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Stress/strain induced flux pinning in highly dense MgB$_2$ bulks

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Stress/Strain Induced Flux Pinning in Highly Dense MgB$_2$ Bulks


Abstract—We have systematically studied the flux pinning behavior of MgB$_2$ bulks synthesized by direct diffusion of Mg into pressed pellets of high purity crystalline B powder, with and without mixing with C and SiC nanoparticles, at a reaction temperature of 850°C for 10 hrs. All of the samples showed very high purity and high density, but their microstructure and flux pinning behavior showed significant differences. It was found that the pure MgB$_2$ agrees with the $\Delta T_c$ pinning model, nano-C doped MgB$_2$ agrees with the $\Delta T_c$ pinning model, while the SiC + MgB$_2$ composite agrees with the $\xi_0$ pinning model (stress/strain field pinning), since the dominant micro-defects that influence the flux pinning in these three samples are different.

Index Terms—Critical current density, flux pinning, MgB$_2$, strain field.

I. INTRODUCTION

SINCE THE discovery of superconductivity in MgB$_2$ [1], its high transition temperature ($T_c \approx 40$ K) and moderately low anisotropy have made it interesting for applications in comparison with both low-$T_c$ and high-$T_c$ superconductors. A number of synthesis methods, such as low temperature reaction, selection of boron powders, and especially carbon and SiC doping [2] have been established in order to improve its originally poor critical current properties under magnetic fields. The upper critical field, $B_{c2}$, especially in thin films, [3] can be hugely increased, exceeding that of Nb-based superconductors at all temperatures. On the other hand, the critical current density, $J_c$, and its behavior in magnetic field have not yet reached their full potential, and the mechanisms of those improvements in flux pinning have not been well understood. The important role of grain boundaries as pinning centers has been emphasized [4]. The intentional addition of defects such as nanoparticles [5] and irradiation damage [6], [7] has been proved to be effective in enhancing both $B_{c2}$ and flux pinning, but an unambiguous discrimination between these two effects has not been formulated yet.

In this paper, we report a systematic study of the flux pinning behavior of highly dense MgB$_2$ bulks synthesized by direct diffusion of Mg into pressed pellets of high purity crystalline B powder, with and without mixing with C and SiC nanoparticles at a reaction temperature of 850°C for 10 hrs. We demonstrate that the grain boundary flux pinning cannot account alone for the enhanced $J_c$ values in magnetic field. On the contrary, we unambiguously show that there is an additional pinning contribution by the stress/strain field around defects introduced by thermal strain during the preparation processing.

II. EXPERIMENTAL

The starting powders of crystalline B, of 99.999% purity, with and without nano-C and crystalline SiC (<30 nm) particles, were mixed and pressed into pellets. The pellets were then put into an iron tube filled with Mg powder (99.8%). The mass ratio between B and Mg was kept at 1:1.2. The samples were sintered at 650–950°C for 10 hrs in a quartz tube, where a flow of high purity argon gas was maintained, and then cooled to room temperature by natural cooling. All of samples were characterized by X-ray diffraction (XRD) and analysed using Rietveld refinement XRD to determine the $a$ and $c$ lattice parameters, and the MgO content. Micro-structural observations were performed by using a scanning electron microscope (SEM) and a high resolution transmission electron microscope (HRTEM). The critical temperature, $T_c$, was defined as the onset temperature at which diamagnetic properties were observed. The Raman scattering was measured by a confocal laser Raman spectrometer (Renishaw inVia plus) with a 100× microscope. The 632.5 nm line of an Ar$^+$ laser was used for excitation, with the laser power maintained at about 20 mW, measured on the laser spot on the samples, in order to avoid laser heating effects on the studied materials. The magnetization of samples was measured at 5 and 20 K using a Quantum Design Physical Properties Measurement System (PPMS) with a magnetic field sweep rate of 50 Oe/s and amplitude up to 9 T. The magnetic $J_c$ was calculated from the height of the magnetization loop, $M$, using the critical state model: $J_c = 12 M_l/[d(\delta b - d)]$, with $b$ and $d$ the dimensions of the samples perpendicular to the direction of applied magnetic field and $1 < \delta$). The magnetoresistivity $\rho(H, T)$ was measured with $H$ applied perpendicular to the current direction, using the four probe method in the temperature range from 4.2 K to 300 K.
K and the field range from 0 T to 9 T. The irreversibility field, \( H_{irr} \), and \( H_{c2} \) could be deduced using the criteria of 0.1 and 0.9 of \( \rho(H,T) \), respectively.

