EUROPEAN PROGRESS TOWARD NANOSTRUCTURE ENGINEERING IN COATED CONDUCTORS

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EUROTAPES collaborative project
(European development of Superconducting Tapes: integrating novel materials and architectures into cost effective processes for power applications and magnets)
Nanotechnology engineering enables to improve ReBCO CC performance

Main Goal

Optimize the pining centres according the specific working conditions \((H,T)\) for CC applications

Applications requiring \(J_c > 10^4 \text{ A cm}^2\) for various superconducting tapes and wires [Shimoyama, SUST 27 (2014)]
Nanocomposite YBCO films and CCs and their final nano-structure deeply differs depending on:

- Growth technique ⇒ Simultaneous or deferred nucleation
- Growth conditions (Rate, Temperature, …)
- Chemistry of secondary phase (or mixed additions)
- % addition
- Substrate

- Strain with the Matrix (Epitaxial or randomly)
- Geometry (nano-rods, nano-particles, …)
- Size, distribution
- Shape / orientation (correlated, isotropic) / size / distribution

Superposition of different dimensionalities in a single material
VORTEX PINNING IN YBCO NANOCOMPOSITES: ANISOTROPY

In field angular $J_c(\theta)$ dependence

$$J_c = J_c^{H/c}(\sin^2\theta/\gamma^2 + \cos^2\theta)$$

Anisotropy of $J_c$ in high $H$ even at $T$ is one of key issue

CSD Nanocomposites with random NP

Nanostrain $\Rightarrow$ quasi-isotropic vortex-pinning with a highly reduced $\gamma_{eff} \sim 1.5 - 2$

PLD Nanocomposites $\Rightarrow$

Mixed Nanocomposites
Tuning the growing conditions

Combination of correlated defects along the c axis and ab-planes

Ercolano et al. SUST 24 (2011)

Llordes, Palau et al. Nat. Mat. 11 (2012)
Single vortex pinning

$E_{\text{int vortex-defect}} > E_{\text{int vortex-vortex}}$

Collective pinning

$E_{\text{int vortex-vortex}}$
**Temperature $J_c(T)$ dependence**

Vortex pinning efficiency at different field / temperatures can be correlated with the nanoscale defect structure.

### Anisotropic strong
- Intrinsic Pinning ($\parallel$ab)
- Stacking faults ($\parallel$ab)
- Twin boundaries ($\parallel$c)
- Dislocations

### Isotropic strong
- Nano-strain

### Isotropic weak
- Point defects
- Oxygen vacancies

Quantify pinning strength and energies associated to different pinning centres

- $J_c^{str}(0), J_c^{wk}(0)$ → strength, density of defects
- $T^*, T_0$ → thermal activation

characteristic vortex pinning energy for each defect

- Anisotropic $T^* \sim 90K$
- Iso-strong $T^* \sim 70K$
- Iso-weak $T_0 \sim 10K$

All three contribute, Isotropic-weak has some relevance

Combination of anisotropic and Isotropic-strong

Anisotropic pinning becomes dominant

VORTEX DYNAMICS IN YBCO NANOCOMPOSITES: CREEP

Vortex Creep

Transport measurements

In general $N \propto J_c$ (intrinsic pinning)

Inverse correlation $J_c \propto 1/N$ at $H//ab$

Range where intrinsic pinning is dominant \(\Rightarrow\) Loss in $U_p$ due to the formation of double kink excitations

Blatter et al. RMP 66 (1994)

Relaxation measurements

Large peak in $S(T)$ observed in YBCO films with parallel columnar defects \(\Rightarrow\) easy expansion of double kinks between adjacent defects

Maiorov et al. Nat Mat. 8 (2009)

Double King formation in correlated defects must be avoid

- $H//ab \Rightarrow$ Intrinsic pinning
- $H//c \Rightarrow$ straight correlated defects, twin boundaries
Defect structure must be engineered according to the operating $H$-$T$ range and considering **vortex pinning & dynamics**

⇒ Mixed microstructure with synergetic vortex pinning centers may good for a wide range of temperature and field
Simultaneous deposition and growth

