Nanocoating of particles for optimal doping and universal enhancement of current-carrying ability in "organic" MgB2-xCx superconductors

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Nanocoating of particles for optimal doping and universal enhancement of current-carrying ability in "organic" $MgB_{2-x}C_x$ superconductors

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The universal approach of liquid mixing has been found to produce "organic" $MgB_{2-x}C_x$ superconductors with structural and supercurrent-carrying properties unattainable by other techniques. We show by transmission electron microscopy combined with energy dispersive spectroscopy that these unique properties are enabled through coating of boron particles with a nanolayer of carbon. The subsequent reaction between carbon-encapsulated boron and magnesium results in enhanced carbon content x in the crystal lattice, as determined by x-ray diffraction pattern analysis. Among various carbon-containing compounds investigated, polycarbosilane has been found to be the optimal dopant for MgB_2 superconductor, producing the largest critical current density due to the formation of wide range of nanodefects with pinning properties within the MgB_2 crystal lattice, as well as due to minimal formation of current-blocking layers around the grains. © *2010 American Institute of Physics.* [doi:10.1063/1.3366610]

Superconductivity, with its zero-resistance below the critical temperature T_c and its capacity to carry high supercurrents in some superconducting materials, enables unique high-current applications, for example, in medicine (superconducting magnets for magnetic resonance imaging). The middle range T_c superconductor MgB_2 discovered in 2001 (Ref. [1]) is one of the most promising materials for these applications. Intensive studies of this superconductor have resulted in significant advances in understanding of current-carrying performance at high magnetic fields. The key feature of the advanced performance is the conversion of MgB_2 into "organic" $MgB_{2-x}C_x$ superconductor,[2] which is relatively easily achievable via chemical doping with carbon-based compounds.

Nano-SiC has been shown to be one of the most effective dopants for enhancement of electromagnetic properties of MgB_2 superconductor.[2–5] However, the critical current density (J_c) enhancement achieved at high fields are usually associated with J_c degradation in low fields due to stronger current carrier scattering and current-blocking effects on grain boundaries.[6] The search for optimal conditions and new methods for converting MgB_2 into $MgB_{2-x}C_x$ has led to a new advanced and, at the same time, simplified approach for the carbon-doping of MgB_2 superconductor. We have dissolved, first, glucose ($C_6H_{12}O_6$) (Ref. [7]) and then a range of other carbohydrates, such as malic acid ($C_4H_6O_5$),[8] in an appropriate solvent (water and toluene, respectively), and then mixed the particular carbon-containing solution with boron powder. This approach assumes extremely homogeneous mixing of raw components enabling enhanced performance of the final $MgB_{2-x}C_x$ superconductor. A reasonable assertion was made that the liquid mixing approach results in a coating of each boron particle with a nanolayer of carbon.[7] However, no evidence for this has been provided so far. In this work, we indeed reveal the thin carbon plating on the surface of the boron precursor powder particles and clarify its role in the enhanced current-carrying ability.

To demonstrate the simplicity of our new approach, we employed table sugar (or sucrose, $C_{12}H_{22}O_{11}$) as a cheap and readily available carbon dopant for MgB_2 superconductor. To prove universality, we show that the liquid mixing approach can be extended to the group of polymer carbon-containing dopants. For this purpose, the effect of polycarbosilane (C_2H_6Si) doping has been investigated. The polycarbosilane is a polymer analog to nano-SiC doping,[9] which is expected to *combine the benefits* of the liquid mixing of carbohydrates and the codoping with C and Si, as it occurs in nano-SiC doping.[2,3]

Pure and doped MgB_2 bulk samples have been prepared using our new liquid mixing approach.[7] To enable a comparative analysis, three dopants, table sugar ($C_{12}H_{22}O_{11}$), malic acid ($C_4H_6O_5$), and polycarbosilane (C_2H_6Si, PCS later in the text), have been added at the level of 10 wt %. The sugar was dissolved in water while the malic acid and the PCS were dissolved in toluene (C_7H_8). After the liquid mixing stage, samples were pressed into pellets, and then heat treated at 700 °C for 30 min in Ar atmosphere, followed by furnace cooling to room temperature.

The critical current density as a function of the applied magnetic field (B_a) has been determined from magnetization measurements using the critical state model for the rectangular geometry of the samples. Transmission electron microscopy (TEM) has been carried out using a JOEL 2011 200
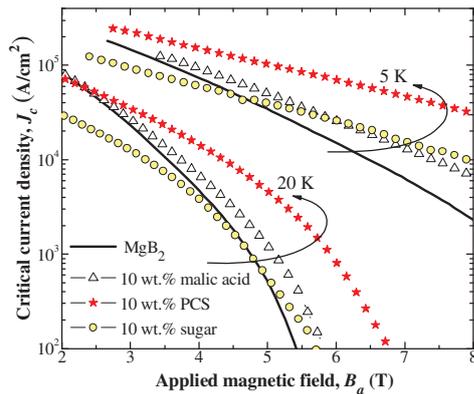
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FIG. 1. (Color online) $J_c(B_a)$ of MgB$_2$ samples with 10 wt % addition of malic acid, PCS, and sugar doping materials.

