Strong enhancement of In-Field Critical Current Density at 20K in MgB$_2$ with Minute Additions of Dy$_2$O$_3$ and B$_4$C

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Abstract - Minute additions of a combination of Dy$_2$O$_3$ and B$_4$C 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$_2$O$_3$ and B$_4$C additions is required to improve pinning without significantly reducing connectivity between grains. The Dy$_2$O$_3$ nanoparticles react with B to form 10-15 nm DyB$_4$ nanoparticles, while B$_4$C supplies carbon into MgB$_2$ crystal lattice and increases the upper critical field. The optimum level of Dy$_2$O$_3$ and B$_4$C additions is ~0.5 wt. % of Dy$_2$O$_3$ and 0.04 wt. % of B$_4$C, yielding a $J_c$ (20K) of 10$^5$ A/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 to 10 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$_2$O$_3$ nanoparticles [7] are effective low-field pinning additives to MgB$_2$. We found that additions of as low as 0.5 wt.% Dy$_2$O$_3$ 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$_4$C has been studied less widely as a carbon dopant, but nevertheless it has been found to be quite effective [20]. Samples reacted with B$_4$C at about 800°C do not contain x-ray diffraction peaks of B$_4$C [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$_2$O$_3$ additions for pinning together with small B$_4$C 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$_2$O$_3$

c) double additions: Mg + xB + 0.5 wt.% of Dy$_2$O$_3$ + yB$_4$C, \( y = 0.02, 0.04 \) and 0.1

For c), x and y are chosen to form MgB$_2$ after the complete decomposition of B$_4$C. 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:

$$ J_c = \frac{4m}{a^2 b L (1-a/3b)} , $$

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%.
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$_2$O$_3$ + (B$_4$C)$_y$ 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$_2$O$_3$-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$_4$C are made to the CS samples, the $J_c$ drops significantly compared to the Dy$_2$O$_3$-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$_2$O$_3$, 37.0 K for 0.5% Dy$_2$O$_3$+ 0.02%B$_4$C, 36.4 K for 0.5% Dy$_2$O$_3$+ 0.04%B$_4$C and 35.3 K for 0.5% Dy$_2$O$_3$+ 0.1%B$_4$C, RS), and/or because there is some negation of the pinning enhancement capability of Dy$_2$O$_3$ by B$_4$C. On the other hand, comparing the RS samples to one another there is no evidence for negation of the pinning enhancement by B$_4$C 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$_4$C additions, but this is as expected from the slight lowering of $T_c$. The benefits of the B$_4$C additions are apparent when field is applied, and it is observed that the $J_c$ crosses over the Dy$_2$O$_3$-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.
IV. CONCLUSIONS

To enhance both pinning and scattering in MgB$_2$, combinations of minute additions of Dy$_2$O$_3$ and B$_4$C 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$_2$O$_3$ and B$_4$C additions is 0.5 wt. % of Dy$_2$O$_3$ and 0.04 wt. % of B$_4$C, yielding a $J_c$ (20K) of $10^5$A cm$^{-2}$ at 2.7 T.

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