INSTITUTE OF PHYSICS PUBLISHING SUPERCONDUCTOR SCIENCE AND TECHNOLOGY

Supercond. Sci. Technol. **19** (2006) 479–483 doi:10.1088/0953-2048/19/6/012

The effect of different nanoscale material doping on the critical current properties of *in situ* processed MgB_2 tapes

Xianping Zhang[1,3], Yanwei Ma[1,4], Zhaoshun Gao[1,3], Zhengguang Yu[1], G Nishijima[2] and K Watanabe[2]

[1] Applied Superconductivity Laboratory, Institute of Electrical Engineering, Chinese Academy of Sciences, PO Box 2703, Beijing 100080, People's Republic of China
[2] High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
[3] Graduate University of Chinese Academy of Sciences, Beijing 100088, People's Republic of China

E-mail: ywma@mail.iee.ac.cn

Received 27 December 2005, in final form 13 February 2006
Published 3 April 2006
Online at stacks.iop.org/SUST/19/479

Abstract

Fe-sheathed MgB_2 tapes were prepared by the *in situ* powder-in-tube technique using nanometre Si/N/C, SiC whiskers and SiC as doping materials, respectively. The doping effect on phase composition, microstructure and critical current properties was investigated. Heat treatment was performed at 650 °C for 1 h under an argon gas atmosphere. All the doped tapes were found to have significantly enhanced critical current density J_C at 4.2 K in magnetic fields up to 14 T compared with their undoped counterparts. Moreover, the tapes doped with nano-SiC had the best pinning performance, while the SiC whiskers and Si/N/C powders showed a similar improved field dependence of J_C compared to undoped samples. At 4.2 K and 10 T, J_C for the nano-SiC doped samples increased by a factor of 32. Even for Si/N/C doped tapes, a 16-fold improvement in the magnetic field J_C was observed. It is inferred that the different chemical properties of the Si and C elements in SiC, SiC whiskers and Si/N/C led to the J_C–B difference.

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

1. Introduction

Due to its high superconducting transition temperature (T_C), weak-link free grain coupling and low material cost, MgB_2 is a promising candidate for electric power and magnetic applications at temperatures below 30 K [1]. For practical applications of superconductors, such as magnets and cables, we have to develop tapes and wires. Most MgB_2 tapes and wires are now fabricated by the so-called powder-in-tube (PIT) method [2, 3]. Coils have been prepared using MgB_2 wires [4]. However, the critical current density (J_C) of MgB_2 decreases rapidly under magnetic fields compared to those for Nb-based superconductors. It is essential to have high J_C in high magnetic fields, and this can be achieved through increasing the number of flux pinning centres and improving the irreversibility field (H_{irr}). As a simple and practical method, chemical doping using different elements/compounds or nano-particles seems to be a very effective way to increase the number of flux pinning centres and H_{irr} in MgB_2. Many materials have been doped in MgB_2 tapes [5–11]. Of all these materials, nano-SiC [12] seems to be very effective in the enhancement of J_C for MgB_2 in the high field regime. Many reports have confirmed this result [13–16]. However, the mechanism of J_C enhancement by SiC doping is still not fully understood. On the other hand, the effect of nanometre Si/N/C and SiC whisker doping on the superconducting properties of MgB_2 has not been reported. In this work, we prepared Fe-sheathed MgB_2 tapes doped

[4] Author to whom any correspondence should be addressed.

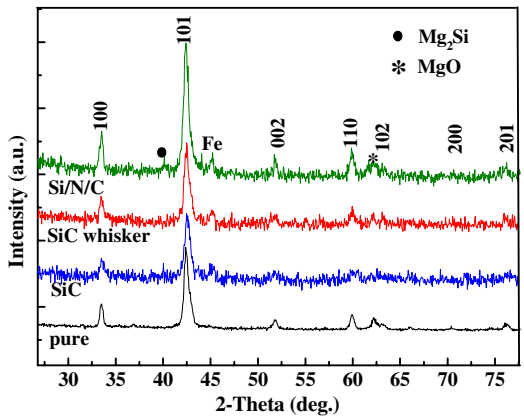

Figure 1. XRD patterns of *in situ* processed doped and undoped tapes heated at 650 °C for 1 h. The measurements were performed after peeling off the sheath materials. The peaks of MgB_2 are indexed, while the peaks of MgO and Mg_2Si are marked by asterisks and solid circles, respectively.