FIG. 3. (Color online) Level of C substitution (x) for B in MgB$_2$ lattice.

KeV analytical electron microscope with a JOEL energy dispersive x-ray spectroscopy (EDS) system. X-ray diffraction (XRD) patterns were obtained on a GBC Mini-Materials Analyser (MMA) x-ray diffractometer, whereas Rietveld refinement of XRD patterns has been used to analyze the crystal structure of the samples.

The liquid mixing of boron with carbon-based dopants resulted in the significant enhancement of the $J_c(B_a)$ for all the samples studied (Fig. 1), which is consistent with previous results.[7,8] The observed improvement of $J_c(B_a)$ is due to the appearance of additional defects, which increase the upper critical field (B_{c2}) through enhanced electron scattering, and improve pinning of magnetic vortices on defects with the size of $\sim 2\xi$,[3–5,10–12] where ξ is the coherence length. TEM investigations (Fig. 2) revealed that typical additional defects induced by doping are (i) *crystal lattice defects*--stacking faults and dislocations [Fig. 2(a)] and nanodomains [Fig. 2(b)], etc.--of <10 nm produced by C substitution, and (ii) *nanoscale impurities* with sizes of $\leq$20 nm (MgO in samples with carbohydrate doping; MgO and Mg$_2$Si in the PCS doped sample) [Fig. 2(c)].
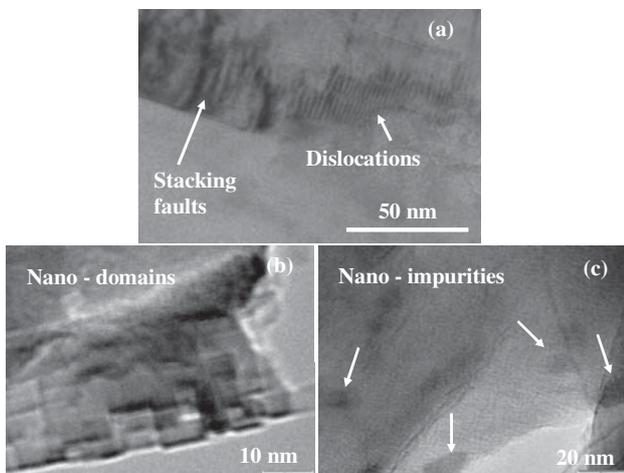

FIG. 2. Typical defects observed in C-doped MgB$_2$ samples: (a) stacking faults and dislocations; (b) nanodomains of <10 nm large size; (c) nanoscale impurities of $\leq$20 nm large.
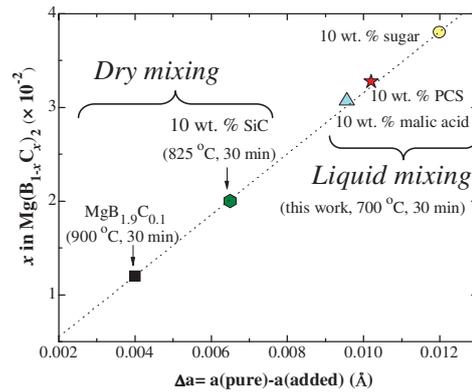
Generally, the crystal lattice is much more defective in doped than in pure MgB$_2$, and hence ξ is smaller (because $B_{c2} \propto 1/\xi^2$ is considerably larger). Therefore, defects with smaller sizes, such as type (i), which are less effective for pure samples with larger ξ, *become effective pinning sites*. This also explains the generally stronger enhancement of $J_c(B_a)$ for the doped samples at lower temperatures (Fig. 1), in which $\xi(T)$ is the smallest.

The $J_c(B_a)$ of the MgB$_2$ sample with PCS doping considerably exceeds those of the MgB$_2$ samples with carbohydrate dopants (Fig. 1). Note, in contrast to oxygen containing carbohydrates, PCS doping *does not introduce excessive oxidation effects* (e.g., for Mg), which result in unwanted sediments around MgB$_2$ grains, reducing the current flow. The level of MgO is 7, 7, 12, and 18 wt % for pure, PCS, malic acid, and the sugar doped MgB$_2$ samples, respectively. Note, the higher level of MgO in the sugar doped sample than in the malic doped sample may be due to both, higher level of oxygen in this compound and water used during the liquid mixing. There could be about 20% variation of MgO content in pure MgB$_2$ samples, depending on preparation route (liquid or dry mixing) at the same conditions and environment. In addition, the large amount (11 wt %) of Mg$_2$Si impurities in PCS doped sample introduce an additional level of lattice distortion [defects of type (i)], resulting in enhanced $J_c(B_a)$ at low temperature (5 K), and these act as pinning centers themselves at higher temperatures, explaining the excellent $J_c(B_a)$ performance in PCS doped MgB$_2$ sample at 20 K (Fig. 1), which far exceeds those of malic acid and sugar doped samples.

