Microstructural landscape and vortex pinning scenarios in REBCO coated conductors prepared at high growth rates

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Motivation and outline

• Excepcional properties of REBCO Coated conductors at ultrahigh magnetic fields: excellent opportunity for compact fusion

• UHF magnets (20 T / 20 K) for fusion require extremely long lengths of CCs (~ 20,000 km/magnet) with high performance ($I_c$ (20T, 20 K))

• High throughput production of CCs is essential to cope with the expected demands: High growth rates of CCs need to be developed

• Understanding the impact of high growth rates on the microstructure and vortex pinning mechanisms of CCs is essential to optimize the potential of CCs

• Reliable methodologies to analyse the influence of high energy neutron irradiation in CCs are required

• Overview of vortex pinning scenarios of CCs prepared at high growth rates
REBCO coated conductors: enabling a new era of fusion energy

I_c(20T,20K) = 350-700 A/cm-w

I_c(20T,4.2K) = 1000-1600 A/cm-w

I_c(0T,77K) = 350-750 A/cm-w

“The highest Field with the lowest cryogenic cost”
The applied superconductivity community is anticipating the virtuous cycle of price reduction and further demand from other electrotechnology applications that are not yet economic at today’s REBCO CC prices.

The development of compact nuclear fusion power generation is the immediate stimulus that has driven exponential annual volume increases.
Coated Conductors: materials objectives

**CHEAPER**

- Ultrafast growth (G)
- Lower capital investment (€)
- Larger area manufacturing (W, L)
- Higher throughput
- Simpler processing
- Simpler architecture
- Higher yield

**BETTER**

- Higher performance: $J_c(B, T)$
- Thicker REBCO films
- More robust
- Customized for Applications
- Thinner substrates ($J_E$)
- Nanostructure control: APCs
- Lower ac losses

**Coated Conductor penetration**

$\frac{C}{P} = \frac{€}{G \times L \times W \times J_c} \left( \text{€ / kA m} \right)$

**Fast growth rate**

**Best combination**

**Nanocomposites**
REBCO growth processing: simultaneous and sequential

**Vapour-solid transformation**
Simultaneous and sequential solid-solid gas mediated

Growth from **vapour phase**
PLD, MOCVD, ME, MBE, Sputt

Growth from **nano crystalline solids**
TFA-MOD, BaF₂

Growth from **liquid phase**
TLAG-CSD, RCE-DR, HLPE, VLS

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**Supersaturation, σ, is the driving force for crystallization: \( \sigma \propto G \) (growth rate)**

\[
\sigma = \frac{(P_{\text{ad}} - P_{\text{ad,e}})}{P_{\text{ad,e}}}
\]

Deposition rate
High vacuum environ.
Simultaneous

\[
\sigma = f \left( \ln \left( \frac{P_{\text{HF}}}{P_{\text{H}_2\text{O}}} \right) \right)
\]

\( P_{\text{HF}} \) = HF partial pressure
\( P_{\text{H}_2\text{O}} \) = water partial pressure
Sequential

\[
\sigma = \frac{(C_\delta - C_e)}{C_e}
\]

RE solubility, Ba-Cu-O liquid

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**Growth rate:**

- Simultaneous: \( G = 0.5 - 25 \text{ nm/s} \)
- Sequential: \( G = 0.5 - 5 \text{ nm/s} \)
- Liquid-soluble: \( G = 10 - 1000 \text{ nm/s} \)

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T. Puig, J. Gutiérrez, X. Obradors Nat Rev Phys (2023, doi.org/10.1038/s42254-023-00663-3); J. Driscoll et al, Nat Rev Mat (2021)
**Transient Liquid Assisted Growth (TLAG)**

A new high throughput non-equilibrium kinetically controlled growth process

- High performance (3 MA/cm² at 77K)
- High throughput
- Simple reactor
- Large area processing
- Low cost/performance method

100 nm/s by **ultrafast-PLD** EuBCO/BHO (transient liquid growth at high T PLD)

- High performance (3 MA/cm² at 77K)
- High throughput
- Simple reactor
- Large area processing
- Low cost/performance method

