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The effect of $ZrSi_2$ and SiC doping on the microstructure and J_c–B properties of PIT processed MgB_2 tapes

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Abstract
We investigated the effect of $ZrSi_2$ and SiC doping on the microstructure, critical current density J_c and flux pinning of Fe-sheathed MgB_2 tapes prepared by the *in situ* powder-in-tube method. Heat treatment was performed at a low temperature of 650 °C for 1 h. The phases, microstructures and flux pinning were characterized by means of x-ray diffraction, scanning electron microscope, magnetic and transport property measurements. It was found that the tapes doped with nanoscale SiC had the best pinning performance, while the $ZrSi_2$ powder showed a similar improved field dependence of J_c compared with undoped samples. J_c values for the SiC doped samples were enhanced by two orders of magnitude at 4.2 K in magnetic fields above 8 T. At 4.2 K and 10 T, the J_c reached $\sim 1.5 \times 10^4$ A cm^{-2}. Moreover, the critical temperature for the doped tapes decreased slightly (<1.2 K). Microstructural analysis shows that very good grain connections or/and grain refinement were obtained for the doped tapes. The mechanism of the enhancement of the flux pinning is also discussed.

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

1. Introduction

The discovery of superconductivity at 39 K in the MgB_2 compound has generated great interest in the field of applied superconductivity. Compared to conventional metallic superconductors (LTS), MgB_2 has advantages of high transition temperature (T_c) and low raw material costs of both B and Mg. MgB_2 wires could become a credible competitor to LTS-based wires or to BSCCO-based wires used in low temperature (<25 K) applications, such as a potential NMR or MRI magnet conductor. Indeed, superconducting MgB_2 tape has been regarded as one of the most promising materials for the next generation of superconductor applications [1]. The method commonly used to fabricate MgB_2 tape is the powder-in-tube (PIT) technique [2, 3]. Many groups have made prototype tapes, using both prereacted (*ex situ*) MgB_2 powder and mixtures of Mg and B powders, which must be reacted to MgB_2 *in situ* within the tape.

By using PIT process, research efforts have been directed towards either improving critical current density (J_c) by improving grain connectivity, or improving in-field performance through introducing pinning centres [4–6]. Several groups have reported that the nanometre-scale SiC doped *in situ* processed tapes show much higher J_c values

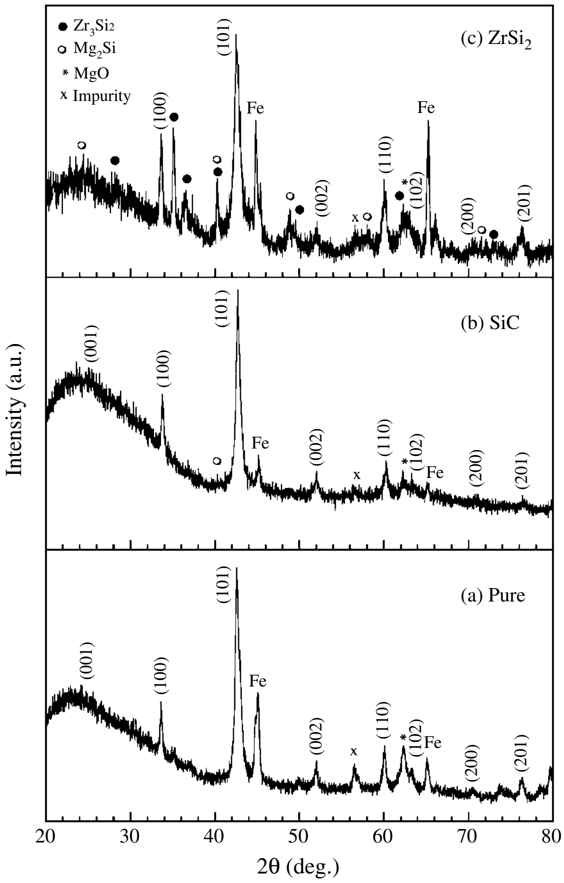

Figure 1. XRD patterns of undoped, $ZrSi_2$ and nano-SiC doped tapes. The data were obtained after peeling off the Fe sheath. The XRD peaks of MgB_2 are indexed, and the peaks of MgO, Zr_3Si_2, Mg_2Si and impurity are marked by asterisks, solid circles, open circles and forks, respectively. The peaks of Fe were contributed from the Fe sheath.

