Strong enhancement of In-Field Critical Current Density at 20K in MgB_2 with Minute Additions of Dy_2O_3 and B_4C

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Abstract **- Minute additions of a combination of Dy_2O_3 and B_4C have been used to enhance both pinning and upper critical field in MgB_2 to the level suitable for MRI applications at 20 K. A delicate balance of Dy_2O_3 and B_4C additions is required to improve pinning without significantly reducing connectivity between grains. The Dy_2O_3 nanoparticles react with B to form 10-15 nm DyB_4 nanoparticles, while B_4C supplies carbon into MgB_2 crystal lattice and increases the upper critical field. The optimum level of Dy_2O_3 and B_4C additions is ~0.5 wt. % of Dy_2O_3 and 0.04 wt. % of B_4C, yielding a J_c (20K) of 10^5A.cm^{-2} at 2.7 T.**

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I. INTRODUCTION

It is expected that MgB_2 will replace Nb-based coils in magnetic resonance imaging (MRI) magnets to operate in cryogen-free environment, making MRI cheaper and more convenient for medical use. Other MgB_2 applications would likely follow ranging from the power transmission lines to satellite and space station protective shields. To secure this development, an improvement in critical current density (J_c) of MgB_2 of by a factor of 3 to10 times is necessary. A critical current density, J_c, of 10^5 A/cm^2 (1.5-5T, 15-26K) is sufficient for many applications. The values must be reached in a simple and cost-effective way.

So far, at ~20K, the best J_c's at < 2 T come from nano-grained [1, 2, 3, 4], nanoparticle added [5, 6, 7, 8] or hot isostatically pressed (HIPed) [9, 10, 11] samples, and at > 2 T come from C-doped samples [12, 13, 14, 15, 16]. While HIPing produces excellent low-field properties [11], for wires there is the problem of reaction with the containment material [17, 18], which is typically iron or stainless steel. We earlier showed that Dy_2O_3 nanoparticles [7] are effective low-field pinning additives to MgB_2. We found that additions of as low as 0.5 wt.% Dy_2O_3 yielded an optimum J_c enhancement. In a separate study, we showed that J_c strongly depends on grain size, and that nanoparticles effectively reduce grain size [4].

For improving J_c beyond 1-2T, doping into the MgB_2 lattice is required because pure MgB_2 has a very low upper critical field along the c-axis [19]. Carbon has been found to be most effective for increasing upper critical field. Several kinds of carbon-containing additions have been employed [12, 13, 14, 15, 16]. B_4C has been studied less widely as a carbon dopant, but nevertheless it has been found to be quite effective [20]. Samples reacted with B_4C at about 800°C do not contain x-ray diffraction peaks of B_4C [14], so the phase is likely to be completely decomposed allowing the C to partially replace the B in the MgB_2 lattice.

As far as known, double 'pinning + doping' additions have not previously been explored to maximise J_c in the intermediate field regime (2-5 T) at ~20 K. In this work, we use a combination of small Dy_2O_3 additions for pinning together with small B_4C additions for

doping. We find that these two kinds of additions act in a complementary and positive way with one another.

II. METHOD

Starting boron purity has a strong influence on current cross-section [21]. The pure chemicals give a factor of 3 higher J_c than the cheap starting precursors [21], but they are very expensive. Hence, without cost reduction they are not of interest for industry.

In this work we use cheap 95-97 % amorphous boron and through pinning and doping additions aim to more than overcome the negative effects of impurities in the boron, which are mainly Mg, C, and O, and H. 99% Mg flake was used for reaction with the boron.

We prepared a range of MgB_2 samples as follows:

a) no additions
b) addition of 0.5 wt.% Dy_2O_3
c) double additions: Mg + xB + 0.5 wt.% of Dy_2O_3 + $y$$B_4C$, y = 0.02, 0.04 and 0.1

For c), x and y are chosen to form MgB_2 after the complete decomposition of B_4C. The $x + 4y$ is close, but slightly less than 2 to account for the partial evaporation of Mg.

For reaction of the powder, we used both conventional sintering (CS) and resistive sintering (RS). Resistive sintering (RS) [4] was undertaken in a vacuum chamber with MgB_2 powder uniaxially pressed in a graphite die with tungsten rods that simultaneously act as electrodes carrying high electrical current up to 1000 A. The electrical current heats the powder up to 1000 ºC. A dense sample with high J_c can be obtained in 5 minutes.