**CSD**

**Low Temp PLD**
A. Quetalto et al, SUST (2023)

**In-situ synchrotron XRD**
Reaching high Growth Rate: A path towards cost reduction

Figure of merit:
\[
\frac{Cost}{Performance} = \frac{total \ cost \ per \ year}{G \times L \times W \times \left(\frac{I_{c-w}}{d}\right)} = \frac{\varepsilon}{kA \times m}
\]

W = tape width
L = tape length
d = tape thickness

T. Puig, J. Gutiérrez, X. Obradors Nat Rev Phys (2023, doi.org/10.1038/s42254-023-00663-3)
The complex defect structure in nanocomposites

Relevant issues: size, dimensionality, orientation, concentration

Different growth methods have modified nanostructures
The complex magnetic phase diagram of nanocomposites

Relevant issue: behaviour of defects as APCs can be classified as weak or strong and isotropic or anisotropic

We need a simple route to classify defects behaviour in terms of vortex pinning centers to follow the differences and the evolution of CCs with different processing methodologies and now with irradiation!
Simultaneous deposition/growth: micro/nanostructure

**BaZrO$_3$ nanocolumns**

**PLD**

Vapour - solid growth: low growth rates (1 - 4 nm/s)

- **(Gd,Y)BCO / BZO nanorods**
  - 5-6 nm diameter, separation: 18 nm
  - Growth rate: 4 nm/s

**A-MOCVD**

Strain field develop around the nanocolumns to reduce boundary energy inducing self-assembly

Oxygen vacancies and misfit dislocations at the interface

*C. Cantoni et al., ACSNano (2011)*


Nanoparticles (Y$_2$O$_3$): Molodyk et al. Sci Reports (2021)

G. Majkic et al., SUST (2020)
Simultaneous growth films: micro/nanostructure

**PLD-LAP (YBCO-BYTO)**

4 nm/s: BYTO nanorods misalignment

~ 20 nm separation

**PLD-HR (EuBCO- BHO)**

5 – 15 nm/s: discontinuous aligned BHO nanorods

20 – 30 nm/s: strongly segmented and misaligned BHO nanorods

Liquid assisted growth: **fast growth rates** (5 - 100 nm/s)


J. Feighan et al., SUST (2021)
Simultaneous growth films: micro/nanostructure

Liquid assisted growth: fast growth rates (20 - 100 nm/s)

PLD-HR (EuBCO- BHO)

4 nm/s: BYTO nanorods
misalignment

Y. Wu et al., Mat & Design (2022)
Shanghai Superconductor Technology

20 – 100 nm/s: strongly segmented and misaligned BHO nanorods
Simultaneous growth of Nanocomposites
Low versus high growth rate

Grown at 0.6 nm/s

High growth rates (10-50 nm/s)

Montecarlo simulations

EuBCO + HfBaO₃ nanorods

20-30 nm/s

10-15 nm/s

Elastic Strain energy model

Engineering landscape by design

LTG – PLD method

SmBCO+BHO upper layer
Low T growth

SmBCO seed layer
High T growth

Y. Yoshida et al, SUST 30 (2017)

Y Ichino et al J.JAP 56 (2017)


Wu, et al, SUST 35 (2022)

Sequential deposition and growth films (CSD, RCE-DR)

Use of complex solutions for spontaneous segregation of nanoparticles (TFA)
\( (\text{BaZrO}_3, \text{BaHfO}_3, \text{Ba}_2\text{YTaO}_6, \text{BaCeO}_3) \)

- J. Gutierrez et al, Nat Mat (2007);

Not suitable for TLAG

\textbf{pn-Nanocomposites:} Colloidal solutions with \textit{preformed nanoparticles} (N. Chamorro, RSC Adv. (2020))

Suitable for TFA and TLAG

- Spinel \((\text{MFe}_2\text{O}_4)\)
- Fluorite \((\text{CeO}_2, \text{ZrO}_2)\)
- Perovskite \(\text{BaMO}_3\) \(\text{(M= Zr, Hf)}\)
- Bronze \(\text{Ba(Ta,Nb)}_2\text{O}_6\)

- P. Cayado et al, SUST (2015)
- X. Obradors et al, SUST (2018)
- D. Garcia et al., to be published

Need to stabilize np in the alcoholic and ionic environment of YBCO precursor solution at high concentrations
Nanoparticles for multifunctional colloidal solutions