than undoped tapes [7, 8]. The suggested possible mechanism is that nano-SiC particles can result in the substitution of C in the B site and the formation of Mg_2Si nanometre inclusions, which greatly enhance the J_c property of MgB_2 in high magnetic fields [7]. Besides SiC doping, Si particles [9] and several silicon compounds, such as $ZrSi_2$, WSi_2 [10] and SiO_2 [8], have also been added into MgB_2, and all of them showed a positive effect in enhancing the J_c property of MgB_2 superconductors. In this work, we have fabricated nanometre-scale SiC and micrometre $ZrSi_2$ doped MgB_2 tapes by using the PIT technique and investigated their doping effects on the microstructure and J_c–B of MgB_2 tapes.

2. Experimental details

Powders of magnesium (99.8% pure), amorphous boron (99.99%) and 5 at.% nanoscale SiC (20–50 nm) or $ZrSi_2$ powders (−325 mesh) powders were used for the fabrication of tapes by the *in situ* powder-in-tube method. The sheath materials chosen for this experiment were commercially available pure Fe. Then the mixture was filled into an Fe tube of 8 mm outside diameter and 1.5 mm wall thickness. After packing, the tubes were swaged and drawn to a wire of

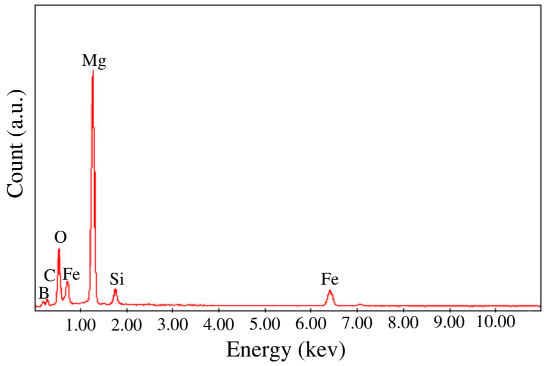

Figure 2. Typical EDX analysis of the SiC doped tapes. The peaks of Fe were contributed from the Fe sheath.

1.5 mm in diameter. The wires were subsequently rolled to tapes of ∼3.2 × 0.5 mm. Finally, the tapes, wrapped in Ta foil, were sintered at temperatures of 650 °C for 1 h in flowing high purity Ar. Undoped tapes were also similarly prepared for comparative study. The phase composition and microstructure were investigated using x-ray diffraction (XRD) and a scanning electron microscope (SEM). Magnetization measurements were performed with a superconducting quantum interference device magnetometer (SQUID). The transport J_c at 4.2 K and its magnetic field dependence were evaluated at the High Field Laboratory for Superconducting Materials (HFLSM), Sendai, by a standard four-probe technique with a criterion of 1 μV cm^{-1}. The I_c measurement was performed for several samples to check reproducibility.

3. Results and discussion

Figure 1 shows the x-ray diffraction patterns of the superconducting cores of the undoped and doped tapes. As we can see, the undoped samples consist of a main phase, MgB_2, with minor impurity phases of MgO present. The same was found to be the case for both SiC and $ZrSi_2$ doped tapes. In the case of SiC-added samples, we could not observe any peaks of SiC, which is similar to previous reports [7, 8]. The weak peak of Mg_2Si is observed in the XRD patterns of the SiC doped tapes if using a high speed scan, but the SEM/EDX analysis clearly shows that both Si and C are present within the MgB_2 core of our doped tapes, as shown in figure 2. In addition, the position of both (100) and (110) peaks slightly shifts to higher angles due to SiC addition (see figure 3), meaning a decrease in the a-axis lattice parameter. However, the position of the (002) peak stays almost unchanged, indicating that nano-SiC doping has little effect on the c-axis. This is in good agreement with a recent report [11]. Further, the full width at half-maximum (FWHM) of the (110) peak for the SiC-added tapes is apparently larger than that of the corresponding peak for the undoped ones (figure 3). This broadening of the FWHM indicates inferior MgB_2 crystallinity and lattice distortion of the core MgB_2, which usually resulted in an enhancement of the flux pinning strength [12]. On the other hand, XRD measurements revealed that 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

