High-\(T_c\) Superconductors - based Nanocomposites with Improved Intergrain Coupling and Enhanced Bulk Pinning

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Abstract — Heterogeneous sonochemical synthesis was used to modify superconducting properties of granular \(\text{YBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{8}\) and \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8\). Sonication of liquid-powder alkane slurries produces material with enhanced intergrain coupling and improved current-carrying capabilities. Co-sonication with metals and organometallics results in highly compact nanocomposites with increased magnetic irreversibility. Ultrasonic irradiation of \(\text{YBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{8}\) carried under partial oxygen atmosphere produces similar morphological effects and increases superconducting transition temperature due to effective surface saturation with oxygen. Detailed chemical and physical characterization of sonochemically prepared high-\(T_c\) nanocomposites is presented.

Index Terms—granular superconductor, critical current, pinning, magnetic irreversibility

I. INTRODUCTION

USEFUL properties of superconductors, such as critical current, critical fields and magnetic irreversibility, strongly depend on the material’s morphology. High-\(T_c\) cuprates, \(\text{YBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{8}\) (YBCO) and \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8\) (BSCCO) are potentially useful mostly in their bulk form. However, achieving high persistent currents in these granular materials is a non-trivial task [1]. BSCCO is highly anisotropic, and very hard and brittle, and critical currents are limited mostly by the intergrain coupling. YBCO, on the other hand, is very sensitive to the oxygen content and distribution, which limits possible technological treatments.

This paper describes a novel method for modification of microstructure and introduction of efficient pinning centers in high-\(T_c\) superconductors. The presented method utilizes high-intensity ultrasonic irradiation for structure modification and preparation of nanocomposites based on high-\(T_c\) superconductors.

II. EXPERIMENTAL

A. Sonochemical Method

Irradiation of liquids with powerful ultrasound induces transient cavitation: nucleation, growth and violent collapse of bubbles [2,3]. The implosive bubble collapse generates localized hot spots with temperatures as high as 5000 K, pressures of about 800 atm, and cooling rates exceeding \(10^9\) K/s, and induces intense shock waves, propagating in the liquid at velocities well above the speed of sound. In powder-liquid mixtures (slurries), shockwaves lead to an extremely rapid mass transfer and induce high velocity collisions among suspended solid particles [2-4]. Such interparticle collisions result in extreme heating at the point of impact, which can lead to effective localized melting and significant increase in the rates of numerous solid-liquid reactions. As a consequence, morphology of the initial material is significantly modified: individual grains are grinded, smoothened and welded together, ultimately resulting to a more compact material. In the case of a superconductor, such morphology change leads to better inter-grain coupling and annealing of the intra-grain defects. Sonication with volatile organometallic compounds leads to in-situ nucleation of nanoparticles, which precipitate on the surface of individual granules, and become trapped between colliding grains. The process is so aggressive that it overcomes usual surface tension limitations, and yields a uniform composite with nanoparticles embedded in the bulk of the slurry. This approach was initially explored in polycrystalline \(\text{MgB}_2\). Resulted \(\text{MgB}_2\)-based nanocomposites with magnetic and non-magnetic embedded nanoparticles exhibited enhanced pinning. Both methods lead to production of novel nanocomposite superconducting materials [4]. Applied to polycrystalline BSCCO, irradiation with high-intensity ultrasound was shown to significantly improve current-carrying characteristics and magnetic irreversibility [5].

