A significant improvement in the superconducting properties of MgB2 by co-doping with graphene and nano-SiC

K S B De Silva  
*University of Wollongong*, kaludewa@uow.edu.au

X Xu  
*University of Wollongong*, xun@uow.edu.au

Xiaolin Wang  
*University of Wollongong*, xiaolin@uow.edu.au

D Wexler  
*University of Wollongong*, david_wexler@uow.edu.au

D Attard  
*University of Wollongong*, darrena@uow.edu.au

See next page for additional authors

Follow this and additional works at: [https://ro.uow.edu.au/engpapers](https://ro.uow.edu.au/engpapers)

Part of the Engineering Commons

https://ro.uow.edu.au/engpapers/5050

**Recommended Citation**

De Silva, K S B; Xu, X; Wang, Xiaolin; Wexler, D; Attard, D; Xiang, F; and Dou, S. X.: A significant improvement in the superconducting properties of MgB2 by co-doping with graphene and nano-SiC 2012, 802-805.  

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
Authors
K S B De Silva, X Xu, Xiaolin Wang, D Wexler, D Attard, F Xiang, and S. X. Dou

This journal article is available at Research Online: https://ro.uow.edu.au/engpapers/5050
A significant improvement in the superconducting properties of MgB₂ by co-doping with graphene and nano-SiC


Institute for Superconducting and Electronic Materials, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia

Received 17 April 2012; revised 22 June 2012; accepted 11 July 2012
Available online 17 July 2012

The effects of graphene (G) and nanosilicon carbide (SiC) co-doping on the superconducting properties of MgB₂ were studied using bulk samples. SiC remains one of the best dopants which can significantly improve the high field performance, while graphene is emerging as a new dopant for MgB₂, which can improve the zero field critical current density ($J_c$). The superconducting properties characterized by $J_c$, the intergrain connectivity, and the critical fields were significantly improved by the use of both SiC and graphene as dopants.

Due to the high critical temperature ($T_c$) of 40 K, intrinsically “weak link” free grain boundaries, and low fabrication cost MgB₂ is believed to be promising to replace conventional low $T_c$ superconductors in many cryogen-free applications, such as magnetic resonance imaging, cavities, flying wheels, high field magnets, etc. For practical applications that require carrying large supercurrents in the presence of a magnetic field improvements in the critical current density ($J_c$) have been the key research topic for MgB₂. So far extensive research has been undertaken to enhance the superconducting properties, such as the critical current density ($J_c$), upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$). A significant improvement in $J_c$ field dependence is one of the most important factors permitting its usage in industrial applications. Chemical doping has been identified as the simplest and cheapest way to improve the electronic structures of superconductors and their superconducting properties. In particular, carbon-containing dopants, including silicon carbide (SiC), nanocarbon, carbon nanotubes (CNTs), hydrocarbon/carbohydrate composites, graphite and graphene are effective means to improve the $J_c$ field dependence and $H_{c2}$ [1–9].

Among all the dopants SiC appears to be the most effective, resulting in a high density of micro-structural defects, favouring superior improvements in the superconducting properties compared with other carbon or carbon-based dopants [1]. However, as in many carbon dopants, SiC also has an adverse effect on $J_c$ in the low field region. On the other hand, graphene is a dopant which can improve $J_c$ in the low field region, through improved inter-grain connectivity [8–10]. In this work we report success with a significant improvement in $J_c$ in both low and high fields in MgB₂ with co-doping of graphene and nano-SiC. Our finding paves the way for MgB₂ to be useful in both high and low field applications.

Graphene and SiC co-doped bulk samples were prepared via a diffusion method from crystalline boron powder (99.999% pure, 0.2–2.4 μm), Mg powder (99% pure, 352 mesh), SiC (99% pure, <30 nm) and highly reduced chemically converted graphene (rCCG) as precursors. The detailed chemical synthesis of rCCG has been described in a previous work [9]. Initially boron and graphene powders were mixed at a weight ratio of MgB₂:graphene:SiC equal to 1:0.025:x, where x = 0, 5, or 7.5 wt.% SiC. The weight ratio of graphene was kept constant at 2.5 wt.% for co-doped samples, as this gave the optimum results in a previous work [8]. Powders were then pressed into pellets 13 mm in diameter and inserted into a soft iron tube at a stoichiometric ratio of Mg to B, plus excess Mg to compensate for the loss of Mg during sintering. The samples were sintered at 800 °C for 10 h in a quartz tube at a heating rate of 5 °C min⁻¹ in high purity argon gas (99.9% Ar). The phase identification and crystal structure investigations...
were carried out using an X-ray diffractometer (GBC MMA) with Cu Kα radiation (λ = 1.54059 Å). A JEOL JSM-7500FA field emission scanning electron microscope equipped with an ultra-thin window (UTW) JEOL hyper-minicup energy dispersive spectrometer was used for scanning electron microscopy (SEM) analysis. Transmission electron microscopy (TEM) was performed on powders using a JEOL 2011 200 keV analytical instrument. The superconducting transition temperature \( T_c \) was determined from the a.c. susceptibility measurements, and the magnetic \( J_c \) value was derived from the width of the magnetization loop using Bean’s model [11] using a physical properties measurement system. The resistivity measurements were conducted using the standard d.c. four probe technique under magnetic fields up to 13 T. The upper critical field \( H_{c2} \) and the irreversibility field \( H_{irr} \) were determined using the 90% and 10% criteria of \( R(T) \) for different applied fields, where \( R(T) \) is the normal state resistance near 40 K. The active cross-section \( A_F \) was calculated from the resistivity \( \rho \) from Rowell’s model [12].

