Flux pinning and inhomogeneity in magnetic nanoparticle doped MgB$_2$/Fe wires

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Abstract.
The effects of magnetic nanoparticle doping on superconductivity of MgB$_2$/Fe wires have been investigated. Fe$_2$B and SiO$_2$-coated Fe$_2$B particles with average diameters 80 and 150 nm, respectively, were used as dopands. MgB$_2$ wires with different nanoparticle contents (0, 3, 7.5, 12 wt.%) were sintered at temperature 750°C. The magnetoresistivity and critical current density $J_c$ of wires were measured in the temperature range 2–40 K in magnetic field $B \leq 16$ T. Both transport and magnetic $J_c$ were determined. Superconducting transition temperature $T_c$ of doped wires decreases quite rapidly with doping level ($\sim 0.5$ K per wt.%). This results in the reduction of the irreversibility fields $B_{irr}(T)$ and critical current densities $J_c(B, T)$ in doped samples (both at low (5 K) and high temperatures (20 K)). Common scaling of $J_c(B, T)$ curves for doped and undoped wires indicates that the main mechanism of flux pinning is the same in both types of samples. Rather curved Kramer’s plots for $J_c$ of doped wires imply considerable inhomogeneity.

1. Introduction
The MgB$_2$ superconductor with transition temperature $T_c \cong 39$ K [1], which is high compared to $T_c \leq 18$ K in commercial superconductors (NbTi, Nb$_3$Sn) has considerable potential for wide spread applications (such as magnets for magnetic resonance imaging). Since pure MgB$_2$ has quite low upper critical field $B_{c2} \sim 18$ T and critical current density $J_c$ which decreases rapidly in magnetic field [2] it has to be modified in order to become useful superconductor.

There has been steady improvement in $B_{c2}$ and in-field $J_c$ of MgB$_2$ achieved mainly by dopant additions to MgB$_2$ [3, 4]. However, further improvement of flux pinning (governing irreversibility field $B_{irr}$ and $J_c(B)$ variation) and intergranular connectivity (affecting the magnitude of resistance and $J_c$) in MgB$_2$ is necessary for its practical applications [5]. Recently, there has been considerable interest in improvement of flux pinning in MgB$_2$ by the use of magnetic nanoparticle additions. Although most publications report enhancement of in-field $J_c$ and $B_{irr}$ [6, 7, 8, 9] upon doping of MgB$_2$ with magnetic nanoparticles, the actual situation is not so clear. In particular, there are some observations of detrimental influence of magnetic nanoparticles on $J_c$ of MgB$_2$ [10, 11] and also direct, transport $J_c$ measurements on MgB$_2$ wires doped with magnetic nanoparticles are still lacking.

Here we present the main results of the systematic study of the effects of Fe$_2$B and SiO$_2$-coated Fe$_2$B nanoparticles on electromagnetic properties ($T_c$, $B_{irr}$, $J_c(B)$) of Fe-sheated MgB$_2$
wires. We selected Fe$_2$B particles because they are not likely to affect Mg/B ratio as pure Fe did [10, 11] and also used somewhat larger than usual particle size (80 nm vs. usual 30–50 nm) in order to check recent suggestion that magnetic pinning force increases with increasing particle size [6]. In addition, we used coated Fe$_2$B particles which on the one hand should alleviate the problems with clustering of magnetic particles and on the other hand can produce multiple/diverse pinning centres causing further increase of flux pinning. Finally, we perform both magnetic and transport measurements of $J_c$ which makes our results unambiguous [12].

