# Sonochemical modification of the superconducting properties of $MgB_2$

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Ultrasonic irradiation of magnesium diboride slurries in decalin produces material with significant intergrain fusion. Sonication in the presence of $Fe(CO)_5$ produces magnetic $Fe_2O_3$ nanoparticles embedded in the $MgB_2$ bulk. The resulting superconductor–ferromagnet composite exhibits considerable enhancement of its magnetic hysteresis, which implies an increase of vortex pinning strength due to embedded magnetic nanoparticles. © *2003 American Institute of Physics.*
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Controlled modification of the pinning properties of bulk granular superconductors is an active area of applied and fundamental research.[1–8] Doping with different metals,[9,10] variation of stoichiometry,[11] and nonsuperconducting phase precipitation[12] are recent examples of the chemical tuning of superconducting materials. Systematic modification of superconductor *morphology* provides another way to influence intergrain coupling and intragrain critical currents.[1,6,13]

Various techniques to control pinning properties of $MgB_2$ have been suggested.[14] Alternative synthetic routes[13,15] and postsynthesis treatments,[16] fabrication of dense wires,[17] pellets,[16] and tapes,[18] annealing in Mg vapor,[19] doping with Na,[20] Co, Fe,[21] Cu, or Ag,[10] introduction of SiC nanoparticles,[22] Ag powder,[23] Ti precipitates,[24] synthesis of $MgB_2$/Mg nanocomposites,[25] intralayer carbon substitution[11,26] have all been reported.

In this letter, we report the sonochemical modification of grain morphology and intergrain coupling of polycrystalline $MgB_2$. The method is further extended for the *in situ* synthesis and embedding of ferromagnetic nanoparticles, which are shown to act as efficient magnetic vortex pinning centers.

In ultrasonically irradiated slurries, turbulent flow, and shock waves are produced by acoustic cavitation. The implosive collapse of bubbles during cavitation results in extremely high local temperatures ($\sim$5000 K)[27,28] and also creates high-velocity collisions between suspended particles with effective temperatures at the point of impact of $\sim$3000 K.[29] These high velocity collisions cause localized interparticle melting and "neck" formation.[27–29] The estimated speed of colliding particles approaches half of the speed of sound in the liquid. $MgB_2$ polycrystalline powder (325 mesh, Alfa Aesar) was ultrasonically irradiated for 60 min at $-5$ °C in 15 ml of decalin (0.13%, 0.26%, 0.5%, and 2% wt, respectively, at 20 kHz and $\sim$50 W/cm$^2$) under ambient atmosphere using direct-immersion ultrasonic horn (Sonics VCX-750). A similar set of slurries was sonicated with the addition of 1.8 mmol of $Fe(CO)_5$. The resulting material was filtered, washed repeatedly with pentane, and air-dried overnight.

Magnetic measurements were conducted using a *Quantum Design* Superconducting Quantum Interference Device (SQUID) MPMS magnetometer. For magnetic measurements, the powder was sintered at room temperature at a pressure of 2 GPa for 24 h. (Study of high-temperature annealing is in progress.) The average sample mass was 10 mg. The magnetic moment was normalized using the initial slope, $dM/dH$, measured at 5 K after zero-field cooling. The slope is proportional to the fraction of the superconducting phase. For materials without magnetic nanoparticles, such normalization gives the volume magnetization. For composites containing $Fe_2O_3$ nanoparticles, the normalization was done after subtraction of the paramagnetic contribution.

Scanning electron micrographs (SEM) were taken on a Hitachi S-4700 instrument. Samples were additionally characterized by powder x-ray diffraction and differential thermal analysis. All reported results were reproduced on more than 25 samples. We use the following sample designations: original $MgB_2$ powder (A) and sintered pellet (AP); $MgB_2$ sonicated in decalin with various loadings of the slurry (pellets: S1, 0.13% wt; S2, 0.26% wt; S3, 0.5% wt; S4, 2% wt); $MgB_2$ sonicated in decalin with 1.8 mmol of $Fe(CO)_5$ (pellets SF1, SF2, and SF3 with the same loading of $MgB_2$ as S1, S2, and S3). SEM images of the original (A and AP) as well as the sonicated samples (S1 and SF1) are shown in Fig. 1. Samples A and AP (a sintered pellet made from sample A) are shown in Figs. 1(a) and 1(b), respectively; no particular structural modification was observed upon making the sintered pellet. In contrast, the sonicated powder used for sample S1 [Fig. 1(c)] and sonicated with $Fe(CO)_5$ for sample SF1 [Fig. 1(d)] have distinctively modified morphologies. Even though the decomposition temperature of $MgB_2$

