Improved critical current densities in MgB$_2$ tapes with ZrB$_2$ doping

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MgB$_2$/Fe tapes with 2.5–15 at. % ZrB$_2$ 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 ZrB$_2$ 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 ZrB$_2$ 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.

The detailed procedure for preparation of MgB$_2$/Fe tapes has been reported elsewhere. $^1$ Mg (325 mesh, 99.8%), B (amorphous, 99.99%), and ZrB$_2$ (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 ZrB$_2$ 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 investigations 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 ZrB$_2$ doped and undoped MgB$_2$ 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 the doped samples because of the superposition of the (220) peak for MgO and the (102) peak for ZrB$_2$. ZrB$_2$ phase can be identified in all the doped samples, and its peak intensities increases in proportion with increasing amount of ZrB$_2$ in the starting powder. For example, the (100) peak of ZrB$_2$ has the same intensity as the (100) peak of MgB$_2$ 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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As shown in the inset to Fig. 2, the $T_C$ onset for the undoped tapes is $\sim 37.1$ K. The $T_C$ decreased with increasing ZrB$_2$ doping level. However, $T_C$ has slightly dropped by 1.2 K for the 15% high ZrB$_2$ 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. On the other hand, all doping slightly depressed $T_C$ (less than 1.2 K), indicating that the dopant incorporates into the MgB$_2$ structure. This may be caused by the ZrB$_2$ dispersion in the MgB$_2$ matrix, the effects of which are proposed to be the change in the electron diffusivities in the $\pi$ and $\sigma$ bands. 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 ZrB$_2$ and MgB$_2$ have an AlB$_2$-type structure, and their lattice parameters are very similar, thus some of the dispersed ZrB$_2$ in MgB$_2$ matrix may be regarded as the defects of the MgB$_2$ grains, similar to the substitution of Mg by Zr in the Zr doped MgB$_2$ samples.

Figure 2 presents the $J_C$ in magnetic fields at 4.2 K for undoped and ZrB$_2$ doped samples. It is noted that the ZrB$_2$ doping significantly enhanced the $J_C$ values of MgB$_2$ tapes in magnetic fields. $J_C$ increased with the increase of ZrB$_2$ doping level, and reached the highest values at 10% doping level. At 4.2 K, the $J_C$ reached 6590 A/cm$^2$ at 9 T, more than 11-fold improvement compared to the undoped tapes.

Then the $J_C$ decreased with further increasing the doping level (e.g., 15%), which may be due to a large amount of ZrB$_2$ introduced. Although MgB$_2$ has relatively large coherence length, the existence of large amounts of impurity phases will bring weak links at grain boundaries. On the other hand, the sensitivity of $J_C$ to magnetic fields was decreased by the ZrB$_2$ doping. Therefore, the ZrB$_2$ 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 ZrB$_2$ doping. Comparing to the previous report, we found that the $J_C$ value of 5% doped MgB$_2$ 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 ZrB$_2$ 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 ZrB$_2$ doped tapes. SEM results reveal that the MgB$_2$ core of the undoped samples was loose with some limited melted intergrain regions. In contrast, much larger melted regions of intergrains were observed in...
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 and Zr (Ref. 12) additives. The grain boundaries may act as pinning centers in MgB$_2$ as in Nb$_3$Sn, but the grain size for all our samples is almost the same ($\sim$0.2 $\mu$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 and/or 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. 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 $\mu$m; the size of dopants will be much larger than those in nanoparticle doped tapes. 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.

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