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Superconducting Properties of Graphene Doped Magnesium Diboride

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1. Introduction

Graphene, carbon in the form of monolayer sheets, has revealed astonishing and unique chemical and physical properties, which have made it an extremely active research topic in both materials science and physics (Novoselov, K. S. et al., 2004). Through chemical and materials integration, graphene is being actively exploited in a range of technological applications (Stankovich, S. et al., 2006). Superconductors can carry electrical current without any energy dissipation. The combination of both graphene and a superconductor into a composite has great potential for electrical devices and large scale applications. MgB$_2$, a superconductor with a simple composition and two-gap feature has great potential for large current carrying applications, as demonstrated through a series of chemical dopings (Dou, S. X. et al. 2007). In the case of graphene’s, the strict two-dimensionality and its high electrical and thermal conductivities, make it an ideal candidate for integrating/doping into MgB$_2$ in order to improve the superconducting properties.

Substitutional chemistry can modify, in a controlled way, the electronic structures of superconductors and their superconducting properties, such as the transition temperature ($T_c$), critical current density ($J_c$), upper critical field ($H_{c2}$), and irreversibility field ($H_{irr}$). In particular, carbon containing dopants, including nano-meter sized carbon (nano-C), silicon carbide (SiC), carbon nanotubes (CNTs) and hydrocarbons/carbohydrates are effective means to enhance the $J_c$ field dependence and $H_{c2}$ (Ma, Y. et al., 2006, Senlouocz, B. J. et al., 2005, Kumakura, H. et al., 2004, Sumption, M. et al., 2005, Kim, J. H. et al., 2006, Wilke, R. H. T. et al., 2008). Upon graphene incorporation into MgB$_2$ it is expected that $H_{c2}$ and the flux pinning properties should be improved. Recently, high-throughput solution processing of large-scale graphene has been reported by a number of groups (Tung, V. C. et al., 2009, Kim, K. S. et al., 2009, Hernandez, Y. et al., 2008, Li, D. et al., 2008, Li, X. et al., 2008, Choucair, M. et al., 2009).

Based on the works of Choucair et al., sufficient quantities of graphene were obtained for doping the bulk MgB$_2$ samples via a diffusion process. It was demonstrate that graphene is the most efficient among all the carbon-based dopants used to date, in terms of enhancing the flux pinning behaviour in MgB$_2$. Very low levels of graphene doping (e.g. 0.9 at%) have been shown to be sufficient to lead to a significant improvement in the critical current density - field performance ($J_c(B)$), with little change in the transition temperature ($T_c$). At 3.7 at% graphene doping of MgB$_2$ an optimal enhancement in $J_c(B)$ was reached by a factor of 30 at 5 K and 10 T, compared to the un-doped reference.
sample. This improvement is believed to be related to: the single carbon sheet two-dimensional (2-D) geometry, the negative thermal expansion coefficient, high electron mobility, low resistivity, high thermal conductivity, and high mechanical strength of graphene. In contrast to many carbon-based dopants, where carbon substitution and hence scattering, is the dominant factor for enhancement of $J_c(B)$, the enhanced flux pinning is largely attributable to strong strain effects induced by the large difference between the negative coefficient of thermal expansion of graphene and the large, anisotropic coefficient of thermal expansion of MgB$_2$.

Fig. 1. Crystal structure of MgB$_2$, $a$=3.086 Å and $c$=3.524 Å (Nagamatsu, J. et al., 2001).

The most exciting result is the soften $E_{2g}$ mode in graphene added samples. It is well known that the superconductivity of intermetallic compound MgB$_2$ is self-optimized both in electronic structure and in phonon dispersion and slim chance is left to improve its superconducting transition temperature, $T_c$, above ~39.4 K (Nagamatsu, J. et al., 2001). Higher $T_c$ of MgB$_2$ and band structure calculation indicate that MgB$_2$ is a phonon-mediated BCS-Eliashberg superconductor with multiple gaps and strong electron-phonon coupling (EPC). As a two-gap superconductor, MgB$_2$ shows two qualitatively different Fermi surfaces: $\sigma$-band with extremely strong pairing strength and $\pi$-band with weak pairing strength. The $\sigma$-band contribution is dominant and specifically the contribution from its coupling with the B-B stretch modes with $E_{2g}$ symmetry in boron layer, the only Raman active phonon modes according to first principle calculation (Kunc, K. et al, 2001). the $T_c$ does not show improvements in the alloys due to carbon substitution and impurity scattering, a tensile strain effects assuredly exist in the alloys judging from both the width of superconducting energy gaps and the phonon behaviors.

