Temperature effect on microstructure and electromagnetic performance of polycarbosilane and sugar-doped MgB$_2$ wires

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Abstract. The effect of processing temperature on structural and superconducting properties of 10 wt.% sugar- and 10 wt.% PCS-doped MgB$_2$ wires is systematically investigated. It is demonstrated that these dopants significantly enhance the electromagnetic performance of Fe-clad MgB$_2$ superconductor and increase its potential for practical application. The enhancement of in-field critical current density ($J_c(B_a)$) and upper critical field ($B_{c2}$) is due to formation of a large amount of lattice defects caused by impurities and C substitution into the MgB$_2$ crystal lattice. High temperature sintering of sugar-doped sample results in as high $B_{c2}$ value as 37 T (at 5 K), which correlates with higher level of C substitution into MgB$_2$ crystal lattice in this sample. In contrast, for PCS doped MgB$_2$ wire higher $B_{c2}$ value (32 T at 5 K) is observed at lower sintering temperatures. In spite of the fact that the level of C in the crystal lattice and $B_{c2}$ value are higher in the sugar doped MgB$_2$ sample, this sample has lower $J_c(B_a)$ when compared to the sample with PCS addition. We speculate that it is due to a higher level of MgO impurities in the sugar doped sample (18.6 wt.% compared to 9.15 wt.% in the PCS doped sample), which results in the dissipation of supercurrent flowing through this sample.

1. Introduction

In recent years the rapid development of MgB$_2$ superconductor has been based on simple fabrication and a relatively high (compared to low temperature superconductors) transition temperature of 39 K in this compound. This temperature enables the application of MgB$_2$ superconductor at temperatures of around 20 K facilitating the use of simple, cost-effective and reliable cryocoolers. Additional benefits of the MgB$_2$ compound are simple crystal structure, low cost of the starting materials, and the fact that grain boundaries have a less detrimental effect on the supercurrent flow than in high temperature superconductors [1]. The MgB$_2$ superconductor is a promising candidate for large scale applications, such as magnetic resonance imaging systems, fault current limiters, and high field magnets [2, 3]. However, the in-field critical current density, $J_c(B_a)$, is still below the practical level. This stimulates the research community to find the way to improve both, the upper critical field value, $B_{c2}$, which set the limit to existence of superconductivity, and $J_c(B_a)$ performance for the desired 20 K application of MgB$_2$ superconductors.
Enormous efforts have been made to improve the superconducting properties of MgB$_2$ via chemical doping. It was experimentally established that a significant enhancement of MgB$_2$ superconducting properties at high fields can be achieved with carbon-based doping. Among nano C-based dopants, nano-SiC holds a leading position for the most effective enhancement of electromagnetic properties of the MgB$_2$ superconductor [4, 5, 6]. Further development of the chemical doping technique resulted in the idea of the “liquid mixing” technique, which was initially developed in our group [7]. Later it was shown that the “liquid mixing” approach is applicable to a wide range of carbohydrates [8] and C-based organic materials [11].

In this paper, we have attempted to improve the $B_c$ and $J_c$ ($B_{a}$) properties of Fe-clad MgB$_2$ wires by addition of a readily available source of carbon - table sugar (or sucrose, C$_{12}$H$_{22}$O$_{11}$), as well as polycarbosilane (C$_2$H$_6$Si), which is a polymer analog to nano-SiC compound [11]. In addition, the effect of sintering temperature on microstructure and superconducting properties of MgB$_2$ samples has been systematically investigated.

2. Experimental

Pure and doped Fe-clad MgB$_2$ wires were fabricated by in-situ processing using the standard PIT technique. Powders of Mg (99% purity, particle size of 1-11 µm) and amorphous B (99% purity) have been used as host materials. The sugar and polycarbosilane (PCS)-doped samples were prepared by the “liquid mixing” approach described in Ref.[7]. The level of added dopants was 10 wt.%. Well mixed powders were packed into Fe tubes and then drawn to a diameter of 1.42 mm. Several short samples from each wire were sintered at temperatures of 650 or 950°C for 30 min followed by cooling to room temperature in the furnace. A high purity argon gas flow was maintained throughout the sintering process to avoid oxidation. Later in the text the samples prepared at 650 or 950°C are designated as MB-650 or MB-950 for reference samples, PCS-650 or PCS-950 for polycarbosilane doped MgB$_2$ samples, and SR-650 or SR-950 for sugar doped MgB$_2$ samples, respectively.

