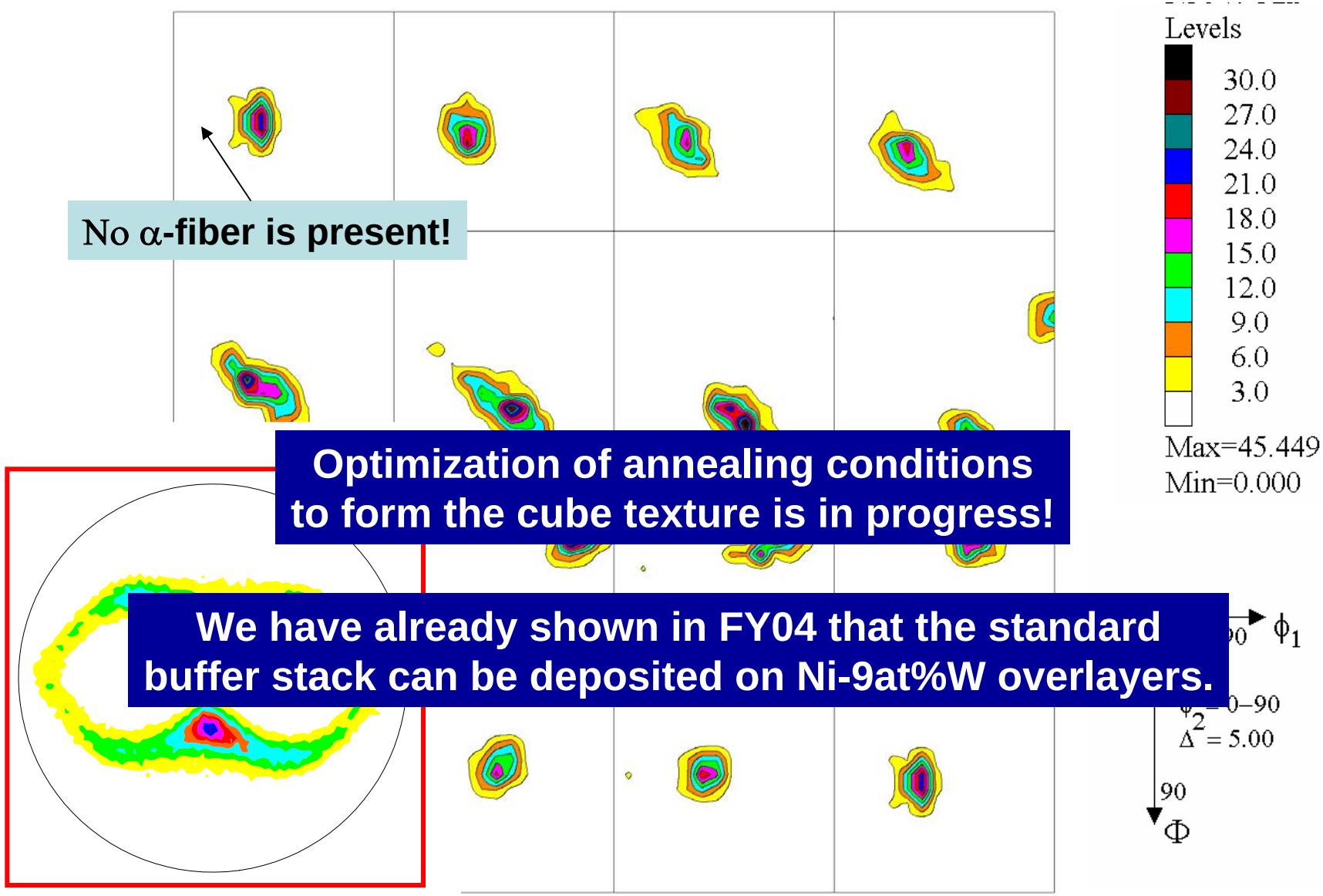


99.9% deformation





With modified rolling conditions, Cu-type rolling texture is obtained for Ni-9.3at%W with no α-fiber present!



Objective 4: Work with vendors in developing the powder metallurgy route for starting coils.

Powder metallurgy (PM) derived coils are potentially much cheaper than vacuum melting followed by hot-rolling derived coils!

- Worked with Ametek Specialty Metals
- Key problem with PM coils: high carbon content
- Carbon alloys with W to form WC which pins grain boundaries and results in retained rolling texture upon annealing
- Several coil fabrication experiments were attempted to reduce the carbon content. However, results were unsuccessful
- Carbon can certainly be removed but requires greater strategic interest by Ametek

Objective 5: Research texture development in strengthened and possibly highly conducting Cu-based alloy substrates

Effort was essentially stopped for first half of this FY:

- Key motivation for conducting Cu-alloy substrate is no longer there since most companies prefer to use a stabilizer layer
- For reduced AC loss applications, a conducting substrate with a conducting buffer stack couples the filaments in the superconducting layer

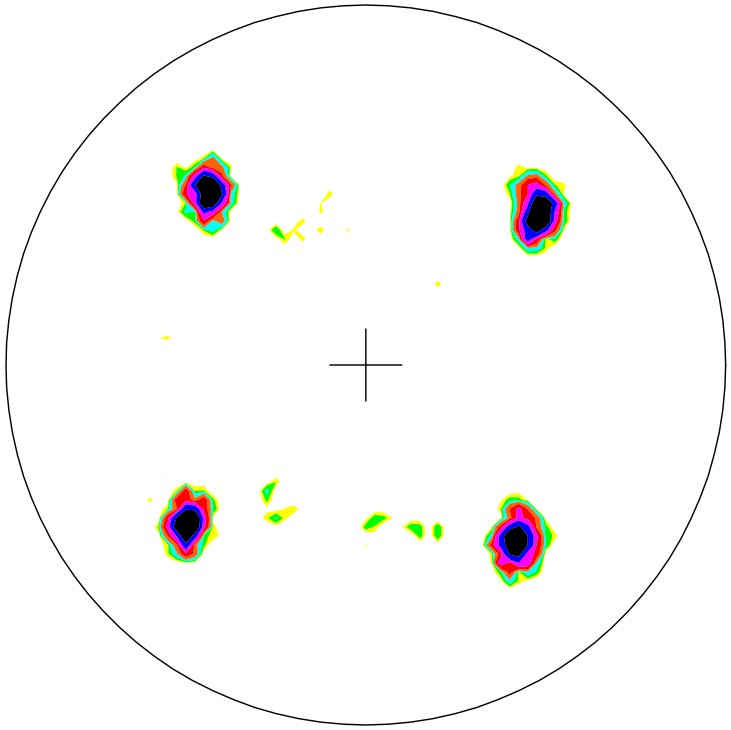
Work on texturing a strengthened Cu alloy was restarted:

- Key motivation was that formation of a sharp cube texture was not possible in Ni-9.3at%W alloy
- Goal established: Develop sharp cube texture in a non-magnetic, Cu-based alloy with a yield strength greater than or equal to 200 MPa

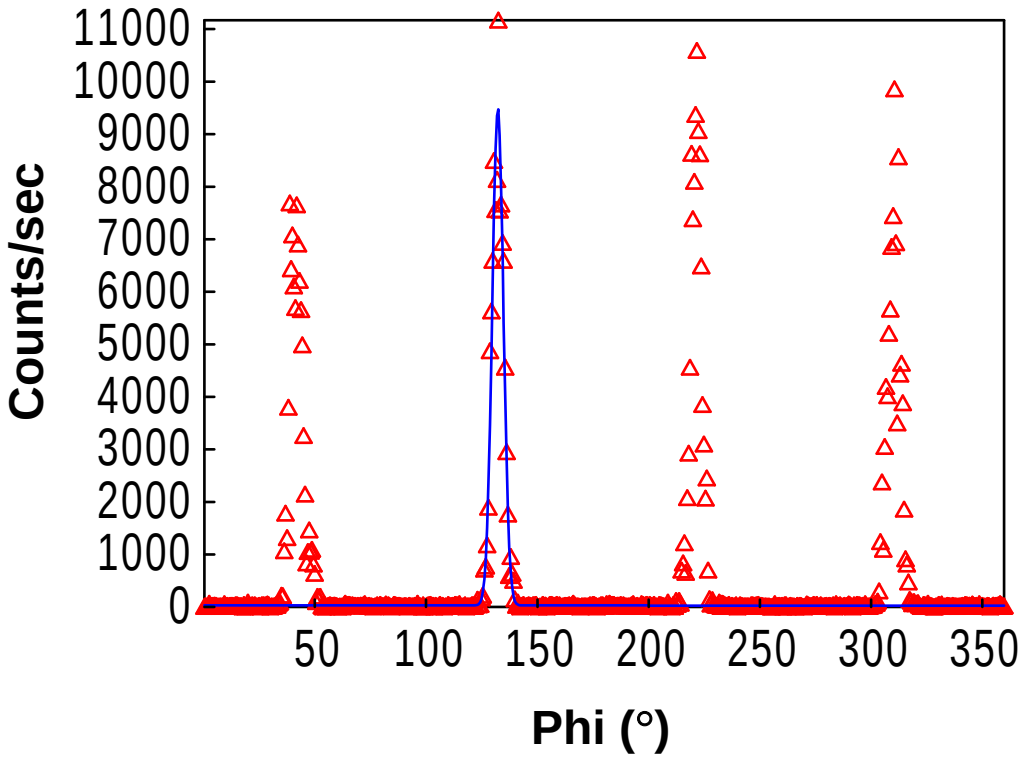
Most alloys studied which met the strength requirement could not be cube textured!

After testing over 10 alloys, an alloy with a potential for a yield strength of greater than 300 MPa was identified

(111) log-scale pole fig.



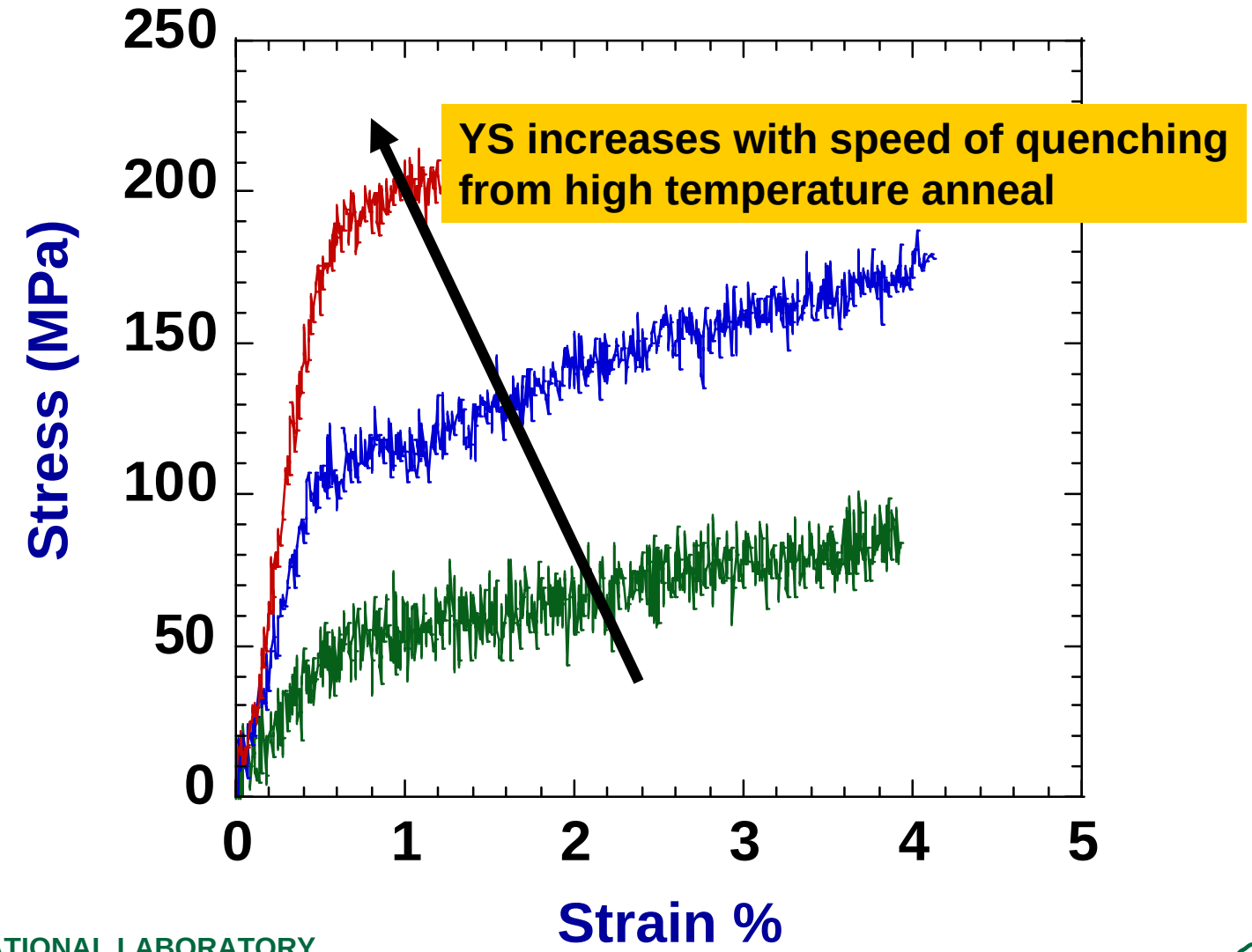
(111) phi-scan



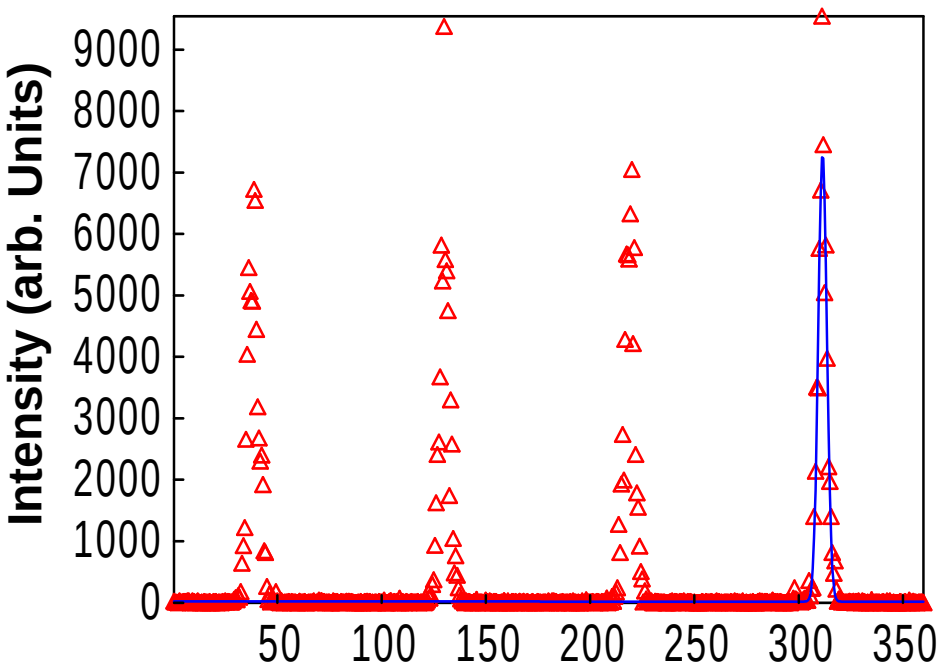
$\Delta\omega$ = 4.2°; 7.8°

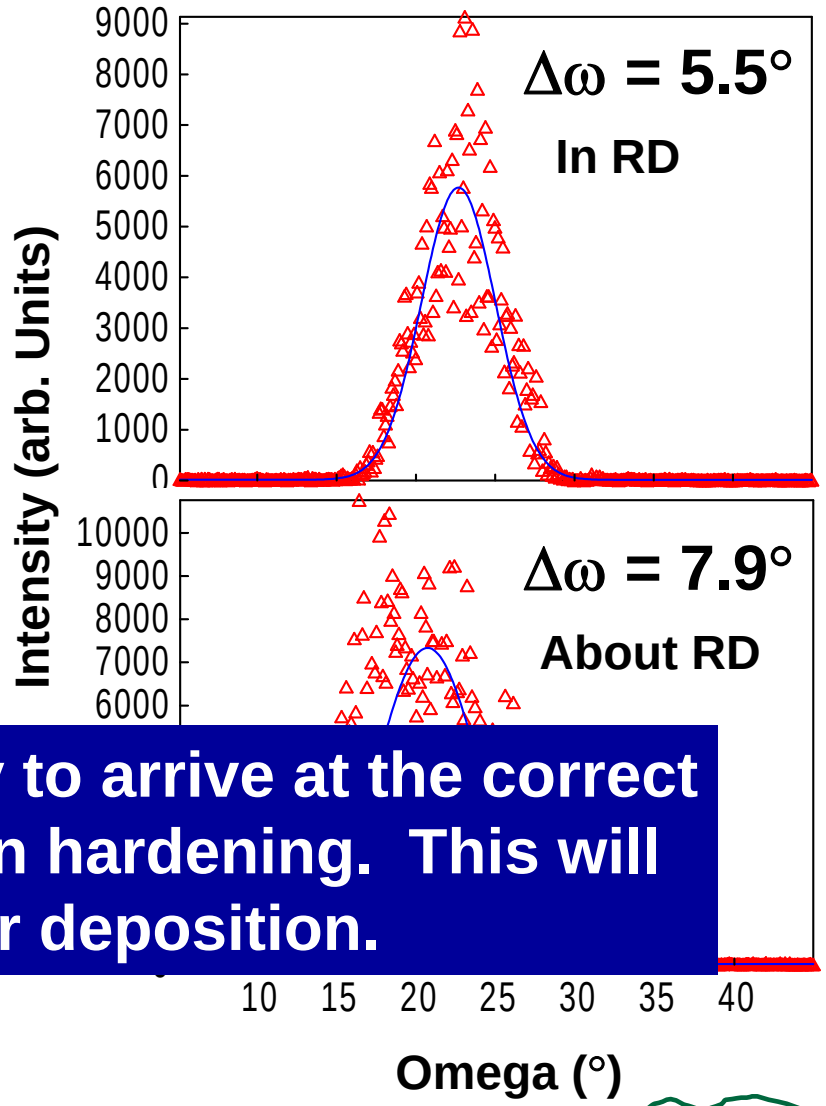
$\Delta\phi$ (measured) = 5.9°

For obtaining a YS over that of pure Cu, precipitation hardening is required



The Cu-alloy is still cube textured in its hardened state





Further work is necessary to arrive at the correct procedure for precipitation hardening. This will be followed by buffer layer deposition.

