

Improved critical current densities in MgB₂ tapes with ZrB₂ doping

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(Received 27 May 2006; accepted 16 August 2006; published online 28 September 2006)

MgB₂/Fe tapes with 2.5–15 at. % ZrB₂ additions were prepared through the *in situ* powder-in-tube method. The phases, microstructures, critical current density, and flux pinning were characterized by means of x-ray diffraction, scanning electron microscope, and magnetic and transport property measurements. Compared to the pure tape, a significant improvement in the in-field J_C was observed for all the ZrB₂ doped samples, while the critical temperature decreased slightly. The highest J_C value was achieved for the 10 at. % doped sample. At 4.2 K, the transport J_C increased by more than an order of magnitude than the undoped one in magnetic fields above 9 T. Nanoscale segregates or defects caused by the ZrB₂ additions which act as effective flux pinning centers are proposed to be the main reasons for the improved J_C field performance. © 2006 American Institute of Physics.
 [DOI: 10.1063/1.2357884]

MgB₂ is considered as a possible substitute for Nb–Ti or high- T_C oxide superconductors operated at around 20 K because of its high transition temperature (T_C) and weak-link-free character. The low material costs, simple structure, and small anisotropy are additional advantages of MgB₂. Therefore, it is thought as the most promising candidate for engineering application, especially for magnetic resonance imaging magnet which prefers to work at cryogen-free circumstances. However, critical current density (J_C) of MgB₂ decreases rapidly under magnetic fields compared to those for the Nb-based superconductors. MgB₂ is a two-gap structure material, and phonon scattering induced by the lattice distortions in this material is very pronounced. This suggests that the upper critical field (H_{C2}) of MgB₂ can be enhanced by introducing electron-scattering defects. It has been demonstrated that C doped thin films have $H_{C2}(0\text{ K})$ of about 50 T.¹ Various dopants^{2–8} have been investigated, leading to a wide variation in the reported values of H_{irr} and J_C . In the case of ZrB₂, we reported earlier that the improved J_C value was observed in 5% ZrB₂ doped MgB₂ tapes when sintered at 600 °C.⁹ Furthermore, an increase in H_{C2} from 20.5 to 28.6 T and enhancement of H_{irr} from 16 to 24 T were obtained in the ZrB₂ doped bulk MgB₂ samples as compared to the binary sample at 4.2 K.¹⁰ This means that ZrB₂ doping is a very promising method for MgB₂ tapes to get higher J_C in high magnetic fields. Therefore, it is very necessary to carry out further investigation on the doping effect of this material due to the lack of systematic study. In this work, a series of ZrB₂ doped MgB₂ tapes was prepared using an *in situ* powder-in-tube method. The highest J_C values were achieved in samples with the 10% ZrB₂ doping level, more than 11-fold improvement compared to the undoped tapes. The field dependence of J_C decreased by the ZrB₂ doping, suggesting that pinning centers effective in a high-field region were possibly introduced.

The detailed procedure for preparation of MgB₂/Fe tapes has been reported elsewhere.¹¹ Mg (325 mesh, 99.8%), B (amorphous, 99.99%), and ZrB₂ (2–5 μm, 99%) powders were used as the starting materials. Mg and B powders were mixed with the nominal composition of 1:2, the ZrB₂ doping levels were 2.5, 5, 10, and 15 at. %, respectively. These mixed powders were packed into Fe tubes, then swaged, drawn, and cold rolled into tapes. The final size of the tapes was 3.2 mm in width and 0.5 mm in thickness. Undoped tapes were similarly fabricated for comparative study. These tapes were heated under an Ar atmosphere up to 800 °C for 1 h, which was followed by a furnace cooling to room temperature.

The phase identification and crystal structure investigation were carried out using powder x-ray diffraction (XRD). Microstructure and composition analyses were performed using a scanning electron microscopy (SEM) equipped with an x-ray energy dispersion spectrum (EDX). dc magnetization measurements were performed with a superconducting quantum interference device magnetometer. The transport current I_C at 4.2 K and its magnetic field dependence were evaluated at the High Field Laboratory for Superconducting Materials in Sendai, by a standard four-probe technique, with a criterion of 1 μV cm⁻¹.

