RAPID COMMUNICATION

Large irreversibility field in nanoscale C-doped MgB2/Fe tape conductors

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Abstract
We investigated the effect of nanoscale C doping on the critical current density $J_c$ and irreversibility field $B_{irr}$ of Fe-sheathed MgB2 tapes prepared by the in situ powder-in-tube method. The tapes were heat treated at 600–950 °C for 1 h. Higher values of $J_c$ and $B_{irr}$ were seen for 5 at.% C-doped MgB2 tapes at higher sintering temperatures. The C-doped samples sintered at 950 °C showed the highest $B_{irr}$, for example at 4.2 K the $B_{irr}$ reached 22.9 T. In particular, at 20 K, $B_{irr}$ for the C-doped tape achieved 9 T, which is comparable to the upper critical field of the commercial NbTi at 4.2 K. This role of nanosized C particles can be very beneficial in the fabrication of MgB2 tapes for magnetic resonance imaging applications at 20 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Compared to conventional metallic superconductors, MgB2 has the advantages of high transition temperature ($T_c$) and low raw material costs for both B and Mg. It is believed that MgB2 can be used with a convenient cryocooler as a conductor for a cryogen-free magnet at elevated temperatures of around 20 K [1]. In particular, recent studies found a significant upper critical field $B_{c2}$ enhancement, $B_{c2}^\perp$ (4.2 K) $\approx$ 35 T and $B_{c2}^\parallel$ (4.2 K) $\approx$ 51 T, in C-alloyed films [2]. Such critical field properties exceed those of any Nb-based conductor at any temperature, suggesting that MgB2 could also be a replacement for the well-known Nb3Sn as a high field magnet conductor.

The method commonly used to fabricate MgB2 tape is the powder-in-tube technique [3]. So far, enormous efforts have been directed towards improving $B_{c2}$ and the in-field critical current density ($J_c$) through the development and application of various methods for fabrication of technically usable materials, such as chemical doping [4–8], irradiation with heavy ions [9] and various processing techniques [10, 11].

Among all the methods, chemical doping is the most promising for applications. Since MgB2 has a relatively large coherence length and small anisotropy, the fluxoids to be pinned are string-like and amenable to pinning by inclusions and precipitates in the grains.

Dou et al [4] have reported that SiC doping can significantly improve the irreversibility field ($B_{irr}$) and $J_c$. Kumakura et al [6] used hydride-based MgB2 powder with SiC dopants in the in situ process, enhancing $B_{irr}$ from 17 T to 22.5 T at 4.2 K. SiC-doped MgB2 has also been attempted by Sumption et al [7] in metal sheathed strands reaching $B_{c2}$ values up to 33 T. Since carbon is widely recognized to enter the structure through replacing boron, it is expected that the carbon, which has one more electron than boron, will donate electrons to the $\sigma$ band. Thus, C doping of MgB2 is believed to be quite a useful means of alloying MgB2 for enhancing $B_{c2}$ and flux pinning [12, 13]. Recently, we have demonstrated that a $J_c$ enhancement by more than one order of magnitude in high magnetic fields can be easily achieved through doping the MgB2/Fe tape with C nanoparticles. The
highest $J_c$ value of tapes was achieved with addition of 5 at.% nano-C [14]. Therefore, we expected that transport measurements in higher fields on C-doped samples would provide additional useful information for understanding the $J_c$ and $B_{c2}$ behaviours of MgB$_2$ tapes. In this work, the effect of sintering temperature on the $J_c$–$B$ property was investigated, and high-field resistive transitions were used to demonstrate the relatively large values of $B_{c2}$ for C-added MgB$_2$ tapes under various heating conditions.

2. Experimental details

Powders of magnesium (99.8%, –325 mesh), amorphous boron (99.99%, 2–5 μm) and carbon nanoparticle powders (20–30 nm, amorphous) were used for the fabrication of tapes by the in situ powder-in-tube method. The nano-C concentration was fixed to be 5 at.%. Details of the tape fabrication procedure have been described elsewhere [14]. The sheath materials chosen for this experiment were commercially available pure Fe. The mixed powder was filled into a Fe tube of 8 mm outside diameter and 1.5 mm wall thickness in air. After packing, the tube was rotary swaged and drawn to wires of 1.5 mm in diameter. The wires were subsequently rolled to tapes of ~3.2 × 0.5 mm. Short samples (~4 cm each), cut from the tapes, were heated in flowing Ar at temperatures ranging from 600 to 950 °C for 1 h. Undoped tapes were also prepared under the same conditions for use as reference samples.

