Flux Pinning and Superconducting Properties of MgB$_2$-Diamond Nanocomposites

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Abstract. The present investigation focuses on a further performance improvement of disk-shaped bulk MgB$_2$ superconductors by means of a nanoscopic diamond powder, using a single-step solid-state reaction process. MgB$_2$ bulks were produced by in-situ solid state reaction in Ar gas using high purity commercial powders of Mg metal and amorphous B mixed in a fixed ratio of Mg:B = 1:2. Further, 0, 0.4, 0.8, and 1.2 wt% of nanoscopic diamond powder was added to improve flux pinning performance of the bulk MgB$_2$ material. All samples were sintered at 775 °C for 3 hours in Ar atmosphere. X-ray diffraction confirmed that the sample consisted mainly of MgB$_2$ phase and a small quantity of MgO phase. DC magnetization measurements showed a sharp superconducting transition with onset $T_c$ at around 39.25 K and 37.42 K for the pure and 0.8 wt.% of nanoscopic diamond powder added samples, respectively. The highest self-field critical current density ($J_c$) around 300 kA/cm$^2$ and 105 kA/cm$^2$ were recorded at 20 K, in self-field and 1.5 T for the sample with 0.8 wt.% of nanoscopic diamond. The present results show that nanoscopic diamond powder is an effective pinning medium for bulk MgB$_2$ and might thus be an alternative to further improve the superconducting performance of the bulk MgB$_2$ material.

1. Introduction

Since the discovery of superconductivity in MgB$_2$ with the highest critical temperature, $T_c$ of 39 K, a significant progress has been made concerning the development of processing techniques, flux pinning, critical current density ($J_c$), large size MgB$_2$ bulk growth [1-5]. To utilize this material for industrial applications, including superconducting super-magnets, a further improvement of critical current density is crucial, especially in sintered bulks [6-7]. Several approaches were established for the processing and fabrication of bulk MgB$_2$ material. MgB$_2$ have been fabricated as a crystal, powder, thin film, macroscopic wire, nanowire or tape using various approaches such as solid state synthesis, mechanical alloying, sol-gel or vapor-transport process [8-9]. MgB$_2$ offers the possibility of wide engineering applications in the temperature range 20-30 K, where conventional superconductors such as Nb$_3$Sn and Ni-Ti alloy are not applicable due to their low $T_c$. Further, the field trapping capability for the practical applications of bulk MgB$_2$ magnets is similar to melt-textured REBa$_2$Cu$_3$O$_y$, which can be utilized as a trapped field magnet in nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) [1-6]. In high magnetic fields MgB$_2$ exhibits a decrease in critical current density, $J_c$, due to its poor grain connectivity and lack of strong pinning centers [14-15]. Earlier studies indicated that an inclusion of nano-dopants enables control of MgB$_2$ microstructure by introducing nano-pinning centers into the superconducting matrix. Nanoscale diamond powder makes it possible to form a high density of nano-inclusions in MgB$_2$ matrix. To improve pinning performance of bulk MgB$_2$ materials, we tried to utilize a nanoscopic diamond powder in combination with optimum sintering temperature.
set in earlier studies [6]. In the present work, we study the effect a nanoscopic diamond powder on bulk MgB$_2$ material by means of X-ray diffraction (XRD), superconducting transition temperature and critical current density at 20 K. The best sample indicated a high critical current density of 298.9 kAcm$^{-2}$ at 20 K and the superconducting transition temperature around 37.5 K.

2. Experimental details

Bulk specimens of MgB$_2$ were prepared by an in situ solid state reaction. The precursor powder materials were Mg powder (99.9% purity, 325 meshes), sub-micron particle sized amorphous B powder (98.5% purity, ~250 nm), and diamond nanoparticles (<10 nm particle size) as nano-dopant. The mentioned powders were weighed 1.5 g in a glove box and thoroughly mixed under argon atmosphere in the same glove box. The Mg and B powders were mixed in the nominal ratio of 1:2 while varying the compositions of the nano-diamond for each sample produced at 0.0, 0.4, 0.8 and 1.2 wt.%. A uniaxial pressing machine was employed to press the precursors into pellets of 10 mm in diameter and 7 mm thickness. The resulting samples were then wrapped in titanium foils and subjected to heat treatment in a furnace, sintered at 775 ℃ for 3 h in flowing Ar atmosphere and finally cooled down to room temperature at a cooling rate of 100 ℃ h$^{-1}$.

![Image](a) Prepared MgB$_2$ pure bulk sample sintered at 775 ℃ (b) Prepared MgB$_2$-nD 0.8 wt.% sintered at 775 ℃. Both samples showed no cracks.

The samples were observed to have no defects when removed from the titanium foils (see fig. 1). We also observed that all samples were carefully fabricated with no indication of cracks. Microstructures of samples were also added and discussed later. The crystal structures and constituent phases were investigated using a high resolution X-ray powder diffractometer (Rigaku/Smart Lab), using Cu K$_\alpha$ radiation with wavelength of 1.5405 Å. The microstructure of samples were investigated using a scanning electron microscope (FESEM, JEOL make, JSM-7100 model). Smaller sized specimens of dimension 2.0×2.0×1.0 mm$^3$ were collected from the sintered pellets and subjected to measurements of the magnetization hysteresis loops (M-H loops) in field range from 0 to 5 T at 20 K and also the critical temperatures ($T_c$) using a SQUID magnetometer (MPMS5minSITO). $J_c$ values were estimated based on the extended Bean’s critical state model using the relation:

$$J_c = \frac{20\Delta M}{a^2d \left( b - \frac{a}{3} \right)}, \quad (1)$$

where $d$ is the sample thickness, a and b are the cross sectional dimensions with $b \geq a$, and $\Delta M$ is the difference of the magnetic moments during increasing and decreasing field in M-H loop [10].
3. Results and discussion

The X-ray diffraction patterns shown in Fig. 2 give information on the crystallographic phases at different doping levels. All three bulk MgB\textsubscript{2}-nD samples consisted mainly of MgB\textsubscript{2} phase and a small quantity of MgO phase.

