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<td>Chemical Emulsion of Radiation Pinning Center Geometries in High Temperature Superconductors</td>
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<td>Dr. Roy Weinstein</td>
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<td>University of Houston</td>
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<td>632 Science &amp; Research Bldg. 1</td>
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<td>Discovery of sub-micron size deposits of (U, Zr, Nd, Ba, O) in Nd123 enabled application of the U/n method to Nd123, resulting in world record Jc. Discovery of an entire class of ~ 200-400 nm size, double perovskite pinning centers, (A,B)REBa2O6, led to ~ 20 new chemical “point” pinning centers, and enabled replacement of successful but expensive and radioactive (U0.8Pu0.2)REBa2O6 pinning centers with inexpensive, non-radioactive (W0.5,Zr0.5)REBa2O6. Additional studies proved that the parent compound used for additives strongly effect the critical parameter of pinning center size. Theoretical studies of the cause of decreasing Jc, when large ion fluences are used to induce pinning, led to postulating a new class of pinning centers based on multiple-in-line-damage (MILD). Achievement of self-assembling chemical columnar structures in YBCO proved the feasibility of our ultimate goal of producing such chemical pinning centers in small enough diameter to play the role of ideal pinning centers.</td>
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(4) Statement of problem studied

Application of high temperature superconductivity (HTS) to motors, power transfer, magnets, levitated transportation, etc., etc., is a great energy saving field of study. In some cases, such as levitation, it enables new classes of applications. Known applications of HTS all require high currents and current densities, $J_c$. All successful applications to date of HTS utilize type II conditions, in which magnetic field penetrates the HTS.

When field penetrates a type II superconductor, within the superconductor the field exists in the form of quantized flux. Each quantum carries a flux of $\phi_0 \approx 2 \times 10^{-7}$ Gauss cm$^2$. When current flows a Lorentz force is generated, and this force moves the fluxoids. Their motion generates an electric field opposing $J_c$. This reduces $J_c$.

As a result, in order to obtain the high $J_c$ needed for applications, the fluxoids must be “pinned” in place. This is done by creating small regions of non-superconducting material within the HTS. These are called “pinning centers.” Pinning centers work by creating an attractive potential to bind the fluxoids.

The work reported here describes our studies to produce more and more effective pinning centers. The newly discovered ways to produce pinning centers, described in section 5, have resulted in increases in $J_c$ by factors of 2 to 30.

(5) Summary of the most important results

a.) MILD Pinning Centers

We reported last year the completion of theoretical work with a surprising conclusion [1-4]. Conventional wisdom, in HTS work, is that the best pinning center is damage having the geometry of a continuous column. Continuous columnar pinning centers (CCPCs) can contain the entire length of a magnetic fluxoid and, as a result, provide the maximum possible pinning potential, $U_{pin}$. It has been broadly assumed that this resulted in the highest $J_c$ and highest operating field.

Our work indicated that these conclusions did not allow for the severe damage which such pinning centers inflict upon HTS microstructure.

Our quantitative models, which included the damage microstructure as part of the problem, indicated that better results would be obtained using multiple-in-line-damage (MILD). MILD pinning centers would result in less overall damage. The lower damage increases the area available for percolation, and hence increases $J_c$. It also decreases the overlap of adjacent damage, and thereby increases the number of pinning centers and hence the maximum pinnable field. We proposed an experiment which can test this model and would, if successful, provide a practical method to produce a markedly superior HTS material. The experiment was designed and constructed in Spring 2003. The experiment was run in August 2003, and is being analyzed.

b.) Self-Assembling Nano-sized Pinning Centers

The best known methods for investigating the optimum size, continuity, density and splay of pinning centers are via experiments utilizing radiation. A successful example of such study is reported in sec. (1), below.
Ideally, once the optimum pinning center geometry is known, one would find a way to produce a non-superconducting chemical deposit with the desired geometry.

The ideal pinning center is not yet completely defined, but it will be close to this: a columnar shape, perhaps 10 to 50 μm long, 4 nm in diameter, splayed uniformly over an angle of ~20°.

Two approaches to such ideal chemical pinning come to mind. The first is to produce the needed columns outside HTS, and introduce these to the powders from which HTS is produced. This has been tried by others, for example, using carbon nano-tubes. This approach has to date been unsuccessful. The HTS chemical environment and processing temperatures destroy the pre-formed columns.

The second approach is to find a chemical process to produce self-assembling columns of nano-sized diameter within the HTS.

We have had initial success with such self-assembling chemical nanostructures. [Not yet published.]

Fig. 1 shows SEM studies of YBCO doped with nano-sized TiO₂ and Pt. A study of various doping levels revealed a region in which self-assembling columnar deposits resulted. These columns are typically 2-10 μm in length, and 400 nm to 1 μm in diameter. A clear increase in $J_c$ is observed in the doping region in which these columns are formed.

