BSCCO 2212 precursor at Nexans:

Current Status and Further Development within EuCARD2

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Outline

- Requirements on Precursor for Ag-sheathed Bi2212 conductors
- Bi2212 precursor technology at Nexans
  - Equilibrium Precursor: Development, Current Status, and Quality
- Major Open Issues
  - Granulated versus Powdered Precursor
  - Optimum cation composition and optimum O contents
- Work within EUCARD2
  - Supplying high-quality precursor to OST.
  - Optimize granulated precursor

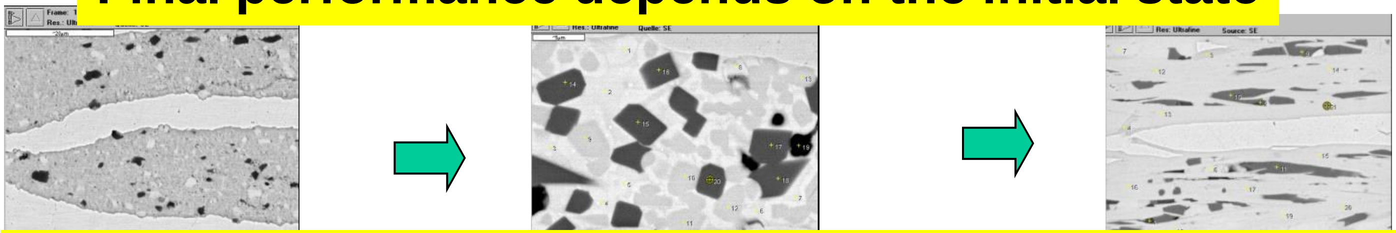
    density homogeneity in granulate; optimum particle size window
  - Optimizing composition including O contents as variable
  - Stabilizing the industrial process for optimum composition

Requirements on Bi2212 precursor

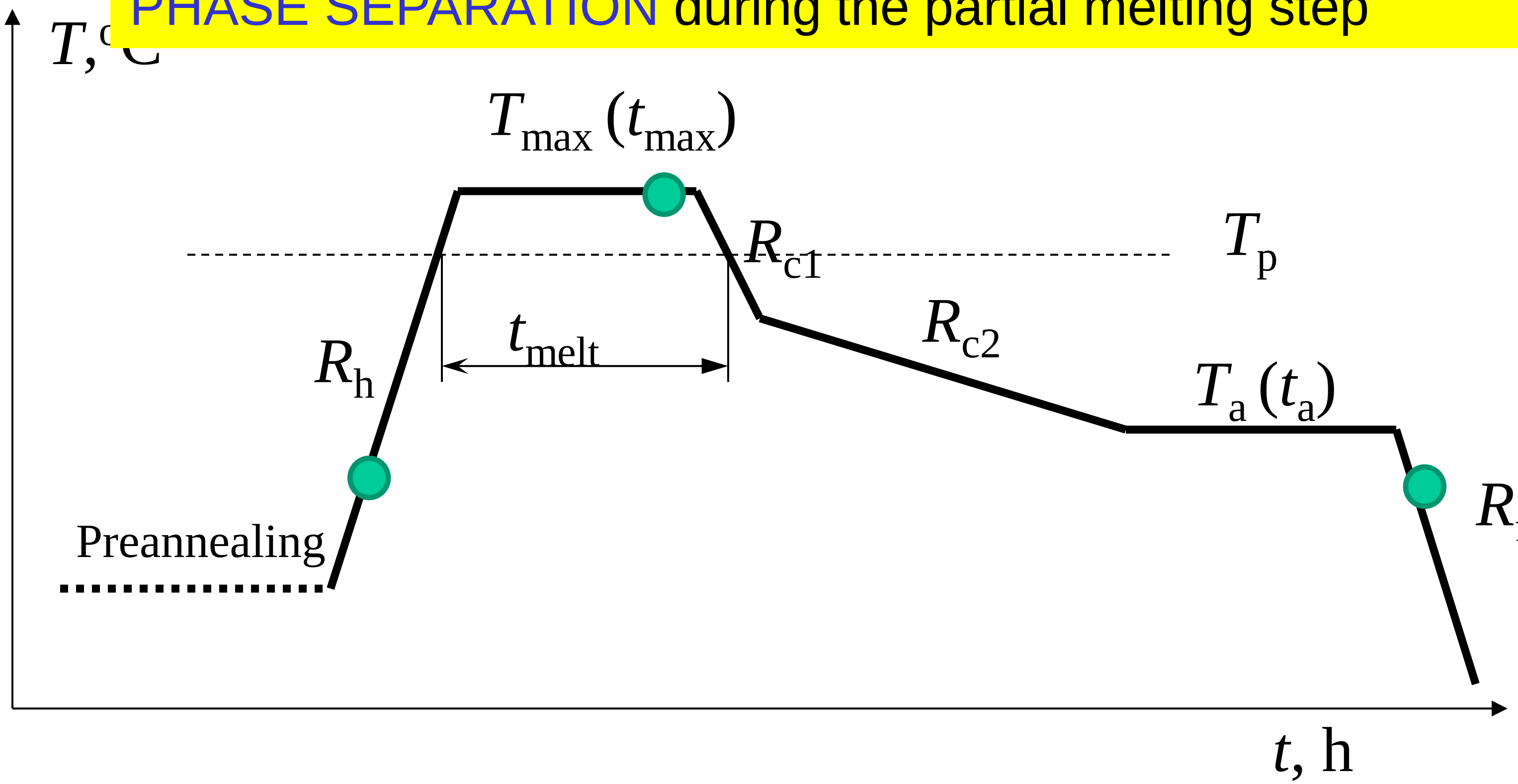
- General for OPIT process
  - Homogeneity
  - Size of hard particles much smaller than filament size
  - Filling / Tapping density to ensure necessray fill factors
  - Flowability……
- Specific for Partial Melt Processing of Bi2212
  - Low C and H_2O contents to avoid bubbling
  - Equilibration state :

Why Precursor matters for Bi2212 Partial Melt Processing ?

Final performance depends on the initial state



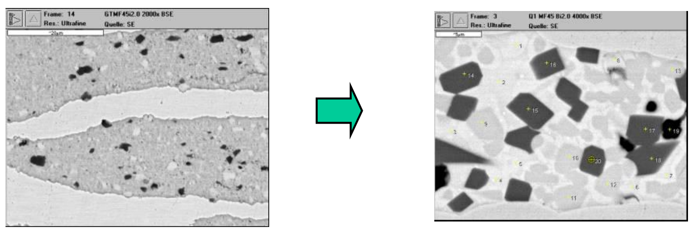
The initial state of precursor predetermines the extent of PHASE SEPARATION during the partial melting step