2. Graphene doped polycrystalline MgB$_2$

MgB$_2$ is an intermetallic, polycrystalline material that had been known since 1953 and was used in the commercial preparation of elemental boron (B). It was not known to be superconducting until this property was accidentally discovered by Jun Akimitsu and his colleagues (Nagamatsu, J. et al., 2001). MgB$_2$ consists of alternating layers of boron and magnesium atoms in a hexagonal structure, as shown in Figure 1. It was analyzed that the crystal structure of MgB$_2$ using by the Rietveld method. It was found that the compound has hexagonal symmetry (Space Group P6/mmm) with the unit cell lattice parameters: $a =$
0.3086 nm and c = 0.3524 nm. Similar conclusions on the crystal structure were soon made on the basis of studies using high resolution transmission electron microscopy (HRTEM), high resolution powder neutron diffraction and electron energy loss spectroscopy. Up to now, large number of experimental and theoretical of works has been studied because of its high $T_c$ of 39 K. Beside the high $T_c$, simple crystal structure, large coherence length, high critical field, transparency of grain boundaries, and low normal state resistivity are a fascinating topic to study for both large scale application and electronic devices. Moreover, the presence of two-gap superconductivity ($\sigma$ and $\sigma^\prime$ band) has been theoretically and experimentally established besides it shows a significant isotope effect like a low temperature superconductor.

2.1 Dual reaction model and C doping effects in MgB$_2$

The “pure” MgB$_2$ is not so good for applications due to the poor flux pinning and low $J_c$, $H_{c2}$ and $H_{irr}$ values. A significant enhancement of critical current density ($J_c$) in MgB$_2$ can be achieved through chemical doping with various kinds of material. Chemical doping is a simple and readily scalable technique. A significant enhancement of critical current density ($J_c$) in MgB$_2$ can be achieved through chemical doping with carbon (C) containing composites or compounds, such as SiC, C, B$_4$C, or carbon nanotubes (CNT), hydrocarbon, carbohydrates etc. The C can enter the MgB$_2$ structure by substituting into boron (B) sites, and thus $J_c$ and $H_{c2}$ are significantly enhanced due to the increased impurity scattering in the two-band MgB$_2$.

In 2007, Dou et al has proposed a dual reaction model based on the following factors to explain the mechanism of enhancing the electromagnetic properties due to the SiC and C doping (Dou, S. X. et al. 2007):

- Demonstrated a dual reaction model in which the C substitution due to nano SiC doping and MgB$_2$ formation take place simultaneously at temperatures
- The C substitution and induced highly localised fluctuation in structure and $T_c$ are responsible for the enhancement in $J_c$, $H_{irr}$ and $H_{c2}$ by SiC doping.
- Disorder created by all means has universal influence on electromagnetic properties of MgB$_2$