### III. RESULTS AND DISCUSSIONS

Three samples appeared to exhibit a high density (about 80% of the theoretical density, compared with about 50% of the theoretical density for in-situ mixed bulk), and no MgO could be detected by XRD. Fig. 1 shows the Rietveld refinement XRD patterns of the pure MgB\(_2\), the nano-C doped MgB\(_2\), and the 10 wt% SiC – MgB\(_2\) composite samples. By using Rietveld refinement analysis, the \( a\)- and \( c\)-axis lattice parameters and SiC content were determined, as shown in Table I, which also gives a comparison of the density, the defect induced \( a\)- and \( c\)-axis lattice strain, the grain size, the percentage of Mg vacancies, \( T_c \), and the residual resistance at 40 K (\( \rho(40\,K) \)) for the three samples. We note that the \( a\)-axis parameter is virtually the same for pure and SiC-doped MgB\(_2\) samples, while the \( c\)-axis parameter is slightly enlarged in the SiC – MgB\(_2\) composite. In contrast, the \( a\)-axis parameter for nano-C doped MgB\(_2\) is reduced, while the \( c\)-axis parameter remains unchanged, as reported by a number of groups. This indicates that the SiC particles remained un-reacted and formed a composite with the MgB\(_2\) in

![Image](https://example.com/image1.png)

**Fig. 1.** XRD patterns of the pure MgB\(_2\), nano-C doped MgB\(_2\), and the 10 wt% SiC – MgB\(_2\) composite samples that were diffusion reacted at 850°C for 10 hrs.

### TABLE I

**SUMMARY OF PHYSICAL PROPERTIES OF PURE, NANO-C AND SiC + MgB\(_2\) COMPOSITE SAMPLES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( D ) (g/cm(^3))</th>
<th>( a)-lattice (Å)</th>
<th>( c)-lattice (Å)</th>
<th>Mg Vacancies (%)</th>
<th>Grain Size (nm)</th>
<th>( T_c ) (K)</th>
<th>( \rho ) (( 40,K )) (( \mu \Omega \cdot \text{cm} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>1.86</td>
<td>3.085, 3.5220</td>
<td>0.208</td>
<td>3.2</td>
<td>~100</td>
<td>38.4</td>
<td>12</td>
</tr>
<tr>
<td>10% SiC</td>
<td>1.91</td>
<td>3.084, 3.5282</td>
<td>0.306</td>
<td>11.3</td>
<td>~100</td>
<td>37.8</td>
<td>16</td>
</tr>
<tr>
<td>C(_a)</td>
<td>1.97</td>
<td>3.075, 3.523</td>
<td>0.216</td>
<td>3.12</td>
<td>~60</td>
<td>36.5</td>
<td>32</td>
</tr>
</tbody>
</table>

The magnetic \( J_c \) versus field at 5 K, 20 K, and 30 K. (b) Upper critical field (\( H_{c2} \)) and irreversibility field (\( H_{irr} \)) as functions of the reduced temperature. The inset shows the resistivity of the three samples as a function of temperature. (c) The normalized \( J_c(T)/J_c(0) \) at field \( H = 0.1 \, \text{T} \) versus reduced temperature (\( T/T_c \)) and fitting of the normalized \( J_c(T) \) with various pinning models for pure, nano-SiC doped, and nano-C doped MgB\(_2\) samples.

