Improvement of critical current density in Fe-sheathed MgB\textsubscript{2} tapes by ZrSi\textsubscript{2}, ZrB\textsubscript{2} and WSi\textsubscript{2} doping

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Abstract

Fe-sheathed MgB\textsubscript{2} tapes were prepared through the in situ powder-in-tube technique by 5 at.\% ZrSi\textsubscript{2}, ZrB\textsubscript{2} and WSi\textsubscript{2} doping, respectively. The doping effect of these compounds on the microstructure and superconducting properties of MgB\textsubscript{2} tapes has been investigated by using x-ray diffraction, scanning electron microscope, transport measurements and DC susceptibility measurements. Compared to the undoped samples, J\textsubscript{c} for all the doped samples were much improved; the best result in terms of J\textsubscript{c} was achieved for ZrSi\textsubscript{2} doping, by up to a factor of 3.4 at 4.2 K in magnetic fields up to 12 T. Moreover, these dopants did not significantly decrease the transition temperature. The J\textsubscript{c}-B curves of WSi\textsubscript{2}-doped tapes show better performance in higher magnetic fields in comparison to undoped tapes, suggesting that pinning centers effective in a high-field region were possibly introduced.
Introduction

The discovery of superconductivity in MgB\textsubscript{2} with a transition temperature (T\textsubscript{c}) of 39 K \cite{1} has led to great progress researches in applied superconductivity because of low materials cost. The crystal structure of this material is an hexagonal AlB\textsubscript{2} type structure consisting of alternating layers of Mg atoms and boron honeycomb layers. Unlike the case of copper oxide superconductors MgB\textsubscript{2} has no weak-link problem at grain boundaries \cite{2}, and is thus a promising candidate for engineering applications in the temperature range of liquid hydrogen (20-30K) where the conventional superconductors cannot play any role due to low T\textsubscript{c}. To achieve high critical current density, different techniques have been developed. Among these techniques, the powder-in-tube (PIT) method has been demonstrated, either with \cite{3-5} or without \cite{6-7} recrystallization after deformation. Iron and its alloy have been found to be useful not only due to non-poisoning to MgB\textsubscript{2} but also due to its ductility, low cost and light weight. Extensive research efforts have been made to improve the J\textsubscript{c} of Fe-sheathed MgB\textsubscript{2} tapes \cite{3, 4}. High critical current density J\textsubscript{c} up to \(10^4 - 10^5\) A/cm\textsuperscript{2} at 10 K was obtained. However, the J\textsubscript{c} value of MgB\textsubscript{2} tapes is relatively low compared to the conventional low temperature superconductors, due to poor grain connections and the lack of flux pinning centers in this material.

On the other hand, the chemical doping is found to be easily controlled and highly efficient in improving J\textsubscript{c} and flux pinning in high-T\textsubscript{c} superconductors \cite{19-20}. Very recently, Dou \cite{8} and Driscoll et al. \cite{9} reported that chemical doping with nano-particles (SiC or Y\textsubscript{2}O\textsubscript{3}) into MgB\textsubscript{2} could significantly enhance J\textsubscript{c}. Cimberle et al. \cite{10} found that J\textsubscript{c} increased somewhat for Li-, Al-, and Si-doped samples. Likewise, Feng claimed much higher J\textsubscript{c} for Ti- and Zr-doped samples at low fields \cite{11-12}.
In this work, we have fabricated separate ZrSi$_2$-, ZrB$_2$- and WSi$_2$-doped MgB$_2$ tapes and investigated those doping effect on the microstructure and Jc of MgB$_2$. Excellent performance of Jc in magnetic fields of up to 12 T has been achieved in doped MgB$_2$ tapes processed at ambient pressure.

**Experimental**

The MgB$_2$ composite tapes with ZrSi$_2$ (or ZrB$_2$ or WSi$_2$) doping were prepared by the *in situ* PIT method with Fe sheath. The doping ratio of Mg:X:B was 5 at.% with X = ZrSi$_2$, ZrB$_2$ and WSi$_2$. Mg (325 mesh, 99.8% in purity), ZrSi$_2$ (or ZrB$_2$ or WSi$_2$) (2~5 µm), and B amorphous (325 mesh, 99.99%) powders were well mixed and ground in air for 1 h. The pure Fe tubes had an outside diameter of 6 mm, a wall thickness of 1.25 mm, and were 5 cm long. One end of the tube was sealed; then the powder mixture was filled into the Fe tube in air. After packing, the other end was crumpled, and this tube was subsequently cold-rolled into a rectangular rod using a groove-rolling machine.