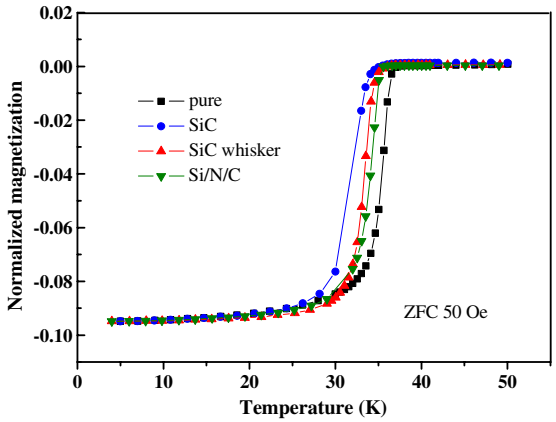

Figure 2. The temperature dependence of the DC magnetic susceptibility curves of all the doped and undoped tapes.

with nanoscale Si/N/C, SiC whiskers and SiC. The difference in microstructure and transport properties caused by various doping is also investigated. This seems to be important for gaining a deeper understanding of the mechanism behind the improvement of J_C in high fields.

2. Experimental details

MgB_2 tapes were prepared by the *in situ* PIT method. The sheath materials chosen for this experiment were commercially available pure Fe. Mg (325 mesh, 99.8%), B (amorphous, 2–5 μm, 99.99%), SiC (10–30 nm, 98%), SiC whiskers (diameter <100 nm, length/diameter >10, 99%) and Si/N/C (amorphous, 12–30 nm, 96%) powders were used as the starting materials. Mg and B powders were mixed with the nominal composition of 1:2; the chemical doping level is 5 at.%. After milling for 1 h, the mixed powder was tightly packed into Fe tubes of 8 mm outside diameter and 1.5 mm wall thickness. The composite tubes were subsequently swaged into rods of 5 mm in diameter, and then the rods were drawn into round wires of about 1.5 mm in diameter. Subsequently, the wires were rolled into tapes. The final size of the tapes was 3.2 mm in width and 0.5 mm in thickness. In order to investigate the effects of chemical doping, undoped tapes were also made. These tapes were sintered in flowing high-purity Ar at 650 °C for 1 h, which was followed by a furnace cooling to room temperature.

The phase constituents and microstructure of the samples were investigated using x-ray diffraction (XRD), energy dispersive x-ray analysis (EDX) and scanning electron microscopy (SEM). For SEM/EDX and XRD analysis, rectangular samples were cut from the tapes, and sheath materials were removed. DC magnetization measurements were performed with a superconducting quantum interference device magnetometer, using small pieces of an MgB_2 layer obtained by removing the sheath material. T_C was defined as the onset temperature at which a diamagnetic signal was observed. The transport current I_C at 4.2 K and its magnetic field dependence were evaluated at the High Field Laboratory for Superconducting Materials (HFLSM), by a standard four-probe technique, with a criterion of 1 μV cm^{-1}. Current leads and voltage taps were directly soldered to the sheath materials of the tapes. A magnetic field was applied parallel to the tape surface. The critical current density J_C was obtained by dividing I_C by the cross-sectional area of the MgB_2 core.

3. Results and discussion

The XRD patterns recorded from undoped and SiC, SiC whisker and Si/N/C doped heat-treated tapes are shown in figure 1. The XRD pattern for the undoped samples reveals that the main phase is MgB_2, with minor impurity of MgO. This is consistent with the oxygen peaks in EDX analysis, which are not shown here. The same was found to be the case for doped samples. The addition of SiC, SiC whiskers and Si/N/C leads to the formation of Mg_2Si as impurity phases. From the XRD pattern we cannot detect any free SiC presence, suggesting that there were reactions between Mg and SiC at a temperature of 650 °C. Additional peaks were found besides those for MgB_2, MgO and Mg_2Si phases, which have been indexed to Fe. This may come from Fe sheath material adhering to the MgB_2 core.

In addition, the full width at half maximum (FWHM) of the (110) peaks of doped samples was larger than that of undoped samples, especially for the SiC doped samples. This reflects the degradation of crystallization caused by various types of lattice defects or intragranular precipitates which usually act as effective pinning centres [17]. Therefore, a larger J_C value of doped samples than undoped ones in high magnetic fields is expected.

