ORNL-AMSC CRADA: Development of 2G YBCO-RABiTS Wires

American Superconductor Corporation

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Overall CRADA Objectives

Assist AMSC's development of a low-cost, robust 2G wire based on RABiTS technology through R&D support

Desirable features of the conductor:

- **Production Cost: <$10/kAm (Broad Market Penetration)**
- **Form – Fit – Function replacement for BSCCO**

Since the start of the CRADA in FY2000, the following has been accomplished

- Transfer of rolling technology for developing biaxially textured metals and alloys
- Transfer of Y_2O_3 seed buffer layer growth in reel-to-reel configurations
- Transfer of sulfur superstructure development in reel-to-reel configurations for high quality seed layer epitaxy
- Transfer of reel-to-reel YSZ and CeO_2 sputtering technology
- Development of solution buffer layer growth technology
- Long length transport characterization, Reel-to-reel X-ray characterizations, etc.

Specific CRADA Objectives

- Assist AMSC in developing a high performance, robust, 10-m RABiTS-based YBCO wire via reel-to-reel processing at all steps….(Marty Rupich)
- Characterize AC losses in AMSC's MOD/RABiTS 2G wire….(Amit Goyal)
- Jointly develop alloy substrates with sharper texture, higher strength, and/or lower magnetism….(Amit Goyal)
- Develop methodologies to characterize and optimize properties of buffer layers using microstructural techniques such as TEM, EBSP, SEM, Auger etc. ….(Amit Goyal)
- Quantify the relationships between "texture" and "J_c" and develop a metric to direct the development of alloy substrates with respect to texture on AMSC's substrates….(Amit Goyal)
- Develop simpler, lower-cost, buffer materials and architectures compatible with AMSC's MOD-YBCO process….(M. Paranthaman)

AMSC-ORNL CRADA Presentation

- **FY 2003 Results**

  2G Development (YBCO/RABiTS) at AMSC (Marty)
  2G wire manufacturing at AMSC
  2G wire characteristics
  Prototype 2000 Amp 2G cable performance

  Characterization of 2G wire (Amit)
  Development of improved substrates
  Correlation of texture to J_c
  Buffer layers: Methodology development and characterization

  Development of low-cost, solution buffer layers (Parans)

- **FY 2003 Performance and FY 2004 Plans (Parans)**
- **Research Integration**

A fundamental understanding of materials & process is required for well-controlled, low-cost, high-yield 2G manufacturing

- Understanding of texture evolution allows defect-free manufacture of long length alloy substrates with controlled texture (length and width), and controlled surface morphology
- Understanding of buffer material properties and deposition processes allows controlled engineering of buffer stacks optimized for cost/performance in long length manufacturing
- Process understanding is necessary to enable scaling of deformation/deposition processes to widths (10cm) and lengths (1 km) required for low-cost, high-yield commercial manufacturing

CRADA based R&D, focused on critical materials and process issues identified by industrial partners, has been a major factor in the rapid development of the 2G wire technology

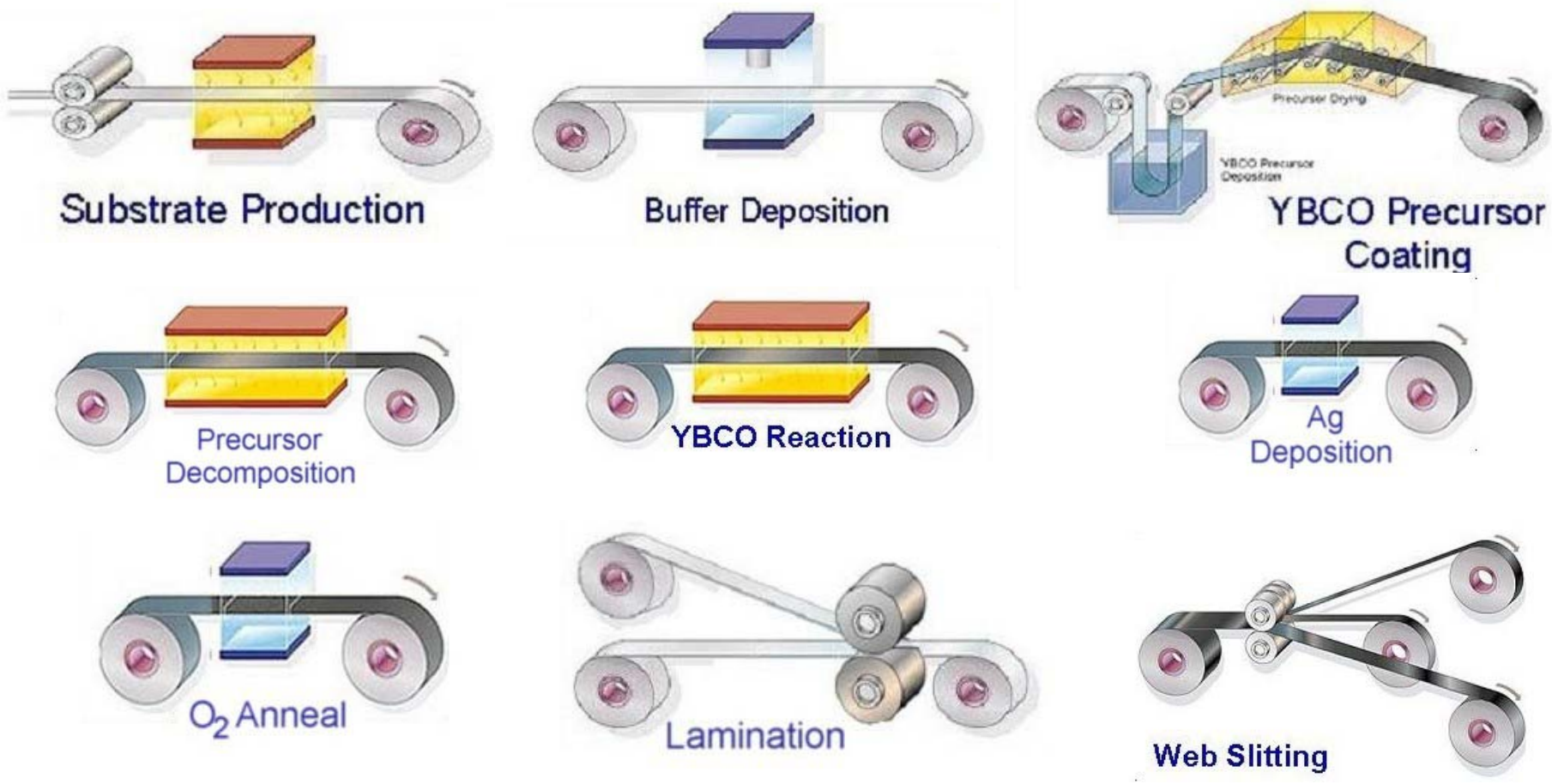
ORNL CRADA focus is on Materials and Process R&D to support 2G development at AMSC

- **Process Development**
  - R&D and development for RABiTS substrates
  - R&D for new low cost/high performance buffer materials and processes
- **Characterization**
  - Characterization of oxygen/metal diffusion through buffer layers
  - Developing substrate characterizations to predict Ic capability
  - Post–process texture characterization
  - AC loss measurements
- **User Facility**
  - Deformation processing user facility
  - In–situ HTS reaction processing and characterization
- **HTS Cable Demonstration**

AMSC Focus is development of 2G manufacturing process with R&D support through CRADA partners

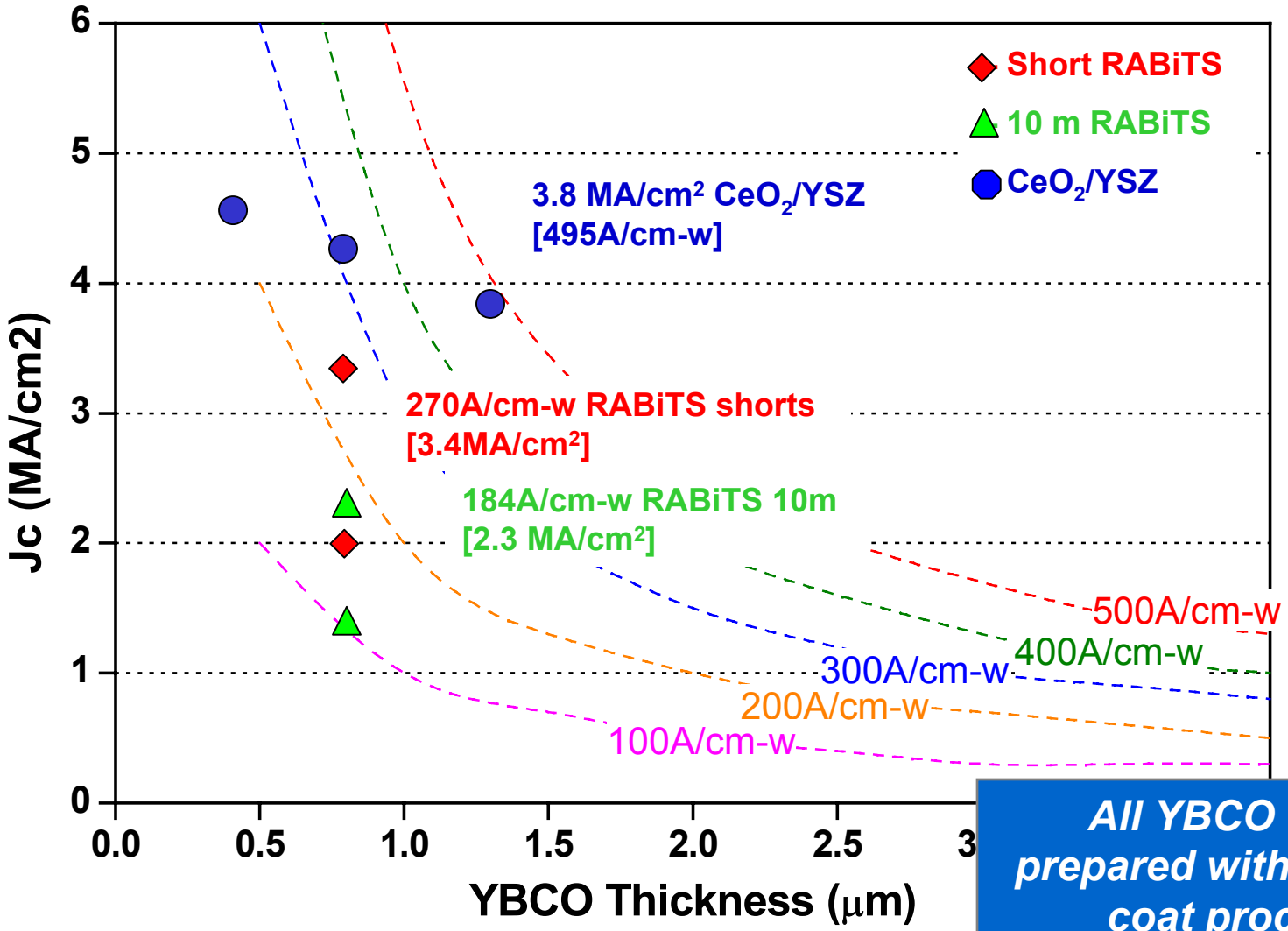
- **MOD/RABiTS process development**
  - high performance
- **Commercial 2G wire**
  - architecture, specifications
- **Manufacturing scale up design/planning**
  - low-cost (capital/operating), high yield, high performance
- **Prototype 2G wire manufacture**
  - customer testing, demonstration projects

AMSC current 2G wire process
(scaleable to 10cm wide web which yields 20 4mm wires)



ORNL CRADA contributes to improving process stability, material uniformity, and product yield

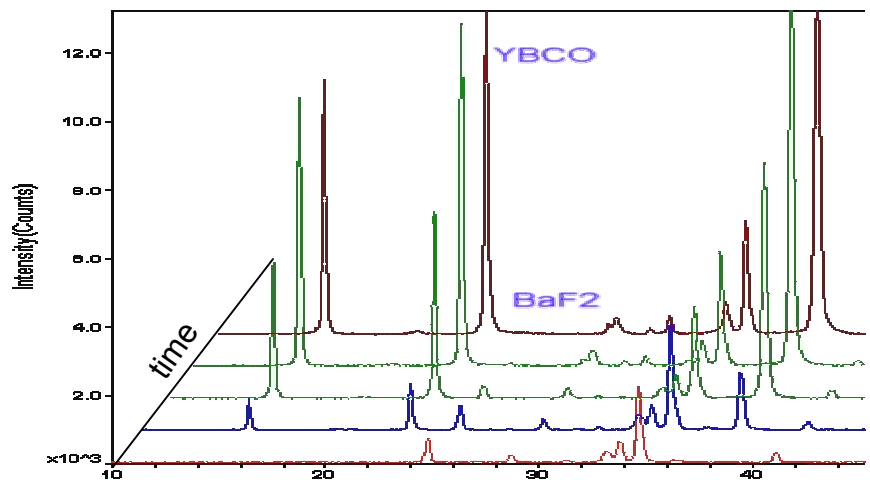
TFA-based YBCO Performance Improved during 2003

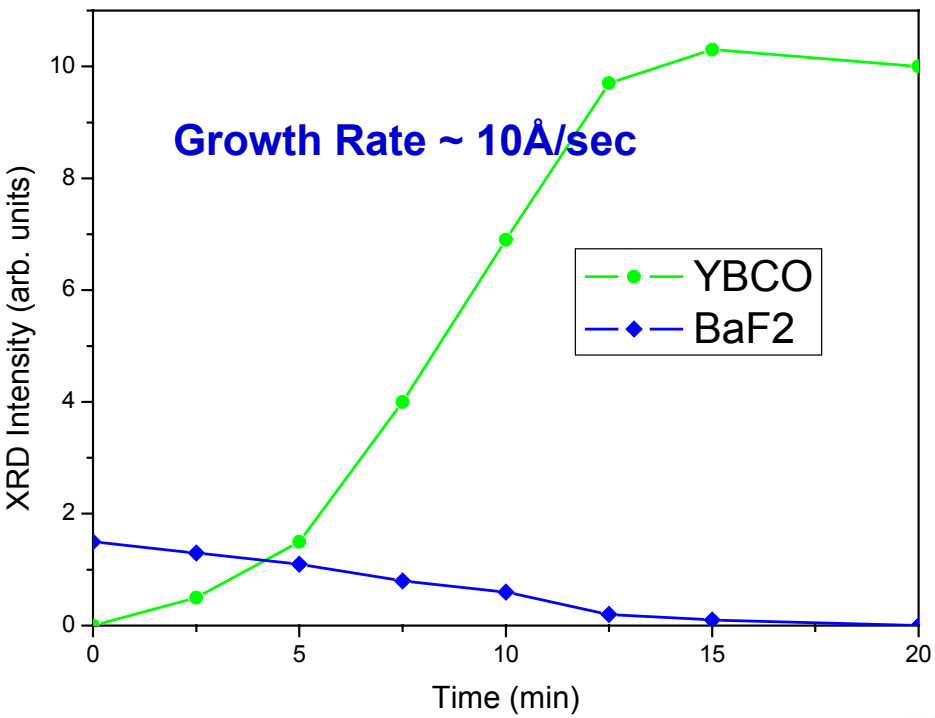


All YBCO films prepared with a single coat process

YBCO Growth Rate Exceeds 10Å/sec

YBCO growth can be determined by xrd or Raman spectroscopy of quenched tapes





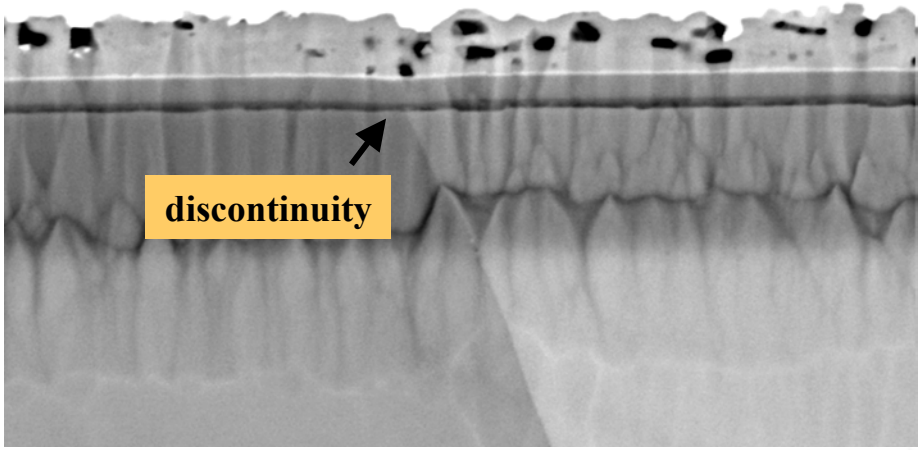
YBCO Growth Rate in continuous process increased by 3–5x in 2003

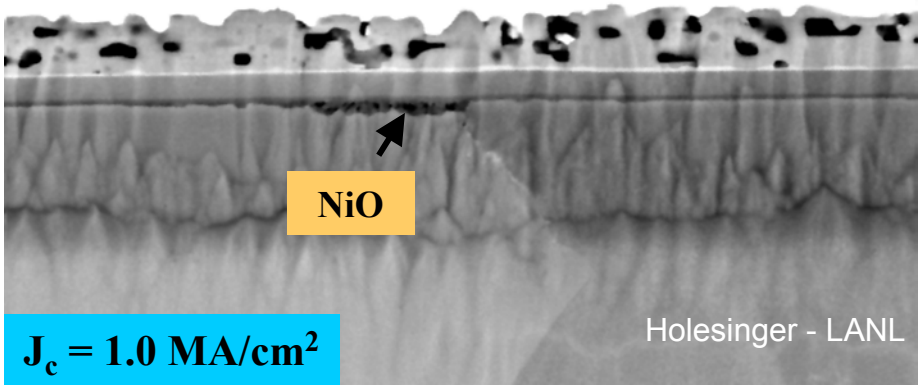
Improvements in substrates, buffer layers and YBCO have contributed to increases in Jc in MOD/RABiTS

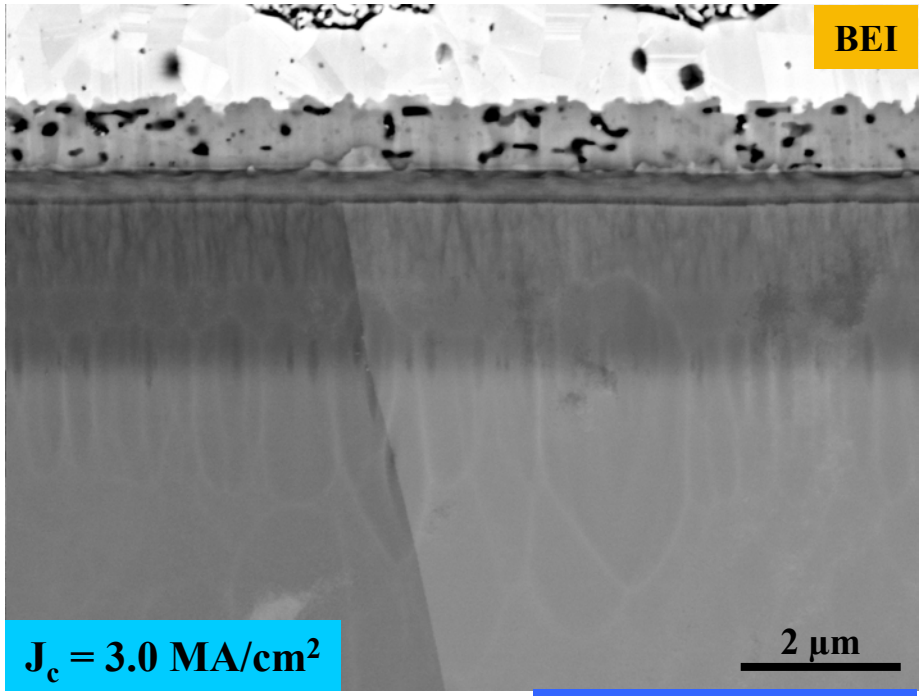
Substrates - Improved texture; reduced GB grooving, smoother surface