B. Sample Preparation

Slurry of 2 wt% of polycrystalline \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}\) (325...
mesh, *Alfa Aesar*) in 20 mL of decane was ultrasonically irradiated for 2 hours at 263 K under a 30 mL/min flow of argon using a direct-immersion ultrasonic horn (Sonics & Materials VCX-750 at 20 kHz, ~50 W/cm²). To produce composite materials, 54 µmol of powdered lead and/or silver (*Alfa Aesar*) were admixed to BSCCO slurry and sonicated under the same conditions. Resulting ultrasonically treated powders were collected by filtration, washed with dry pentane (30 mL×5), and air-dried overnight. Dry powders were pelletized at room temperature at a pressure of 2 GPa for 24 hours, maintaining an average sample mass of ~70 mg. In order to compare the results with other studies, we have used here a standard annealing procedure (850 °C in air for 48 hours, followed by a rapid quenching to the room temperature). We note, however, that properties of nanocomposites can be further optimized by modifying the annealing protocol (e.g., constant-temperature melting and recrystallization in switching atmosphere).

Slurry of 2 wt% polycrystalline YBa$_2$Cu$_3$O$_{7-δ}$ (*Alfa Aesar*) in 20 mL of decane was ultrasonically irradiated for 2 hours at 263 K under a 30 mL/min flow of argon, using a direct-immersion ultrasonic horn (Sonics & Materials VCX-750 at 20 kHz, ~50 W/cm²). Ultrasonically treated powders were collected by filtration, washed with dry pentane (30 mL×5), and air-dried overnight. To sustain the necessary sonochemical conditions while introducing controlled amount of oxygen into a reaction vessel, sonochemical irradiation of YBCO slurries in ethylene glycol was performed under partial oxygen flow (Ar: 20 mL/min, O$_2$: 10 mL/min). To produce composite materials, 2% YBCO slurry was sonicated with 18 µmol F(CO)$_5$ and 180 µmol of F(CO)$_5$, respectively. Resulting ultrasonically treated powders were collected by filtration, washed with dry pentane (30 mL×5), and air-dried overnight. Dry powders were pelletized at room temperature at a pressure of 2 GPa for 24 hours, maintaining an average sample mass of ~50 mg. No post-sonication annealing was performed for YBCO samples.

C. Measurements and Characterization

All samples were characterized by scanning electron microscope (SEM) imaging, powder x-ray diffraction, localized energy-dispersive x-ray spectroscopy (EDX), x-ray photoelectron spectroscopy (XPS), thermogravimetric analysis and differential scanning calorimetry. Morphology of superconducting powders was examined on a Hitachi S-4700 SEM equipped with an Energy Dispersive X-Ray Analysis unit. Surface chemical composition of modified powders was monitored by using X-ray Photoelectron Spectroscopy (XPS) and localized EDX. XPS analysis was conducted on a Physical...
Electronics PHI 5400 X-Ray Photoelectron Spectrometer, maintaining the pressure below $2.5 \times 10^{-8}$ torr.

Magnetic measurements were performed on Quantum Design MPMS. Magneto-optical imaging was done on a custom-built system with Bi-doped iron garnet in-plane Faraday indicator films. Transport measurements were performed with a standard 4-probe technique on a Quantum Design PPMS.

III. RESULTS

A. BSCCO-based Nanocomposites

SEM images of pelletized BSCCO-based nanocomposites are shown in Fig.1 – (a) BSCCO before irradiation with ultrasound; (b) BSCCO sonicated at 2% wt slurry for two hours; (c) BSCCO sonicated with lead powder; (d) BSCCO sonicated with 180 µmol of Fe(CO)$_5$.

Magnetic measurements were performed on Quantum Design MPMS. Magneto-optical imaging was done on a custom-built system with Bi-doped iron garnet in-plane Faraday indicator films. Transport measurements were performed with a standard 4-probe technique on a Quantum Design PPMS.