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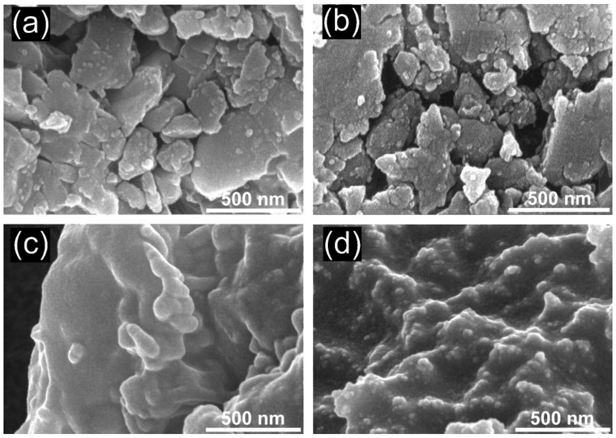


FIG. 1. Scanning electron images of (a) original $MgB_2$ powder, sample A; (b) $MgB_2$ pellet, sample AP; (c) $MgB_2$ sonicated in decalin, sample S1; and (d) $MgB_2$ sonicated in decalin with $Fe(CO)_5$, sample SF1.

($\sim$1100 K)[14] is lower than the effective local temperatures achieved during transient cavitation, the initial material apparently undergoes surface melting, as implied by Fig. 1(d). This can be attributed to extremely high cooling rates ($>10^9$ K/s)[29,30] leading to formation of smooth welded grains in sonochemical process. In the case of a superconductor, such morphological changes produce better intergrain coupling and annealing of the intragrain defects, consistent with our observations. Sonication of $MgB_2$ powder in decalin with $Fe(CO)_5$ is accompanied by the *in situ* sonochemical formation of iron oxide nanoparticles[31] directly on $MgB_2$ grain surfaces, while concurrent ultrasound-driven melting results in embedding of $Fe_2O_3$ nanoparticles into the $MgB_2$ matrix, Fig. 1(d). The embedded particles act as efficient pinning centers where magnetic interaction with Abrikosov vortices provides extra force in addition to the core pinning. Similar enhancement was reported in 1966 for Hg–In alloys with mechanically dispersed Fe nanoparticles.[32,33] Related recent work has also examined the effect of magnetic particles placed on the surface of low-$T_c$ superconducting films.[34–36] Our method is to embed ferromagnetic nanoparticles into high-$T_c$ superconductors.

Figure 2 shows $M(T)$ curves measured in magnetic field of 10 Oe after zero-field cooling (ZFC). The superconducting transition temperature remains unchanged, $T_c \approx 38.5$ K.

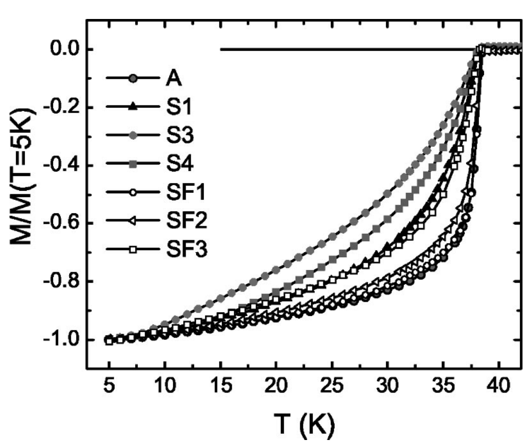


FIG. 2. Zero-field cooled magnetization measured in $H = 10$ Oe, normalized to its value at 5 K. The paramagnetic contribution for SF samples was subtracted using Curie–Weiss law measured up to 150 K.

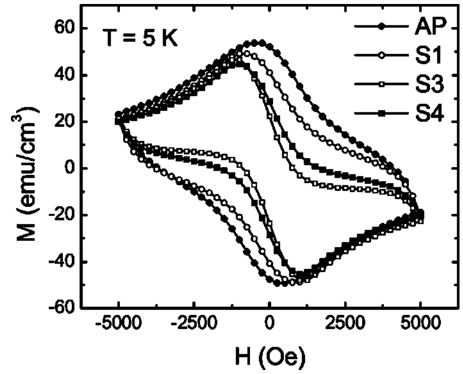


FIG. 3. Magnetization loops at $T = 5$ K for sonicated samples S1, S2, and S3 compared to the original sample AP. Width of the hysteresis loops is reduced, but the Meissner expulsion is not.

