Optimization of Carbon Encapsulated Boron Doping for High-Performance Bulk Sintered MgB$_2$

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Carbon has been a standard doping agent in MgB$_2$ for long time. It, however, has also participated in a non-uniform distribution of the constituents throughout the bulk MgB$_2$. To address this issue, carbon encapsulated boron (CEB) was used instead of the manually added mixture of boron and carbon. The previous studies confirmed that only low concentrations of carbon in CEB were effective for synthesis of a high-performance bulk MgB$_2$. Here, a further step in optimization carbon content in CEB is reported. Carbon content in CEB varied as 1, 1.1, 1.35, 1.5, and 1.9 wt%. X-ray diffraction (XRD) results depict a slight shift in peaks corresponding to $a$–$b$ plane, indicating carbon substitution into the lattice. High superconducting critical current density in self-field, such as 660, 550, and 435 kA cm$^{-2}$, was observed in the samples with 1.5 wt% CEB at 10, 15, and 20 K, respectively. In addition, $J_c$ of 75 kA cm$^{-2}$ at 2 T and 20 K was observed in the 1.5 wt% CEB sample, which is thrice the value observed in the pure sample, with a minute tradeoff in $T_c$ (around 37.5 K). Scanning electron microscope (SEM) images reveal that small particles of size ranging from 50 to 200 nm contribute to $J_c$ improvement. Energy-dispersive X-ray (EDX) results show carbon uniformly distributed throughout the bulk.

1. Introduction

Discovery of superconductivity in MgB$_2$\cite{1} attracted research focus from trendy superconductors (intermetallic,\cite{2} cuprates, etc.). The reason was the specific position of this material among other superconductors, being much closer to conventional ones,

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as the products require stability and reliability over long run. To enable a commercial production, we opted carbon encapsulated boron (CEB), where carbon uniformly coats nano-sized boron. In our previous works, we reported that a low concentration of carbon (less than 3 wt%) resulted in a high critical current density. In opposite, higher concentrations of carbon resulted in a degradation of critical temperature and formation of undesired Mg–C–B phases. The size of CEB particles is in nanometer order, which also aids in improving self-field $J_c$. So, we need to perfectly optimize the carbon content to obtain best performance for commercialization. In this work, we tried to vary the carbon wt% from 1 to 1.9 wt% and to tune the product properties.

2. Results and Discussion

X-ray diffraction (XRD) results in Figure 1 show a slight shift of the (110) peak toward higher diffraction angles in proportion with carbon wt%. This tells us that there is carbon substitution in the lattice, and the amount of shift is proportional to the amount of carbon substituted. The lattice parameters were calculated using Bragg’s law. The lattice parameter $a$ (equivalent to $b$) was calculated using (110) peak, parallel to $ab$-plane, whereas $c$ was calculated using (002) peak, perpendicular to $ab$-plane. The standard lattice parameters of pure MgB$_2$ are $a = b = 3.086$ Å and $c = 3.524$ Å. $a$ drops with increasing carbon content, up to 1.5 wt%, but above 1.5 wt%, it starts to increase. This is because when carbon substitutes boron in the lattice, the lattice parameter shrinks, as the carbon atoms have a lower atomic radius compared with boron. The amount of decrease in the lattice parameter is, thus, proportional to the amount of carbon substitution. $c$ stays unchanged, as there is no shift in (002) peak. All the changes happen in $ab$-plane, and there is no shift in (00l) diffraction peaks. This is due to hexagonal arrangement of Mg and B layers in the MgB$_2$ lattice. More detailed information can be found in Table 1.

Figure 2 shows sharp transition, which indicates high quality of the MgB$_2$ bulks. The onset superconducting temperature results (Figure 3).

Table 1. Lattice parameters and crystallite size calculations from XRD data. Large reduction and smallest crystallite size are observed in CEB 1.5 wt%–based MgB$_2$ bulk.

| CEB wt% | Lattice parameter $a$ [Å] | Lattice parameter $c$ [Å] | Crystallite size [nm] |
|---------|--------------------------|--------------------------|----------------------|
| 0       | 3.086                    | 3.524                    | ≈27                  |
| 1       | 3.0854                   | 3.524                    | 21                   |
| 1.1     | 3.0849                   | 3.524                    | 21.3                 |
| 1.35    | 3.0826                   | 3.524                    | 21.3                 |
| 1.5     | 3.0798                   | 3.524                    | 17.1                 |
| 1.9     | 3.0830                   | 3.524                    | 19.8                 |