- free and reactive C is the key to searching for better dopants
- Fig. 2 shows the effects of sintering temperature on the $J_c$(H) for different carbon based dopants. The hydrocarbon and SiC doped MgB$_2$ show significant enhancement in $J_c$ for the samples sintered at lower temperature, whereas the carbon and CNT doped MgB$_2$ need to be sintered at higher temperature for high $J_c$. The low sintering temperature results in small grain size, high concentrations of impurities and defects, and large lattice distortion, which are all responsible for a strong flux pinning force (Soltanian et al., 2005, Yamamoto et al., 2005). Furthermore, the hydrocarbon and SiC can release fresh and active free carbon at very low temperature, which means that the carbon substitution effects take place simultaneously with the MgB$_2$ formation. A high sintering temperature will perfect the crystallization and decrease the flux pinning centers in the MgB$_2$ matrix. That is the reason why high sintering temperature degrades the $J_c$ performance. Although high sintering temperature has the same shortcomings in nanosized carbon and CNT doped MgB$_2$, the carbon substitution effects improve their $J_c$ values. The high sintering temperature is necessary for carbon and CNT doped MgB$_2$ because the carbon and CNT are quite stable at low temperature and the substitution effects are absent if the sintering temperature is not high enough.
Fig. 2. The critical current density ($J_c$) at 4.2 K versus magnetic field for wires of pure MgB$_2$ and MgB$_2$ doped with C, SiC, SWCNTs, and malic acid that were sintered at different temperatures (Dou et al., 2002; Yeoh et al., 2006; Dou et al., 2007; Kim et al., 2008).

### 2.2 Gram-scale production of graphene

Graphite is the most common allotrope of carbon. The name is derived from the Greek verb graphein, ‘to write’, which relates very literally to the compound we now know as graphene, as single sheets of graphene were first isolated by simply tracing a sample of bulk graphite across a substrate in a process known as micromechanical cleavage (Novoselov, K. S. et al., 2004). Further attempts to synthesize isolated graphene have been based on intercalation (Li, X. et al., 2008), sonication in various solvents (Hernandez, Y. et al., 2008) and the chemical reduction of graphite to yield few-layer graphite oxide (Li, D. et al., 2008). Approaches developed for the production of carbon nanotubes have also been explored, but so far they have only been able to produce graphitic film (Dikin, D. A. et al., 2007). However, single- and few-layer graphene sheets have been grown epitaxially by the chemical vapour deposition of hydrocarbons on metal and nonmetal substrates, substrate-free deposition and by thermal decomposition of SiC. Given the lack of a reliable top-down approach for the large-scale production of graphene, attention has turned to bottom-up approaches that might be able to deliver the economies of scale that are found in the chemical and pharmaceutical industries. Choucair et al. have demonstrated that single-layer graphene can be synthesized by low-temperature flash pyrolysis of a solvothermal product of sodium and ethanol, followed by gentle sonication of the nanoporous carbon product (Choucair, M. et al., 2009).

All solvothermal reactions were performed in a Teflon-lined Parr Instrument Company 4749 reactor having a maximum volume of 23 ml. A typical synthesis consists of heating a 1:1 molar ratio of sodium (2 g) and ethanol (5 ml) in a sealed reactor vessel at 220°C for 72 h to yield the solid solvothermal product—the graphene precursor. This material is then rapidly pyrolysed, and the remaining product washed with deionized water (100 ml). The suspended solid is then vacuum filtered and dried in a vacuum oven at 100°C for 24 h. The final yield of graphene is approximately 0.1 g per 1 ml of ethanol—typically yielding ~0.5 g...
2.3 Graphene doping effects in MgB$_2$

Based on the works of Choucair et al., sufficient quantities of graphene were made available for doping the bulk MgB$_2$ samples. The bulk MgB$_2$ samples were fabricated via a diffusion process. The crystalline boron powder (0.2 to 2.4 µm) of 99.999% without and with graphene was prepared by ball milling with toluene medium. Then, the powders were dried in a vacuum oven to evaporate the medium. These powders were mixed and pressed into pellets. The pellets were then put into an iron tube filled with Mg powder (-325 mesh 99%). The samples were sintered at 850°C for 10 hrs in a quartz tube; the heating rate was 5°C/min under high purity argon (Ar 99.9%) gas. The phase and crystal structure of all the samples were investigated by X-ray diffraction (XRD). $T_c$ was defined as the onset temperature at which diamagnetic properties were observed. The magnetic $J_c$ was derived from the width of the magnetization loop using Bean’s model by a Physical Properties Measurement System (PPMS). Transport measurements for resistivity ($\rho$) were done using a standard AC four probe method. In addition, $H_{c2}(T)$ and $H_{irr}(T)$ were defined as the fields where the temperature dependent resistance at constant magnetic field $R(H_{c2}, T) = 0.9R_{ns}$ and $R(H_{irr}, T) = 0.1R_{ns}$ with $R_{ns}$ being the normal state resistance near 40 K. The hysteresis loops of the MgB$_2$ sample every 1.5 K in the 17-35 K range. The symmetric hysteresis loops with respect to the magnetic field indicate the dominance of bulk pinning up to temperatures near $T_c$.