The phase investigation was performed using a X-ray diffractometer with CuKα radiation. The fraction of phases and lattice parameters were estimated via Rietveld refinement of the XRD patterns. The microstructure of samples were investigated by Scanning Electron Microscopy (SEM). The magnetization of the superconducting cores extracted from the wires were measured at 20 K using a Physical Property Measurement System (PPMS, Quantum Design) with a magnetic field applied perpendicular to the wire long axis. The magnetic $J_c$ was derived from the width of the magnetization loop ($\Delta M$) using the critical state model [10] and relation $J_c = \frac{30\pi \Delta M}{4d}$, where $d$ is a diameter of sample. To eliminate a sample size effect on the magnetic $J_c$ values [9] all samples for measurement were shaped to the same length of 3.5 mm for systematic comparison.

3. Results and discussion

XRD pattern observed on samples fabricated at temperatures of 650 and 950°C are presented in Fig. 1 (a) and Fig. 1 (b), respectively. Data obtained by Rietveld refinement (crystal lattice parameters and phase fraction), as well as some superconducting characteristics for the samples studied are summarized in Table 1.

As can be seen, all samples investigated have MgB$_2$ as the main phase and some amount of MgO. It is to be noted that pure and PCS-doped MgB$_2$ samples have nearly similar amount of MgO phase, while in sugar doped samples higher levels of MgO are detected (Table 1). It is due to the fact that table sugar (or sucrose) originally has high amount of oxygen in its compound (C$_{12}$H$_{22}$O$_{11}$). In PCS-doped samples, a high level (17.21 wt.%) of Mg$_2$Si phase was observed for sample sintered at low (650°C) temperature, but it dropped to nearly zero (0.15 wt.%) in the sample treated at high (950°C) temperature (Fig. 1 and Table 1). This behaviour is similar to nano-SiC doping, which was obtained earlier by number of authors [12, 13, 14]. In PCS-doped
samples, free atoms of Si and some of the C (released after PCS decomposition at 300°C [11]) form SiC compound at temperature of 950°C (Fig. 1(b)).

Figure 1. X-ray diffraction pattern of samples sintered at temperatures of (a) 650°C and (b) 950°C.

Generally, the C-based doping results in the reduction of the lattice parameter \(a (\Delta a)\) due to C substitution for B in the MgB\(_2\) crystal lattice, while lattice parameter \(c\) remains unaffected. The large the \(\Delta a\) value the higher the level of incorporated C is within the MgB\(_2\) lattice [16, 17]. Analysis of results obtained (Table 1) indicate that: i) PCS doping results in a smaller level C substitution for B in MgB\(_2\) lattice than sugar doping at both temperatures studied; and ii) the higher the sintering temperature, the larger the level of C is substituted for B in both samples.

Table 1. Some parameters of samples studied. Lattice parameters \(a\) and \(c\) are defined from XRD pattern; \(\Delta a\) defines changes in the \(a\) lattice parameter as a result of C incorporated into the MgB\(_2\) lattice on B sites; \(x\) - actual level of C in Mg(B\(_{1-x}\)C\(_x\))\(_2\) estimated from \(\Delta a\) values [17].