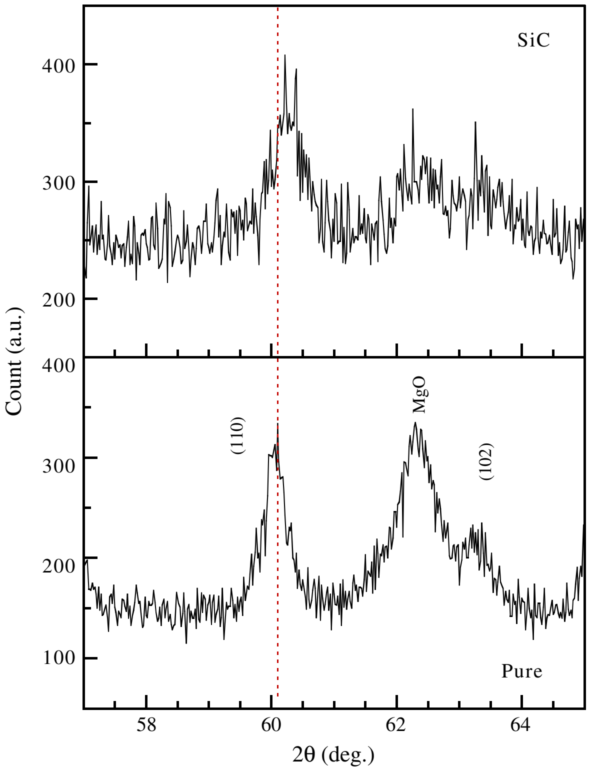

Figure 3. The enlarged view of XRD patterns near the (110) peak for undoped and nano-SiC doped tapes.

there were reactions between MgB_2 and $ZrSi_2$, in agreement with the previous report [10].

It should be noted that our present undoped tapes have a rather high content of MgO, which may come from the Mg source and the fabrication process. This is also demonstrated by the lower T_c (see figure 6). Upon doping with either SiC or $ZrSi_2$, both dopants would react with Mg, resulting in the formation of Mg_2Si or others as the impurity phases. The formation of Mg_2Si would decrease the content of MgO. This viewpoint is supported by the recent report that MgB_2 forms more easily at low temperature by the reaction of Mg with SiC powder [8].

Figure 4 shows the transport critical current density at 4.2 K in magnetic fields up to 14 T for the $ZrSi_2$ and SiC doped tapes. Only data above 4 T are shown, because in the lower field region, I_c was too high to be measured. From figure 4 we immediately notice that both doped samples exhibited a superior field performance and higher values of J_c than the undoped samples in magnetic fields of up to 14 T. In other words, the irreversibility field (H_{irr}) of doped samples is significantly higher than for undoped ones. This suggests that both $ZrSi_2$ and SiC doping are enhancing H_{irr}. It is striking that, in contrast with the previous report [10], the magnetic field dependence of J_c for $ZrSi_2$ doped tapes does change with the $ZrSi_2$ addition in our study. At present, the reason is not completely understood. A possible explanation may be related to the different $ZrSi_2$ powders employed and different deformation processes in the two investigations. When we compare the $ZrSi_2$ and the SiC doped tapes, we should note the difference of the J_c–B property. The J_c value of SiC doped tapes was higher than that of $ZrSi_2$ doped tape in

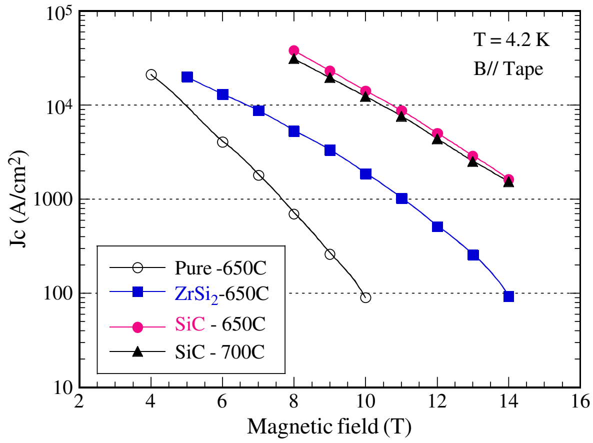

Figure 4. Transport J_c at $T = 4.2$ K as a function of applied fields for undoped and doped samples. The measurements were performed in magnetic fields parallel to the tape surface.