Self-assembled perovskites

\[ \text{BaZrO}_3 \text{ (BZO), BaHfO}_3 \text{ (BHO), Ba}_2\text{YTaO}_6 \text{ (BYTO) Ba}_2\text{Y(Nb}_{0.5}\text{Ta}_{0.5})\text{O}_6 \text{ (BYNTO)} \ldots \]

Mixed targets from stoichiometric powders

PLD, e-beam, MOCVD, HLPE

- Simultaneous growth
- Interfacial energies and strain
- Diffusion length of the respective atomic species
- Temperature
- Grown Rate (i.e. laser repetition rate)
- Growth direction (vicinality of the substrate)

Self-assembled c axis oriented rods

Vortex pinning mostly ascribed to self-assembled secondary phases and associated interfacial strain
Mixed PLD nanocomposites BYNO +BYTO (BYNTO)

Combination of correlated defects along the c axis and ab-planes

→ Complex and rich microstructure and capacity to tune the $J_c(\theta,H,T)$ dependence

Single (BYTO 5%) and mixed doping (BYNTO 5%) of YBCO on STO

Dense and fine columnar structure ($d \sim 5$ nm))

- straight and partially interrupted columns in BYTO
- splayed and continuous nanocolumns in mixed BYNTO

F. Rizzo, et al., submitted
$J_c$ properties BZO – BYTO - BYNTO APC

LN2 T range;

- BZO effective at low field
- BYNTO and BYTO at higher fields ⇒ Among highest values of $B_{\text{irr}}$ (BYNTO) = 11 T for $H//c$
- BYNTO (mixed doping) more effective in both high field and low T regimes

F. Rizzo, et al., submitted
YBCO + BYNTOP on metallic template

YBCO + BYNTO on metallic ABAD CeO₂/YSZ/SS

- Multi-layers approach to avoid reactivity with the CeO₂ layer
- YBCO-BYNTO (150 – 250 nm) / YBCO (10-60nm) / ABAD

- Higher $T_c$: similar to STO ($\approx 88$ K);
- Good $J_c$ performances: closer to STO at lower T (to be still optimized);
- Formation of pinning effective BYNTO self assembled columns (to be still optimized, work is ongoing)
**Density and morphology of defects can be tuned with** \( f_{\text{Dep}} \)

- Very narrow BYNTO segmented nanocolumns
- \( \text{Y}_2\text{O}_3 \) plates
- Antiphase boundaries
- Stacking faults
- Dislocations

Increasing \( f_{\text{Dep}} \)  
- Density of the nanorods ↑
- Diameter ↓
- Density of \( \text{Y}_2\text{O}_3 \) plates ↑

**Matching effect for** \( B \parallel c \)

- End of \( J_c \) plateau
- \( F_p \) maximum (T independent)
- Peak in N value

High \( F_{p\text{max}} \) (25 GN/m³) among the highest values in literature!

- Anticorrelation N - \( J_c \) bellow the matching field (nanocolumns)
- High \( J_c \) → Intermediate \( \text{Y}_2\text{O}_3 \) particles and SF hinder the half loops and double kink structures

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**ANISOTROPY AT 77 K – SHIFTING PEAKS**

Complex $J_c$ anisotropy (off axis peaks shifting towards the ab peak)

- Matching effect with c-axis component of applied field
- Region of N-Jc anticorrelation above the matching field

**THICK PLD BHO - YBCO FILMS ON TECHNICAL SUBSTRATES**

YBCO + 5 - 6 mol% BaHfO$_3$ (BHO)

<table>
<thead>
<tr>
<th>Thickness, µm</th>
<th>$J_c$, MA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

77K, self-field

Ni-5W

ABAD-YSZ

5 µm thick BHO-doped YBCO layers:

- $I_c \sim 350$ A/cm-width on ABAD-YSZ
- $I_c \sim 450$ A/cm-width on Ni-5W

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**Influence of the Substrate**

$R = 0.7$ nm/s

BHO-YBCO on ABAD-YSZ

Different defect landscape depending on the substrate used:

- Fan-shaped BHO nanorods with diameter of (4 ± 2) nm and large splay (up to 20°)
- $Y_2O_3$ plates
- Y124 intergrowths

YBCO + 5 mol% BHO

Stainless steel / ABAD-YSZ / PLD-CeO$_2$
RABiT Ni-5 at.% W / CSD-La$_2$Zr$_2$O$_7$/ CSD-CeO$_2$

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M. Sieger et al., IEEE TAS (EUCAS 2017) in preparation
Influence of the growth rate

- Growth rate 0.4 – 6.6 nm/s still epitaxial growth
- Changing distribution of pinning centers from splayed nanorods to mixture of segmented nanorods and ab-oriented platelets

**DOPED YBCO FILMS ON ABAD-YSZ**

BHO show a larger $J_c$ enhancement at low T
- Large splay nanorods
- Week pinning??

