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# Effect of Nano-Particle Doping on the Upper Critical Field and Flux Pinning in $\text{MgB}_2$

S. X. Dou, S. Soltanian, W. K. Yeoh, and Y. Zhang

**Abstract**—The effect of nano particle doping on the critical current density of  $\text{MgB}_2$  is reviewed. Most nano-particle doping leads to improvement of  $J_c(H)$  performance while some shows a negative effect as with Cu and Ag. Nano-carbon containing dopants have two distinguishable contributions to the enhancement of  $J_c$  field performance: increase of upper critical field and improvement of flux pinning. Among all the dopants studied so far, nano SiC doping showed the most significant and reproducible enhancement in  $J_c(H)$ . The nano SiC doping introduced many precipitates at a scale below 10 nm, which serve as strong pinning centers.  $J_c$  for the nano SiC doped samples increased by more than an order of magnitude at high fields and all temperatures compared to the undoped samples. The significant enhancement in  $J_c(H)$  of nano-SiC doping has been widely verified and confirmed, having a great potential for applications. An attempt is made to clarify the controversy on the effects of nano Fe and Ti doping on  $J_c$ .

**Index Terms**—Critical current, doping, magnesium diboride, silicon carbide.

## I. INTRODUCTION

THE DISCOVERY of the new superconductor,  $\text{MgB}_2$  [1], has opened a window of opportunity for applications in the temperature and field regime otherwise unattainable by conventional superconductors. During the past three years,  $\text{MgB}_2$  has been fabricated in various forms, including single crystals, bulk, thin films, tapes and wires. In particular, enormous efforts have been directed to improvement of the critical current density ( $J_c$ ) through development and application of various novel techniques for fabrication of technically usable  $\text{MgB}_2$  materials. Attempts to enhance  $H_{c2}$  and flux pinning have been made by using a number of techniques, including addition and substitution, irradiation, and various types of thermomechanical processing. Many dopants have been studied for improving  $J_c(H)$  performance in the field and impressive progress has been made. There is an urgent need to have a clear picture of all the doping work. In this article, we review the current status of doping effects on  $J_c$  and  $H_{c2}$  of  $\text{MgB}_2$ . We will also introduce new data to clarify the controversial problems on the effects of some types of element doping.

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## II. CARBON DOPING

The effect of C-doping on superconductivity in  $\text{MgB}_2$  compound has been extensively studied. The results on C solubility and the effect of C-doping on  $T_c$  reported so far vary significantly due to the precursor materials, fabrication techniques and processing conditions used [2]. From the application point of view, the effect of C doping on the flux pinning properties is crucially important. The author's group has reported a significant improvement in  $J_c(H)$  and  $H_{irr}$  in  $\text{MgB}_2$  through doping with nano-SiC [3], nano-C [4] and nano-carbon tubes [5]. It is clear from previous work that complete substitution of C for B causes a drastic depression in  $T_c$ , which is very undesirable for improving  $J_c$  at high temperatures. The authors' group has designed compromise synthesis conditions that limit the degree of C substitution, which can cause disorder at the B position, and at the same time can introduce nano-additives to act as effective pinning centers in  $\text{MgB}_2$ . Among various carbon precursors, carbon nano-tubes (CNT) are particularly interesting as their special geometry may induce more effective pinning centers compared to other carbon-containing precursors. The authors' group studied the effect of doping with CNT on the  $T_c$ , lattice parameters,  $J_c$  and flux pinning on  $\text{MgB}_{2-x}\text{C}_x$  with  $x = 0, 0.05, 0.1, 0.2$  and  $0.3$  [6]. The carbon substitution for B was found to enhance  $J_c$  in magnetic fields but depress  $T_c$ . The depression of  $T_c$ , which is caused by the carbon substitution for B, increases with increasing doping level, sintering temperature and duration. The inset to Fig. 1 shows the  $T_c$  dependence on the sintering temperature of 10% CNT doped  $\text{MgB}_2$ , indicating that the C substitution for B clearly increased at 1000 C. By controlling the extent of the substitution and addition of CNT one can achieve the optimal improvement of  $J_c$  and flux pinning in magnetic fields while maintaining the minimum reduction in  $T_c$ .  $J_c$  was enhanced by two orders of magnitude at 8 T and 5 K (Fig. 1). The partial C substitution for B caused disorder at the B position that can lead to intrinsic scattering and hence the enhancement of  $H_{c2}$  [8].