For reference, conventionally sintered (CS) samples were made by mixing and grinding powders in a mortar for 60 min. Pellets of 5 mm diameter were uniaxially pressed, wrapped with Ta foil in the presence of excess Mg shavings and sintered at 900ºC for 15 min. using heating and cooling rates of 15 ºC/min.

Samples were characterised using a Quantum Design Magnetic Properties Measurement System (MPMS) in a magnetic field up to 5 Tesla. The J_c was derived from the irreversible magnetic moment (m) using the critical state formula:

$$J_c = \frac{4m}{a^2 bL(1-\frac{a}{3b})} \quad , \qquad (1)$$

where a, b and L are sample dimensions ($a<b<<L$) and the magnetic field is applied along the direction of L.

Scanning electron microscopy (SEM) was used to evaluate the density of the material and to perform element analysis. The SEM images of RS samples show low porosity (the pores are black areas in Fig.1) of ~10 %. The light grey background in Fig.1 is MgB_2. The dark grey crystals are higher-boron compounds. The CS reference samples had a porosity of ~ 50%.

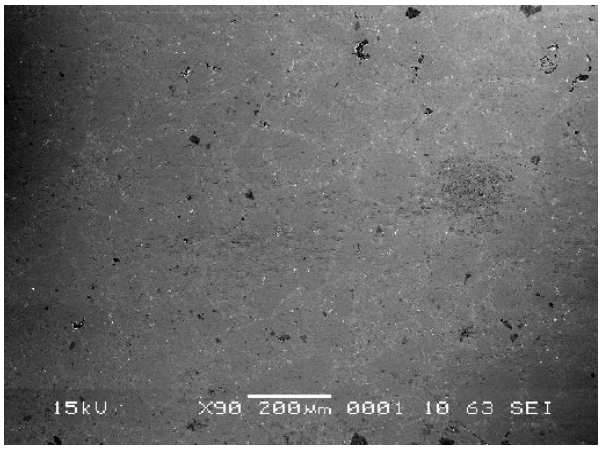

Fig. 1. Typical RS sample showing a high density of material.

III. CRITICAL CURRENT DENSITY AS FUNCTION OF MAGNETIC FIELD

Figure 2 shows critical current density as a function of magnetic field for MgB_2 + 0.5 wt.% Dy_2O_3 + $(B_4C)_y$ compared to pure MgB_2 samples, prepared either by CS (lower curves) or RS (higher curves) methods. In spite of the low purity of amorphous boron, record high values of bulk self-field critical current density (J_c) at 20 K of near-10^6 A/cm^2 were achieved for the best samples. The RS samples show J_c values which are a factor of up to 6 higher than the CS samples. This difference cannot alone be explained by the higher sample densities of RS samples. The origin of the J_c difference is related to the presence of sub-grains in the RS samples, and a large number of associated grain boundary dislocations [4].

The smallest difference between RS and CS samples is observed for the Dy_2O_3-added samples. This appears to be because of the very large pinning enhancements caused by these additions, *i.e.* it is difficult to enhance J_c significantly further through RS than is already achieved using CS. Once small additions of B_4C are made to the CS samples, the J_c drops significantly compared to the Dy_2O_3-added CS samples. There are two possible reasons for this, either because the T_c is lowered (the values are 37.5 K for both pure MgB_2 and MgB_2 + 0.5% Dy_2O_3, 37.0 K for 0.5 % Dy_2O_3+ 0.02%B_4C, 36.4 K for 0.5 % Dy_2O_3+ 0.04%B_4C and 35.3 K for 0.5 % Dy_2O_3+ 0.1%B_4C, RS), and/or because there is some negation of the pinning enhancement capability of Dy_2O_3 by B_4C. On the other hand, comparing the RS samples to one another there is no evidence for negation of the pinning enhancement by B_4C additions. Indeed, all the RS samples show high J_c values. There is a small reduction in self-field J_c due to the B_4C additions, but this is as expected from the slight lowering of T_c. The benefits of the B_4C additions are apparent when field is applied, and it is observed that the J_c crosses over the Dy_2O_3-added sample at ~2 T.

Figure 3 shows J_c (20K) versus applied magnetic field for the optimum 'pinned+doped' higher field (>2T) performing sample of this study to the best literature data for differently C-doped samples. The inset to Fig. 3 shows J_c(20K) on a linear scale versus field for the optimum sample compared to a C-doped sample. It is clear from Fig. 3 that the properties of the optimum sample of this study exceed the properties of other C-doped samples in fields of up to more than 3T. This is because of the beneficial effect of the *combination* of pinning and light C-doping. Fig. 3 shows that heavier C-doping is clearly beneficial above around 3.25 T. Below 3.25 T, the C doped samples have a lower J_c than the samples of this study because a) C-doping lowers T_c by ~22 K/at.%, which impacts strongly on J_c at 20K, and b) there is no clear nanoparticle pinning enhancement.