2. Experimental

Undoped and doped Fe-sheeted MgB$_2$ wires were prepared by the in-situ powder-in tube-method. Magnetic Fe$_2$B and SiO$_2$-coated Fe$_2$B particles with average diameter 80 nm and 150 nm, respectively, were used as dopands. Magnetic particles were prepared via aqueous chemical synthesis [13] and characterised with X-ray powder diffraction, electron microscopy and magnetization measurements [14]. Powders of magnesium (Mg, 99%) and amorphous boron (B, 99%) were well mixed in mortar. For preparation of the doped MgB$_2$ wires 3, 7.5 and 12 wt.% of Fe$_2$B and SiO$_2$-coated Fe$_2$B particles were added. Mixed powders were filled into pure Fe tube of 10 mm and 6.5 mm outer and inner diameter, respectively. The tubes were drawn to wires of 1.41 mm diameter. Finally, the reaction heat treatment was performed at 650°C and 750°C for 60 min in pure argon atmosphere.

Phase composition of the superconducting cores of all prepared MgB$_2$ wires was examined by the X-ray powder diffraction. XRD patterns were taken at room temperature using an automatic Philips powder diffractometer, model PW1820 (Cu Kα radiation, graphite monocromator, proportional counter), in Bragg-Brentano geometry. The diffraction intensity was measured in the angular range $20^\circ \leq 2\theta \leq 70^\circ$. Magnetization was measured at temperatures of 20 K and 5 K in magnetic fields up to 9 T using Physical Property Measurement System (PPMS, Quantum Design). Magnetic critical current density values were determined from the magnetic hysteresis loops using the critical state model. The resistance $R(T, B)$ of the prepared samples was measured in the temperature range 2–40 K in applied magnetic fields up to 16 T using AC current ($I = 1$ mA, $f = 18.4$ Hz) [15]. The transport $J_c(B)$ curves were obtained from $V – I$ curves measured using the pulse method (rectangular pulses with a duration of 0.5 ms with maximum current 320 A) at 20 K and 5 K. The samples for transport measurements (~ 1.5 cm long with wire diameter 1.41 mm and core diameter 0.8 mm) were fitted with two current and four voltage leads with average spacing 0.3 cm. The resistance and $V – I$ curves at each sample were measured at different sections of the wires (voltage leads) to obtain useful informations about homogeneity of the wire [15]. All measurements presented in the paper were made on the section of the wire showing the highest $B_{c2}$ and $J_c$.

3. Results and discussion

All following results were obtained at the samples annealed at 750°C. XRD patterns of all samples showed well developed MgB$_2$ phase with approximately the same crystallite size ~ 20 nm and also a presence of MgO phase. Samples doped with Fe$_2$B (Figure 1) showed also presence of FeB and Fe$_2$B crystalline phases with amount which increased with increasing doping level. Since the Fe$_2$B/SiO$_2$ particles were in amorphous state [14] and doping level was very low, presence of the Fe$_2$B/SiO$_2$ particles could not be detected in XRD patterns of the Fe$_2$B/SiO$_2$ doped MgB$_2$ samples (Figure 2). However, XRD pattern of the sample doped with 7.5 wt.% of the Fe$_2$B/SiO$_2$ particles showed minor phase FeB. Also, in Fe$_2$B/SiO$_2$ doped wires the amount of MgO phase increased with increasing doping level. The appearence of FeB phase and the increase of the amount of MgO phase with increasing doping with Fe$_2$B/SiO$_2$ particles indicate that to some extent a reaction between Mg, B and nanoparticles occured during annealing of wires.
In Figures 3 and 4 resistance $R$ versus temperature $T$ plots for undoped and doped MgB$_2$ wires in applied magnetic fields are shown. (Larger resistance of samples doped with 3 wt.% of nanoparticles is due to the larger distance between the voltage leads in these wires.) Strong shift of the superconducting transition temperature $T_c$ for undoped MgB$_2$ wire with magnetic field is observed, which is a consequence of the weak flux pinning in undoped bulk MgB$_2$ samples [2, 4]. For doped wires (both Fe$_2$B and Fe$_2$B/SiO$_2$ particles) $T_c$ decreases as the doping level increases. Shifting of $T_c$ towards lower temperatures and broadening of the transition with the increasing magnetic field is more pronounced for doped MgB$_2$ wires than for undoped one, indicating that the enhancement of the flux pinning in doped wires was not achieved.