## III. NANO-SiC DOPING

The exceptional properties of SiC as a dopant have been systematically studied by the authors' group and other groups during the last two years. Doping  $\text{MgB}_2$  with nano-particle SiC can significantly enhance  $J_c$  in high fields with only slight reductions in  $T_c$  up to a doping level as high as 30% of B [7]. In fact, we obtained the highest  $J_c$  values in magnetic fields at 20 K ever reported for  $\text{MgB}_2$  wires and bulk [3], [8]. Compared to the undoped sample, the  $J_c$  for the 10 wt% SiC doped sample increased by a factor of 32 at 5 K and 8 T, and 42 at 20 K and

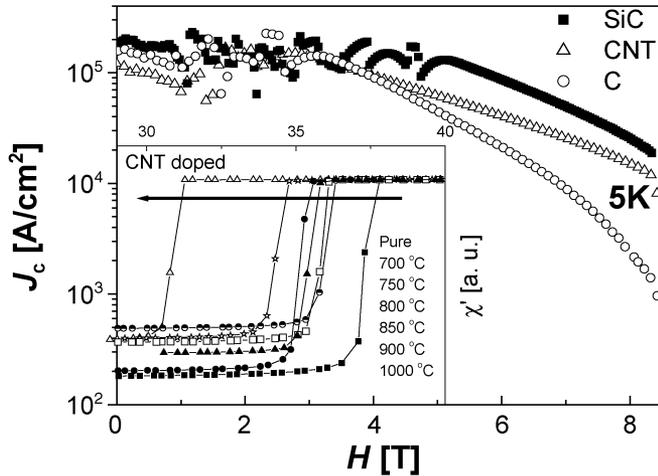


Fig. 1. Comparison of  $J_c$  at 5 K for 10 wt% C, CNT and SiC doped  $MgB_2$  with undoped  $MgB_2$ . Inset: magnetic AC susceptibility as a function of temperature for  $MgB_{1.8}C_{0.2}$ . Carbon added was in the form of carbon nano-tubes.

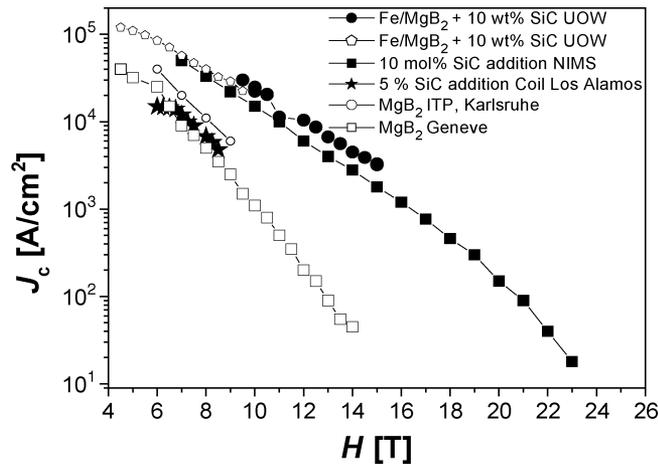


Fig. 2. Comparison of transport  $J_c$  for SiC doped  $MgB_2$  wires with the best undoped  $MgB_2$  wire from various groups.

5 T, respectively. Fig. 2 shows a comparison of transport  $J_c(H)$  for SiC doped  $MgB_2$  at 4.2 K by the author's group [3], [9], Matsumoto *et al.* [10], and Serquis *et al.* [11], along with data on recently reported state-of-the-art wires [12], [13].  $J_c$  for nano SiC doped wires is an order of magnitude higher than for the state-of-the-art Fe/ $MgB_2$  tapes.