Requirements on Bi2212 precursor

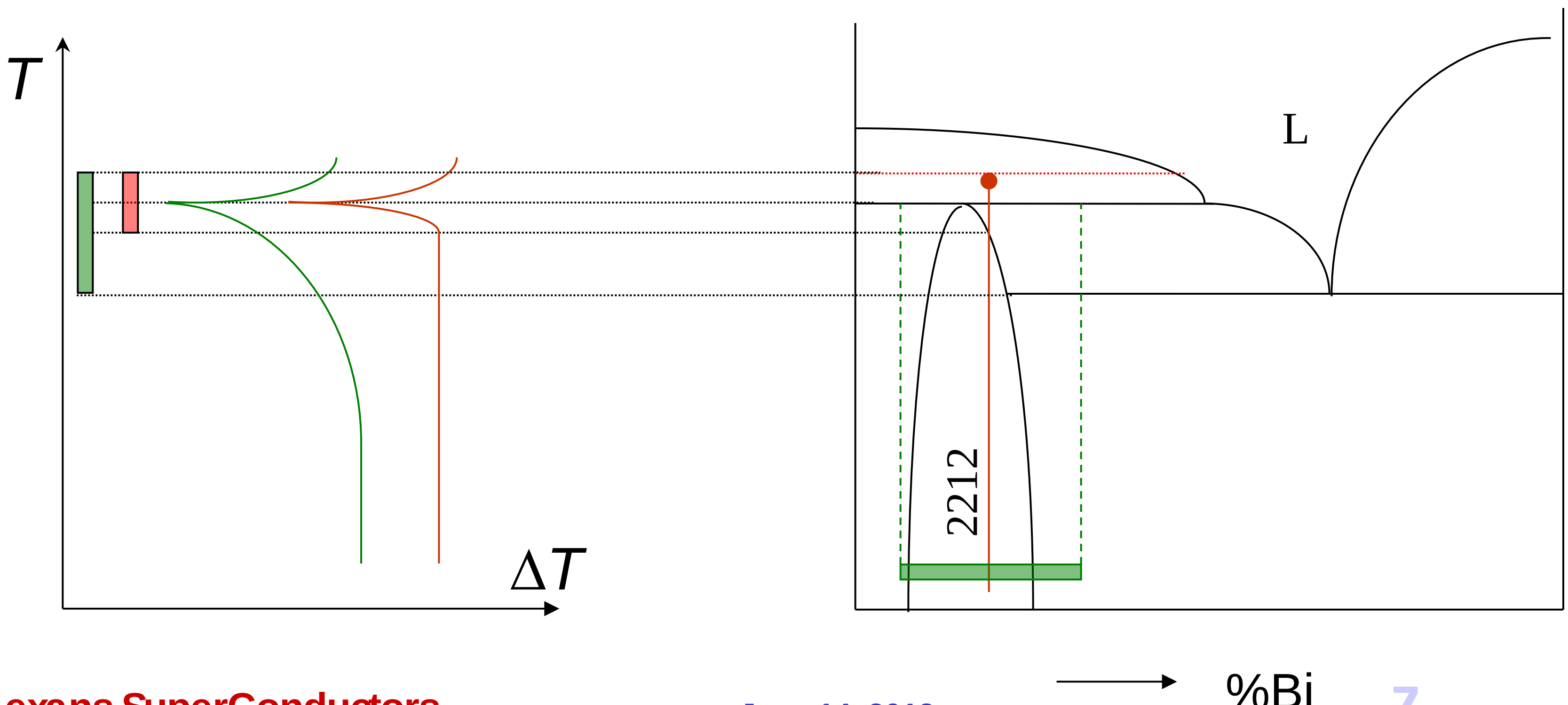
- General for OPIT process
  - Homogeneity
  - Size of hard particles much smaller than filament size
  - Filling / Tapping density
  - Flowability……
- Specific for Partial Melt Processing of Bi2212
  - C contents
  - Equilibration state that minimizes
    PHASE SEPARATION during partial melting
  - .

Concept of EQUILIBRIUM precursor



Minimize PHASE SEPARATION by
- choosing proper composition;
- making precursor as close

to **EQUILIBRIUM** as possible



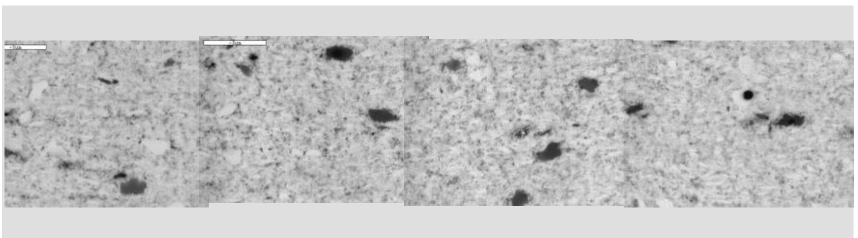
Equilibrium vs Non-Equilibrium Precursors: 1. Proof-of-Principle

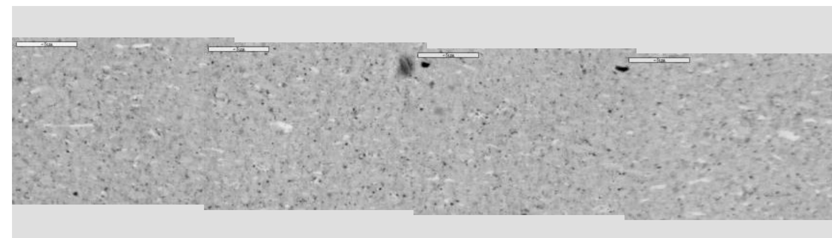
Equilibrium

Green Tapes

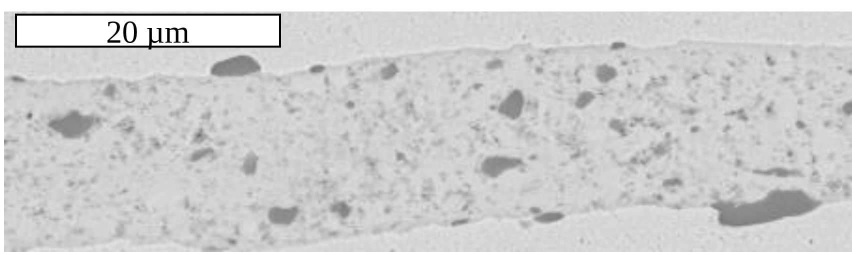
Non-Equilibrium

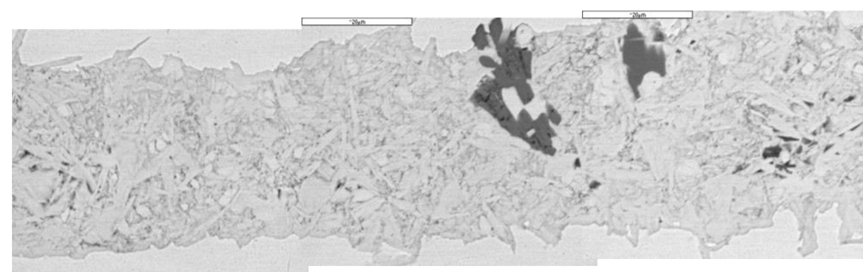
looks more uniform in the Green tape





Tapes after heating close to melting (864°C)



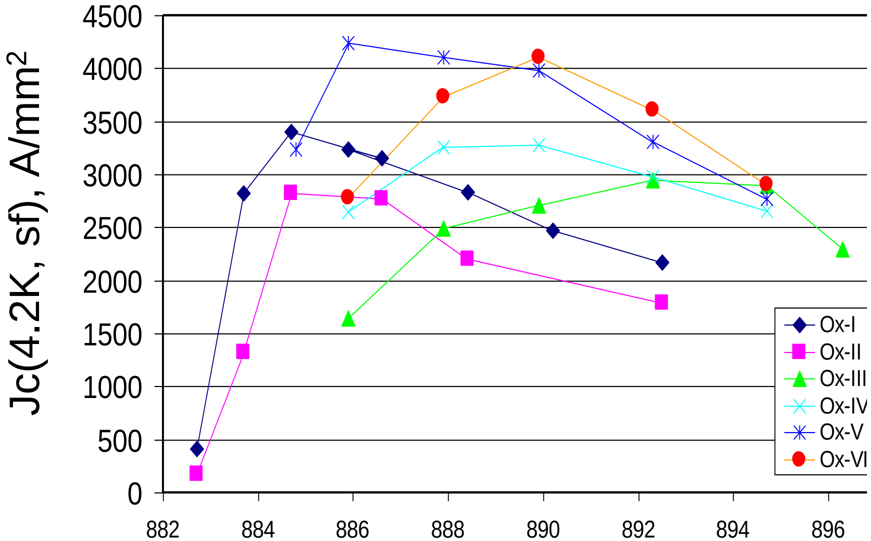


is more uniform close to melting

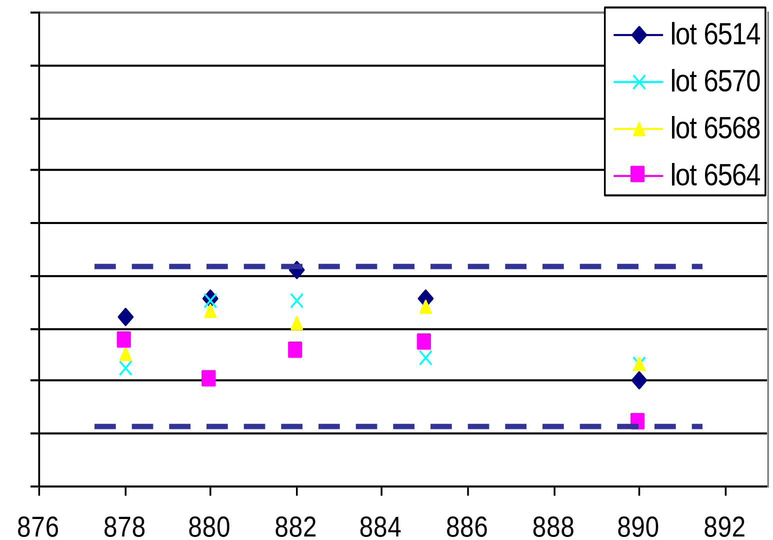
Equilibrium vs Non-Equilibrium Precursors: 2. Jc (OST results 2002-2003)