In order to precisely evaluate the $B_{c2}$ values at elevated temperatures, resistive transition measurements were made on 1.5 cm long tapes at the High Field Laboratory for Superconducting Materials (HFLSM) in Sendai. The resistance versus temperature curves were measured in magnetic fields up to 17 T by a four-probe method using a 20 T superconducting magnet. Four-point transport resistive measurements in high magnetic fields up to 26 T at 4.2–10 K were also made using a 28 T hybrid magnet. The distance between the voltage taps was 5 mm. The applied current was 100 mA. The temperature of the tapes was changed by the combination of He gas cooling and heating, and the temperature of the tape was monitored with a thermometer attached directly to the tape. A magnetic field was applied parallel to the tape surface and perpendicular to the current flow. Values of $B_{c2}$ were obtained taking the 10% points of the resistive transition. The transport $J_c$ at 4.2 K and its magnetic field dependence were evaluated by a standard four-probe technique with a criterion of 1 μV cm$^{-1}$. Magnetic fields were applied parallel to the tape surface by employing either a newly developed 18 T cryogen-free superconducting magnet [15] or the 28 T hybrid magnet at the HFLSM.

3. Results and discussion

Figure 1 shows the $J_c$ at 4.2 K in magnetic fields up to 18 T for 5 at.% C-doped MgB$_2$ tapes sintered at various temperatures. The $J_c$ values of an undoped tape heated at 800 °C are also included as a standard.

![Figure 1. Transport $J_c$ at 4.2 K in magnetic fields up to 18 T for 5 at.% C-doped MgB$_2$ tapes sintered at various temperatures. The $J_c$ values of an undoped tape heated at 800 °C are also included as a standard.](image)

In order to precisely evaluate the $B_{c2}$ values at elevated temperatures, resistive transition measurements were made on 1.5 cm long tapes at the High Field Laboratory for Superconducting Materials (HFLSM) in Sendai. Figure 2 shows the magnetic field dependence of the transport $J_c$ at 4.2 K for pure and 5% C-doped MgB$_2$/Fe tapes. Again, both $J_c(B)$ values of C-doped MgB$_2$ tapes were higher than for the pure MgB$_2$ sample, and the tape heated at 950 °C still exhibited the largest $J_c$ value. Specifically, C-doped tapes showed a much smaller dependence of $J_c$ on magnetic field due to the addition of C, which can be explained by the introduction of effective pinning centres in higher fields. However, the $J_c$ of the undoped tape decreased rapidly with increasing magnetic field. In addition, the $J_c$ value of the pure sample fell to 10 A cm$^{-2}$ at 16 T. For the C-doped tape sintered at 950 °C, on the other hand, $J_c$ higher than 10 A cm$^{-2}$ was observed at 23 T. Clearly, doping with C significantly improved the $B_{c2}$ values of MgB$_2$ tapes well above 20 T.

