Improved upper critical field in bulk-form magnesium diboride by mechanical alloying with carbon

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High-energy milling of magnesium diboride (MgB_2) prereacted powder renders the material largely amorphous through extreme mechanical deformation and is suitable for mechanically alloying MgB_2 with dopants including carbon. Bulk samples of milled carbon and MgB_2 powders subjected to hot isostatic pressing and Mg vapor annealing have achieved upper critical fields in excess of 32 T and critical current density approaching 10^6 A/cm^2. © *2005 American Institute of Physics.*
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Recent studies of magnesium diboride thin films by Braccini *et al.*[1] found $H_{c2}(0 \text{ K})^{\parallel} > 50$ T for C-doped MgB_2 films. Fits to the data using the two-gap model of H_{c2} of Gurevich[2] showed an extrapolated $H_{c2}(0 \text{ K})^{\parallel}$ (H parallel to the Mg and B planes) of ~ 70 T and $H_{c2}(0 \text{ K})^{\perp}$ exceeding 40 T.[1] Such critical field properties exceed those of any Nb-based conductor at any temperature, suggesting that MgB_2 could be a viable replacement for Nb_3Sn as a high field magnet conductor. Masui *et al.*,[3] Ohmichi *et al.*,[4] and Kazakov *et al.*[5] have reported carbon-doped single crystals with $H_{c2}(0 \text{ K})^{\parallel}$ in excess of 30 T. Untextured carbon-doped filaments fabricated by a chemical vapor deposition (CVD) method can achieve upper critical fields in excess of 30 T at 4.2 K.[6] The measured H_{c2} in this case is the higher parallel critical field $H_{c2}^{\parallel}(0 \text{ K})$, rather than the lower, perpendicular critical field that controls the bulk J_C. One immediate question is how thin films and bulk differ. A partial answer was given by Braccini *et al.*[1] who noted that the *c*-axis parameter of the highest H_{c2} films was expanded relative to C-doped bulk samples, which have lower H_{c2} values.

Several groups[7–10] have also produced wires containing SiC, the latter finding that H_{c2} could attain values as high as the CVD filaments of Wilke *et al.*[6] In fact there is increasing suspicion that one of the beneficial effects of SiC addition occurs by C doping of the MgB_2. In general there is good agreement that C doping of MgB_2 is a useful means of alloying MgB_2, even if the best bulk H_{c2} values are only about half those of the best thin films. The present Letter discusses the *ex situ* synthesis of alloyed MgB_2 powder using high energy ball milling of MgB_2 with C. Since a major goal of MgB_2 technology is the fabrication of high critical current density, multifilament wire suitable for magnet applications, we need a scalable bulk process capable of producing carbon-doped precursor powder. One such method is provided by this paper.

The composition of carbon-doped MgB_2 is commonly given using the format $Mg(B_{1-X}C_X)_2$. Alfa–Aesar prereacted MgB_2 powder was mixed with powdered graphite in the following proportions: $0.1C + 0.9MgB_2$ (nominal $X = 0.0525$)

and $0.3C + 0.7MgB_2$ (nominal $X = 0.17$). The mixtures were high energy ball milled in a Spex 8000M mixer/mill with a WC milling container and milling media. Powders were milled until no graphite peak was discerned in the x-ray diffraction (XRD) pattern, which took 10 h for $X = 0.0525$ and 25 h for $X = 0.17$. The milled powders were then cold isostatic pressed to form pellets that were welded into evacuated stainless steel tubes and hot isostatic pressed (HIP) at 1000 °C and >30 ksi for 200 min. These HIP-treated pellets were cut apart and examined. They were black, lusterless, and lacked mechanical strength. These features were attributed to incomplete reaction due to a deficiency of Mg with respect to (B+C) resulting from adding C to the *ex situ* powder without adding Mg. Accordingly, portions of the HIP-treated pellets were welded into evacuated stainless steel tubing with a quantity of Mg metal that was about half the volume of the MgB_2 pellet. MgB_2 pellets and Mg metal were arranged in such a way that the sample would be exposed to Mg vapor, while limiting exposure to liquid Mg, as described by Braccini *et al.*[11] These sealed MgB_2+Mg packages were heat treated at 900 °C for 5 h and cooled at a rate not faster than 100 °C/h so as to fully react the B and C with Mg. After cutting the samples free from the steel, the samples were found to be black in color, to gain luster when polished, and to be dense and hard. However, even after this Mg vapor anneal, the x-ray intensities were reduced and the peaks broadened as compared with unmilled powders.