Carbon-based doping results in the reduction of the a-lattice parameter (Δa in Fig. 3) due to the C substitution for B sites in the MgB$_2$ crystal lattice.[13] Generally, the larger the Δa value, the higher is the level of C (x) substituted for B in MgB$_2$, producing a denser network of microstructural defects [type (i)] crucial for enhancement of current-carrying ability in the MgB$_{2-x}$C$_x$ superconductor. The results in Fig. 3 show that the liquid mixing approach promotes the enhanced incorporation of C on B sites in the MgB$_{2-x}$C$_x$ crystal lattice during the sintering when compared to the conventional dry-mixed samples prepared with SiC (Ref. 14) and C (Ref. 15) nanodopants.
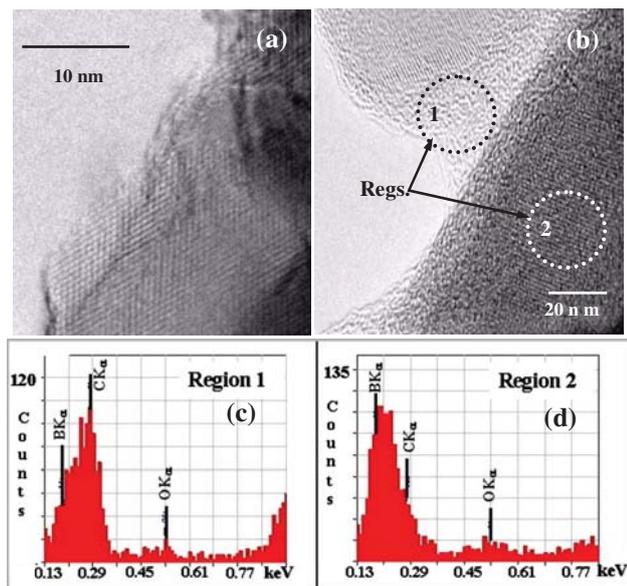
FIG. 4. (Color online) TEM images of crystalline boron nanoparticles: (a) as received; (b) coated by an amorphous carbon nanolayer. [(c) and (d)] EDS spectra obtained from regions 1 and 2 in (b).

To clarify the role of the liquid mixing approach for promoting C substitution in the MgB_2 lattice (Fig. 3) and enhancing $J_c(B_a)$ of MgB_2 with the dopants studied (Fig. 1), TEM analysis of boron nanoparticles after liquid mixing with C-based compounds was performed. Crystalline boron was used in order to boost the contrast between B and amorphous C in TEM observations. First, the surface of the reference crystalline boron nanoparticles (as obtained from a supplier) was examined. The lattice fringes associated with crystalline boron continue all the way along to the edge of the sample, consistent with the presence of clean crystallites, free from any significant surface contamination [Fig. 4(a)].

Next, TEM observation was performed on the boron +sugar slurry, which was dried after liquid mixing of these elements in distilled water. An amorphous layer, 10–20 nm thick, was consistently observed at the edges of the crystalline B-particles [Fig. 4(b)], and analyzed using EDS. The EDS spectrum associated with region 1 reveals a high amount of carbon (at an energy of ~ 0.29 keV) [Fig. 4(c)], whereas the spectrum associated with region 2 (at ~ 0.18 keV) indicates that boron is the dominant element in this region [Fig. 4(d)]. Due to the low count rate generated by the small areas (~ 25 nm), it was difficult to precisely evaluate the concentration of B and C elements in these regions. However, the TEM observations supported by the EDS spectra unambiguously demonstrate the formation of the carbon-rich nanolayer, which coats the B particles after liquid mixing.

The TEM images obtained for malic acid and PCS doped samples are very similar to those shown in Fig. 4, but for latter the B particles are coated by a mixture of amorphous C and Si, as confirmed by EDS analysis.

This coating configuration offers the most possible homogeneity of mixing and an optimal reaction area between boron and carbon. In addition, decomposition of the studied C-based dopants at low temperatures (<300 °C) assures a two-stage process:[7] (i) formation of fresh carbon and (ii) subsequent MgB_2 formation, which assures effective chemical doping of MgB_2 superconductor by C, and results in the dramatic enhancement of electromagnetic properties in $MgB_{2-x}C_x$ material. This process has been generalized to the so-called dual reaction model,[2] which works for various combinations of multielement dopants releasing fresh carbon in the first stage (which does not necessarily involve liquid mixing).

In summary, we have demonstrated that developed liquid mixing approach results in the formation of an extremely reactive C-rich nanolayer on the surface of the boron particles. During subsequent reaction with Mg and B powders, this configuration promotes a higher level of carbon substitution into the MgB_2 crystal lattice. This substitution generates a denser network of pinning sites and results in enhanced $J_c(B_a)$ performance at high fields. The results of this work show that the liquid mixing approach can be effectively employed for polycarbosilane doping of MgB_2 superconductor, which results in the dramatic enhancement of the critical current density in this material at high fields. Moreover, the approach of liquid pretreatment is generally expected to create a nanoscale coating on host particles, independent of the liquid solution and the host particles, which would make this process extremely efficient for relevant technologies in different areas of science.

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