Buffers - Improved texture; superior oxygen/metal diffusion barrier properties (reduced defects, smoother interfaces)

HTS - Improved chemistry, optimized reaction processing (faster growth rates, reduced second phases)







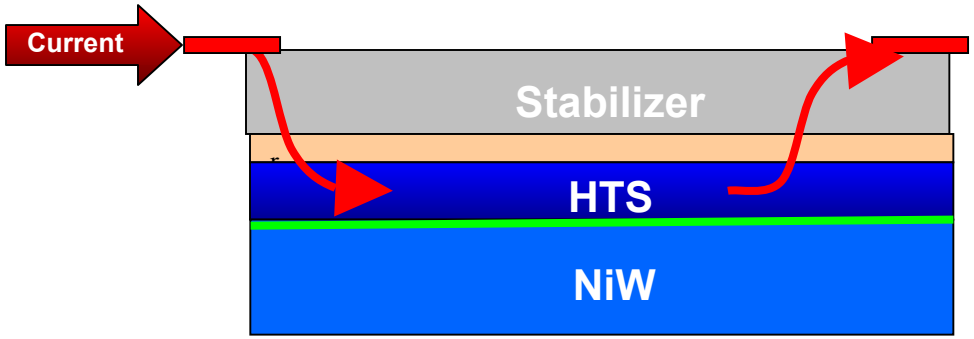
T. Holesinger/LANL

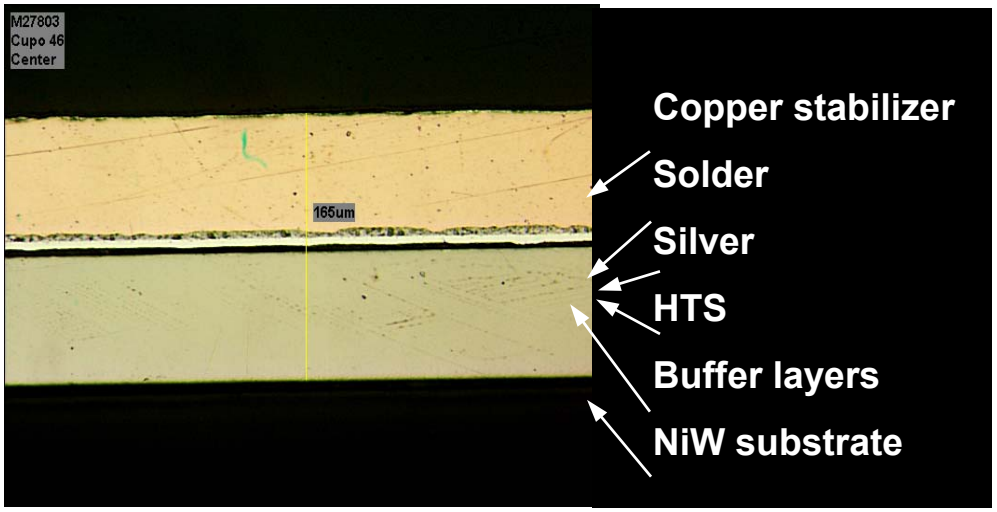
"Real World" 2G Conductor Design and Properties
-----Neutral Axis (NA) 2G Wire----

HTS Customers require more than high Ic

Neutral Axis Commercial 2G Wire

- Electrical/thermal stability
- Simple current injection
- Mechanical stability





2G (NA) wire meets or exceeds 1G wire mechanical properties

AMSC 2G wire ordered for Prototype 1 Meter Power Cable in April 2003

Order Specifications

30 – 1.5 meter wires

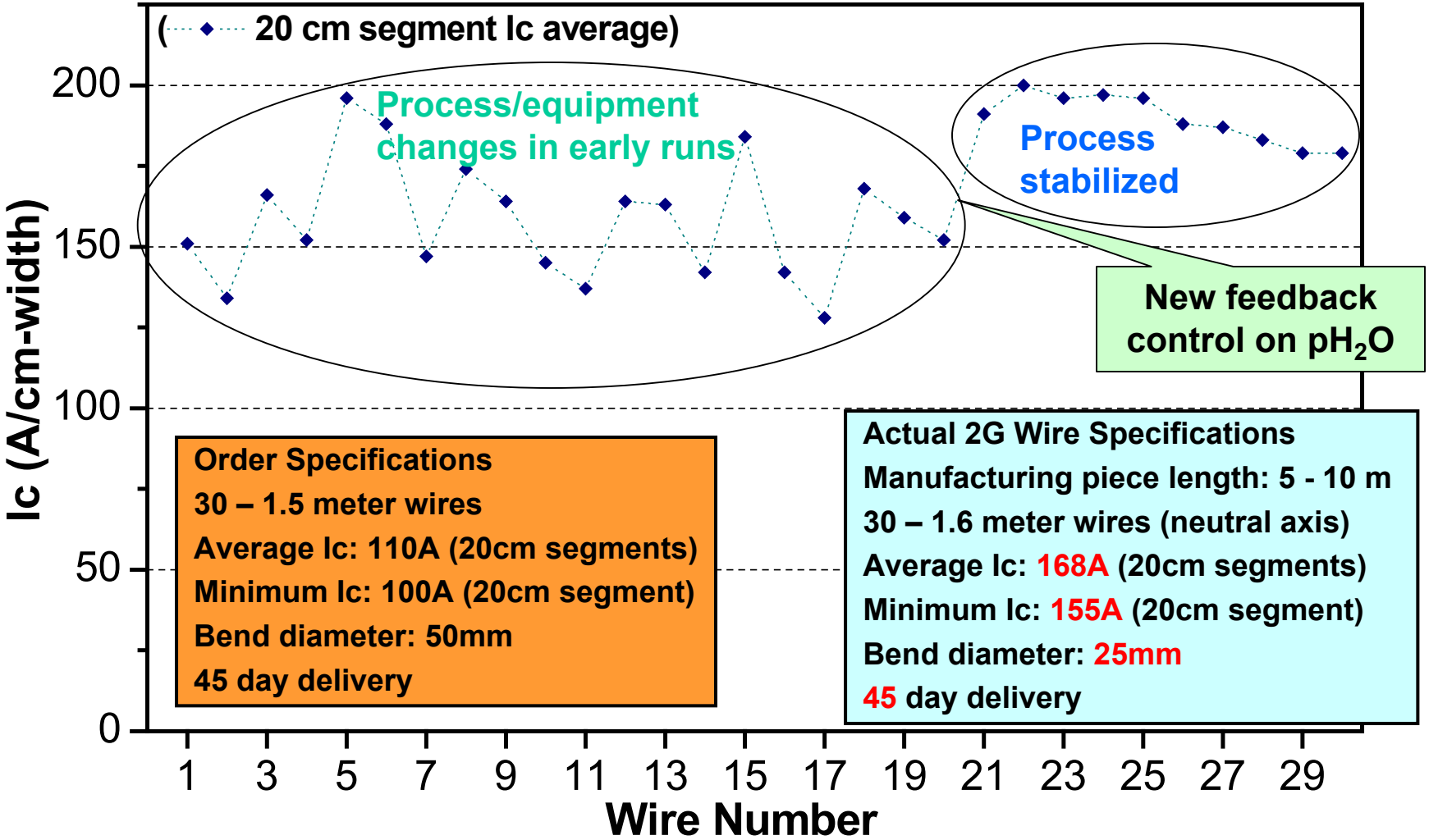
Average Ic: 110A (20cm segments)

Minimum Ic: 100A (20cm segment)

Bend diameter: 50mm

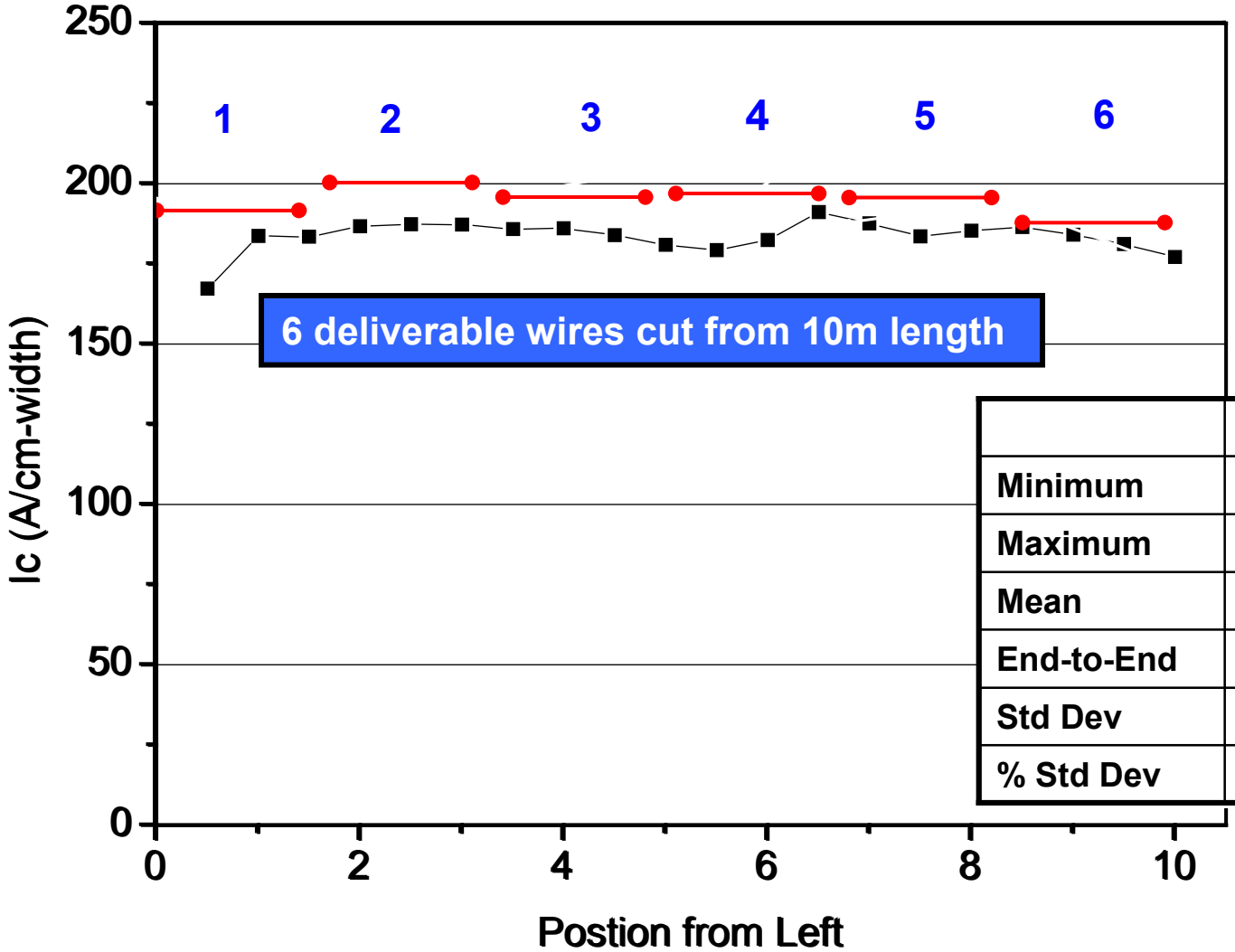
45 day delivery

30 wire order manufactured while commissioning with new YBCO reaction oven developed under ATP



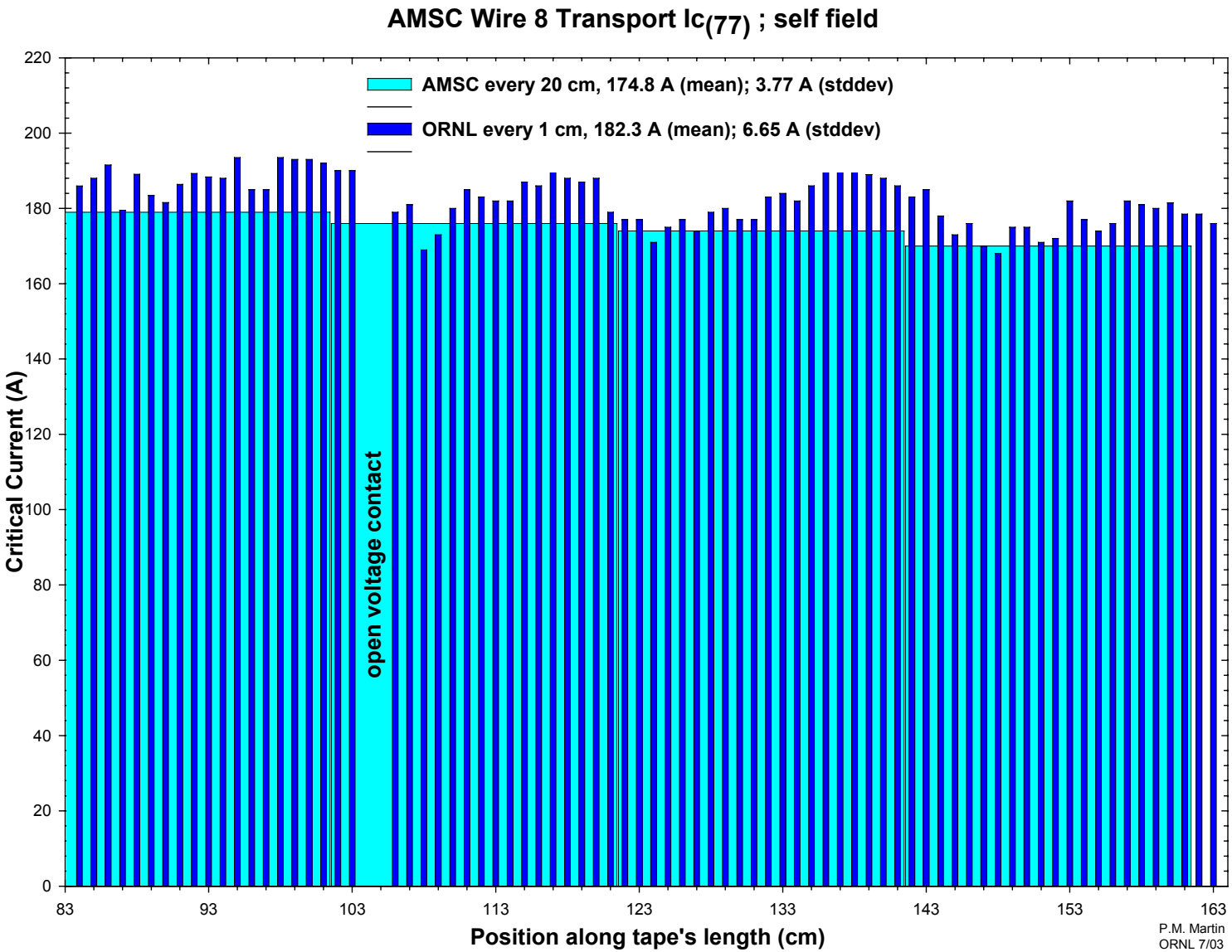
Wires delivered to Ultera (Southwire/NKT) for cable assembly on May 25

Champion 10 m wire had end-to-end Ic of 184A



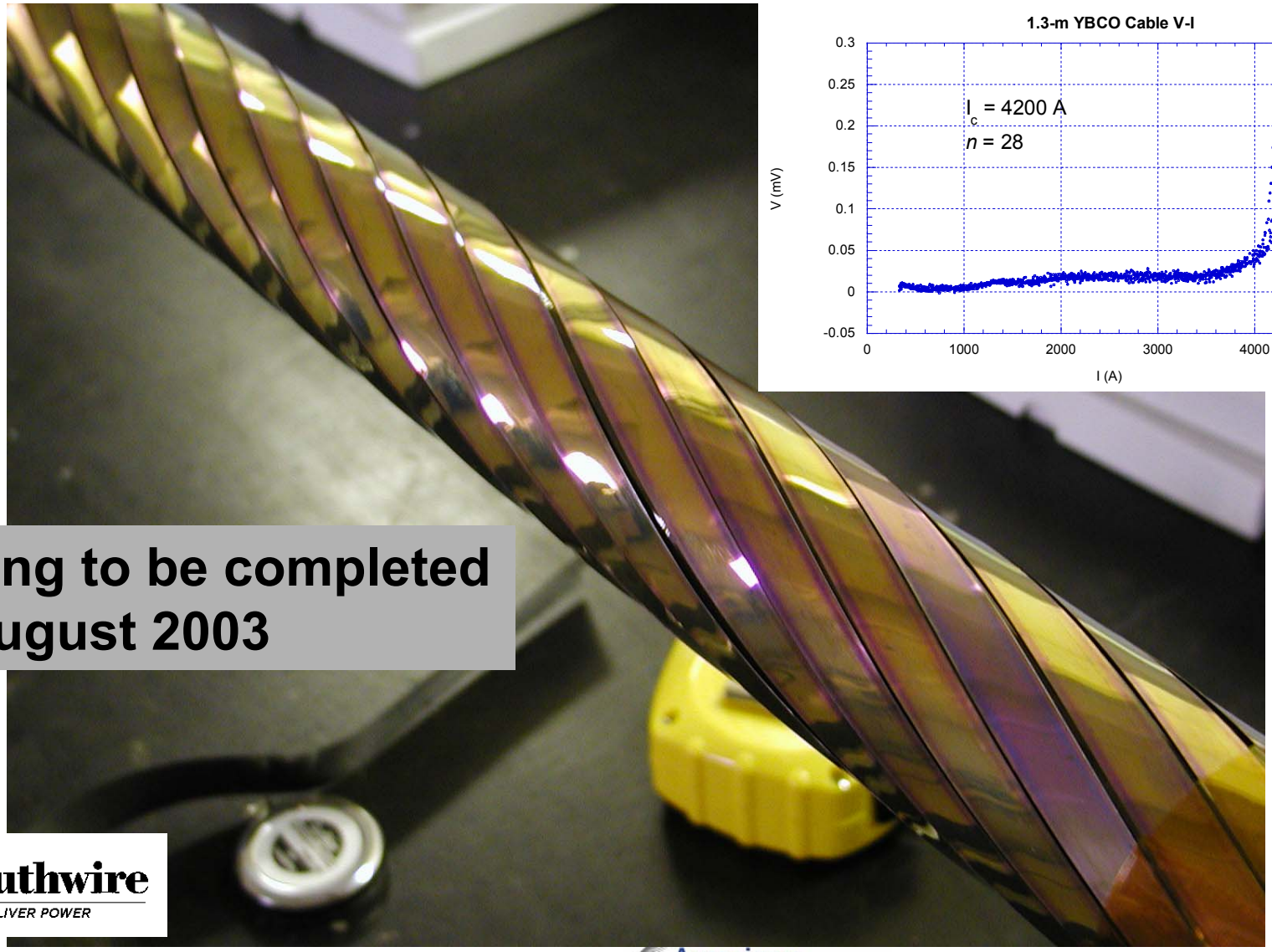
	Ic (A/cm-w)
Minimum	167
Maximum	191
Mean	183
End-to-End	184
Std Dev	5.0
% Std Dev	2.7%

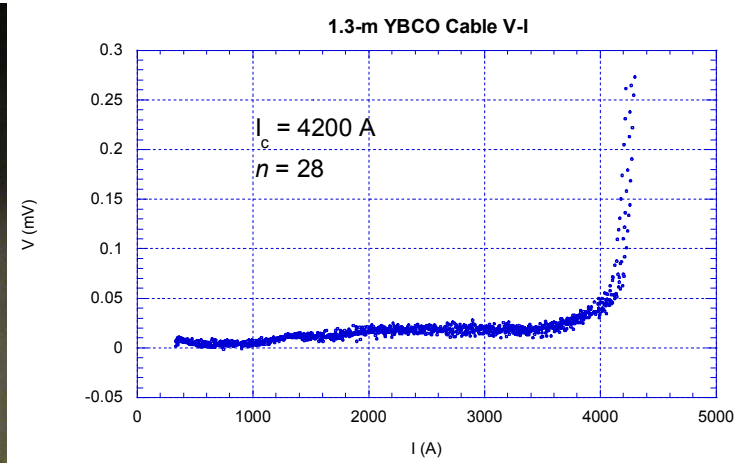
Current Homogeneity confirmed at 1 cm scale at ORNL