Figure 2 shows the magnetization as a function of temperature for all the samples. It is noted that T_C (onset) of all doped tapes was a little lower than that of undoped tapes. For the SiC doped samples, T_C dropped to 35 K, about 1.5 K lower than the T_C value of undoped samples. Meanwhile, the T_C values of SiC whisker and Si/N/C doped samples only drop slightly, ~0.5 K. The depressed T_C of doped samples is possibly attributed to the dopant incorporation into the MgB_2 structure, and the reaction between Mg and Si or the substitution of B by C is proposed to be responsible for the dopant incorporation [5], which also results in the broadening of the XRD peaks in figure 1. The T_C transition width of SiC

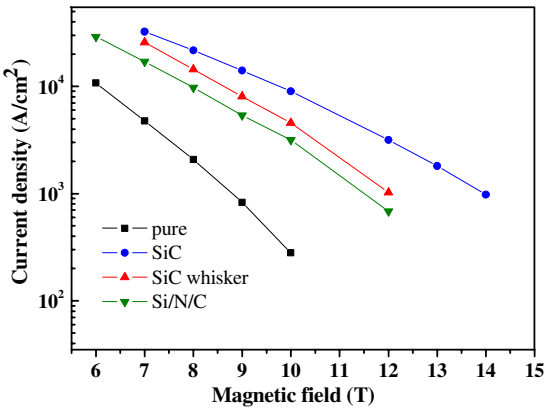

Figure 3. J_C–B properties of Fe-sheathed undoped and nano-SiC, SiC whisker and Si/N/C doped tapes heated at 650 °C for 1 h. The measurements were performed in magnetic fields parallel to the tape surfaces at 4.2 K.

doped samples is bigger than that of undoped samples, which may be due to the larger amount of impurity phases formed in the samples.

Figure 3 shows the field dependence of transport critical current densities of undoped and various doped tapes. Here, in the low-field region below 6 T, I_C could not be measured because of the heat generation at the current contacts. Clearly, the J_C values of all the doped samples were much improved compared to the undoped samples in all fields. Moreover, all the doped samples show much weaker field dependence of J_C than the undoped one. This means that effective pinning centres are introduced in the doped samples [18]. It is known that when the impurity phases have a size smaller than 10 nm, which is the coherence length of MgB_2, they can act as effective pinning centres. Therefore, the excellent J_C field performance may mainly be attributed to nanoscale impurity precipitates or/and reaction-induced products induced by doping. The SiC doped tape exhibited much higher J_C than the undoped one; J_C increased by a factor of 10 at 4.2 K, 8 T, and a factor of 32 at 4.2 K, 10 T. The Si/N/C doped samples have relatively inferior J_C properties in comparison with the SiC or SiC whisker doped ones, but still have 16 times larger J_C value than the undoped samples at 4.2 K, 10 T. Compared to the Si/N/C doping, SiC whisker addition shifted the J_C–B curves upwards but did not change the field dependence of J_C.

Typical micrographs of the fractured core layers for undoped and SiC, SiC whisker and Si/N/C doped samples are displayed in figure 4. It can be seen that a rough and porous microstructure is observed in the undoped MgB_2 samples (see figure 4(a)). The porous microstructure of MgB_2 directly means a reduction of the effective current path. However, the SiC doped sample has fewer voids and seems very dense (see figure 4(b)) and consequently the connections between grains are much improved. This is in accordance with the high J_C values of SiC doped samples in figure 3. As for the SiC whisker and Si/N/C doping, the connections between grains are also improved compared to the undoped ones, as shown in figures 4(c) and (d). This may partially explain the J_C–B property difference between doped and undoped samples. Nevertheless, the difference in microstructure by SEM observation alone cannot explain the enhancement of J_C–B properties shown in figure 3, since the grain coupling mainly increases the J_C values, but hardly changes the J_C field dependence. So it is speculated that more effective flux pinning