| Sample   | \(c\) | \(a, \Delta a\) | \(x\) | non-s/c | FWHM of \(T_c\) | \(B_{c2}\) |
|----------|-------|-----------------|-------|---------|----------------|----------|
|          | Å     | Å               | Å     | %       | (101) peak, deg. | (5 K), T |
| MB-650   | 3.521(1) | 3.081(0)       | -     | 8.55 (MgO) | 0.5          | 36.8     | 21     |
| SR-650   | 3.523(1) | 3.071(0)       | 0.010 | 2.3     | 16.36 (MgO) | 0.626    | 35.0   | 34     |
| PCS-650  | 3.527(0) | 3.076(0)       | 0.005 | 2.3     | 7.70 (MgO)  | 0.542    | 34.5   | 32     |
|           |        |                 |       |         | 17.21 (Mg\(_2\)Si) |          |        |
| MB-950   | 3.530(0) | 3.087(0)       | -     | 7.34 (MgO) | 0.364        | 38.3     | 17     |
| SR-950   | 3.527(0) | 3.072(0)       | 0.014 | 2.3     | 18.06 (MgO) | 0.508    | 36.2   | 37     |
| PCS-950  | 3.528(0) | 3.077(0)       | 0.010 | 2.2     | 9.15 (MgO)  | 0.396    | 36.6   | 30     |
|           |        |                 |       |         | 0.15 (Mg\(_2\)Si) |          |        |

Critical temperature \(T_c\) values of the studied samples are presented in Table 1. In carbon-doped samples the decrease in \(T_c\) is due to carbon being incorporated into the structure [5, 18, 19, 20]. At sintering temperature of 650°C, the \(T_c\) value of PCS-650 sample is lower
compared to SR-650 sample in spite of the fact that the level of C substitution is higher in SR-650 sample. This is due to high level of impurities in PCS-650 sample (Table 1), which result in inhomogeneity of this sample and reduce its \( T_c \). However, higher sintering temperature (950\(^{\circ}\)C) results in better crystallinity and homogeneity of all samples, and, thus, higher \( T_c \) values in all samples. For more homogeneous samples (SR-950 and PCS-950), the higher the level of C in the MgB\(_2\) lattice, the lower \( T_c \) value is (Table 1).

SEM images of microstructure are quite similar for all studied samples. To demonstrate the typical microstructure of doped samples subjected to high and low sintering temperatures, images of PCS-doped samples are presented in Fig. 2. It is clear that sintering at 650\(^{\circ}\)C yields samples with small loosely connected grains (Fig. 2(a)), while high temperature sintering (950\(^{\circ}\)C) results in samples with larger and better consolidated grains (Fig. 2(b)). This conclusion is also supported by FWHM (Full Width at Half Maximum) values estimated from XRD patterns of studied samples (Table 1). In particular, the FWHM values for all samples decrease with increasing sintering temperature indicating growth of grain size in the samples. Also, FWHM values of C-doped samples are larger than those for reference MgB\(_2\) sample due to worse MgB\(_2\) crystallinity associated with C-substitution for B in these samples, and reduction of grain size compared to reference sample, which is generally induced by doping [15]. Note that high values of FWHM are obtained for sugar doped samples. This is a collective effect of several factors, including the high level of C substitution into the MgB\(_2\) lattice, and high intrinsic strain caused by large amount of MgO impurities and defects generated by C-substitution.

![Figure 2](image)

**Figure 2.** SEM images of the microstructure of the PCS-doped MgB\(_2\) samples fabricated at (a) 650\(^{\circ}\)C and (b) 950\(^{\circ}\)C.

The upper critical field \( B_{c2}(T) \) values were obtained from the \( \rho(B_{a}, T) \) curves using the criteria of \( B_{c2}(T) = 0.9 \times \rho(B_{a}, T) \) (Fig. 3). The \( B_{c2}(5 \text{ K}) \) values for samples studied were estimated by a linear extrapolation of the \( B_{c2}(T) \) curves, and resulting values are presented in Table 1. As can be seen, the doping of MgB\(_2\) with C-based dopants increases \( B_{c2} \) values when compared to pure sample. The highest (among other samples studied) \( B_{c2} \) value of 37 T was obtained for the sugar doped wire sintered at 950\(^{\circ}\)C. This value is the highest for nano-C doped samples reported in the literature [18, 19, 20].

The observed enhancement of \( B_{c2} \) in PCS and sugar-doped samples is due to structural changes, which affect the scattering mechanism in the two-band MgB\(_2\) superconductor [21]. A higher level of C substitution (higher \( x \) value) in the sugar doped samples correlates well with a more significant enhancement of the upper critical field, as observed for SR-650 (\( x = 2.3 \% \),
Figure 3. The upper critical field vs. temperature dependance, $B_{c2}(T)$, for the samples studied. Scatter represents experimentally observed data, while line shows corresponding linear extrapolations.