![X-ray diffraction patterns](image)

**Figure 2.** X-ray diffraction patterns of bulk MgB\textsubscript{2}-diamond nanocomposites produced using the mixture of the amorphous boron powders in sintering process. All samples are sintered at 775 °C for 3h in argon atmosphere.

From previous research, we know that the nanoscale diamond should be reflected as an impurity phase in the MgB\textsubscript{2} material, with intensity depending on the initially added weight percentage of the nanoscale diamond. However, the main reflection of the nano-diamond (111) could not be seen in the XRD patterns due to an overlap with the MgB\textsubscript{2} (101) peak. Therefore, we were able to observe only MgO impurity by XRD, similar to our earlier reports [11-12].

Temperature dependence of magnetization curves was measured on the MgB\textsubscript{2} samples with a varying content of nano-diamond powder in a magnetic field of 1 mT. The critical temperature (\(T_{c,\text{onset}}\)) decreased with increasing nanoscale diamond content (Fig 3a). Note that a high \(T_c\) (onset) of 39.25 K was observed for a sample produced without nano-diamond. Here we obtained \(T_c\) (onset) around 37.3 K for 0.8 wt% of nano-diamond. This clearly indicates that we have to find an optimum between superconductivity degradation and pinning enhancement.

To see the effect of nano-diamond addition on critical current density, \(J_c\) was determined from magnetization hysteresis loops (\(M-H\) loops) detected by a SQUID magnetometer in applied magnetic fields from 0 to 5 T at 20 K. Fig 3(b) shows \(J_c\) values at 20 K as a function of applied magnetic field for the bulk MgB\textsubscript{2} material with varying content of nano-diamond. The MgB\textsubscript{2} sample with 0.8 wt% of nano-diamond powder exhibited higher critical current density than a pure MgB\textsubscript{2} material as well as the 0.4 wt% and 1.2 wt% samples. \(J_c\) increment at higher field has improved for the doped samples as shown on the graph (see inset Fig. 3c), which also supports the fact that the flux pinning mechanism has been enhanced through controlled nanodiamond doping. The self-field critical current density around 300 kA/cm\textsuperscript{2} was observed at 20 K for the best sample as compared to the \(J_c\) of 278 kA/cm\textsuperscript{2} for the pure sample. We can say that optimization was effective for the 0.8 wt.% nano-diamond added sample. The critical current density in high magnetic fields also improved (see inset Fig. 3b). In the MgB\textsubscript{2} sample with 1.2 wt% of nano-diamond powder, the critical current density decreased by a small value when compared with the pure sample. Thus, performance of the bulk MgB\textsubscript{2} material can be improved by optimizing the amount of nano-diamond powder in bulk MgB\textsubscript{2} material. The present study supports the suggestion that the nanoscale diamond can serve as a strong pinning medium to improve flux pinning of MgB\textsubscript{2} bulks at high magnetic fields.
Figure 3. (a) Superconducting transition in the bulk MgB$_2$-diamond nanocomposites produced using the mixture of the amorphous boron powders in sintering process. (b) The field dependence of the critical current densities for the same material at $T = 20$ K. (c) The effect of pinning centers at higher fields. All samples are sintered at 775 °C for 3h in argon atmosphere.

The elementary pinning force of grain boundaries in MgB$_2$ is dependent on its nanostructural control. $J_c$ at low field is simply determined by the connectivity, grain size, and elementary pinning force of the grain boundaries. The effects of grain connectivity and grain size on critical current density and flux pinning are analysed. There is qualitative agreement between grain-boundary pinning mechanism and the experimentally observed grain-size dependence of flux pinning in bulk MgB$_2$ [13].

Figure 4. Micrograph of samples, both low and high magnification for diamond-added MgB$_2$ with different percentage contents.

The results of the microstructural analysis show the refined grains in the diamond added sample and we emphasize that these grains help in enhancing $J_c$. Although the percentage of the dopant added is low, this grain refinement behavior is in agreement with previous literature [15-16]. Therefore, the diamond nanoparticles may provide nucleation centers for MgB$_2$ and tightly bound to them [14]. These intergrain nano sized inclusions created by nanodiamond acts as strong pinning centres and are responsible for the improved flux pinning which are optimally distributed in the 0.8wt%-nD sample.
4. Conclusions

MgB$_2$-diamond nanocomposite was successfully synthesized by a solid state sintering process. X-ray diffraction indicated that all samples were single phase MgB$_2$ along with a small quantity of MgO. DC susceptibility vs. temperature measurements showed a sharp superconducting transition around 38 K for the doped samples. The magnetization measurements showed that 0.4 wt%, 0.8 wt% or 1.2 wt% of nanodiamond did not affect the critical temperature much as compared to pure MgB$_2$ materials. The grain morphology of the sample was improved. The critical current density and irreversibility field values were improved by nano-diamond addition to bulk MgB$_2$. The best $J_c$ value at 20 K was around 300 kA/cm$^2$ in self-field and 175 kA/cm$^2$ at 1 T for the 0.8 wt% of the nano-diamond content. This work shows that doping by nano-diamond particles is a promising way to improve performance of MgB$_2$ bulk materials.

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