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Microstructure and high critical current density of *in situ* processed MgB_2 tapes made by WSi_2 and $ZrSi_2$ doping

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WSi_2- and $ZrSi_2$-doped Fe-sheathed MgB_2 tapes were prepared through the *in situ* powder-in-tube method. Both WSi_2- and $ZrSi_2$-doped tapes were found to have significantly increased critical current density J_c at 4.2 K in magnetic fields up to 12 T than their undoped counterpart. Scanning electron microscopy investigation revealed that the WSi_2 and $ZrSi_2$, doping enhanced intergranular connectivity, thus raising J_c by more than a factor of 2.2 and 3.4, respectively. Moreover, the critical temperature for the doped tapes decreased slightly (less than 0.7 K). It was also found that the improved field dependence of the WSi_2 tapes was due to the pinning by possible segregates or defects caused by the WSi_2 addition. This role of WSi_2 and $ZrSi_2$ may be very beneficial in the fabrication of MgB_2 tapes for a large range of applications.
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The recent discovery of magnesium diboride (MgB_2) with its superconducting transition temperature at 39 K has generated much interest in both fundamental research and applications.[1,2] In addition to the chemical simplicity and low cost, a T_c of 39 K is high enough for use at temperatures (10–20 K) easily accessible to cryocoolers. Therefore, MgB_2 is a possible candidate as a substitute for Nb–Ti or high-T_c oxide superconductors operated at around 20 K. Indeed, although considerable progress has already been made, the best critical current densities J_c reported so far on MgB_2 wires or tapes fabricated using the powder-in-tube (PIT) method[3–5] are well below those of bulk samples prepared under high pressure,[6,7] due to poor grain connections and the lack of flux pinning centers in this material. Significant improvement of the J_c is required by either increasing Bc_2 or introducing pinning centers.

Defects and segregates are known to act as effective flux pinning centers in high-T_c superconductors. Therefore, irradiation defects, chemical doping, the introduction of impurities or substitutions on the Mg or on the B site have been studied in MgB_2 samples.[8–11] Although these were surely effective in increasing inductive critical current density, the improvement in the transport J_c was not significant. More recently, SiC and Y_3O_2 doping has been reported to strongly improve the J_c in MgB_2 superconductors.[12,13] They claimed that a high density of dislocations and nanometer-sized inclusions observed inside MgB_2 grains could act as pinning centers. This leads us to expect that other materials can also be effective in increasing J_c values. On the other hand, the key applications of MgB_2 superconductors will be for wires and tapes. It is thus highly desirable that synthesis of a highly dense, high critical current capacity phase is possible at ambient pressures to enable large-scale applications.

In this letter, we show that much improvement of J_c is achieved by the addition of $ZrSi_2$ and WSi_2 in Fe-sheathed MgB_2 tapes by the PIT process.

Mg (325 mesh, 99.8% in purity), B (325 mesh, amorphous, 99.99%) and 5-at.% WSi_2 or $ZrSi_2$ powders (2–5 μm) were used for the fabrication of tapes by the *in situ* PIT method. The sheath materials chosen for this experiment were commercially available pure Fe. Then the mixture was filled into a Fe tube of 6-mm outside diameter and 1.25-mm wall thickness. After packing, the tubes were subsequently cold-rolled into a rectangular rod using a groove-rolling machine. The rods were subsequently rolled to tapes of 4×0.5 mm. Finally, the tapes were sintered at 600 °C for 1 h in argon. Undoped tapes were also similarly prepared for comparative study. The phase composition and microstructure were investigated by x-ray diffraction (XRD) and scanning electron microscope (SEM). Dc magnetization measurements were performed with a superconducting quantum interference device magnetometer. Magnetization curves were also measured with a vibrating sample magnetometer. 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. The I_c measurement was performed for several tape samples to check reproducibility.

Figure 1 shows the XRD patterns for three tapes. These are undoped, WSi_2- and $ZrSi_2$-doped heat-treated tapes, respectively. Note that the peaks of Fe were contributed from the Fe sheath. It can be seen that all the peaks are attributed to pure MgB_2 in the case of the undoped MgB_2 sample, suggesting the good structure quality. The same was found to be the case for the WSi_2- and $ZrSi_2$-doped samples. However, the WSi_2-doped MgB_2 tape has additional peaks besides MgB_2 phase, which have been indexed to the WSi_2 compound. Due to the high x-ray scattering factor of the heavy element W, the relative intensities of MgB_2 peaks are smaller than those of WSi_2 peaks. By contrast, the addition of $ZrSi_2$ leads to the formation of Zr_3Si_2 and Mg_2Si as the major impurity phases; there are no peaks corresponding to pure $ZrSi_2$, suggesting that there were reaction between MgB_2 and $ZrSi_2$.