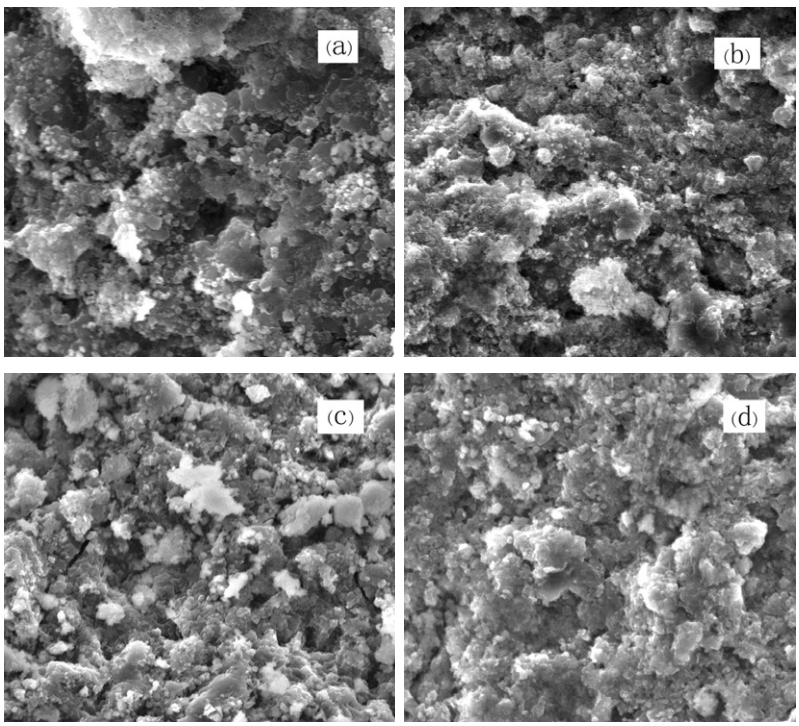

Figure 4. SEM images of the undoped (a) and (b) nano-SiC doped, (c) SiC whisker doped, (d) Si/N/C doped samples after peeling off the Fe sheath materials.

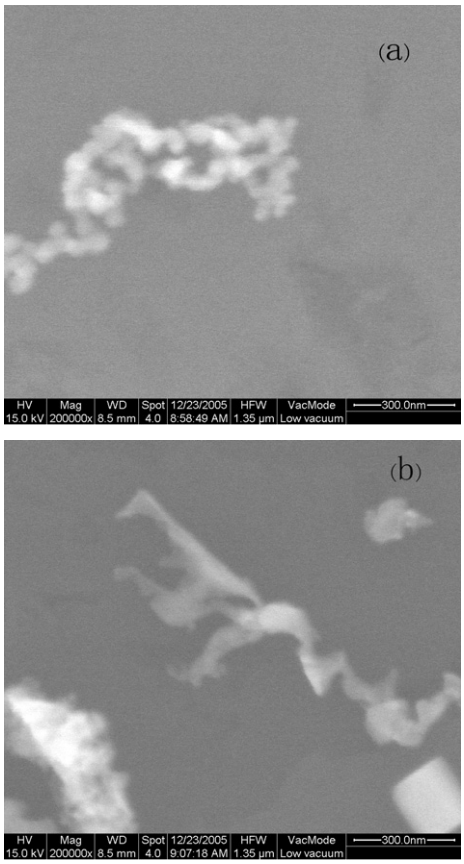

Figure 5. SEM images of nano-SiC (a) and SiC whisker (b) dopants.

centres caused by different doping are the main reason for better J_C–B characteristics.

All the doped tapes exhibited a superior field performance and higher J_C values than the undoped tapes in a magnetic field up to 14 T. It is believed that a large amount of nanoprecipitates and lattice distortions in the MgB_2 matrix, which can serve as pinning centres, are the dominant mechanism responsible for higher J_C values in high magnetic fields. Note that there is J_C–B difference among the doped samples. The J_C value of SiC doped tapes was higher than that of SiC whisker doped tape in high magnetic fields, suggesting that SiC doping is more effective in improving flux pinning than SiC whisker addition. As there are similar types of nano-inclusions in SiC and SiC whiskers, the strong enhancement of J_C–B properties in SiC doped samples may be caused by much higher reactivity of SiC powder compared to SiC whiskers. The micrographs of SiC and SiC whisker powders used for doping are shown in figure 5. It can be seen that the SiC powder mainly comprises nanoparticles (see figure 5(a)), while the SiC whisker is composed of nanofibres (see figure 5(b)). Obviously, the surface area of SiC nanoparticles is relatively large compared with that of the nano-whiskers, and this is very beneficial to the J_C–B enhancement of MgB_2. On the other hand, the Si/N/C doped tapes exhibited the lowest J_C value compared to the SiC and SiC whisker doped samples. This may be due to the lower chemical reactivity of the Si or/and C element in Si/N/C than that in SiC at a temperature of 650 °C. It has been reported that the reactivity of source dopants has a large effect on the J_C–B properties of MgB_2; for instance, the reactivity of B_4C with magnesium and boron was found to be much higher than that of graphite. Hence, substantially enhanced J_C values under high fields were observed in the B_4C doped MgB_2 samples [19]. Clearly, our data for the J_C difference between the SiC and Si/N/C doped samples further supports this viewpoint.