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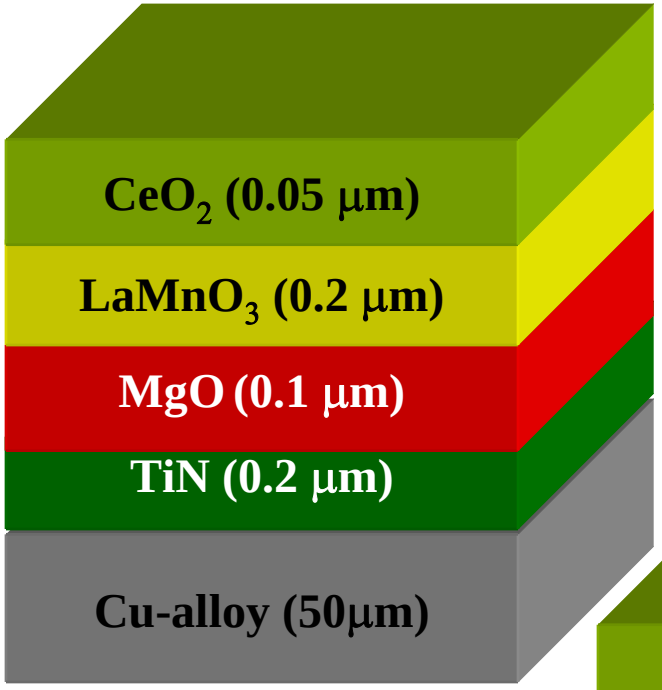
Buffer layer stacks for Cu-based substrates have been previously developed at ORNL

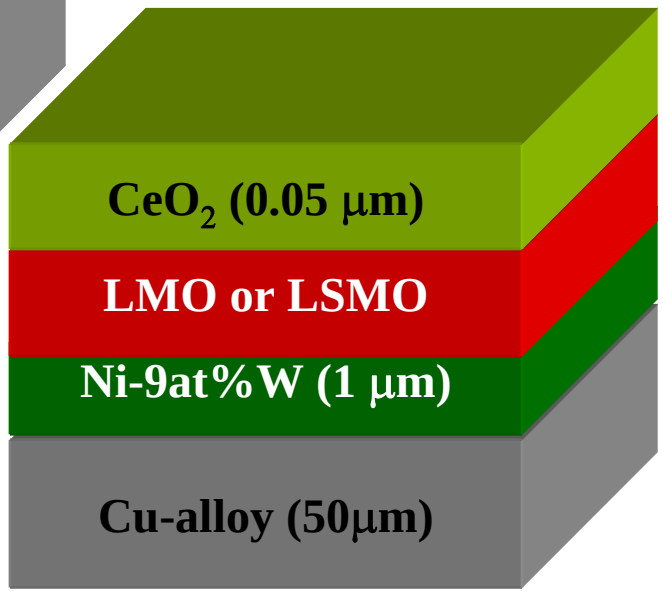


YBCO Compatible

O and Cu barrier

O diffusion barrier

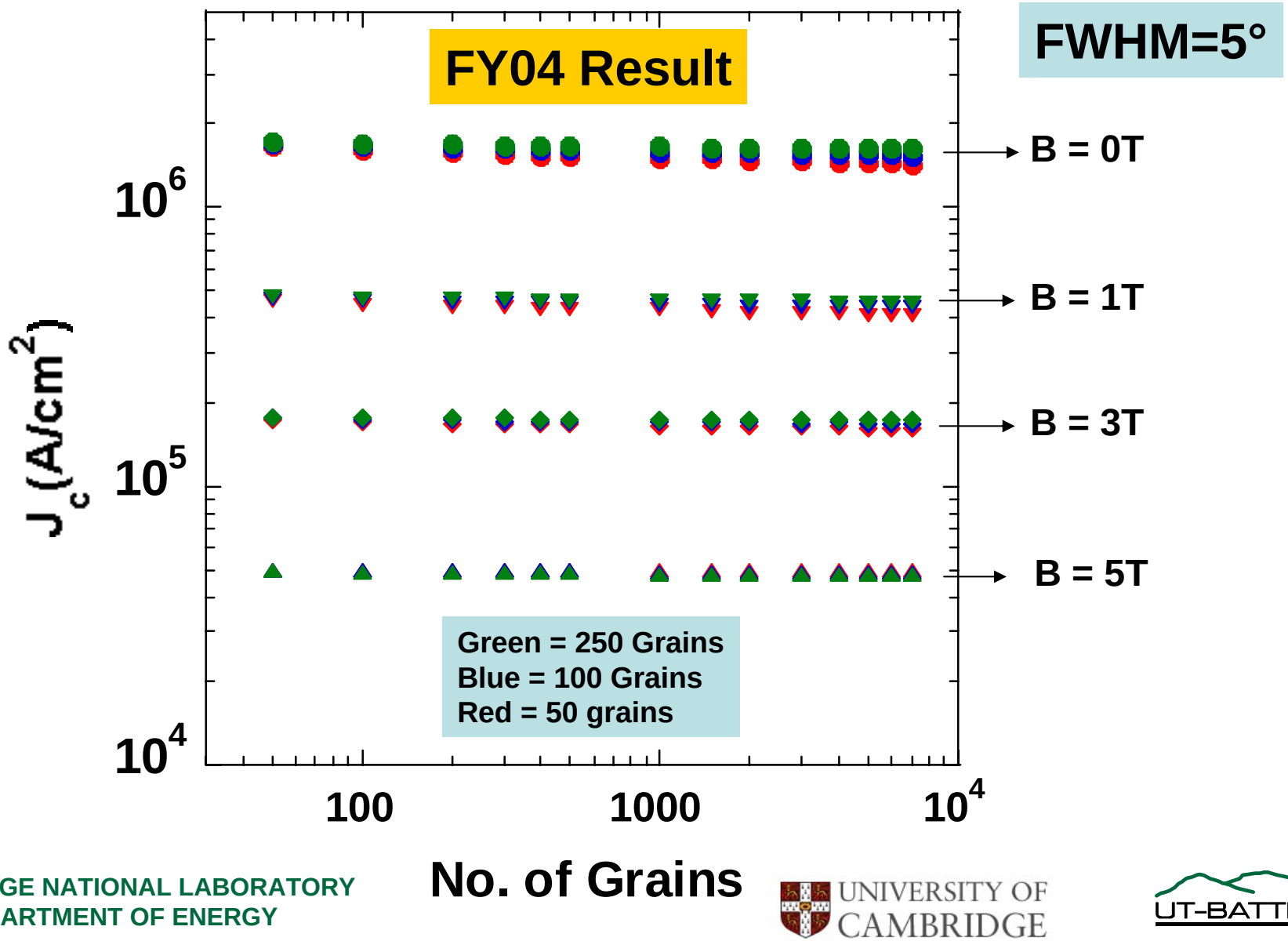
Cu diffusion barrier



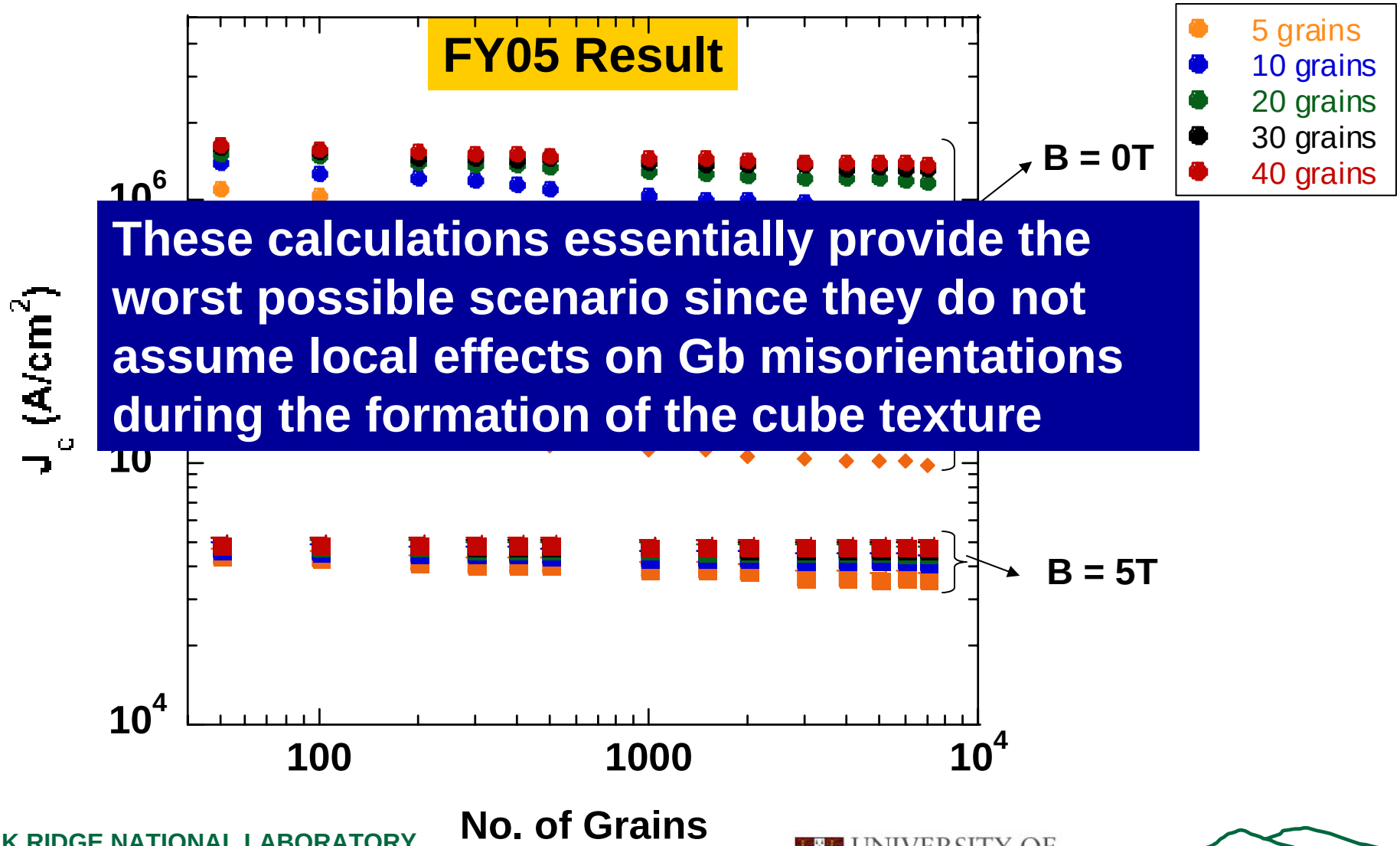
YBCO Compatible

O and Cu barrier

Objective 6: Extend percolation calculations in applied magnetic fields to conductors less than 50 grains wide.



J_c drop is insignificant for filaments as narrow as 10 grains wide

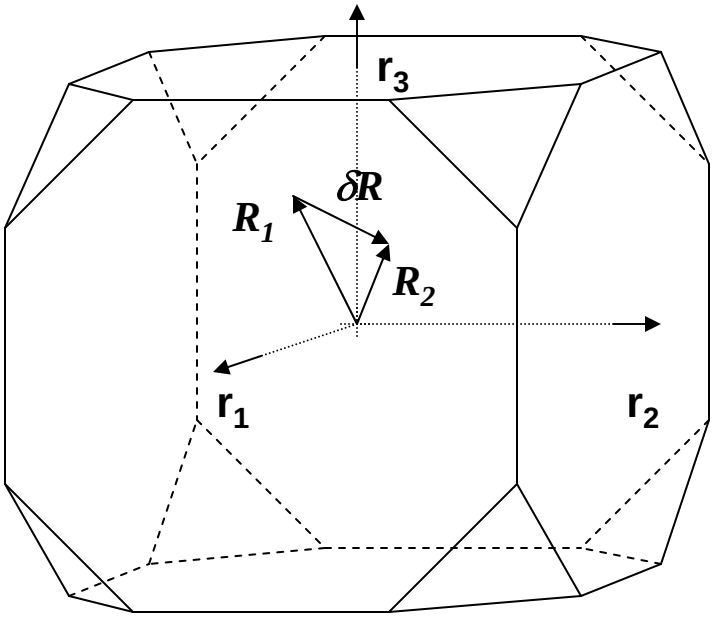


These calculations essentially provide the worst possible scenario since they do not assume local effects on Gb misorientations during the formation of the cube texture

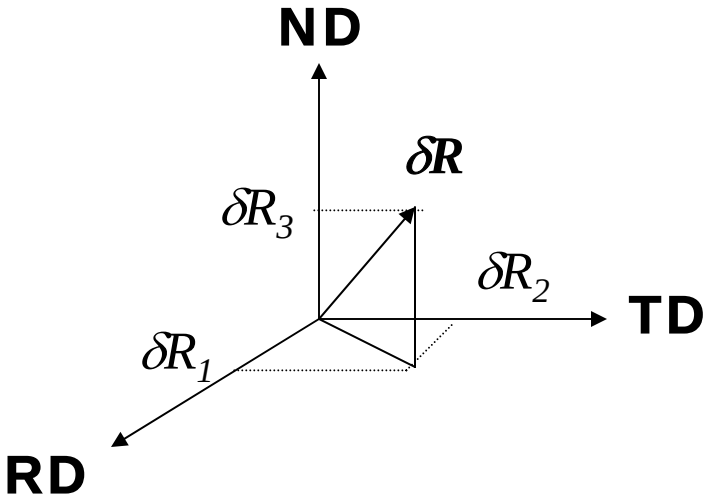
Objective 7: Develop methods to separate in-plane and out-of-plane misorientations from EBKD measurements in YBCO and correlate with J_c.