Figure 1. XRD of MgB$_2$ with several wt% CEB-based bulks. Shift in [110] peaks can be observed, whereas [002] peaks remain unchanged.
bulk with 1.5 wt% CEB exhibited the highest value among all other bulks, 435 kA cm\(^{-2}\) at self-field, 20 K (inset of Figure 4). At low fields close to self-field as well as high fields (2–4 T), \(J_c\) of the 1.5 wt% CEB-based bulk was high. These values are higher than in MgB\(_2\) doped by carbohydrates\(^{[32]}\). Moreover, the tradeoff between \(T_c\) reduction and \(J_c\) improvement was not as good as in the present case. This behavior can be explained by the diffraction data obtained from XRD. We calculated the crystallite sizes for all the bulks using Scherrer’s equation

\[
\tau = K\lambda/\beta\cos(\theta)
\]

Here, \(\tau\) is the crystallite size, \(K\) is the dimensionless shape factor (\(\approx 0.9\)), \(\lambda\) is the X-ray wavelength (Cu-K\(_{α}\) = 1.54 Å), \(\beta\) is the FWHM (highest intensity peak—(101) peak), and \(\theta\) is the Bragg angle. Usually, Scherrer’s formula can be used only on grains smaller than micrometer. In case of in-situ sintered bulk MgB\(_2\), the crystallite size lies around 15–37 nm\(^{[33]}\) and hence, the formula can be used without any restriction. Note that the FWHM of the diffraction peak can be affected by various parameters such as lattice strain due to C substitution, natural defects, etc. As all the bulks are processed in similar conditions, we assume that the contribution of the external factors is the same for all bulks and can be omitted during comparison. Another notable issue is the overlap of MgO highest intensity peak (200) with MgB\(_2\) (101) peak. To ensure that there was no influence on the MgO peak, we have performed Rietveld refinement analysis on the diffraction pattern (using materials analysis using diffraction [MAUD]) and calculated the FWHM of MgB\(_2\) diffraction peak. Simultaneously, we calculated the phase fraction of MgO in the bulks. It was 5, 3.5, 3, 4.7, and 4.9 wt% in 0, 1, 1.1, 1.35, 1.5, and 1.9 wt% CEB-based MgB\(_2\) bulks, respectively. All the bulks had very low MgO content (<5 wt%), which ensured low or none influence on FWHM calculations of (101) MgB\(_2\) diffraction peak. In Table 1, we can find the lowest crystallite size \(\approx 17\) nm in MgB\(_2\) with 1.5 wt% CEB, which resulted in a high self-field \(J_c\), as grain boundary pinning is prominent at low fields. In high fields, high \(J_c\) is observed because of high defect density created by high carbon substitution into the lattice, as seen on lattice parameters. In addition, the lattice distortion created by maximum doping results in a high impurity scattering, which aids an additional pinning. This indicates that 1.5 wt% CEB is optimal amount for maximum substitution of carbon into lattice and most effective in improving the critical current density. Any further excess of carbon content is for the performance detrimental\(^{[32]}\). This bulk subjected to much lower temperatures, exhibited extremely large critical current densities, such as 660 kA cm\(^{-2}\) at self-field and 10 K, 550 kA cm\(^{-2}\) at self-field and 15 K, and 100 kA cm\(^{-2}\) at 3 T and 10 K (see Figure 5). In addition, the irreversibility field measured at 10 K was extremely high, up to 20 T (extrapolation), which is very interesting for upcoming high-field applications, such as particle accelerators\(^{[34]}\), Axion dark matter experiments\(^{[35]}\), and magnetic confinement fusion reactors\(^{[36]}\). The present irreversibility field values are far above those of conventional Nb\(_3\)Sn superconducting magnets. Some studies of MgB\(_2\) report \(H_{irr}\) at 4.2 K close to 42 T in thin films, and 44 T (theoretically) at 0 K\(^{[37]}\). Here, we note that relaxation in MgB\(_2\) is very weak, and therefore, \(H_{irr}\) can be expected very close to \(H_{irr}\). \(H_{irr}\) perpendicular to \(ab\)-plane for various thin films.
ranged at 10 K from 7 to 17 T. In addition, regular bulk MgB\textsubscript{2} prepared under similar conditions showed $H_{c2}$ (0 K) to be around 16–18 T,\textsuperscript{[3]} which are comparable with our results at 10 K. These results show that the present extrapolated $H_{c2}$ value for 1.5 wt\% CEB is almost equivalent to that of thin films and had improved over regular processed bulk MgB\textsubscript{2}. In other studies, heavy carbon doping (\textasciitilde10–30 wt\%) in MgB\textsubscript{2} thin films showed promising $H_{c2}$ values, up to 60 T, but at expense of $T_c$ degradation.\textsuperscript{[38,39]} High $H_{c2}$, such as \textasciitilde37 T, was observed at 10 K in 10 wt\% SiC-doped MgB\textsubscript{2} tape,\textsuperscript{[37,40]} where Mg\textsubscript{2}Si and Mg–Si–O–C-based secondary phases formed nano-pinning centers helping in increasing $H_{c2}$. In this case, however, obtaining a uniform SiC distribution and uniform pinning centers throughout the matrix is always a challenge. Marzik et al. showed a projection of 37 T $H_{c2}$ at 0 K in 7.4 wt\% C-doped MgB\textsubscript{2}, however, at a great loss of $T_c$, which dropped to 29 K.\textsuperscript{[41]} With the plasma-assisted carbon doping, one can expect a uniform C distribution, but the technique has not yet been optimized. Great prospects were expected when 10 wt\% double-walled carbon nano-tubes were used to dope MgB\textsubscript{2} bulks.\textsuperscript{[26]} The authors predicted the $H_{c2}$ of 42 T at 4.2 K. Elsewhere,\textsuperscript{[32]} carbon doping via the addition of 10–20 wt\% of malic acid resulted in enhancement of superconducting properties. However, $J_c$ was not as good as our present results. Moreover, the $H_{c2}$ at 20 K of MgB\textsubscript{2} bulk with 1.5 wt\% CEB around 8 T (obtained via extrapolation) is also higher than that of malic acid-doped MgB\textsubscript{2}.\textsuperscript{[32]} Similar studies were performed using graphene-coated boron, which was prepared via hydrothermal methods. Their studies revealed the homogeneous graphene coating in the microstructure and also similar irreversibility field values.\textsuperscript{[42]}

