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Magnetic nanoparticles in MgB_2: Vortex pinning, pair breaking and connectivity

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The results indicating magnetic flux pinning in MgB_2 wires doped with three types of magnetic nanoparticles (MNP) are reported. The magnetic state of MNPs, both as-prepared and inside the MgB_2 core, was determined with magnetization and ac susceptibility measurements. The competition between detrimental influence of doping (reduced connectivity, pair breaking) and enhanced flux pinning leads to deterioration of electromagnetic properties of doped wires at high MNP content, whereas light doping causes an enhancement of critical current density, J_c, and/or irreversibility field, B_{irr}, for all our MNPs. For Ni and dextrin coated $NiFe_2O_4$ MNPs the enhancement of J_c was comparable to that achieved with the best nonmagnetic dopands. Detailed analysis indicates the contribution of magnetic flux pinning including the matching effects in flux pinning on MNPs.

1. Introduction

Magnetism and superconductivity are probably the most interesting phenomena in solid state physics. These phenomena are generally considered to be competing, but the development of hybrid superconducting/magnetic nanostructures [1,2] and the discovery of Fe-based high-T_c superconductors [3] challenge this view. In particular, in well-designed hybrid systems magnetism and superconductivity show cooperative behaviour, such as enhancement of the flux pinning in a superconductor [1]. However, these findings are well established [1] in thin films (2D), whereas for probably more interesting bulk (3D) superconductors [4] the situation is far from being clear [5].

Nanostructuring MgB_2 seems especially interesting because of multicomponent superconductivity [6] and applicative potential of MgB_2 and because of novel effects in flux pinning in nanostructured MgB_2 [7]. Indeed, already the addition of SiC (nonmagnetic) nanoparticles (NNP) caused strong enhancement of flux pinning in MgB_2 wires [8], but the required amount of NNP ($\geq$10 wt%) produce a large amount of nonsuperconducting phases, which in porous in situ prepared samples strongly reduce connectivity between MgB_2 grains, thus J_c at all fields and temperatures [8,9]. This detrimental effect of NNPs can possibly be avoided by the use of MNPs, which interact much stronger with vortices than NNPs and the range of this magnetic interaction is larger than that involved in flux pinning at NNPs [2,9]. Thus, the required volume fraction of MNPs is likely to be lower than that of NNPs, which makes this magnetic pinning (MP) more effective at lower fields and may also diminish the problem of connectivity. In order to improve properties of MgB_2 over the whole field range, $B \leq B_{c2}$ (with B_{c2} being the upper critical field), the co-doping, combining MP on MNPs with carbon doping (which boosts B_{c2} of MgB_2 [10]), is proposed (e.g. [11]). However, the results of numerous studies of MNP doped bulk MgB_2 e.g. [12–22] are inconclusive and provide no clear evidence that MP is achieved. Further, as pointed out earlier [12,19,20], the majority of studies of MgB_2 doped with MNPs (and all studies reporting an enhancement of J_c upon doping) report J_c determined from magnetization measurements (J_{cm}) only. It is also known that J_{cm} in porous ceramic samples, derived from an approximate model and dependent on the shape, size, density, texture and homogeneity of the sample, is not as reliable as the directly obtained transport J_c. This was demonstrated in [19] where the same MgB_2 wire doped with 3 wt% of SiO_2coated MNPs showed the same J_{cm} as undoped wire, whereas its transport J_c (like its B_{irr}) was considerably lower than that of undoped wire. Also, the field and temperature dependencies of J_{cm} in ceramic MgB_2 samples differ from those of J_c [23]. Further, in all previous studies, including ours [5,11,12] no proper characterization of magnetic state of MNPs, both before and after annealing within the MgB_2 core of the wire has been reported. Clearly, in such circumstances the attribution of any enhancement of either J_c or J_{cm} to magnetic pinning is quite unreliable. (Some other problems/shortcomings in the literature data as well as the comparison of some ours with literature data can be found in [11,12,20,21].)