P.M. Martin
ORNL 7/03

YBCO Demonstration Cable Assembled by Ultera
Ic = 4200A n = 28





Testing to be completed by August 2003

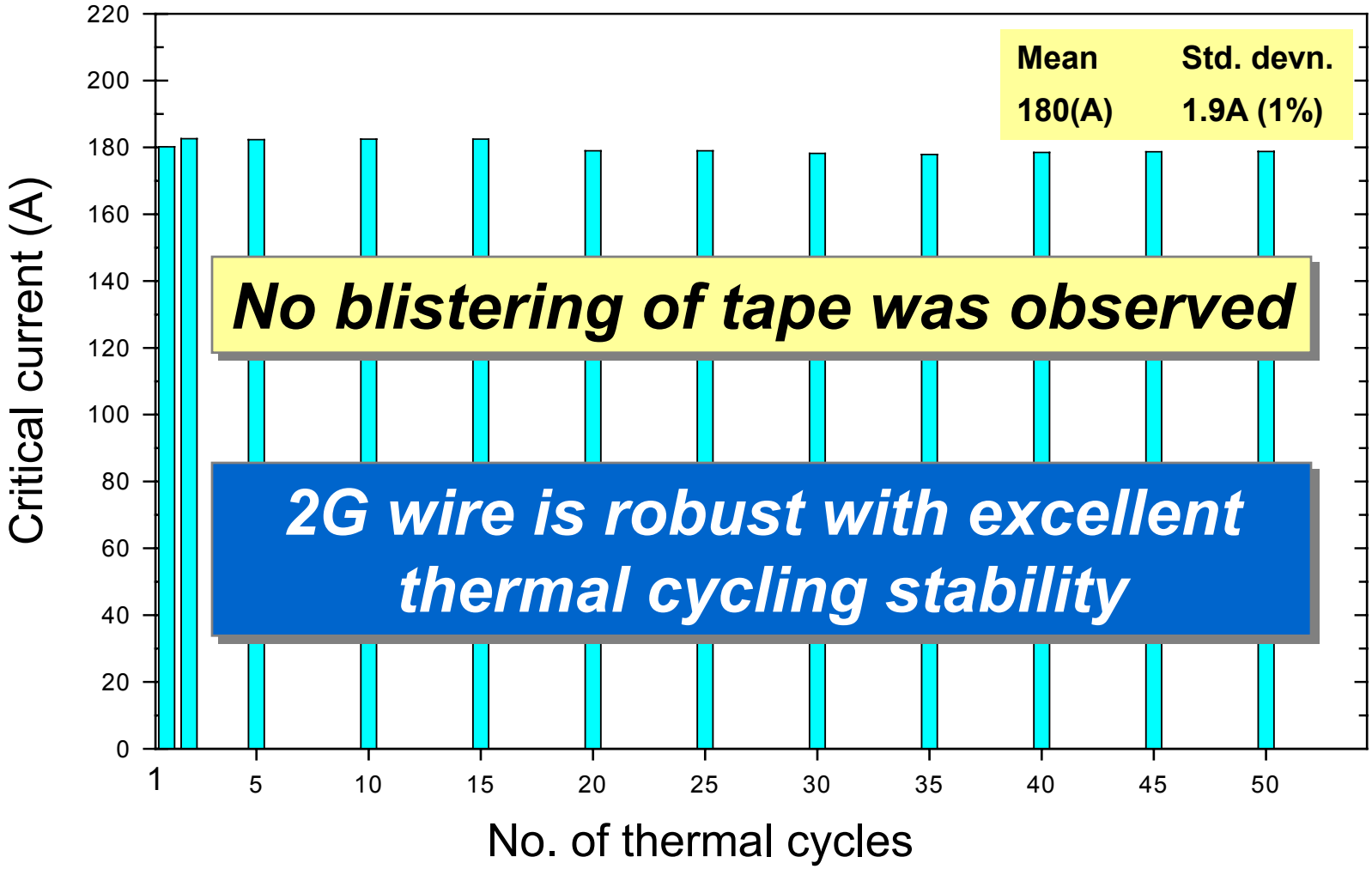
Southwire
WE DELIVER POWER

ORNL CRADA contributions have contributed significantly to the rapid progress of AMSC 2G wire process over past year

- Substrates:
  - Significant improvements in substrate texture
  - Stable manufacturing process
- Buffers
  - Texture improvements
  - Improved oxygen/metal diffusion
  - Stable, reproducible deposition processes

Result has been continually improving performance of 2G wire leading to first power cable demonstration

AMSC's Neutral Axis, 2G wire tested for thermal cycling stability



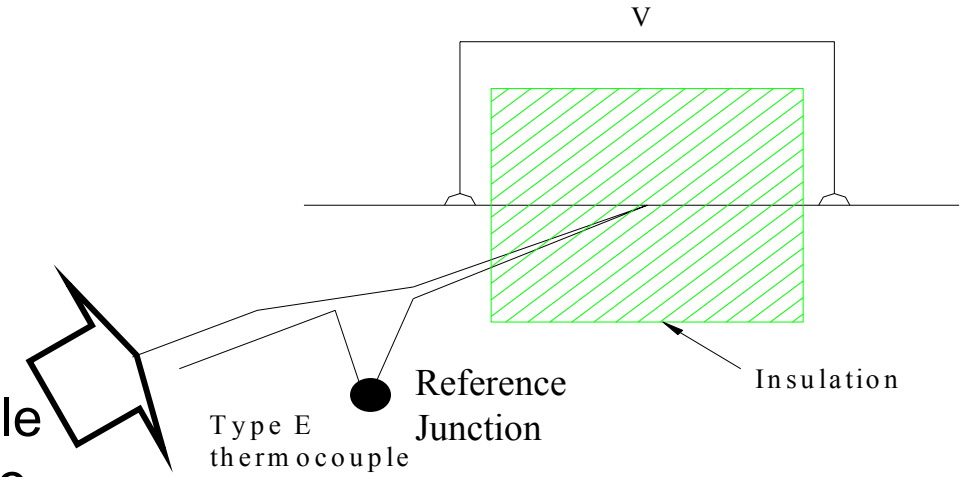
No blistering of tape was observed

2G wire is robust with excellent thermal cycling stability

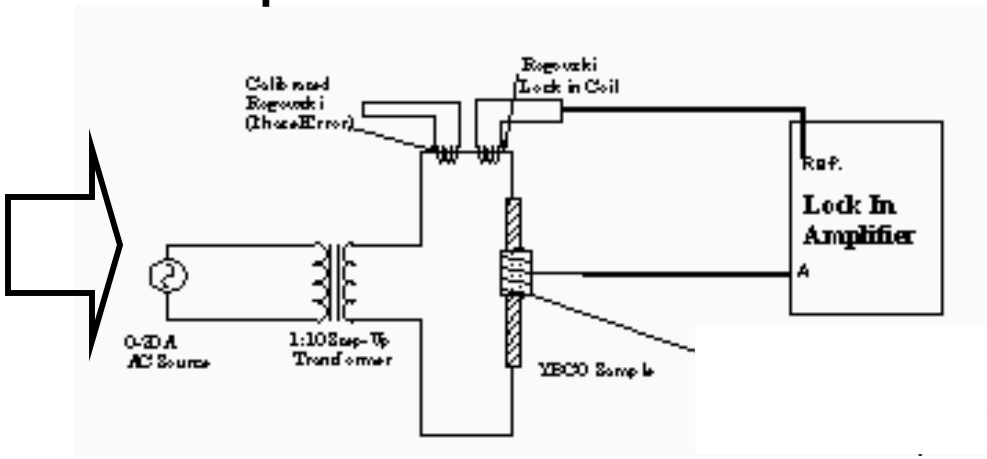
Transport AC losses of AMSC 2G Tape measured at ORNL

- **Sample characteristics**
  - Ni 5%W 75 μm substrate
  - Critical current of 110 A
  - YBCO thickness of 1 μm
- **Thermal measurement**
  - Comparison of thermocouple response from AC current to known heat input
- **Electrical Measurement**
  - Spiral voltage tap configuration
  - $Q = I\,V\cos(\theta_{sample} - \theta_{calib})$

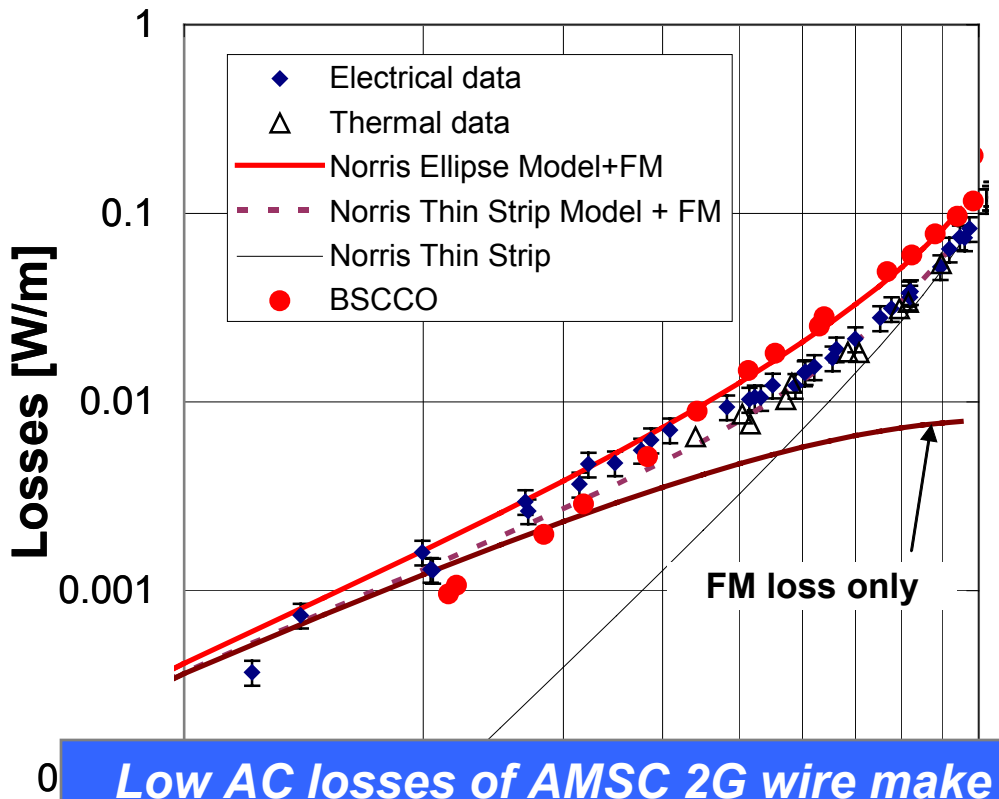
Setup of thermal measurement



Setup of electrical measurement



Norris thin strip model + ferromagnetic loss from Ni-5at%W provided good agreement with both thermal and electrical data



AC losses for YBCO on Ni-5at%W conductors are lower than those for typical BSSCO tapes for I_{peak}/I_c greater than 0.5

For cable applications, I_{peak}/I_c is anticipated to be between 0.5-0.7. In this range, ferromagnetic losses and hysteretic losses are comparable

Low AC losses of AMSC 2G wire make it suitable for cable applications and some coil applications

Specific applications may benefit from NMA (Ni-Cr-W) susbtrates

[BSCCO losses scaled down to account for difference in I_c.

Development of Improved Substrates

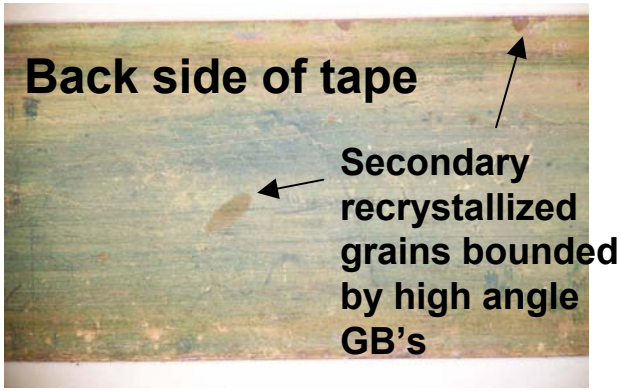
Objectives:

- Obtain sharper textures
- Develop a stable processing window for fabricating long and wide metal/alloy tape

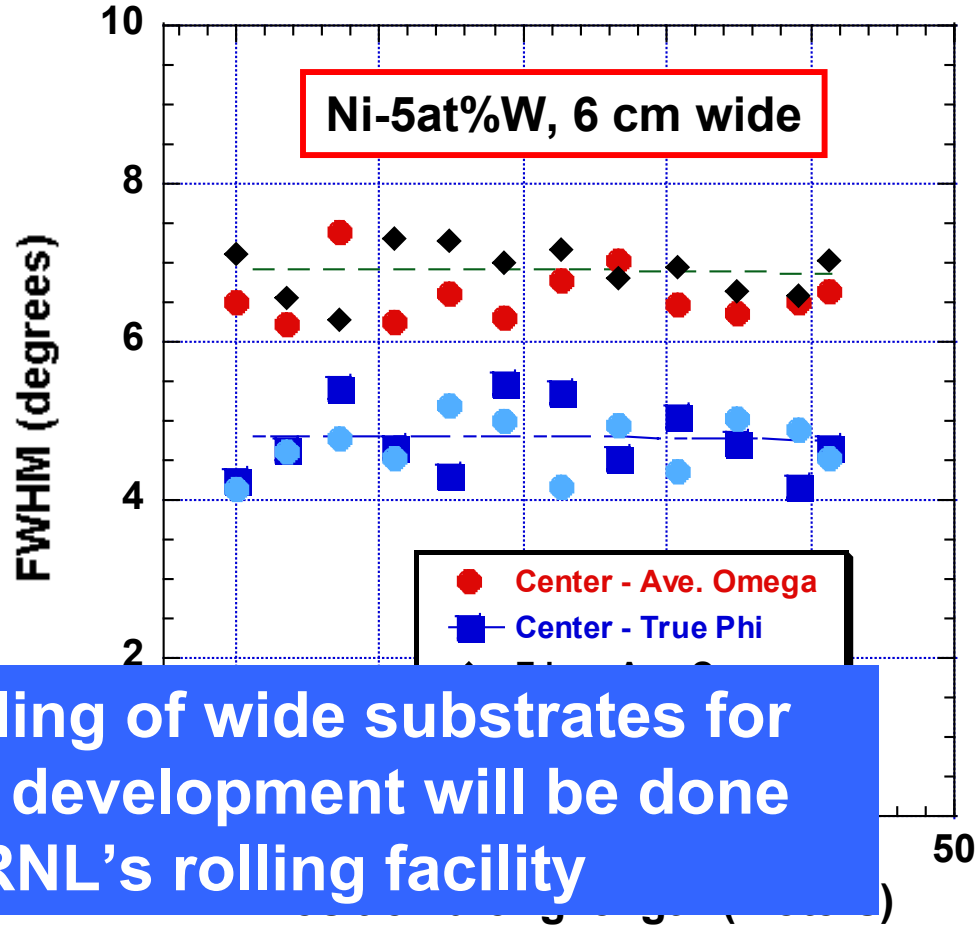
Approach:

- Develop appropriate rolling parameters for long and wide substrates
- Develop suitable annealing conditions which permit formation of sharp textures with no secondary recrystallization

Secondary recrystallization (SR)



Processing of wide webs is critical for low-cost manufacturing



Long length rolling of wide substrates for AMSC scale-up development will be done using ORNL's rolling facility

Texture is homogeneous along the length and width of alloy strips

Control of Secondary Recrystallization

- Surface energies play a key role in secondary recrystallization
- Modification of surface energies can provide a route to control onset of secondary recrystallization

ORNL Base Program Findings:

In certain Ni or Ni-based alloys, significant differences are observed when annealing in different atmospheres such as:

- flowing 4%H_2 in Ar → Recrys. Temp.
- high vacuum → ↑
- presence of sulfur (10^{-5}-10^{-7} Torr) → ↓
- presence of water (10^{-5}-10^{-7} Torr) → ↑

Investigate annealing of Ni-10at%Cr-2at%W non-magnetic alloy developed in the ORNL-AMSC CRADA and AMSC's Ni-5at%W alloy

Control of Secondary Recrystallization

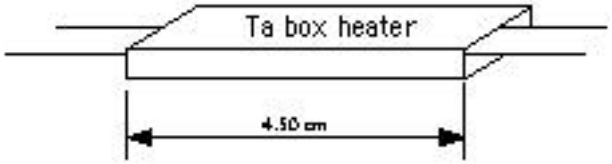
FY 2002:

ORNL-AMSC developed non-magnetic substrate: Ni-10at%Cr-2at%W
- **True in-plane FWHM = 7.4°**
- **Maximum annealing temp. before onset of secondary recrystallization was ~1050°C.**

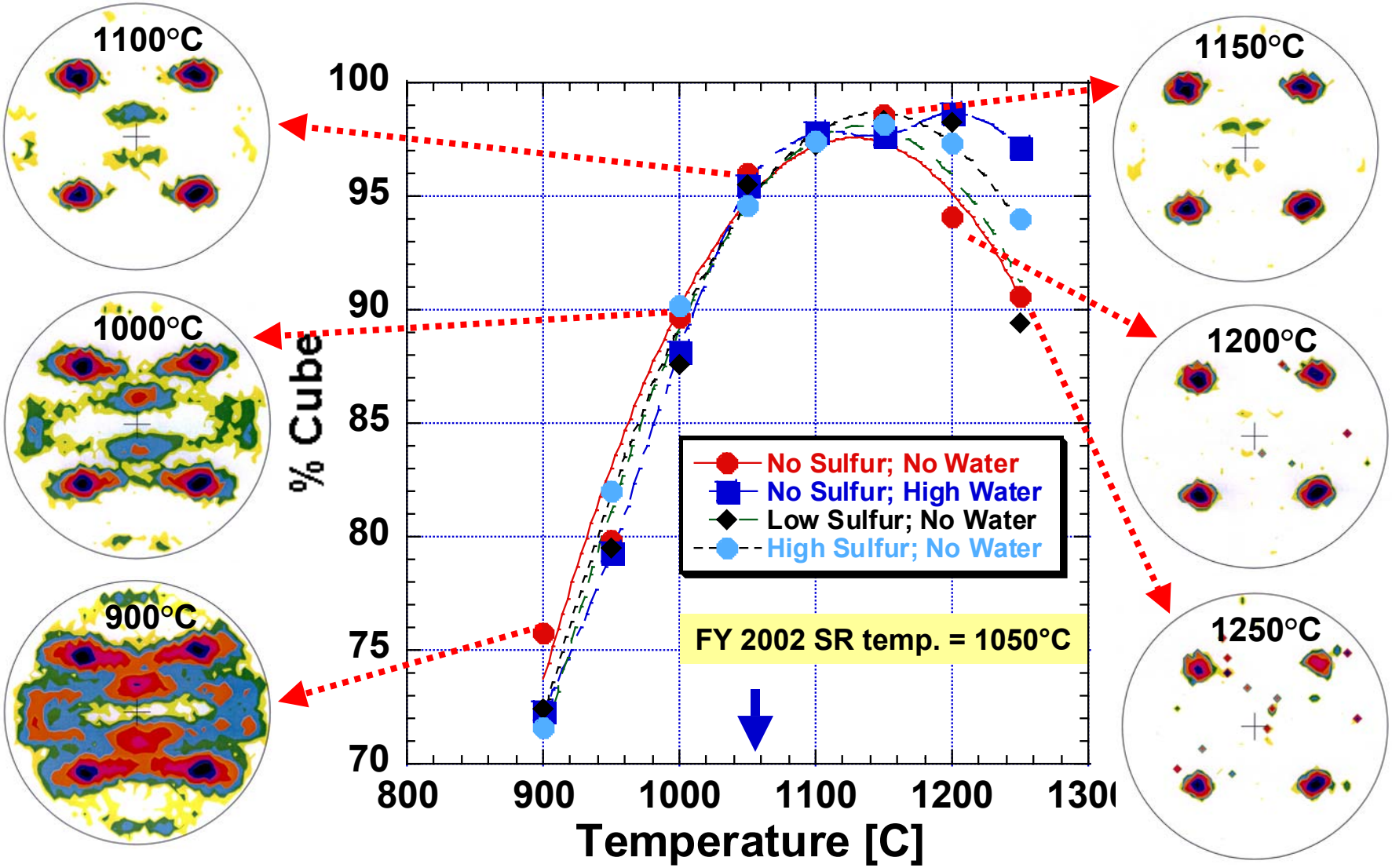
AMSC's substrate for development: Ni-5at%W
- **True in-plane FWHM = 6°**
- **Maximum annealing temp. before onset of secondary recrystallization was ~1150°C.**