Angular dependence

- Reduced peak for $B \parallel ab$ due to defects
- Broad peak for $B \parallel c$ for large splay of BHO nanocolumns
- Significantly reduced anisotropy for with mixed APC
- $N$ lower in doped samples $\rightarrow$ APC promote a higher creep rate
- Inverse $N(\theta) - J_c(\theta)$ correlation $H/ab$ (double kink excitations)
- *quasi-locked in state* manifested at 40 K as thermal activation is diminished
Sequential deposition and growth method

BaZrO$_3$ (BZO), BaHfO$_3$ (BHO), Ba$_2$YTaO$_6$ (BYTO) Ba$_2$Y(Nb$_{0.5}$Ta$_{0.5}$)O$_6$ (BYNTO) …

**ReBCO Precursor Solution**

- Addition of metal-organic salts
- Spontaneous Segregation
- Colloidal Solution: Preformed Nanoparticles

- Sequential growth
- Precursor Solution (TFA, Low Fluorine, TLAG)
- Deposition technique (spin coating, dip coating, slot die coating, ink jet printing)
- Growth conditions ($T$, Heating rate, $PO_2$, $PH_2O$, Gas velocity, $P_{total}$)

Self-assembled **randomly oriented** nanoparticles

Vortex pinning mostly ascribed to distributed **local lattice distortions** (nanostrain) induced by defects generated due to the presence of nanoparticles
High performance of CSD-YBCO nanocomposites

CSD YBCO nanocomposites with different spontaneous segregated NP (BZO, BYTO, Y$_2$O$_3$,..)

Enhanced performance at all temperatures

Incoherent YBCO-NP interfaces give rise to high density of Y248 intergrowths (stacking faults) ⇒ Nanostrain associated to intergrowths


Strong strain effects are generated at the partial dislocations
HIGH PERFORMANCE OF CSD-YBCO NANOCOMPOSITES

CSD YBCO nanocomposites with different spontaneous segregated NP (BZO, BYTO, \(Y_2O_3, \ldots\))

**H***: single vortex pinning regime

\[
\frac{J}{J_{\text{max}}} = \frac{J_c(H^*)}{J_{c_{\text{max}}}} = 0.5J_{c_{\text{sf}}}^2
\]

\(T=77K\)

\[
\rho_{\text{dislocation}} = \frac{\pi \delta \delta_{ab}}{\Delta x \Delta y(r_{SF})} \left( n_{SF} \delta_{ab} + 2 \sum_{i=1}^{n_{SF}} r_{SF} \right)
\]

- Partial Dislocation
- Y124 intergrowth
- \(r_{SF}\)

**Pristine**

- \(H^*=77K\)
- \(J_c(H^*)=0.9J_{c_{sf}}\)

**Best route to obtain high density of NP without segregation**

**Mixed Nanocomposites** (BZO/YO, BYTO/YO, BZO/BYTO) with optimized growing conditions \(\rightarrow\) high density of short SF defect landscape

**Vortex Pinning Contributions in CSD Nanocomposites**

**Isotropic Strong**

- *Iso-weak*
- *Iso-strong*

**Anisotropic H∥ab**

- SF correlated defects along the a-b planes

**Isotropic-weak**

- Weak pinning contribution: Cu-O cation vacancies
- New point defects effective at low temp.