For cubic materials, this was made possible in FY04 by manipulations in Rodrigues Space using a misorientation difference vector δR

Asymmetric region of Rodrigues space for cubic materials

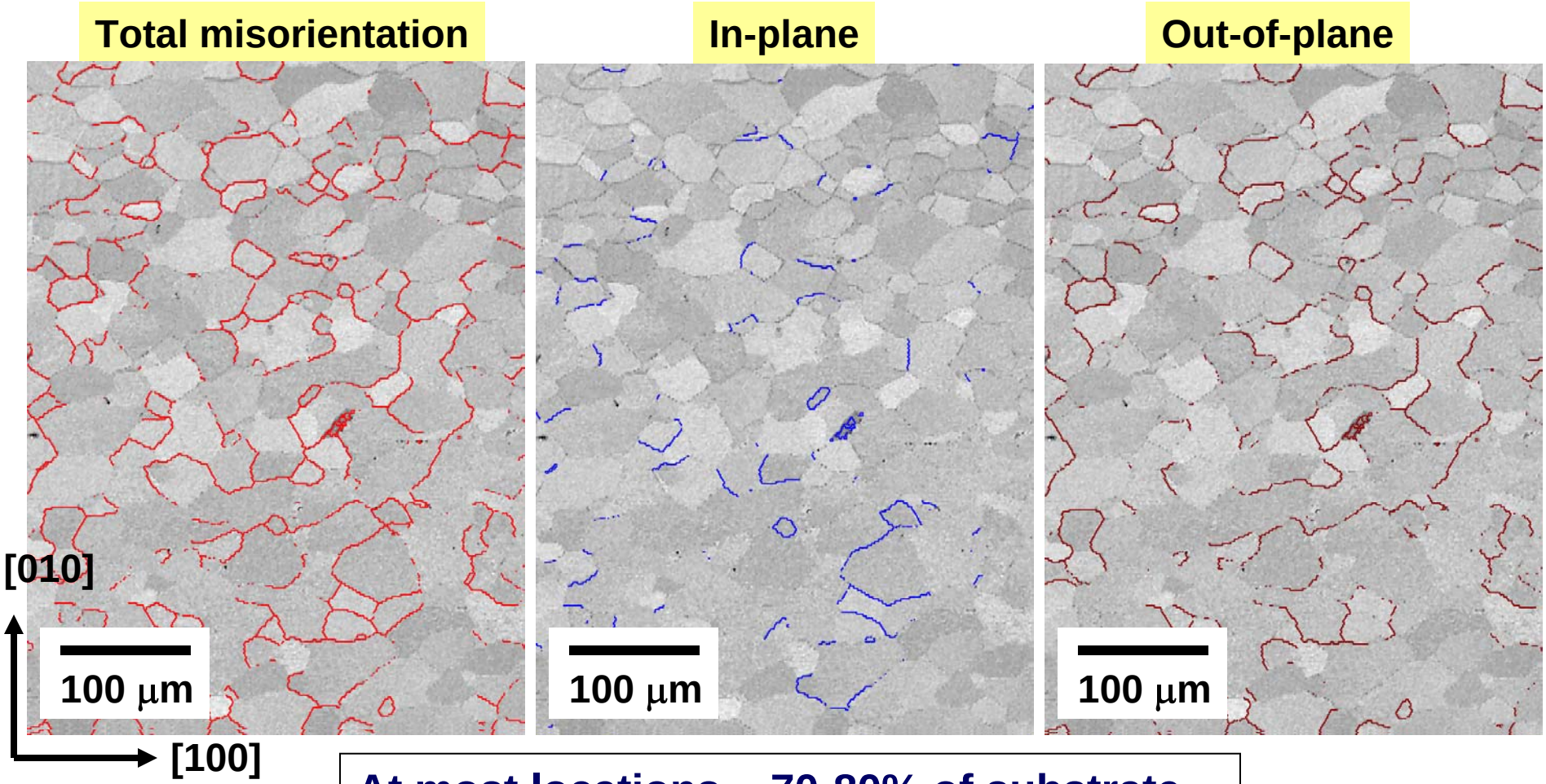


Projection of the Rodrigues difference vector give the in- and out-of-plane misorientations



While this is much more complicated for materials with lower symmetry, we accomplished our goal this FY!

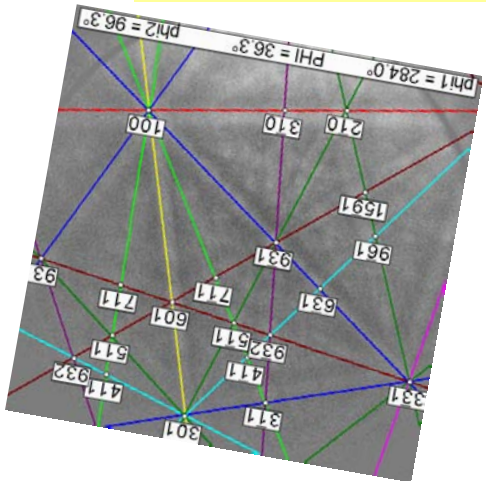
FY04: Grain boundary (GB) maps from CeO_2 cap layer of fully-buffered RABiTS with all GB's greater than 4°

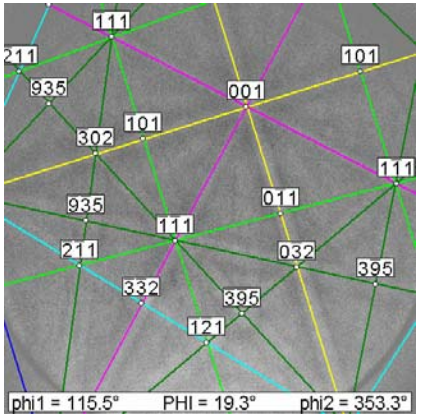


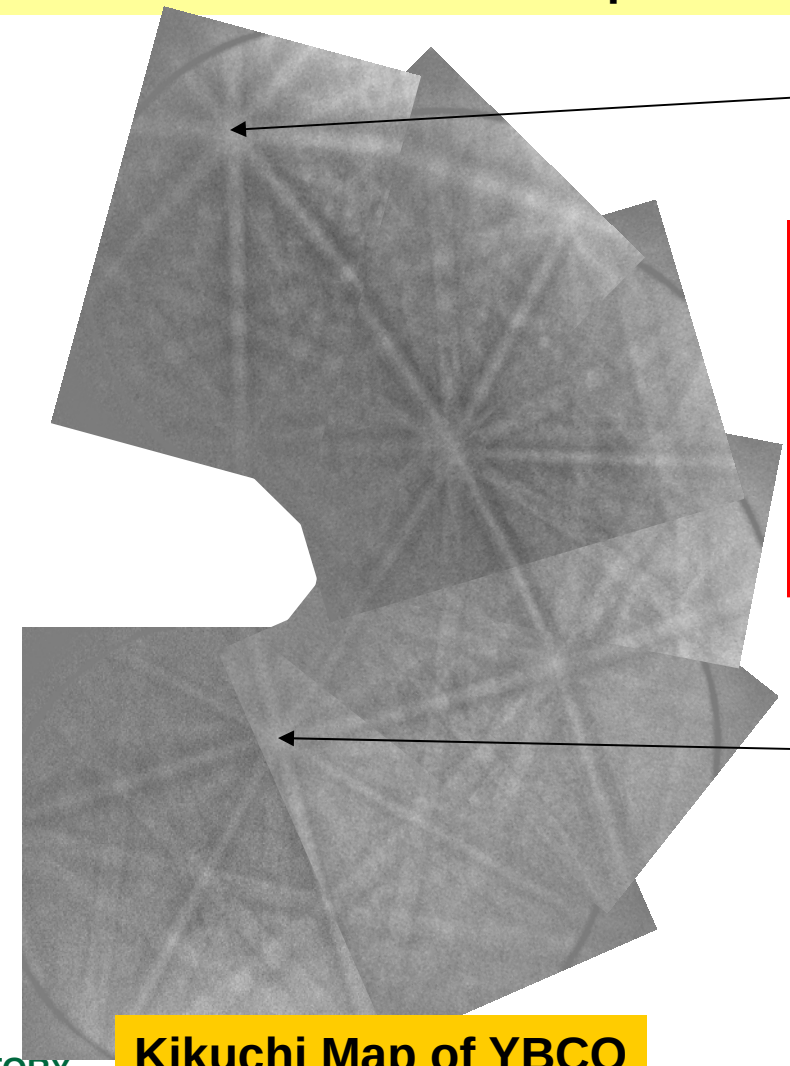
At most locations ~ 70-80% of substrate is single crystal-like w.r.t. in-plane texture

Automated indexing of YBCO with the correct crystal symmetry reflectors gives erroneous results

This is because it is not possible to distinguish between a a-axis and a c-axis orientation based on interplanar angles alone!







A-axis

C-axis

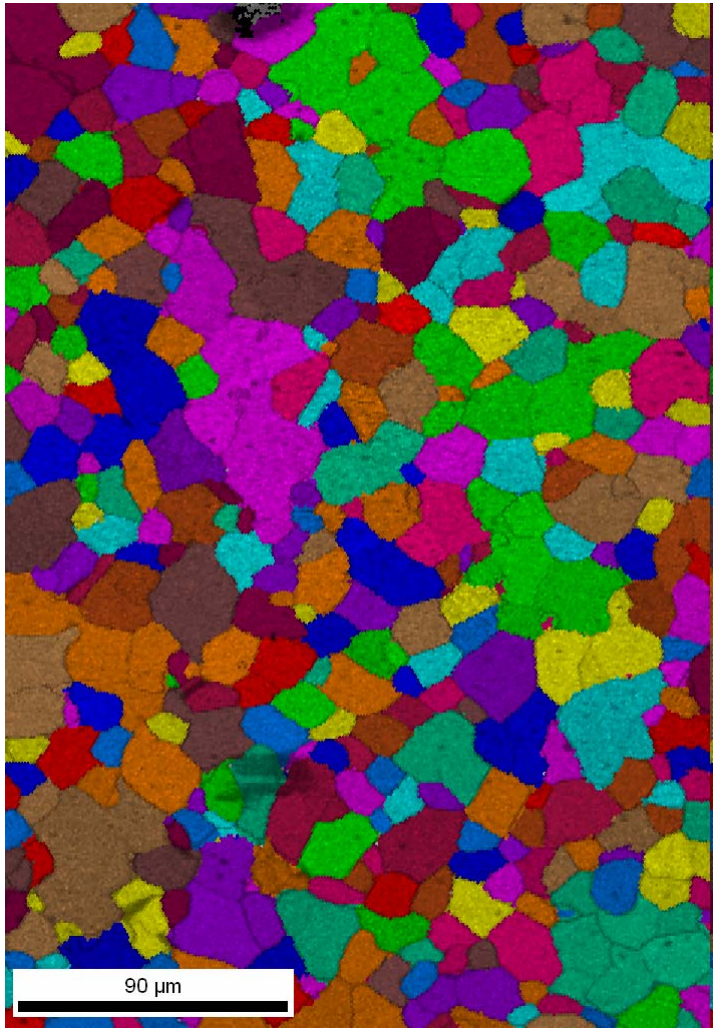
Indexing the YBCO pattern as a cubic pattern has been suggested before, but is crystallographically incorrect!

Kikuchi Map of YBCO

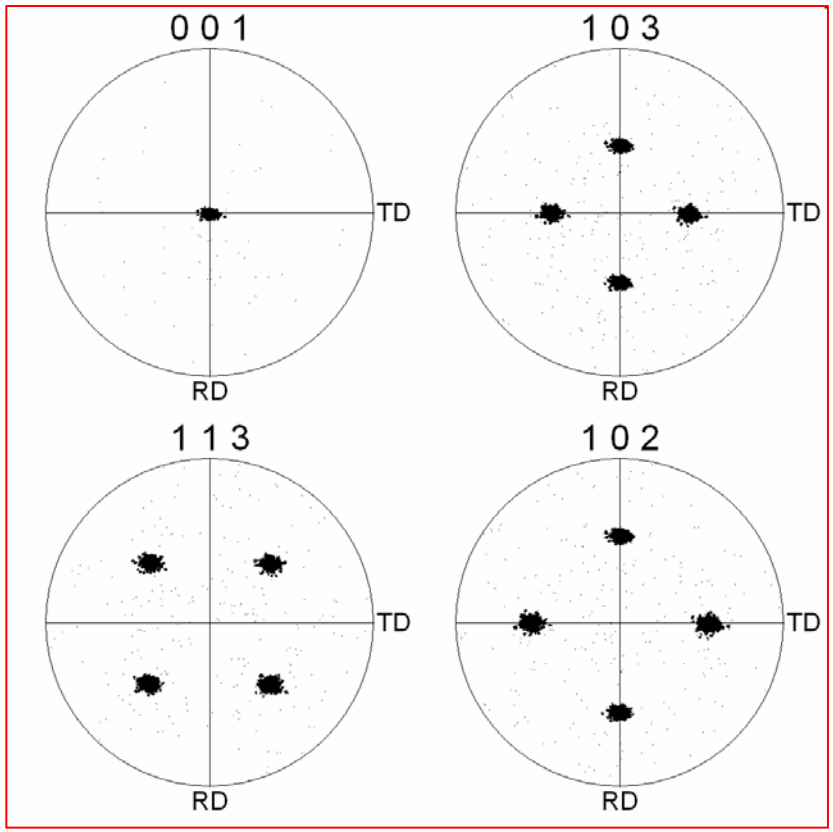
New methodology was developed for accurate indexing of electron backscatter Kikuchi diffraction patterns from YBCO

- Use of band widths as well as interplanar angles for indexing
- Choice of right reflectors for indexing
- New procedure to determine if indexing in an automated run is accurate (since the usual parameter "confidence index" cannot be used since c-axis and a-axis solutions get the same number of votes)
- New procedure to correct for incorrect indexing since the usual methodology based on confidence index does not work

Orientations in a 0.12 μm YBCO film with a J_c over 4 MA/cm^2. No grain boundary meandering is observed for such thin films

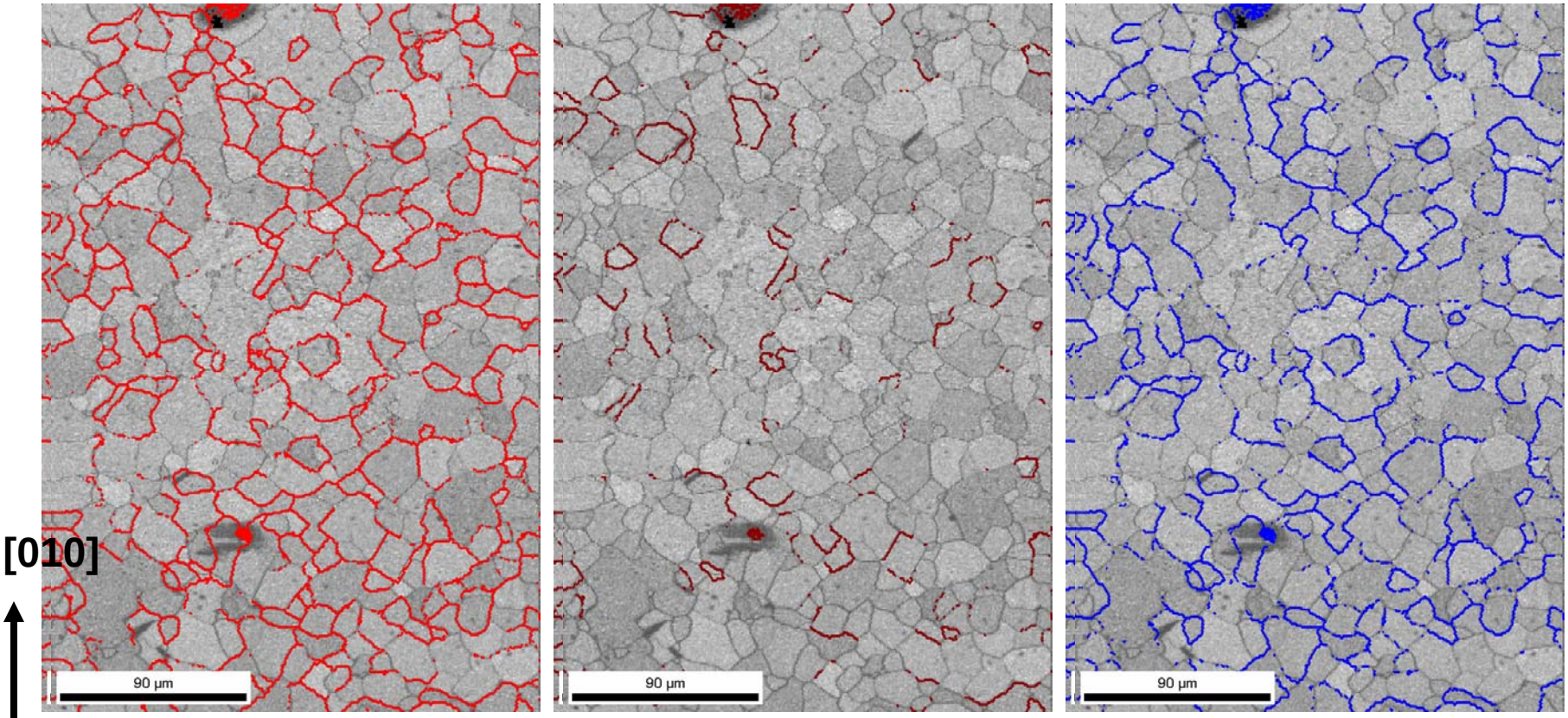


Pole figures for YBCO



GB maps in a 0.12 μm YBCO film with a J_c over 4 MA/cm^2. All GB's greater than 4° are shown

Total misorientation | **In-plane** | **Out-of-plane**



[010]

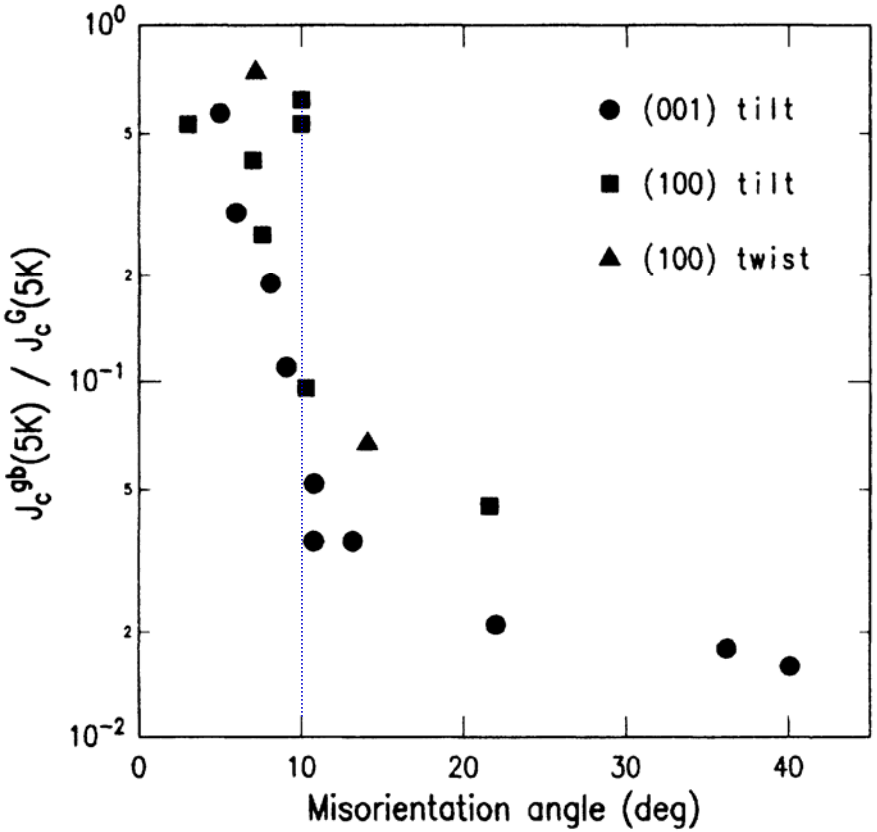
[100]