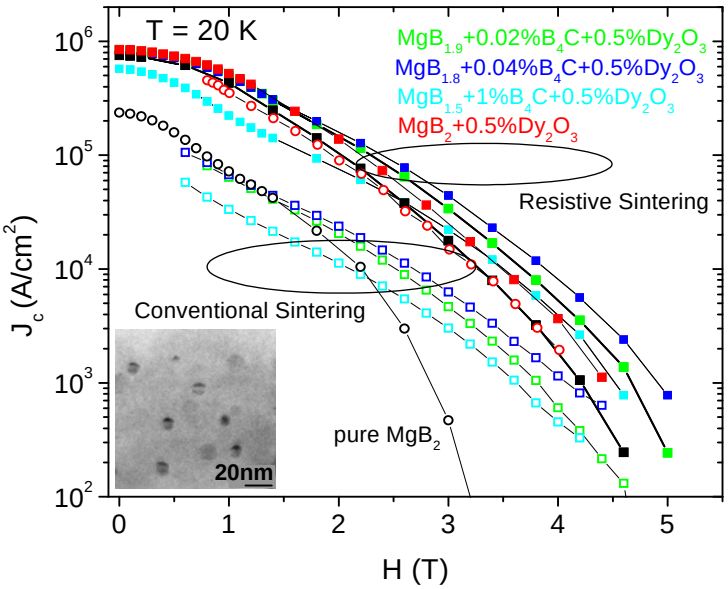

Fig. 2. J_c (20K) versus applied magnetic field for different CS and RS MgB_2 samples. Inset shows DyB_4 nanoparticles in the MgB_2 matrix in a CS MgB_2+0.5 wt. % Dy_2O_3 sample.

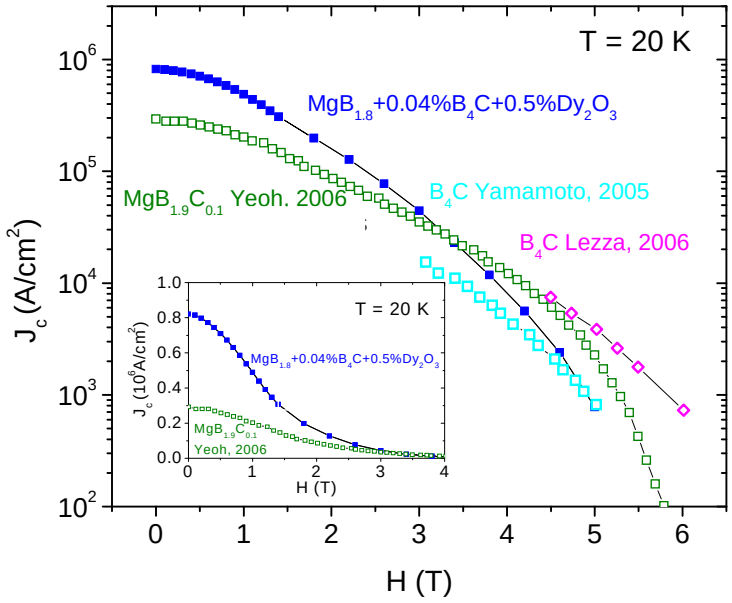

Fig. 3. J_c (20K) versus applied magnetic field for the optimum RS 'nanopinned + doped' MgB_2 sample compared to C-doped and B_4C-doped MgB_2 from the literature. Inset shows J_c(20K) on a linear scale versus field for optimum RS 'nanopinned + doped' MgB_2 sample compared to a C-doped sample.

IV. CONCLUSIONS

To enhance both pinning and scattering in MgB_2, combinations of minute additions of Dy_2O_3 and B_4C were made to samples which were subsequently resistively sintered. A delicate

balance of the additions is necessary to achieve enhancements of the in-field critical current density at 20 K. Dense, resistively sintered samples show excellent critical current densities in magnetic fields up to 5 T. The improvement in J_c (20 K,<3.25 T) over literature data in this regime comes *both* from the pinning and scattering enhancements. The optimum amount of Dy_2O_3 and B_4C additions is 0.5 wt. % of Dy_2O_3 and 0.04 wt. % of B_4C, yielding a J_c (20K) of $10^5 A \cdot cm^{-2}$ at 2.7 T.

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