Significantly enhanced critical current densities in MgB_2 tapes made by a scaleable nanocarbon addition route

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Nanocarbon-doped Fe-sheathed MgB_2 tapes with different doping levels were prepared by the *in situ* powder-in-tube method. Compared to the undoped tapes, J_c for all the C-doped samples was enhanced by more than an order of magnitude in magnetic fields above 9 T. At 4.2 K, the transport J_c for the 5 at. % doped tapes reached 1.85×10^4 A/cm^2 at 10 T and 2.8×10^3 A/cm^2 at 14 T, respectively. Moreover, the critical temperature for the doped tapes decreased slightly. Transmission electron microscopy showed a number of intragranular dislocations and the dispersed nanoparticles embedded within MgB_2 grains induced by the C doping. The mechanism for the enhancement of flux pinning is also discussed. These results indicate that powder-in-tube-processed MgB_2 tape is very promising for high-field applications. © *2006 American Institute of Physics*.
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The discovery of superconductivity at 39 K in the MgB_2 compound has generated great interest in the field of applied superconductivity.[1] Compared to conventional metallic superconductors, MgB_2 has advantages of high transition temperature (T_c) and low raw material costs of both B and Mg. Indeed, superconducting MgB_2 tape has been regarded as one of the most promising materials for the next generation of superconductor applications.[2,3] The method commonly used to fabricate MgB_2 tape is the powder-in-tube technique.[4–6]

So far, enormous efforts have been directed toward improving critical current density (J_c) through the development and application of various techniques for fabrication of technically usable materials, such as doping with elements or compounds,[7–10] hot isostatic pressing,[11] irradiation with heavy ions.[12] Among all the methods, chemical doping is the most promising way for large-scale applications. Many dopants have been attempted in order to increase H_{c2} or introduce pinning centers to improve J_c, notably in high magnetic fields (H).

Especially, many groups have focused on studying the effect of C-doping on superconductivity in MgB_2 compound, since C element is widely recognized to enter the structure through replacing boron.[13–16] Several groups have also reported that the nanoscale SiC-doped MgB_2 wires and tapes exhibited much higher J_c values of MgB_2 than those of undoped ones.[7,17] In fact, there is increasing suspicion that one of the beneficial effects of SiC addition occurs by C doping of the MgB_2.[18] Therefore, from the application point of view, C doping of MgB_2 is a quite useful means of alloying MgB_2 for enhancing H_{c2} and flux pinning. Actually, carbon,[19] diamond,[9] and carbon nanotube[20] have recently been added into MgB_2, and all of them showed a positive effect in enhancing the J_c property of MgB_2 superconductors through magnetic measurement (no transport J_c data are available). However, the effect of pure nano-C doping on J_c-H properties of Fe-sheathed MgB_2 tapes has not been reported. In this work, we will present results on doping MgB_2/Fe tapes with nanometer C particles to achieve an improvement of critical current density by more than one order of magnitude in high magnetic fields.

Powders of magnesium (99.8%, −325 mesh), amorphous boron (99.99%), and carbon nanoparticle powders (20–30 nm, amorphous) were used for the fabrication of tapes by the *in-situ* powder-in-tube method. The C doping ratio was varied from 2.5 to 20 at. %. 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 to two rod types of 5 mm (Batch I) and 3 mm (Batch II) in diameter and then drawn to wires of 1.5 mm in diameter. The wires were subsequently rolled to tapes of $\sim3.2\times0.5$ mm. Short samples (~4 cm each), cut from the tapes, were wrapped in Ta foil and heat treated at 650 °C or 750 °C for 1 h in flowing high-purity Ar, and then cooling in the furnace to room temperature. Undoped tapes were also prepared under the same conditions for use as reference samples.