Then, the rods were cold-rolled into a tape with a thickness of about 0.5 mm and a width of about 4 mm. These tapes were cut into short pieces and then heated up to 600° C in 40 min in a flow of Ar. After 1 h heat treatment, the tapes were furnace-cooled to room temperature. Undoped MgB$_2$ tapes were similarly prepared for comparison.

Phase identification was performed by an x-ray diffraction (XRD) method after mechanically peeling off the sheath materials. Microstructural observation was carried out by scanning electron microscopy (SEM). DC magnetization measurements were performed with a superconducting quantum interference device magnetometer (SQUID). Magnetization curves were measured with a vibrating sample magnetometer (VSM). Using a conventional four-probe resistive method, the transport critical current (Ic) of
short tapes was measured at 4.2 K. The criterion for the Ic definition was 1 µV/cm. A magnetic field up to 12 T was applied parallel to the tape surface. The Ic measurement was performed for several tape samples to check reproducibility.

**Results and discussion**

The phases present after the heat treatment were determined by XRD with Cu Kα radiation at room temperature, as shown in Fig. 1. The XRD pattern for the undoped samples reveals that MgB₂ was obtained as the nearly single phase. Note that the peaks of Fe were contributed from the Fe sheath. The XRD spectrums for ZrB₂ and WSi₂ samples show that in addition to MgB₂, large quantities of pure dopants, ZrB₂ and WSi₂, are presented. Clearly, MgB₂ is inert with respect to ZrB₂ and WSi₂ at 600 °C. Note that due to the high x-ray scattering factor of the heavy element, Zr and W, the relative intensities of MgB₂ peaks are smaller than those of ZrB₂ and WSi₂ peaks even for the doping level = 5 at.%. By contrast, ZrSi₂ samples consist of MgB₂ as the main phase. The addition of ZrSi₂ leads to the formation of Zr₃Si₂ and Mg₂Si as the major impurity phases; there are no peaks corresponding to pure ZrSi₂, suggesting that there were reaction between MgB₂ and ZrSi₂. It is worth noting that the position of MgB₂ peaks could not be changed with these three materials doping, which is much different from the results in Zn and Al-doped samples [13-14].

Figure 2 shows the superconducting transition curves for the doped and undoped samples determined by susceptibility measurements. Samples were zero-field cooled and then warmed from 5 K in an applied field of 10 Oe. All the doped tapes show a relatively sharp transitions, suggesting a fairly strong coupling of grains. The highest transition temperature (Tc onset =35.7 K) is observed in the pure MgB₂ samples. As can be seen, all doping slightly decreases Tc (less than 1 K), indicating that the dopant
incorporates into the MgB$_2$ structure. Superconducting transitions, with an onset at 35.2 K, are seen for the ZrSi$_2$ and ZrB$_2$ samples, while WSi$_2$ samples have T$_c$ onset of 35.0 K. Our observations are in good agreement with previous reports, in which the transition temperature decreases at various rates for different doping with Al, Zr, Ti, Si, Li and SiC [10, 11, 13, 15, 18].

Figure 3 summarizes the J$_c$ values at 4.2 K as a function of magnetic fields for our MgB$_2$/Fe tapes with and without doping. The magnetic field was applied parallel to the tape surface. It can be seen that the J$_c$ values are much improved by doping in MgB$_2$ tapes with ZrSi$_2$, ZrB$_2$ and WSi$_2$, respectively. Clearly, the largest J$_c$ values were achieved in the ZrSi$_2$-doped samples, more than three times higher than the undoped ones. Similarly, in the ZrB$_2$- and WSi$_2$-doped tapes, we also obtained the J$_c$ values being at least twice as large as those of pure tapes. At 4.2 K and in a field of 10 T, the undoped samples showed J$_c$ values of about 820 A/cm$^2$, while the doped tapes showed higher values in the same field, namely, ZrSi$_2$-doped tapes = ~3000 A/cm$^2$; WSi$_2$ tapes: ~1900 A/cm$^2$; ZrB$_2$ tapes: ~1700 A/cm$^2$. More importantly, for the WSi$_2$-doped tapes the field dependence of J$_c$ was evidently different for other three samples (undoped, ZrSi$_2$- and ZrB$_2$-doped). The Jc-B curves became flatter than those of other ones in higher field region. Such a difference can be explained in term of higher flux pinning effect. This is demonstrated by Fig. 4, which shows the field dependence of volume pinning forces Fp(H) at 22 K for the undoped and WSi$_2$-doped tapes. Here Fp(H) is obtained from the hysteresis in magnetization curves and is normalized by the maximum volume pinning force F$_{p,max}$ at the same temperature. Although the positions of the maximum pinning force for both tapes (undoped and WSi$_2$-) are the same, the pinning force over B$_{Fp,max}$ is apparently larger in the WSi$_2$-doped tapes, suggesting that pinning centers
effective in a high-field region were possibly introduced.