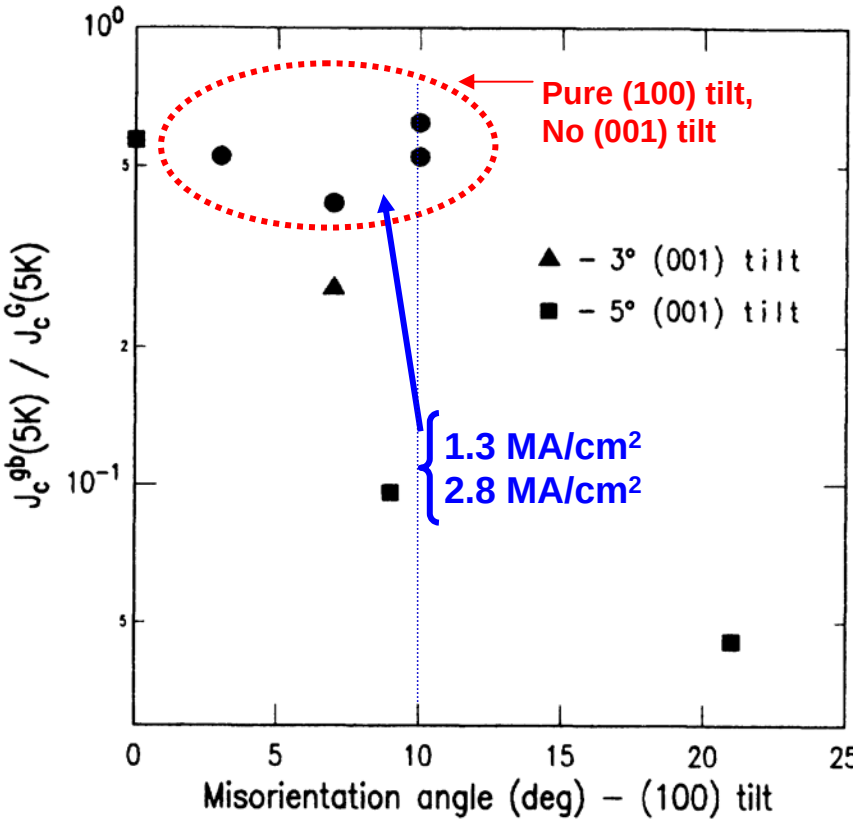
90 μm

At most locations ~ 70% of the YBCO film has no grain boundaries with respect to in-plane misorientations at the 4° criterion.

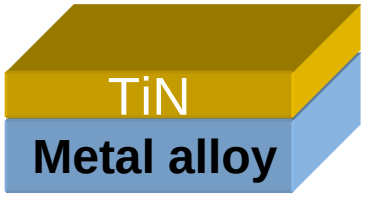
Observations are consistent with Dimos et al.'s work

Ref: Dimos et al., Phys. Rev.B, 41, 4038 (1990)

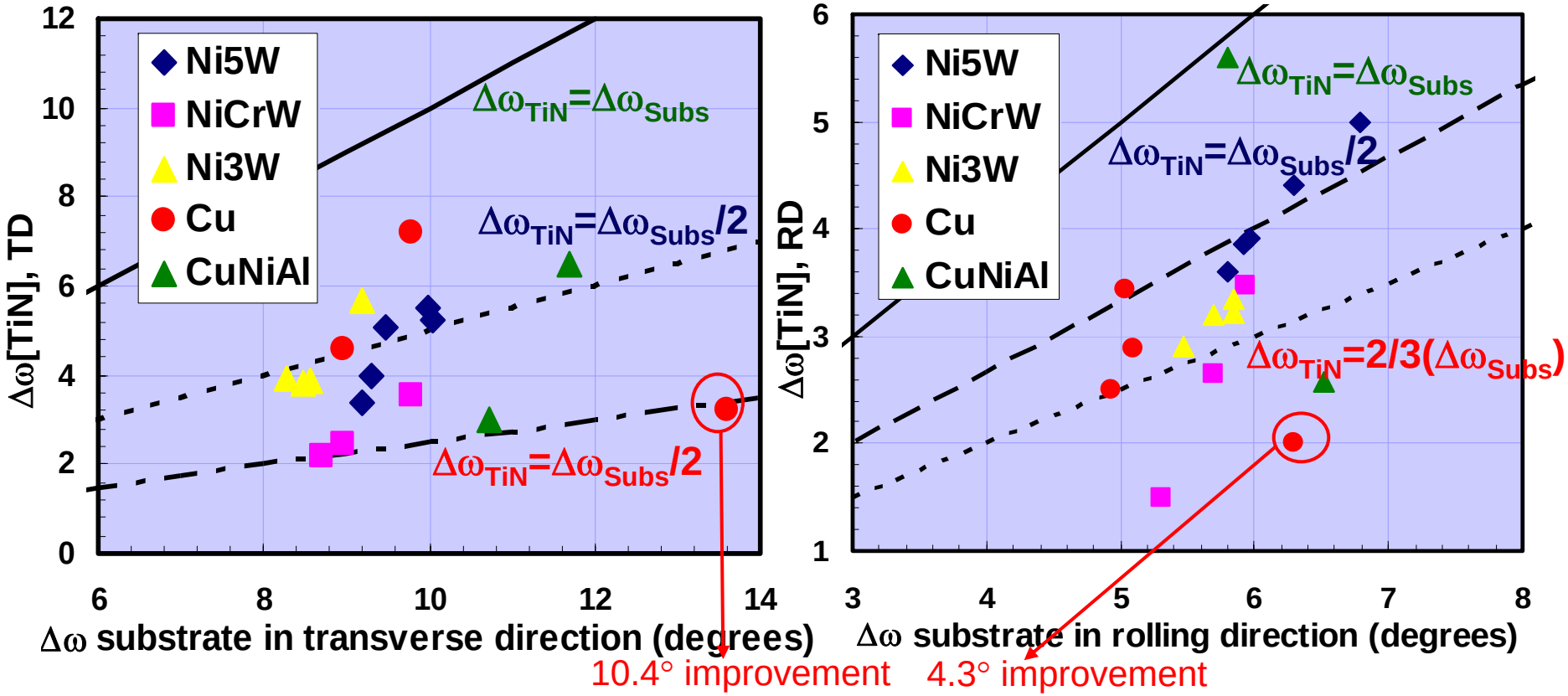




Objective 8: **Determine the relative effects of in-plane and out-of-plane misorientations on J_c by fabricating YBCO films with *same in-plane but different out-of-plane misorientations*.**



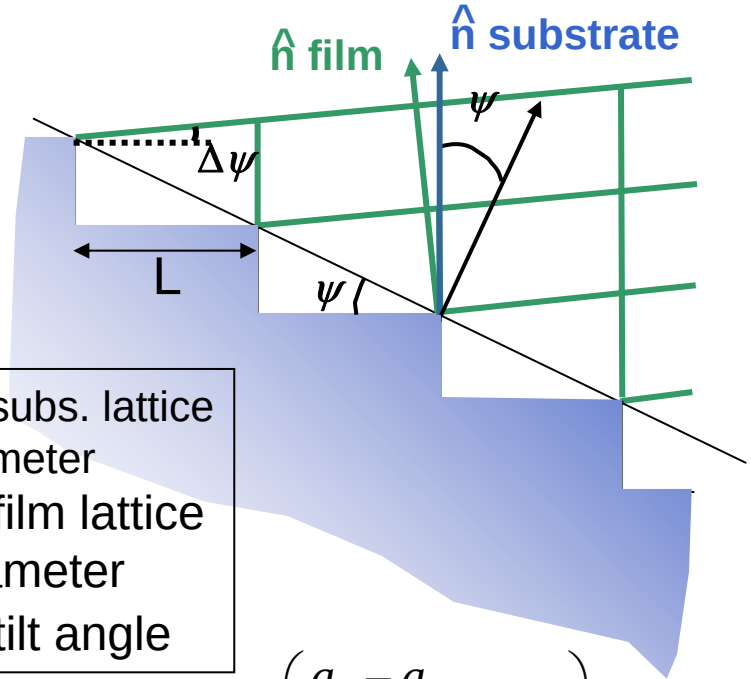
TiN seed layers result in significant sharpening of the out-of-plane full-width-half-maximum (FWHM)



Mechanisms for tilted epitaxy and sharpening of the out-of-plane texture FWHM

Two possibilities exist:

1. Strain in coherent growth
(Nagai, 1971)

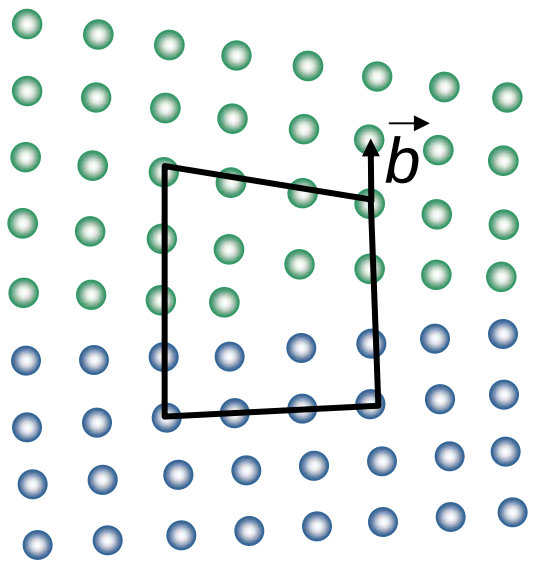


a_s = subs. lattice parameter
a_f = film lattice Parameter
ψ = tilt angle

$$\Delta\psi = \tan^{-1}\left(\frac{a_s - a_f}{a_s}\tan\psi\right)$$

c-axis tilts toward surface normal if $a_f < a_s$

2. Misfit dislocations (incoherent)
(Olsen and Smith, 1975; Ayers et al., 1991)



$$\Delta\psi = f \cdot b_{\perp} / b_{//}$$

c-axis tilts toward surface normal if $a_f > a_s$; much larger tilts are possible

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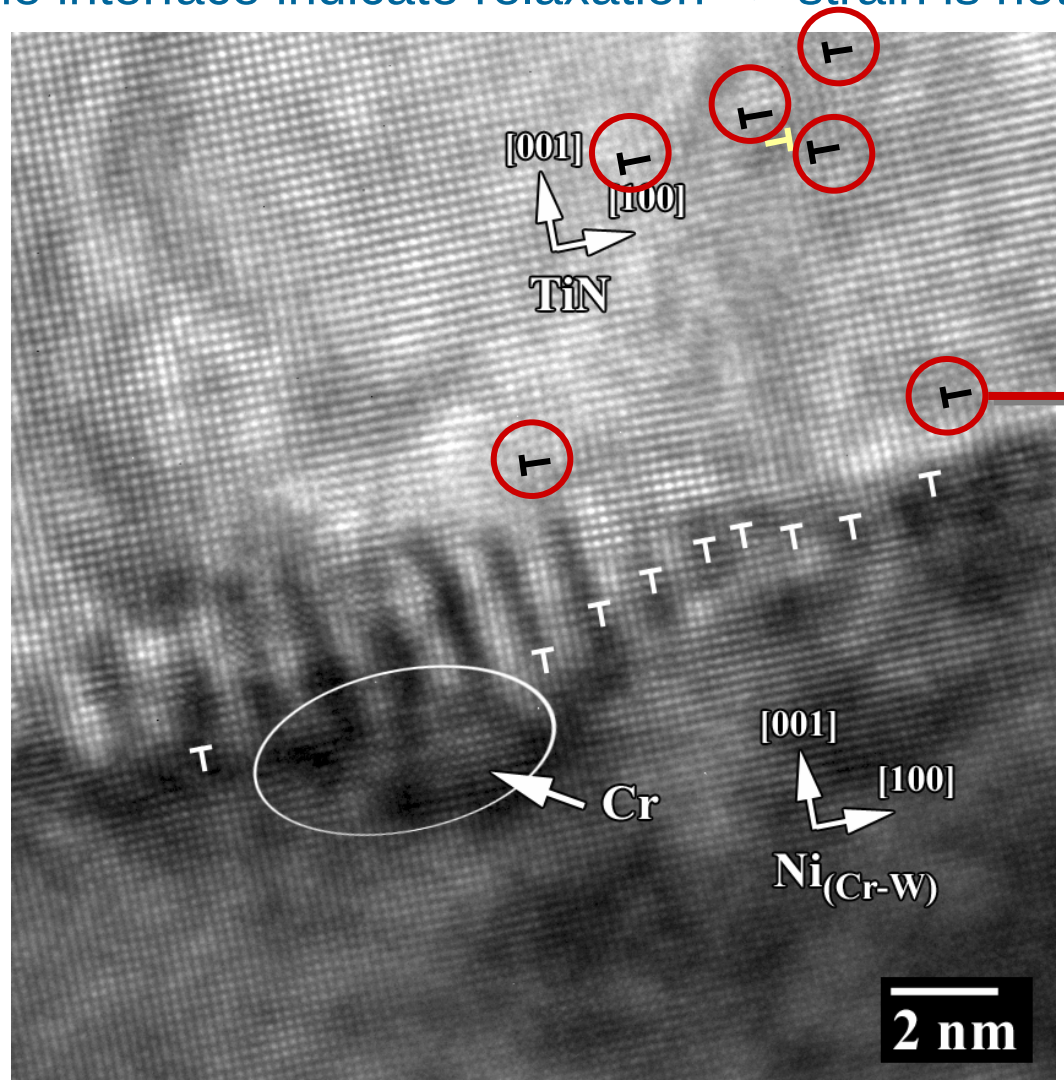
What is the operative mechanism for TiN seed layers?