Based on the abovementioned discussion, we can conclude that the present results represent an optimized scenario with improved superconducting performance of bulk MgB\textsubscript{2}, while maintaining the uniform carbon doping and high $T_c$ when compared with other carbon doping techniques.

Furthermore, we constructed flux pinning diagram based on Dew–Hughes general expression, which is plot of the normalized flux pinning force ($f_p = F_p/F_{p,max}$) against reduced magnetic field ($h = H/H_{irr}$). Here, $H_{irr}$ is the irreversibility field, and $F_p$ is the flux pinning force calculated as a product of magnetic field induction and critical current density. When compared with the reference undoped MgB\textsubscript{2} bulk, the $f_p(h)$ peak of the MgB\textsubscript{2} bulk with 1.5 wt\% CEB is slightly shifted toward higher fields, which indicates a slight pinning contribution from carbon substitution (Figure 6). Thus, the decrease in crystallite size contributed to pinning improvement at low fields.

**Figure 5.** Superconducting critical current density of CEB 1.5 wt\%-based MgB\textsubscript{2} bulk at various temperatures. At 10 K, the $J_c$ reached 660 kA cm\textsuperscript{-2}.

**Figure 6.** Flux pinning diagrams of the 1.5 wt\% CEB-based MgB\textsubscript{2} bulk and a reference normal MgB\textsubscript{2} bulk. The 1.5 wt\% CEB MgB\textsubscript{2} bulk shows a slight increase in peak position as well as the curve width.

**Figure 7.** Flux pinning diagrams of the 1.5 wt\% CEB-based MgB\textsubscript{2} bulk at various temperatures. The normalized flux pinning force at high fields increases with reduction in operating temperature, but the peak position does not shift.
whereas carbon substitution aided in improving high field pinning. Similar scenarios were seen when carbohydrates were doped in the bulk MgB2 system. There also the basis hypothesis is carbon substitution.\(^{32}\) In the flux pinning diagrams of best sample for various temperatures (Figure 7), the peak position does not shift much. We tried to calculate parameters \(p\) and \(q\) pertaining to Dew–Hughes expression (Equation (2)), via curve fitting to get deeper understanding on flux pinning mechanisms. \(A\) is a numerical parameter, whereas \(p\) and \(q\) are power-law describing parameters, which explain the actual pinning mechanism.

\[
f_p = A(h)^p(1 - h)^q
\]  

(2)

We obtained \(p = 0.5 \pm 0.05, q = 2 \pm 0.15\), and \(A = 3.5 \pm 0.4\). The fit curve is plotted as blue line in Figure 6, labelled as curve fit. According to the Dew–Hughes, the maximum position \(h_{\text{max}}\) can be estimated by the value \(p/(p + q)\), which is equivalent to 0.2 from the curve fit parameters. These parameters strongly indicate that the primary pinning mechanism is grain boundary pinning, which is expected in the bulk MgB2 system. In addition, the FWHM of pure as well as CEB-based MgB2 is slender/smaller than theoretical one because of the anisotropy in the system. The theoretical model was prepared, assuming an isotropic material, whereas MgB2 is anisotropic.\(^{43}\) To get deeper insight, we also calculated flux pinning diagrams of best sample at various temperatures (see Figure 7), and the peak positions lie around 0.2. This shows that the dominant pinning mechanism remains grain boundary pinning at various temperatures in the CEB-based MgB2 bulks. To support the superconducting performance results, we performed scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) (see Figure 8). The EDX spectrum revealed that the carbon distribution was uniform throughout the matrix. The high magnification images depicted fine particles of the size range 50–200 nm, similar as the precursor CEB particle size.

