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Effect of Addition of TiO₂/SiO₂ Nanoparticles on \( H_{c2} \) and \( H_{\text{irr}} \) in MgB₂ Bulks

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Abstract— In this paper, MgB₂ bulks were prepared with doped TiO₂ nanoparticles surface-modified by 5-10% SiO₂. Quantitative X-ray diffraction (XRD) analysis was performed to obtain the weight fraction of impurities using the Rietveld method. The effects of addition of TiO₂/SiO₂ nanoparticles on the critical temperature (\( T_c \)), the upper critical field (\( H_{c2} \)), and the irreversibility field (\( H_{\text{irr}} \)) as a function of doping rates at 750°C are reported. It has been found that the addition of TiO₂/SiO₂ nanoparticles resulted in small depressions in \( T_c \), while the \( H_{c2} \) and \( H_{\text{irr}} \) performances were improved due to TiO₂/SiO₂ nanoparticle doping.

Keywords—upper critical field; irreversibility field; doping; magnesium diboride; TiO₂/SiO₂

I. INTRODUCTION

The superconductivity at 39K discovered in MgB₂ [1] has aroused much interest in practical applications. Its low cost, high critical temperature (\( T_c \)), freedom from weak-links [2], [3], and multiple energy gaps [4], [5], [6] offer the possibility for application in magnets and various electronic applications. However, the significant potential of MgB₂ for applications is limited by poor flux pinning and the relatively low upper critical field (\( H_{c2} \)) and irreversibility field (\( H_{\text{irr}} \)). So far, substitution and addition have been widely used to improve the critical current density (\( J_c \)), \( H_{c2} \), and \( H_{\text{irr}} \) improvement by substitution. Currently, only Al replacing Mg and C replacing B have been possible for higher doping level [7], [8], [9], [10]. Other substituting dopants, such as the transition metal elements (Fe, Y, Ti, Zr) in the Mg sub-lattice are limited to very low concentration [11], [12], [13], [14]. Compound additions, such as SiC [8], B₃C [15], Y₂O₃ [16], SiO₂ [17], [18], and TiO₂ [19] have exhibited positive effects on \( J_c \), \( H_{c2} \), and \( H_{\text{irr}} \). Therefore, adding nanoparticles which cause compositional and nanostructural changes in MgB₂, has been proved to be an effective way to enhance the performance of MgB₂.

Among these dopants, the authors’ group found that \( J_c \) could be improved by TiO₂ doping under low magnetic fields, while SiO₂ doping played a role under high magnetic fields. Perner et al. [17] have reported that the optimum SiO₂ doping level of around 2 wt.% improved the flux pinning ability of MgB₂. In our recent study of the effect of atmosphere on the \( J_c \) of MgB₂, it was suggested that the particular amount of O₂ might play a very important role [20]. This is another reason why metal oxides, in particular, have attracted attention rather than other compounds. These results motivated us to add TiO₂ and SiO₂ nanoparticles into MgB₂ simultaneously. In order to make homogeneous samples by co-doping, TiO₂ nanoparticles coated by 5-10% SiO₂ were used. In this paper, we performed a systematic study of \( H_{c2} \) and \( H_{\text{irr}} \) performances for samples sintered at the temperature of 750°C, and we have found an enhancement of the \( H_{c2} \) and \( H_{\text{irr}} \) for MgB₂ samples with 5-10wt% TiO₂/SiO₂ doping, along with a small depression in \( T_c \).