the high magnetic fields, suggesting that nano-SiC doping is more effective in improving flux pinning than micrometre $ZrSi_2$ addition. Compared to the undoped tapes, the SiC doped tapes heated at 650 °C reveal the highest J_c values, increased by more than two orders of magnitude in higher magnetic fields. At 4.2 K, the transport I_c reached 164 A at 8 T ($J_c = \sim 3.8 \times 10^4$ A cm^{-2}) and 62 A at 10 T ($J_c = \sim 1.5 \times 10^4$ A cm^{-2}). These data for J_c–B are quite comparable to the best results recently achieved for the nano-SiC doped MgB_2 tapes using MgH_2 + B powder [8]. It is noted that the J_c difference between tapes sintered at 650 and 700 °C are quite small as shown in figure 4, but the tape sintered at 700 °C seems to show a slightly weaker field dependence of J_c. This indicates that more nanoparticles acting as effective pinning centres are formed due to the higher sintering temperature.

To confirm the enhanced flux pinning ability in MgB_2 tapes with SiC and $ZrSi_2$ doping, figure 5 presents the normalized volume pinning force $F_p(B)/F_p^{max}$ as a function of magnetic field at 5 and 20 K for undoped and doped tapes heated at 650 °C. It is clear that the pinning force of both $ZrSi_2$ and SiC doped tapes is much larger than for the undoped ones over 1 T, indicating enhanced flux pinning in high fields. The samples with the SiC doping show the highest flux pinning force among the samples studied: the field where the maximum $F_p(B)$ occurs is shifted to higher fields: e.g., at 20 K, the maximum $F_p(B)$ difference is 0.4 T between the SiC doped and undoped samples, while at 5 K, the F_p^{max} of SiC doped samples is up to 2 T—compared to the 1.2 T maximum of undoped ones. As we can see, $ZrSi_2$ particle also shows a pinning force enhancement, but it is not as strong as with nano-SiC. The maximum $F_p(B)$ is only shifted to higher field by 0.2 T for the $ZrSi_2$ doped tapes in comparison to the undoped ones. Briefly, these results clearly demonstrated that the enhanced flux pinning as a result of SiC and $ZrSi_2$ doping should be responsible for the excellent transport J_c–B properties of doped samples.

As shown in figure 6, the T_c onset for the undoped samples heated at 650 °C is ~35.2 K. For the SiC doped samples, T_c only drops slightly, 1.2 K, indicating that SiC doping in MgB_2 tapes has little effect on T_c, which is quite important

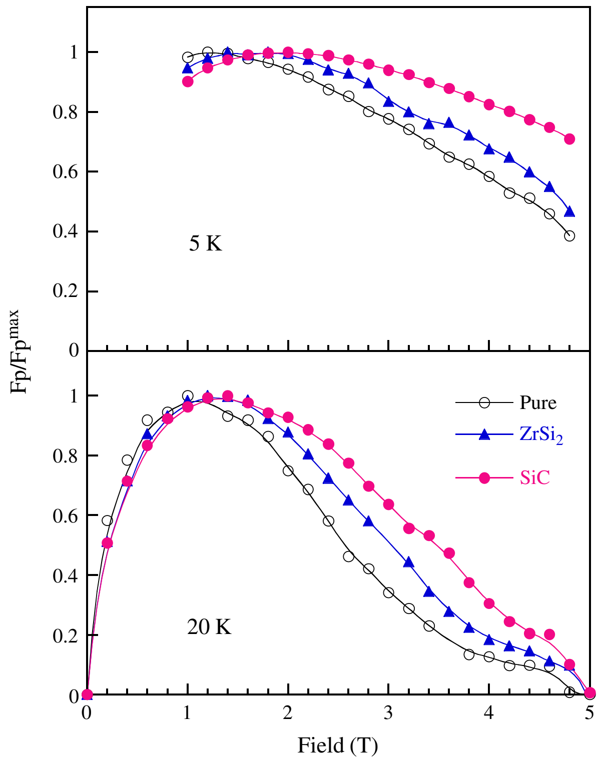

Figure 5. Volume pinning force F_p versus B at various temperatures for undoped and doped tapes.