Figure 1 shows the XRD patterns of the series of *in situ* processed MgB_2 tapes with different C doping as well as the XRD pattern of the starting nano-C powder. As can be seen, the undoped samples consist of a main phase, MgB_2, with a small amount of MgO present. In the C-doped samples, extra peaks of Mg_2C_3 appear as impurity phases, which increase as the doping level increases. Note that there are no peaks related to C in the XRD patterns of the C-doped tapes due to the amorphous C powder used. At the same time, by increasing the C doping level, there is a significant shift of the (110) peaks to the higher angle that indicated a distortion of lattice parameter. These results suggest that the substitution of C in

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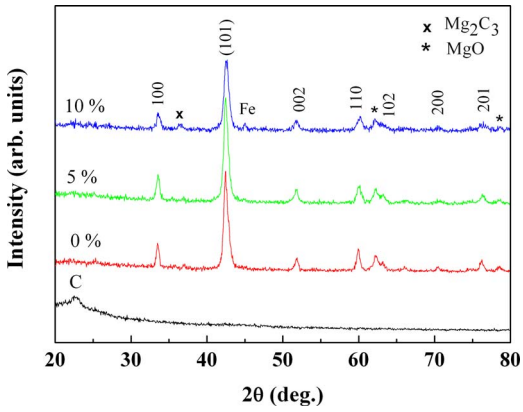

FIG. 1. (Color online) XRD patterns of undoped and nano-C-doped tapes. The data were obtained after peeling off the Fe sheath. The peaks of Fe were contributed from the Fe sheath.

the B site actually occurred, which is consistent with recent results of MgB_2 bulks doping with C or carbon nanotube.[19,20]

Susceptibility measurements revealed that the T_c onset for the undoped tapes is ~36.5 K. The T_c decreased with increasing nano-C doping level. However, T_c has slightly dropped by 3.5 K for the 15% high C-doped tapes while only 1.5 K decrease in T_c was observed in the 5% doped samples. This clearly indicates that C doping has little effect on T_c, which is in good agreement with recent paper.[19] As reported by Wilke *et al.*,[14] T_c may be used as an indicator of how much carbon is incorporated into the MgB_2. Therefore, these results suggest that some amounts of C powders were substituted in the B position in our samples.

Figure 2 shows the transport J_c at 4.2 K in magnetic fields for Fe-sheathed MgB_2 tapes with various amounts of nano-C doping from 0 to 20 at. % that were heat treated at 650 °C (Batch I). The J_c values of the 5% C doped tape that was sintered at 750 °C are also included. Only data above 6 T are shown, because at lower field region, I_c was too high to be measured. The striking result of Fig. 2 is that all the doped tapes showed an enhancement of more than one order of magnitude in J_c-H performance in fields above 9 T. The highest J_c value of the Fe-sheathed tapes was achieved in the 5% nano-C addition, then further increasing the C-doping

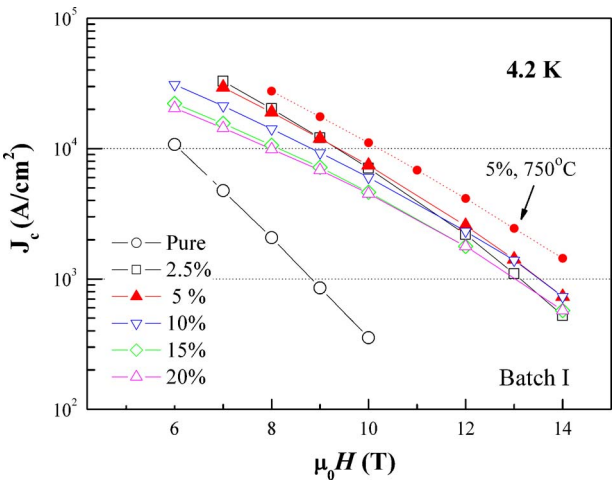

FIG. 2. (Color online) Transport critical current densities of Fe-sheathed tapes with nano-C doping level from 0 to 20 at. %, which were heat treated at 650 °C (Batch I), at 4.2 K in magnetic fields. The J_c values of the 5% C-doped tape that was sintered at 750 °C are also included.

