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Olga V. Shcherbakova
University of Wollongong, olga@uow.edu.au

Alexey V. Pan
University of Wollongong, pan@uow.edu.au

Emil Babic
University of Zagreb

S. X. Dou
University of Wollongong, shi@uow.edu.au

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“Organic” $\text{MgB}_{2-x}\text{C}_x$ superconductor with high performance enabled by liquid mixing approach

O. V. Shcherbakova¹, A. V. Pan¹, E. Babić², and S. X. Dou¹

¹Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia

²Department of Physics, Faculty of Science, University of Zagreb, 10002 Zagreb, Croatia

E-mail: olga@uow.edu.au (O. V. Shcherbakova)

Abstract. Comparative analysis of structural and electromagnetic characteristics have been performed on nano SiC- and polycarbosilane-doped MgB_2 samples prepared by the dry and liquid mixing approaches. The total benefit of liquid mixing approach for fabrication of “organic” MgB_2 superconductor with excellent electromagnetic performance has been demonstrated.

1. Introduction

The “middle temperature” MgB_2 superconductor (with $T_c = 39$ K) discovered in 2001 [1] has been regarded as a very promising candidate for high current applications in the temperature range of 20 to 25 K. The progress in development and fabrication of this material made its performance highly efficient for medical applications, such as magnetic resonance imaging systems (MRI). Extensive investigation and study of MgB_2 superconductor has resulted in a significant breakthrough for the performance of this conductor at high fields (required for applications in high field magnets). This breakthrough has been achieved with introduction of carbon into the crystal lattice of MgB_2 via chemical doping with nano-C or C-based compounds.

Chemical doping is easy and a relatively cheap and effective approach for enhancement of MgB_2 superconducting properties. The high values of critical current density ($J_c(B_a)$, B_a is an applied magnetic field), irreversibility (B_{irr}) and upper critical (B_{c2}) fields of MgB_2 superconductor achieved by nano SiC and C doping are bright examples of this technique [2, 3, 4, 5, 6, 7]. There are, however, some unavoidable obstacles which reduce the effectiveness of this method.

First of all, it is extremely difficult to homogeneously distribute a small amount of nano-dopant among matrix elements. This is because any dry mixing results in the formation of large particle agglomerates. This unavoidably results in inhomogeneity of the final MgB_2 material, which is not desirable from the applications point of view.

Second, nano particles used for chemical doping always have a wide distribution of particle size. While small particles have better reactivity with matrix elements, large particles have poor reactivity and remain unreacted in the system. This was demonstrated on the samples with nano-SiC doping [8]. Unreacted dopants are less desirable, because they result in reduction of superconducting volume and degrade the current flowing through the superconductor.

Third, the vast majority of the nano dopants employed have been introduced into the MgB₂ matrix in passivated state. In this case, the surface of the nano particles is contaminated (by oxide compounds, for example), which degrades their reactivity and, hence, doping effectiveness. That is why for various forms of nano C doping, C substitution for B cannot be achieved at the same temperature as MgB₂ formation and requires a much higher annealing temperature.

Therefore, in our group we have developed a new advanced and, at the same time, simplified *liquid mixing* approach [9] for the fabrication of “organic” MgB_{2-x}C_x superconductors. This approach results in extremely homogeneous mixing of raw components and enables enhanced performance of the final MgB_{2-x}C_x superconductors.

The idea behind the liquid mixing approach can be extended to a wide group of polymer dopants. In this work, one of these materials, polycarbosilane, has been investigated. Polycarbosilane (C₂H₆Si, PCS later in the text) is a polymer analogous to SiC [10] and can be expected to combine the benefits of the liquid mixing of carbohydrates [9] and the co-doping of C and Si, as in nano SiC doping [2, 3]. In addition, we have performed a comparative study of samples with nano-SiC and polymer PCS dopants prepared by dry and liquid mixing techniques. The absolute benefit of liquid mixing approach for formation of “organic” MgB_{2-x}C_x superconductors is demonstrated.