Reel-to-reel annealing system

- **Resistive heating of a tantalum box through which the substrate passes**
- **rapid heating rate**

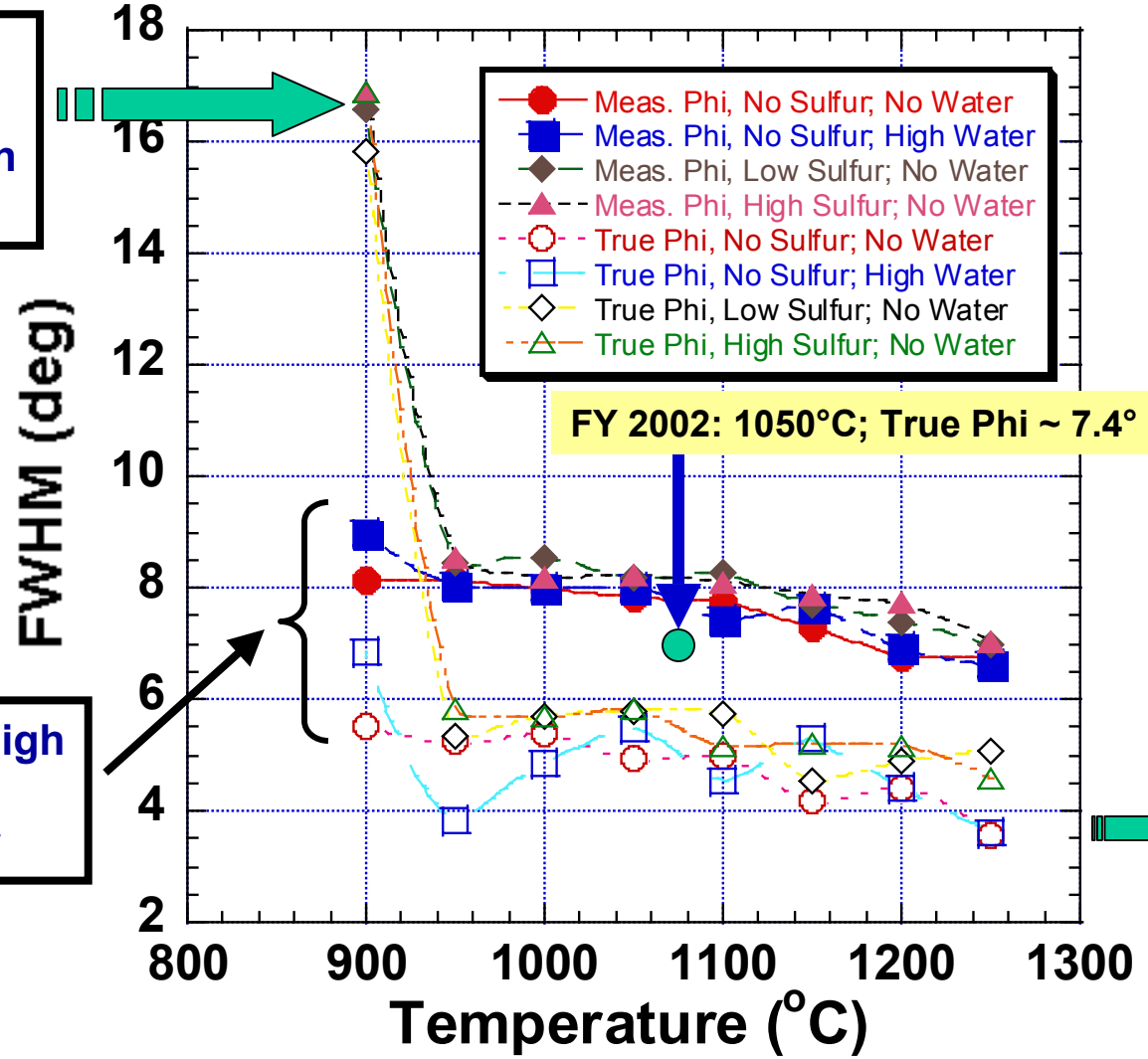


For Ni-10at%Cr-2at%W substrates, the SR temperature is enhanced by 100-150°C



There are differences in the formation of the cube texture when annealing under different environments

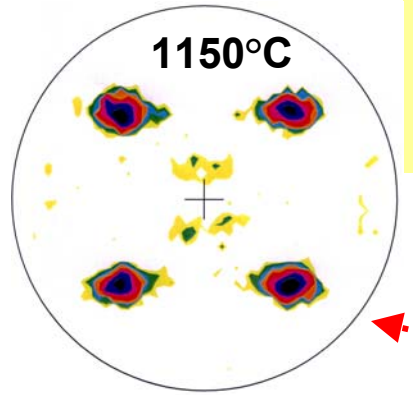
In the presence of sulfur, cube texture formation is sluggish

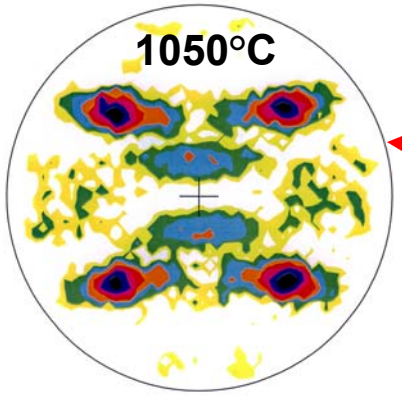


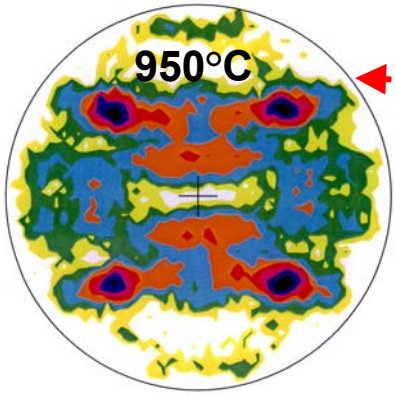
In vacuum and high water, textures develops rapidly

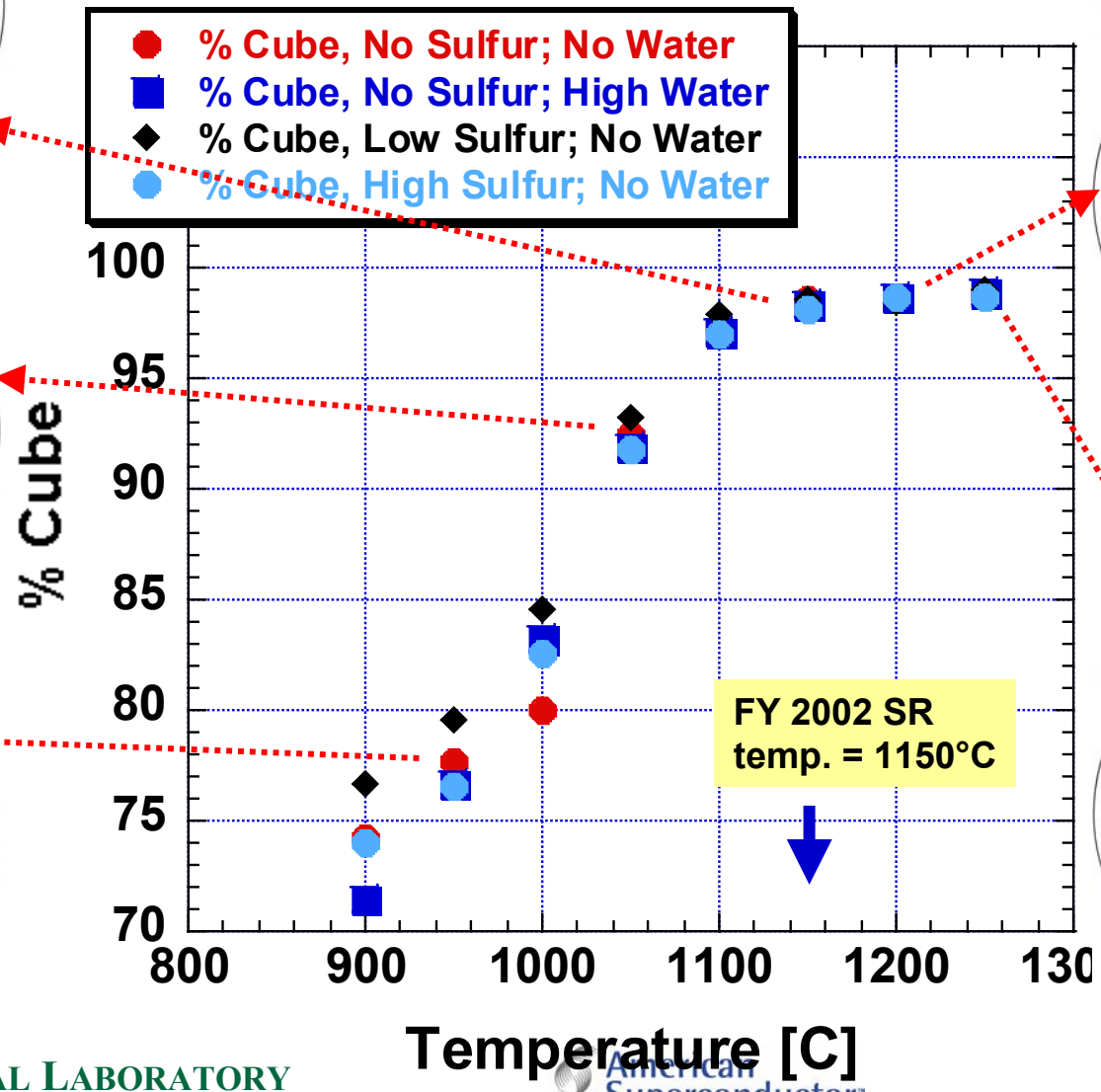
Even after onset of SR, texture continues to sharpen in the cube textured material

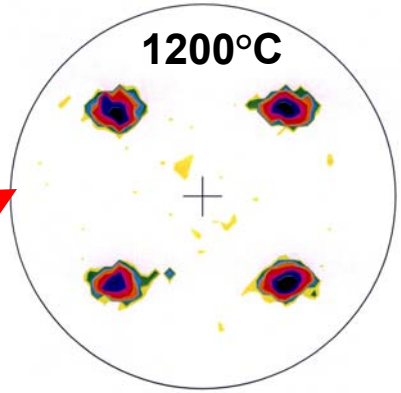
For Ni-5at%W substrates, annealing temperatures can be increased to 1250°C resulting in improved texture without SR

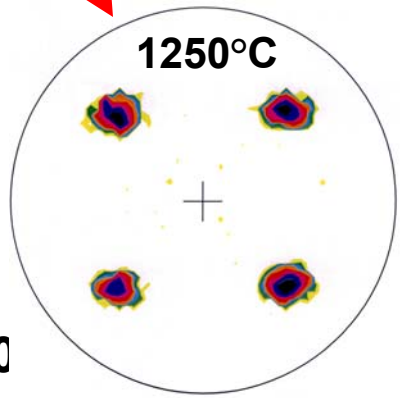




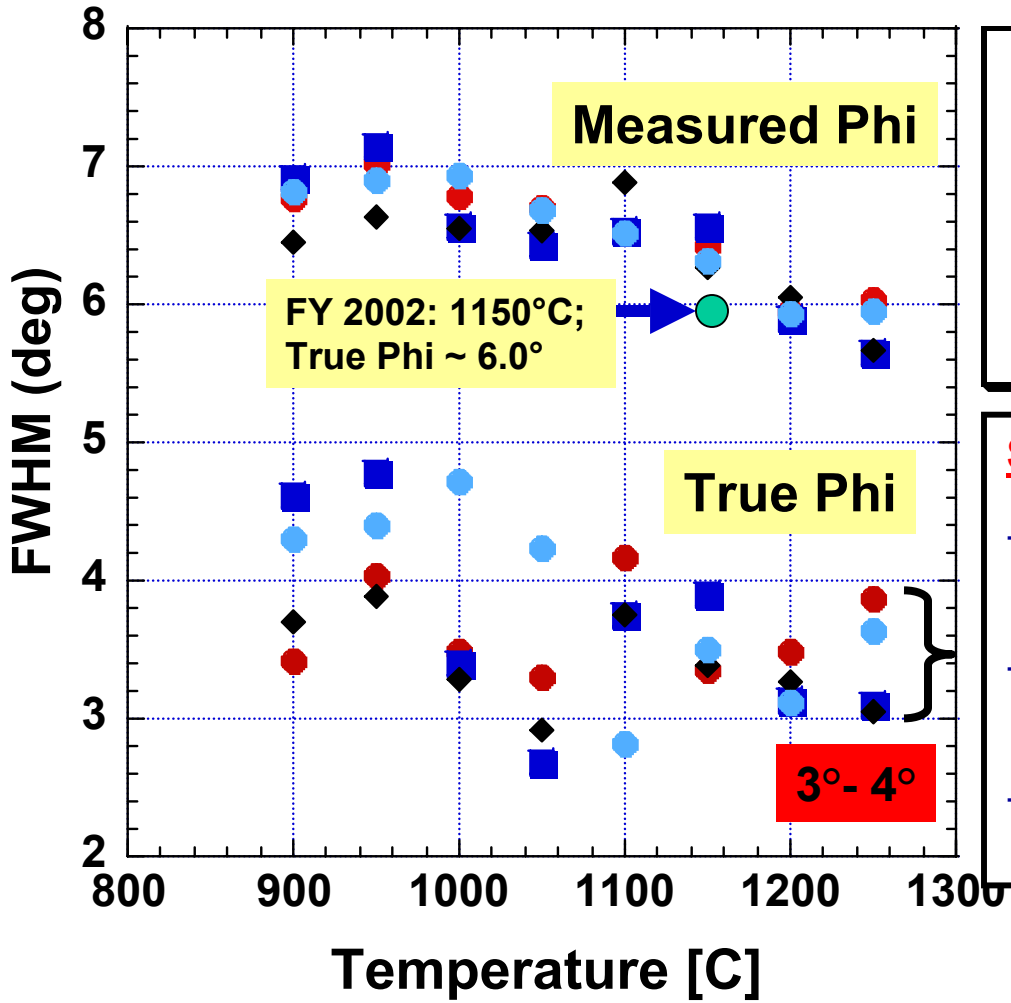








Texture sharpens up substantially in the Ni-5at%W tape at higher temperatures!



- Meas. Phi; No sulfur; No Water
- Meas. Phi; No Sulfur; High Water
- Meas. Phi; Low Sulfur; No Water
- Meas. Phi; High Sulfur; No Water
- True Phi; No sulfur; No Water
- True Phi; No Sulfur; High Water
- True Phi; Low Sulfur; No Water
- True Phi; High Sulfur; No Water

SUMMARY:

- SR temp. increased 100°C by controlling the annealing environment
- True in-plane textures of 3-4° FWHM obtained
- Very high cube texture fraction was obtained

SUMMARY: Substrate Work

FY 2002:

AMSC's substrate for development: Ni-5at%W
- True in-plane FWHM = 6°
- Maximum annealing temp. before
- onset of secondary recrystallization was ~1150°C

ORNL-AMSC developed non-magnetic substrate: Ni-10at%Cr-2at%W
- True in-plane FWHM = 7.4°
- Maximum annealing temp. before onset of secondary recrystallization was ~1050°C

FY 2003 Results:

AMSC's substrate for development: Ni-5at%W
- True in-plane FWHM improved to 3-4° from 6°
- Annealing temperature increased by 100°C to 1250°C
- High cube fractions obtained

ORNL-AMSC developed non-magnetic substrate: Ni-10at%Cr-2at%W
- True in-plane FWHM improved to 4-5° from 7.4°
- Annealing temperature increased by 100°C-150°C to 1200°C
- High cube fractions obtained

ORNL R&D Supports AMSC 2G Substrate Development:

1) Wide substrates required for low-cost manufacturing
2) Sharper textures enables improved performance
3) Control of texture improves yield and throughput

Explore next level of detail in texture: GBMD's

Objectives:

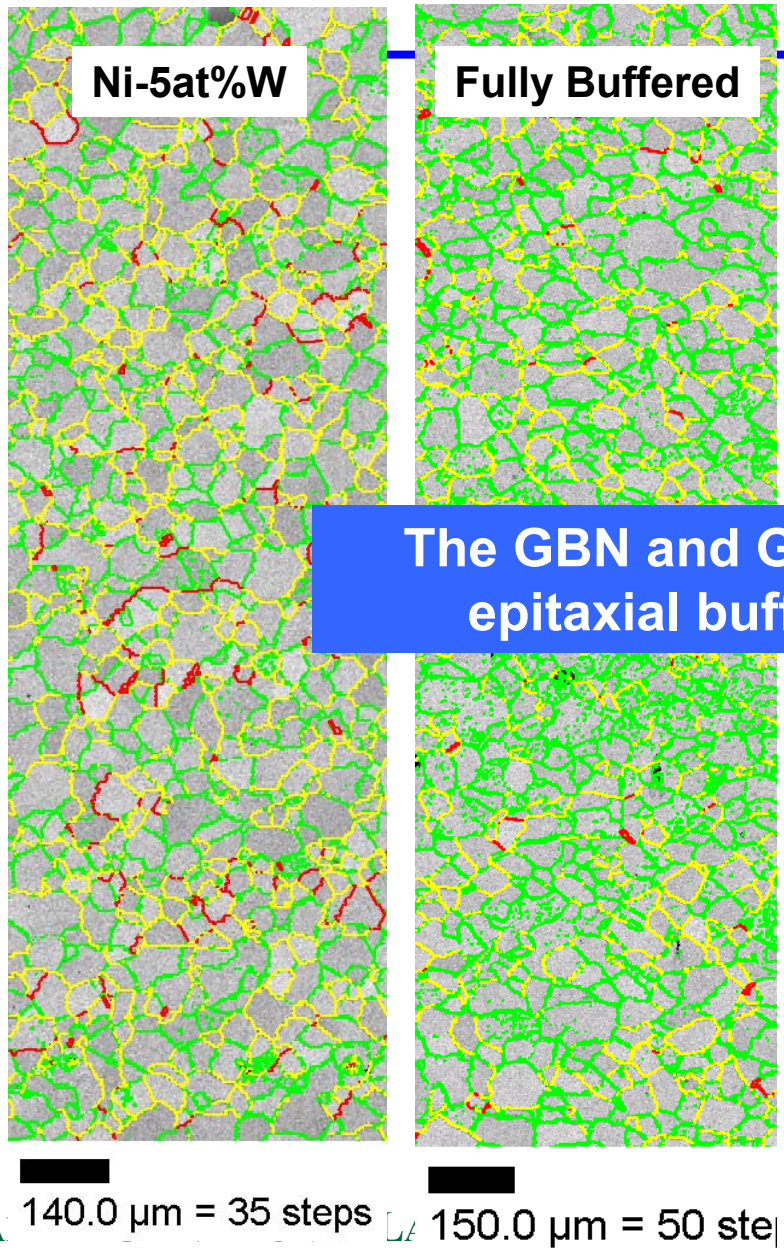
(a) Do slight changes in annealing of substrate modify the grain boundary networks (GBN) and grain boundary misorientation distributions (GBMD)?