Some superconducting properties were then evaluated resistively with small transport currents of ~ 0.25 A/cm^2 in a 9-T Quantum Design physical properties measurement system (PPMS) and then with the 65-T short pulse magnet at the National High Magnetic Field Lab (NHMFL) in Los Alamos, NM. $H_{c2}(T)$ was defined by the 90% normal state resistance transition[11] giving values about 5–10 % lower than would be obtained by the 95–99 % transitions.[6] The hysteretic magnetization ΔM of bulk samples was also measured in an Oxford Instruments vibrating sample magnetometer (VSM), from which the critical current density $J_c(H,T)$ was calculated assuming fully connected samples using the expression $J_c(H,T) = \Delta M \times 12b/(3bd - d^2)$ where b and d are the width and thickness of a rectangular section bar.

Figure 1 compares $H_{c2}(T)$ of our samples to those of an $X = 0.035$C filament of Wilke *et al.*[6] Our $X = 0.0525$ sample

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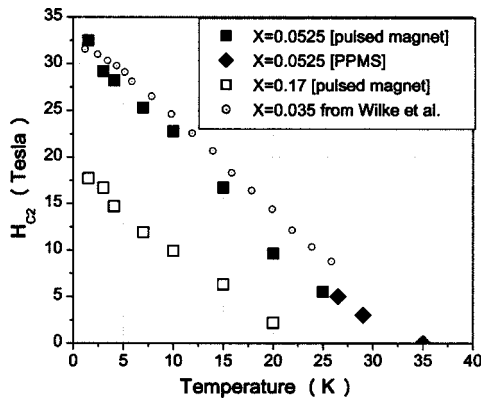
FIG. 1. H_{c2} defined by the 90% normal state resistivity of our carbon-doped samples and final onsets of full normal-state resistance for the sample of Wilke *et al.*[6]

had T_c of 35 K and $H_{c2}(0\ \mathrm{K}) \sim 33$ T, and our nominal X =0.17 sample had T_c of 22 K and ~ 19 T $H_{c2}(0\ \mathrm{K})$. The CVD filament[6] exhibited very similar properties to our X =0.0525 sample, given that $H_{c2}(T)$ was determined from the highest fraction of the transition, rather than the 90% transition as here.[6,12] These data also agree well with single crystal data for which an estimated maximum $H_{c2}^{\parallel}(0\ \mathrm{K}) \sim 29$ T at X=0.05 (Ref. 3) was reported.

To determine how much carbon was successfully incorporated into the lattice, Fig. 2 compares a-axis lattice parameters in the literature.[5,13–15] Both single crystal data sets (Kazakov *et al.*[5] and Lee *et al.*[15]) are rather linear in C content. Fitting the Kazakov *et al.*[5] data produces the following relationship:

$$a = 3.084\,39x - 0.3153, \tag{1}$$

where x is the carbon content given by $\mathrm{Mg(B_{1-x}C_x)_2}$.

Lattice parameters determined from high resolution x-ray diffraction measurements are presented in Table I along with the carbon content of the lattice calculated using Eq. (1). This calculation suggests that x=0.051 of the nominally X=0.0525 sample (Sample A) was incorporated into the lattice. For the nominal X=0.17 carbon-doped sample (Sample B), only about 40% of the available carbon was incorporated into the lattice (x=0.069). Between X=0.0525 and X=0.17 we experienced diminishing efficiency of carbon incorporation, as previously observed by Bharathi *et al.*[14]

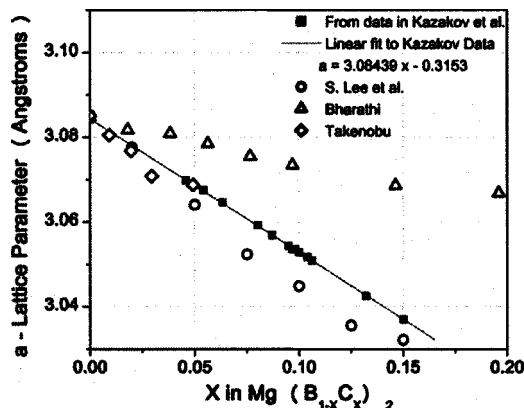TABLE I. Properties of C-doped milled samples.