II. EXPERIMENTAL

MgB₂ bulks were prepared by the in-situ method. Powders of Mg (99%), amorphous B (99%) were used as starting materials. TiO₂ nanoparticles (15 nm) with a purity of 99.7% and surface modified by 5-10% SiO₂ were used as the dopant. The doping ratios were 0, 5, and 10 wt% and the sintering temperature was 750°C. Amorphous boron powder was dried for 9 days in oven at 120°C before mixing with the Mg powders. The powders were well ground and pressed into stainless steel tubes with 10mm outer diameter and 7mm inside diameter, using a 5 ton press. This packing process was carried out in air. The samples were heated from room temperature to the sintering temperatures in a tube furnace under Ar atmosphere at ambient pressure, and kept at the sintering temperature for 1 hour. The samples were then furnace cooled to room temperature. The obtained MgB₂ samples were examined by a Phillips PW1730 X-ray power diffractometer with CuKα radiation (\( \lambda = 1.5418 \)Å). The X-ray diffraction (XRD) patterns were collected over a 20 range from 20° to 80° with a step size of 0.02°. The quantitative phase analysis was carried out based on the XRD patterns. Magnetic measurement
of the samples were conducted in a commercial Quantum Design Physical Properties Measurement System (PPMS). The samples were cut into a rectangular shape for measurements. Their dimensions were accurately measured by a digital micrometer. The typical dimensions of the samples used for magnetization measurement were 0.5mm x 2.5mm x 4.5 mm. 

Hc2 and Hirr were defined as $H_{c2} = 0.9R(T_c)$ and $H_{irr} = 0.1R(T_c)$ from the resistance ($R$) versus temperature ($T$) curve. Details of the sample compositions, heat treatment conditions, and measured superconducting properties of all the un-doped and doped MgB2 samples are given in Table 1.

### III. RESULTS AND DISCUSSION

Fig. 1 contains the powder XRD patterns of MgB2 samples with various doping ratios of TiO2/SiO2 at the sintering temperature of 750°C. MgO is the major impurity in all the samples. As the doping ratio increases from 0 wt% to 10 wt%, the amount of MgO obviously increases. The reason can be attributed to a reaction between the starting material Mg and the oxygen introduced by the dopant TiO2/SiO2 nanoparticles. Mg2Si can be observed in the samples with TiO2/SiO2 doping. It is formed by the reaction of Mg and SiO2. The amount of Mg2Si seems to increase with increasing doping ratios. In addition, there are no peaks corresponding to TiO2 (or Ti-containing compounds). However, energy dispersive x-ray spectroscopy (EDX) shows that the element Ti exists in the bulk samples. It is therefore suggested that the very weak XRD intensity of TiO2 nanoparticles (as a second phase) is the main reason for the absence of TiO2 peaks in the XRD patterns. Specifically, MgB2 samples doped with TiO2/SiO2 nanoparticles had larger full width at half maximum (FWHM) values of the (110) peak than the pure sample, as described in Table 1. This indicates that small grains and various types of lattice defects or intra-granular precipitates [21] exist in the doped samples. This result might be related to lattice disorder due to oxygen doping into the MgB2 lattice or Mg deficiency due to the existence of Mg2Si. From Table 1, we can see that $T_c$ for the TiO2/SiO2 doped samples was slightly depressed, due to impurity scattering. In addition, as the doping ratio increase, resulting in reduction of the superconducting volume of MgB2, the self-field $J_c(0)$ dropped slightly at 20K.

The resistivities, $\rho$, for the doped and un-doped samples sintered at 750°C are shown in Fig. 3. It can be observed that the resistivities for the doped sample are much higher than for the un-doped one. This trend is quite similar to that shown by SiC doped samples.

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**TABLE 1 Measured data for un-doped and doped MgB2 samples**

<table>
<thead>
<tr>
<th>samples</th>
<th>sintering conditions</th>
<th>MgO at%</th>
<th>Mg2si at%</th>
<th>$\rho_{20K}$ ($\mu\Omega cm$)</th>
<th>$\rho_{300K}$ ($\mu\Omega cm$)</th>
<th>$\Delta\rho$ ($\mu\Omega cm$)</th>
<th>RRR</th>
<th>FWHM(110) (°)</th>
<th>$T_c$ (K)</th>
<th>$J_c(0)$ (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-doped MgB2</td>
<td>750°C 1H</td>
<td>5.7</td>
<td>30.1</td>
<td>79.7</td>
<td>49.6</td>
<td>2.7</td>
<td>0.44</td>
<td>37.8</td>
<td>5.17×10⁵</td>
<td></td>
</tr>
<tr>
<td>MgB2 + 5% TiO2/SiO2</td>
<td>750°C 1H</td>
<td>17</td>
<td>1</td>
<td>122</td>
<td>215</td>
<td>93.1</td>
<td>1.8</td>
<td>0.52</td>
<td>36.2</td>
<td>4.27×10⁵</td>
</tr>
<tr>
<td>MgB2 + 10% TiO2/SiO2</td>
<td>750°C 1H</td>
<td>21</td>
<td>9</td>
<td>166</td>
<td>252</td>
<td>86.8</td>
<td>1.5</td>
<td>0.71</td>
<td>35.6</td>
<td>3.381×10⁵</td>
</tr>
</tbody>
</table>

