Superconducting properties of MgB2: Polycarbosilane versus conventional Nano-SiC doping

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Abstract—The effect of polycarbosilane (PCS) doping on the superconducting properties of MgB$_2$ was systematically investigated. Highly reactive C and Si appeared after PCS decomposition facilitating incorporation of C into the MgB$_2$ lattice, as well as the reaction between Si and Mg, resulting in formation of a large number of small Mg$_2$Si particles within MgB$_2$ grains. C-substitution induced crystal lattice defects and impurities act as strong pinning centers, significantly improving $J_c(B)$ performance in the high field region. The differences in the effects of SiC and PCS doping have been studied and are described to the structural transformation that occurs in MgB$_2$ after doping with these two materials.

I. INTRODUCTION

INTENSIVE study of the superconducting properties of MgB$_2$ material for the last few years has revealed a great potential for practical application of this superconductor due to its attractive high critical temperature, $T_c$, strong grain connectivity and low anisotropy [1]. The major concern of weak pinning in pure MgB$_2$ has been overcome with the help of cheap and effective chemical doping with different elements. Among them, SiC doping appeared to be the most effective for significant improvement of high field $J_c(B)$ performance of MgB$_2$ with only a slight reduction in $T_c$ [2], [3]. Since the discovery of this effect, it has been difficult to imagine the practical application of MgB$_2$ without SiC doping.

Recently it was found that doping MgB$_2$ with carbohydrates (sugar and malic acid) can be even more effective for improvement of the $J_c$ performance of bulk MgB$_2$ material in both self and high field regions [5], [6]. From those reports it became clear that better distribution of doping material and the appearance of highly reactive fresh carbon are crucial for the $J_c$ enhancement. In the case of nano-SiC doping, free carbon appears after the reaction between Si and Mg, which takes place at 600 °C [4]. However, C released during this reaction does not seem as reactive as unpassivated C, which appears after decomposition of carbohydrates at relatively low temperatures (< 200 °C) [5], [6]. To introduce unpassivated, highly reactive carbon, we have employed organic polycarbosilane ((C$_3$H$_6$Si)$_n$) compound. This is a polymer analog to SiC addition, but thanks to its low decomposition temperature, this material can introduce fresh C into the MgB$_2$ system, as in the case of carbohydrates. However, compared to carbohydrates, this composition does not include oxygen in its structure, which could be more desirable for MgB$_2$, the properties of which are very sensitive to oxidation.

In this work, a systematic study of the polycarbosilane (denoted as PCS in the text) doping effect on the structure and superconducting properties of MgB$_2$ bulk material is presented and compared with the conventional nano-SiC doping.

II. EXPERIMENTAL PROCEDURE

MgB$_2$ bulk samples were prepared by an in-situ reaction technique. Powders of Mg (99%), amorphous B (99%), and PCS were used for fabrication of pure and 1, 5 and 10 wt.% doped PCS samples. Then mixtures of powders were pressed into pellets, sealed in stainless steel tubes, and sintered at a temperature of 850 °C for 1 h. For comparison, two samples with an atomic ratio of Mg$_{12}B_{X}X_{0.1}$, where X is PCS or SiC powder (with particle size less then 15 nm) were prepared and sintered at 650 °C for 1 h. A flow of high purity Ar gas was maintained throughout the sintering process to avoid oxidation.

The phase identification and crystal structure investigation were carried out using powder x-ray diffraction (XRD) with CuK$_{a1}$ radiation. The nanostructure of samples was studied with the help of transmission electron microscopy (TEM). The magnetization of samples was measured over a temperature range of 5 to 20 K using a Physical Properties Measurement System (PPMS). The magnetic $J_c$ was derived from the height of the magnetization loop using a critical state model. Due to a considerable dependence of the magnetic $J_c$ on the size of the MgB$_2$ samples fabricated by the in-situ reaction process [7], all the samples for measurement were shaped to the same size of 1 x 2.2 x 3.5 mm$^3$ for consistent comparison. The critical temperature, $T_c$, was determined as the onset of diamagnetism by measuring the real part of the ac susceptibility.