The superconducting transition temperature in zero applied field $T_{c0}$ was determined from $R(T, B)$ curves as the temperature at which resistance vanishes. Dependence of $T_{c0}$ on doping level is shown in Figure 5. $T_{c0}$ decreases quite rapidly with the doping level, namely 0.72 K/wt.%
and 0.45 K/wt.% for Fe$_2$B and Fe$_2$B/SiO$_2$ doped wires, respectively. For comparison, a rate of decrease of $T_c$ in SiC doped MgB$_2$ is about 0.2 K/wt.% [16, 17]. Magnetic moment of the Fe$_2$B and Fe$_2$B/SiO$_2$ particles probably caused Cooper pair breaking and additional reduction of $T_c$.

The irreversibility field curves $B_{irr}(T)$ were deduced from resistivity measurements using the criteria of $R(B_{irr}, T_{irr})$ equals 10% of the resistance of the wire immediately above the superconducting transition [18]. $B_{irr}(T)$ curves are shown in Figure 6. Irreversibility field curve for undoped wire is in accordance with previously published data for high quality MgB$_2$ wires [15, 19]. Samples with higher doping level (both Fe$_2$B and Fe$_2$B/SiO$_2$ particles) have lower values of $B_{irr}$ in the whole temperature range due to the lower $T_c$ of the doped samples. Besides, the $B_{irr}(T)$ variation for doped MgB$_2$ wires increases slower with decreasing temperature than for undoped wire indicating that the vortex pinning was not enhanced in the doped wires.

Field dependence of magnetic and transport critical current density $J_c$ is shown in Figures 7 and 8. Transport $J_c$ have larger values than magnetic $J_c$ for all samples which is in accordance with results given in [12]. We consider transport $J_c$ to be more accurate $J_c$ of the wires because they are obtained directly from the measured $V$ - $I$ curves and magnetic $J_c$ are calculated using a model. Furthermore, in magnetic measurements $J_c$ flows along the circumference of the wire, not along the length of wire. There is, in general, a good qualitative agreement between magnetic and transport $J_c$s of our samples. However, near overlap of magnetic $J_c(B)$ curves for undoped and 3 wt.% Fe$_2$B/SiO$_2$ doped at 5 K illustrates the danger of using magnetic $J_c(B)$ only. As observed in Figures 7 and 8, $J_c(B)$ curves for undoped and doped (both Fe$_2$B and Fe$_2$B/SiO$_2$) MgB$_2$ wires follow approximately the same trend both at high (20 K) and low (5 K) temperature implying that the main pinning mechanism is the same. Indeed, when plotted against normalised magnetic field $B/B_{irr}$, curves for undoped and doped samples almost overlap, particularly at 5 K (Figures 9 and 10). (The deviation from scaling of $J_c(B)$ in doped samples at 20 K is associated with the proximity of $T_c$: $J_c(B)$ for sample with lowest $T_c$ deviates most from $J_c(B)$ for undoped sample.) Regarding these results, magnetic pinning of the vortices in the magnetic nanoparticle doped MgB$_2$ wires probably was not accomplished. Lower values of the $J_c$ as well as the $J_c(B)$ variation for the doped wires is consistent with the irreversibility curves (Figure 6).

The rates of suppression of $T_c$ and $B_{irr}(T)$ in wires doped with Fe$_2$B and SiO$_2$-coated Fe$_2$B particles, respectively, show that the magnetic effect prevails. MgB$_2$ wires doped with SiO$_2$-coated Fe$_2$B particles also have better $J_c(B)$ performance than the Fe$_2$B doped wires probably
due to the smaller amount of the magnetic material. Indeed, we note very similar effects of 3 wt.% Fe$_2$B and 7.5 wt.% Fe$_2$B/SiO$_2$ on $T_c$, $B_{irr}$ and $J_c$ (Figures 6–10). Similar behaviour was observed previously in Fe doped MgB$_2$ [10, 11].