In order to precisely evaluate the $B_{c2}$ values at elevated temperatures, we performed the resistance versus temperature systematically with increasing sintering temperatures. All the C-doped samples sintered at different temperatures exhibited superior $J_c$ values compared to the pure tape in measuring fields of up to 18 T. The tape sintered at 950 °C revealed the highest $J_c$ values with excellent $J_c$–$B$ performance compared to all other samples: at 4.2 K, the transport $J_c$ reached $2.11 \times 10^4$ A cm$^{-2}$ at 10 T, over an order of magnitude larger than for the undoped sample. Furthermore, for C-added tapes, the field dependence of the $J_c$ became weaker with increasing heat treatment temperature. This behaviour is quite in contrast to the SiC-doped case [16], where the $J_c$–$B$ curves were independent of the sintering temperature. In fact, it is recognized that the higher the sintering temperature, the more the fine nanoscale particles scatter within the grain, as supported by the TEM observations [14], and perhaps the larger the proportion of C that is substituted for B in MgB$_2$ [12, 13, 17]. Therefore, our C-doped samples heated at higher temperatures showed a better field performance and higher $J_c$, indicating that a higher annealing temperature enhances flux pinning thus improving the high-field $J_c$. To identify the critical current properties in higher magnetic fields above 18 T, transport $J_c$ measurements were carried out by using the hybrid magnet at the HFLSM in Sendai.
measurements on the pure and C-added MgB$_2$ tapes in various magnetic fields by the four-probe resistive method. With increasing magnetic field, both the onset and zero resistive points of the superconducting transition curve shifted towards low temperatures for MgB$_2$ tapes, as typically shown in figure 3. The $T_c$ of the pure sample was 36.5 K. For the C-doped tape sintered at 800°C, $T_c$ decreased by 1.8 K. By contrast, $T_c$ was depressed to about 34.2 K for the doped sample heated at 950°C. This indicates that the extent of the C substitution reaction increases with increasing sintering temperature, resulting in $T_c$ depression, which is in agreement with a recent report [17]. As we can see, although the pure sample has a higher $T_c$ value at zero field, $T_c$ was depressed more severely in the undoped sample compared to the C-doped one by the applied magnetic field.

Figure 4 shows the temperature dependence of $B_{irr}$ for the pure tapes and tapes with added C, obtained from the 10% values of their corresponding resistive transitions. Clearly, the $B_{irr}$ of the C-doped tapes increased more rapidly with decreasing temperature than that of the undoped one. It is noted that both the $B_{irr}$ curves for doped tapes showed a crossover with the pure sample at higher temperature, for instance the crossover at 26 K for an 800°C curve but at 29 K for the 950°C curve. Although the addition of C introduced a degradation of $T_c$, the C-doped tapes show a higher $B_{irr}$ in the low temperature region. In fact, the C-doped samples sintered at 950°C showed the highest $B_{irr}$. Additionally, $B_{c2}$ has also been found to increase at temperatures below 29 K with C doping as shown in the inset of figure 4. This increase in the critical fields is believed to be due to the substantial substitution of boron for carbon, as evidenced by the change in the lattice parameter, which will be reported elsewhere [18].

Figure 4 also suggests that the higher sintering temperature led to higher $J_c$ and $B_{irr}$ values in C-doped MgB$_2$ tapes, a result indicating that flux pinning was enhanced by the carbon substitution for B with increasing annealing temperature, quite similar to the data of Dou et al [17]. Highly dispersed nanoparticles are believed to enhance the flux pinning directly, in addition to the introduction of pinning centres by carbon substitution, resulting in enhancement of $J_c$ and $B_{irr}$ values. Therefore, nano-C powder has proved to be one of the most promising dopants for MgB$_2$ wires and tapes with high $J_c$ besides SiC.

It is also interesting to note from figure 4 that at 4.2 K, $B_{irr}$ for the C-doped tape heated at 950°C reached 22.9 T, compared to 16 T for the undoped one. This is consistent with $B_{irr}$ data being determined by the transport $J_c(B)$ measurements (see figure 2). The $B_{irr}$ value of 22.9 T, which is even slightly higher than that of SiC-added MgB$_2$ tapes using MgH$_2$ + B powders [6], was comparable to the $B_{c2}$ of a conventional bronzed-processed Nb$_3$Sn conductor. Most importantly, at 20 K, $B_{irr}$ reached 9 T for C-doped tapes heated at 950°C, which was comparable to the $B_{c2}$ at 4.2 K of commercial NbTi conductors [19].

4. Conclusions
In summary, we have synthesized nano-C doped MgB$_2$/Fe tapes by applying heat treatments at 600–950°C. Higher values of $J_c(B)$ and $B_{irr}$ were seen for C-doped MgB$_2$ tapes.
at higher sintering temperatures. In particular, the tapes with added C showed a $B_{ir}$ value comparable to that of commercial NbTi at 4.2 K. This role of nanosized C particles can be very beneficial in the fabrication of MgB$_2$ tapes for magnetic resonance imaging applications at 20 K.

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