Flux pinning behavior of MgB$_2$ doped with Fe and Fe$_2$O$_3$ nanowires

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Abstract

MgB$_2$ bulks doped with Fe and Fe$_2$O$_3$ nanowires are prepared by hybridized diffusion method. The doping effect on superconductivity transition temperature, $T_c$, critical current density $J_c$, and flux pinning behavior have been studied. It is found that both $T_c$ and $J_c$ of MgB$_2$ show quite different features for these two kinds of nanowires. Fe$_2$O$_3$ nanowires significantly suppress both $T_c$ and $J_c$ of MgB$_2$, whereas Fe nanowires do improve the flux pinning behavior of MgB$_2$ although the $T_c$ is slightly suppressed.

1. Introduction

Since the discovery of superconductivity at 39 K in MgB$_2$, great deals of studies for its basic research and practical applications have been performed [1-4]. In order to improve the current carrying properties in high field, many methods have been utilized to enhance the pinning force. Nano-particles or powders, such as carbon, Ti, Zr, Y$_2$O$_3$, Dy$_2$O$_3$, and Ho$_2$O$_3$ have been introduced as nano-pinning-centers [5–10]. Among them, the dopants with strong magnetic moment have attracted extensive attentions since they may work as magnetic pinning centers in MgB$_2$, since the magnetic impurities usually have a stronger interaction with magnetic flux line than nonmagnetic impurities and thus exert a stronger force to trap the flux lines if they can be properly introduced into the superconducting matrix. In our previous work, it was observed that some magnetic HoB$_4$ particles were formed to be as effective pinning centers in Ho$_2$O$_3$ doped MgB$_2$. Other magnetic particles including Fe, and Fe$_2$O$_3$ have also been added into MgB$_2$ as pinning centers. Prozorov et al. prepared MgB$_2$ bulk embedded with Fe$_2$O$_3$ particles through application of a sonication technique and enhancement of flux pinning behavior was found in their samples [11]. Dou et al. have studied the effect of nano-scale iron particles addition on $T_c$ and $J_c$ in both bulk and thin film MgB$_2$ and demonstrated that the particle iron doping depresses both $T_c$ and $J_c$ of MgB$_2$ superconductor in both samples [12]. (Mg$_{1-x}$Fe$_x$)$_2$B$_2$ with $x = 0 - 0.4$ was prepared by Gao et al., using mechanically alloying and vacuum annealing. They found that the solubility of Fe in MgB$_2$ phase decreased with increasing annealing temperature as confirmed with x-ray diffraction and Mossbauer spectra [13].

Iron nanowires are another kind of nano-scale material, which is different from the iron nano-particles used in previous work [11-13]. Because of its special one dimensional geometry (high aspect ratio and nanometer diameter), doping effects of Fe nanowires in MgB$_2$ superconductor may be different from that of Fe nano-particles as well as...
nano diamonds [14]. Besides being as magnetic pinning centers, Fe nanowires may play as line pinning centers if nanowires are embedded in the MgB₂ superconductor matrix.

In this paper we reported the result of the doping effects of Fe and Fe₂O₃ nanowires, on superconductivity of MgB₂ bulks prepared by hybridized diffusion method. We observed that Fe₂O₃ nanowires significantly suppress both $T_c$ and $J_c$ of MgB₂, whereas Fe nanowires do improve the flux pinning behavior of MgB₂.

2. Experimental

Pure MgB₂ sample and samples with composition of MgB₂+0.5 wt%Fe, MgB₂+1.0 wt%Fe, MgB₂+0.5 wt%Fe₂O₃, MgB₂+1.0 wt%Fe₂O₃ were prepared with a hybridized diffusion method with starting powder materials of amorphous B (99.9% nano-powder of 30–50 nm), Mg (99.5% micro-powder of around 10 microns), and Fe and Fe₂O₃ (99.9% nanowires with diameter of 10-20 nm, length 1 micron). The stoichiometric amount of B and Fe plus y% portion (0 < y < 30) of stoichiometric amount of Mg were mixed and well ground in a glove-box for 1 h, the mixed powders were pressed into pellets of a diameter of 5 mm with thickness of 2 mm, and then sealed in iron tubes with excess Mg. Although only y% amount of Mg was added in the precursor pellets, the other amount of Mg, 100-y%, was added into the sample through diffusion method. The diffusion reaction was performed at 900 °C for 2–5 h in flowing Ar, and finally quenched to room temperature.