MgB$_2$/Fe monofilament wires were prepared by an in situ reaction process and the powder-in-tube method. Magnesium (99%, 325 mesh), and the different boron powders with the nominal atomic ratio of Mg : B = 1.1 : 2 were mixed through grinding and were put into Fe
tubes with a length of 140 mm, an outer diameter (O.D) of 10 mm, and an inner diameter (I.D) of 8 mm. The packing process was carried out in air. Both ends of the tubes were sealed with aluminum pieces, and then the tubes were drawn to a wire with a diameter of 1.4 mm. Short wire samples (4 cm each) were sealed with Zr foil, then sintered with a heating rate of 5 °C min⁻¹ in flowing high purity Ar to 700-800 °C and held at the final temperature for 30 minutes, followed by a furnace cooling to room temperature. The transport current (I) at 4.2 K was measured by the standard dc four-probe resistive method with a criterion of 1 μV cm⁻¹ in magnetic fields up to 12 T. Tc was determined using the standard ac four-probe method.

In addition, Hc2(T) and Hirr(T) were defined as the fields where the temperature dependent resistance at constant magnetic field R(Hc2, T) = 0.9Rns and R(Hirr, T) = 0.1Rns, respectively, with Rns being the normal state resistance near 40 K. Mg(B1-xCrx)2 with x=0, 0.037, was used. The composition of graphene doped MgB2 were 0, 3.7 at%, and as such, the samples are designated as G000, and G037 respectively.

### 2.3.1 XRD analysis for bulk samples

Fig. 4 shows XRD patterns for the pure and graphene doped MgB2 samples. All the peaks are inherent to MgB2. No impurity phase was detected in the XRD data, however a slight peak shift to higher angle is noted for the G087 samples. MgO, which is commonly present in most bulk MgB2 samples is absent in all the samples.

The lattice parameters, a, c, the ratio of a/c, grain size, strain, and full width at half maximum of the representative peak (110) calculated from the XRD patterns are shown in Table 1. Both the a-axis and c-axis parameters vary little with increasing graphene doping level of 3.7%, apart from G087 sample, which shows a notable decrease in the a-axis parameter, suggesting that carbon (C) likely substitutes into the boron (B) sites, leading to a slight drop in Tc (36.7 K) for the G087 sample. It was also observed that the full width at half maximum (FWHM) of the (110) peak increases with increasing graphene doping level. Such a peak broadening is caused by both grain size reduction and an increase in lattice strain. The calculated results on grain size and lattice strain from a Williamson-Hall plot (Williamson, G. K., and Hall, W. H., 1953) are given in Table 1. Transition temperatures (Tc) for the graphene doped samples were determined by AC susceptibility measurements. Also, the Tc onset determined from the AC susceptibility measurement is 38.9 K for the un-doped sample, dropping only slightly to 37.7 and 36.7 K for the G037 and G087 samples, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Constants</th>
<th>Grain Size (nm)</th>
<th>Strain (%)</th>
<th>FWHM (110) (°)</th>
<th>Tc (onset) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G000</td>
<td>3.084(1) 3.525(1)</td>
<td>1.143(1)</td>
<td>216(10)</td>
<td>0.1198(188)</td>
<td>0.288 38.9</td>
</tr>
<tr>
<td>G037</td>
<td>3.082(1) 3.527(1)</td>
<td>1.144(1)</td>
<td>170(8)</td>
<td>0.1685(250)</td>
<td>0.400 37.7</td>
</tr>
<tr>
<td>G087</td>
<td>3.075(1) 3.525(1)</td>
<td>1.146(1)</td>
<td>171(11)</td>
<td>0.1782(330)</td>
<td>0.414 36.7</td>
</tr>
</tbody>
</table>