**Staking Faults**: multiple pinning sites of different dimensionality
Stacking Faults avoid the Double Kink Formation (H//ab)

Pristine YBCO

Inverse correlation $J_c$ and $N$

$\mu_0 H_{\text{ab}} (T)$

$T (K)$

$\theta (°)$

Small $H$-$T$ Region dominated by SF pinning

Direct correlation $J_c$ and $N$

$H_{\text{cross}}$

a-b planes $\rightarrow$ strongly correlated planar defects

Large region dominated by Intrinsic pinning (double kink excitations)

Creep $\uparrow\uparrow$

Creep $\downarrow\downarrow$

F. Vallès et al. Submitted
Stacking Faults avoid the double kink formation ($H_{//ab}$)

Pristine YBCO

**Inverse correlation $J_c$ and $N$**

Nanocomposites → Strongly distorted matrix due to the presence of SF

The region dominated by SF pinning is enhanced to higher fields ⇒ **Reduce $H$-$T$ region with double king excitations**

Creep ↓↓

F. Vallès et al. Submitted
(Y,Gd)BCO+12%BHO films with different Y and Gd ratios.

- BaCeO$_3$ formation reduces as the Gd content increases
- $J_c \sim 2$ MA/cm$^2$ for 200 nm on tapes
- Similar $T_c$ values than in STO.

- GdBCO +12%BHO on SC $\Rightarrow F_p \sim 16$ GN/m$^3$
- YGdBCO +12%BHO on tape $\Rightarrow F_p \sim 5$ GN/m$^3$
  (higher than the pristine sample on STO)
- Promising results but still limited by pores in the matrix $\Rightarrow$ further optimization is required

CSD with Preformed Nanocrystals / Nanoparticles

Oxide nanoparticles can be stabilized in the YBCO precursor solution at high concentrations. Better control of size, density and stability is achieved. New phases must be explored (magnetic NP).

Requirements:
- Small size (< 10 nm range)
- Narrow size dispersion
- High concentrations (~100 mM)
- Highly crystalline
- Highly dispersive
- Stable in alcoholic media
- Stable in YBCO ionic environment

CSD YBCO Nanocomposites (ZrO$_3$ preformed NP)

- Reactivity (BaZrO$_3$)
- NC with homogeneous dispersion of NC

Improved $J_c$(H) performance

K. De Keukeleere et al.; Adv. Electr. Mater. (2016); 2; 1600161

NON-REACTIVE PREFORMED BaZrO$_3$ and BaHfO$_3$ NANOPARTICLES

- Higher concentration of Np without current blocking
- No $T_c$ reduction up to 25 %

- No reactivity nor coarsening occurs
- High homogeneity in Np dispersion

- $J_c$ (sf) = 3-5 MA/cm$^2$ at 77 K, 200 nm
- High performance at all temperatures
THICK NANOCOMPOSITES WITH PREFORMED NANOPARTICLES

- Colloidal solutions compatible with IJP
- Thick layer and CC are reachable

IJP single deposition

Increase of $I_c$ with thickness by IJP deposition of nanocomposites

Well dispersed NP

700-850 nm single deposited BZO nanocomposites with $J_c = 3$-$3.5$ MA/cm$^2$ at 77K, sf, $I_c \sim 240$ A/cm-w 77, sf

$700 \text{nm} - 20\%\text{BZO}$

$I_c(5K, 9T) \times 12$

$I_c(77K, 3T) \times 12$

$J_c = 3$-$3.5$ MA/cm$^2$ at 77K, sf, $I_c \sim 240$ A/cm-w 77, sf
IJP single deposition on ABAD substrates

1 μm single IJP deposited tape, $I_c \sim 100$ A/cm-w at 77 K, sf

500 nm single IJP deposition on ABAD substrates

150 nm YBCO+12% BZO

250 nm YBCO pristine

700 nm 12%M BZO on Bruker substrate

$J_c^{SF} = 1.4$ MA/cm² at 77 K

Same dependence than in sc

Promising results but still limited by pores in the matrix $\rightarrow$ further optimization is required

SQUID meas.