Figure 7. Magnetic (open symbols) and transport (solid symbols) critical current density versus applied magnetic field for undoped and doped (Fe$_2$B and Fe$_2$B/SiO$_2$) MgB$_2$ wires at 20 K.

Figure 8. Magnetic (open symbols) and transport (solid symbols) critical current density versus applied magnetic field for undoped and doped (Fe$_2$B and Fe$_2$B/SiO$_2$) MgB$_2$ wires at 5 K.

Figure 9. Transport critical current density $J_c$ versus normalised magnetic field $B/B_{irr}$ for undoped and doped (Fe$_2$B and Fe$_2$B/SiO$_2$) MgB$_2$ wires at 20 K.

Figure 10. Transport critical current density $J_c$ versus normalised magnetic field $B/B_{irr}$ for undoped and doped (Fe$_2$B and Fe$_2$B/SiO$_2$) MgB$_2$ wires at 5 K.

Kramer’s plots $J_c^{1/2} B^{1/4}$ versus $B$ are shown in Figure 11. Rather curved Kramer’s plots for doped wires indicate considerable inhomogeneity of the samples. During the preparation of the samples agglomeration of the Fe$_2$B and Fe$_2$B/SiO$_2$ particles probably occurred because of their magnetic interaction. This probably enhanced the detrimental effects of magnetic particles on electromagnetic properties of MgB$_2$ wires.

Preliminary measurements on wires prepared at 650°C show qualitatively the same variations of $T_c$, $B_{irr}(T)$ and $J_c(B)$ as those described above in this paper. The only difference is that corresponding $B_{irr}(T)$ and $J_c(B)$ are somewhat higher as is usual for MgB$_2$ wires prepared at lower sintering temperature [20].
Figure 11. Kramer’s plots for undoped and doped (Fe$_2$B and Fe$_2$B/SiO$_2$) MgB$_2$ wires.

4. Conclusion
A comprehensive study of the irreversibility fields $B_{irr}(T)$ and critical current densities $J_c(B)$ (both magnetic and transport) of undoped and doped with different amounts of Fe$_2$B (80 nm) and SiO$_2$-coated Fe$_2$B (150 nm) magnetic nanoparticles MgB$_2$/Fe wires does not show any enhancement of flux pinning associated with the magnetic interaction between vortices and magnetic nanoparticles. Moreover, rather good scaling of $J_c(B)/B_{irr}$ curves for doped wires with that for undoped wire seems to indicate that the dominant pinning mechanism is the same (grain boundary pinning) both in undoped and doped samples. We observe, however, rather strong suppresion of the transition temperature $T_c$, $B_{irr}(T)$ and $J_c(B)$ with increasing content of the magnetic addition (Fe$_2$B) which probably indicates that the magnetic pair breaking prevails in doped samples. These detrimental effects are probably aided by an inhomogeneous distribution of the magnetic dopands, as evidenced by strongly curved Kramer’s plots of doped samples.

Altogether, our study indicates that in conventionally prepared MgB$_2$ wires (i.e. when no special care is taken to prevent agglomeration of the magnetic particles [6] and/or to density of the superconducting core [21]) the magnetic nanoparticles with size $\geq$ 50 nm are unlikely to cause any enhancement of flux pinning. It also shows that only the magnetic measurements of $J_c(B)$ for MgB$_2$ samples doped with magnetic nanoparticles are not sufficient to conclude whether the flux pinning is enhanced or not. However, our study shows neither that magnetic pinning does not exist nor that is not more efficient than bulk pinning on normal particles. All it shows is that the situation with magnetic flux pinning in bulk MgB$_2$ samples is much more complex than that encountered in thin films [22].

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