A factor of 3 better performance (dip-coated tapes)

Dip Coated Jc optimization in Nexans Equilibrium Lots



non - Equilibrium powder evaluation



OXFORD INSTRUMENTS

Superconducting Technology

Equilibrium vs Non-Equilibrium Precursors:
3. Reproducibility in short samples

NIMS dip-coated Tapes
Postannealed at 300°C

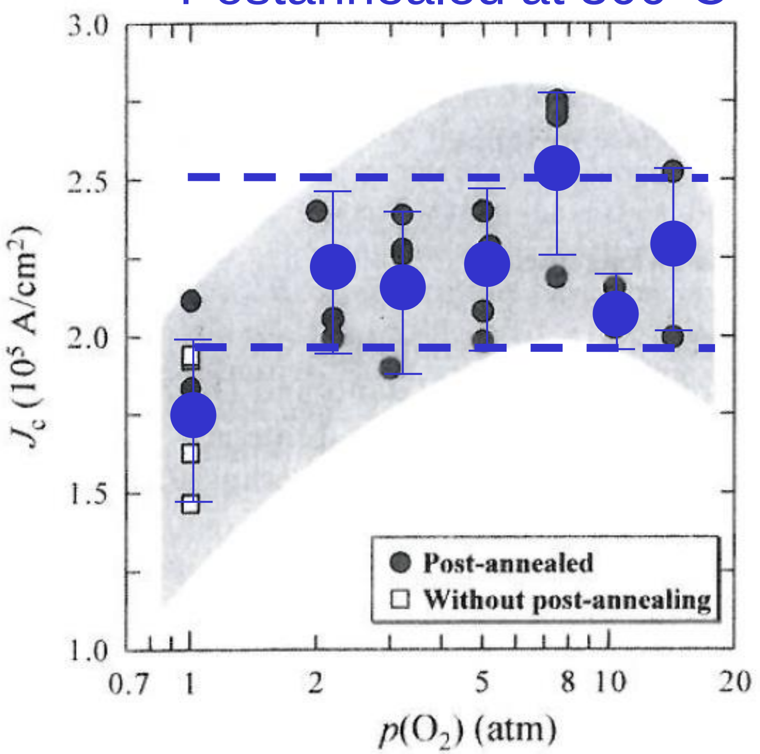
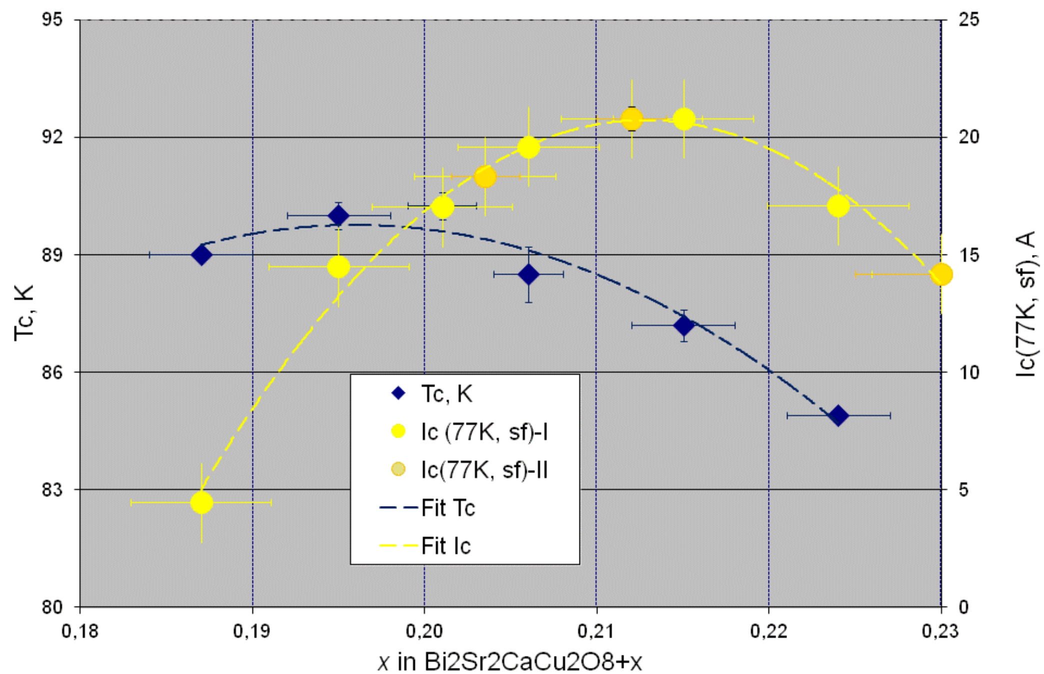


Fig. 2. Correlation between the $p(O_2)$ at the post-annealing process and the J_c value in 10 T at 4.2 K.