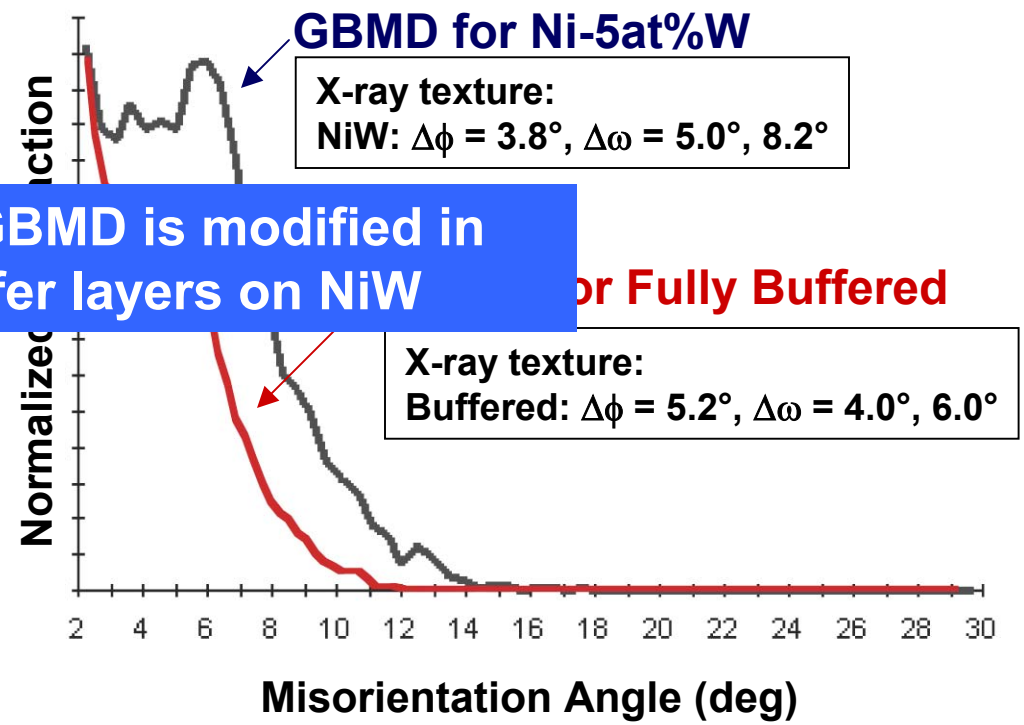
(b) To determine if GBN and GBMD are modified in epitaxial oxide layers

The experiment:

- Three different annealing conditions for Ni-5at%W substrates
- Same epitaxial layers – Y_2O_3/YSZ/CeO_2 and YBCO deposited under identical conditions
- GBN and GBMD were measured in large areas by electron backscatter Kikuchi diffraction
- Samples J_c's were: High (1.6 MA/cm^2), medium (1.1 MA/cm^2) and low (0.75 MA/cm^2)

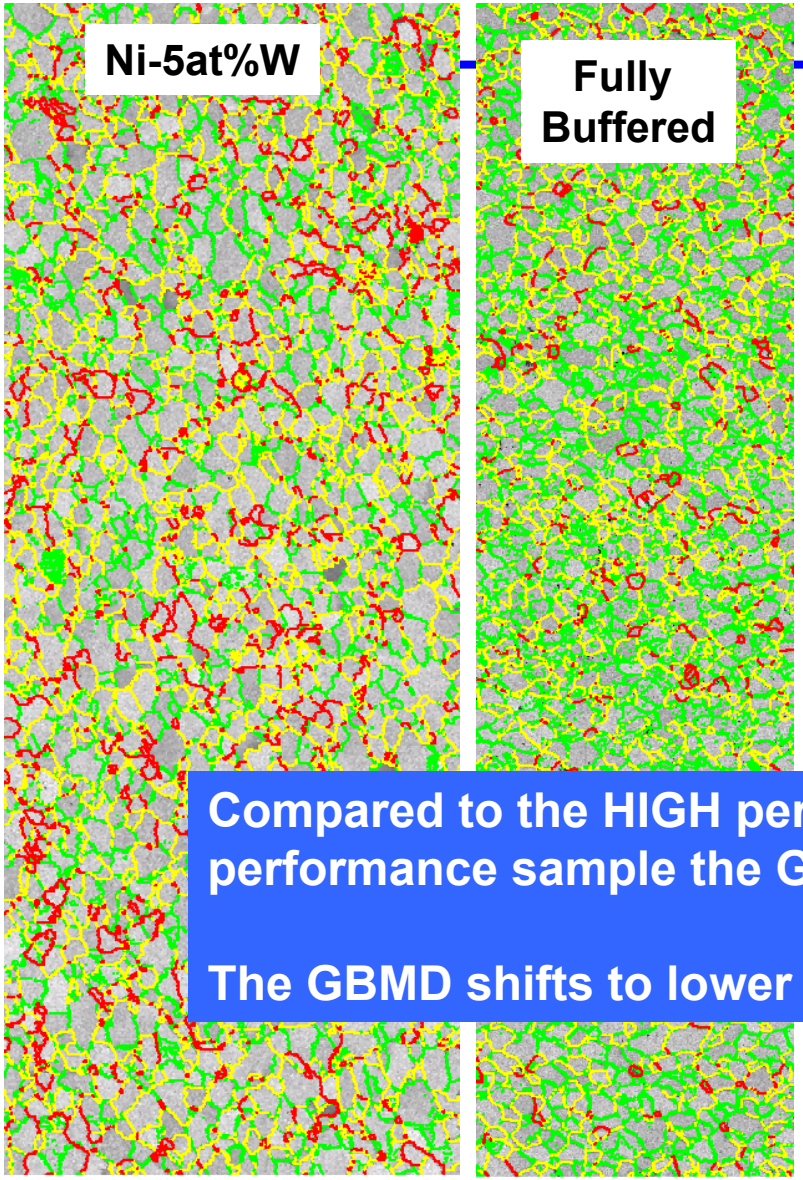
High Performance Samples: J_c = 1.6 MA/cm^2 for 0.4 μm YBCO

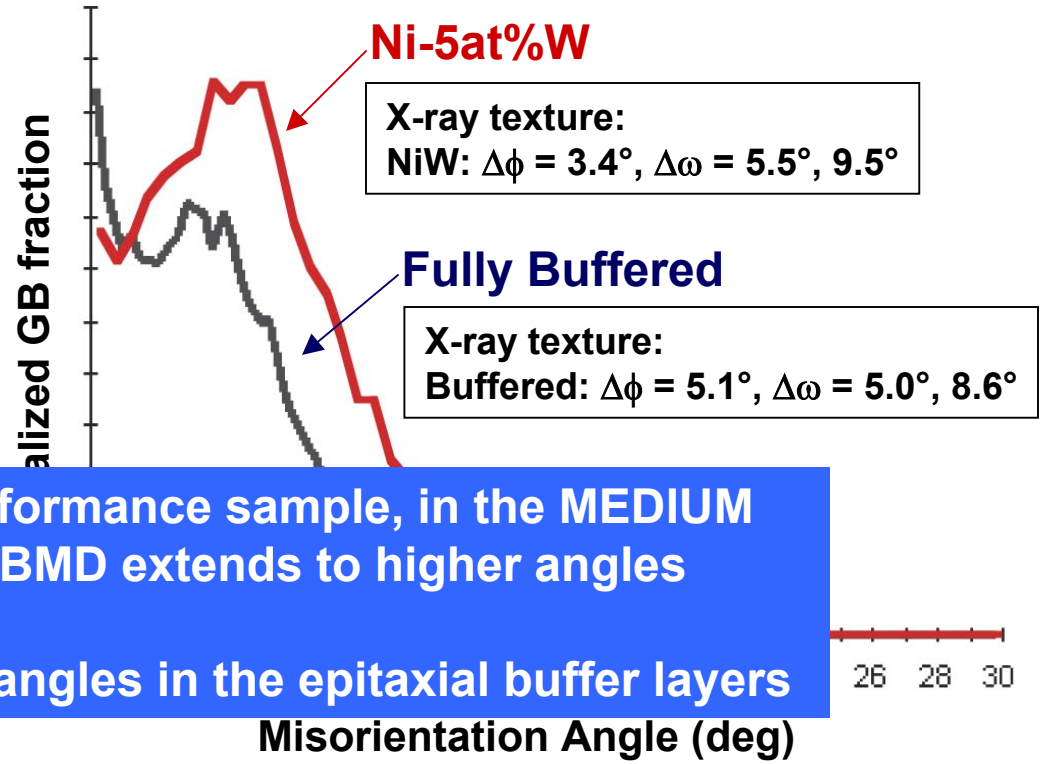




The GBN and GBMD is modified in epitaxial buffer layers on NiW

Medium Performance Samples: J_c = 1.1 MA/cm^2 for 0.4 μm YBCO





Compared to the HIGH performance sample, in the MEDIUM performance sample the GBMD extends to higher angles

The GBMD shifts to lower angles in the epitaxial buffer layers

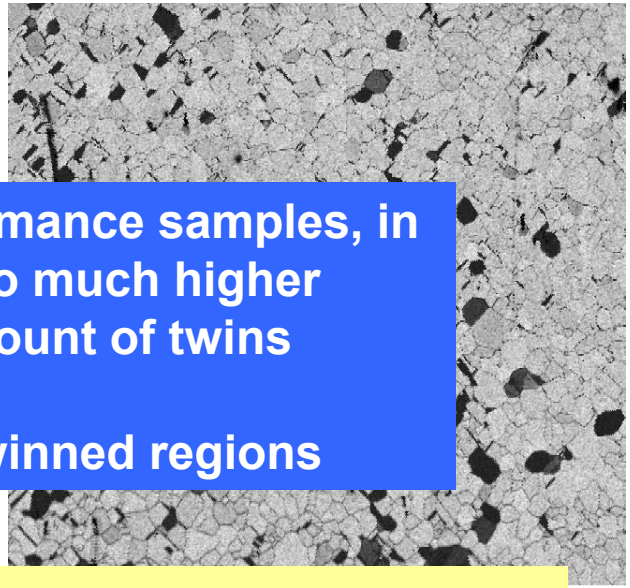
180.0 μm = 45 steps

180.0 μm = 45 st

Low Performance Samples: J_c = 0.75 MA/cm^2

X-ray texture:
NiW: $\Delta\phi$ = 5.3°, $\Delta\omega$ = 6.2°, 9.6°

Buffered substrate



Compared to the HIGH and MEDIUM performance samples, in the LOW performance the GBMD extends to much higher angles and the samples has significant amount of twins

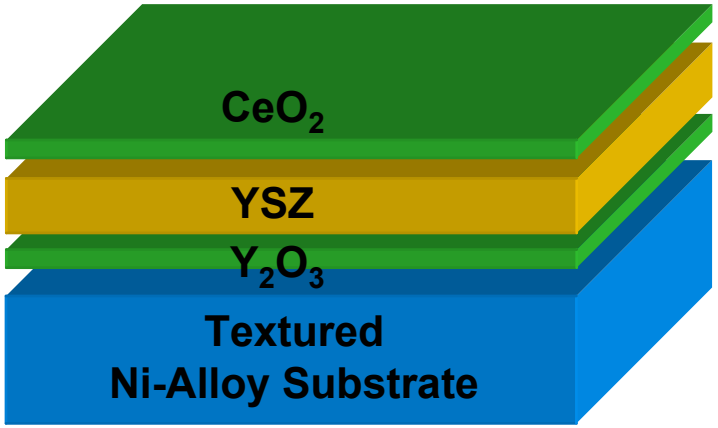
Growth of buffer layers is affected in the twinned regions

GB

Summary:

- Controlled changes in annealing conditions affect grain boundary networks and grain boundary misorientation distributions
- Grain boundary networks and grain boundary misorientation distributions are modified in epitaxial layers on the metal/alloy substrate

AMSC Standard RABiTS™ Architecture: *Benchmarking of buffer characteristics*



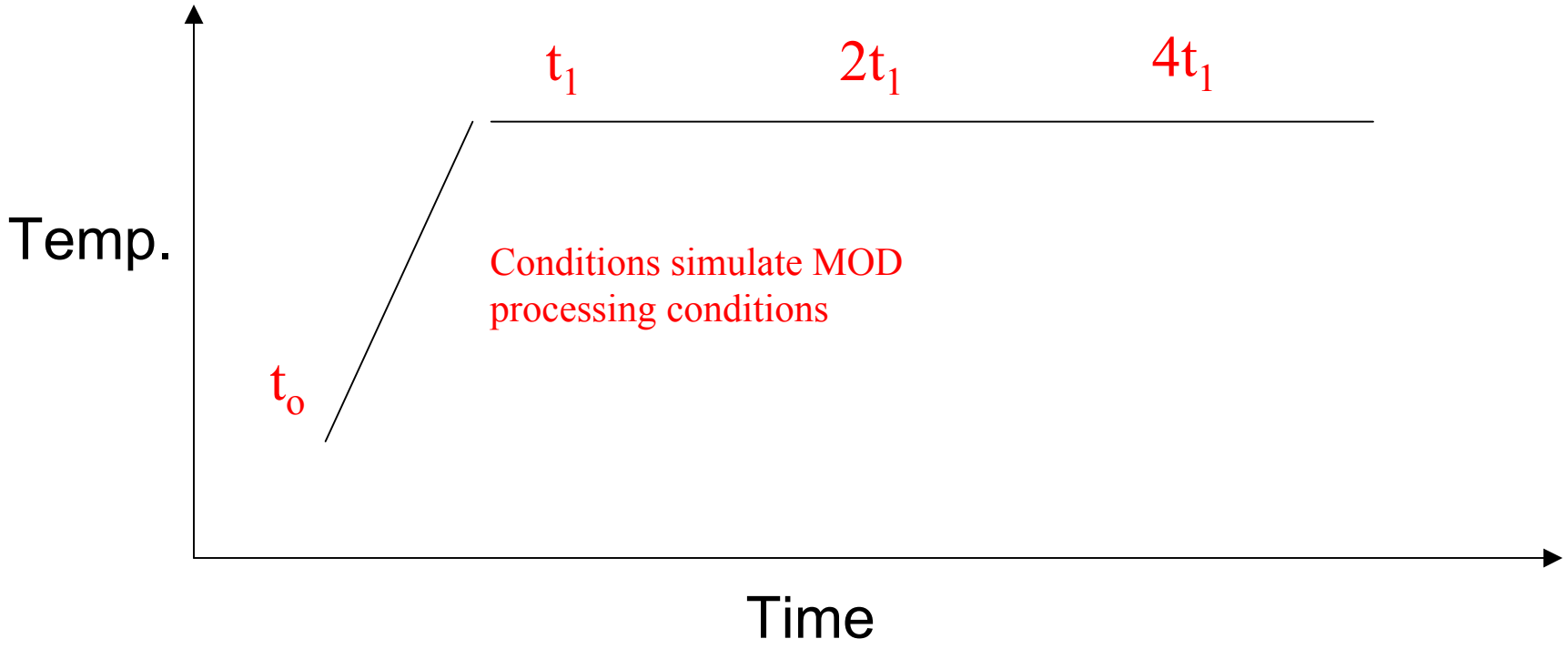
Objectives:

- **Benchmark standard buffer with respect to metal/oxygen diffusion**
- **Establish differences between GB's and intragranular regions**
- **Characterize the metal/oxide interface**
- **Engineer cost/performance of the buffer stack**

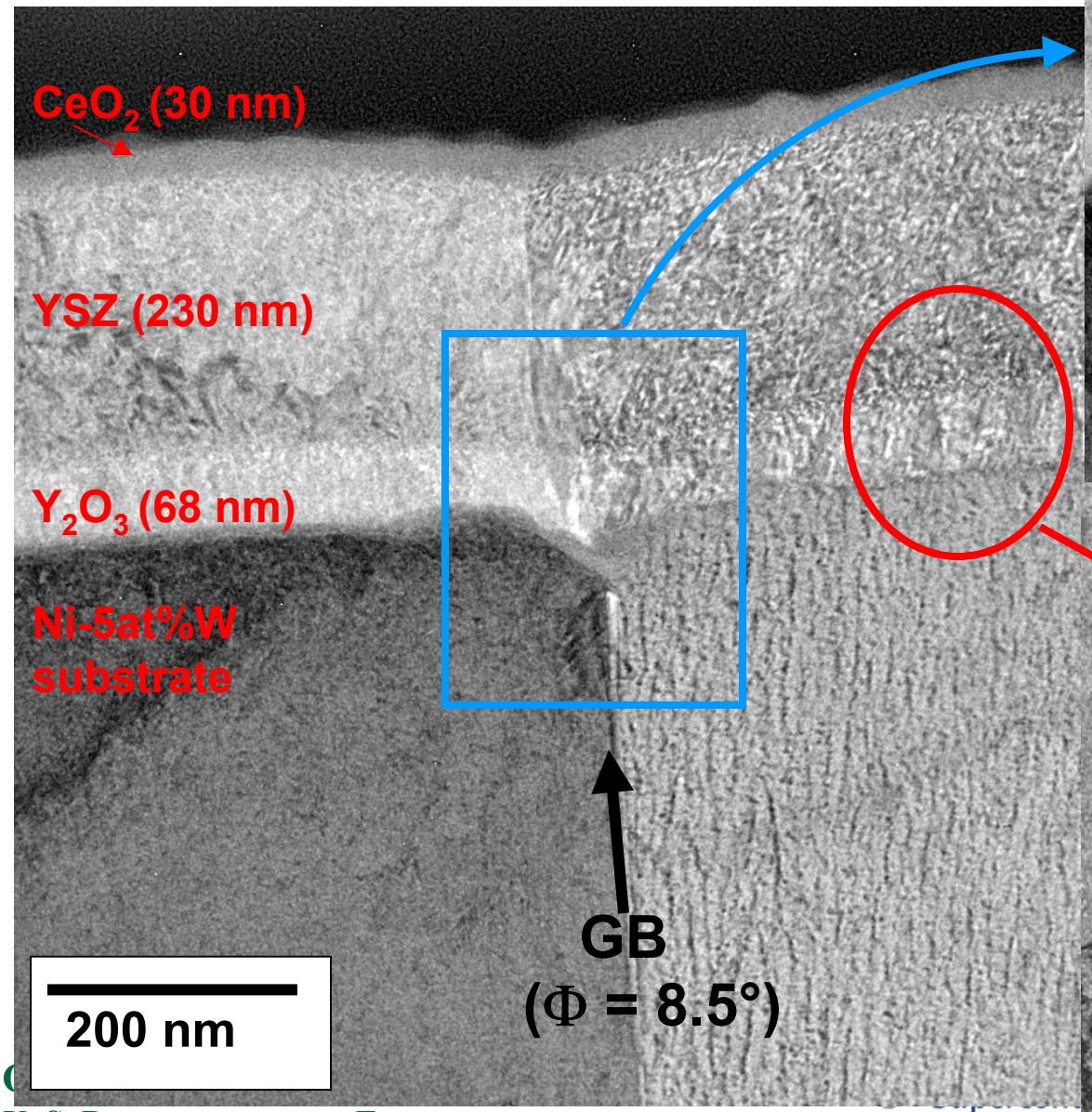
Microscopy techniques and X-ray diffraction studies were performed at ORNL to further the materials understanding of buffer properties which is being applied to AMSC 2G wire process