2. Experimental

Bulk samples of pure, 10 wt.% nano-SiC and PCS-doped MgB₂ have been prepared *in-situ* by hand mixing of Mg, B and doping materials (dry mixing technique). The 10 wt.% PCS-doped MgB₂ bulk sample was fabricated using our new liquid mixing approach [9]. After PCS compound was dissolved in toluene (C₇H₈), an appropriate amount of B powder was added to dopant in the solvent and well mixed with a mortar and pestle by hand. After the liquid mixing stage, the wet slurry of boron, dopant, and solvent was dried in a vacuum chamber at a slightly elevated temperature (200°C) overnight to remove the remaining solvent and moisture. After drying, the powder was ground, mixed with Mg powder, and ground again. The Mg+2B+dopant mixture was pressed in stainless steel tube (at pressure of 12 MPa) and encapsulated with Fe plugs using a hydraulic press for formation of MgB_{2-x}C_x sample in a pellet form. Pressed samples were heated at the rate of 5 °C/min and sintered at 700°C for 60 min, followed by furnace cooling to room temperature. Detailed description on fabrication of pure and 10 wt.% nano-SiC doped MgB₂ can be found in Ref. [7], and for PCS-doped MgB₂ prepared by dry mixing in Ref. [10]. In Figures and Table “PCS-dry” and “PCS-liquid” denote PCS-doped MgB₂ samples prepared by dry and liquid mixing techniques, respectively.

The lattice parameters and impurities phase fraction of MgB_{2-x}C_x samples were estimated via Rietveld refinement of X-ray diffraction (XRD) patterns. The $J_c(B_a)$ curves were derived from the height of magnetization loops measured on a Physical Property Measurement System (PPMS, Quantum Design) in fields of up to 8 T, using the critical state model [11]. The magnetic critical current density was calculated using the relation $J_c = \frac{20\Delta M}{a(1-\frac{a}{3b})}$, where a and b are the dimensions of a bar shaped sample perpendicular to the magnetic field direction ($a < b$), ΔM is the width of hysteresis loop. All the samples for magnetic measurement were shaped to the same size of $a = 0.05$ cm, $b = 0.2$ cm, and $c = 0.3$ cm for consistent comparison. The $B_{c2}(T)$ values were obtained from resistivity (ρ) versus temperature curves measured by 4-points technique using criteria of $B_{c2}(T) = 0.9\rho(B_a, T)$.

3. Results and discussion

The results on structure and phase analysis obtained from Rietveld refinement of XRD patterns are presented in Table 1. In the MgB₂ hexagonal cell, the a -lattice parameter is reduced with addition of C-based dopants (Table 1), while the c -lattice parameter does not change significantly

(3.524 ± 0.002 nm). The reduction in the a -value is associated with partial carbon substitution on B sites in the MgB₂ crystal lattice. The smaller the a -value, the higher the level of carbon that has been introduced into the lattice. The actual level of C substitution (x in Mg(B_{1-x}C_x)₂, Table 1), has been calculated from the change in the a -parameter of the crystal lattice [12].

One level (10 wt.%) of doping by analogous compounds (nano-SiC and polymer PCS) and employed preparation techniques have notable influence on phase and structure formation in samples studied (Table 1). Among samples prepared by dry mixing approach, PCS doping results in higher level of C substitution for B, and larger amount of Mg₂Si phase, compared to sample with nano-SiC doping. It can be explained by the fact that PCS initially contains higher level of C in its compound (C₂H₆Si). Some C could be introduced by toluene, which also has high amount of carbon (C₇H₈). In addition, disordered Si and C atoms released after decomposition of PCS at temperature of 300 °C [10] appears in a highly reactive (unpassivated) form when the MgB₂ formation reaction starts at 650°C, promoting the enhanced incorporation of C on B places in MgB₂ lattice during the heat treatment. In case of nano-SiC doping, according to dual reaction model proposed by Dou et al.[7], which is based on two stage process described in Ref.[9], free carbon on the atomic scale also appears after reaction between Mg and Si, which takes place at temperature of about 600 °C [14]. However, lower value of x as well as relatively small amount of Mg₂Si phase in nano-SiC doped sample indicate on worse reactivity of nano elements, probably due to inhomogeneous particles distribution or their agglomeration.