To the best of our knowledge, this represents the first successful attempt to produce self-assembling columnar pinning centers within the HTS environment.

While these columns represent a significant step forward, they do not complete the job. Ti enters the YBCO matrix, and lowers $T_c$. Consequently this particular solution is not optimum.

We will seek other self-assembling nano-diameter chemical centers which do not decrease $T_c$. Until these are found, the result reported here serves as proof that self-assembling chemical nano-structures, for use as pinning centers, are an attainable goal.

c.) Two foreign-elements (chemical pinning centers)

We have discovered a new class of chemical pinning centers which pin better than any prior chemical deposits [5]. The general form of these centers is

$$(A_xB_{1-x})REB_{2}O_{6}$$

where RE is a rare earth type such as Sm, Nd or Y, A is a member of the group U, W, Mo or others, and B is a member of the group Pt, Zr, or others, x+y=1 and $|x-y| <= 0.1$. These deposits are stable double perovskites of uniform size (300 ± 100 nm) and spherical shape.

Since at least 18 new compounds are predicted (more likely well over 20) it is impossible for a group our size to investigate all of them. We have therefore (a.) published these results for others to work on [5], (b.) formed collaborations to work on some of the resulting areas of interest and (c.) pursued what we consider to be the most promising resulting lines of research.

i.) Improvement of $Y_{123}$

$J_c$ in $Y_{123}$ is tripled by pinning centers of composition

$$(U_{0.4} Pt_{0.6})Ba_{2}O_{6}$$

Such pinning raises two objections: (1.) fear of U (not rational, but real) and (2.) cost of Pt. We have therefore studied two substitutions in $Y_{123} + U + Pt$:

$$U \rightarrow W, \text{ and}$$

$$Pt \rightarrow Zr$$

We have learned, so far, to double $J_c$ using W [6].

ii.) There is emerging data from Chinese groups, Japanese groups, and our own work that major gains in $J_c$ can be obtained by reducing the size of pinning centers to ~ 100 nm. The
improvement is not directly due to the small size. Rather, decreasing size permits an increase in the number of pinning centers for a given mass of the dopants. A limited weight % of non-stoichiometric chemicals can be added. For example, reducing deposit diameter by a factor of 2 permits an increase in the number of pinning centers by 8.

We are studying methods to decrease size of pinning center deposits. In one line of these studies, \((U, Pt)SmBa_2O_6\) in Sm123, we are using the following approaches:

a.) A reduced melt time for the HTS texturing.

b.) A mechanical “crusher” to reduce the dopant chemical size to < 100 nm.

c.) Substitution of “soft” compounds containing the dopant for hard compounds.

Thus melt time has been studied in the range 1 min. – 4 hours, and resultant size effects observed. Compounds of varying hardness, \(UO_2\), \(UO_3\) and \(UO_4 \cdot 2H_2O\) have been used to introduce \(U\) (here soft compounds are seen to improve \(J_c\) by a factor of two) [7]. In addition, a “crusher” is being studied with aim to reduce the caliber of dopants. The problem of removing the impurities added by the crusher balls is being attacked.

d.) A physics “puzzle” has developed. In \(Y123 + U + Pt\), the pinning deposits form \((U_{0.6}Pt_{0.4})YBa_2O_6\), a double perovskite. If only \(U\) is added (no \(Pt\)), deposits form \((U_{0.4}Y_{0.6})BaO_2\), a single perovskite. Both types of deposits are stable, essentially spherical, and ~ 300 nm in size. Nevertheless, the double perovskites pin very well, while the single perovskite shows no pinning effect. The two deposits are expected to pin equally unless the single perovskite is superconducting or magnetically anomalous.

This anomaly is being pursued by additional measurements, but initial results are now being published [8].

c.) \(Nd123\). One of our goals for the present grant was to improve \(J_c\), in the Nd123 superconductor, by the method of introducing \(^{235}U\) and then irradiating with thermal neutrons to fission the \(U\). In earlier works we had shown that the \(U\) must be introduced in small deposits (< 1 \(\mu m\)), closely spaced (< 5.4 \(\mu m\)).

Work, in collaboration with G. Krabbes, IFW, Dresden Germany, and M. Murakami, ISTEC, Japan had failed to achieve small deposits, despite three separate attempts to solve the chemistry by adding (i) \(U, Pt\); (ii) \((U, Pt)YBa_2O_6\); and (iii) \((U, Pt)NdBa_2O_6\).

In a “return to basics,” we introduced \(U\), alone, to Nd123. We observed formation of small deposits. These were found to contain Zr, but no Zr had been added. However, the samples had been supported on rods of yttria-stabilized zirconium, and clearly the Zr had migrated from the rod. Guided by this accidental observation, we introduced controlled amounts of Zr, using \(ZrO_2\). We soon obtained profuse small deposits, ~ 400nm, in the chemical form of a double perovskite, \((U_{0.2}Zr_{0.8})NdBa_2O_6\) [9].