Nakane et al (2004), Physica C 412-414, 1163-6

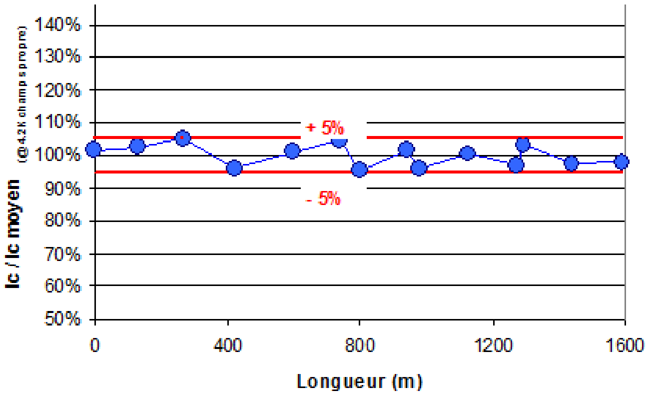
OST wire PMM110106

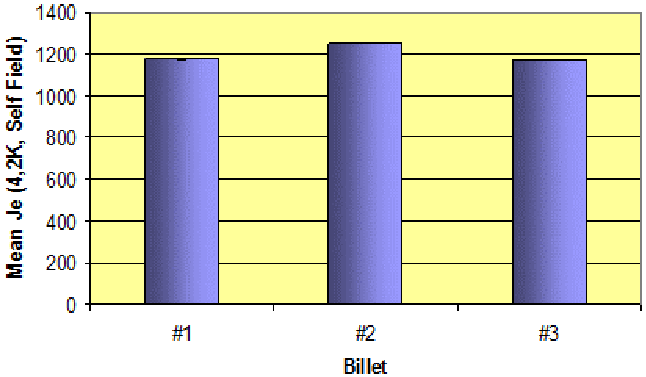


Rikel et al (2012) ASC, Portland

Equilibrium vs Non-Equilibrium Precursors:
4. Industrial Reproducibility

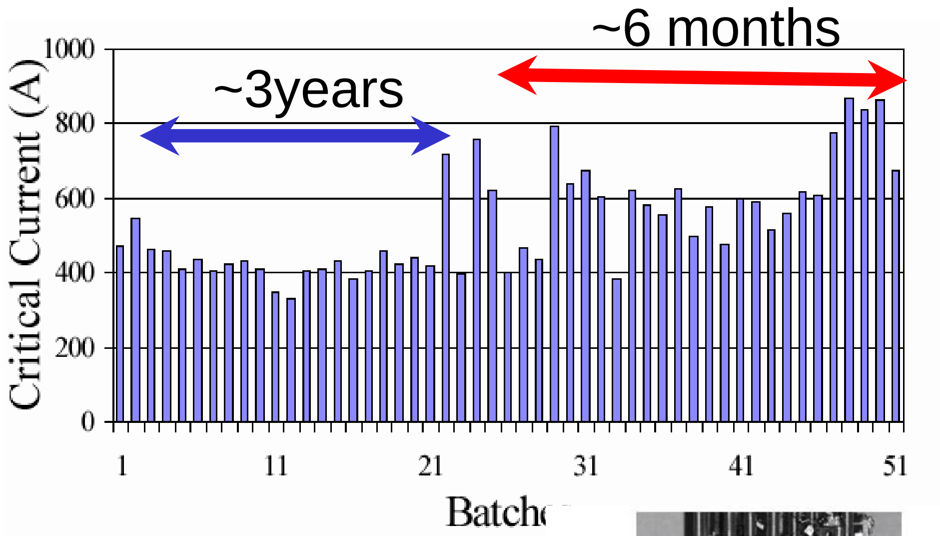
Nexans experience





C.E.Bruzek et al EUCAS 2003
ASC 2004

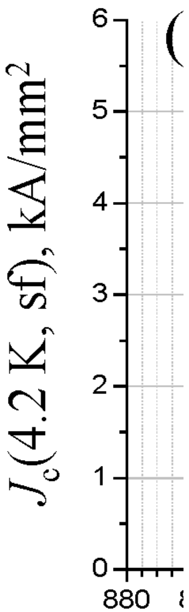
OST experience

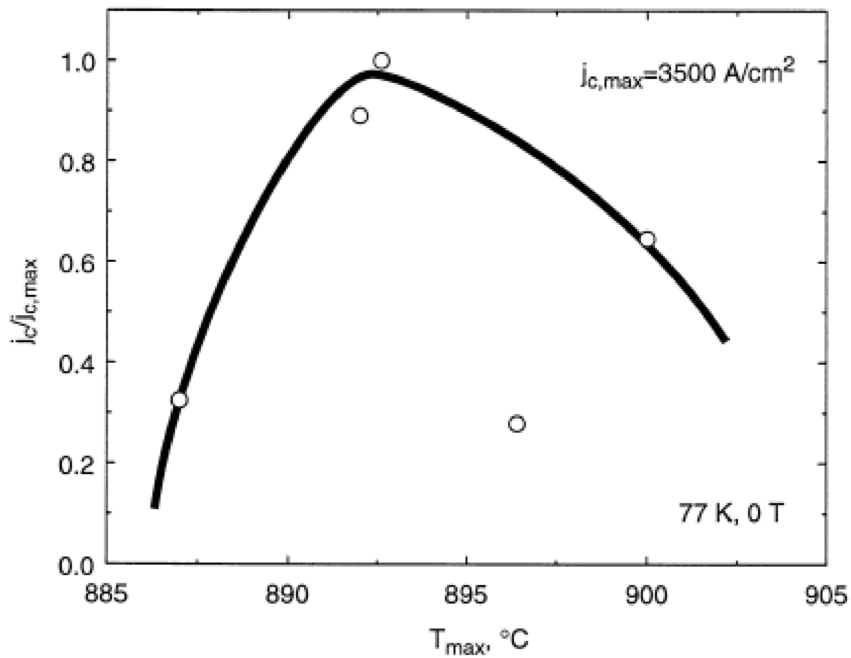


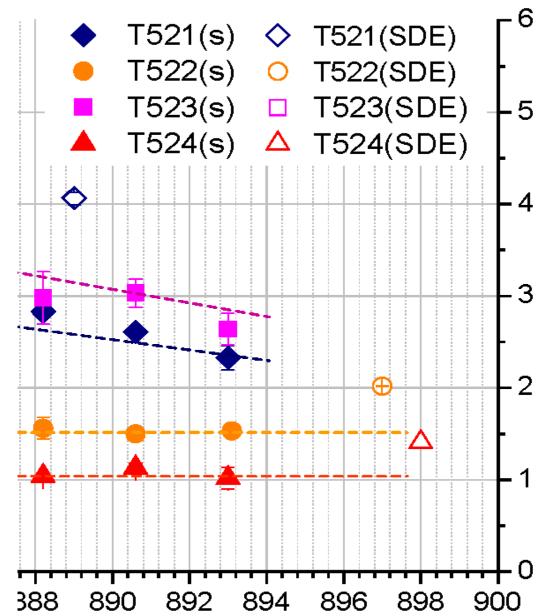
K. R. Marken et al,
ICMC 2003

FIGURE 2. The 5 tesla insert magnet which achieved 25 T central field.

Equilibrium vs Non-Equilibrium Precursors: 5. Step like Jc vs Tm



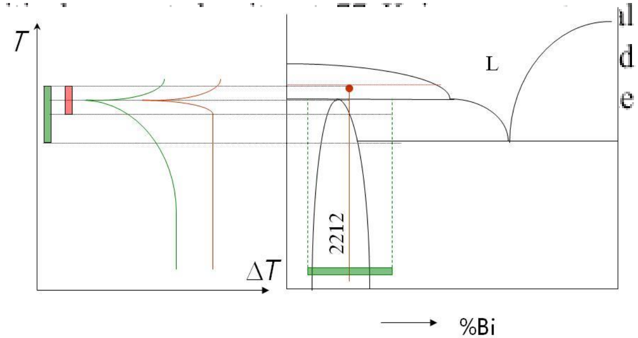




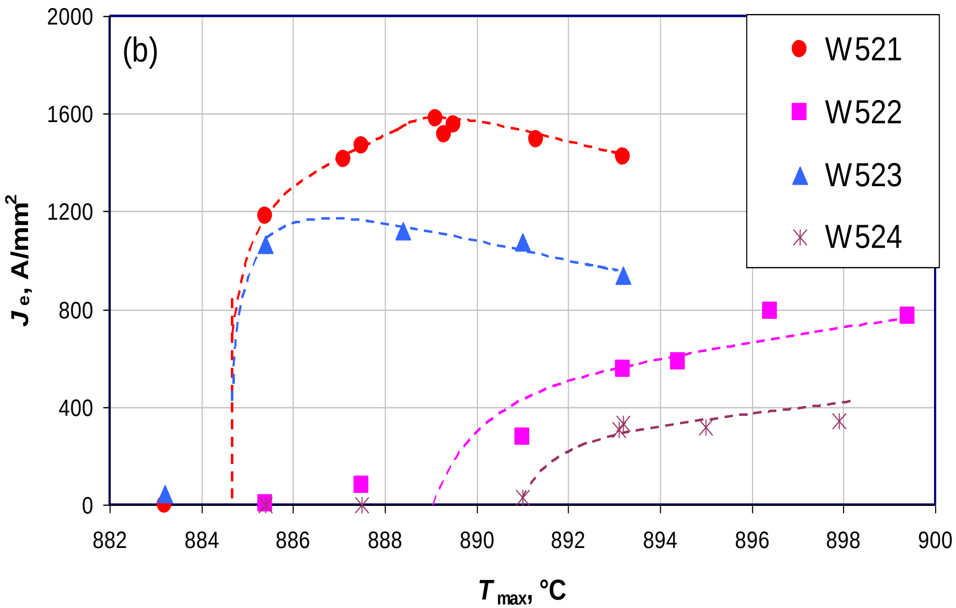
- Very uniform distribution of melting point over macroscopic lengths

Fig. 2. Influence of the maximum processing temperature T_{max} on
the normalized c
field of fully proc
in the same fur
maximum j_c was

Lang et al

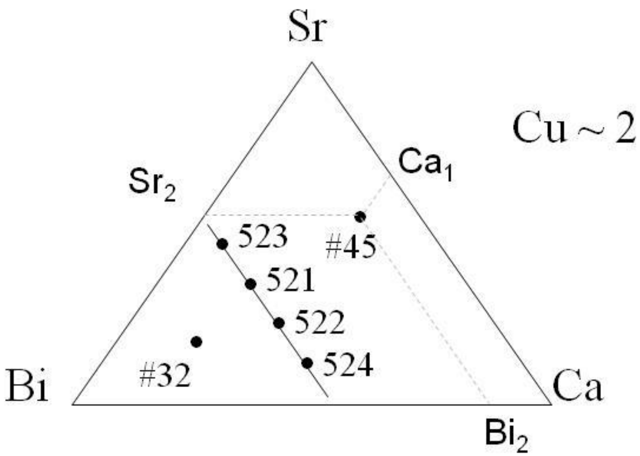


Equilibrium vs Non-Equilibrium Precursors.
6. Effect of Cation Composition



W521-524 2.14 : (2.86–*x*) : *x* :2.00

Sr/Ca = 2.25, 2.18, 1.75, 1.34



H. Miao et al 2006 *Adv Cryo Eng*. **52B**, p. 673, (2006) [Proc. ICMC 2005]
M. Rikel et al 2006 *J Phys: Conf Ser.*, **43** (2006) 51–54 [Proc. EUCAS 2005]

- Why overall composition of Bi2212 has such a strong effect on performance of round wires and tapes ?