Crystalline structure of sample was investigated by powder x-ray diffraction (XRD) using an X’pert MRD diffractometer with Cu Kα radiation and the microstructure was analyzed by scanning electron microscope (SEM). DC magnetization measurements were performed on the Quantum Design SQUID (superconducting quantum interference device) magnetometer. Samples with a size of $1 \times 1 \times 0.5$ mm$^3$ were cut from each cylinder for magnetic measurements. Critical current density, $J_c$ values were deduced from the width of the magnetization hysteresis loop with a criterion of $J_c = 10^5$ A/cm$^2$.

3. Results and discussion

X-ray diffraction patterns of 3 typical samples are shown in Fig. 1(a). MgB₂ is still the main phase observed in these samples; however, impurity phases such as MgO are detected. As shown in the XRD pattern, no free Fe is detected in doped samples. The diffraction peaks of FeB are detected in 1.0wt%Fe₂O₃ doped sample. In the samples prepared with conventional solid state reaction method, excessive free Mg is often observed in Fe-doped MgB₂, due to the reaction between B and Fe [15]. However, in our present samples there was no free Mg been observed although FeB was observed. This may be attributed to the unique features of hybridized diffusion method where only a small portion of Mg is packed in the pellets and majority of Mg is introduced through diffusion from outside. For Fe doped samples, their lattice parameter $c$ obtained from Rietveld refinements of the XRD data reveals no decrease of the lattice parameter along the $c$-axis indicating that Fe substitution for Mg is too low to be observed. Whereas for MgB₂+1 wt%Fe₂O₃, the lattice parameter $c$ was found slightly shrunk, indicating that a certain amount of Fe was doped into the lattice of MgB₂. This presumption is also supported by the results of DC magnetization.

Fig. 1. (a) XRD patterns for the Fe nanowires and Fe₂O₃ nanowires doped MgB₂; (b) The temperature dependent magnetization (ZFC) at 10 Oe for the Fe nanowires and Fe₂O₃ nanowires doped MgB₂.
Fig. 1(b) shows the temperature dependence of magnetization for all samples in this work in a field of 10 Oe in a \textit{zero field cooling} ZFC process. The superconducting transition temperature, $T_c$, is depressed more severely for samples doped with Fe$_2$O$_3$ nanowires than for those with Fe nanowires. For undoped sample, the $T_c$ obtained as the onset of magnetization curves is 37.6 K with a transition width of 1.6 K. For the Fe$_2$O$_3$-doped samples, the transition temperature onsets are depressed by 2.8 K and 4.4 K, respectively. This result is consistent with the above-mentioned lattice shrinkage of MgB$_2$ as well as with our previous report on Fe nano-particle doping effect on MgB$_2$ [15] which revealed that the depression of $T_c$ at low doping level was due to the substitution Fe for B. At the same time, the transition width is broadened severely, being increased to about 5 K. This broadened transition of Fe$_2$O$_3$-doped samples may be caused by the MgO impurity and other inhomogeneity in the samples.

![Figure 2](image1.png)

**Figure 2.** (a) $J_c(H)$ behavior for the Fe$_2$O$_3$ nanowires doped MgB$_2$. (b) $J_c(H)$ behavior for the Fe nanowires doped MgB$_2$.

![Figure 3](image2.png)

**Figure 3.** Temperature dependence of $H_{irr}$ for the MgB$_2$ doped with Fe nanowires. Inset: Curves of $H_{irr}$ versus temperature for Fe$_2$O$_3$ nanowire doped MgB$_2$.