B. YBCO-based Nanocomposites

Morphological changes induced by ultrasonic treatment in YBCO, Fig.4, are similar to MgB$_2$ [4] and BSCCO nanocomposites. However, superconducting properties did not significantly improve and even somewhat deteriorated. It became apparent that notorious sensitivity of YBa$_2$Cu$_3$O$_{7-\delta}$ to the oxygen content was the primary reason. In polycrystalline YBCO, grain boundaries are usually more oxygen deficient, compared to the bulk. Indeed, probing the sonicated materials with XPS revealed distinct changes in the chemical surface composition of sonicated YBCO. A single O 1s peak of the starting material, Fig.5(a), is broadened in YBa$_2$Cu$_3$O$_{7-\delta}$ irradiated with high-intensity ultrasound, and its intensity decreases. Additional lower-energy O 1s peak, Fig.5(b), can be attributed to formation of new surface layers [7,8]. Appearance and growth of oxygen peak with lowered energy, and in drop of the original oxygen peak intensity in the samples examined with XPS, confirms decrease of the surface oxygen concentration. Thus, despite the obvious rounding and fusion of the individual grains seen in SEM images of sonochemically irradiated grains, its overall structure becomes chemically less homogeneous. Apparently, ultrasound irradiation apparently disrupts oxygen content in the melted surface layers, forming non-superconducting phases. In particular, formation of trace amounts of surface $Y_3BaCuO_5$ phase and BaCuO$_2$ compound within the bulk YBa$_2$Cu$_3$O$_{7-\delta}$ matrix has been previously reported [3]. These freshly formed non-superconducting layers enfold the superconducting grains, leading to the weakening of intergrain magnetic field was used. Bright spots on the left image are the places of trapped flux, most probably inside the larger grains. The sonicated sample (right image) shows a much more uniform Meissner screening and is, therefore, more homogeneous, which correlates well with morphological changes observed in Fig.1. Since irradiated with ultrasound slurry contains both ceramic powder and soft metal granules, interparticle collisions lead to a significant size reduction and plastic deformation of softer metallic component. The latter then acts as welding or soldering material, further improving the intergrain coupling at the point of contact. Better intergrain coupling leads to the enhanced magnetic properties of sonicated BSCCO [5]. However, the effect is even more pronounced in nanocomposites made with superconducting lead and non-superconducting silver (not shown here). Magnetic measurements, shown in Fig.3, demonstrate more than two-fold enhancement of the magnetic irreversibility in nanocomposites as compared to non-modified BSCCO. The problem is that this enhancement is significant only below ~30 K and quickly diminished above. A number of factors can be responsible for this behavior, among which are non-uniform thermal expansion of nanocomposite and dimensional crossover of flux pinning in BSCCO [5]. However, current research indicates that with proper modification of the synthesis and annealing protocols, the observed enhancement can be extended to higher temperatures.
coupling and to reduction of the total volume of superconducting phase. However, this adverse effect can be minimized and ultimately reverted by adjusting the synthesis protocol. Sonochemical reactions are normally carried under the flow of inert [2]. Since there is no excess oxygen in the reaction vessel, oxygen content in the surface layers of superconducting YBa$_2$Cu$_3$O$_{7-\delta}$ grains inevitably decreases. To maintain the oxygen content in sonochemically treated YBa$_2$Cu$_3$O$_{7-\delta}$, irradiation of slurries was performed under partial oxygen flow in an oxygen rich solvent. It was assumed that during the sonolysis, a fraction of diatomic oxygen molecules undergoes dissociation to yield highly reactive atomic oxygen species. Remarkably, such treatment not only inhibited the oxygen loss, but apparently allowed effective saturation of surface layers with oxygen. This conclusion was ultimately confirmed by the magnetic measurements: transition temperature of YBCO sonicated under partial oxygen flow increased, compared to the initial material.

Fig. 5(c) shows XPS spectra for sonicated YBCO treated with ultrasound in partial oxygen flow. The undesirable low-energy peak, attributed to formation of surface non-superconducting phases, almost disappeared and the peak corresponding to the oxygen in Cu-O planes was recovered. Measurements of the magnetic moment after zero-field cooling were performed in a 10 Oe external magnetic field. The normalized by the value at 5 K, the results are shown in Fig.6. The inset shows zoomed region in the vicinity of the transition temperature clearly demonstrating the enhancement of the overall superconducting behavior.

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