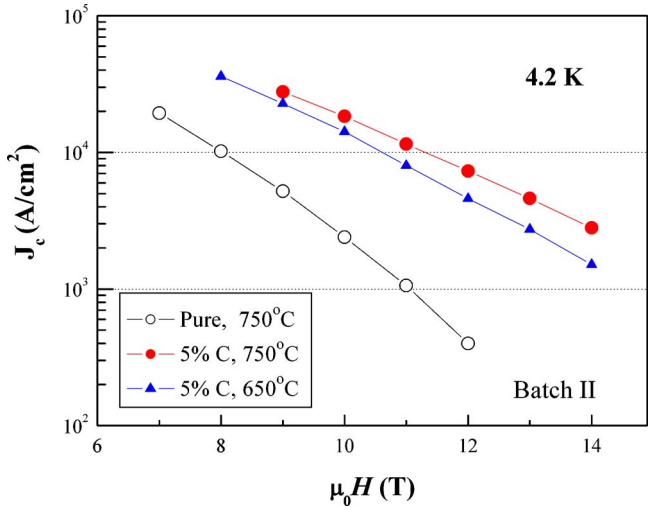

FIG. 3. (Color online) Transport J_c-H properties at 4.2 K for Fe-sheathed undoped and 5 at.% nanosized C-doped tapes (Batch II).

ratio caused a reduction of J_c in magnetic fields below 10 T. At 4.2 K and 10 T, J_c for the 5% doped samples is ~21 times larger than that of the undoped tapes. At higher doping levels ($x>5\%$), although the J_c in the low-field region was depressed, the rate of the J_c drop is much slower than for all other samples, clearly indicating strong flux pinning induced by the C doping. The higher the doping lever, the stronger the flux pinning in high fields. Besides, the J_c values of the 5% C-doped sample were much enhanced when the sintering temperature was further increased to 750 °C. At the same time, the sample showed slightly better J_c field performance too. High J_c values of 1.1×10^4 A/cm^2 at 10 T and 1.4×10^3 A/cm^2 at 14 T were observed for the samples sintered at 750 °C.

Figure 3 shows the magnetic-field dependence of the transport J_c at 4.2 K for pure and 5% C-doped MgB_2/Fe tapes annealed at 750 °C (Batch II). Several conclusions can be drawn from Fig. 3. First, high J_c values were achieved in both the undoped and the C-doped tapes in terms of Batch II samples. Second, again, all the $J_c(H)$ curves for doped tapes have a much higher J_c, more than an order of magnitude larger than for the undoped sample at fields above 10 T. The doped tapes heated at 750 °C reveal the highest J_c values compared to all other samples in our experiment: At 4.2 K, the transport J_c reached 1.85×10^4 A/cm^2 at 10 T and 2.8×10^3 A/cm^2 at 14 T, respectively. Even for the C-added tapes sintered at 650 °C for 1 h, we observed J_c values of 1.5×10^4 at 10 T and 1.6×10^3 A/cm^2 at 14 T, respectively. The J_c-H properties of our C-doped MgB_2 tapes are much better than the MgB_2 bulk or wires made by nanocarbon[19] and carbon nanotube[21] doping. To our knowledge, the J_c results mentioned here are the highest for the Fe-sheathed MgB_2 tapes reported to date. On the other hand, samples heated at 750 °C have a better field performance and higher J_c than samples sintered at 650 °C, indicating that the sintering temperature has a significant effect on the $J_c(H)$ characteristics for C-doped samples. A higher annealing temperature promotes the C-substitution reaction for B,[15] thus enhancing flux pinning and improving the high-field J_c.[20] It should be noted that this behavior is quite different from that of SiC-doped samples, in which the J_c is insensitive to the sintering temperature above 650 °C.[21]