We investigated the reason for the $J_c$ difference for tapes with and without doping. Figure 5 shows the typical SEM images of the fractured core layers for different doped tapes, as well as the undoped tapes. A rough and porous microstructure is observed in the pure MgB$_2$ tapes. However, all three doped tapes have a higher density with few voids, suggesting the improved coupling of grains. This important enhancement of the MgB$_2$ core quality is believed to be responsible for the higher transport $J_c$ in the doped tapes. The grain boundaries may act as pinning centers in MgB$_2$ as in Nb$_3$Sn [17]. However, in contrast to previous work on doping for reducing grain size [11, 12], our high magnification images for all tapes indicated that the grain size is almost the same (~ 0.2 µm), which further confirmed that the $J_c$ difference in these tapes is not due to the grain-size difference but due to the improved grain coupling.

The high performance of $J_c$ in the whole range of magnetic fields up to 12 T in the three kinds of doped samples might be largely attributed to densification effect and a good connection between grains. Our results are in consistent with recent reports, in which doping MgB$_2$ with Ti, Si and Zr showed an improvement of $J_c$, likely mainly due to the densification effect [10-12]. Feng and co-workers claimed that in Zr- and Ti-doped cases, with increasing doping level, the samples become denser, and the $J_c$ increases. However, the improvement in the microstructure is not significant until the doping level reaches 10%. As the doping level increases to 10%, the density of the sample sharply increases and, at the same time, the $J_c$ enhanced significantly. As the doping level further increases to 40%, the $J_c$ decreases rapidly although the samples are still quite dense [11-12]. Based on our present preliminary results, it is speculated that further improvement in $J_c$ will be achieved upon optimization of doping level.
On the other hand, in our present study, the size for added powders is around 2-5 µm, which may be too large for strong flux pinning. This is the reason why the difference of pinning forces between WSi2 doped and undoped tapes is small as shown in Fig. 4. It is evident that incorporating SiC (or Y2O3) nanoparticles together with Mg and B powders results in the formation of MgB2 with a uniform dispersion of nano-precipitates, which can act as strong pinning centers [8-9]. Thus we can expect that Jc(H) and irreversibility field (Hirr) can be improved significantly by doping MgB2 with nano-particles ZrSi2, ZrB2 and WSi2, respectively.

In a word, the present results clearly showed that the ZrSi2, ZrB2 and WSi2 doping in MgB2 seems an effective and easily controlled method to improve Jc. This method is very suitable for the industrial scale fabrication of MgB2 tapes and bulks because these doped samples are prepared at ambient pressure.

Conclusions

In summary, the Fe-sheathed tapes of the MgB2 pure and doped with ZrSi2, ZrB2 and WSi2 have been prepared through the \textit{in situ} PIT method. The transport Jc measured at low temperature indicates an improvement of the critical current density for all the doped tapes, the best result being achieved by the ZrSi2 doping (about a factor 3.4 in the Jc values). At 4.2 K and in a field of 8 T, the Jc of ZrSi2-doped tapes reaches a higher value about 10^4 A/cm². The Jc-B curves of WSi2-doped tapes show better performance in higher magnetic fields in comparison to undoped tapes, suggesting that pinning centers effective in a high-field region were possibly introduced. Densification of MgB2 core was observed for all the doped tapes. This densification is also effective to improve Jc.
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Figure captions

Figure 1 X-ray diffraction patterns for the undoped and all the doped samples heated at 600 °C for 1h. The data were obtained after peeling off the Fe-sheath. The XRD peaks of MgB$_2$ are indexed, and the peaks of WSi$_2$, ZrB$_2$, Zr$_3$Si$_2$ and Mg$_2$Si are marked by squares, asterisks, solid circles and open circles, respectively. The peaks of Fe were contributed from the Fe sheath.

Figure 2 Normalized magnetic susceptibility vs temperature for all the doped and undoped tapes. The inset shows the enlarged view near the superconducting transitions.

Figure 3 Jc-B properties of Fe-sheathed undoped and all the doped tapes heated at 600 °C for 1h. The measurements were performed in magnetic fields parallel to the tape surface.

Figure 4 The normalized volume pinning forces of undoped and WSi$_2$-doped tapes at 22 K.

Figure 5 SEM images of the fractured MgB$_2$ core layers of Fe-sheathed undoped and all the doped tapes heated at 600 °C for 1h. (a) undoped, (b) ZrSi$_2$, (c) ZrB$_2$, (d) WSi$_2$. 


Fig. 1  Ma et al.
Fig. 2  Ma et al.
Fig. 3  Ma et al.
Fig. 4  Ma et al.
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