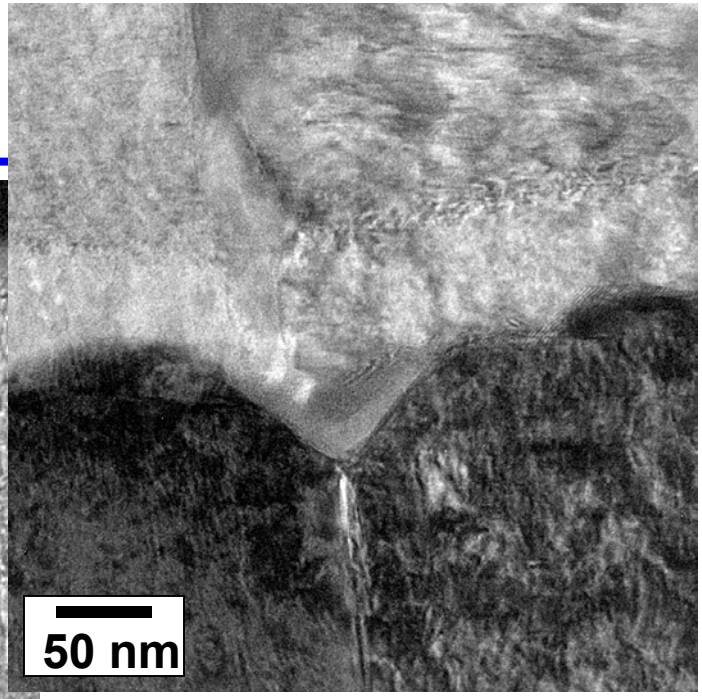
Examination of AMSC buffered substrates

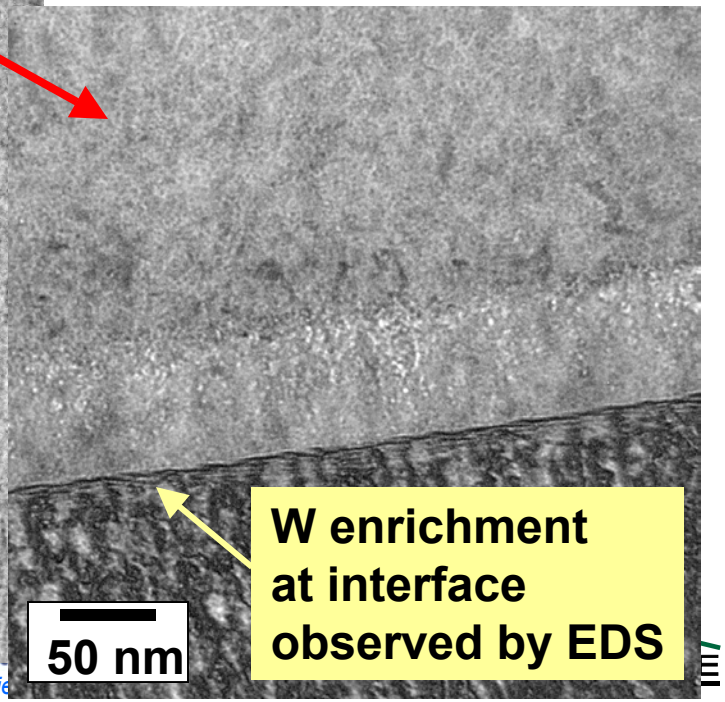
- First establish a benchmark for as-processed buffer layers with respect to metal/cation diffusion, etc.
- Examine buffered substrate after it has been subjected to annealing treatments at high temperature simulating MOD processing conditions for fabrication of thick YBCO films



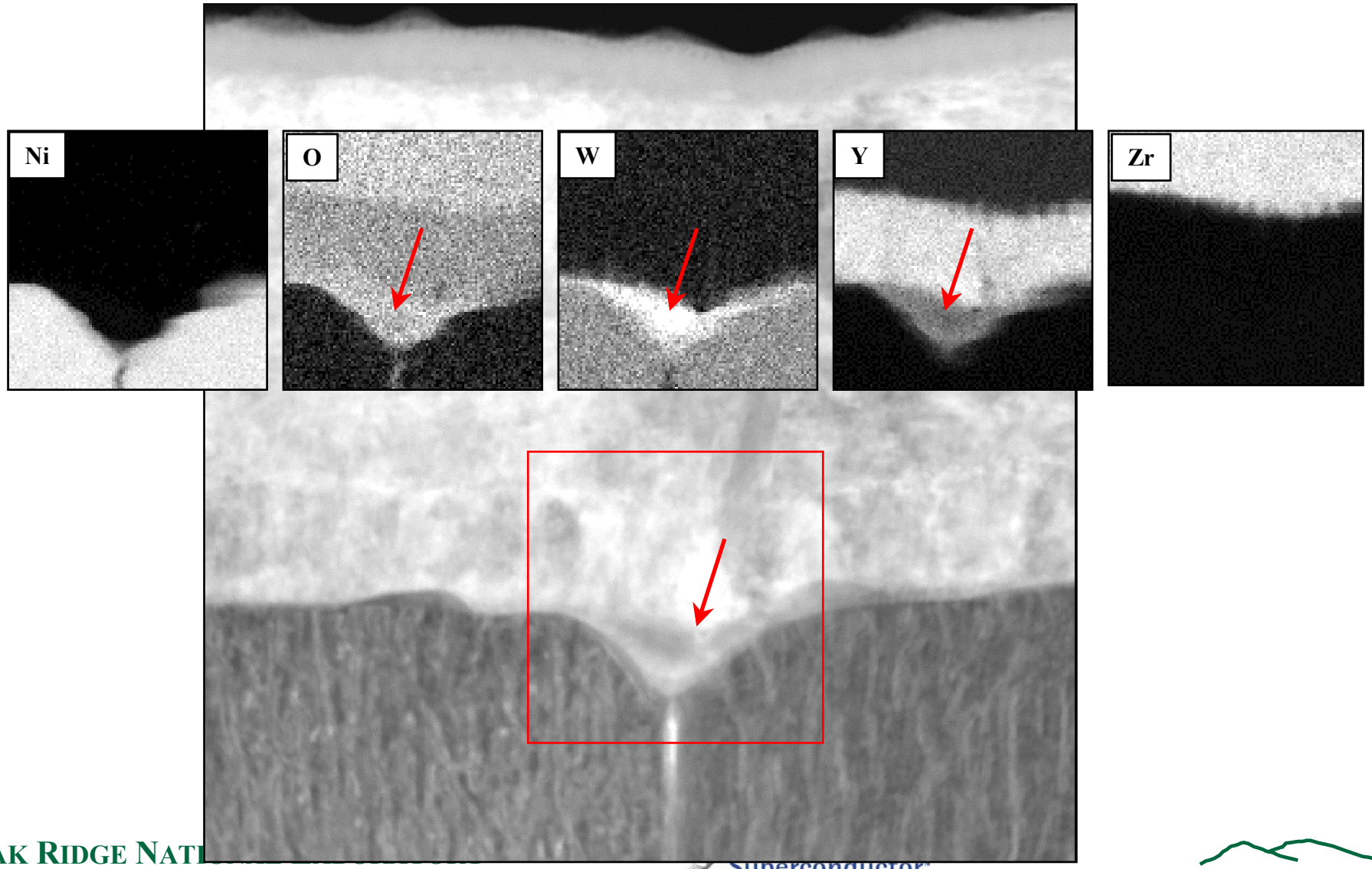
TEM of as-processed AMSC standard buffer layer stack on Ni-5at%W (t_0)



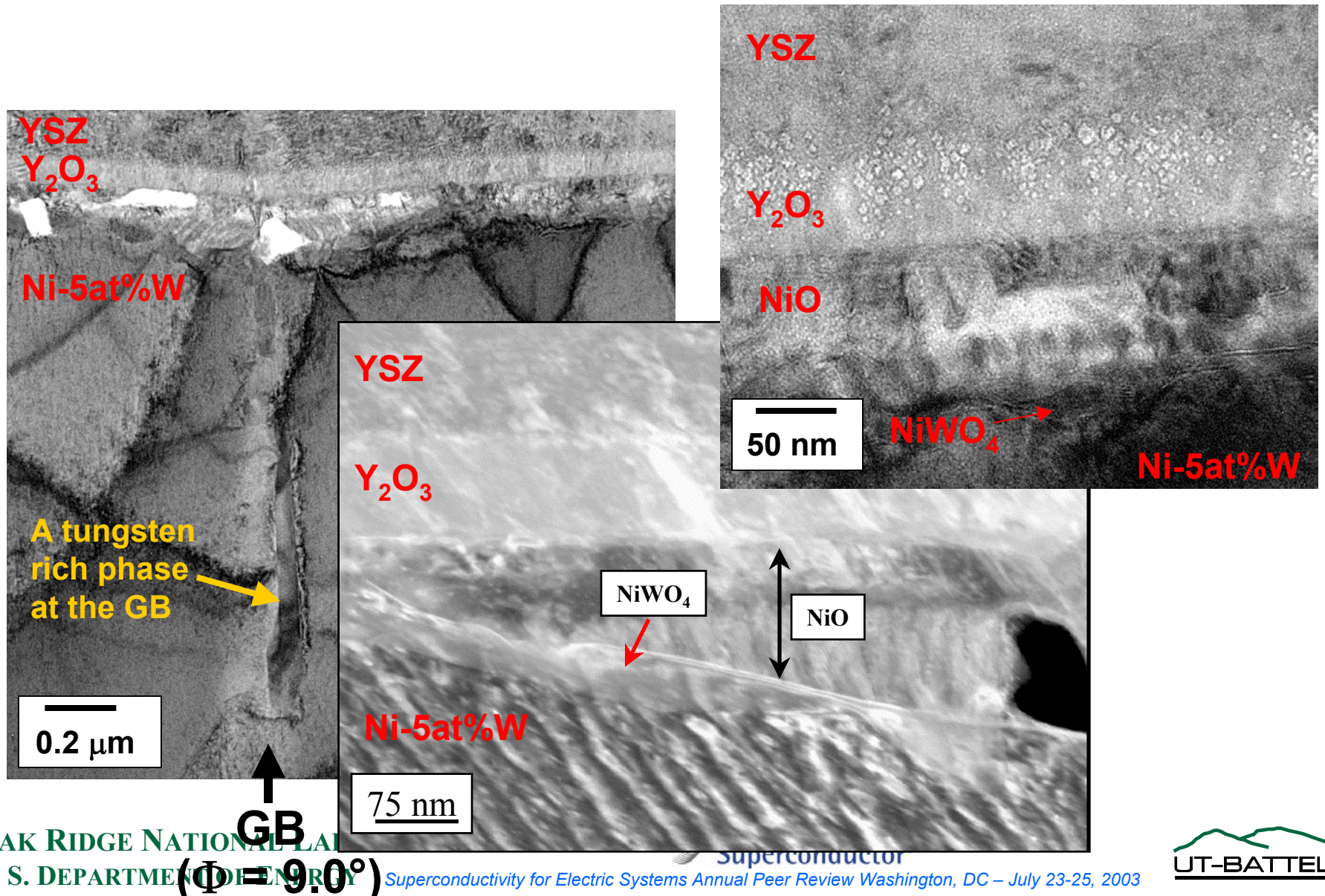




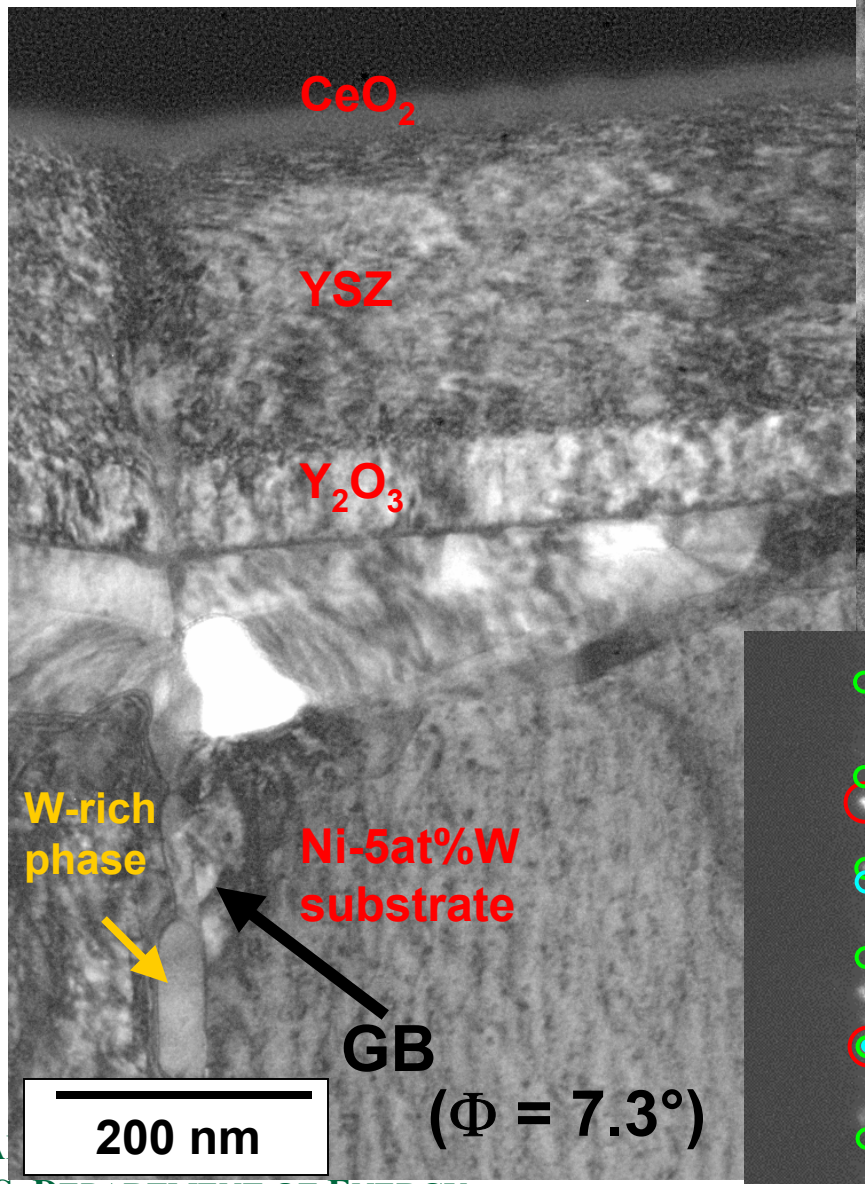
A tungsten yttrium oxide phase is formed at the grain boundary groove

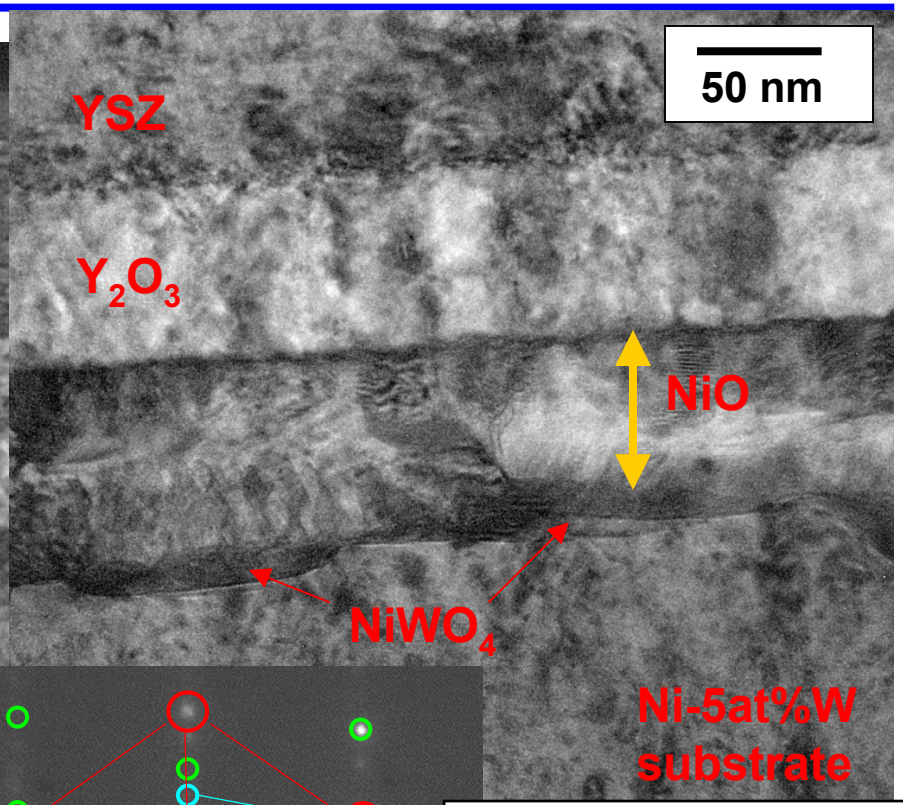


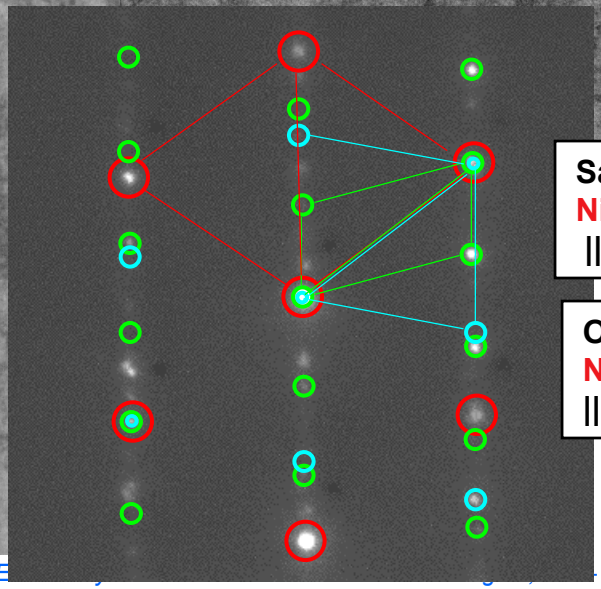
$NiWO_4$ and NiO are formed upon annealing for time = $2t_1$



$NiWO_4$ and NiO increase slightly in thickness after annealing for an time = $4t_1$