Dislocations at the interface indicate relaxation => strain is not a big component



Unbalanced dislocations with Burgers vector // [001] can explain tilt

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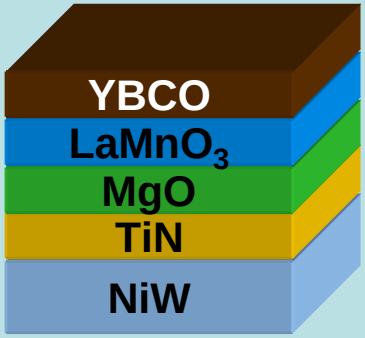
Samples with different out-of-plane but similar in-plane FWHM

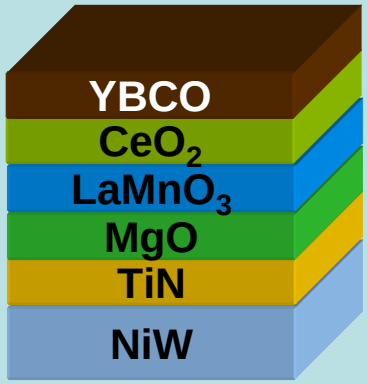
CASE 1

Sharper Δω transferred to YBCO, Δϕ same as substrate



CASE 2

Δω in YBCO broader by 3°, Δϕ same as substrate



Ni3W Δω, R	Ni3W Δω, T	Ni3W Δϕ
5.8°	8.5°	8.2°

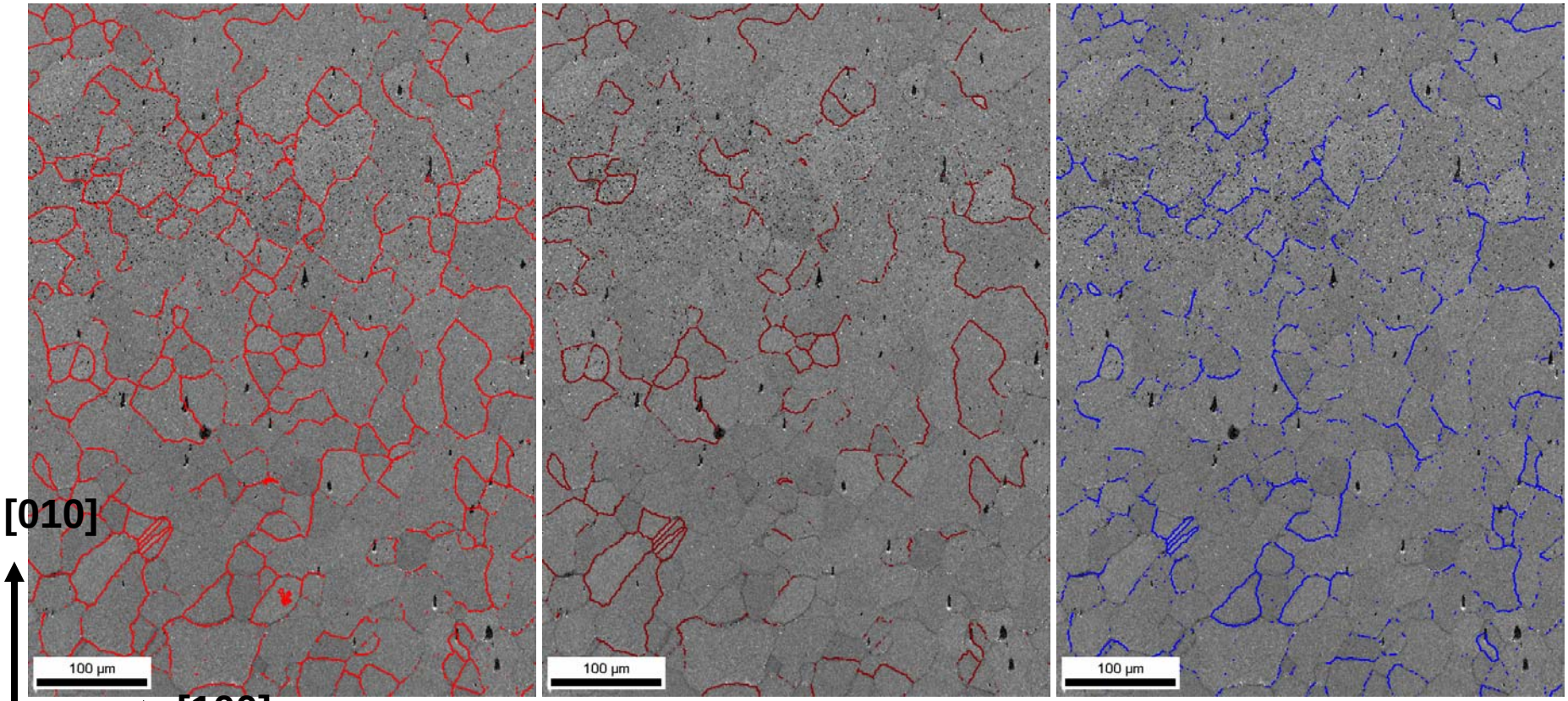
Different out-of-plane FWHM

#	YBCO Δω, R	YBCO Δω, T	YBCO Δϕ
1	3.1°	4.1°	7.5°
2	6.3°	7.5°	7.9°

Similar in-plane FWHM

GB's greater than 4° in sample with sharper out-of-plane full-width-half-maximum (FWHM)

Case 1: YBCO/LMO/MgO/TiN/NiW



[010]

[100]

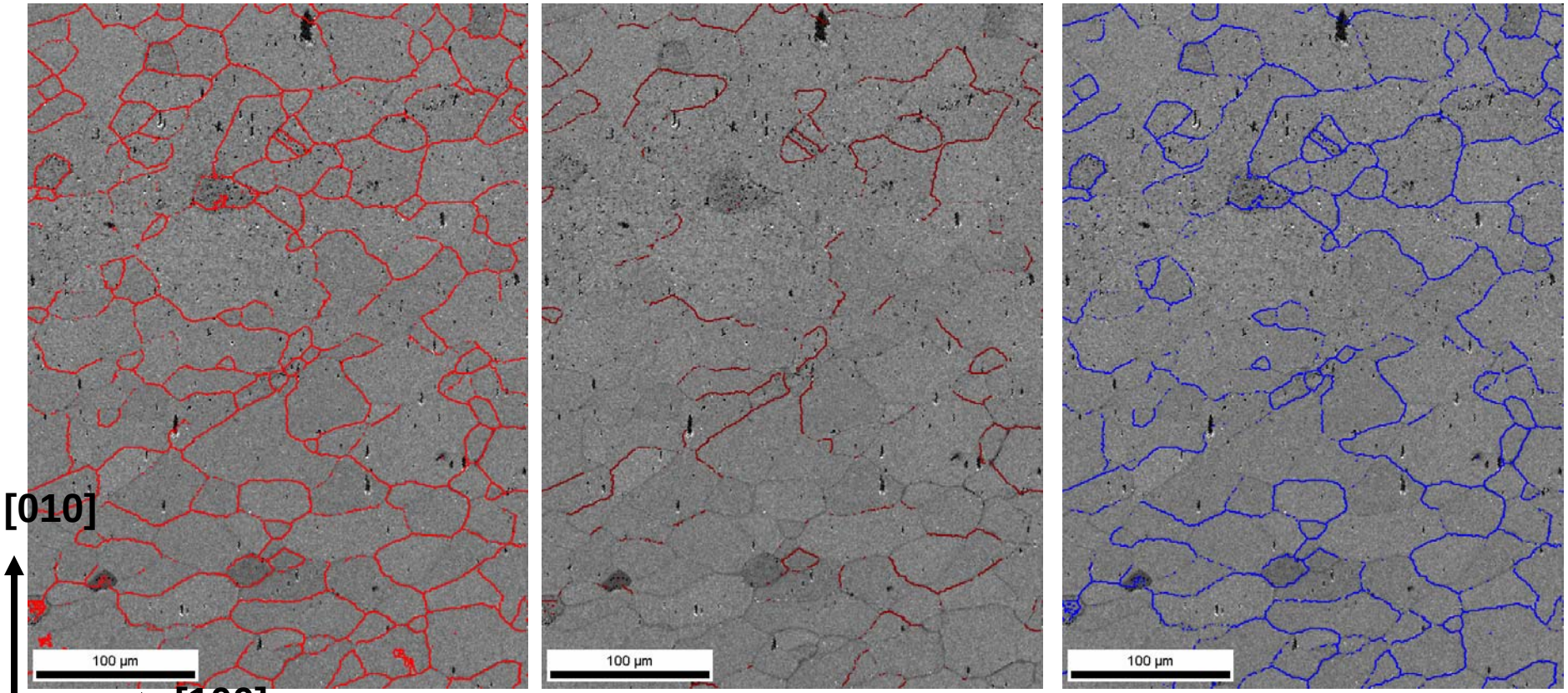
100 µm

~70% area is single crystal-like w.r.t. in-plane misorientations!

~60% area is single crystal-like w.r.t. in-plane misorientations!

GB's greater than 4° in sample with broader out-of-plane full-width-half-maximum (FWHM)

Case 2: YBCO/CeO_2/LMO/MgO/TiN/NiW



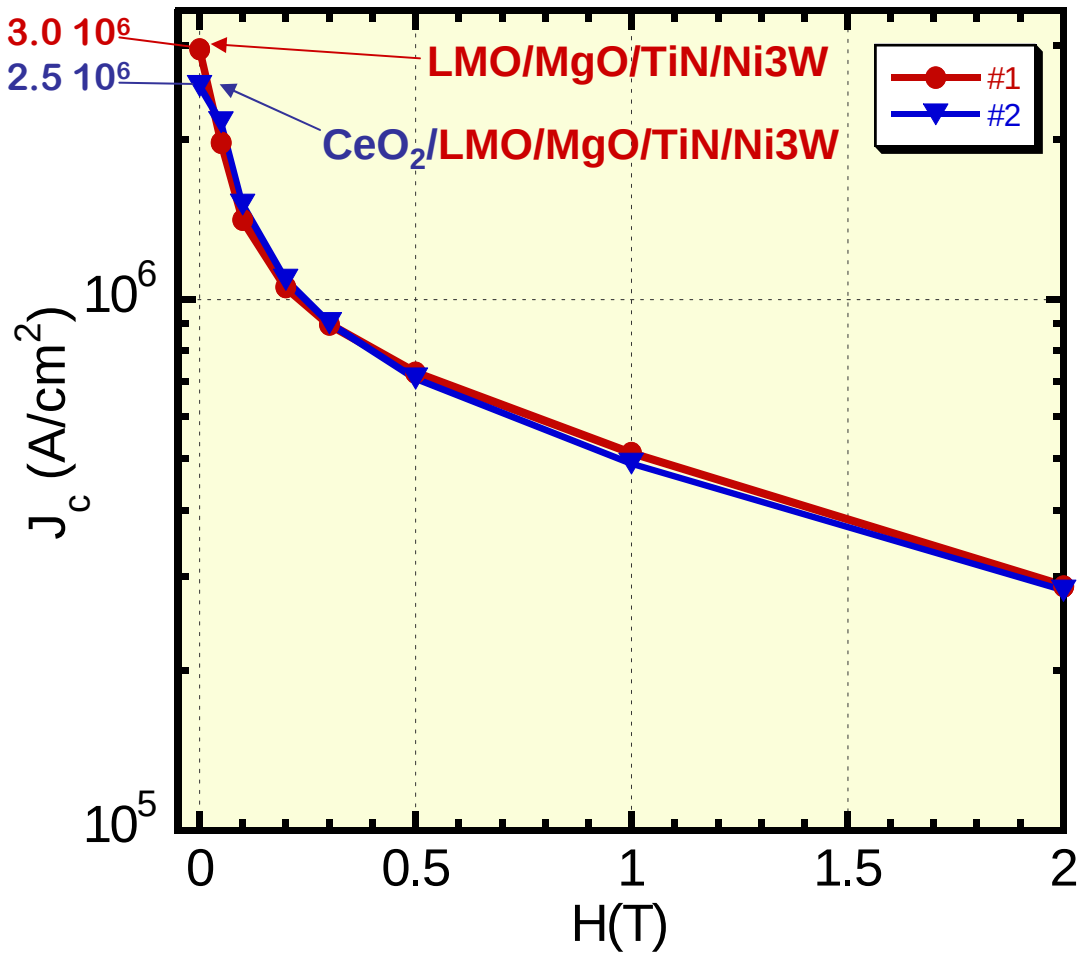
[010]

[100]

100 µm

~70% area is single crystal-like w.r.t. in-plane misorientations!

So how does out-of-plane sharpening affect J_c?



Similar J_c is seen for samples with similar in-plane texture but significantly different out-of-plane texture!

J_c appears to correlate primarily with in-plane misorientations!

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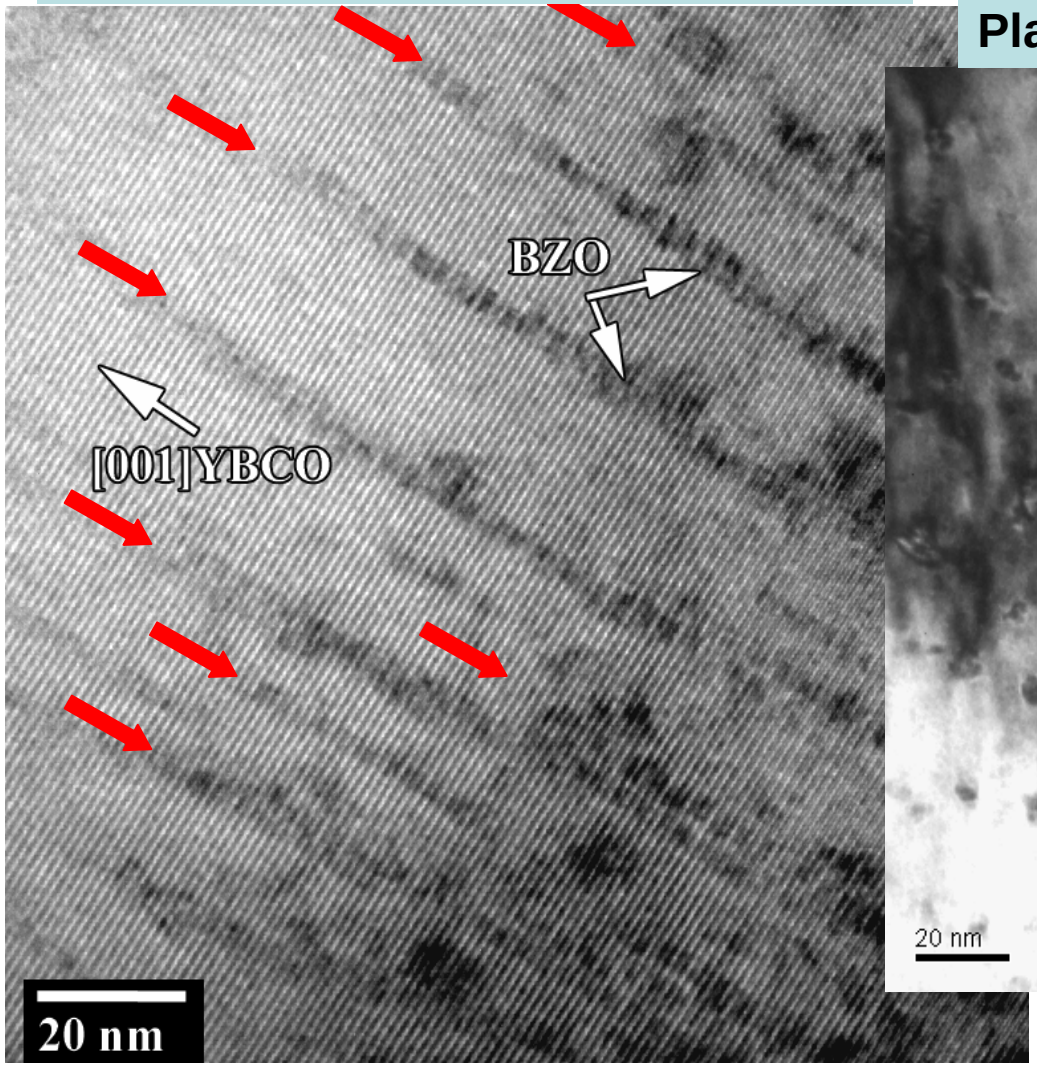
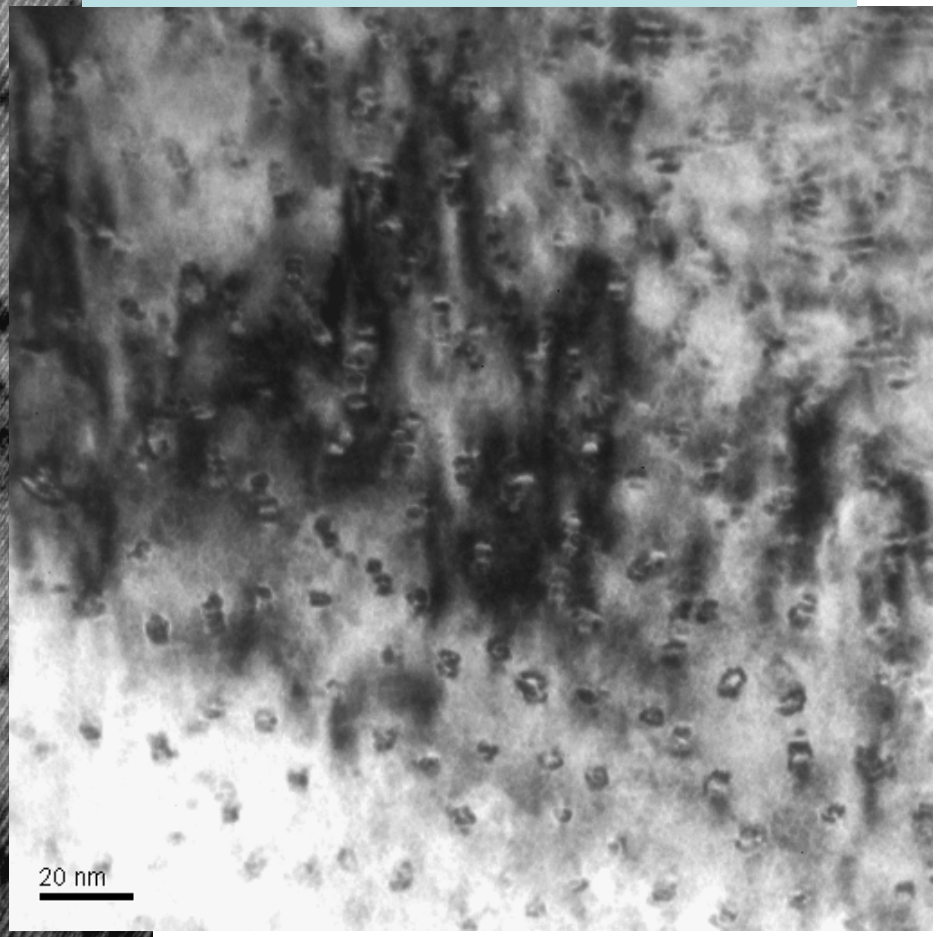
Objective 9: Enhance pinning in YBCO thick films on RABiTS