We found that the large deposits of \(Nd_2Ba_3Cu_4O_{10}\) (Nd422), usually found in Nd123 (see Fig. 2a), were diminished in size to ~ 1 \(\mu m\), as seen in Fig. 2b, due to the presence of the Zr. Also, the addition of \(U\) and Zr together resulted in the 400 nm deposits of the \((U_{0.2}Zr_{0.8})NdBa_2O_6\). (See Fig. 2c.)

Upon neutron irradiation, to fission the \(U, J_c\) was found to be increased by over an order of magnitude. This resulted in a new world record \(J_c\) in Nd123: \(J_c = 274 \text{ kA/cm}^2\).

This is just 2% short of a new record for any textured high \(T_c\) superconductor. Since the samples used were hurriedly made, we believe we will be able to improve \(J_c\), and eclipse the record \(J_c\) for any form of HTS.

\(J_c\) was measured via trapped field. Fig. 2d shows the striking rise in trapped field. Trapped field is proportional to \(J_c\), and it is seen that trapped field, and hence \(J_c\), is increased by a factor of 6.2 at optimum irradiation fluence. However, \(J_c\) is usually quoted at constant field. The
correction factor for the increased field is 1.8. Thus the total increase in \( J_c \) due to irradiation, is a factor of \( 6.2 \times 1.8 = 11.2 \).

In addition, both the refined Nd422 and the (U,Zr) deposits act as pinning centers. We estimate the increase in \( J_c \) due to this chemical pinning by referring to prior work we did on Y123, and find it to be 2.6. Thus the total increase in \( J_c \) by this "U/n" process is 11.2 x 2.6 = 29.

The specific radioactivity of the resulting superconductor was found to be 100 nanocuries/gram.

(6) Listing of all publications under this grant:

(a) Papers published in peer-reviewed journals


Roy Weinstein, Alberto Gandini, Ravi-Persad Sawh, and Drew Parks, “Improved pinning center morphology in HTS, with order-of-magnitude increase in Jc and Bp, compared to columnar pinning,” Tsinghua Journal of Science & Technology special issue: Advances in High Tc Superconductors,” Vol 8, Number 3, (June 2003) pp 266-279.


(b) Papers published in non-peer reviewed journals or in conference proceedings

13th International Symposium on Superconductivity, Tokyo, Japan, October 15, 2000


Applied Superconductivity Conf, 2000, Virginia Beach, Sept 17-22, 2000


104th Annual Meeting of American Ceramics Society, St. Louis, MO, April 28-May 1, 2002


Applied Superconductivity Conf, 2002, Houston, TX, August 4-9, 2002


Applied Superconductivity Conf. 2002, Houston, TX, August 4-9, 2002.—Invited Paper

American Physical Society 2003 March Annual Meeting, Austin, TX (March 3-7, 2003)

American Physical Society 2003 March Annual Meeting, Austin, TX (March 3-7, 2003)

American Physical Society 2003 March Annual Meeting, Austin, TX (March 3-7, 2003)

Oral presentation at PASREG 2003 (Jena, Germany) June 30, July 2, 2003;

Invited talk to PASREG 2003 (Jena, Germany) June 30, July 2, 2003;

(c.) Papers presented at meetings, but not published in conference proceedings

(d.) Manuscripts submitted, but not published


(e.) Technical reports submitted to ARO

None.

(7) List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project.

Faculty: Dr. Roy Weinstein

Staff: Mr. Drew Parks
       Mr. Ravi-Persad Sawh

Post-Doc: Dr. Alberto Gandini (earned Ph.D. August 2001)

Grad Students: Goro Osabe (Ph.D. expected May 2005)
               Jiafu Tang (Ph.D. expected May 2005)
               Alfred Michael


*All of the above students are at University of Houston, except for Adenike Olanrewaju who is a student at Texas Southern University, an Historically Black University, and is part of a 10-year outreach program run by our UH group and TSU.

(8) Report of inventions (by title only)

(a.) MILD Pinning Centers
(b.) Production Test for Ag-BiSCCO tape
(c.) Pinning centers with 2 foreign elements
Bibliography


(10) Appendixes

Fig. 1. SEM study of melt-textured Y123 doped with nano-sized TiO$_2$ and Pt. The visible columns are self-assembled nano-diameter columnar pinning centers, formed within the HTS chemical environment.
**Fig. 2a.** SEM study shows ordinary Nd123 including large (light) areas of Nd422.

**Fig. 2b.** After Zr is added, Nd422 is refined and increases $J_c$.

**Fig. 2c.** After U is added to [Zr+Nd123] very small deposits of $(U_{0.5}Zr_{0.5})$NdBa$_2$O$_6$ form, and increase $J_c$ further.

**Fig. 2d.** After irradiation by thermal neutrons, trapped field is increased further. Quasi-columnar pinning centers increase $J_c$ to record 274 kA/cm$^2$. 