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Scanning electron microscope (SEM) images for the un-doped sample and the 10% TiO2/SiO2 doped one at two different magnifications are shown in Fig. 2(a)-(d). From the low magnification images (a) and (b), we can observe similar microstructures, consisting of fully round and smooth holes. Comparing Fig. 2(c) and (d), we can see that the un-doped sample shows noticeably better density and connectivity. The difference between the resistivities at 40K and 300K, $\Delta\rho$, values of MgB2 bulks were 49.6 $\mu\Omega$ cm for the un-doped sample and 86.8 $\mu\Omega$ cm for the 10% doped sample, respectively. The low $\Delta\rho$ values are considered to originate from the good connectivity of the sample [22]. This is consistent with the higher low field $J_c$ in the un-doped sample (Table 1). As Fig.2(c) and (d) shows, the grain size of the doped samples appears to be smaller than for the un-doped one, which is consistent with the broadening of the (110) X-ray peaks.

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Figure 1 XRD pattern of MgB2 samples with various doping rates at sintering temperature of 750°C.

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**FIGURE 1 XRD pattern of MgB2 samples with various doping rates at sintering temperature of 750°C.**
As \( \rho \) increases, \( H_{c2} \) and \( H_{irr} \) show an increasing trend as shown in Fig. 4. The straightforward explanation is that the doped samples are dirty, as the residual resistivity ratio (RRR), defined as \( R(300K)/R(40K) \), is found in Table 1 to also decrease with increasing doping level. Although Klie et al. [23] reported that most oxygen doping would result in second phases of MgO or BOx with large particle size at the grain boundaries, several other reports [24], [25], [26] have revealed that there are nano Mg(B,O)2 precipitates inside the MgB2 grains, which have desirable effects on superconducting performance. Our current study on the effect of processing atmosphere on the superconducting properties of MgB2 [20] have showed a high density of Mg(B,O)2 precipitates and of grain boundaries as results of oxygen doping. These desirable nanoprecipitates inside the MgB2 grains result in lattice distortion and shorten the mean-free path \( \lambda \) of the superconducting electrons [25]. Therefore, the coherence length \( \xi \) is decreased due to the relation: \( 1/\xi = 1/\xi_0 + 1/\lambda \), where \( \xi_0 \) is the value of \( \xi \) for the pure superconductor. According to \( H_{c2} = \Phi_0/(2\pi\mu_0\xi^2) \), where \( \Phi_0 \) is the superconducting flux quantum and \( \mu_0 \) is the magnetic permeability, \( H_{c2} \) will increase as \( \xi \) decreases. Both the \( H_{irr} \) and the \( H_{c2} \) slopes are found to be significantly higher for the doped samples. The best performance is shown in the 10% TiO2/SiO2 doped sample, which has a large FWHM of the (110) peak for the MgB2 phase and a large \( \rho \) value at 40K, as shown in Table 1. This provides direct evidence that the lattice defects and precipitates are essentially beneficial for enhanced \( H_{irr} \) and \( H_{c2} \) for MgB2 bulks.

IV. SUMMARY

In this paper, MgB2 bulks doped with TiO2 nanoparticles surface-modified by 5-10% SiO2 were fabricated. The effects of the doping with TiO2/SiO2 nanoparticles on \( T_c \), \( H_{c2} \) and \( H_{irr} \) have been investigated. It has been found that the additive TiO2/SiO2 nanoparticles resulted in small depressions in \( T_c \), while \( H_{c2} \) and \( H_{irr} \) performances were improved due to the TiO2/SiO2 doping. The best performance was shown by the 10% TiO2/SiO2 doped sample. The enhancement of \( H_{c2} \) and \( H_{irr} \) can be attributed to the existence of precipitates induced by the TiO2/SiO2 doping.

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