Figure 2 shows transport I_c and J_c as a function of mag-

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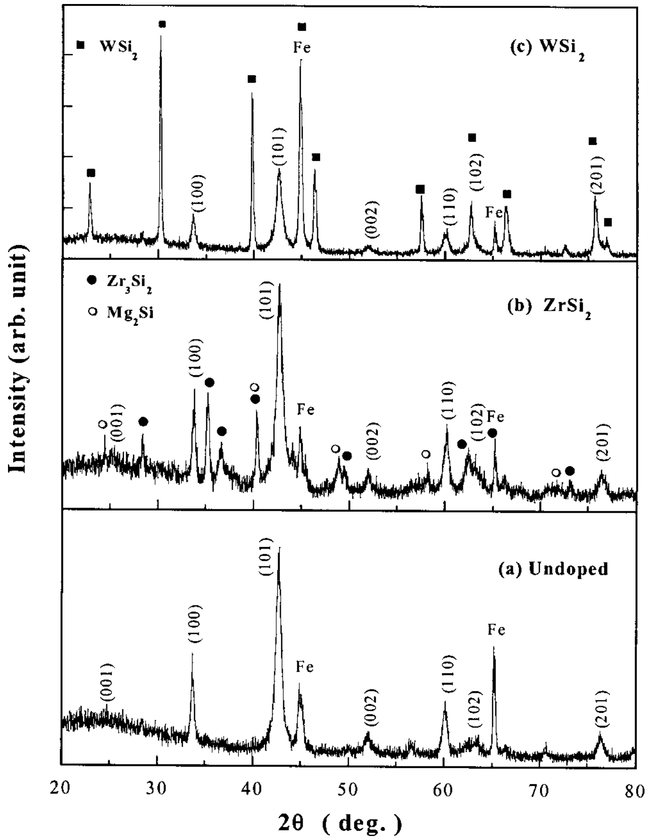

FIG. 1. XRD patterns of undoped, WSi_2-, and $ZrSi_2$-doped samples heated at 600 °C for 1 h. The data were obtained after peeling off the Fe-sheath. The XRD peaks of MgB_2 are indexed, and the peaks of WSi_2, Zr_3Si_2, and Mg_2Si are marked by squares, solid circles and open circles, respectively. The peaks of Fe were contributed from the Fe sheath.

netic field at 4.2 K for our undoped, WSi_2- and $ZrSi_2$-doped tapes. Only data above 4 T are shown, because at lower field region, I_c was so high that strong heating at the current contacts precluded the collection of reliable data. Clearly, both WSi_2- and $ZrSi_2$-doped tapes had a much higher J_c than the undoped tape in magnetic field. The best result was achieved by the $ZrSi_2$ doping, at 4.2 K and in a field of 8 T, the J_c of

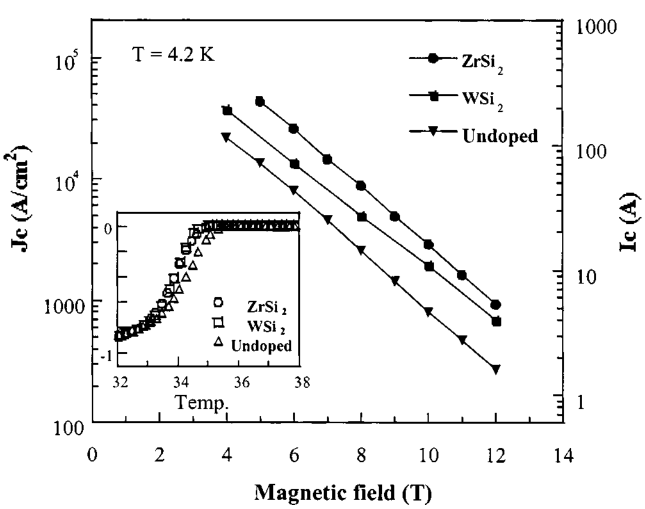

FIG. 2. J_c and I_c vs applied field at 4.2 K, for undoped, WSi_2-, and $ZrSi_2$-doped samples heated at 600 °C for 1 h, as measured by transport. The measurements were performed in magnetic fields parallel to the tape surface. Inset: ZFC dc magnetization as a function of temperature for all three samples.