Curves in Fig. 2 were normalized by the magnetization value at 5 K, and the paramagnetic contribution for the SF samples was subtracted. Figure 3 shows the effect of sonication on the magnetization loops measured at 5 K for samples with different initial loading of $MgB_2$ slurries. The loops become less hysteretic and more asymmetric for loading up to 1% wt, after which the effect diminishes. This is as expected for the material, where intragrain defects are annealed during sonication and most of the grains are fused together. This also provides the evidence that Meissner expulsion in granular superconductors is mostly due to intragrain shielding and not to weak intergrain coupling.

As shown in Fig. 4, the situation is different for the samples sonicated with $Fe(CO)_5$. The magnetization loops are more hysteretic compared to sample A. However, the hysteresis decreases with increasing $MgB_2$ loading. This is in agreement with the results of Fig. 3 where the optimum effect of sonication was achieved for 0.5% wt of $MgB_2$ slurry. Figure 5 shows magnetization loops measured in sample SF3 at 30 and 42 K. The curve at 42 K is well described by the Langevin function, indicative of a superparamagnetic behavior. The hysteresis at $T = 42$ K is due to some magnetic anisotropy and dipole–dipole interactions[37] of the dispersed $Fe_2O_3$ nanoparticles, and it is much smaller than the hysteresis due to pinning. We verified this conclusion by measuring remnant magnetization as a function of temperature.

The irreversibility practically disappears at $T_c$. The difference, $\Delta M = M(30\ \mathrm{K}) - M(42\ \mathrm{K})$, shown by solid squares

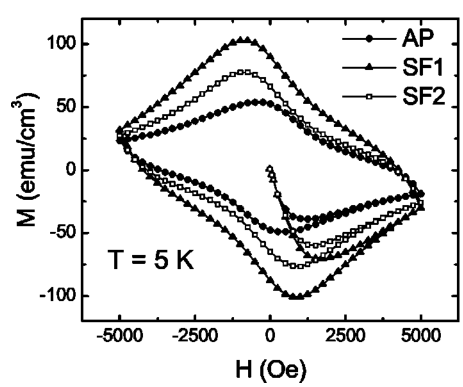


FIG. 4. Magnetization loops measured at $T = 5$ K in $MgB_2$ sonicated in decalin with $Fe(CO)_5$. The hysteresis is largest for the lowest loading of $MgB_2$.

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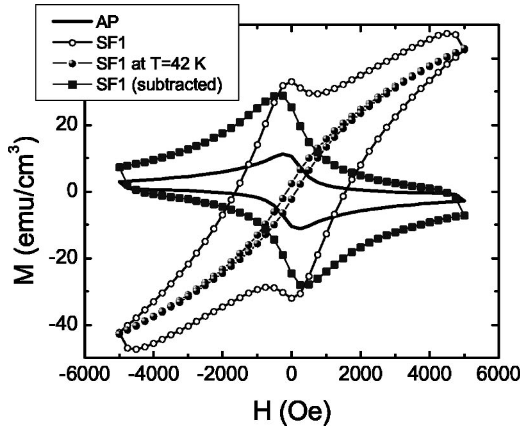


FIG. 5. Open symbols—measured magnetization loops for sample SF1; filled squares−same curve with paramagnetic contribution subtracted; filled circles–$M(H)$ curve measured at $T=42$ K. The solid line is the $M(H)$ curve of the unmodified $MgB_2$, sample AP measured at 30 K.

in Fig. 5 is typical for a superconductor with significant pinning. The solid line shows magnetization curve of the original sample AP. The comparison indicates more than twofold enhancement of pinning.

In conclusion, a method of a controlled modification of the superconducting properties of magnesium diboride is described. Ultrasonic cavitation leads to a significant change in morphology without affecting chemical composition. Sonication in decalin results in a granular superconducting material with significant intergrain fusion and a much less defective structure compared to the original $MgB_2$ powder. Sonication in decalin with the addition of $Fe(CO)_5$ produces a superconductor–ferromagnet composite in which ferromagnetic nanoparticles are embedded into the $MgB_2$ matrix. These particles act as efficient pinning centers. Our continuing research indicates that the described experimental technique and conclusions are applicable to other granular superconductors, such as $YBa_2Cu_3O_7$.

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