Requirements

NP solution

- Small-size < 10 nm
- Non-aggregation in alcohol solution
- High concentrations in alcohol solution (≥ 100 mM)

Stabilization in YBCO precursor solution

- NPs compatible and stable in YBCO precursor solution
  - non-aggregation
  - no precipitation

Compatibility with CSD-TLAG process

- NP composition non-reactive with YBCO
- High-thermal stability of NP composition

Reactivity - ZrO₂ NPs

- Pushing effect - CeO₂ NPs

Aggregation

- Coarsening

Multifunctional colloidal ink
(Patent EP22382741)

BaMO$_3$ (M= Zr and Hf) Nanoparticles

**BaZrO$_3$ NC**

- 7 ± 2 nm
- 10 ± 2 nm
- 5 ± 1 nm

**BaHfO$_3$ NC**

- 11 ± 3 nm
- 6 ± 2 nm
- 5 ± 1 nm

- Stable solutions (size/surface stability) for months
- Tuneable NP size from 4-20 nm

Nanoparticles induce stacking faults at the incoherent interface
Incoherent YBCO-BaZrO$_3$ interfaces give rise to high density of Y248 intergrowths and associated nanostrain.

Incoherent interface is associated to the random orientation of the nanoparticles.

Strong strain effects are generated at the partial dislocations.

Nanostrain is controlled by random nanoparticles.

Partial dislocations surrounding SFs: source of isotropic nanostrain

Nanostrain can be easily measured by XRD and it controls the concentration of dislocations (TEM analysis) and nanometric disorder.

Vortex pinning is closely correlated to nanostrain

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

\[ \delta_i \sim 0.8 \text{ nm} \]

Plan view TEM

Sequential deposition and growth films: micro/nanostructure

TFA

BZO

BZO

BZO

STO

(110) BZO pole

TLAG

c-YBCO

STO
Weak pinning contribution: cation-oxygen vacancy clusters

Atomic scale defects (<1 nm) demonstrated

Cu – O vacancies within Y248 intergrowth → weak pinning ??

Avoids the Stoichiometry Catastrophe

Cluster with ferromagnetism confirmed by XMCD synchroton radiation

TFA-BHO pn-nanocomposites by Flash Heating

Flash heating (20 °C/s): 20%M BHO (5 nm)

Flash Heating strongly avoids NP coarsening
- Higher concentration of short SFs: higher density of partial dislocations
- NP size very close to the optimal size for vortex pinning (5-8 nm)

\[ n_{np} \approx 40 \times 10^{22} \text{m}^{-3} (x2,5) (\approx 8 \% \text{ vol}) \]

NPs random fraction: 94%

Short SFs are promoted! (20 – 30 nm)
Vol density partial dislocation: \( \approx 2.3 \% \text{ vol} \)

J Mat Chem C (2019)
UltraThin Once Coating (UTOC): a route to small NPs

Multideposition with ultrathin repetition thickness (30 nm): CuO layers at the interfaces!

BZO and BHO nanoparticles are confined due to CuO barriers at the interface: coarsening is limited

Very high concentration of small and dispersed NPs
Volume similar to the optimal in simultaneous growth approach

T. Izumi et al., SUST (2018)
M. Miura et al., NPG Asia Materials (2017)
Magnetic field dependence of $J_c(B,T)$: single vortex to collective pinning

Region I: single vortex pinning ($H^*$)
Region II: collective vortex pinning
Region III: thermal activation effects very relevant (close to $H_{irr}(T)$)

Accommodation magnetic field $H^*(T)$: very useful parameter to monitor efficiency and concentration of APCs

A decrease of $\alpha$ values when the nanoparticle concentration is increased (enhanced vortex pinning)
Vortex pinning consequences at high growth rate: PLD-HR

EuBCO + HfBaO$_3$ nanorods

Y. Iijima, CCA 2023

Aligned long nanorods are not essential at low T - high H

Nanostrain is the most relevant parameter controlling single vortex pinning (CSD-TFA and CSD-TLAG)

H* enhanced by nanostrain H//c and H//ab

F. Vallés et al, Comm Mat 3,45 (2022)

Close relationship among dislocation density and nanostrain
Synergistic combination of Nps and nanostrain: enhanced vortex pinning