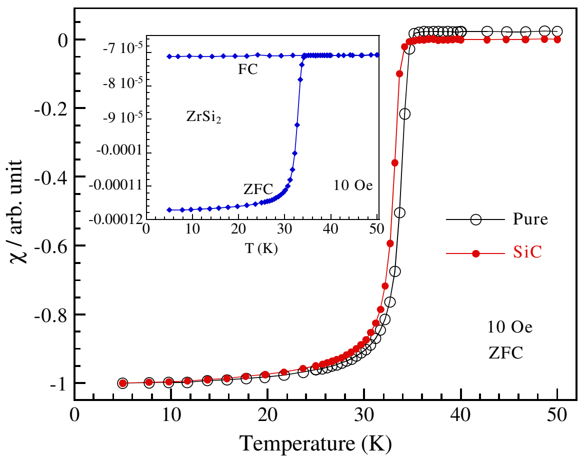

Figure 6. Normalized magnetic susceptibility versus temperature for all the doped and undoped tapes.

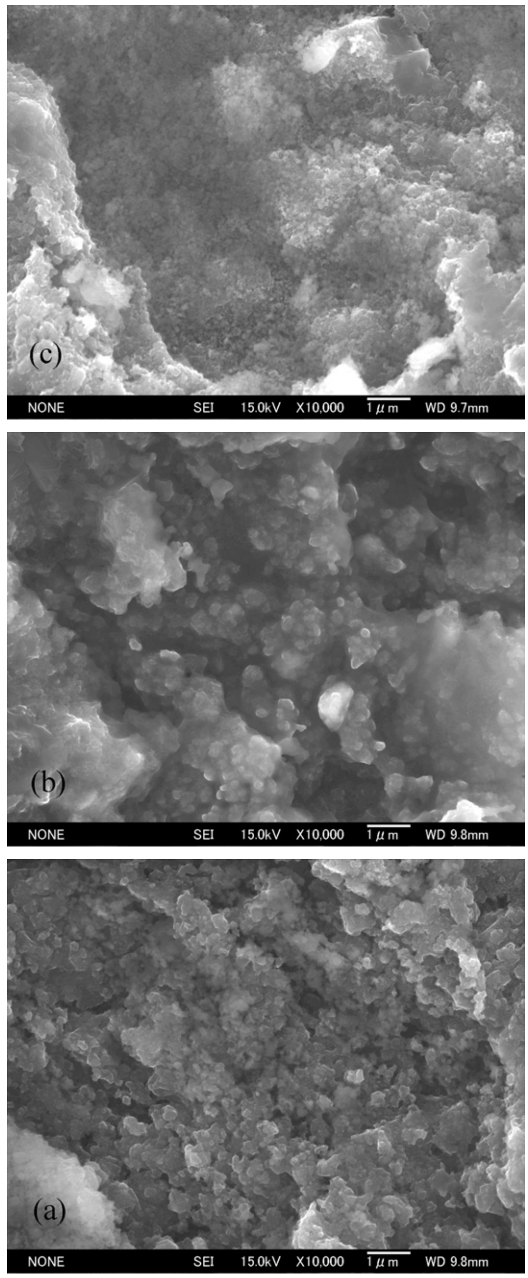

Figure 7. Typical SEM images of the fractured MgB_2 core layers of heat-treated Fe-sheathed tapes: (a) undoped, (b) $ZrSi_2$ doped, (c) SiC doped.

for practical applications. Note that the T_c decreases with increasing sintering temperature. T_c reaches 33.7 K for the tapes heat treated at 700 °C. Meanwhile, the onset T_c of the tapes with $ZrSi_2$ addition reaches 34.2 K, and also decreases slightly, compared to the undoped ones. On the other hand, all doping slightly depressed T_c (<1.2 K), indicating that the dopant incorporates into the MgB_2 structure. It is interesting to note that the $ZrSi_2$ sample shows relatively large diamagnetic signal at temperatures of above T_c, which might be related to the ferromagnetic Fe particles coming from the iron sheath, as supported by the XRD data. Further study is now in progress.