According to the XRD patterns (Fig. 1a) the dominant phase within all the samples was MgB₂. As the SiC doping level increased Mg₂Si and unreacted SiC peaks can be seen with more pronounced peak intensities [13]. Figure 1b–f shows the field emission scanning electron microscopy (FESEM) backscattered images for doped and co-doped samples. There are four distinct grey scale intensities present in the images, with the backscattered images showing increasing brightness with atomic number. Region 1 is the darkest phase, indicating that it has the lowest relative atomic number. This phase is present at all levels of doping, and increases with the amount of SiC and graphene doping. EDS analysis confirmed the presence of Mg and B only in this phase (B-rich phase). Region 2 shows a lighter grey scale than region 1, indicating a higher relative atomic number. EDS confirmed the presence of Mg and B only, however with a higher Mg:B ratio being responsible for the increased grey scale intensity. The area fraction of region 2 increases with the doping level and always shows a higher area fraction than region 1. Region 3 is the most prominent phase in all samples, however, the relative amount decreases with the level of doping. EDS analysis of this area confirmed the presence of Mg, B, C, O and Si. Region 4 shows the brightest grey scale level, indicating that this phase has the highest relative atomic mass. EDS analysis confirmed the presence of Mg, B, C, O and Si, with significantly higher Si and O concentrations. The relative amount of this phase increased with the level of SiC doping. From the above observations it is clear that the addition of SiC contributes to the formation of Mg₂Si and B-rich phases, which has a favourable effect on improving flux pinning due to the formation of normal superconducting interfaces [14]. Figure 1d, is an enlarged view of the area circled in Figure 1e, which reveals the fine distribution of region 4 in the main MgB₂ matrix.

Preliminary TEM investigations were performed on powders prepared by the gentle grinding of bulk samples followed by deposition onto holey carbon support films. Here a 5 wt.% SiC co-doped sample was selected, due to the excellent \( J_c \) performance in low fields. While further investigation of sectioned bulk samples is required to fully characterise the distributions of minor phases, including Mg₂Si, MgO and unreacted SiC, the TEM investigations revealed that MgB₂ in the co-doped samples contained large concentrations of defects, typical of carbon-doped specimens. Furthermore, excess carbon was also present, both in the form of graphene or graphite and amorphous carbon. The TEM results obtained from the co-doped sample containing 5 wt.% SiC are shown in Figure 2. In the low magnification bright field image (Fig. 2a) the large circled area contains both MgB₂, confirmed by the electron diffraction pattern obtained from the large circled region, and either graphene or a graphitic decomposition product of the original graphene additive, as indicated by the diffraction spots.
grain connectivity were observed as one of the main benefits gained through graphene doping on MgB₂ [8,9]. This may be due to the presence of remaining graphene or graphitic decomposition products, as is evident in the TEM analysis, which could reside between grains, resulting in greater connectivity [9]. According to Rowel [12] factors such as porosity, density and the presence of impurities in the grains or on the grain boundaries need to be considered, as some factors affect the inter-grain connectivity while others affect the resistivity of the grains themselves, which ultimately affects the resistivity of the sample. Carbon substitution at boron sites increases the resistivity due to increased electron scattering and disorder. Doped and co-doped samples containing 5 wt.% SiC show better homogeneity, compared with 7.5 wt.% SiC-doped and co-doped samples, due to the low levels of secondary phases such as Mg₂Si and unreacted SiC, which reflect better grain connectivity, as is evident from the XRD analysis, FESEM images and A_F values. However, with increasing doping level higher resistivities were observed in the doped samples, due to both inferior grain connectivity and the higher carbon substitution. The presence of non-superconducting phases such as Mg₂Si and SiC leads to a shortened electron mean free path l, resulting in a reduced coherence length ε according to the equation 1/ε = 1/l + 1/ε₀ [16]. The residual resistivity ratio (RRR) gives a clue to the reduction in crystallinity or increased disorder, therefore decreased values of RRR for the doped samples compared with the undoped ones reflect the effect of doping on the disorder of the samples [17].