Cross-section TEM of YBCO/RABiTS

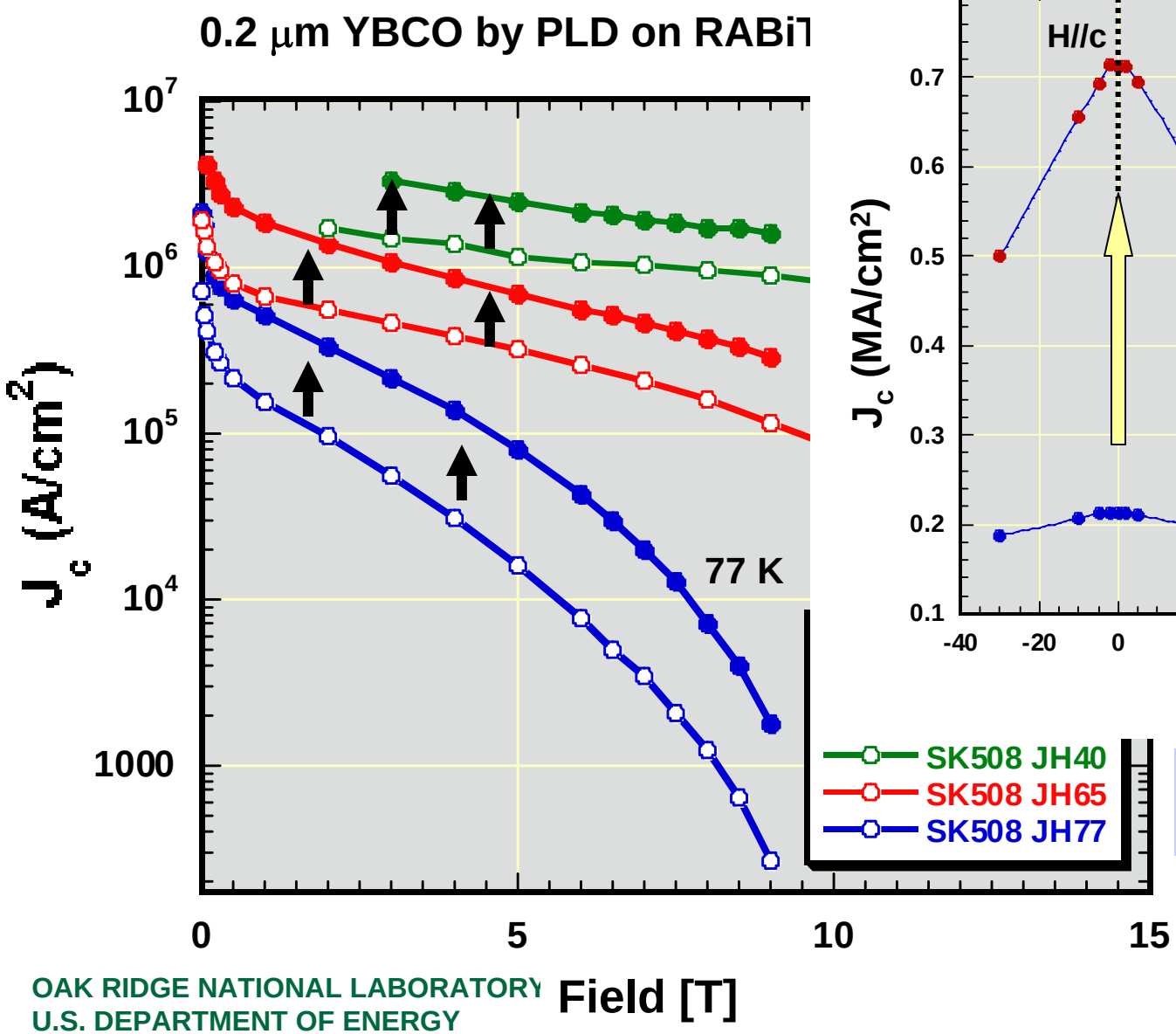


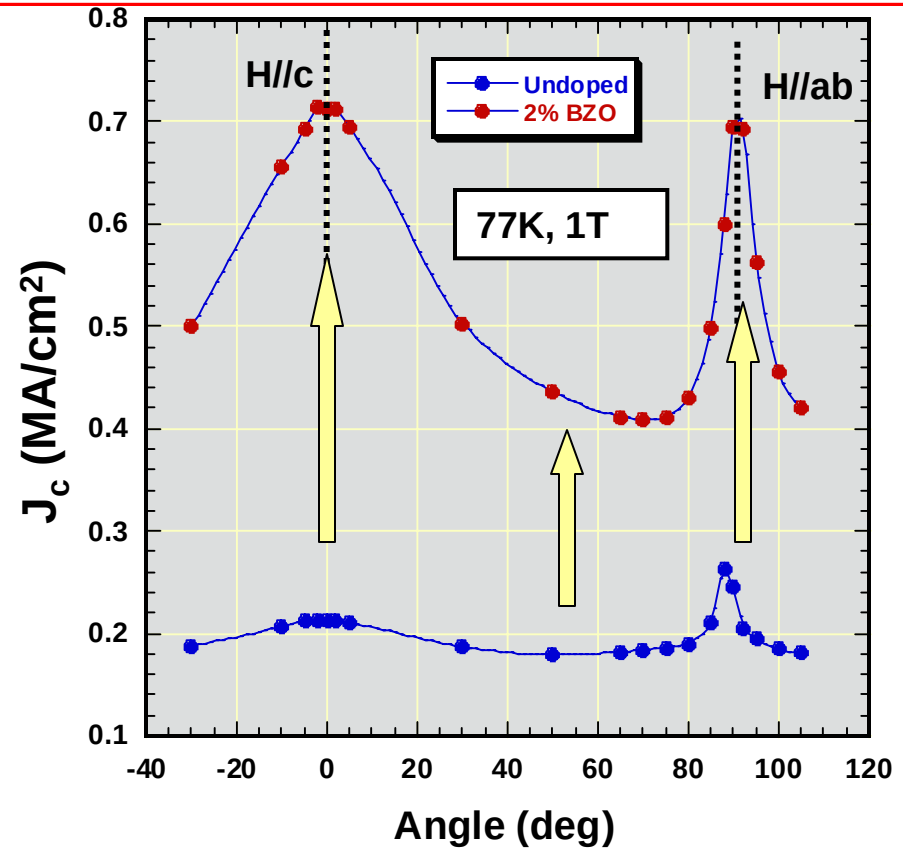
Plan view TEM of YBCO/RABiTS



20 nm

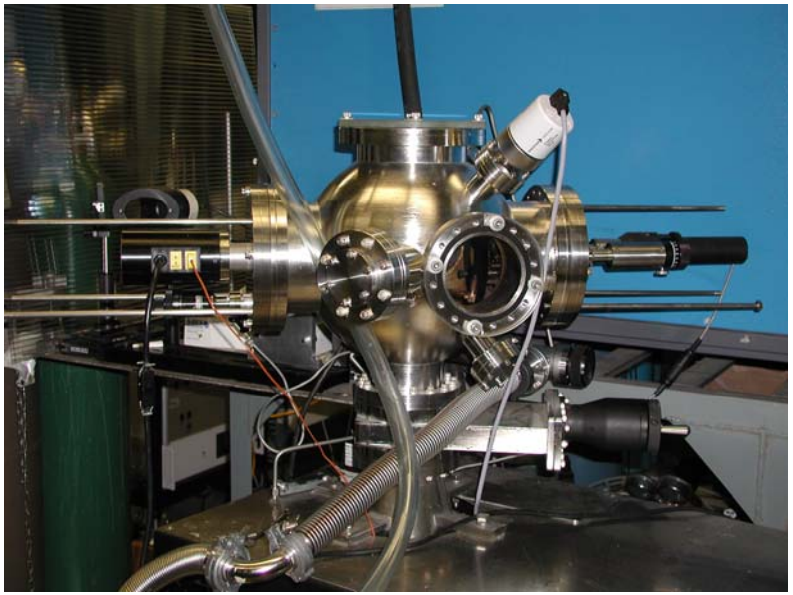
*Intra*granular J_c can be significantly enhanced by incorporation of self-aligned nanodots in YBCO on RABiTS





Significant enhancement in J_c is observed

Method used to incorporate self-aligned nanodots & nanorods

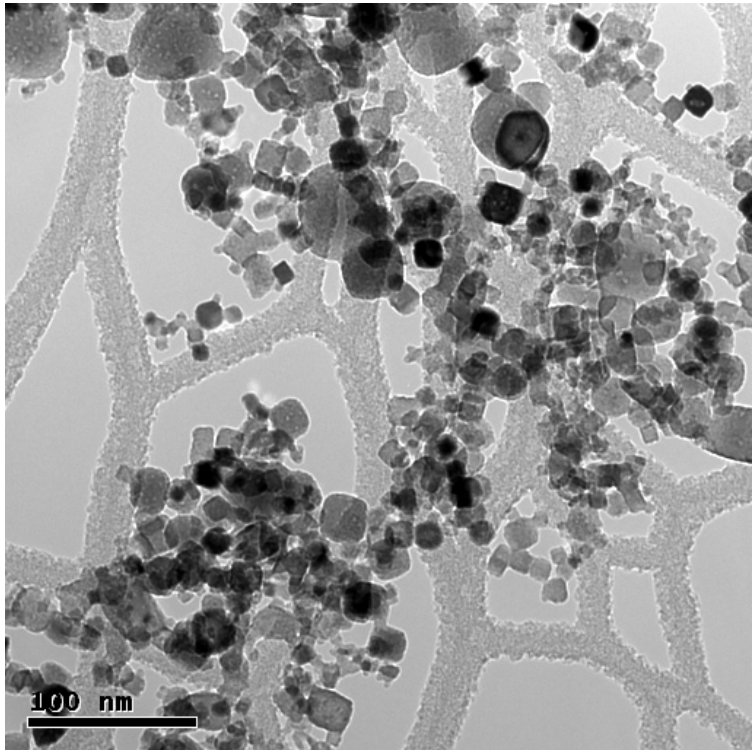


PLD YBCO deposition system

- XeCl(308nm) excimer laser Model LPX 305
- Rep. Rate: 10-20 Hz
- Subs. Temp. = 790°C
- PO2 = 120 mTorr

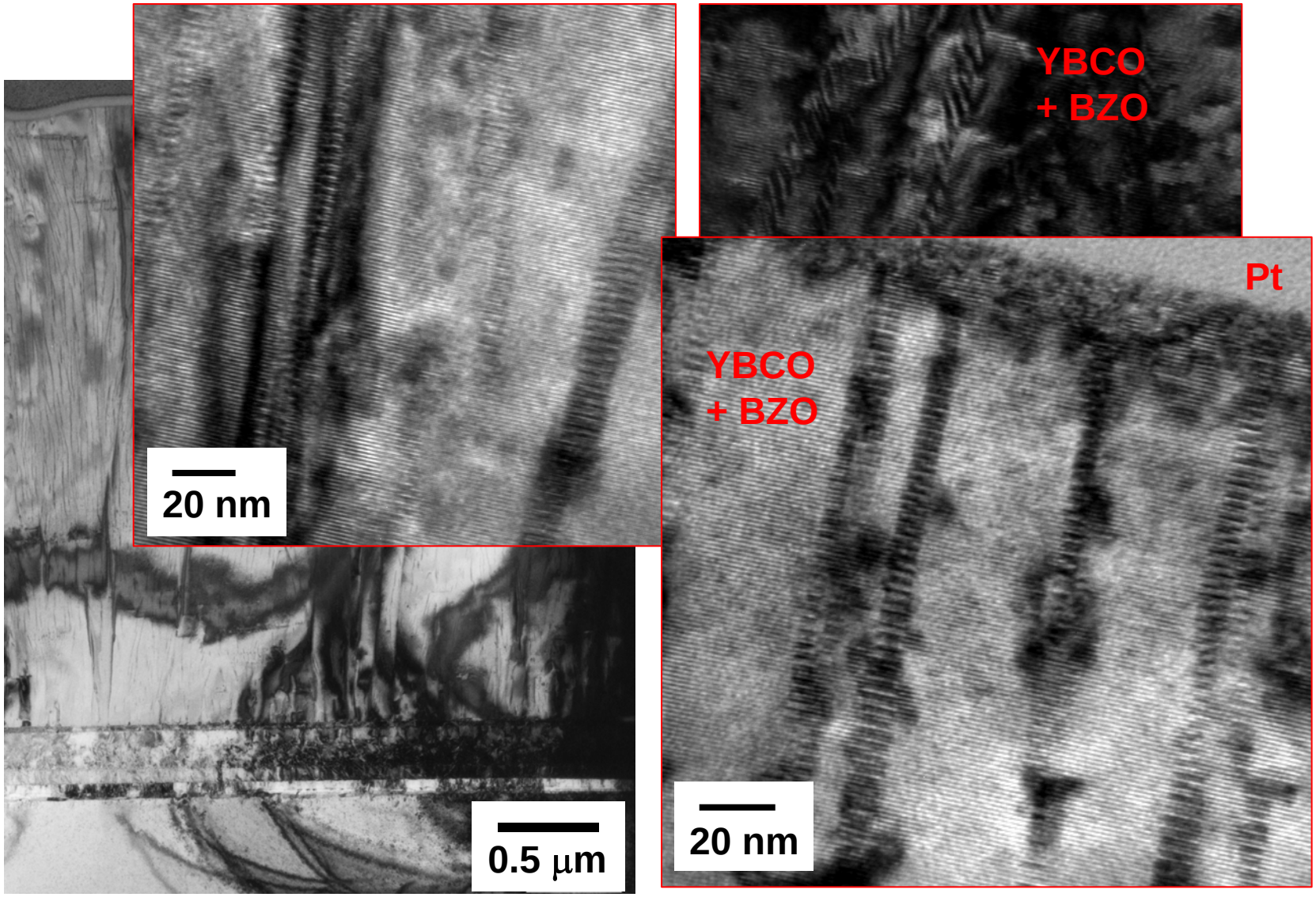
Substrate used: RABiTS

Use a single sintered target of YBCO mixed with $BaZrO_3$ nanoparticles



Commercially available powder from Sigma-Aldrich Co. Not expensive!

3 μm thick films on RABiTS: Self-assembled nanodots and nanorods extend all the way through the film thickness!