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Here we report some results from our systematic study of the influence of MNP additions on electromagnetic properties of MgB_2 wires [5] which indicate the MP contribution to flux pinning in our samples. First, we establish the magnetism of MNPs, before and after addition to the wire. Next, we look for the enhancements of B_{irr} (including possible matching effects), J_c and pinning force density, $F_p = J_cB$, in selected samples. We also note the influence of the nonsuperconducting phases on connectivity, thus B_{irr}, J_c and T_c of the studied wires.

2. Experimental procedures

Nanoparticles of uncoated and dextrin coated ferrites (AFe_2O_4 with A=Fe, Co, Ni and Mn) with size ranging from 5 to 25 nm [11,20], as well as those of uncoated and silica coated borides (Fe_2B, Co_2B, FeCoB, FeNiB and NiCoB) with size ranging from 15 to 250 nm [24,25] were prepared by coprecipitation from solution. Commercial nanoparticles of carbon (C) protected Fe, Co and Ni, as well as Dy_2O_3, Eu_2O_3, all with size 20–30 nm were purchased from NanoAmor, Inc., USA. All particles were fully characterized with XRD, SEM/EDS and magnetometry (SQUID MPMS5 and VSM) [24,25]. Most MNPs used in this work were single-domain magnets with blocking temperatures T_b below room temperature (RT), thus were superparamagnetic for $T \geq$ RT. Undoped and doped Fe-sheathed MgB_2 wires were prepared by the in situ powder in tube (PIT) technique [11,12] and annealed for 1 h at 650 °C (or 750 °C) in a pure Ar atmosphere [11,12]. Usually, the wires with two or more MNP contents were prepared [12,19–21]. All wires were characterized by microscope, XRD and SEM/EDS (including elemental mapping). Some wires (their bare cores) were also investigated with high resolution ac susceptibility [26]. Both magnetic ($T \geq 5$ K, $B \leq 5.5$ T) and electric transport measurement were performed on wires and/or their bare cores. The resistance of the wires, both intact and without Fe-sheathing, was measured with low frequency ac method in the temperature range $T \geq 1.5$ K and magnetic field $B \leq 16$ T [8,12]. Transport critical current of wires was obtained from $I - V$ curves measured using the pulse method [8,12].