Figure 3 shows the in-field $J_c$ performance at 5 and 20 K for undoped, SiC-doped and co-doped bulk samples of MgB₂. The $J_c$ curves for the co-doped samples show a significant improvement over the undoped and doped samples at both 5 and 20 K. In a zero field (20 K) the sample co-doped with graphene and 5 wt.% SiC showed a quite high critical current density value of $5.77 \times 10^3 \text{ A cm}^{-2}$, and showed a 40% improvement compared with the undoped sample. It should be noted that the reduction in $T_c$ for this sample was less than 1 K, compared with the undoped sample. The enhancement in $J_c$ in a zero field can mainly be attributed to good connectivity. According to the resistivity analysis this sample exhibits the highest value of $A_F$, indicating an excellent grain to grain connectivity. The sample co-doped with graphene and 7.5 wt.% SiC shows a remarkable value of $J_c$, $2.08 \times 10^5 \text{ A cm}^{-2}$ at 5 K and 8 T, which is similar to the highest $J_c$ ever reported for bulk samples [6]. This is a nearly 46 times improvement compared with the undoped sample. The high level of carbon substitution at boron sites and the presence of a nano-sized Mg₂Si impurity phase significantly improved $J_c$ in high fields, by enhancing $H_{c2}$ and flux pinning (see Fig. 1d).

The temperature dependence of the upper critical ($H_{c2}$) and irreversibility ($H_{irr}$) fields are shown in the Figure 4. It can be seen that both $H_{c2}$ and $H_{irr}$ increased dramatically in all doped samples, compared with the undoped samples. The highest improvement in critical field was observed in the co-doped sample with 7.5 wt.% SiC. Such an improvement in the critical field was gained due to several reasons, such as (i) C substitu-

---

**Table 1. Critical temperature ($T_c$), resistivity at 40 and 300 K, residual resistivity ratio (RRR), and active cross-section ($A_F$) of undoped, SiC-doped and co-doped MgB₂ bulk samples.**

<table>
<thead>
<tr>
<th>SiC doping level (wt.%)</th>
<th>$T_c$ (K)</th>
<th>$\rho$ (\mu\Omega \text{ cm})</th>
<th>RRR</th>
<th>$A_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>300 K</td>
<td>40 K</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>38.87</td>
<td>46.65</td>
<td>12.74</td>
<td>3.65</td>
</tr>
<tr>
<td>5</td>
<td>38.13</td>
<td>40.20</td>
<td>12.80</td>
<td>3.14</td>
</tr>
<tr>
<td>5 + G</td>
<td>38.12</td>
<td>38.18</td>
<td>12.40</td>
<td>3.07</td>
</tr>
<tr>
<td>7.5</td>
<td>36.10</td>
<td>83.66</td>
<td>52.12</td>
<td>1.60</td>
</tr>
<tr>
<td>7.5 + G</td>
<td>35.60</td>
<td>87.00</td>
<td>52.00</td>
<td>1.67</td>
</tr>
</tbody>
</table>
tion for B sites, which results in an increase in intraband scattering, (ii) the formation of nano-domain structure, and (iii) the formation of a Mg$_2$Si impurity phase [18].

The effects of co-doping with graphene and nano-SiC with MgB$_2$ were systematically investigated. A significant improvement in critical current density in low fields was observed in the sample co-doped with graphene and 5 wt.% SiC, with only a small depression in $T_c$. This indicates that inter-grain connectivity was the dominant factor governing the performance of $J_c$ in zero fields, while high $H_{c2}$ and flux pinning govern the $J_c$ performance in high fields in graphene and nano-SiC with MgB$_2$ bulk samples. By combining the advantages of strong flux pinning with SiC doping and good connectivity with graphene doping co-doping is a novel approach that can be used to improve the superconducting properties in both low and high fields.

This research was performed with the support of the Australian Research Council (ARC) through project LP0989352. The authors would like to thank Dr S. Gambir and G.G. Wallace for providing graphene for this study, and P. Shamba, O. Shcherbakova, and W.X. Li for their helpful discussions. This work was supported by Hyper Tech Research Inc., OH, and the University of Wollongong.