In comparison with all other doping, the special features of nano-scale SiC doping into  $MgB_2$  are the significant magnitude and the wide range of temperatures up to  $T_c$ . According to the two-gap superconductivity theory [14], nano SiC doping could lead to C substitution for B, which will result in scattering. This accounts for the enhancement of  $J_c(H)$  over a wide temperature range for the SiC doped sample. Fig. 3 shows a record high  $H_{c2}(0)$  value of 37 T for a nano-SiC doped sample of bulk  $MgB_2$  obtained from transport measurements as reported by Serquis *et al.* [15]. The strong upturn of  $H_{c2}(T)$  at low temperatures indicates impurity scattering on the Mg sites. The additional impurities at nano scale introduced by SiC doping can serve as strong pinning centers to improve flux pinning within

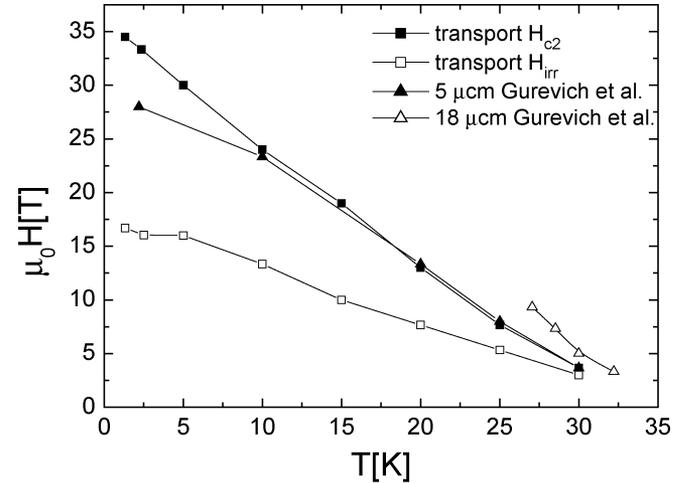


Fig. 3. Comparison of  $H_{c2}$  and  $H_{irr}$  for SiC doped  $MgB_2$  with Mg-vapor treated  $MgB_2$  [15].

a certain field region. The potential pinning centers introduced by SiC doping include highly dispersed  $MgSi_2$ , BC,  $BO_x$  and  $SiBO_x$ , which are all at a scale below 10 nm and can act as strong pinning centers. In addition, the extensive network of nano-domain defects at a scale of 2–3 nm would provide effective collective pinning at all the temperatures up to  $T_c$  [16]. These results suggest that we can manipulate the processing parameters that lead to the improvement of either  $H_{c2}$  or flux pinning or of both at the same time.

Matsumoto *et al.* [10] has confirmed that SiC improved  $J_c$  by an order of magnitude and  $H_{irr}$  went from about 17 T to about 23 T. M Sumption *et al.* showed a significant improvement in pinning force density (from transport  $J_c$ ) vs B at 4.2 K for the SiC doped  $MgB_2$  wires, compared to undoped ones [17]. These results demonstrated that the enhancement effect on  $J_c - H$  performance by nano-SiC doping is highly reproducible.

#### IV. Si AND SILICATE DOPING

Si and silicides, including  $WSi_2$ ,  $ZrSi_2$ ,  $MgSi_2$  and  $SiO_2$ , have been found to have a positive effect on  $J_c - H$  performance as dopants in  $MgB_2$ . Ma *et al.* have reported the effects of  $ZrSi_2$ ,  $WSi_2$ ,  $ZrB_2$ ,  $Mg_2Si$  and  $SiO_2$  on the  $J_c - H$  behavior [18]. They found that the  $J_c$  was enhanced by all these dopants except for  $SiO_2$ . These compounds act as pinning centers in the form of additives. The extent of  $J_c$  enhancement depends on the additive contents and processing conditions. However, the enhancement of  $J_c$  by these dopants is much less significant compared to SiC doping [2]. Cimerle *et al.* found that doping with a small amount of Li, Al and Si showed an increase in low-field  $J_c$ , but there is no improvement in  $H_{irr}$  [19]. Wang *et al.* has studied the effect of nano-Si particle (<100 nm) and coarse Si particle doping in  $MgB_2$  on the  $J_c - H$  performance [20]. They found that the nano particle doping enhanced the flux pinning while the coarse one had a negative effect. Neutron diffraction indicates that there is no substitution of Si at either the B or Mg positions. The enhanced flux pinning is attributed to impurity inclusions including reaction products,  $Mg_2Si$  and un-reacted nano Si particles.