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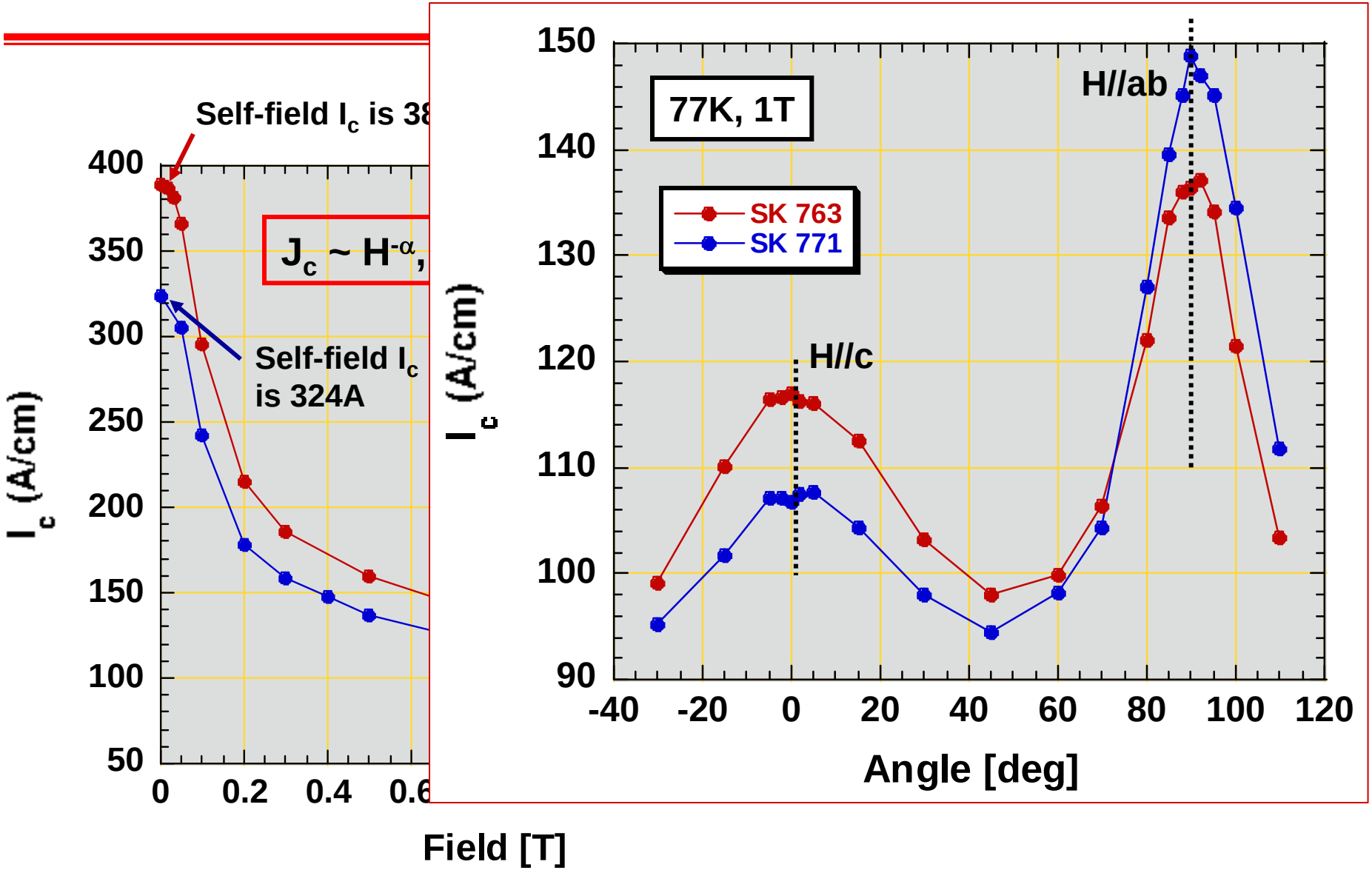
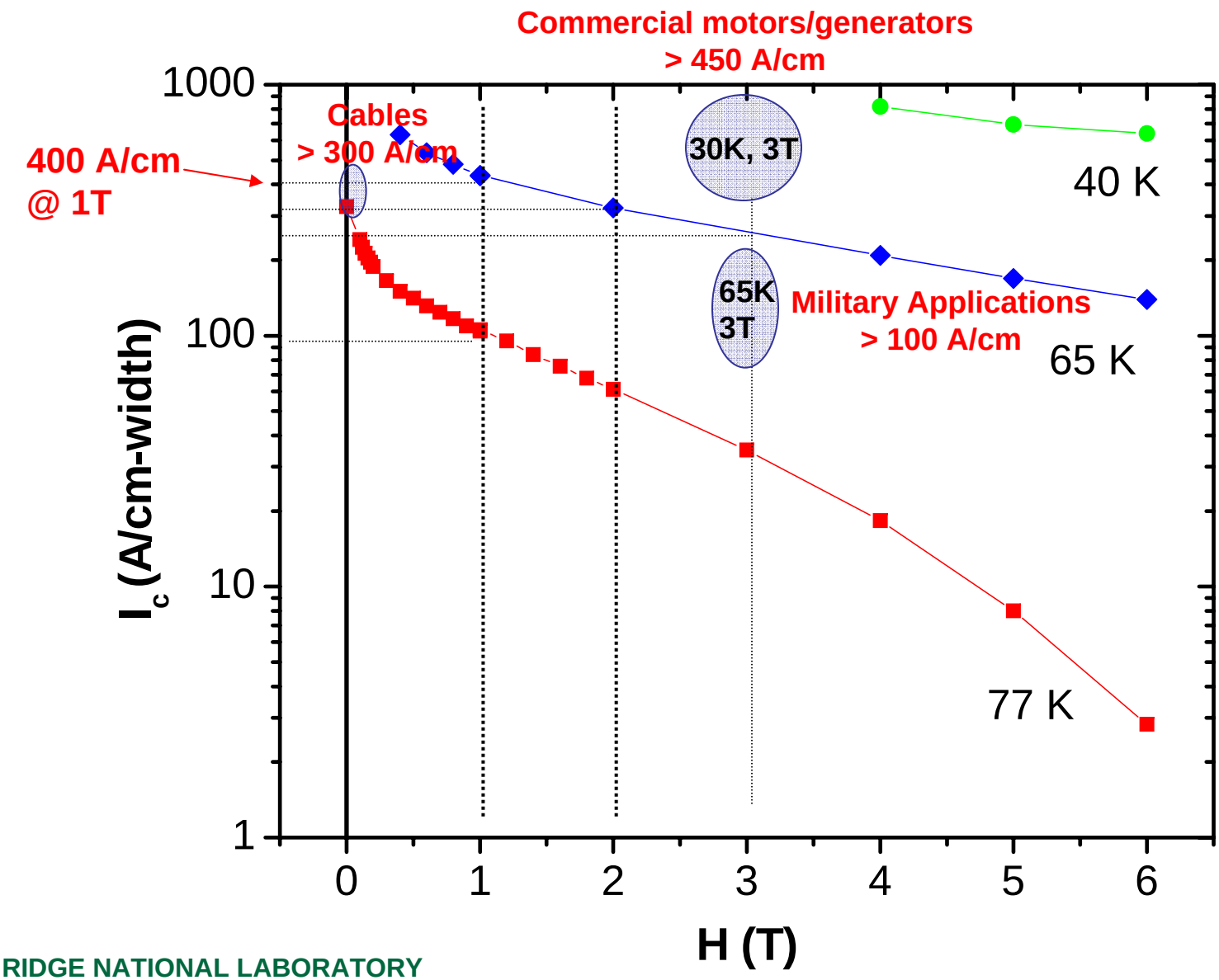
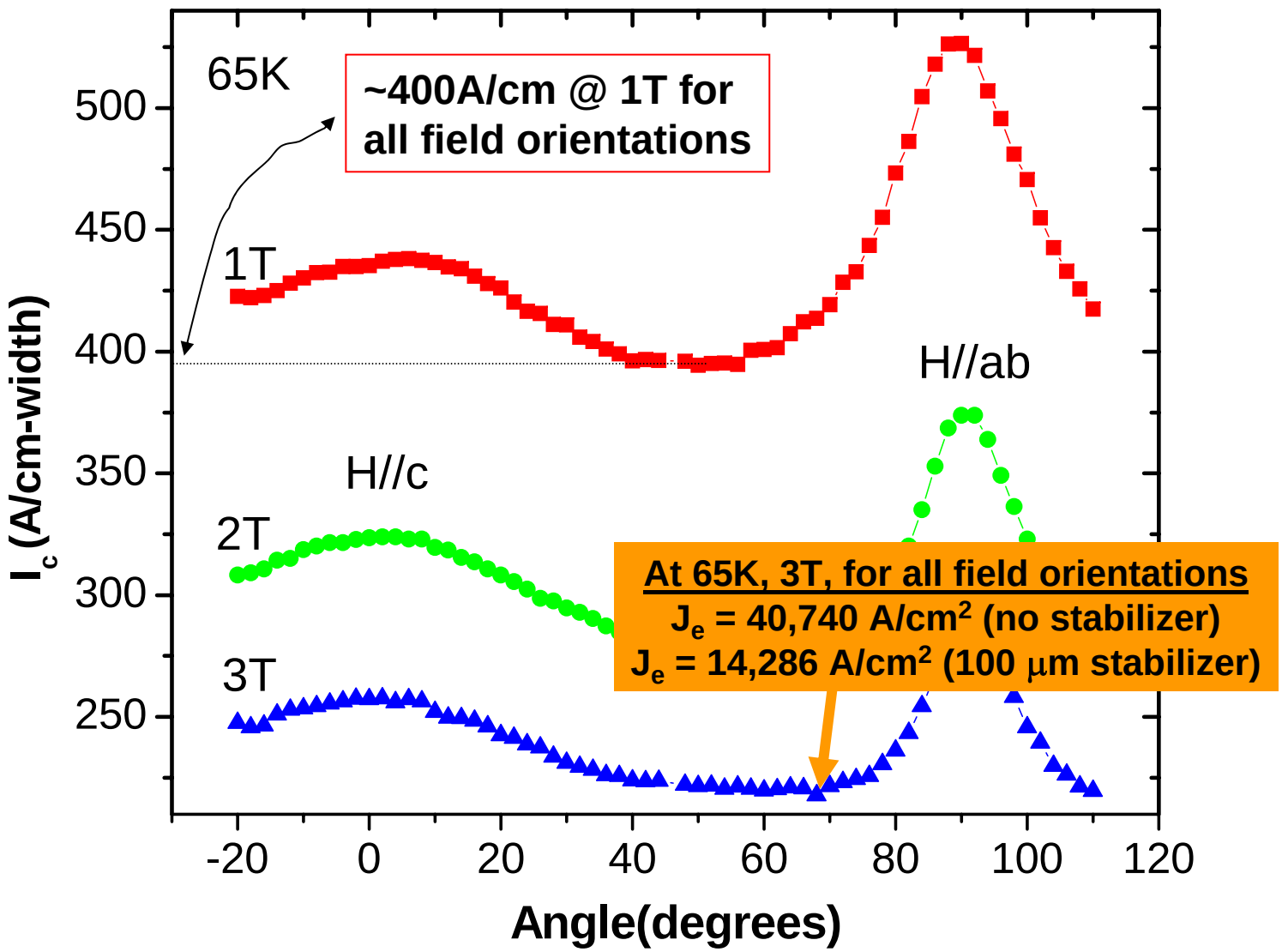
Under best conditions, promising results are obtained!



High I_c's are obtained at higher fields and lower temperatures due to strong pinning defects in the film!



Angular dependence of J_c shows peaks for both H//c and H//ab



Presentation Outline

- **FY 2005 Results**

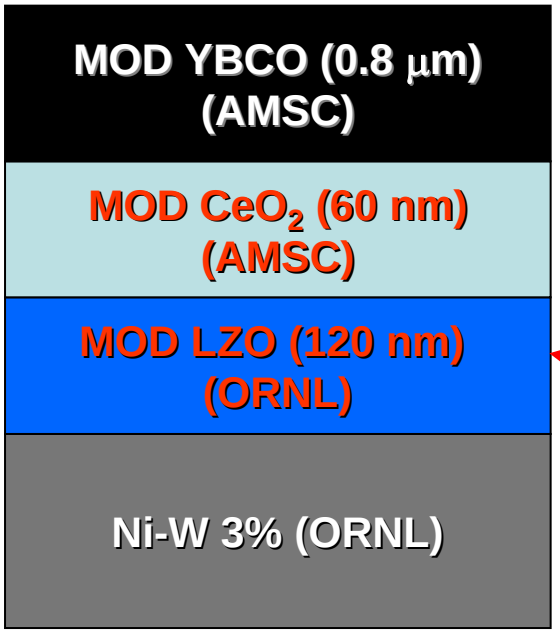
  Rolling of substrates **(Amit)**
  Development of robust buffers
  Development of texture in Cu-based, conductive RABiTS
  Development of texture in Ni-based, non-magnetic RABiTS
  Percolation calculations in applied fields
  Separation of in-plane and out-of plane misorientations in YBCO
  Enhancement of intragranular-J_c

  Development of solution buffers **(Parans)**

- **FY 2005 Performance and FY 2006 Plans** **(Parans)**
- **Research Integration**

Objective 10: Development of low-cost, solution buffer layers

FY04 Results: First two-layer all-MOD buffer for a low-cost RABiTS process; 140 A/cm-width (77K,sf) performance demonstrated



Why is the performance not as good as all PVD buffers?

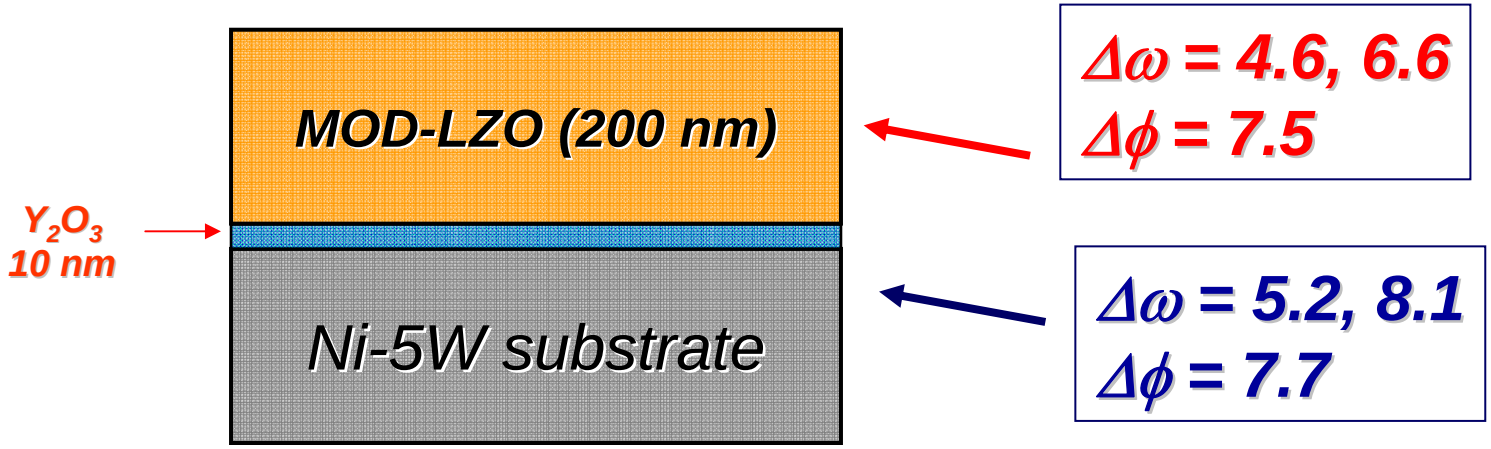
$\Delta\omega = 6.6, 10.2$
$\Delta\phi = 8.1$

$\Delta\omega = 5.2, 8.1$
$\Delta\phi = 7.7$

Lattice mismatch of LZO with Ni: 7.9%

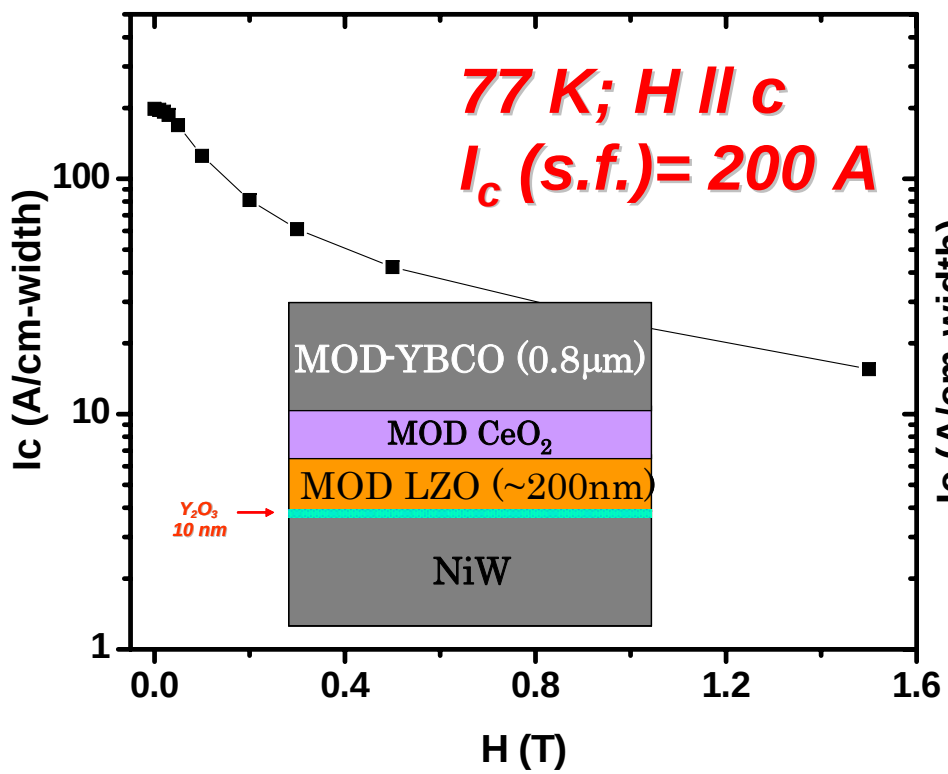
Texture of LZO can be significantly improved

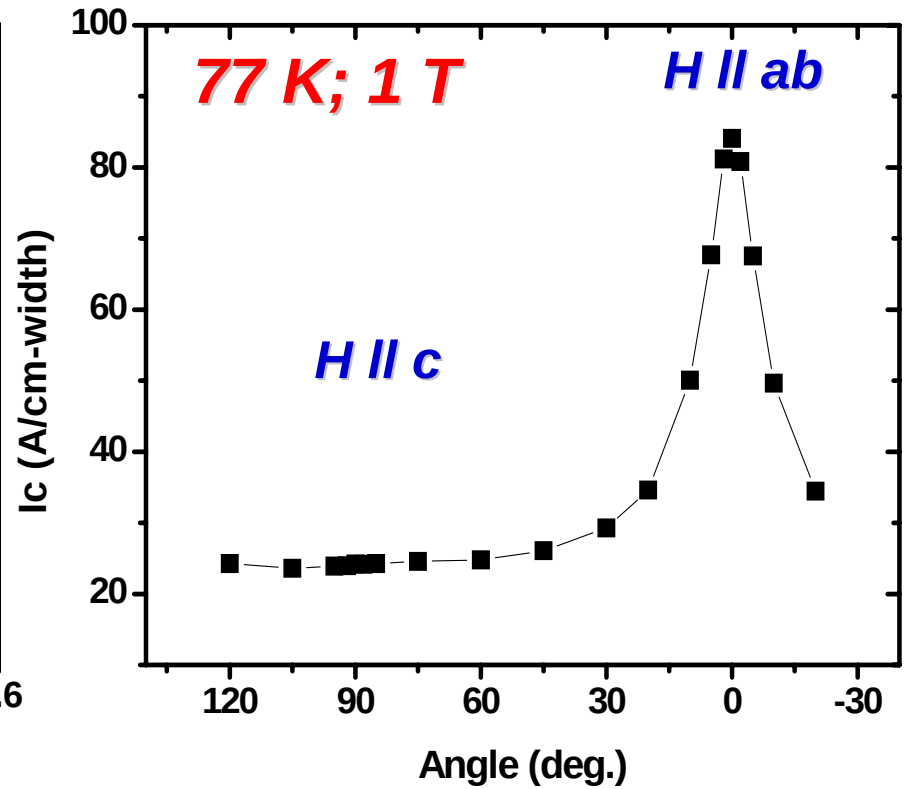
Insertion of a thin layer of Y_2O_3 changes the texture of LZO



Lattice mismatch of LZO with Ni has been reduced by introducing Y_2O_3 layer

Performance of MOD LZO/CeO_2/YBCO stack improved to 200 A/cm





Is the performance of the stack being limited by MOD LZO or MOD CeO_2 compared to all PVD buffer stack with a performance of 250 A/cm width?