III. RESULTS AND DISCUSSION

Differential thermal analysis (DTA) of the PCS precursor powder (not presented here) showed an exothermal peak at a temperature of 470 °C. According to the specification, PCS...
TABLE I
SUMMARY OF PARAMETERS OF STUDIED SAMPLES

<table>
<thead>
<tr>
<th>N</th>
<th>Sample</th>
<th>Sintering profile</th>
<th>Lattice parameters, Å</th>
<th>Actual C (x) in MgB$_2$-$_x$C$_x$</th>
<th>Mg$_2$Si phase, wt. %</th>
<th>$T_c$, K</th>
<th>$J_c \times 10^{4}$, A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MgB$_2$</td>
<td>(850 °C×1 h)</td>
<td>a: 3.0808, c: 3.5210</td>
<td>-</td>
<td>-</td>
<td>38</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>1 wt.% PCS</td>
<td>(850 °C×1 h)</td>
<td>a: 3.0790, c: 3.5216</td>
<td>0.006</td>
<td>≤ 5</td>
<td>37.2</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>5 wt.% PCS</td>
<td>(850 °C×1 h)</td>
<td>a: 3.0744, c: 3.5229</td>
<td>0.019</td>
<td>11</td>
<td>36.1</td>
<td>0.60</td>
</tr>
<tr>
<td>4</td>
<td>10 wt.% PCS</td>
<td>(850 °C×1 h)</td>
<td>a: 3.0716, c: 3.5236</td>
<td>0.028</td>
<td>46</td>
<td>35.5</td>
<td>1.40</td>
</tr>
<tr>
<td>5</td>
<td>MgB$_2$</td>
<td>(650 °C×1 h)</td>
<td>a: 3.0828, c: 3.5198</td>
<td>-</td>
<td>-</td>
<td>37.4</td>
<td>0.03</td>
</tr>
<tr>
<td>6</td>
<td>MgB$<em>{1.0}$SiC$</em>{0.1}$</td>
<td>(650 °C×1 h)</td>
<td>a: 3.0754, c: 3.5216</td>
<td>0.022</td>
<td>27</td>
<td>34.6</td>
<td>1.50</td>
</tr>
<tr>
<td>7</td>
<td>MgB$<em>{1.9}$PCS$</em>{0.1}$</td>
<td>(650 °C×1 h)</td>
<td>a: 3.0730, c: 3.5310</td>
<td>0.030</td>
<td>44</td>
<td>35.0</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Fig. 1. The x-ray diffraction patterns of pure and PCS or SiC doped MgB$_2$ samples. The XRD pattern of PCS precursor powder after DTA study is also presented on the bottom.

Fig. 2. Actual C substitution level in B site in 1, 5, and 10wt.% PCS doped MgB$_2$ samples (this work), SiC [12], and C [13] doped MgB$_2$.

Melts at temperatures above 300 °C, which is correlated with our result (470 °C). XRD results on PCS powder heated up to 900 °C revealed that PCS was transformed into amorphous silicon carbide (SiC) compound (see bottom of Fig. 1). Its transformation to SiC compound with a small excess of C takes place between 700 and 800 °C [8]. Therefore, we can assume that in the temperature interval between 470 °C and 700–800 °C, the PCS system is decomposed and consists of disordered Si and C atoms.

The XRD patterns for the studied MgB$_2$ samples with and without PCS or SiC doping are presented in Fig. 1. All samples had a small peak at 2θ = 62.3° related to MgO phase. The Mg$_2$Si peaks appeared in the samples with PCS and SiC doping. Increasing the PCS doping level resulted in increasing the relative amount (which is correlated with the height of the corresponding peak) of non-superconducting Mg$_2$Si phase in MgB$_2$ samples. In the 1 wt.% doped PCS sample the amount of Mg$_2$Si phase was presumably less than 5 wt. % and could not be detected with x-ray diffraction. It is to be noted that in the SiC doped sample a small peak of unreacted SiC has appeared, while in samples with PCS additions there were no other peaks except those related to MgB$_2$, MgO, and Mg$_2$Si phases.