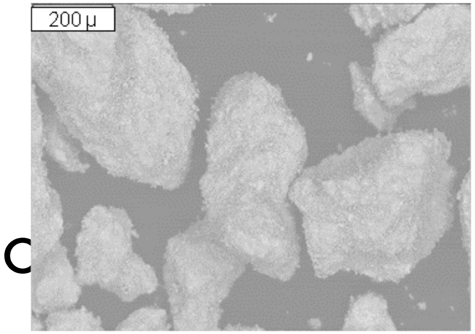
Equilibrium Precursor Technology (EP 1 659 104 B1)

- Characterization // Conditioning of Raw Materials
- Mixing oxides
- Melt Casting oxide mixtures

  Melt Quenching // Spray drying
- Thermomechanical processing to reach equilibrium and control size of second phases

  Annealing – Jet Milling – Compacting – Annealing – ....
- Final Product:
  - Powder or Pressed Rods
  - Granulate

Granulated Precursor



- Introduced to solve the problem of high C contents

  can be annealed at higher T than powder to decompose SrCO

- Advantages

  > Lower C contents attainable

  > Fill factors intermediate between powder and rods

  > Flowability better than that of powder

  > Easy filling the billets (no sticking to tools)

  > Better Jc achieved by Nexans (France & Korea), Supercon, Supramagnetics, but

  not OST, where Jc were in average ~10% worse.

Precursor Technology Development

- Equilibrium Rods/Powder (2002-2004)
  - Nexans SMES project (~ 400 kg precursor)
  - OST 25 T magnet project + R&D (~50 kg)
- Collaboration with OST on optimizing precursor composition (2004-2005)
  - $Bi_{2.17}Sr_{1.94}Ca_{0.89}Cu_{2.00}$ cation composition (Lot 521) = Nexans Standard
- Granulated Precursor (2005-2006)

Quality Control

Attribute	Target Levels	Test
Cation Composition	Bi : Sr : Ca : Cu 2.16 : 1.95 : 0.89 : 2.00 ± 0.03 : 0.03 : 0.015: 0.03	**XFA**
Cation Impurities	H: < 50 ppm Fe: < 50 ppm (?) Zn: < 20 ppm	**IR for H** **ICP**
Carbon	20 - 50 ppm for granulate 50-150 ppm for powder	IR Leco
Grain Size d: 10, 50, 90	d10 < 0.5 µm; d50 < 2 µm; d90 < 5 µm	Laser granulometry
Fill density : g/cm^3	1.5 (powder) to 1.9-2.5 (granulate)	weight
Melting Temperature, with Ag	Onset in 100% O2: 883 ±2°C	DTA/TGA
Phase State	Phase composition should correspond to equilibrium state for a given overall composition	2theta XRD Rietveld Refinement
Extent of equilibration	Fraction of intergrowths in 2212 phase < 1%	2theta XRD
Particle size (granulate)	100-500 µm (empirical)	sieving
Storage and shipment	Dry, < 10^{-5} at static P_{H2O}, P_{CO2}	Monitor & record: sensors

Questions to be addressed

Attribute	Target Levels	Test
Cation Composition	Bi : Sr : Ca : Cu 2.16 : 1.95 : 0.89 : 2.00 ± 0.03 : 0.03 : 0.015: 0.03 Is this sufficient?	**XFA**
Cation Impurities	H: < 50 ppm Fe: < 50 ppm (?) Zn: < 20 ppm	**IR for H** **ICP**
Carbon	20 - 50 ppm for granulate 50-150 ppm for powder	IR Leco
Grain Size d: 10, 50, 90	d10 < 0.5 µm; d50 < 2 µm; d90 < 5 µm	Laser granulometry
Fill density : g/cm^3	1.5±0.2 (powder) to 1.8-2.5 (granulate)	weight
Melting Temperature, with Ag	Onset in 100% O2: 883 ±2°C How to control low temperature event?	DTA/TGA
Phase State	Phase composition should correspond to equilibrium state for a given overall composition	2theta XRD Rietveld Refinement
Extent of equilibration	Fraction of intergrowths in 2212 phase < 1% ?	2theta XRD
Particle size (granulate)	Particle size window	Sieving, OM, SEM
Storage and shipment	Dry, < 10^{-5} at ? static P_{H2O}, P_{CO2}	Monitor & record: sensors

Major Issues

- Requirements on Precursor for Ag-sheathed Bi2212 conductors
- Bi2212 precursor technology at Nexans
  - Equilibrium Precursor: Development, Current Status, and Quality
- Granulated versus Powdered Precursor
- Optimum cation composition and optimum O contents
- Work within EUCARD2
  - Supplying high-quality precursor to OST.
  - Optimize granulated precursor
  - optimum particle size window; density homogeneity in granulate
  - Optimizing composition including O contents as variable
  - Stabilizing the industrial process for optimum composition

Outline

- Requirements on Precursor for Ag-sheathed Bi2212 conductors
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    density homogeneity in granulate; optimum particle size window.
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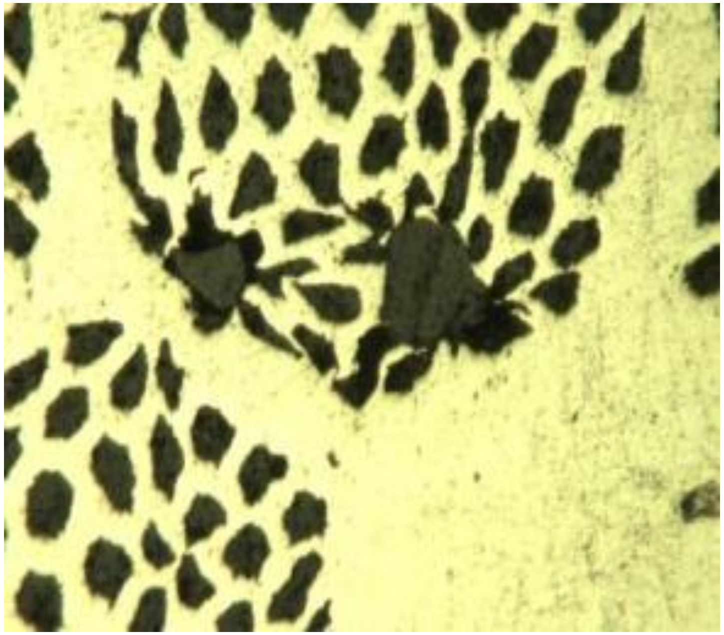
Why Granulated Precursor shows 10% worse perfromance? New Data from OST



- Hard Bi2212 particles forming when drawing wires made using granulates 78 and 80 (small powder batches), but not 77 (large batch)

Formation of Hard Particles. Two Hypotheses

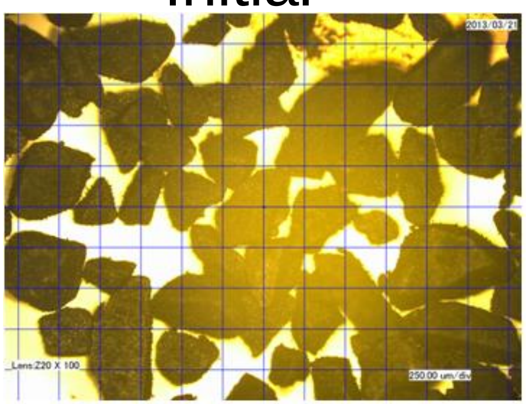
Formation of hard particles may stem from too broad particle size distribution or reflect density inhomogeneity in the granules due to