In the case of PCS-doped MgB₂ sample prepared by liquid mixing, the x -value and amount of Mg₂Si are notably higher compared to the dry-mixed samples. In our previous work Ref.[13], we have demonstrated that liquid mixing technique enables coating of boron particles with a nano-layer of carbon and silicon mixture. Our results indicate that liquid mixing approach results in more efficient doping, which assures the maximum surface for reaction and clean interfaces between boron and the doping elements in the nano-layer, in contrast to the arrangement obtained by dry-mixing of nano-powders.

Table 1. Some structural and superconducting parameters of samples studied.

Sample	Anneal. temp., °C	a , nm	x in MgB _{2-x} C _x	Mg ₂ Si, wt. %	FWHM (101), degree	T_c , K	B_{c2} , (5 K) T
MgB ₂	825	3.0850	-	-	0.3340	37.2	19
nano-SiC	825	3.0750	0.020	6.2	0.4840	36.0	28
PCS-dry	850	3.0746	0.028	9.7	0.5140	35.1	30
PCS-liquid	700	3.0741	0.033	11.2	0.5520	34.7	32

FWHM (Full Width at Half Maximum) values of (101) peak for samples investigated are summarized in Table 1. FWHM value can be used for calculation of crystalline size, which is proportional to grain size. The higher FWHM values correspond to smaller grain size. The microstructure investigation has shown a general reduction in MgB₂ grain size caused by SiC doping. This is likely due to the fact that Mg₂Si particles formed at lower temperature (about 600 °C [14]) act as nucleation centers for MgB₂ grain formation. This point of view together with large FWHM value support the idea that liquid mixing approach enables the formation of small grain size due to homogenous distribution of possible nucleation sites (in the form of nano C or Mg₂Si impurities) as it occurs in PCS-doped MgB₂ sample (PCS-liquid in Table 1).

Importantly, increasing width of peak and, therefore, FWHM value is caused by several factors, including grain size, level of C-substitution, lattice strain caused by lattice defects

(vacancies, interstitial, substitutions, stacking faults, etc)[15]. Therefore, large FWHM values also indicate on high level of defects in the sample. Indeed, higher level of carbon substitution on boron sites and the appearance of a high level of nano inclusions promote greater crystal lattice distortion and result in formation of denser network of crystal lattice or “secondary” defects (dislocations, stacking faults, nano-domains, etc.) in doped samples. Hence, the highest density of “secondary” defects is generated in PCS-doped sample fabricated by liquid mixing technique, which has the highest level of C-substitution and largest amount of Mg₂Si impurities (Table 1).

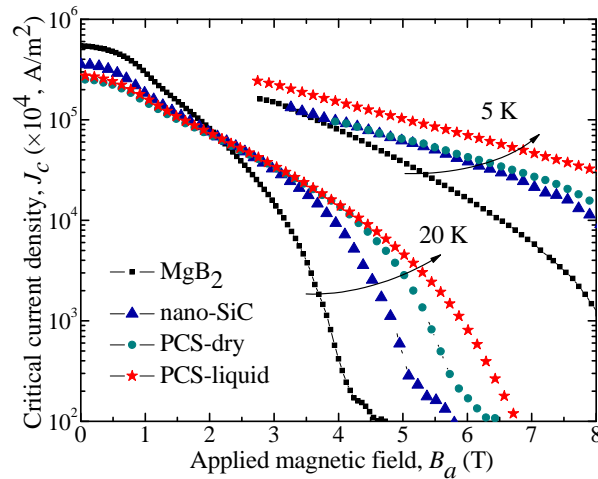


Figure 1. $J_c(B_a)$ performance of samples prepared by dry (MgB₂; nano-SiC MgB₂, denoted as nano-SiC; PCS-doped MgB₂, denoted as PCS-dry) and liquid mixing (PCS-doped MgB₂, denoted as PCS-liquid) approaches.

The critical temperature, T_c , reduces as the level of C-substitution on B site, x , increases in the samples (Table 1). This behaviour is commonly observed in MgB_{2-x}C_x superconductors.