3. Results and discussion

A broad scope of our research is illustrated by over eighty MgB_2 wires prepared so far. A rate of success (an improvement upon doping) is about 10% and a study of about 15% of samples has not been completed. Here, we focus on some samples showing an improvement in electromagnetic properties upon doping and, as first, briefly review some properties of the employed nanoparticles. The average size of magnetic core of Ni/C, NiCoB and dextrin coated Fe_3O_4 nanospheres (determined by combining SEM, XRD and magnetization studies [11,12,21]) was 17, 17 and 5.2 nm, respectively. For other dextrin coated ferrite particles (A=Mn, Co, Ni) XRD pattern was indicating an amorphous structure and an analysis of magnetization measurements indicated a core size 2–3 nm. Fig. 1 illustrates the magnetic states of Ni/C, NiCoB and dextrin coated Fe_3O_4 and $NiFe_2O_4$ MNPs via the low-field zero field cooled (ZFC) and field cooled (FC) magnetization measurements in the temperature range 5–300 K and corresponding coercive fields, H_c. The magnetizations, M_s, (including that of coating) at $T = 5$ K and field $B = 5$ T were 42.5 Am^2/kg, 32.5 Am^2/kg, 12.1 Am^2/kg and 7.6 Am^2/kg. We note quite low magnetizations of dextrin coated ferrites which is partially due to dextrin coating and is also due to small size of ferrite cores with significant fraction of atoms forming the surface layer with disordered spins which interacts/binds to the coating [11,27,28]. Indeed, a detailed study of γ-Fe_2O_3 thin platelets [29] showed that spins in the surface layer may even develop spin glass like order which strongly reduces total magnetization and enhances H_c below the freezing temperature of the surface layer, probably via pinning effect of the spin glass layer on the single domain core of the platelet. Similar effects were found also in studies of ferrite nanoparticles [30–32]. These studies revealed that in addition to particle size the method of preparation also affects the magnetic properties, probably via the effect on the cation disorder, both in the surface layer and in the core [30,31]. Fig. 1 (left) shows that all MNPs exhibit partial blocking of magnetic moments with blocking temperatures, $T_b \geq 300$ K, 150 K, 46 K and 5.1 K for Ni/C, NiCoB and coated Fe_3O_4 and $NiFe_2O_4$ particles, respectively. As expected, T_b increases with size of particles (and also M_s) and all these MNPs are at least partially superparamagnetic at room temperature, which should make their agglomeration during mixing with Mg and B powders less likely [11,12,21]. We note, however, that FC magnetization of Ni/C particles decreases only a little with temperature, which probably indicates a dominant ferromagnetic behaviour which is not surprising considering weak magnetic anisotropy of fcc Ni. Further, for all MNPs in Fig. 1 merging of ZFC and FC magnetizations occurs at temperatures well above T_b, which reflects a rather broad distribution of particle sizes [25]. Such behaviour is particularly pronounced for Fe_3O_4 particles which are mixture of rods (≈25%) and spheres (≈75%) with very different sizes and properties [11] and show very small maximum of ZFC magnetization (Fig. 1, left). This is likely to affect flux pinning, homogeneity and connectivity in MgB_2 wires doped with these MNPs.

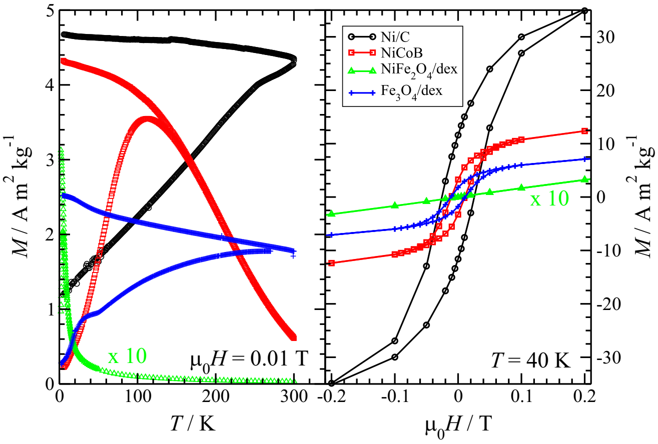

Fig. 1. Zero field cooled and field cooled magnetization curves measured in applied field 0.01 T (left) and magnetic hysteresis curves measured at 40 K (right) of the selected nanoparticles.

The hysteresis curve of all MNPs at $T = 40$ K shown in Fig. 1 (right) corroborates the previous discussion. In particular, H_c and M_s of dominantly ferromagnetic Ni/C particles decreased relatively little on increasing temperature from 5 K to 40 K (just above T_c of MgB_2), whereas those of partially or fully superparamagnetic NiCoB and dextrin coated ferrite particles decreased dramatically. Moreover, $NiFe_2O_4$ particles at 40 K show non-hysteretic (super) paramagnetic variation of magnetization with field.

As seen in Fig. 2 annealing (1 h at 650 °C) of MNPs with Mg and B powders during production of wires causes pronounced change in magnetic properties of all MNPs other than Ni/C. In Ni/C doped wires (not shown) neither magnetization nor X-ray study revealed interaction of particles with host [12]. In contrast, all, magnetization, T_b and H_c (Fig. 2) of wires doped with coated Fe_3O_4 and $NiFe_2O_4$ particles increased strongly in respect to corresponding values of as-prepared particles (Fig. 1). In particular, T_b, M_s and H_c of Fe_3O_4 doped wire were about four-, three- and six-fold larger