- using different compacting technologies
- multiple compaction steps necessary for the required yield when using small powder batches

- Quick test: Uniformity of granule response to small loads (1 to 50 bar)

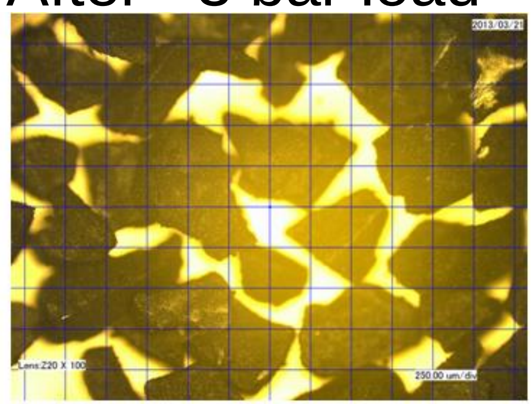
82215123121 (200-500 µm)

Initial



3 mm

After ~3 bar load

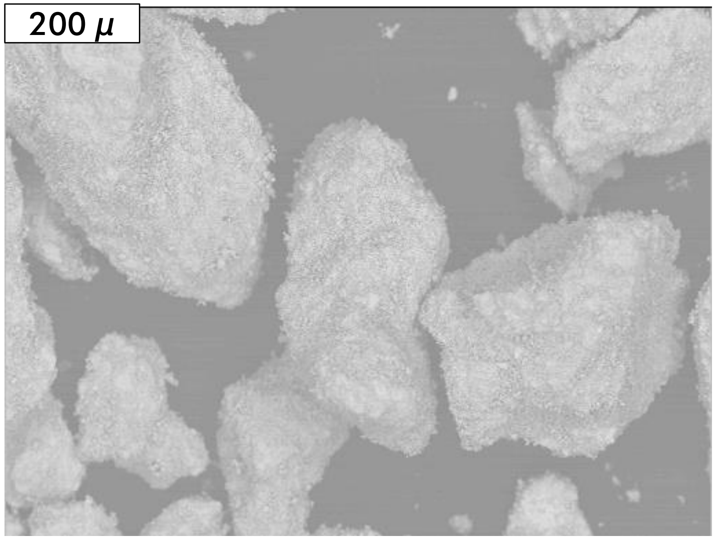


3 mm

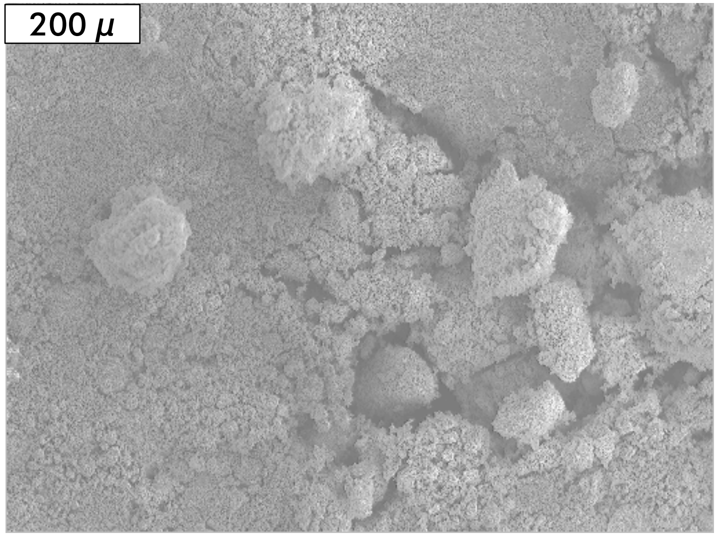
Response to small Loads. Lot 80.

8011322331 (100-500 µm)

Initial



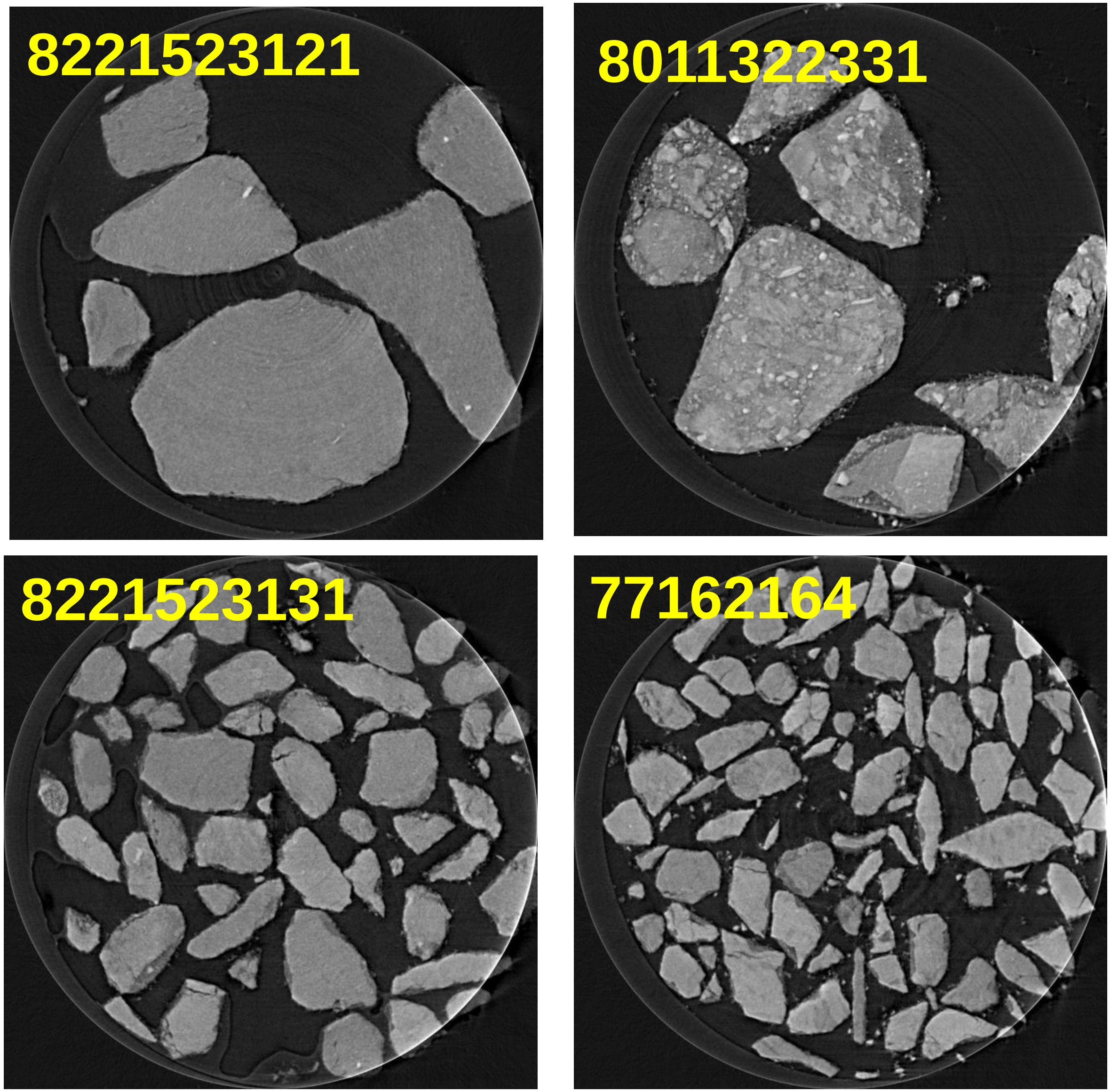
After ~3 bar load



- Old lot 80 seems less homogeneous than new lot 82

Nexans

Confirmation by μ-CT from ESRF



- Granulate 82 is much more homogeneous than 80 and even 77

- Inhomogeneity of lot 77 may come not from compacting but from exposure of the 3.5-year old material to environment