- 850 nm YBCO+12% BZO
- 700 nm YBCO+12% BZO (Bruker tape)
- 150 nm YBCO+12% BZO
- 250 nm YBCO pristine

T=77K

$J_c/J_{c,max}$ vs B (T)
Non-Fluorinated precursors

BaCO₃(s) + CuO(s) + Y₂O₃

Liquid-Solid reaction

CSD-TRANSIENT LIQUID ASSISTED GROWTH (TLAG)

- Faster diffusion - faster growth rate (x100)
- Highly simplified reactor
- More environmental friendly
- Highly epitaxial
- extremely low porosity. J_c(77K) = 3 MA/cm²

Growth process can strongly modify the nano(microstructure) of these films

Addition of a Y-Cu pervoskite block
Nanoscale ab-grains
Antiphase boundaries

Opportunity to play with new pinning landscapes
Industrial involvement in PLD CC processing

- Capability to process 4mm wide HTS tapes with a max. single piece tape length of 600m
- Capability to process 12mm wide HTS tapes with a max. single piece tape length of 100m

Nanocomposites fully implemented (600 m long tapes)

- \( I_c \) Uniformity along 4mm wide wires at 77K
  Reel-to-Reel hall-probe measurement of 4mm wide, 600 m long tapes along the entire tape length at 77K for defect detection and uniformity control

- \( I_c \) performance at ultra-high fields

Bamboo-like nano-columns firework structure with very pronounced deviation from H//c

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YBCO nanocomposite (typically BZO)

\( Y_2O_3 \) or \( A_2O_3 \) (0.1 \( \mu \)m) Planarization

YSZ bi-axially textured, ABAD (1.8-2.5 \( \mu \)m)

CeO\(_2\), PLD in situ (60-100 nm)

600 m long 4mm wide Cr-Ni SS (100\( \mu \)m)

\( \text{Cu encapsulation} \)

\( \text{Ag cap layer} \)

\( \text{YBCO nanocomposite (typically BZO)} \)

\( \text{Y}_2\text{O}_3 \) or \( \text{Al}_2\text{O}_3 \) (0.1 \( \mu \)m) Planarization

YSZ bi-axially textured, ABAD (1.8-2.5 \( \mu \)m)

CeO\(_2\), PLD in situ (60-100 nm)

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\( \text{SuperPower for 42T insert magnet} \)

\( \text{SuperPower R&D: 30-80 m} \)

\( \text{Bruker production line} 550-609 m \)

\( \text{One tape shown in this plot is at 23.8° between B and tape plane, other tapes are at B || tape orientation} \)

\( \text{Shanghai SC} \)

\( \text{SuNAM} \)

\( \text{M3-1216-2 N13} \)

\( \text{S2 M56} \)

\( \text{1254 M4 396 NH} \)

\( \text{S1P} \)

\( \text{S1P 2nd from top} \)

\( \text{S1P Bottom} \)

\( \text{Shanghai SC} \)

\( \text{Shanghai SC Cu} \)

\( \text{Shanghai SC Laminated} \)

\( \text{SuNAM} \) 100% SC

\( \text{Courtesy of A.Usoskin based on D. Abraimov, D.C. Larbalestier et al. (NHMFL) WAMHTS-4 Barcelona in Feb. 2017} \)
Pilot line for industrial HTS wire production
Capacity 150 km/yr (@ 12 mm-width)
Typical production tape length: 300 m

CSD for complete layer architecture
YBCO /CeO₂ /La₂ZrO₇/Ni RABiT
• Length up to 500m
• Width 4-40mm
• Capacity >100km/a

Over 200 m: \( I_c \approx 700 \, \text{A}, I_{c,\text{min}} = 600 \, \text{A} \)

Improved wire performance
12 mm tape, 77 K, self field
Tapestr measurement, 1 mm resolution, 1 \( \mu \text{A/cm} \)

150mx10m, 310±10A (77K,sf)
Homogeneity <5%

Homogeneous 100 m SDP-Y₂O₃ layer @ 35m/h
10 m CZO buffer @ 28 m/h
10 m of YBCO

Bruker & SuperOx substrates

4x25m annealing furnace

Reel-to-reel IJP pilot plant all CSD

different wire types

THEVA

CSD 2G CC

PVD 2G CC
CONCLUSIONS AND PROSPECTS

• Large knowledge in the correlation between vortex pinning and APC & Natural Defects in ReBCO films has been achieved allowing to identify the best pinning landscapes

• PLD: Mixed of random and correlated defects: Better pinning performances for most regimes of magnetic field and temperatures.

• CSD: Mixed spontaneous segregated NP and preformed NP: Good pinning performances with combination of weak and strong pinning centers

• PLD & CSD thick nanocomposite films have been integrated on technical substrates

• New approaches for fast growth rates & long length CC nanocomposite development represent the major present efforts
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