Figure 1 shows the XRD patterns for the series of ZrB₂ doped and undoped MgB₂ tapes. For the pure tapes, a small amount of MgO was detected as an impurity phase. We could not clearly see the existence of MgO from the XRD patterns of doped samples because of the superposition of the (220) peak for MgO and the (102) peak for ZrB₂. ZrB₂ phase can be identified in all the doped samples, and its peak intensities increase prominently with increasing amount of ZrB₂ in the starting powder. For example, the (100) peak of ZrB₂ has the same intensity as the (100) peak of MgB₂ at 2.5% doping level, but exceeds it with higher doping level. In contrast to the experiments by Bhatia *et al.*,¹⁰ a peak shift is not identified clearly in the XRD pattern for our tapes. This may be due to different methods used in XRD analysis. No other impurity phase was found from the XRD patterns, very similar to earlier reports.^{9,10}

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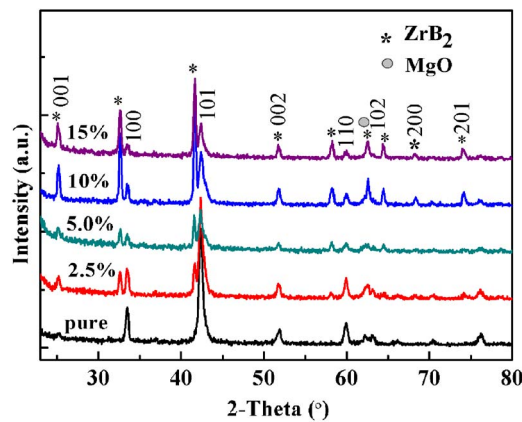


FIG. 1. (Color online) XRD patterns of *in situ* processed undoped and all the ZrB₂ doped tapes. The peaks of MgB₂ are indexed, while the peaks of MgO and ZrB₂ are marked by circles and asterisks, respectively.

As shown in the inset to Fig. 2, the T_C onset for the undoped tapes is ~ 37.1 K. The T_C decreased with increasing ZrB₂ doping level. However, T_C has slightly dropped by 1.2 K for the 15% high ZrB₂ doped tapes while around 0.5 K decrease in T_C was observed in the 10% doped samples, which is in good agreement with the previous report.⁹ On the other hand, all doping slightly depressed T_C (less than 1.2 K), indicating that the dopant incorporates into the MgB₂ structure. This may be caused by the ZrB₂ dispersion in the MgB₂ matrix, the effects of which are proposed to be the change in the electron diffusivities in the π and σ bands.¹⁰ However, the superconducting transition widths were hardly changed with the 10% doping level, and became a little broader only at a 15% doping level. As we know, both ZrB₂ and MgB₂ have an AlB₂-type structure, and their lattice parameters are very similar, thus some of the dispersed ZrB₂ in MgB₂ matrix may be regarded as the defects of the MgB₂ grains, similar to the substitution of Mg by Zr in the Zr doped MgB₂ samples.¹²

Figure 2 presents the J_C in magnetic fields at 4.2 K for undoped and ZrB₂ doped samples. It is noted that the ZrB₂ doping significantly enhanced the J_C values of MgB₂ tapes in magnetic fields. J_C increased with the increase of ZrB₂ doping level, and reached the highest values at 10% doping level. At 4.2 K, the J_C reached 6590 A/cm² at 9 T, more than 11-fold improvement compared to the undoped tapes.

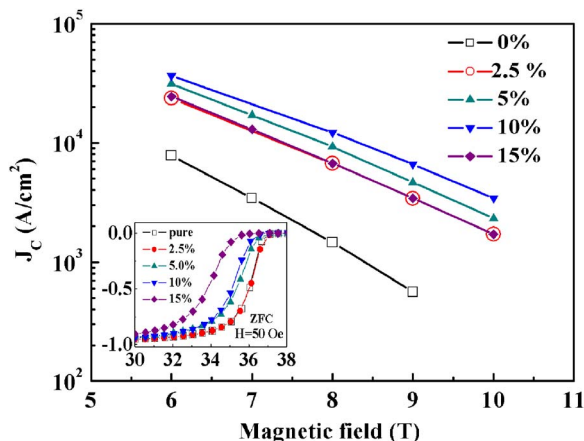


FIG. 2. (Color online) Transport J_C - B properties at 4.2 K for undoped and ZrB₂ doped tapes with different levels. The measurements were performed in magnetic fields parallel to the tape surface at 4.2 K. The inset shows T_C for these samples.