For a comparison, only a slight drop of $T_c$ is observed in Fe nanowires doped samples and the transition temperatures 37 K and 37.2 K respectively, depressed only by 0.6 K and 0.4 K. This is consistent with the XRD analysis which shows iron nanowires are not doped into the MgB$_2$ lattice. Moreover, these two samples exhibit a sharp superconducting transition with a width less than 1 K, showing a good quality and uniformity. Therefore, a conclusion can be drawn that iron nanowires do not depress the superconductivity of MgB$_2$.

The different results of samples doped with two kinds of nanowires may be due to the different chemical reactivity of Fe nanowires and Fe$_2$O$_3$ nanowires. For Fe$_2$O$_3$ nanowires doped MgB$_2$, because oxygen is easy to react with magnesium to form MgO, some Fe$_2$O$_3$ may react with Mg in MgB$_2$, which destroys the structure of Fe$_2$O$_3$ nanowires and releases some free Fe atoms. These free Fe atoms are relatively active and easy to be doped into MgB$_2$ lattice.
However, for Fe nanowires doped MgB$_2$, since no oxygen is involved and Fe nanowire structure is relatively stable in the MgB$_2$ environment. This result is also different from our previous report on the effect of iron nano-particle doping in MgB$_2$ [15], in which we found that the iron nano-particle are relatively active to MgB$_2$ compared with the iron particles with a micron size.

Figs. 2(a) shows the curves of critical current density, $J_c$, versus applied magnetic field for all these samples at various temperatures. The $J_c$ values for Fe$_2$O$_3$ nanowire doped samples are severely suppressed with increasing doping level. The values are $4.5 \times 10^5$ A/cm$^2$, $3.8 \times 10^5$ A/cm$^2$, and $6.0 \times 10^5$ A/cm$^2$, respectively, for undoped MgB$_2$, 0.5wt%Fe$_2$O$_3$-doped, and 1wt%Fe$_2$O$_3$-doped samples at 10 K, self field. The difference between $J_c$ values of these samples is not significant in low field; however, the depression effect of the applied field on $J_c$ is significant in high field region. These values reduce to $6.7 \times 10^3$ A/cm$^2$, $1.8 \times 10^3$ A/cm$^2$, and $1.0 \times 10^3$ A/cm$^2$, respectively under 4 T at the same temperature. The depression of $J_c$ values may be attributed to the reduction of the irreversibility field. Fig. 3(a) shows the $H_{irr}$ of Fe$_2$O$_3$ nanowires doped MgB$_2$, in which the values of $H_{irr}$ are drastically suppressed by the Fe$_2$O$_3$ nanowire dopants.

Quite different from doping effect of Fe$_2$O$_3$ nanowires, no significant depression on $J_c$ is observed for iron nano-wires doped samples. As shown in the inset of Fig. 2(b), $J_c$ values of iron nanowires doped samples exhibit no enhancement in low field region; however, values of $J_c$ are enhanced in high fields at 10 K, 20 K and 30 K. In a field of 4 T, the 1.0wt%Fe-doped MgB$_2$ sample yields the best result of $J_c$ of $1.1 \times 10^4$ A/cm$^2$ at 10 K and $2.2 \times 10^2$ A/cm$^2$ at 20 K. As shown in Fig. 3(b), the irreversibility field is improved with increasing of iron nanowires doping level at all temperatures studied in this work. This results are also quite different from those for iron nano-particle doped-MgB$_2$ [15], which confirms that iron nanowires are effective pinning centers for MgB$_2$ superconductor.

4. Conclusion

In summary, MgB$_2$ bulks doped with Fe and Fe$_2$O$_3$ nanowires have been prepared by hybridized diffusion method. The doping effect on superconductivity transition temperature, $T_c$, critical current density $J_c$, and flux pinning behavior are quite different for these two kinds of nano-dopants. Fe$_2$O$_3$ nanowires are chemically active to MgB$_2$, easy to be doped into MgB$_2$, resulting in a drastic suppression on both $T_c$ and $J_c$ of MgB$_2$. Fe nanowires are relatively stable in MgB$_2$, acting as effective pinning center when buried into the MgB$_2$ matrix.

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References