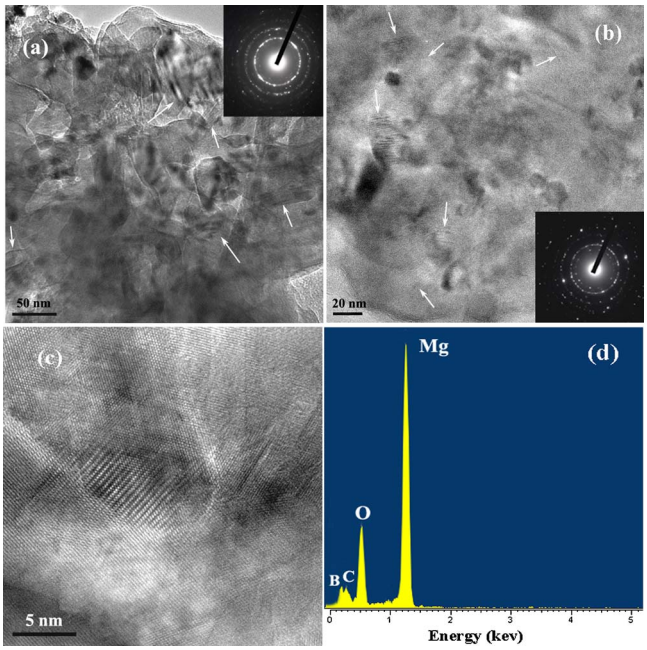

FIG. 4. (Color online) TEM micrographs showing the nanoparticle inclusions and dislocations of the C-doped samples. Some of the dislocations have been labeled using white arrows. The diffraction pattern of each sample is shown in the corner of the corresponding image. (a) Low-magnification micrograph for samples sintered at 650 °C. (b) High-magnification micrograph for samples sintered at 750 °C. (c) Image of nanoparticle showing lattice fringes. (d) The energy dispersive spectroscopy element analysis of MgB_2 grains.

When comparing the tapes between Batch I and Batch II, we should note the J_c difference. The J_c values of the Batch I tapes were lower than those of the corresponding second batch samples. This J_c difference can be explained by the difference in packing density of MgB_2 between the samples. With increasing the swage percentage reduction, the stress applied to the MgB_2 during the swaging increases, and a higher packing density of MgB_2 is obtained. Actually, from Figs. 2 and 3, the J_c-H curves of Batch II tapes were shifted upward compared to Batch I samples, but the field dependence of J_c was not changed, suggesting that the J_c increase for Batch II is clearly attributable to the improvement of the grain connectivity as a consequence of densification of the tape core.

In order to understand the mechanisms for the enhancement of J_c at higher fields in the nano-C-doped samples, a TEM study was performed. Figure 4 shows the typical low-magnification and high-resolution TEM micrographs for the C-doped tapes. TEM images showed that the grains size is less than 100 nm, but in some areas this is hard to distinguish as the grains are so well consolidated. This is because partial melting occurs in the C-doped sample, resulting in an excellent grain connection. Both the selected diffraction (SAD) patterns, shown in the corner of the Figs. 4(a) and 4(b), consist of well defined ring patterns, meaning a very fine grain size. However, the SAD patterns also suggest that the samples sintered at 750 °C were very well crystallized compared to tapes heated at 650 °C. More notably, the TEM examination revealed that there are a number of impurity phases in the form of nanometer-size inclusions (1–20 nm in size) inside grains in the nano-C-doped samples [see Figs. 4(a) and 4(b)]. The higher the sintering temperature, the more the finer nanoscale particles scattering within the grain [Fig. 4(b)]. Some of nanoparticles embedded in the MgB_2 grains have a thin and clear interface boundary [Fig. 4(c)]. The energy dispersive spectroscopy analysis of the grains revealed the presence of uniformly distributed Mg, B, C, and O [Fig. 4(d)]. This suggests that the inclusion nanoparticles might be unreacted C, BO_x, and BC or MgO and Mg_2C_3 detected by XRD. In addition, a large number of dislocations are present in the MgB_2. Some of these dislocations are indicated by white arrows. The high defect density is consistent with the reduced T_cs of the C-doped samples. These nanosized inclusions and intragrain defects created by C doping can serve as strong pinning centers to improve flux pinning. This is clearly demonstrated by the superior J_c-H performance of the C-doped samples, as shown in Figs. 2 and 3. Accordingly, a high density of flux-pinning centers and good grain connection for the MgB_2 phase are responsible for the excellent performance in our doped tapes.

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