The a and c lattice parameters of the hexagonal structure of MgB$_2$ were calculated using XRD patterns, and the results are presented in Table I. As can be seen, the a lattice parameter is decreased with increasing PCS addition level (which is consistent with the gradual shifting of the (110) peak to higher 2θ values with increasing PCS doping level, noticeable in Fig. 1), but no systematic change was observed in the c lattice parameter ((002) peak). This behavior coincides well with the changes in the lattice parameters caused by carbon substitution for boron in MgB$_2$. The observed systematic shrinkage of the a-lattice parameter with increasing PCS doping level is explained by increasing carbon content in the MgB$_2$ lattice. The actual level of carbon substitution for B has been estimated from the a-axis change [11]. Corresponding values are presented in Table I.

It is interesting to compare the C substitution level in PCS and SiC-doped MgB$_2$ samples. Fig. 2 presents data for 1, 5 and 10 wt.% PCS-doped MgB$_2$ samples sintered at 850 °C for 1h and data for SiC doped MgB$_2$ samples reacted at 825 °C for 30 min [12]. The results observed indicated better reactivity of disordered Si and C (or amorphous SiC) released after PCS decomposition (or transformation) with precursor magnesium and boron powders, compared to nano-SiC particles. For instance, the C substitution level in 5 (10) wt.% PCS samples is about 25 (12)% higher than in 5 (10) wt.% SiC doped MgB$_2$. It is to be noted that the high level of C substitution could be reached at a rather low sintering temperature (650 °C). Compared to nano-C doping, in the MgB$_{1.9}$SiC$_{0.1}$ sintered at 900 °C (marked as a triangle in Fig. 2) the level of C-substitution is about 0.012 [13], while for MgB$_{1.9}$PCS$_{0.1}$ sintered at 650 °C (see Table I) this value has reached 0.03. A low sintering temperature is beneficial for improvement of pinning and high field $J_c(B_{H})$ performance, as will be discussed later. Therefore, it is important...
that C-substitution for B can be achieved at a relatively low sintering temperature.

Critical temperature values, \( T_c \), for the studied PCS samples are presented in Table I. It is clear that \( T_c \) decreased faster with increasing C substitution level. For instance, for pure MgB\(_2\) \( T_c \) of 38 K was observed, while this value dropped to 36.1 and 35.5 K for samples with 5 and 10 wt.% of PCS, respectively. \( T_c \) values for PCS doped samples are slightly lower than those for SiC doped MgB\(_2\) [12]. This fact again indicates the higher level of C substitution in PCS samples due to the better reactivity of fresh molecular C revealed after PCS decomposition at \( T > 470 \degree C \).

The effect of PCS doping on \( J_c(B) \) performance is shown in Fig. 3 and explained with the help of TEM nanostructure investigation (Fig. 4). It is well known that grain boundaries provide an essential contribution to the pinning strength in polycrystalline MgB\(_2\) material (see [14], [15], and ref. therein). The lower sintering temperature results in formation of smaller MgB\(_2\) grains and impurities that promote stronger pinning and result in higher \( J_c(B) \) performance. In the samples studied, the size of grains varied from 50 to 200 nm [see Fig. 4(a)]. The electron diffraction pattern shown in the corner of Fig. 4(a) reveals the mixed microstructure of the sample (as evidenced by the appearance of large spots related to the bigger grains, which were framed by a typical spotty ring shape related to fine MgB\(_2\) grains) and the existence of impurity phases such as MgO and Mg\(_2\)Si (see also XRD patterns in Fig. 1). MgO and Mg\(_2\)Si particles were well distributed in the sample [Fig. 4(a)] and had a size of about 10–20 nm [Fig. 4(b)], which is only a factor of 2 larger than the coherence length (\( \xi \approx 5 \text{ nm} \)) in MgB\(_2\) superconductor [9], [10]. This makes them possible candidates for pinning (if in sufficient quantity), because each vortex line has the diameter of the normal core of 2\( \xi \)(T).