CTA: Conventional Thermal Annealing (0.4 °C/s)
FH: Flash heating (20ºC/s) - Enhanced vortex pinning

A leap increase of $H^*$ beyond nanostrain NP diameter $\sim \xi_{ab}$ (coherence length)

Nanostrain & NPs (4-8 nm): Synergistic effect for enhanced vortex pinning

Z. Li et al, J Mat Chem C (2019)
A. Palau et al., SUST (2018)
Enhanced vortex pinning by nanoparticles (UTOC)

CSD-TFA growth: (Y,Gd)Ba\textsubscript{1.5}Cu\textsubscript{3}O\textsubscript{x} / BHO

\[ J_{hc}^{NPS} \alpha N_{np} \frac{\mu_0 H_c^2 \pi \xi^2 D}{4 \xi} \alpha N_{np} \left( \frac{1}{\lambda^2 \xi} \right) \]

Very small BHO NPS achieved with UTOC (∼7 nm) with coatings of 30 nm

Very small BHO NPs contribute as APCs

M. Miura et al., NPG Asia Materials (2017)
Anisotropy of superconducting properties

Effective anisotropy decrease due to nanostrain (SFs) and nanoparticles

\[ \epsilon_{\text{eff}}(\theta) = \left[ \cos^2 \theta + \gamma_{\text{eff}}^2 \sin^2 \theta \right]^{1/2}. \]

Isotropic and anisotropic pinning contributions

L. Soler et al, Nature Communications (2020)
N. Pompeo et al., SUST (2020)
J. Banchewski et al, to be published
Anisotropy of superconducting properties

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J. Banchewski et al, to be published
Strong/Weak Vortex Pinning Contributions: temperature dependence

\[ J_c(T) = J_{c_{\text{iso-wk}}}(T) + J_{c_{\text{iso-str}}}(T) + J_{c_{\text{aniso-str}}}(T) \]

- **Anisotropic strong**
  - Nanorods (H//c)
  - Intrinsic Pinning (H//ab)
  - Stacking faults (H//ab)
  - Twin boundaries (H//c)

- **Isotropic strong**
  - Nano-strain
  - Nanoparticles

- **Isotropic weak**
  - Point defects, Oxygen and cationic vacancies

\[ J_{c_{\text{strong}}}(T) = J_{c_{\text{str}}}(0) \exp \left[ -3 \left( \frac{T}{T^*} \right)^2 \right] \]

\[ J_{c_{\text{weak}}}(T) = J_{c_{\text{wk}}}(0) \exp \left( -\frac{T}{T_0} \right) \]

- \( J_{c_{\text{str}}}(0) \rightarrow \) density of strong defects
- \( T^* \rightarrow \) characteristic vortex pinning energy of strong defects
- \( J_{c_{\text{wk}}}(0) \rightarrow \) density of weak defects
- \( T_0 \rightarrow \) characteristic vortex pinning energy of weak defects

We can quantify the pinning strength and energies associated to different pinning centres.

We assume additive effects of strong and weak APCs.

*References*


G. Blatter et al., RMP, 66: 1125 (1994)
Strong/Weak/Isotropic-Anisotropic Vortex Pinning Contributions: temperature dependence

Considering the same density of defects ($J_c(0)$)

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

Combination of anisotropic and Isotropic-strong

All three contribute, Isotropic-weak has some relevance

Anisotropic pinning becomes dominant

$H//c: 1T$
Pinning contributions in nanocomposite films: very high magnetic fields (35 T)

\[ J_c(T) = J_c(0)^{iso-wk} \exp(-T/T_0) + J_c(0)^{iso-str} \exp(-3(T/T^*_{iso-str})^2) + J_c(0)^{aniso-str} \exp(-3(T/T^*_{aniso-str})^2) \]

- Very different magnetic field dependences for weak and strong pinning defects
- Weak pinning defects may play a critical role at very high magnetic fields and low temperatures

F. Vallés et al, Comm Mat 3,45 (2022)
Phase diagrams of vortex pinning strength

CSD nanocomposites: Single Vortex Pinning vs collective pinning

- Isotropic pinning dominates most of phase diagram (H//c)
- Isotropic and anisotropic pinning with similar relevance in most of the phase diagram (H//ab)
Vortex pinning consequences at high growth rate: TLAG-CSD