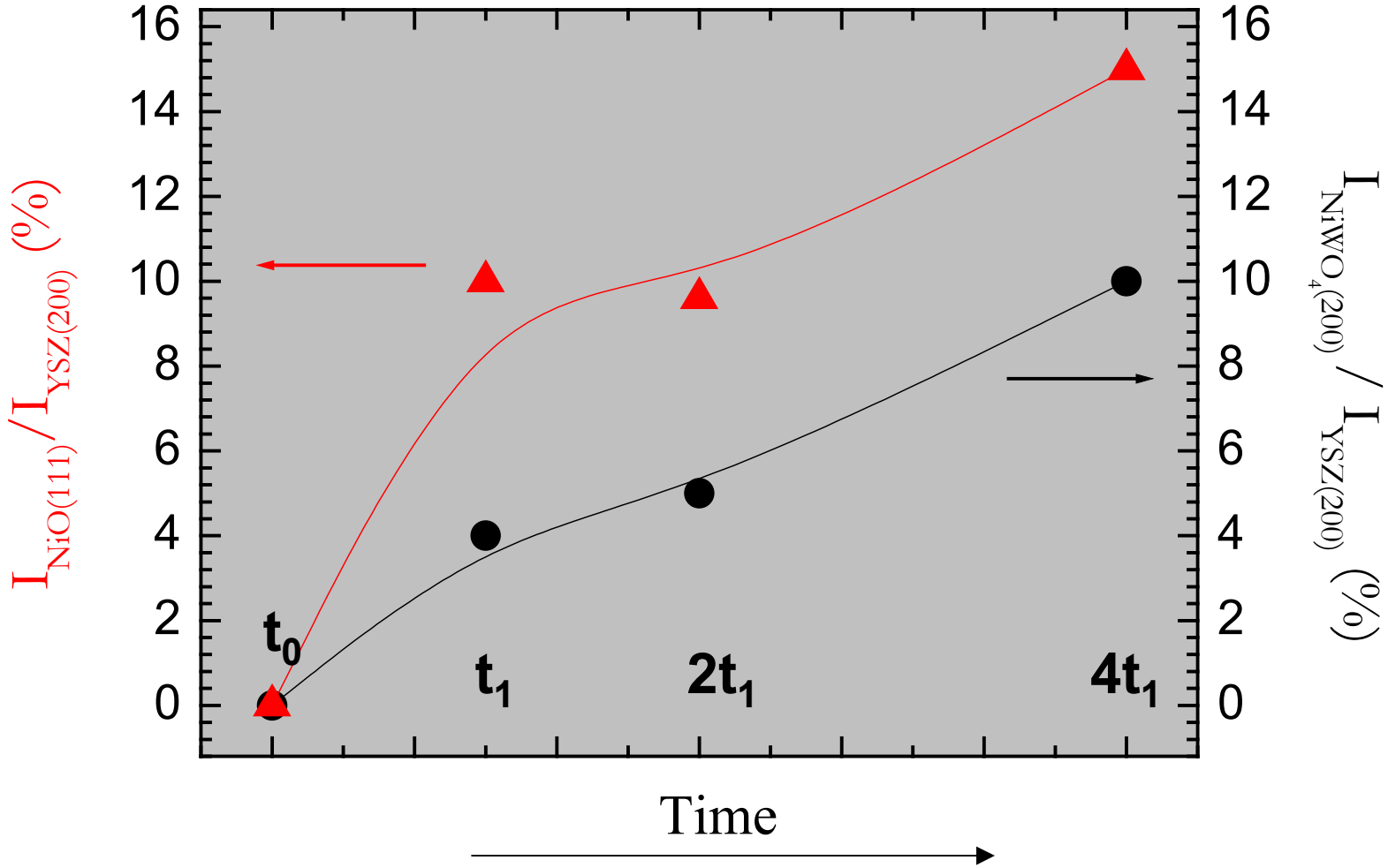




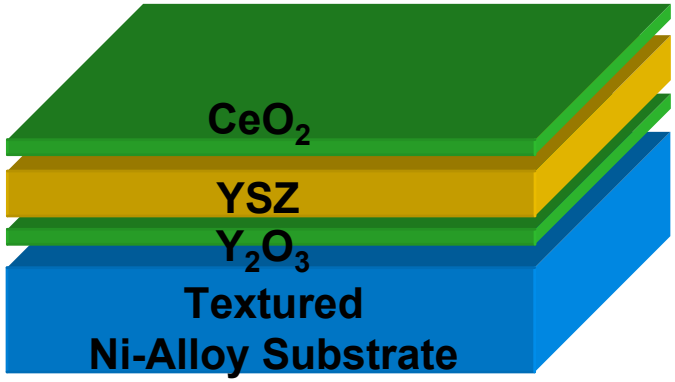
Sample Normal
Ni(W) <200> || $NiWO_4$ <100> || NiO <111>

Overlapping Reflection
Ni(W) (111) || $NiWO_4$ (102) || NiO (200)

X-ray cannot accurately show how much oxide thickness is increasing due to texture effects

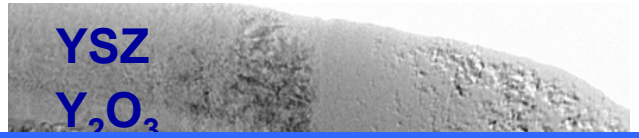


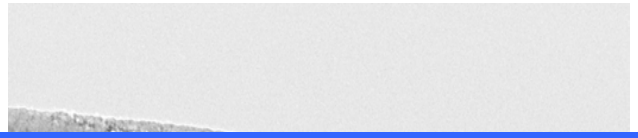
Y_2O_3 is an effective oxygen barrier



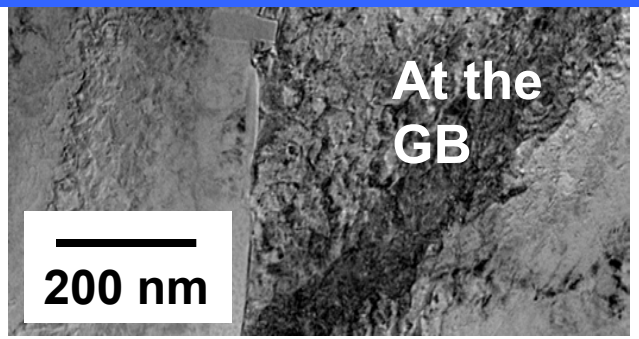
Sample annealed for time $2t_1$

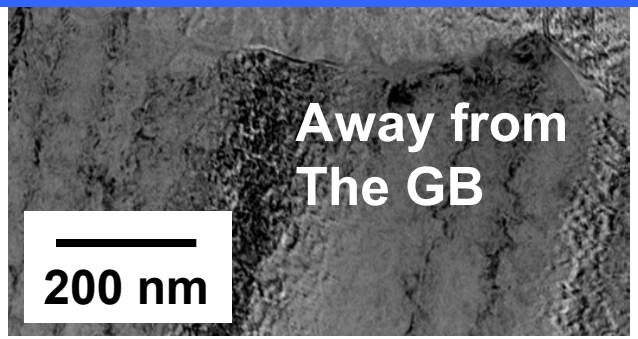
- NiO layer thickness increases with decrease in Y_2O_3 thickness
- It is thicker than for standard material annealed for time $4t_1$





Knowledge of the diffusion characteristics of buffer layers is being used to improve cost/performance of the buffers in AMSC 2G wire



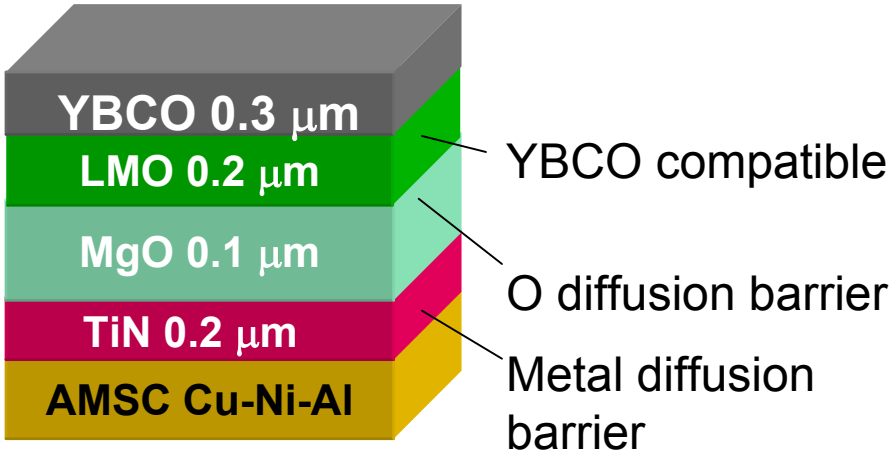


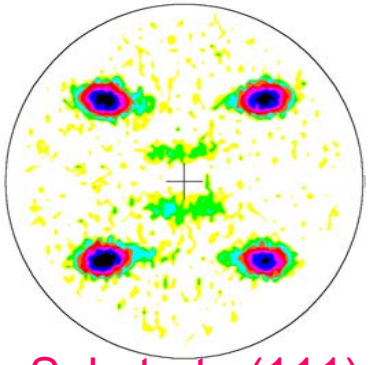
Buffer layer development for non-magnetic substrates: J_c = 2MA/cm^2 on AMSC Cu-Ni-Al alloy

- ***Composition: Cu-Ni48% with 1-1.5%Al, Yield Stress = 130 MPa***
- ***Substantial $\Delta\omega$ improvement occurs in TiN***
- ***PLD YBCO 0.3 μm thick***

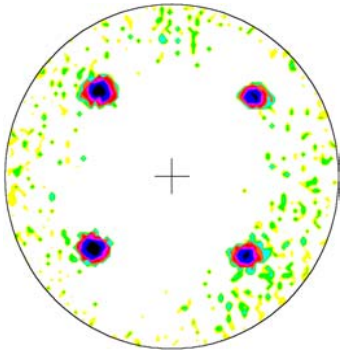
	$\Delta\omega$,t	$\Delta\omega$,r	$\Delta\phi$	True ϕ
alloy	10.73	6.52	8.05	5.1
TiN	3.01	2.57	5.72	5.4
MgO	2.99	2.74	5.54	
LMO	4.01	3.30	6.48	
YBCO	4.00	2.81	6.45	6.0

Buffer layer configuration





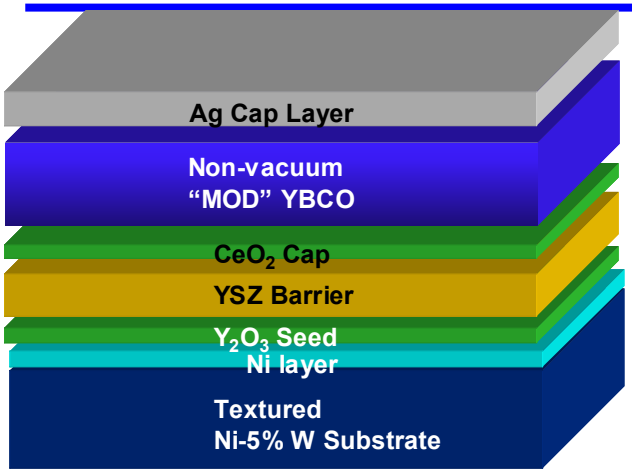
Substrate (111)



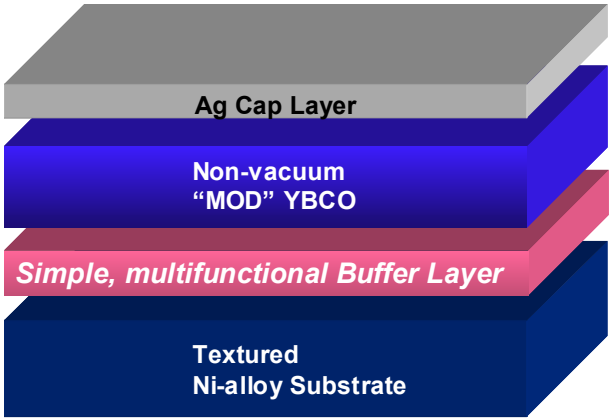
TiN (111)

Buffer layers for AMSC non-magnetic substrates such as Cu-Ni-Al and Ni-Cr-W alloys are being developed

Development of Solution Buffer Layers



Current Architecture; FY 2003



Possible Future Architecture

OBJECTIVE:

Develop lower-cost (capital/operational/materials) buffer materials and/or deposition processes that are compatible with the TFA-YBCO process

APPROACH:

Metal-organic deposition (MOD)

CANDIDATE MATERIALS:

$La_2Zr_2O_7$ (LZO) (seed & barrier; alkoxide); CeO_2 (cap; acac)

Solution deposition of buffer layers offers potential cost advantage relative to PVD processes

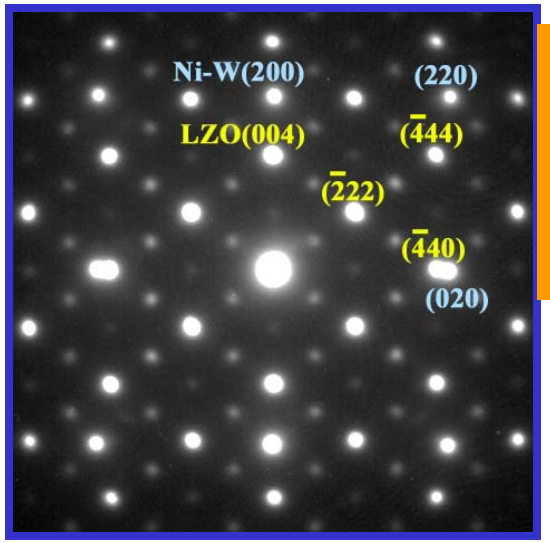
- **Solution coating is amenable to complex oxides**
- **Industrial coating previously demonstrated with RE_2O_3 buffers on 10 meter lengths of Ni (same process as AMSC developed for MOD YBCO coatings)**
- **Current Challenges are:**
  - **Deposition directly on alloy substrates (Ni-W, Ni-Cr-W)**
    - Understanding role of S superstructure in MOD process
  - **Achieving texture comparable to PVD buffers**
    - $\Delta\Phi = 5.2°$, $\Delta\omega = 4.0°$ (Phi=0); $6.0°$ (Phi=90)
  - **Growth of buffer layers with suitable barrier layer properties and mechanical properties**
  - **Compatible with TFA-based YBCO process**

Challenge is to match performance of AMSC's current PVD buffer stack in long length at lower cost

Goal is to replace one or more PVD layers in the current AMSC buffer stack with MOD layers

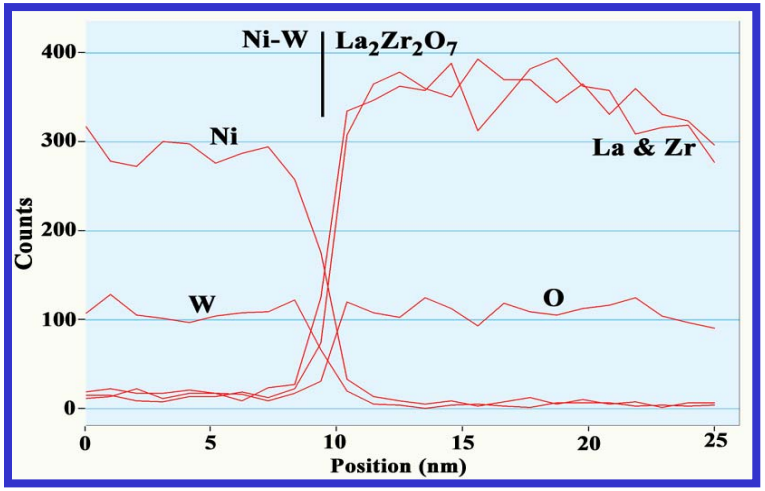
1. Evaluate MOD LZO seed as replacement of Y_2O_3 seed layer
2. Evaluate MOD LZO barrier as replacement of YSZ barrier layer
3. Test compatibility of MOD CeO_2 cap layer with MOD-YBCO
4. Evaluate LZO as a multifunctional seed/barrier as replacement of Y_2O_3/YSZ

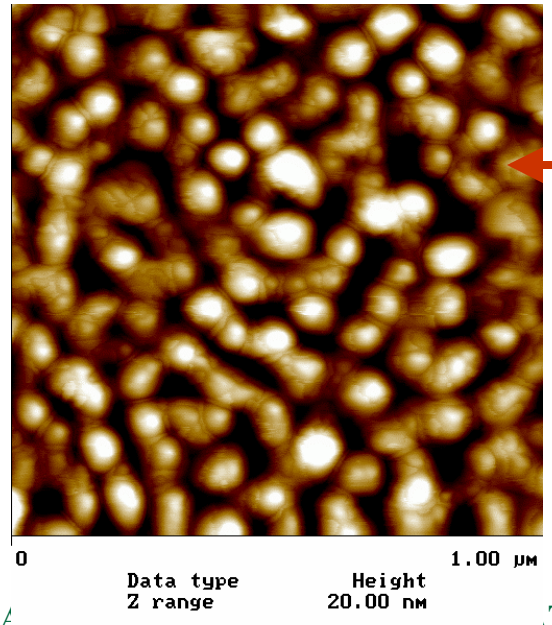
LZO seed layer grown cube-on-cube directly on Ni-W



SAD pattern of LZO/Ni-W shows cube-on-cube texture

Line scale profile shows sharp LZO/Ni-W interface





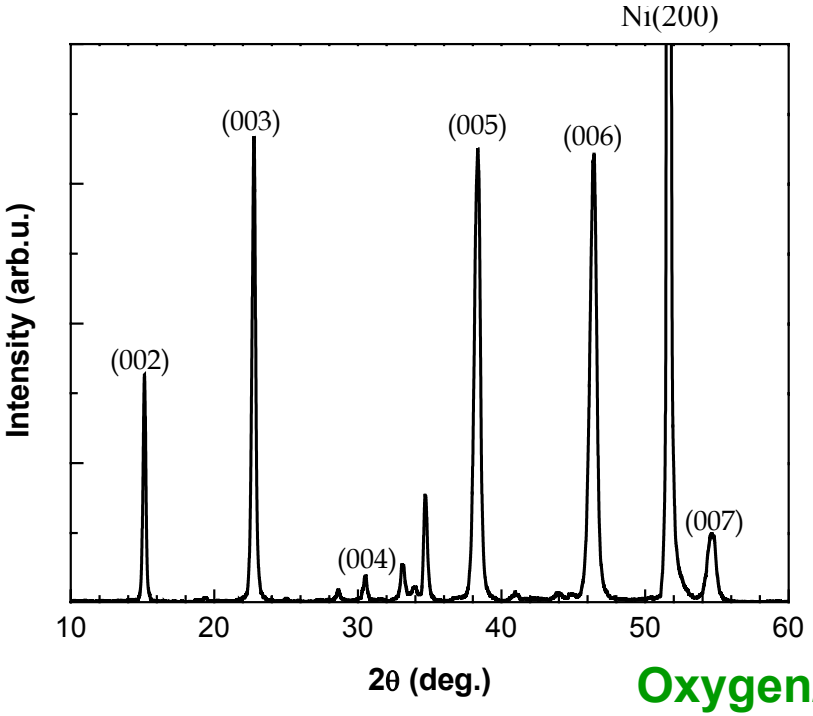
AFM LZO surface

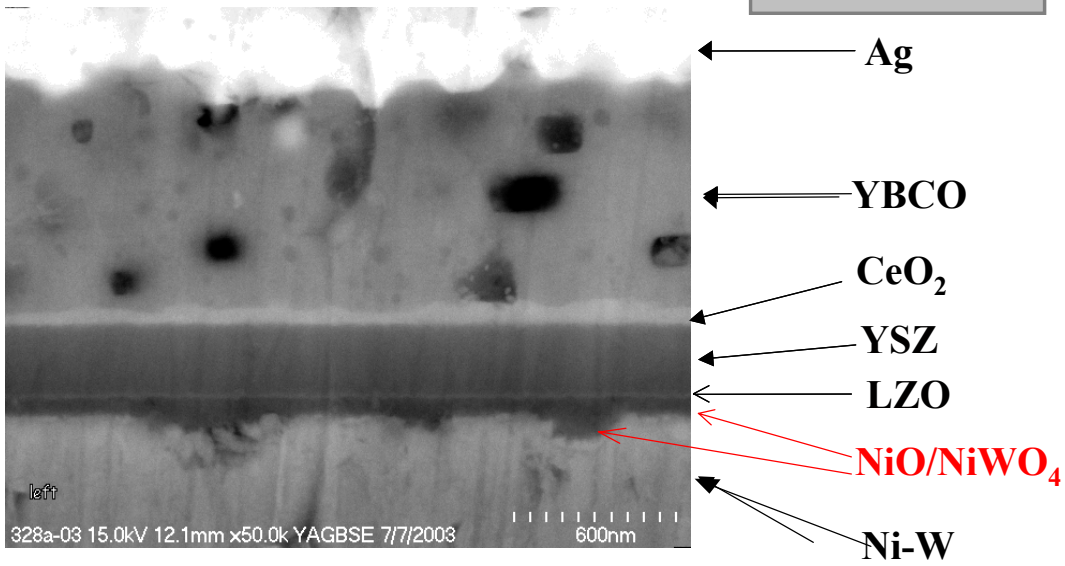
20 nm LZO seed layers are grown with reproducible textures over meter lengths of NiW substrate

LZO seed tested with AMSC YSZ/CeO_2/YBCO

YSZ/CeO_2/YBCO grown epitaxial on LZO

J_c of up to 2.3 MA/cm^2 (184A/cm-w) (short sample, 77K, sf)