Table 1. The full width at half maximum (FWHM) of the (110) peak, the lattice parameters, and the transition temperature (Tc) for the MgB2 samples, made with 0, 3.7, and 8.7 at% graphene doping via a diffusion process (Xu, X. et al., 2010).
2.3.2 Critical current density

Graphene is the most efficient among all the carbon-based dopants used to date, in terms of enhancing the flux pinning behaviour in MgB$_2$. Very low levels of graphene doping (e.g. 0.9 at%) have been shown to be sufficient to lead to a significant improvement in the critical current density - field performance ($J_c(B)$), with little change in the transition temperature ($T_c$). At 3.7 at% graphene doping of MgB$_2$ an optimal enhancement in $J_c(B)$ was reached by a factor of 30 at 5 K and 10 T, compared to the un-doped reference sample. In contrast to many carbon-based dopants, where carbon substitution and hence scattering, is the dominant factor for enhancement of $J_c(B)$, the enhanced flux pinning is largely attributable to strong strain effects induced by the large difference between the negative coefficient of thermal expansion of graphene and the large, anisotropic coefficient of thermal expansion of MgB$_2$.

The common format Mg(B$_{1-x}$C$_x$)$_2$ with $x=0$, 0.037, and 0.087 was used. The composition of graphene doped MgB$_2$ were 0, 3.7, and 8.7 at%, and as such, the samples are designated as G000, G037, and G087, respectively. Fig.5 shows the magnetic $J_c(B)$ curves at 5 K and 20K for all the samples, which were sintered at 850°C for 10 hours. The $J_c(B)$ values for all the doped samples are higher than the un-doped sample at high fields. The sample G037 gives the highest $J_c$ at high fields: $J_c$ increases by a factor of 30 at 5 K for the field of 10 T, as compared to the un-doped sample, G000. Even though the $J_c$ in the low field regime is depressed, a higher doping level (G087), still results in the rate of $J_c$ dropping much slower than the un-doped sample, clearly indicating strong flux pinning induced by the graphene doping. The most significant effect of graphene doping is the high effectiveness of graphene to improve flux pinning at lower doping levels, which distinguishes graphene from any other C containing dopants, for example, the $J_c$ for G037 reached 20,000 A/cm$^2$ at 5 K and 8 T, exceeding or matching the best $J_c$ resulting from dopants such as SiC, CNT, and carbohydrates at their optimal doping level of 10 at%, as well as nano-C at its optimal...
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Fig. 5. Magnetic critical current density as a function of magnetic field at 5 K and 20K for with and without graphene doped bulk samples. 5 at% nano-C doped sample for a comparable result at the same sample preparation route (Xu, X. et al., 2010).

doping level of 5-6.4 at.%. In the latter case, the $T_c$ is substantially reduced to temperatures as low as 30 K. Compared to the graphite doped MgB$_2$ pallets prepared through the ball-milling and HIP the $J_c$ of graphite doped MgB$_2$ is better than graphene doping at 5 K (Yamamoto et al., 2005), but at 20K, the $J_c$ for graphene doping is much better than graphite. For example, the $J_c$ for the graphene doped MgB$_2$ at 20 K and 6 T is larger than that for graphite doped MgB$_2$ by a factor of 50 (Yamamoto et al., 2005). In comparison, low levels of graphene doping have little effect on $T_c$ and cause only a very small increase in impurities, not compromising the significant enhancement in $J_c$ in high fields by the degradation in low-field $J_c$, which is a common issue for all other C based dopants. In order to see the difference with other C based dopants, the same preparation route was applied to 5 at% nano-C doped sample and the resultant decrease in $J_c$ at 20K can be seen in the figure 5, because the $T_c$ for nano- C doped MgB$_2$ is only 34K.