All these results support the crystallite size refinement as well as impurity scattering through the matrix via carbon substitution and fine grain structure in final microstructure. Both these effects helped in improving \(J_c\) in the whole field range. This technique aids in synthesizing stable high-performance bulk MgB2 reliable for use in commercial applications.

3. Conclusions

By optimizing carbon content in CEB, we succeeded to prepare a high-performance sintered bulk MgB2. Carbon (1.5 wt%) in CEB was found to result in the best performance with a tremendous \(J_c\) of 660 kA cm\(^{-2}\) at 10 K, self-field. \(H_{c2}\) (calculated by extrapolation) was also substantially improved, being almost equivalent to some of the best reported values. XRD results explain the maximum carbon substitution in 1.5 wt% CEB-based bulk, via (110) peak shift, reflecting a change in the crystallite size calculated using Scherrer’s equation \(M–T\) loops showed that the reduction in \(T_{c, \text{onset}}\) was proportional to the carbon substituted into the lattice. In addition, \(\Delta T_c < 1\) K for all bulks proved high quality. Flux pinning diagrams revealed that, while the dominant pinning came from grain boundaries, there was a considerable effect from increased electron impurity scattering caused by carbon substitution. This resulted in an increase in \(H_{c2}\), high field \(J_c\), as well as the curve width of flux pinning diagrams. Microstructural analysis revealed small MgB2 particles and uniform carbon distribution that supported all our assumptions. In summary, the 1.5 wt% carbon concentration in CEB was found to be beneficial to fabricate high-performance MgB2 bulks, suitable for a wide range of applications.

4. Experimental Section

To optimize the CEB amount for obtaining the possible highest \(J_c\), a series of bulk MgB2 was synthesized by in situ solid state reaction, with concentrations of CEB, such as 1, 1.1, 1.35, 1.5, and 1.9 wt%. Along with these specimens, a reference bulk MgB2 (pure/0 wt%) was also prepared in the same manner. The precursors were commercial powders (Furu-uchi Chemical Corporation) of amorphous Mg powder (99.9% purity, 200 meshes) and CEB powder (PAVZYUM—50–200 nm). One gram of MgB2 was synthesized with Mg and CEB components weighing 0.529 and 0.471 g, respectively, which was a molar ratio of 1:2, as required. These powders were rigorously mixed and ground in a glove box to avoid oxide formation. This mixture was then pressed into 20 mm diameter, 7 mm thick pellets using a uniaxial hydraulic press with a force of 20 kN. These pellets were immediately wrapped into titanium (Ti) foils and heat treated at 775 °C for 3 h in a tube furnace in Ar atmosphere. The Ti foil acts as protection from Mg oxide formation during the sintering, as at around 250 °C, all oxygen around the Ti foil transforms into the titanium oxide. The density of all the bulk specimens is \(1.3 \text{ g cm}^{-3}\), which is common for a regular sintered MgB2 bulk (50% porosity).\(^{44}\) We observed similar values in our bulk MgB2 material produced by the sintering process.\(^{43}\) Because of the huge porosity, the density is almost half the theoretical value (2.6 g cm\(^{-3}\)). The constituent phases in the final samples...
were identified with a high-resolution automated X-ray powder diffractometer (RINT2000) with a step size of 0.01° from 10° to 90°, using Cu-Kα radiation generated at 40 kV and 30 mA. Rietveld analysis was done to find out the phase fraction of all constituent phases detected from XRD. The microstructure of these samples was later studied with field-emission scanning electron microscope (FE-SEM). To study the carbon distribution in the matrix, we used EDX analysis.

For SQUID measurements, specimens with the dimensions of \(\approx 1.5 \times 1.5 \times 0.75 \text{ mm}^3\) were cut from MgB\(_2\) bulk samples. Critical temperature \((T_c)\) and current critical density \((J_c)\) were measured using SQUID Magnetometer (Quantum Design, model MPMS5). \(J_c\) was calculated from magnetization hysteresis loops \((M-H)\) using the extended Bean critical state model \(^{[6]}\)

\[
J_c = 20 \Delta m / [\alpha^2 (b - a)/3]\]  
(3)

In this equation, \(a\) and \(b\) are cross-sectional dimensions, \(b > a\), and \(c\) is the thickness of the specimen \((a, b, \text{and } c \text{ in } \text{mm})\), and \(\Delta m\) (in emu units, \(1 \text{ emu} = 10^{-3} \text{ Am}^{-2}\)) is the difference in magnetic moments during increasing and decreasing field in the \(M-H\) loop.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bulk MgB\(_2\), carbon encapsulated boron, optimization, sintering

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