In order to understand the mechanism for the enhancement of J_c at high fields, we studied the differences in microstructure of the tapes with and without doping. Figure 7 shows the typical SEM images of the fractured core layers for undoped and doped samples. SEM results clearly 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 $ZrSi_2$ doped tapes, resulting in the better connectivity between the MgB_2 grains and increased J_c as mentioned before. On the other hand, the SiC doped samples had quite uniform microstructure with fewer voids, which also improved the linkages of grains. It is noted that we could not observe appreciate difference

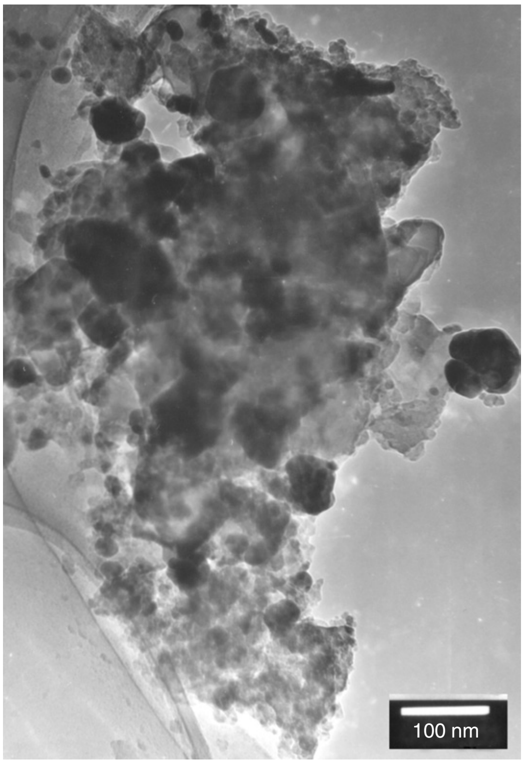

Figure 8. TEM image of the SiC doped tape. MgB_2 grains with the size of <100 nm are clearly shown.

in grain size between the undoped and $ZrSi_2$-added tapes. However, the grain size decreased drastically with the nano-SiC addition, with average values of ~200 and ~80 nm, for the undoped and doped tapes, respectively, as shown in figures 7 and 8. Obviously, the fine grain size would create many grain boundaries that may act as effective pinning centres, which might be one of reasons for the enhanced J_c–B performance.

The significant enhancement of J_c and the improved irreversibility behaviour in the $ZrSi_2$ and SiC doped MgB_2 samples may be attributed to a good connection between grains and strong pinning in the samples. As revealed by microstructural analyses, the improvement in the grain connectivity as a consequence of densification of the tape core is effective for enhancing the J_c–B properties. This was also corroborated by many recent results [5, 6]. However, this factor alone cannot fully explain the experimental results because the grain coupling mainly increases the J_c values, and hardly changes the magnetic field dependence of J_c, as reported previously [8, 10]. Therefore, the excellent J_c field performance is mainly due to nanoscale impurity precipitates or/and substituted crystal lattice defects introduced by SiC and $ZrSi_2$ doping. As supported by XRD and SEM/EDX results, $ZrSi_2$ addition resulted in Zr_3Si_2 and Mg_2Si as the major impurity phases, while high contents of Mg_2Si, other impurity phases and large numbers of grain boundary structure were observed in the SiC doped samples sintered at low temperature. These reaction-induced products or the grain boundary structure can serve as strong pinning centres improving flux pinning, as evidenced by figure 5. As we have shown before, the enhanced pinning force with $ZrSi_2$ is not as strong as with nano-SiC; the reason is that the grain size of the $ZrSi_2$ powder used was larger (~44 μm), so more large impurity phases introduced would not be effective pinning centres but act to reduce the superconducting volume. On the other hand, more nanoscale precipitates matching the coherence length well and grain boundary structures introduced by nano-SiC doping can act as strong pinning centres; thus the superior J_c–B characteristic. Accordingly, the results of the present work indicate that a combination of improving grain coupling, reduced grain size and the strong flux pinning caused by nano-SiC doping is responsible for the significant enhancement of the J_c–B performance in high magnetic fields. Note that further improvement in J_c–B is expected on optimizing the processing parameters or utilization of nanometre $ZrSi_2$ particles.

4. Conclusions

In summary, we have synthesized $ZrSi_2$ and SiC doped MgB_2/Fe tapes by the *in situ* powder-in-tube method. The J_c–B characteristics have been significantly improved in both doped tapes, in comparison with the undoped ones. These excellent values can be attributed to the very good grain connections as well as the strong flux pinning obtained in these doped tapes. This role of $ZrSi_2$ and SiC may be very beneficial in the fabrication of MgB_2 tapes for a large range of applications.

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