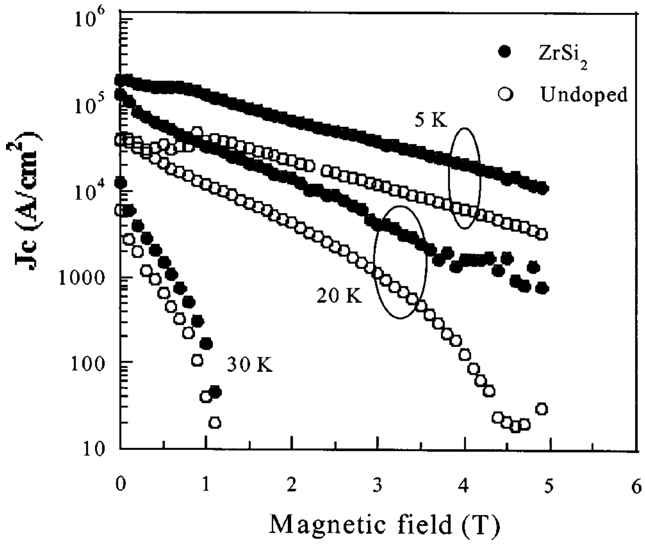

FIG. 3. Magnetic field dependence of J_c for the undoped and $ZrSi_2$-doped samples heated at 600 °C for 1 h at various temperatures, as measured by magnetization.

$ZrSi_2$-doped tapes reached a higher value around 10 kA/cm^2, a factor of 3.4 higher than for the undoped one, while for the WSi_2-doped tape, at 8 and 10 T, J_c reached 5 and 2 kA/cm^2, respectively (about a factor of 2.2 in the J_c values). It can also be seen that the WSi_2 sample revealed a significant improvement in J_c field performance compared to the undoped tape. Such a difference can be explained in term of higher flux pinning effect. This is demonstrated by the field dependence of volume pinning forces for the undoped and WSi_2 tapes (not shown here), Although the positions of the maximum pinning force ($B_{Fp\text{-max}}$) for both tapes are the same, the pinning force over $B_{Fp\text{-max}}$ is apparently larger in the WSi_2 sample, suggesting that effective pinning centers were possibly introduced with increasing field and thus resulting in the improved field dependence of J_c in a high-field region. It is worth noting that compared to the undoped tape, the critical temperature for the WSi_2- and $ZrSi_2$-doped samples slightly decreased by only 0.5 and 0.7 K, respectively, as shown in the inset of Fig. 2. This shift suggests that incorporation of additive elements into the MgB_2 actually occurred.

Figure 3 presents J_c for undoped and $ZrSi_2$-doped samples as a function of magnetic field at various temperatures, as calculated from magnetization loops $M(H)$ using the critical state Bean model and assuming uniform J_c flowing through the entire sample. Compared with the transport and magnetization J_c data, two significant observations are recorded. First, the $ZrSi_2$ sample revealed a higher J_c than the undoped sample at all temperatures and in the entire field region, which is well consistent with the transport J_c–B curves shown in Fig. 2. Second, the transport J_c was larger than the magnetic one at a fixed T and H (e.g., at 4.2 K and 5 T, respectively) and can be understood in terms of criteria fixed for two independent experiments.

In order to investigate the reason for the J_c improvement, we studied the differences in the microstructures of the tapes with and without doping. Figure 4 shows the typical SEM images of the fractured core layers for undoped, WSi_2- and $ZrSi_2$-doped samples. Clearly, well-developed grains can be seen in all three samples. However, the undoped sample