4. Conclusions

Fe-sheathed MgB_2 tapes doped with nanoscale Si/N/C, SiC whiskers and SiC have been prepared through the *in situ* PIT method. Our experiments showed that the field dependence of transport critical current is strongly influenced by the source dopants. The SiC doped tapes exhibited better intergranular connection and many more pinning centres, thus raising J_C by more than a factor of 32 compared to undoped tapes at 4.2 K, 10 T. This may be because of the particular chemical properties of nano-SiC particles. This is very important in the material selection for chemical doping for the fabrication of MgB_2 tapes.

Acknowledgments

We thank Yulei Jiao, Ling Xiao, S. Awaji, Xiaohang Li and Liye Xiao for their help and useful discussions. This work is partially supported by the National Science Foundation of China under Grant Nos 50472063 and 50377040 and National '973' Program (Grant No. 2006CB601004).

References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimisuet J 2001 *Nature* **410** 63
[2] Glowacki B A, Majoros M, Vickers M, Evetts J E, Shi Y and McDougall I 2001 *Supercond. Sci. Technol.* **14** 193
[3] Serquis A *et al* 2002 *Appl. Phys. Lett.* **82** 2847
[4] Fang H, Putman P T, Padmanabhan S, Zhou Y X and Salama 2004 *Supercond. Sci. Technol.* **17** 717
[5] Jiang C H, Nakane T and Kumakura H 2005 *Supercond. Sci. Technol.* **18** 902
[6] Wang J, Bugoslavsky Y, Berenov A, Cowey L, Caplin A D, Cohen L F, MacManus-Driscoll J L, Cooley L D, Song X and Larbalestier D C 2002 *Appl. Phys. Lett.* **81** 2026
[7] Fu B Q *et al* 2002 *J. Appl. Phys.* **92** 73
[8] Ma Y, Kumakura H, Matsumoto A and Togano K 2003 *Appl. Phys. Lett.* **83** 1181
[9] Senkowicz B J, Giencke J E, Patnaik S, Eom C B, Hellstrom E E and Larbalestier D C 2005 *Appl. Phys. Lett.* **86** 202502
[10] Nakane T, Takeya H, Fujii H and Kumakura H 2005 *Supercond. Sci. Technol.* **18** 521
[11] Pachla W, Morawski A, Kovac P, Husek I, Mazur A, Lada T, Diduszko R, Melisek T, Strbik V and Kulczyk M 2006 *Supercond. Sci. Technol.* **19** 1
[12] Sumption M D, Bhatia M, Dou S X, Rindfliesch M, Tomsic M, Arda L, Ozdemir M, Hascicek Y and Collings E W 2004 *Supercond. Sci. Technol.* **17** 1180
[13] Soltanian S, Wang X L, Horvat J, Dou S X, Sumption M D, Bhatia M, Collings E W, Munroe P and Tomsic M 2005 *Supercond. Sci. Technol.* **18** 658

[14] Kumakura H, Kitaguchi H, Matsumoto A and Hatakeyama H 2004 *Appl. Phys. Lett.* **84** 3669
[15] Ma Y *et al* 2006 *Supercond. Sci. Technol.* **19** 133
[16] Sumption M D, Bhatia M, Collings E W, Rindfleisch M, Tomsic M, Soltanian S, Dou S X and Collings E W 2005 *Appl. Phys. Lett.* **86** 092507
[17] Yamamoto A, Shimoyama J, Ueda S, Katsura Y, Iwayama I, Horii S and Kishio K 2005 *Appl. Phys. Lett.* **86** 212502
[18] Ma Y, Zhang X, Nishijima G, Watanabe K, Awaji S and Bai X 2006 *Appl. Phys. Lett.* **88** 072502
[19] Yamamoto A, Shimoyama J I, Ueda S, Iwayama I, Horii S and Kishio K 2005 *Supercond. Sci. Technol.* **18** 1323