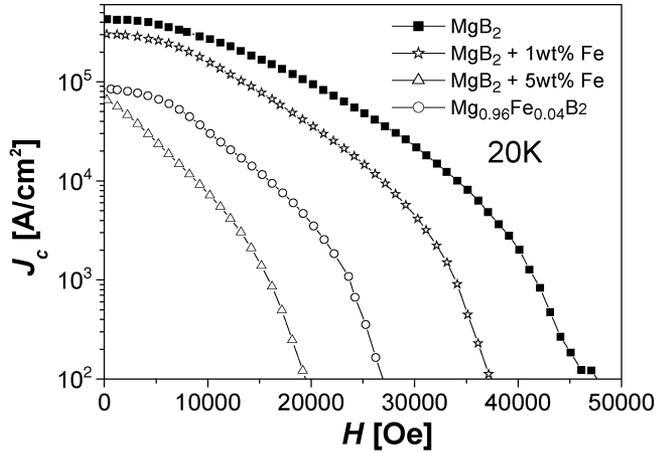


Fig. 4.  $J_c(H)$  curves for undoped and Fe-doped MgB<sub>2</sub> samples at 20 K for different doping levels.

### V. METAL ELEMENT DOPING

Jin *et al.* studied the effect of several metal elements including Fe, Mo, Cu, Ag and Y on the  $J_c - H$  behavior of MgB<sub>2</sub>. They found that these elements were not incorporated into the lattice and had negative effect on the  $J_c - H$  characteristics, but with Fe being the least damaging element while Cu, Y and Ti were the most detrimental elements [21]. The elements Cu, Ag, Y and Ti react with Mg while Fe, Ag and Ti react with B to form intermetallics. This is in contrast to work that has claimed that Fe addition acted as a source of effective pinning centres and improved the  $J_c - H$  performance [22].

Fe doping was further studied by the author's group using nano-scale Fe powder. It was found that nano-scale Fe particle doping depressed both  $T_c$  and  $J_c(H)$  in both bulk and thin film samples as shown in Fig. 4 [23]. By using nano-scale Fe powder the interface area was increased substantially and the ferromagnetic effect of Fe on the surrounding superconductor became more pronounced, resulting in a strong depression in  $T_c$  and superconductor volume which reduced  $J_c$ . Because of their high reactivity, in the in-situ process the nano-scale Fe particles reacted with B to form FeB and Fe<sub>2</sub>B which were homogeneously distributed within the matrix of bulk and thin film MgB<sub>2</sub>. Fe substitution for Mg is unlikely but remains inconclusive. The strong depression in  $J_c(H)$  performance by nano-Fe particle doping is attributable to the decoupling effect of Fe-containing particles within the grains and at grain boundaries.

Zhao *et al.* have doped MgB<sub>2</sub> with Ti and Zr, and the  $J_c$  improved at 4 K [24]. However, the improvement in  $J_c(H)$  was unclear at temperatures above 20 K. Finnemore *et al.* used the CVD technique to co-deposit Ti with boron to form fiber TiB and TiB<sub>2</sub> [25]. When this fiber reacted in Mg vapor to transform boron into MgB<sub>2</sub>, the resulting conductor had a  $J_c$  of  $5 \times 10^6$  A/cm<sup>2</sup> at 5 K and self field. The samples show a fine dispersion of Ti without precipitation of TiB<sub>2</sub> at grain boundaries, which is to be contrasted with the precipitation of TiB<sub>2</sub> in the solid state reaction route. Prikhna *et al.* have achieved better  $J_c - H$  performance of Ti doped MgB<sub>2</sub> using a high pressure of 2 Gpa [26]. Their interpretation was that the role of Ti addition is due to the absorption of hydrogen impurity to form TiH in the