We could not see any change in the relative intensity of the MgO peak with increasing PCS doping level. Hence, we assumed that \( J_c(B) \) improvement with increasing PCS addition level was due to an increased amount of Mg\(_2\)Si phase (see the relative intensity of the Mg\(_2\)Si peak in Table I). In addition, a higher level of C substitution induced higher amount of crystal lattice defects (such a dislocations and stacking faults) as a result of atomic displacement. Impurities and crystal lattice defects are well known to strengthen the pinning force in MgB\(_2\) samples. However, increasing the amount of non-superconducting Mg\(_2\)Si phase obstructed the current flow between MgB\(_2\) grains and resulted in decreasing self field \( J_c \) values in PCS doped compared to pure MgB\(_2\) samples (see Fig. 4 and Table I). For instance, the \( J_c \) (0 T, 20 K) value of \( 4.5 \times 10^5 \text{ A/cm}^2 \) for pure MgB\(_2\) drops to \( 2.6 \times 10^5 \text{ A/cm}^2 \) for 10 wt.% PCS doped MgB\(_2\) sample.

The \( J_c(B) \) curves for MgB\(_{1.9}\)PCS\(_{0.1}\) and MgB\(_{1.9}\)SiC\(_{0.1}\) samples sintered simultaneously at 650 \degree C for 1 h are presented.
in Fig. 5 for comparison. It is clear that $J_c(B_{\text{H}})$ performance for the PCS doped sample is higher than that for the SiC doped sample at all studied temperatures and field ranges. We believe that $J_c(B_{\text{H}})$ improvement in the case of PCS doping was due to the appearance of highly reactive amorphous C after PCS decomposition, resulting in a higher level of C substitution (0.03 for the PCS doped versus 0.02 for the SiC doped) (see Table I). In addition, amorphous Si appearing after PCS decomposition easily reacted with Mg, resulting in a large amount of small Mg$_2$Si phase precipitates distributed within MgB$_2$ grains. For instance, the relative intensity of the Mg$_2$Si peak estimated from the XRD pattern is 44% for PCS and 26% for SiC doped samples (see Table I).

As can be seen, less degradation of self field $J_c$ has been observed in PCS doped sample compared to nano-SiC doped sample (see Fig. 6 and Table I). This behavior is not completely understood by this time. The increased amount of Mg$_2$Si phase in PCS doped samples should result in a greater reduction of the superconducting volume and $J_c$ behavior in both PCS and SiC-doped samples.

With its high critical current density of $3 \times 10^4$ A/cm$^2$ (5 K and 8 T) (Fig. 5) the PCS doping has competitive in field properties with samples doped with recently reported carbohydrates [6], such as 30wt.-% of acetic acid, having $J_c$ (5 K, 8 T) of $2.2 \times 10^4$ A/cm$^2$. However, PCS resulted in a slight reduction at low field. This reduction is hardly observed for carbohydrates ($J_c$ (0T, 20K) of $3.6 \times 10^4$ A/cm$^2$ for PCS versus $4 \times 10^4$ A/cm$^2$ for 30 wt.-% of acetic acid).

IV. CONCLUSION

The effect of PCS doping on the superconducting properties of MgB$_2$ was systematically investigated and compared with the effects of the conventional nano-SiC doping. The PCS amorphous-like state enables efficient homogeneous doping which is difficult to achieve by mixing of nanopowders, such as nano-SiC. In addition, the low decomposition temperature of organic PCS provides dispersed and highly reactive C and Si molecules, facilitating reactions with Mg and B powders. A low sintering temperature hosted formation of small MgB$_2$ grains and a greater amount of grain boundaries, as well as a large amount of defects caused by a higher level of C substitution and the appearance of MgO and Mg$_2$Si impurity phases that were small and well distributed inside MgB$_2$ grains. All these structural modifications merged into significant improvement of pinning strength and hence, $J_c(B_{\text{H}})$ behavior in the high field region of PCS doped MgB$_2$, when compared to the conventional nano-SiC doping. The properties of PCS doped MgB$_2$ are competitive with those of recently reported carbohydrates.

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