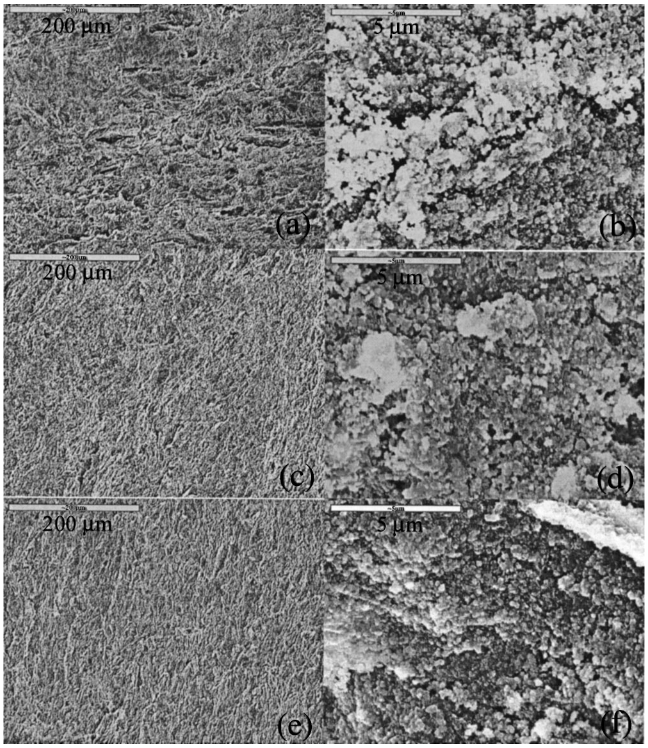

FIG. 4. SEM images of the fractured MgB_2 core layers of Fe-sheathed tapes, where (a) and (b) are from undoped, (c) and (d) are from WSi_2-doped, and (e) and (f) are from $ZrSi_2$-doped samples.

has more voids formed by the evaporation of Mg and the grains are not well connected [Figs. 4(a) and 4(b)]. In other words, weak links exist at the grain boundaries of this sample, and thus introduce a strong limitation to the flow of currents. In contrast, both WSi_2- and $ZrSi_2$-doped samples have a higher density with fewer voids, resulting in the better connectivity between the MgB_2 grains. The best microstructure is observed in the $ZrSi_2$ sample [Figs. 4(e) and 4(f)]. However, in contrast to previous work on doping for reducing grain size,[14,15] our high magnification images for all three tapes indicated that the MgB_2 grain size is almost the same ($\sim$0.2 μm), which further confirmed that the J_c difference in all three tapes is not due to the grain-size difference, but due to the improved grain coupling. We should note here that the initial grain size of WSi_2 and $ZrSi_2$ was 2–5 μm; however, such large grains were not detected in either sample. From the microstructure data we thus conclude that the main beneficial effect of the doping is the improvement of the intergrain connectivity. Also, the enhanced field dependence of the WSi_2 sample is due to the pinning by possible segregates or defects caused by the WSi_2 addition.

Our results are in consistent with recent reports, in which doping MgB_2 with Ti and Zr showed an improvement of J_c, likely due mainly to the densification effect.[14–16] As were demonstrated by several authors,[2,17] the high-density samples have high superconducting homogeneity and strong intergranular current flow as determined by magneto-optical studies. The fact was also corroborated by recent result of Serquis *et al.*[18] They found that for the MgB_2 wires prepared by PIT, they could either increase or decrease the J_c greatly, depending on the certain conditions. Based on microstructural analyses and magnetization data, they claimed that the main J_c limiting factor is connectivity, while intragrain pinning, or grain size are issues of secondary order. Clearly, our data of the high performance of J_c in the whole range of magnetic fields up to 12 T in the WSi_2 and $ZrSi_2$ samples further supports this viewpoint. We should note that the WSi_2 and $ZrSi_2$ grain size used was 2–5 μm. In the SiC and Y_2O_3 addition, which is significantly effective in increasing J_c in the high-field region, nanometer-sized particles were employed.[12,13] Therefore, further improvement in J_c is expected upon either utilization of fine WSi_2 and $ZrSi_2$ particles or optimization of the level of WSi_2 and $ZrSi_2$ doping.

In summary, we have investigated the effect of WSi_2 and $ZrSi_2$ addition to MgB_2 tapes. WSi_2 and $ZrSi_2$ doping improved intergranular connection thus raising J_c by more than a factor of 2 and 3.4, respectively. For the $ZrSi_2$ sample, the J_c value was up to about 10 kA cm^{-2} at 4.2 K and 8 T. Furthermore, the improved field dependence of the WSi_2 tapes was due to the pinning by possible segregates or defects caused by the WSi_2 addition. This role of WSi_2 and $ZrSi_2$ may be very beneficial in the fabrication of MgB_2 tapes for a large number of applications.

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