C. Scheuerlein et al (2013)

First Tasks within EUCARD2

Task 1. Production of BSCCO2212 precursor granulate

Subtask 1.1. Production

10 kg standard (521-like) composition

Subtask 1.2. Effect of particle size in the granulate on processing BSCCO2212 round wires

Goals:

- Optimize the particle size window

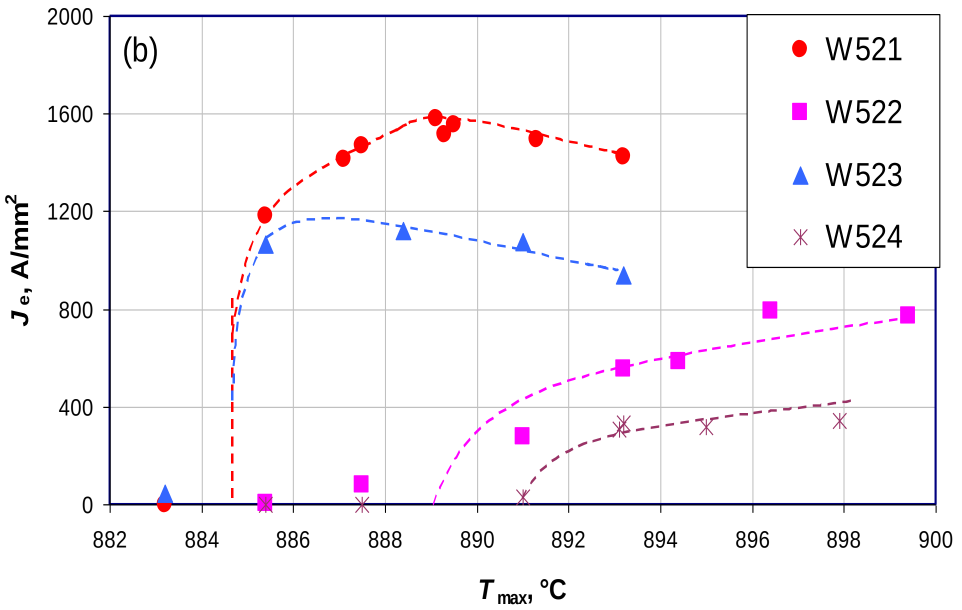
The precursor produced in subtask 1.1 will be classified in fractions with various particle size windows, e.g.,

- powder
- 200-500 µm [standard]
- 100 to 200 µm,
- 50 to 100 µm

Task 2. Compositional studies:

Subtask 2.1. Preliminary studies of BSCCO2212 bulk with various Sr/Ca ratio and O contents

Effect of Cation Composition on Wire Perfromance



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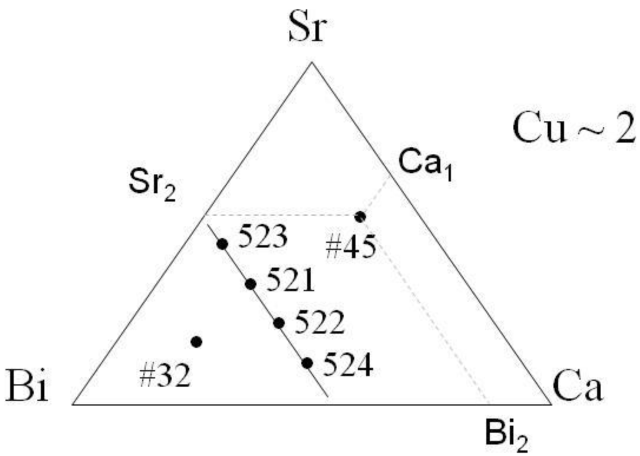

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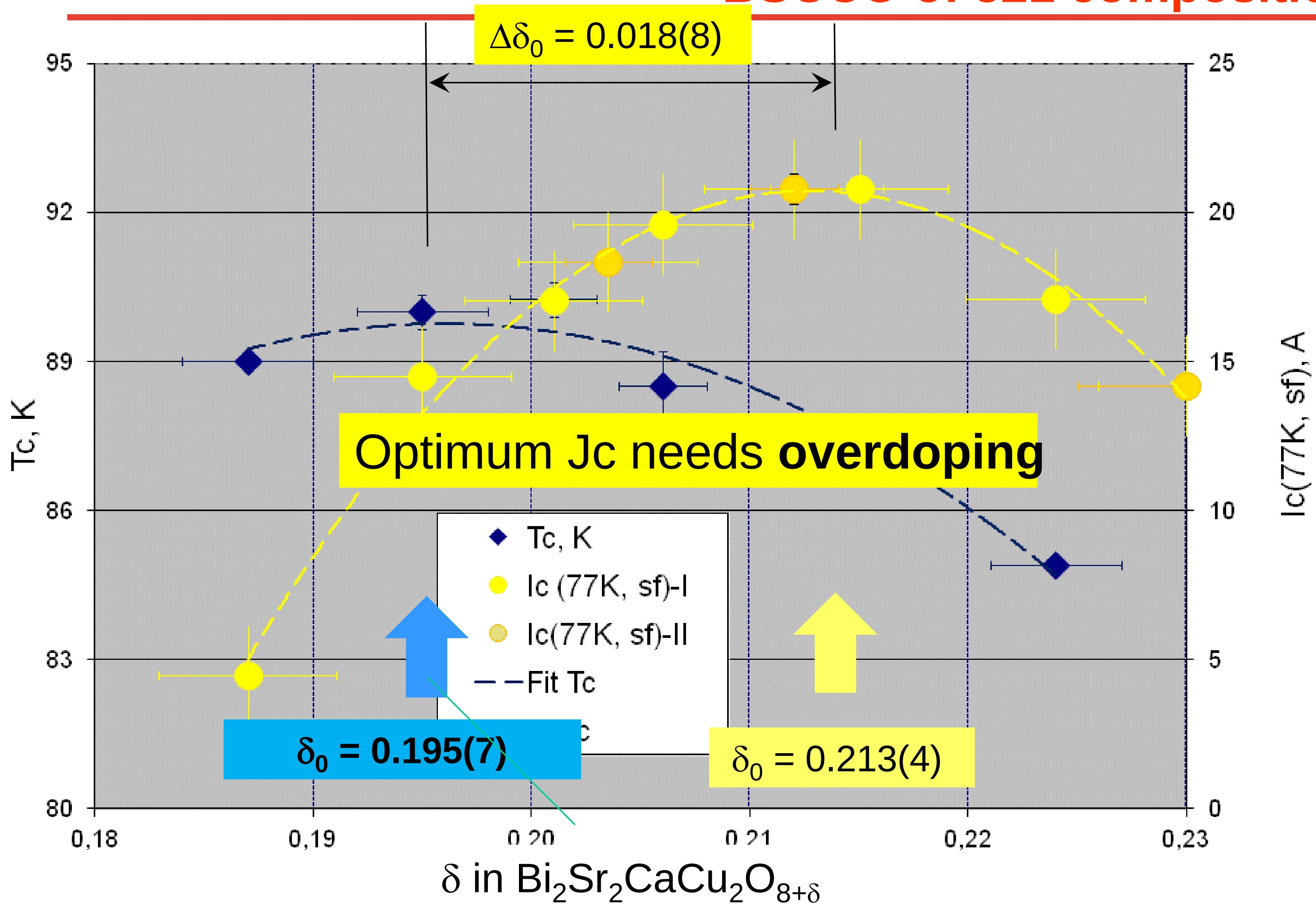
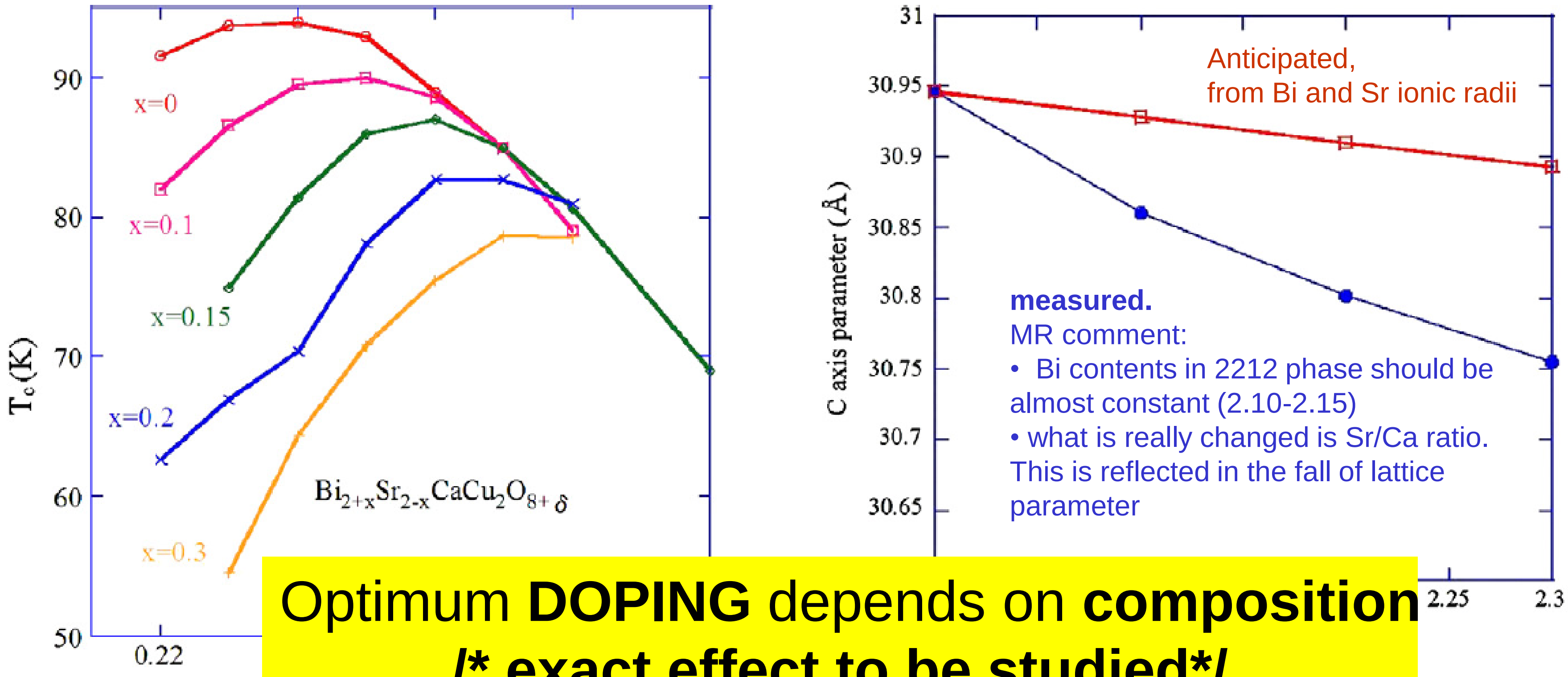
- Why overall composition of Bi2212 has such a strong effect on performance of round wires and tapes ?