50 nm/s → 1500 nm/s

2.5 MA/cm²

$J_c(5 \text{ K})$ MA/cm²

$J_c(77 \text{ K})$ MA/cm²

Rich vortex pinning determined by the defect microstructure of high growth rates

Tune charge carrier density by oxygen overdoping

Pinning force $F_p = \sum_{i}^{Np} f_{p,i} (B, T) \propto J_c$

$f_p \propto E_c$ condensation energy

$J_d^2 \propto n_s E_c \quad \rightarrow \quad J_c^2 \propto n_H H_0$ (H$_0$ from in-plane magnetoresistance)

(three independent experimental parameters)

$n_H$ and $E_c$ increases in the overdoped state, and consequently $J_c$ should increase

$p_{opt} = 0.16$ holes/CuO$_2$-plane: optimal doping for maximum $T_c$

$p^* = 0.19$ holes/CuO$_2$-plane: Critical doping (QCP)

Carrier concentration effects: oxygen overdoping

- Carrier concentration determined by Hall effect (100 K)
- Overdoping is achieved by oxygen excess

YBCO PLD and TFA – CSD thin films

- Fermi surface reconstruction at the Quantum Critical Point ($p^* > p_{opt}$): large increase of the carrier density $n$ (cylindrical Fermi surface)
- Non-unique relation between the charge carrier density $n$ and doping, $p$.

Strong increase of $J_c$ in the overdoped state

$J_c(p^*) \approx \frac{1}{5} J_d(p^*) = 90 \text{ MA/cm}^2$

$J_d(p^*) \approx 500 \text{ MA/cm}^2$

Strong increase of $J_c$ with $n_H$ (x4 from $p_{opt}$ to $p^*$)

$J_c(p_{opt}) \approx \frac{1}{10} J_d(p_{opt})$

$J_d(p_{opt}) \approx 330 \text{ MA/cm}^2$

Overdoping is a robust method to reach ultrahigh $J_c(H)$

A. Stangl et al, Scientific Reports (2021)
Strong increase of $J_c$ in the overdoped state of nanocomposites

- Nanoparticles increase of $J_c$.
- Influence of carrier concentration through thermodynamic parameters.

$$J_{co}^{NPs} \propto N_{np} \frac{\mu_0 H_c^2 \pi \xi^2 D}{4 \xi} \propto N_{np} \left( \frac{1}{\lambda^2 \xi} \right)$$

M. Miura et al, NPG Asia Materials (2022)
TFA-REBCO film growth with UTOC nanoparticles
Strong increase of $J_c$ in the overdoped state of nanocomposites

**Diagram:**
- Graph (d) shows the variation of $J_c$ with $p$ for different composites.
- Graph (b) illustrates the dependence of $J_c$ on $\mu_0 H$.

**Equations:**
- $J_c(p^*) \approx \frac{1}{3} J_d(p^*)$
- $J_c(p^*) \approx \frac{1}{5} J_d(p^*)$

**References:**
- Miura et al., NPG Asia Materials 2022
# Comparison between different growth processes

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T. Puig, J. Gutiérrez, X. Obradors Nat Rev Phys (2023, doi.org/10.1038/s42254-023-00663-3)
Conclusions and take away message

- Coated conductors are unique superconducting materials that are set to enable UHF magnets for compact fusion
- Very long lengths of CCs are required so high throughput production is required at low cost keeping high performance
- Ultrafast REBCO growth rates are required to reduce the figure of merit cost/performance (€/kA m)
- Nanostructure deeply differs between simultaneous and sequential deposition and growth methodologies
- Reliable and fast characterization methodologies are required to identify the efficient APCs at different temperatures and magnetic fields
- Liquid assisted growth methodologies are very promising to increase throughput
- TLAG-CSD is an emerging low cost (low CAPEX-ultrafast growth) route to nanocomposite CCs with preformed nanoparticles
- We need to follow systematic studies of modifications of vortex pinning landscapes with irradiation using well established methodologies: ICMAB is open to collaborate in this challenge!
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