Oxygen/metal diffusion properties not established

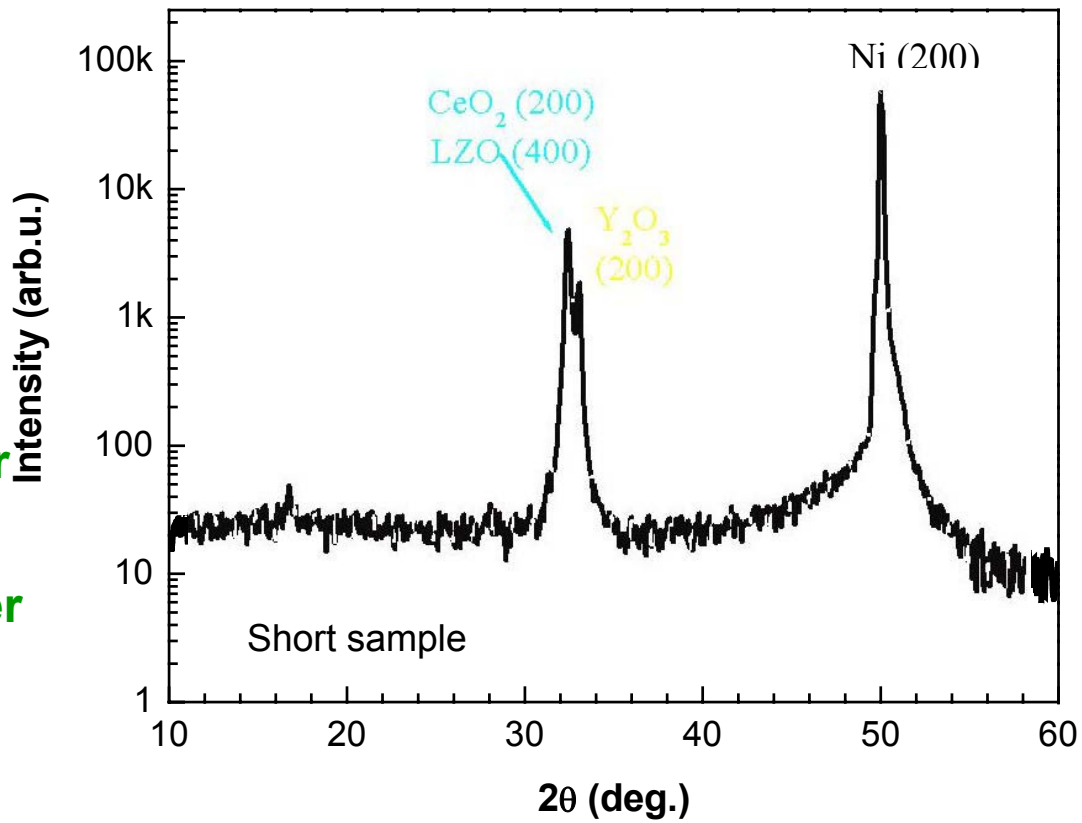
Solution deposited LZO is a promising replacement for PVD deposited Y_2O_3 seed layer

MOD LZO/CeO_2 layer stack deposited on Y_2O_3 seed layer

An MOD process was developed for depositing both LZO and CeO_2 buffer layers.

- 80 – 100 nm LZO barrier deposited in single coat on Y_2O_3/NiW
- CeO_2 cap layer deposited on LZO from $Ce(acac)_3$ precursor solution
- Both solution deposited buffer layers show single texture

CeO_2/LZO/Y_2O_3/Ni-W XRD

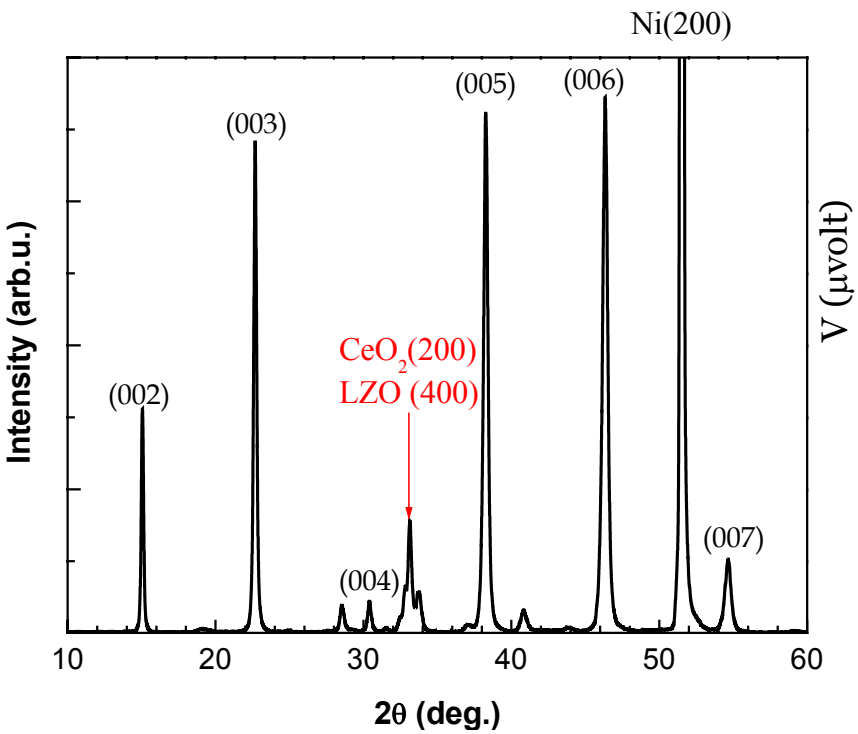


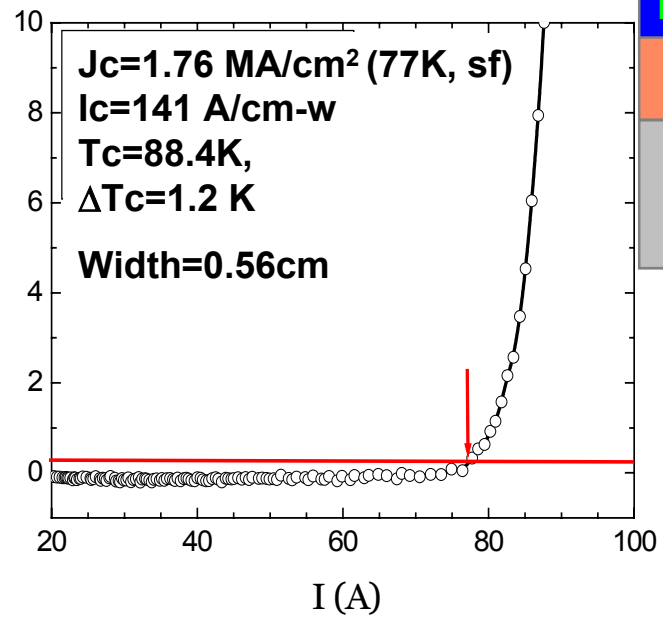
Textured MOD LZO barrier (~ 100 nm/coat) and MOD CeO_2 cap layers were deposited on Y_2O_3 seeds

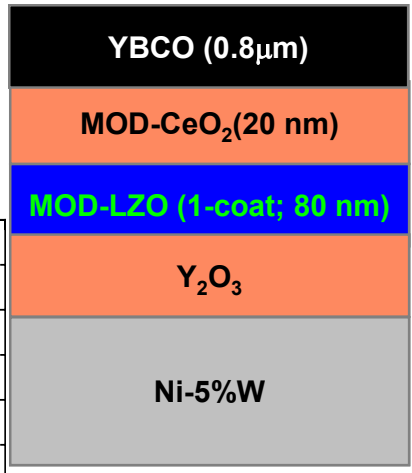
YBCO films deposited on MOD CeO_2/LZO buffer

J_c of up to 1.76 MA/cm^2 (141 A/cm-w)

TFA based YBCO nucleated and grows on MOD CeO_2 cap layer



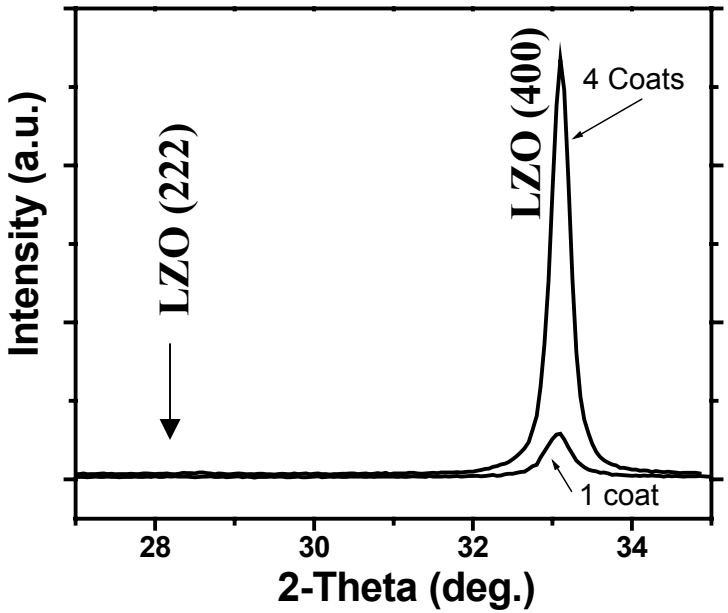




Proof-of-principle demonstration of a solution deposited barrier/cap buffer compatible with TFA based YBCO precursors

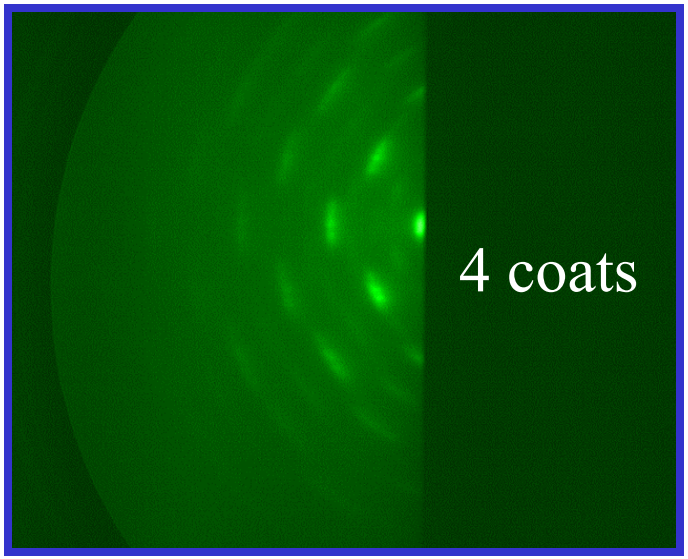
Thick LZO layer can function as seed/barrier replacement

80 nm LZO deposited in 4-coats on Ni-W substrate (in short lengths)

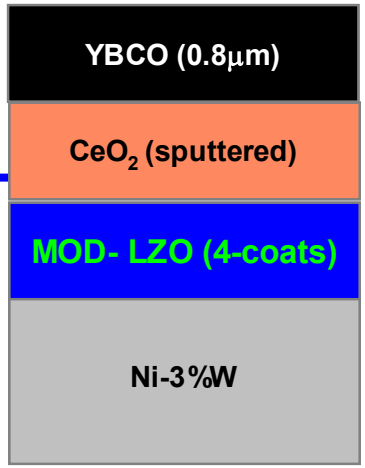


⇐ LZO grows with epitaxial texture

RHEED: no evidence of Polycrystalline LZO at the surface

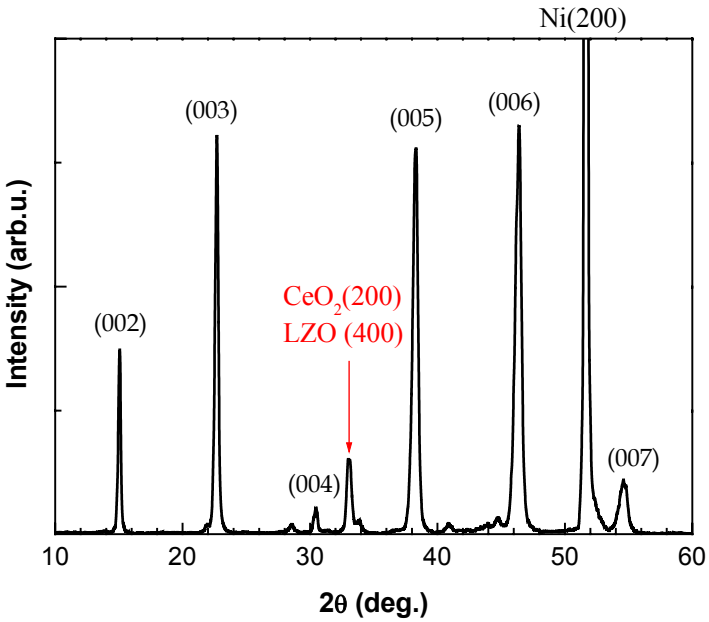


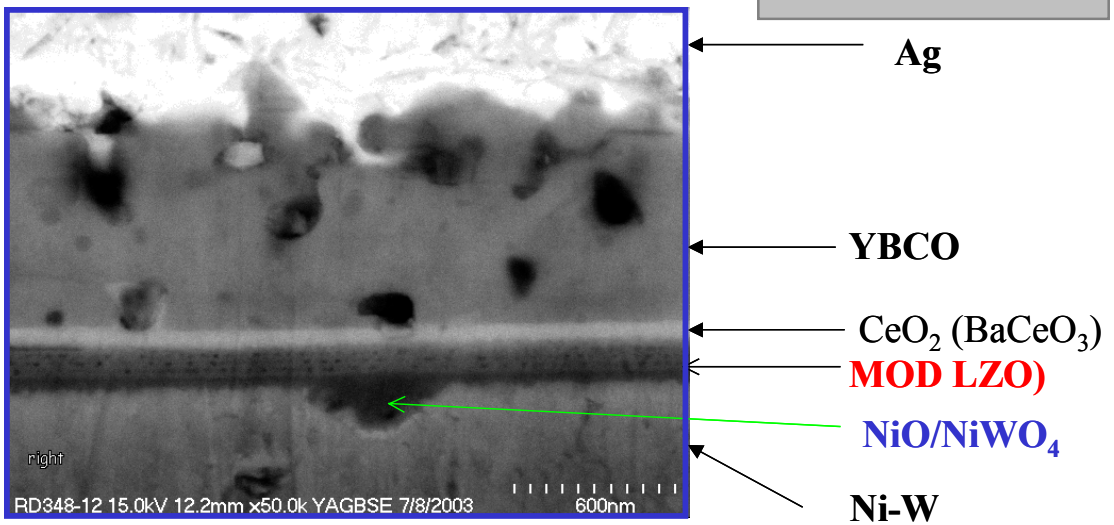
LZO seed/barrier tested with AMSC CeO_2/YBCO



CeO_2/YBCO grown epitaxial on LZO

J_c of 1.7 MA/cm^2 (135A/cm-w) (short sample, 77K, sf)





Oxygen/metal diffusion properties of 80 nm LZO seed/barrier appear acceptable – needs confirmation

Proof-of-principle demonstration of a solution deposited seed/barrier layer that supports high J_c YBCO films

Summary

- **Low-cost solution deposition of buffer layer proof-of-principle demonstrated for seed, barrier and cap layers**
- **Solution buffer layers compatible with AMSC's TFA-based YBCO deposition**
- **Champion performance of solution based buffers (short samples) is approaching that of AMSC's standard PVD buffers**
- **Remaining Issues**
  - Determining oxygen/metal diffusion properties of solution based buffers
  - Establishing reproducibility of solution based deposition process to yield high-J_c with no defects
  - Extending process to long length (10 meter) and evaluating defect and manufacturing issues
  - Detailed analysis of manufacturing cost relative to current PVD deposition processes

Successful development of solution based buffer deposition process represents a path to further reduction in cost of 2G wire

FY 2003 Performance

FY2003 Plans

- Jointly develop improved alloy substrates in long lengths
- Characterize the relationships between "texture" and "J_c," on AMSC substrates

FY2003 Performance

- ✓ Jointly developed Ni-W5% and Ni-Cr-W substrates with sharper texture and increased secondary recrystallization temperature.
- ✓ Mapped process space to allow precise control of alloy texture evolution in long length manufacturing process
- ✓ True in-plane improved to FWHM of 3-4°
- ✓ Correlated the J_c of MOD YBCO/RABiTS tapes with grain boundary networks of buffer/substrate.
- ✓ Established that controlled changes in annealing conditions modify the grain boundary networks
- ✓ Grain boundary networks are modified in epitaxial buffer layers on metal tapes

FY 2003 Performance Cont'd.

FY2003 Plans (cont'd)

- Develop simpler, faster, lower-cost, alternate buffer layer architectures that are compatible with the TFA-YBCO process

FY2003 Performance

- ✓ MOD $La_2Zr_2O_7$ and CeO_2 evaluated as potential buffer layers
- ✓ 80- 100 nm LZO deposited in a single coat directly on NiW
- ✓ Demonstrated MOD of CeO_2 cap that are compatible with the TFA-YBCO
- ✓ Proof-of-principle of MOD LZO as seed/barrier layer demonstrated
- ✓ High I_c/J_c MOD YBCO demonstrated on MOD buffers
  - I_c of 184 A/cm-w on MOD LZO seeds
  - I_c of 141 A/cm-w on MOD LZO barrier and CeO_2 cap
  - I_c of 135 A/cm-w on MOD LZO seed and barrier

FY 2003 Performance Cont'd.

FY2003 Plans (cont'd)	FY2003 Performance
• Develop methods to fully characterize the properties of barrier layers using microstructural techniques	✓ Developed appropriate methodologies and improved materials science understanding of buffer layer characteristics ✓ AMSC is utilizing improved understanding of the RABiTS template in the 2G wire process
• Characterize AC losses in AMSC YBCO on RABiTS	✓ AC losses on AMSC 2G tape were measured ✓ AC losses of 2G wire are acceptable for cable and most coil applications

FY 2003 Performance Cont'd.

FY2003 Plans (cont'd)

- Assist AMSC to demonstrate a high performance, 10-m, continuously processed YBCO tape on RABiTS, fabricated via reel-to-reel processing at all steps

FY2003 Performance

- ✓ AMSC's wire carried an I_c (critical current) of over 100 Amps per centimeter of width over 10 meters. (October 29, 2002).
- ✓ This was the first demonstration of the Long-Length Second Generation HTS Wire Goal Set by U.S. Department of Energy.
- ✓ AMSC' wire now has an I_c of over 180 A/cm in 10 meter lengths.
- ✓ AMSC's 2G wire is hermetic and robust with excellent thermal cycling stability.
- ✓ Conductor development in the ORNL AMSC CRADA has led to the world's first demonstration of 1.25 meter long YBCO cable carrying an I_c of > 4000 A.

FY 2004 Plans

- Assist AMSC in producing pilot line quality (10cm wide by 100m long) alloy substrates using the ORNL rolling mill facility with clean room
- Demonstrate scalability of continuous processing of the MOD-YBCO on RABiTS through implementation of 4 cm wide process
- Assist AMSC in producing 20 meter lengths of 2G wire with an I_c of 250 A/cm from the 4cm wide manufacturing process
- Demonstrate a low-cost (MOD buffer deposition) in 1-10 m lengths with I_c, mechanical properties and diffusion properties comparable to AMSC PVD buffer stack
- Optimize buffer layer stack for long length production of YBCO coated conductors
- Further correlate "texture" to J_c to facilitate the improvement of the texture of AMSC alloy substrates. Analyze the importance of out-of-plane misorientations with respect to J_c.

Research Integration

- Weekly teleconferences
- CRADA meetings at AMSC and ORNL
- Personnel exchange – use of ORNL ACCL facilities by AMSC staff
- Several joint publications
- Joint invention disclosures
- Many joint presentations

This is an intrinsically integrated project between ORNL and American Superconductor Corporation