Tc & Ic vs δ in OST RW BSCCO of 521 composition



Data of Yamashita et al (2010)

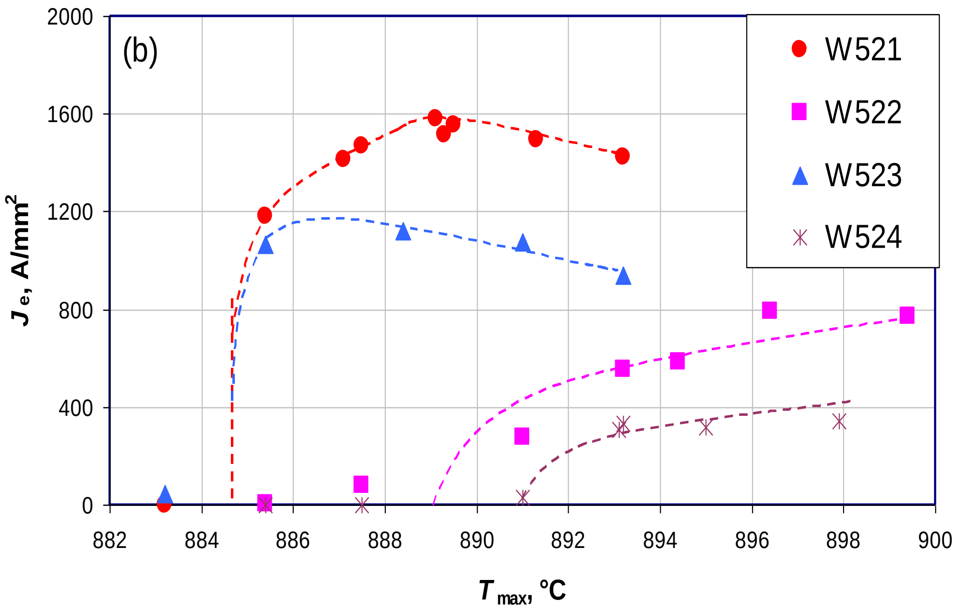
S. Yamashita et al. / Physica C 470 (2010) S170–S172 S171



Optimum DOPING depends on composition
/* exact effect to be studied*/

Yamashita et al (2010) studied single crystals grown from powders of $B_{i2+x}Sr_{2-x}Ca_1Cu_2$ cation compositions and annealed to have various O contents. They found that the crystals with smaller Sr/Ca ratio have maximum Tc at stronger overdoping levels. Though the real compositions were not measured, the Sr/Ca ratio in the 2212 phase should scale with that in the overall composition (Rikel et al 2006). Thus, our observation that maximum of Jc(δ) in round wires is at higher δ than in the bulk may stem from the difference in $T_c(\delta)$ for bulk (Sr/Ca = 2.45±0.02) and round wire (Sr/Ca = 2.20±0.03). We should first measure Tc of the wires.

Effect of Cation Composition on Wire Performance



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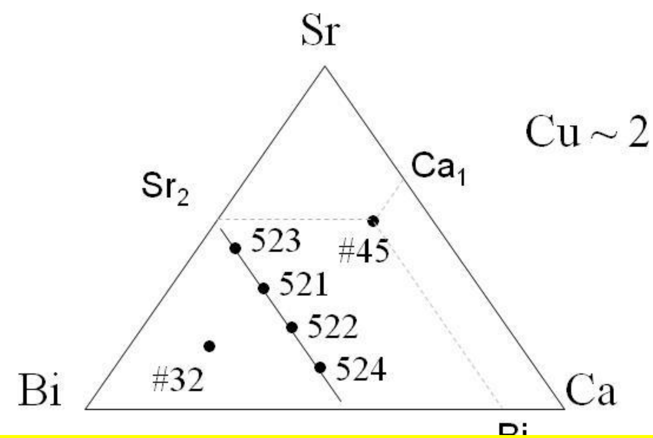

What is the contribution of O doping level in the Jc difference ?

M. Rikel et al 2006 *J Phys: Conf Ser.*, **43** (2006) 51–54 [Proc. EUCAS 2005]

- Why overall composition of Bi2212 has such a strong effect on performance of round wires and tapes ?

Preliminary Compositional Studies of Bulk Samples. Current Status and Nearest Plans

- Bulk rods (5 and 8 mm diameter) of $Bi_{2.15}Sr_{2.85-x}Ca_xCu_{2.00}O_{8+\delta}$ compositions Melt Cast

Sr/Ca	x(*)	$\delta_{optimum}$ for	
		Tc[(a)]	Jc(77 K,sf)
2.47	0.82	0.190(5)	0.203(3)
2.18	0.90	0.195(7)	0.214(3)
1.76	1.03	0.225	?
1.34	1.22	0.240	?

(*) will be checked by XFA after homogenization

  - DTA/TGA done. Heat Treatment designed. Samples processed
  - XRD and SEM/EDX in progress
- Dip-Coated Tapes 521-524 (from OST and NSC) sent to FNAL (Tengming Shen) for Partial Melt Processing
- Samples, Bulk Rods & Tapes (if possible) will be annealed at NSC to vary δ from 0.180 to 0.250
- Tc & M(T,B) will be studied to choose NEW COMPOSITION for testing in wire

Major Plans within EUCARD2

- Supplying high-quality precursor to OST
- Optimizing composition including O contents as variable
- Stabilizing the industrial process for optimum composition

Thank you