Nominal X	a (Å)	c (Å)	Calculated X	ρ (40 K) ($\mu\Omega$ cm)	RRR
0.0525	3.0683(2)	3.5267(5)	0.051	960	1.185
0.17	3.062(3)	3.526(7)	0.069	9000	1.037

Figure 3 shows $J_C(H,T)$ of the samples. J_C of the X =0.0525 sample had a maximum approaching 10^6 A/cm^2, similar to values in the literature for HIP processed *ex situ* MgB$_2$.[16] The X=0.17 sample had maximum J_C depressed two orders of magnitude, with depressed irreversibility fields $H^*(T)$ as well (defined as the field at which J_C vanishes). As noted by comparing Figs. 1 and 3, $H^*(T)$ is of order one half $H_{c2}(T)$, for example 6 T at 20 K vs 10 T at 20 K for the X =0.051 sample. This is consistent with $H_{c2}(T)$ being determined by the highest $H_{c2}(T)$ path in the samples that corresponds to $H_{c2}^{\parallel}(T)$, whereas $H^*(T)$ is determined by the breakup of the fully connected path that starts to occur in the vicinity of $H_{c2}^{\perp}(T)$.

As shown in Table I, the normal state resistivity values were two to three orders of magnitude higher than those measured in carbon-doped single crystals[5] or in good undoped samples.[17,11] The normal state resistivity of the X =0.17 sample [$\rho(40\ \mathrm{K})$=9000 μohm cm was nearly a factor of 10 higher than that of the X=0.0525 sample 960 μohm cm]. Such values are indicative of reduced connectivity,[18] a conclusion supported by their essentially metallic temperature dependence and residual resistivity ratio (RRR) values (1.185 for X=0.0525 and 1.037 for X =0.17). It is interesting that the $J_c(H,T)$ values can still approach 10^6 A/cm^2, even with this high resistivity. Like some SiC-doped wires of Dou *et al.*[8] with high $\rho(40\ \mathrm{K})$ values, it appears that the inferred poor connectivity of the samples is not a barrier to attaining high J_c values. An additional intrinsic source of high resistivities in both samples is likely due to incomplete recovery of milling-induced disorder during heat treatment, as supported by the weak XRD patterns with broad peaks. Such inhibited recovery is generally not observed in undoped samples, leading to the conclusion that the presence of carbon hinders eliminating defects after milling. The low J_C of the X=0.17 sample and the conclusion that not all of the C is incorporated into the lattice indicates addi-
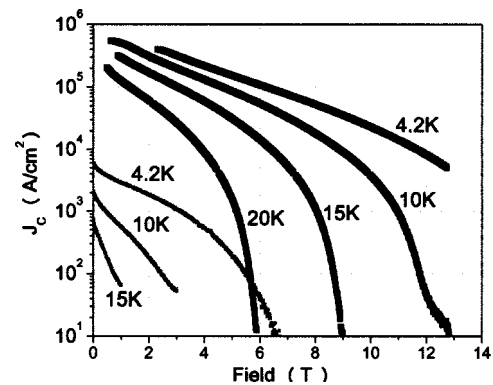

FIG. 2. a-axis lattice parameter as a function of carbon content. Data from Kazakov *et al.*,[5] Takenobu *et al.*,[13] Bharathi *et al.*,[14] and Lee *et al.*[15]

FIG. 3. Magnetization $J_c(H,T)$ values derived for X=0.0525 (thick lines) and X=0.17 (narrow lines). Comparison of the fields at which J_c tends to zero are about half the values of $H_{c2}(T)$ found in Fig. 1.

tional obstruction by residual C phases, as has been seen in some C-doped films.[19]

In summary we have shown that milling C with MgB_2 can produce $H_{c2}(0 \text{ K})$ equal to that obtained for single crystals and CVD filaments. Lattice disorder introduced in the milling process is indicated by weakened XRD patterns, high normal state resistivity, and a low-temperature upturn in $H_{c2}(T)$.

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