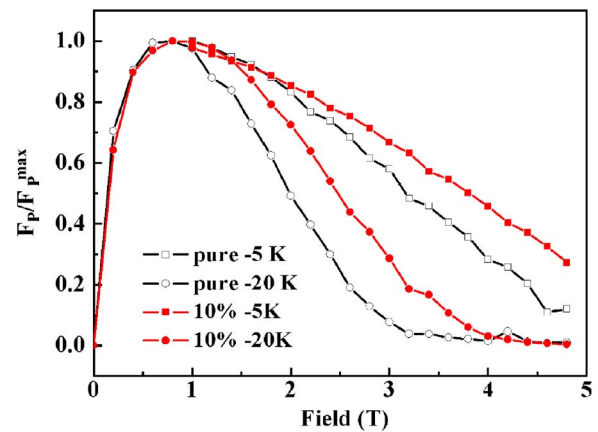


FIG. 3. (Color online) Normalized volume pinning force (F_p/F_p^{\max}) vs magnetic field (T) at 5 and 20 K for undoped and 10% ZrB₂ doped tapes.

Then the J_C decreased with further increasing the doping level (e.g., 15%), which may be due to a large amount of ZrB₂ introduced. Although MgB₂ has relatively large coherence length, the existence of large amounts of impurity phases will bring weak links at grain boundaries.¹³ On the other hand, the sensitivity of J_C to magnetic fields was decreased by the ZrB₂ doping. Therefore, the ZrB₂ addition is supposed to introduce effective pinning centers in high field. This speculation is supported by the volume pinning force data plotted in Fig. 3, which clearly demonstrates an improved flux pinning ability by ZrB₂ doping. Comparing to the previous report,⁹ we found that the J_C value of 5% doped MgB₂ tapes was much enhanced in the present work, in which a higher sintering temperature of 800 °C was employed. Therefore, more small segregates or defects could be introduced by ZrB₂ addition at higher temperatures, thus enhancing flux pinning and improving the high-field J_C .

Figure 4 shows the typical SEM images of the fractured core layers for undoped and ZrB₂ doped tapes. SEM results reveal that the MgB₂ core of the undoped samples was loose with some limited melted intergrain regions. In contrast, much larger melted regions of intergrains were observed in

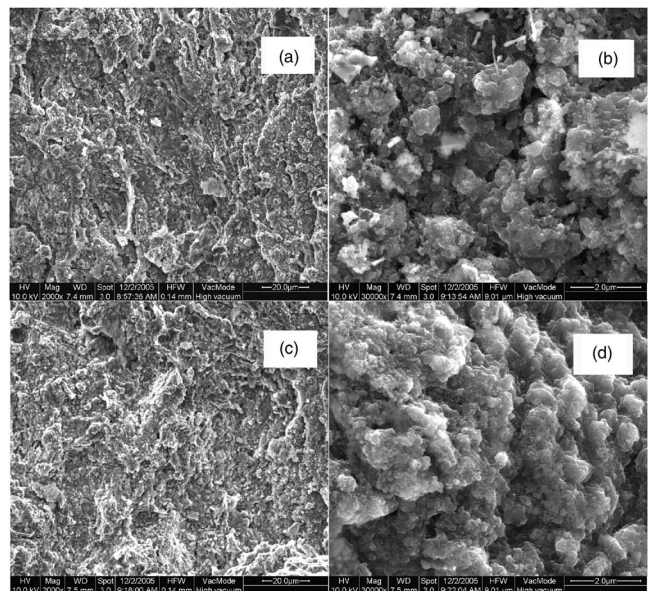


FIG. 4. SEM images of the undoped [(a) and (b)] and 10% [(c) and (d)] ZrB₂ doped samples after peeling off the Fe sheath. The left and right columns show images with low and high magnifications, respectively.