![Image](https://example.com/image2.png)

**Fig. 2.** (a) The magnetic \( J_c \) versus field at 5 K, 20 K, and 30 K. (b) Upper critical field (\( H_{c2} \)) and irreversibility field (\( H_{irr} \)) as functions of the reduced temperature. (c) The normalized \( J_c(T) \) at field \( H = 0.1 \, \text{T} \) versus reduced temperature (\( T/T_c \)) and fitting of the normalized \( J_c(T) \) with various pinning models for pure, nano-SiC doped, and nano-C doped MgB\(_2\) samples.

The SiC-doped sample. It is also confirmed by the \( T_c \) and resistance results that there is a small drop (0.6 K) in \( T_c \) and little increase in \( \rho(40\,K) \) (from 12 \( \mu \Omega \cdot \text{cm} \) to 16 \( \mu \Omega \cdot \text{cm} \)) for the SiC-doped sample and a large drop (1.9 K) in \( T_c \) and a large increase in \( \rho(40\,K) \) (32 \( \mu \Omega \cdot \text{cm} \)) for the nano-C doped sample, as shown in Table I and the Fig. 2(b) inset.

Fig. 2(a) shows the magnetic \( J_c \) versus field at 5 K, 20 K, and 30 K for pure, nano-SiC doped, and nano-C doped MgB\(_2\) samples. A \( J_c \) of 5.8 \times 10^4 A/cm\(^2\) in self-field and 1.9 \times 10^4 A/cm\(^2\) in 4 T at 20 K for SiC-doped MgB\(_2\) is higher than the \( J_c \) of 4.1 \times 10^3 A/cm\(^2\) in self-field and 1.4 \times 10^3 A/cm\(^2\) in 4 T at...
20 K for pure MgB₂. It can be noted that, in comparison with the pure sample, the SiC-doped sample shows significantly improved pinning, since \( J_c \) is improved in all fields and all temperatures (5 K, 20 K, and 30 K), while the nano-C doped sample only shows improved pinning and \( J_c \) at high field and low temperature. Fig. 2(b) shows the upper critical field \( (H_{c2}) \) and the irreversibility field \( (H_{irr}) \) as functions of the temperature for these three samples. The inset shows the resistivity of the three samples as a function of temperature. As can be seen, \( H_{irr} \) and \( H_{c2} \) of both nano-C doped MgB₂ and the SiC–MgB₂ samples are significantly improved in comparison with the pure sample, and \( H_{irr} \) and \( H_{c2} \) of the SiC–MgB₂ sample are much higher than those of the nano-C doped sample.

The results reported above give rise to a very interesting phenomenon, in that nanosize particle inclusions alone (nano-SiC particles here), with almost no C substitution, can evidently induce strong pinning in MgB₂, so as to improve \( J_c \) and \( H_{c2} \). In order to understand the pinning mechanism in these three samples, we return to analysing the experimental temperature dependence of \( J_c \). According to the model of thermally activated flux motion and the model of collective flux pinning [8]–[12], flux pinning mechanisms are mainly classified into two or three types: (i) \( \delta T_c \), due to the spatial fluctuation of the Ginsburg-Landau coefficient associated with the transition temperature \( T_c \); (ii) \( \delta I \), which is induced by the spatial fluctuation of the effective mass related to the charge carrier mean free path \( l \), or (iii) \( \delta \varepsilon \), which is due to the stress/strain field. The temperature dependence of the critical current density \( J_c(T) \) can be expressed as:

\[
J_c(T) \approx J_c(0) f(t) \quad (1)
\]

with

\[
f(t) = \left(1 - t^2\right)^X \left(1 + t^2\right)^Y \quad (2)
\]

where \( J_c(0) \) is \( J_c \) at the temperature of 0 K, and \( t \) is the normalized temperature \( t = T/T_c \). The association with the different pinning models is given by [8]–[12]:

- when \( X = 7/6 \) and \( Y = 5/6 \), \( \delta T_c \) pinning model;
- when \( X = 5/2 \) and \( Y = -1/2 \), \( \delta I \) pinning model;
- when \( X = 7/6 \) and \( Y = -11/6 \), \( \delta \varepsilon \) pinning model.