The transport current $J_{ct}$-B performance of the two kinds of the samples sintered at temperatures from 700 °C to 800 °C, denoted by, WG37S7, WG37S8 for 3.7 at% graphene doped and WG0S7, and WG0S8 for undoped wire sample, respectively, is shown in Figure 6. It can be clearly seen that $J_{ct}$ of samples prepared from the doped wire sample showed better performance in the field range of 4 to 15 T. This indicates that the most significant effect of graphene doping is the high effectiveness of graphene to improve flux pinning at lower doping levels. The strong enhancement in the flux pinning may be attributable to a combination of C substitution for B and thermal strain-induced defects. It is very surprising that if compared to the magnetic $J_{cm}$ with the bulk MgB$_2$ samples via a diffusion process under magnetic fields of 5 to 10 T, the transport $J_{ct}$ increment with the wire MgB$_2$ via the powder-in-tube (PIT) method is tremendous lower from Fig.6. The transport current capacity is the real useful $J_c$ that flows through the whole of the sample. It can be understand, the difference between $J_{cm}$ and $J_{ct}$ in MgB$_2$ may be related to features of the microstructure of the superconducting MgB$_2$ core, such as porosity, agglomeration of...
superconducting crystals, and fraction of impurities as the main secondary phase by different fabricated processing (Horvat, J. et al., 2008). It is clearly that the graphene doped bulk sample via the diffusion process had the highest mass density, which improved the most inter-grain connectivity to improve the \( J_c \) so much. At the same time, according to the Rowell connectivity analysis, the calculated active cross-sectional area fraction \( (A_F) \) represents the connectivity factor between adjacent grains, which is estimated by comparing the measured value with that of a single crystal. (Rowell, J. M., 2003). The \( A_F \) for all wire samples via the powder-in-tube (PIT) method is almost half of the bulk sample via diffusion process. With the wire doped samples, the \( A_F \) value was increased as the sintering temperature increased. This indicates that additional grain growth occurs due to high temperature sintering. The larger grains are also accompanied by improved density and grain connectivity. So, in order to improve the \( J_c \) of the wire sample, the key point is how to improve the inter-grain connectivity.

2.3.3 Flux pinning mechanism

Regarding the flux pinning mechanism, it is established that the core interaction, which stands for the coupling of the locally distorted superconducting properties with the periodic variation of the superconducting order parameter is dominant over the magnetic interaction for MgB\(_2\) due to its large GL coefficient \( \kappa \) (\(~26\) in MgB\(_2\)). The core interaction includes two types of mechanism: \( \delta T_c \) and \( \delta l \) pinning. The \( \delta T_c \) pinning refers to the spatial variation of the GL coefficient associated with disorder due to variation in the transition temperature \( T_c \), while \( \delta l \) pinning is associated with the variation in the charge-carrier mean free path \( l \) near lattice defects. According to the collective pinning model, the disorder induced spatial fluctuations in the vortex lattice can be clearly divided into different regimes depending on the strength of the applied field: single-vortex, small-bundle, large-bundle, and charge-density-wave (CDW)-type relaxation of the vortex lattice. The crossover field, \( B_{sb} \) is defined as a field separating single vortex regime into small bundles of vortices. Below \( B_{sb} \) \( J_c \) is almost field independent. The \( B_{sb} \) as a function of reduced temperature \( (t=T/T_c) \) is described by the equation (Qin, M. J. et al, 2002):
\[ B_{sb} = B_{sb}(0) \left( \frac{1 - t^2}{1 + t^2} \right)^{2/3} \]  

(1)

for \( \delta T_c \) pinning,

\[ B_{lb} = B_{lb}(0) \left( \frac{1 - t^2}{1 + t^2} \right)^2 \]  

(2)

for \( \delta l \) pinning.

To define the pinning mechanism in our graphene doped samples, the crossover field, \( B_{sb} \), as a function of temperature with graphene doped sample (G037) is plotted in Figure 7 as red squares. \( B_{sb} \) is defined as a field where \( J_c \) drops by 5% only compared to \( J_c \) at zero field. It can be seen that the curve for \( \delta T_c \) pinning calculated from Eq. (1) is in a good agreement with the experimental data, whereas, the curve for \( \delta l \) pinning according to Eq. (2) does not fit to the experimental data. For polycrystalline, thin film, and single crystalline MgB\(_2\) samples, it has been found that the dominant pinning mechanism is \( \delta T_c \) pinning, which is related to spatial fluctuation of the transition temperature while most C-doped MgB\(_2\) samples displayed \( \delta l \) pinning mechanism (Wang, J. L. et al., 2008) as a result of strong scattering and hence the shortening of the mean free path \( l \) owing to the presence of large amount of impurities in the doped samples. This is reflected by the significant increase in the residual resistivity. The local strain was suggested to be one of potential pinning centres.