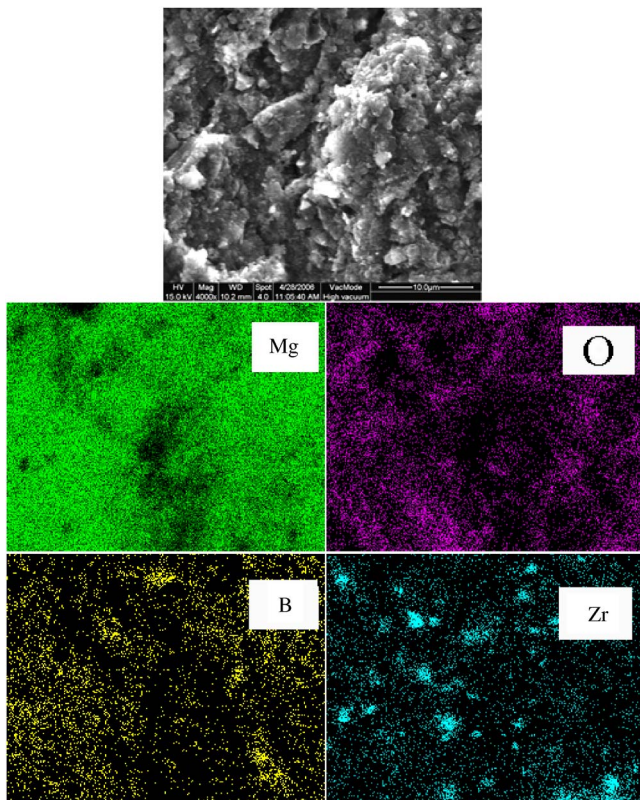


FIG. 5. (Color online) EDX mapping images of the 10% ZrB_2 doped samples after peeling off the Fe sheath.

the ZrB_2 doped tapes, resulting in the better connectivity between the MgB_2 grains. This microstructural change is consistent with previous reports of other borides^{14,15} and Zr (Ref. 12) additives. The grain boundaries may act as pinning centers in MgB_2 as in Nb_3Sn ,¹⁶ but the grain size for all our samples is almost the same ($\sim 0.2 \mu\text{m}$) observed from high magnification images [see Figs. 4(b) and 4(d)], indicating that the enhanced J_C of the ZrB_2 doped samples is not due to the grain-size difference. In addition, the good grain coupling mainly increases the J_C values, hardly changing the field dependence of J_C . From the EDX mapping images (see Fig. 5) of the 10% ZrB_2 doped samples we can see that although there are some segregations of Zr, the Zr element was observed all over the MgB_2 core. Accordingly, it seems that ZrB_2 or Zr atoms formed solid solution with MgB_2 during the sintering process, thus introducing more point defects or nanoparticles that can act as pinning centers. Therefore, the excellent J_C field performance is primarily due to nanoscale impurity precipitates or/and substituted crystal lattice defects introduced by ZrB_2 doping. The reduced T_C 's of the ZrB_2 doped samples further support this viewpoint.

All the doped tapes exhibited a superior field performance and higher J_C values than the undoped tapes in a magnetic field up to 10 T, especially for 10 at. % doping level. The mechanism for the significant improvement of J_C - B performance may be explained by better connection between the grains and very strong pinning force in ZrB_2 doped samples. Feng *et al.* reported that the addition of Zr element enhances the J_C - B characteristics of MgB_2 tape.¹² They concluded that the enhancement of J_C - B properties in high magnetic field is due to the reduction of grain size and small ZrB_2 particles formed by the Zr additive. In our experiment, no obvious grain-size difference could be observed

between the doped and undoped samples. By EDX mapping analyses we find that Zr element distributes all over the MgB_2 core. It is speculated that the distribution or solid solution of ZrB_2 or Zr with MgB_2 is the main reason for the enhancement of flux pinning ability in our experiment. Moreover, from the shape of the F_p profiles in Fig. 3 we can see that the relative pinning force is more remarkable at 20 K, suggesting that further improvement of J_C - B performance is expected for the ZrB_2 doped samples at higher temperatures. As the main working temperature of MgB_2 is around 20 K, the ZrB_2 doping is a very favorable method for the fabrication of applicable MgB_2 tapes. It should be noted that the size of ZrB_2 particles used was 2–5 μm ; the size of dopants will be much larger than those in nanoparticle doped tapes.^{2,8} As the fine precipitates can work effectively as pinning centers, further J_C - B improvement is expected upon utilization of finer ZrB_2 particles.