As shown in Fig. 2(c), normalized \( J_c(T) \) for SiC + MgB₂ composite is well fitted over the main temperature range with the model of \( \delta \varepsilon \) pinning (stress/strain field pinning), while nano-C doped MgB₂ agrees with the \( \delta I \) model and pure MgB₂ agrees with the \( \delta T_c \) model, both in agreement with our previous reports [11], [12].

So far, we know that considering the dominant pinning mechanisms for the three samples, the pure and nano-C doped samples exhibit normal features, as in previous reports [11], [12], but for the stress/strain field pinning mechanism dominated SiC-doped sample, we need to know: (a) what is the original type of pinning for the SiC-doped sample; (b) what is the cause of the stress and strain; (c) where and how does it occur, since there is no C or very low C substitution and almost no MgO or other impurity phases in the sample. To answer these questions, we have conducted Raman measurements and TEM and HRTEM observations on the three samples.

Fig. 3 shows the normalized ambient Raman spectra of the three samples sintered at 850°C for 10 hrs. The line spectra correspond to the spectra at 300 K (black) and after exposure to a 5 T field at 300 K (red), at 10 K (blue), and after exposure to a 5 T field at 10 K (pink), respectively.
are slightly increased by the 5 T treatment at 10 K for all three samples. This is the sign of flux pinning induced irreversible magnetostriction strain or of lattice distortion [18], which indicates that the flux pinning in the doped samples is much stronger than that in the pure MgB₂.

Fig. 4 shows TEM and HRTEM images for three samples: (a) the pure MgB₂ (scale bar 100 nm), (b) the nano-C doped sample (scale bar 200 nm), (c) the SiC-doped sample (scale bar 100 nm), and (d) an HRTEM image of the SiC-doped sample. It can be seen that different types of defects exist in the three samples. There are black spots about 50 nm to 100 nm in size in the pure MgB₂ sample, which are believed to show Mg vacancy areas and are common in all three samples, but there are smaller black spots (around 25 nm in size) in the nano-C doped sample, which are believed to represent residual nano-sized carbon and localized C substitution areas. A more interesting feature in the SiC-doped sample is that a high density of wave fringes was observed in the MgB₂ near the interfaces with SiC. Careful examination indicated that these fringes were induced by lattice mismatch between the two layers, so dislocations, lattice distortions, and nanosized disorder areas (as shown in Fig. 4(d)) were commonly observed in areas with fringes. The lattice distortion observed in TEM and HRTEM confirmed the Raman spectroscopy results described above [19].

IV. SUMMARY

Dense pure, nano-C doped, and SiC-doped MgB₂ bulks with almost no other (MgO) impurity phases were successfully synthesized, and the connectivity was significantly enhanced compared to a mixed powder in situ sample. It was found that the flux pinning mechanism of the pure MgB₂ agreed with the δTc pinning model, that of the C-substituted MgB₂ agreed with the δl pinning model, while the composite MgB₂ that had SiC without C substitution agreed with the δe pinning model (stress/strain field pinning). The dominant micro-defects as flux pinning centers in these samples included Mg vacancy caused lattice mismatch and non-uniform lattice strain, which existed in all the samples. C-substitution caused a high density of lattice mismatch defects, which performed in a similar way to high level Mg-vacancies (in XRD measurements) and highly uniform lattice strain, which caused α-axis lattice scattering, decreased the mean free path (l), and increased the resistivity. However, in the SiC-MgB₂ composite without C substitution, there was highly non-uniform ε-axis lattice strain due to the thermal strain induced by different thermal expansion coefficients between SiC and MgB₂, which caused a high density of lattice distortions, disorder, and dislocations around the SiC. The Raman measurements after high field and low temperature cycling indicated the existence of residual thermal strain and irreversible flux pinning induced strain.

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