Magnetic field dependance of the critical current density, $J_c(B_a)$, and temperature dependance of the upper critical field, $B_{c2}(T)$, for the samples studied are shown in the Fig. 1

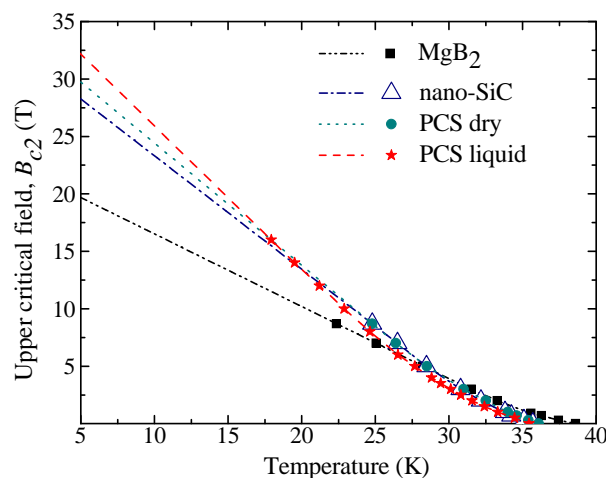


Figure 2. Temperature dependance of the upper critical field, $B_{c2}(T)$, for the samples studied.

and Fig. 2, respectively. As can be seen, in-field $J_c(B_a)$ and lower temperature ($T < 25$ K) $B_{c2}(T)$ performances for “organic” $\text{MgB}_{2-x}\text{C}_x$ superconductors are significantly higher than those for undoped one. Linear extrapolation of $B_{c2}(T)$ curve for PCS-doped sample prepared by liquid mixing yields $B_{c2}(5\text{ K})$ of 32 T, which is the highest value among samples studied (Fig. 2).

Observed enhancement of $J_c(B_a)$ and $B_{c2}(T)$ in studied $\text{MgB}_{2-x}\text{C}_x$ superconductors are due to formation of additional defects induced by Si and C co-doping. These defects lead to enhanced electron scattering and, therefore, increase the upper critical field values. On the other hand, dense network of defects with the size of $\sim 2\xi$, where ξ is the coherence length, improves pinning of magnetic vortices and, hence, in-field $J_c(B_a)$ performance. The pinning sites induced by nano-SiC and PCS doping include: (i) *grain boundaries* and (ii) *crystal lattice defects*, generated by nano scale Mg_2Si impurities and C-substitution for B in $\text{MgB}_{2-x}\text{C}_x$ samples [2, 3, 7, 10]. It is clear that PCS-doped MgB_2 sample prepared by liquid mixing approach, which enables formation of the smallest grain size, the highest level of C-substitution and the largest amount of Mg_2Si impurities, shows superior $J_c(B_a)$ and $B_{c2}(T)$ performances among other samples studied, prepared by dry mixing technique.

We believe that an outstanding advantage of liquid mixing approach is in the most possible homogeneous distribution of dopant and maximal reaction area between boron and dopant. Moreover, liquid mixing approach employed for carbohydrates and polymer C-based materials lead to two-stage process [9]: (i) formation of fresh carbon and (ii) MgB_2 reaction, which was generalized to the so-called dual reaction model [7].

4. Conclusion

We have performed structural and electromagnetic analysis of “organic” $\text{MgB}_{2-x}\text{C}_x$ superconductors with nano-SiC and PCS dopants prepared by conventional dry and new liquid mixing techniques. It is demonstrated that the liquid mixing enables effective doping, which assures: i) highly homogeneous mixing of host and doping materials; ii) coating of boron particles by nano-layer of amorphous carbon and silicon mixture, which facilitate C-substitution in MgB_2 crystal lattice; iii) high level of small and well dispersed within the sample Mg_2Si impurity phase; iv) small grain size; and, therefore, v) formation of microstructure with high amount of small optimally distributed defects, which improve pinning and enhance electron scattering of final material. The liquid mixing approach employed for PCS dopant results in formation of “organic” $\text{MgB}_{2-x}\text{C}_x$ superconductor with excellent electromagnetic performance, which is important result of this work. As shown, the PCS doping outperforms nano-SiC doping, which was considered as the best dopant so far.

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