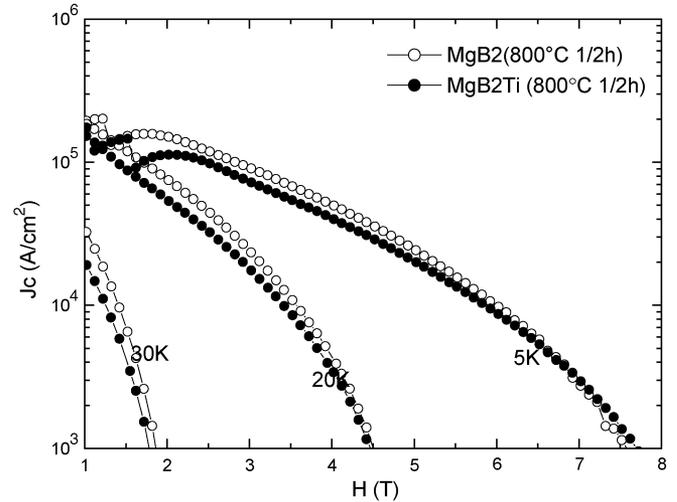


Fig. 5.  $J_c$  vs  $H$  for 10 wt% nano-scale Ti doped and undoped MgB<sub>2</sub>. This may be attributable to the scattering at Mg sites as a result of Al substitution for Mg. However, the authors' group attempted to confirm this but failed.

TABLE I  
SUMMARY OF VARIOUS DOPANTS ON  $J_c(H)$

Dopants	SiC	CNT, C	Si, MSi <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	Ti, BN	Fe, Al, Si <sub>3</sub> N <sub>4</sub> , Ag
Effect of $J_c(H)$	+++	+++	++	+	+-	--
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sample. However, for the normal unpressurized condition there is no hydrogen in the samples.

Thus, the effect of Ti doping remains unclear. Recently, the authors' group has carried out a systematic study on the effect of addition of nano-Ti. The results showed no improvement in  $J_c$  by nano-Ti doping as shown in Fig. 5, consistent with previously reported results using a nominal composition of Mg<sub>1-x</sub>Ti<sub>x</sub>B<sub>2</sub> [27]. It is evident that the effect of Ti doping on  $J_c$  is insignificant.

Al substitution for Mg has been studied by a number of groups with the major emphasis on the effect on  $T_c$ . Recently, Berenov *et al.* used a low level of Al, 1–2.5 at% doping, to minimize the reduction in  $T_c$ ; the  $J_c$  was enhanced for a doping level of 1 at% Al at 5 K and 5 T [28].

### VI. OXIDE AND OTHER COMPOUND DOPING

Wang *et al.* doped MgB<sub>2</sub> with nanoparticles of Y<sub>2</sub>O<sub>3</sub>, and obtained a significant improvement in the irreversibility field ( $H_{irr} = 11.5$  T) at 4.2 K due to the introduction of dispersed inclusions such as YB<sub>4</sub> [29]. However, the improvement in  $H_{irr}$  for the doped samples is less significant at 20 K. Both Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> doping was found to be detrimental to  $T_c$  and  $J_c$  of MgB<sub>2</sub> produced by the in-situ reaction route [30], [31].

The authors' group has studied doping effects on  $T_c$  and  $J_c - H$  behavior using nitride compounds including Si<sub>3</sub>N<sub>4</sub> and BN [32]. It was found that Si<sub>3</sub>N<sub>4</sub> reacted with Mg to form MgSi<sub>2</sub>, causing degradation in both  $T_c$  and  $J_c - H$  behavior. In contrast, BN is highly compatible with MgB<sub>2</sub>. There is little effect on  $T_c$  and  $J_c - H$  characteristics up to 20% addition, using an in-situ reaction route at an annealing temperature of 800°C (Table I).

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