American Superconductor™

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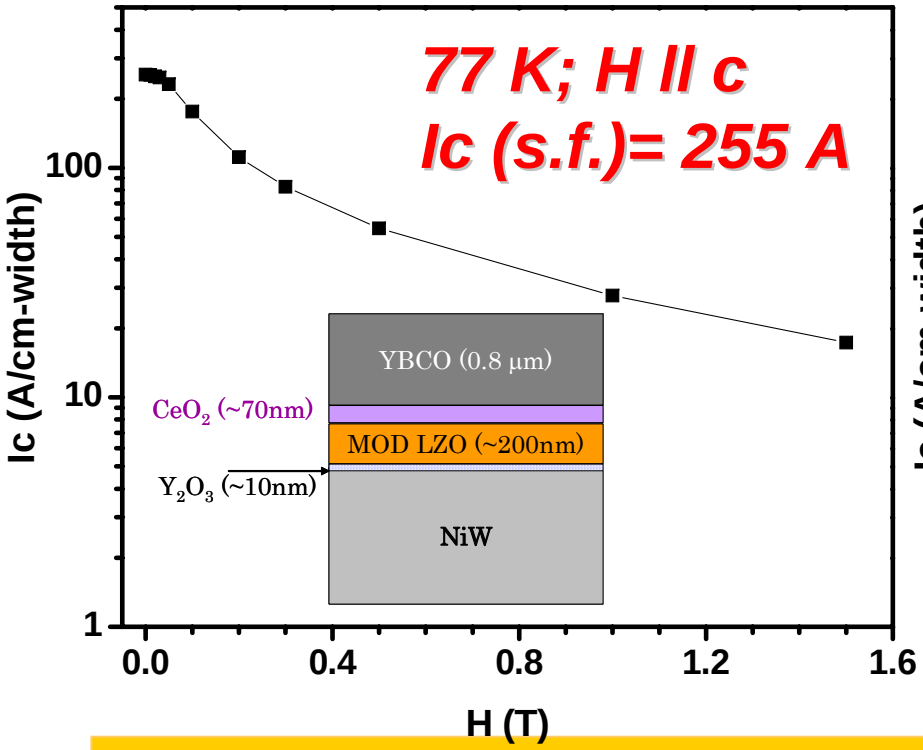
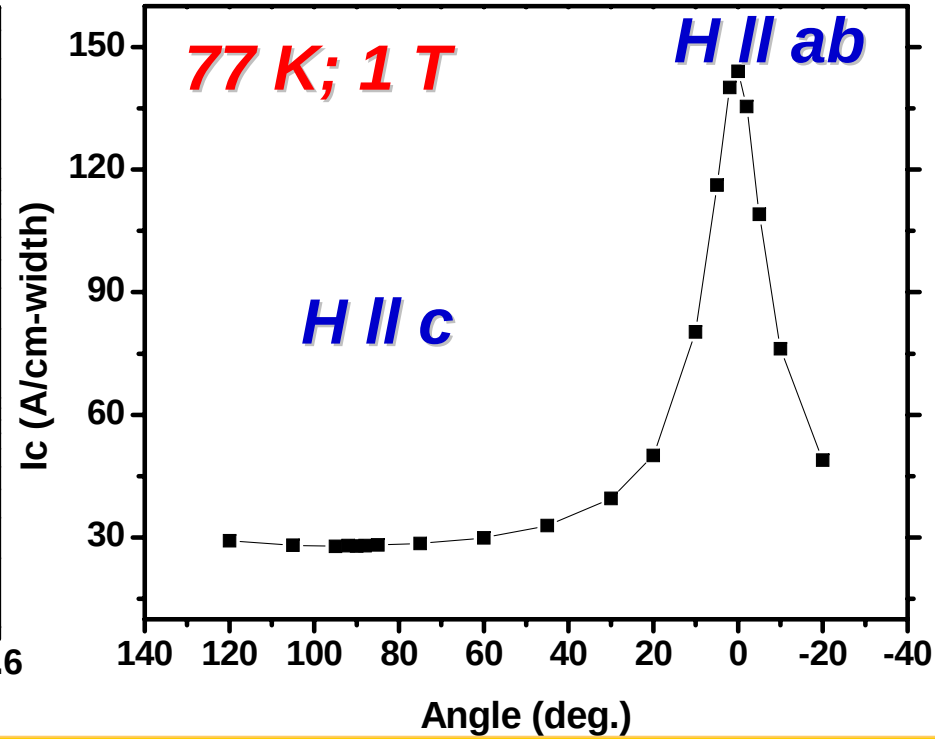
Replacing the MOD CeO_2 with rf sputtered CeO_2 cap layer results in 255 A/cm



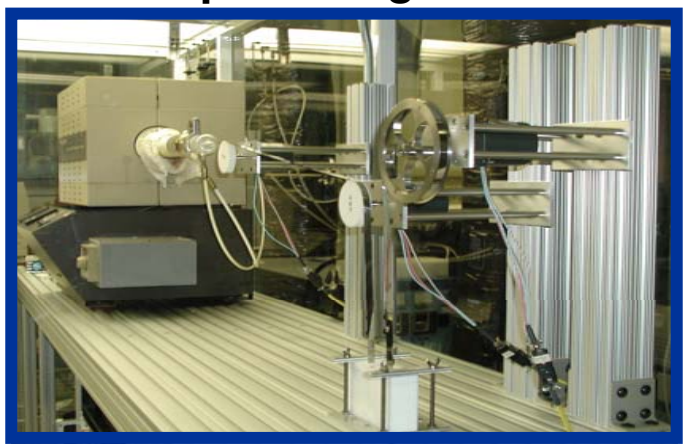


X-ray characterization indicated that there was no difference in the texture, however increased reaction of MOD CeO_2 resulting in higher $BaCeO_3$ was observed

We are also exploring a solution route for replacing the thin Y_2O_3 seed layer

MOD Buffer Scale-up Goal: To produce 100-150 nm Layer in a Single Coat

Dip-coating unit



Slot-die coater

- **One-pass coating process required for commercial applications**
  - **Essential to reduce equipment and labor cost for commercial manufacturing**
- **Developed experimental conditions to coat > 100 nm LZO layers/pass**
  - **Coating speed: > 120 m/hr**
- **Developed process conditions to produce textured LZO layers**
- **Evaluation of slot-die coated buffers is in progress**

Slot-die Coating technology transferred from AMSC to accelerate solution based buffer development

FY 2005 Plans and Performance

FY2005 Plans

- **Use ORNL rolling mill facility for fabrication of long and wide NiW substrates for R&D and scale-up at companies. Address any key issues encountered.**

FY2005 Performance

- ✓ **Fabricated over 2.5 km of 4 cm wide substrates with exceptional surface quality and texture**
- ✓ **ORNL's rolling facility was the primary facility used by AMSC for scale-up research towards wide substrates**

FY 2005 Plans and Performance

FY2005 Plans

- **Develop robust buffers on ORNL Ni-W substrates in reel-to-reel configurations, both internally and assist scale-up activities at companies.**

- **Research texture development in substrates with higher tungsten content, particularly the nonmagnetic, Ni-9.3at%W substrate.**

FY2005 Performance

✓ **Developed conditions to grow all PVD CeO_2/YSZ/Y_2O_3 buffers in a reel-to-reel configuration with excellent texture and diffusion barrier properties**

✓ **Quality of 1 cm RABiTS template successfully extended to 4 cm wide process at AMSC**

✓ **Under typical rolling conditions, a texture transition occurs for NiW alloys with W greater than 6.5 at%**

✓ **With modified rolling conditions, Cu-type rolling texture is obtained for Ni-9.3at%W with no α-fiber present**

FY 2005 Plans and Performance

FY2005 Plans	***FY2005 Performance***
• **Work with vendors in developing the powder metallurgy route for starting coils.**	✓ **Worked with Ametek on the powder metallurgy route to remove carbon for starting NiW coils. Carbon removal continues to be problem in PM coils.**
• **Research texture development in strengthened and possibly highly conducting Cu-based alloy substrates and deposit previously developed epitaxial buffer layers on them.**	✓ **A Cu-alloy substrate with a yield strength of ~200 MPa and a potential for 300 MPa was identified. Good cube texture was obtained for this alloy.**

FY 2005 Plans and Performance

FY2005 Plans

- **Extend percolation calculations in applied magnetic fields to conductors less than 50 grains wide.**
- **Develop methods to separate in-plane and out-of-plane misorientations from electron backscatter Kikuchi diffraction (EBKD) measurements in materials with lower-than-cubic crystal symmetry (YBCO) and correlate with Jc.**

FY2005 Performance

- ✓ **Percolations were extended to conductors less than 50 grains wide. J_c drop was found to be insignificant for filaments ≥ 10 grains**
- ✓ **New methodology was developed for accurate indexing of electron backscatter Kikuchi diffraction patterns from YBCO**
- ✓ **A methodology was developed which allows extraction of in-plane and out-of-plane components from the total misorientation for materials with lower crystal symmetry such as YBCO**

FY 2005 Plans and Performance

FY2005 Plans	***FY2005 Performance***
• **Determine the relative effects of in-plane and out-of-plane misorientations on Jc by fabricating and characterizing YBCO films with the same in-plane but different out-of-plane misorientations.**	✓ **Detailed grain boundary maps of the out-of-plane, in-plane and total misorientations, indicate that the J_c correlates primarily with in-plane misorientations**
• **Improve Jc/Ic and pinning in thick REBCO films on RABiTS**	✓ **Pinning by self-assembled nandots and nanorods has been extended to thick PLD films on RABiTS**

FY 2005 Plans and Performance

FY2005 Plans

- **Fabricate 100-150 nm thick LZO solution based buffer layers on NiW RABiTS substrates. Demonstrate suitability of an all-solution buffer layer process.**

FY2005 Performance

- ✓ **Developed process conditions to grow >100 nm thick LZO in a single pass using slot-die coating**
- ✓ **Proof-of-principle demonstration of MOD-LZO barriers as replacement for PVD-YSZ; Ic of 255 A/cm or a J_c of 3.2 MA/cm^2 was demonstrated on MOD-LZO**
- ✓ **I_c of 200 A/cm or a J_c of 2. 5 MA/cm^2 was demonstrated on improved MOD CeO_2/LZO buffers**

FY2006 Plans

- **Use ORNL rolling mill facility for fabrication of long and wide NiW substrates for in-house R&D as well as scale-up at companies.**

- **Continue work on texture development of higher W content substrates.**

- **Further optimize process conditions to obtain a higher yield strength while maintaining a cube texture in new Cu-alloy. Deposit previously identified buffer stacks for Cu and test YBCO performance on them.**

- **Explore improvement in interfacial strength of metal/seed layer by modifications during buffer layer deposition.**

FY2006 Plans

- **Further develop slot-die coating of solution buffers, such as LZO and CeO_2.**
- **Perform through-thickness measurements of grain boundary networks in YBCO, separate component into in-plane and out-of-plane and correlate to transport properties of the film.**
- **Confirm percolation calculation results by performing measurements on filamentized samples.**
- **Continue work to explore ways to improve flux-pinning in *in-situ* and *ex-situ* REBCO films on RABiTS.**

Research Integration: *Interactions with Companies*

- **American Superconductor Corporation (AMSC)**
  - Have a CRADA with AMSC and work on substrates is a significant component of the CRADA
  - A majority of wide area substrates for scale-up studies at AMSC were rolled in the ORNL rolling mill facility with clean room

- **MetOX**
  - Provided both textured alloy as well as buffered RABiTS substrates for growth of YBCO

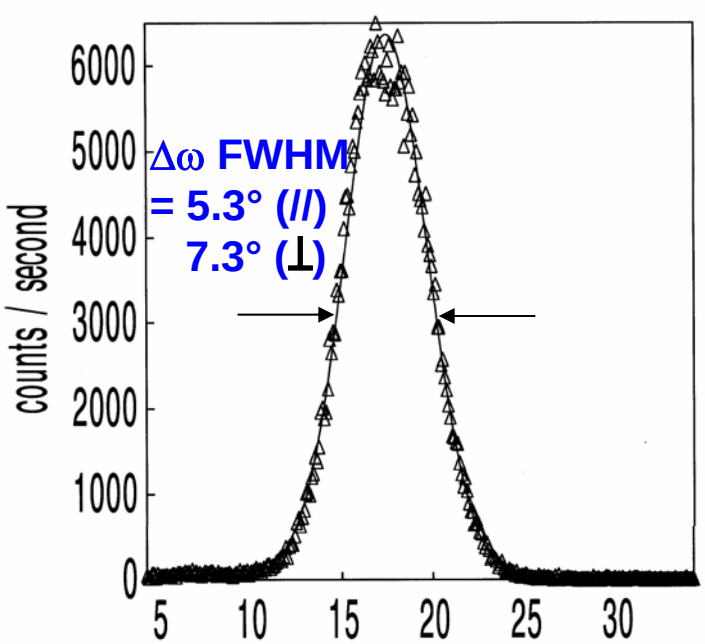
- **Ametek Corporation** - Developing fabrication of starting coils
- **Hamilton Precision Metals** - Developing rolling & slitting process for coil
- **Flowserve Corporation** - Development of vacuum cast starting materials
- **Several other proprietary vendor companies**

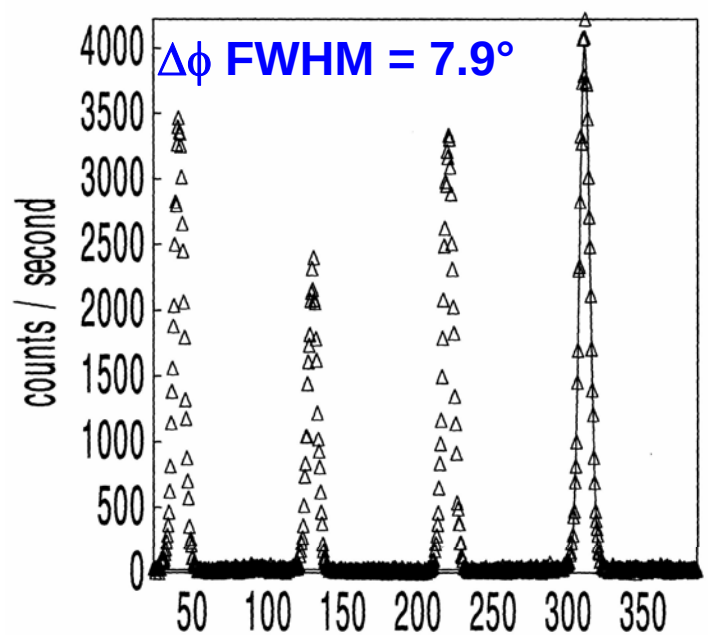
A new ORNL CRADA has been initiated in FY05 with Metal Oxide Technologies Inc. (MetOx)

- **Houston-based small business company.**
- **<u>High-rate MOCVD</u> for buffers and YBCO growth.**

- Recent results since CRADA initiation in July 05
  - –ORNL 1μm YBCO (PLD) on <u>MetOx R2R MOCVD buffers</u> / ORNL Ni-3%W:

J_c = 1 MA/cm² at 77K and sf





~ 94% cube.

MetOx

Research Integration:

Collaborated with the following researchers at universities:

- **University of Cambridge:** N. Rutter
- **Washington State University:** D. Field
- **University of Tennessee:** T. Aytug, S. Sathyamurthy

Have provided substrates and/or YBCO/RABiTS to the following:

- **University of Missouri-Rolla:** J. Switzer
- **University of California at Santa Barbara:** F. Lange
- **University of Wisconsin, Madison:** E. Hellstrom

Research Integration: *Interactions with national laboratories*

Have provided substrates and/or YBCO/RABiTS to the following:

- **NIST: N. Cheggour, J. Ekin, W. Wong**
- **SNL: P. Clem, M. Siegel**
- **NREL: R. Bhattacharya**
- **AFRL: T. Haugan, P. Barnes**

Communications:

- **Many publications**
- **Numerous presentations**
- **Several patents issued as well as filed**
- **Information also dispersed via regular CRADA teleconferences/meetings/annual reports**