$B_{c2} = 34$ T) and SR-950 ($x = 3.2\%$, $B_{c2} =37$ T) samples. However, it is not the case for PCS-doped wires. As can be seen, the $B_{c2}$ value is as high as 32 T for PCS-650 sample having lower level of C-substitution ($x = 1.2\%$, Table 1) compared to 30 T for PCS-950 sample with higher level of C-substitution ($x = 2.2\%$). This implies that electron scattering on MgO and large amount of Mg$_2$Si (17.21 wt.%) impurities, as well as defects caused by these impurities

Figure 4. (a) 20 K $J_c(B_a)$ performances of PCS and sugar-doped MgB$_2$ samples sintered at temperature of 950°C. b) Normalized volume pinning force ($F_p/F_{p,max}$) versus reduced magnetic field ($B_a/B_{irr}$) at 20 K with fitting curves.
(dislocations, staking faults, etc.), and small grain size play the major role for improvement of the upper critical field in PCS-650 sample. Indeed, it was emphasized above that the amount of Mg$_2$Si impurities drops to nearly zero at PCS-950 sample. Combining this fact with large better crystalline and consolidated grains formed at 950$^\circ$C, the electron mean free path and a coherence length were increased, but $B_{c2}$ value was decreased in PCS-950 sample in spite of the fact that the level of C substitution was nearly doubled.

The critical current density, $J_c(B_a)$, however, shows a different trend (Fig. 4(a)), that is the higher in-field $J_c(B_a)$ performance is observed for the PCS-950 sample compared to the SR-950 sample. It is interesting to note that the normalized pinning force ($F_p/F_p^{\text{max}}$, Fig. 4(b)) for SR-950 wire outperforms one for PSC-950 wire at high magnetic fields. Fits to the experimental $F_p/F_p^{\text{max}}$ curves for these samples are made using equation $F_p/F_p^{\text{max}} \propto b^p(1 - b)^q$, where $b = B_a/B_{irr}$ (Fig. 4(b)). The fitting parameters $p = 0.5$ and $q = 2.2 \pm 0.2$ have been obtained for the PCS-950 and SR-950 samples at $T = 20$ K. According to the Dew-Hughes model [22], these values correspond to normal core pinning on surface pins, such as grain boundaries, crystal lattice defects (dislocations, staking faults, etc.) As demonstrated above, the level of these defects generated by high level of MgO impurities and C-substitution is higher in SR-950 sample and should result in stronger pinning, higher $B_{c2}$ and therefore $J_c(B_a)$ values compared to PCS-950 sample. However, the $J_c(B_a)$ performance observed in Fig. 4(a) does not follow this prediction. We believe that this occurs due to formation of the large amount of MgO phase, which likely results in formation of supercurrent blocking layers around the grains and reduces the total critical current density in the sugar doped sample.

4. Conclusion

Effect of processing temperature on structure and superconducting properties of PCS and sugar doped MgB$_2$ wires has been investigated. It is observed that increasing sintering temperature results in higher level of C substitution on B site in MgB$_2$ crystal lattice. This substitution is larger in sugar doped sample compared to PCS doped sample. Increasing sintering temperature results in higher $B_{c2}$ values for sugar doped samples. The $B_{c2}$ value of 37 T (at 5 K) is estimated for SR-950 sample, which exceeds the $B_{c2}$ values achieved by nano-C doping. In contrast, $B_{c2}$ decreases in PCS-doped samples with increasing sintering temperature. The in-field $J_c(B_a)$ performance in doped wires is improved compared to reference wire due to enhanced $B_{c2}$ values and stronger pinning on lattice defects caused by impurities and C substitution. However, the high level of MgO impurities (up to 18 wt.%) reduces transparency for current flow and results in lower $J_c(B_a)$ performance of sugar doped sample compared to PCS doped sample.

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