In summary, we have studied the effect of ZrB_2 doping on the J_C - B properties of MgB_2 tapes prepared by an *in situ* powder-in-tube method. The phase compositions, microstructure, flux pinning behavior, and transport property were investigated by x-ray diffraction, scanning electron microscopy, dc susceptibility measurements, and transport measurements. It is found that the J_C values have been significantly improved by ZrB_2 doping. The highest J_C value was achieved for the 10 at. % doped samples. The enhanced field dependence of the ZrB_2 doped tapes is mainly due to more possible segregates or defects caused by ZrB_2 doping.

The authors thank Ling Xiao, Yulei Jiao, Xiaohang Li, Jiandong Guo, G. Nishijima, and Liye Xiao for their help and useful discussion. This work is partially supported by the National Science Foundation of China under Grant Nos. 50472063 and 50377040 and the National "973" Program (Grant No. 2006CB601004).

¹C. Braccini *et al.*, Phys. Rev. B **71**, 012504 (2005).

²S. X. Dou, S. Soltanian, J. Horvat, X. L. Wang, S. H. Zhou, M. Ionescu, H. K. Liu, P. Munroe, and M. Tomsic, Appl. Phys. Lett. **81**, 3419 (2002).

³R. H. T. Wilke, S. L. Bud'ko, P. C. Canfield, D. K. Finnemore, R. J. Suplinskas, and S. T. Hannahs, Phys. Rev. Lett. **92**, 217003 (2004).

⁴B. J. Senkowicz, J. E. Giencke, S. Patnaik, C. B. Eom, E. E. Hellstrom, and D. C. Larbalestier, Appl. Phys. Lett. **86**, 202502 (2005).

⁵J. Wang, Y. Bugoslavsky, A. Berenov, L. Cowey, A. D. Caplin, L. F. Cohen, J. L. MacManus-Driscoll, L. D. Cooley, X. Song, and D. C. Larbalestier, Appl. Phys. Lett. **81**, 2026 (2002).

⁶R. Flukiger, H. L. Suo, N. Musolino, C. Beneduce, P. Toulemonde, and P. Lezza, Physica C **385**, 286 (2003).

⁷H. Kumakura, H. Kitaguchi, A. Matsumoto, and H. Hatakeyama, Appl. Phys. Lett. **84**, 3669 (2004).

⁸Yanwei Ma, Xianping Zhang, G. Nishijima, K. Watanabe, S. Awaji, and Xuedong Bai, Appl. Phys. Lett. **88**, 072502 (2006).

⁹Yanwei Ma, H. Kumakura, A. Matsumoto, H. Hatakeyama, and K. Togano, Supercond. Sci. Technol. **16**, 852 (2003).

¹⁰M. Bhatia, M. D. Sumption, E. W. Collings, and S. Dregia, Appl. Phys. Lett. **87**, 042505 (2005).

¹¹Xianping Zhang, Yanwei Ma, Zhaoshun Gao, Zhengguang Yu, G. Nishijima, and K. Watanabe, Supercond. Sci. Technol. **19**, 479 (2006).

¹²Y. Feng, Y. Zhao, A. K. Pradhan, C. H. Cheng, J. K. Yao, L. Zhou, N. Koshizuka, and M. Murakami, J. Appl. Phys. **92**, 2614 (2002).

¹³C. H. Jiang, T. Nakane, and H. Kumakura, Supercond. Sci. Technol. **18**, 902 (2005).

¹⁴T. Nakane, H. Takeya, H. Fujii, and H. Kumakura, Supercond. Sci. Technol. **18**, 521 (2005).

¹⁵A. Yamamoto, J. Shimoyama, S. Ueda, I. Iwayama, S. Horii, and K. Kishio, Supercond. Sci. Technol. **18**, 1323 (2005).

¹⁶C. B. Eom, Nature (London) **411**, 558 (2001).