Fig. 7. The crossover field \( B_{sb} \) as a function of temperature with graphene doped sample (G037) (Xu, X. et al., 2010)

However, we do not have strong evidence that the dominant pinning in the graphene doped MgB2 is due to the local strain effect alone. In contrast, the graphene doping sets an exceptional example, following the \( \delta T_c \) pinning rather than \( \delta l \) pinning mechanism. This demonstrates the unique feature of the graphene doping. The amorphous phases can also
act pinning centres, which is in favour for $\delta T_c$ pinning. Although the graphene doped samples have a lot of defects these samples contain low concentration of impurities compared to the samples by other forms of carbon dopants. One of major differences of graphene doping from other dopants is that the samples are relatively pure as evidenced by the low resistivity ($20 \mu\Omega\text{cm}$) in the graphene doped samples. Normally, the resistivity in carbon doped MgB$_2$ ranges from $60 \mu\Omega\text{cm}$ to as high as $300 \mu\Omega\text{cm}$. The high electrical connectivity is beneficial for $J_c$ in low magnetic fields and high field performance; however we can not find any correlation between electrical connectivity with the $J_c$ in the case here. The graphene doped samples have higher resistivity than the un-doped MgB$_2$ sample ($3 \mu\Omega\text{cm}$), indicating electron scattering caused by graphene doping levels. But, it should be pointed out that the increase in resistivity is much smaller than for any other forms of carbon doped MgB$_2$. Which is shown in Figure 8.

2.3.3 $E_{2g}$ mode and Raman peak shift

Tensile strain effects on superconducting transition temperature ($T_c$) was observed in graphene-MgB$_2$ alloys to pursue high $T_c$ in multi-gap superconductors. The enhancement of energy gap for $\pi$-band indicates the weak rescale of density of state on Fermi surface. The $E_{2g}$ mode split into two parts: one dominant soften mode responding to tensile strain and another harden mode responding to carbon substitution effects.

![Fig. 8. The temperature dependence of the resistivity ($\rho$) measured in different fields for doped and undoped samples.](image)

The existence of soften $E_{2g}$ mode in bulk samples suggests that modified graphene-MgB$_2$ alloys are the potential candidates for the high performance superconducting devices. To confirm the effect of tensile strain on EPC, Raman scattering was employed for measurement of phonon properties by a confocal laser Raman spectrometer (Renishaw inVia plus) with a 100× microscope. The 514.5 nm line of an Ar$^+$ laser was used for excitation and several spots were selected on the same sample to collect the Raman signals to make sure that the results were credible. Fig. 9(a) shows the typical spectrum of pure MgB$_2$ consisting of three broad peaks. The most prominent phonon peak located at lower frequency ($\omega_2$: centered at $\sim$600 cm$^{-1}$) is assigned to the $E_{2g}$ mode. The other two Raman bands ($\omega_1$: centered at 400 cm$^{-1}$ and $\omega_4$: centered at 730 cm$^{-1}$) have also been observed earlier.
in MgB\textsubscript{2} and attributed to phonon density of states (PDOS) due to disorder. The EPC strength in MgB\textsubscript{2} depends greatly on the characteristic of \( E_{2g} \) mode, both frequency and FWHM, while the other two modes, especially the \( \omega_4 \) mode, are responsible for the \( T_c \) depression in chemically doped MgB\textsubscript{2} (Kunc, K. et al, 2001). The graphene addition in MgB\textsubscript{2} induces splitting of \( E_{2g} \) mode: one soften mode (\( \omega_2 \)) and another harden mode (\( \omega_3 \)), as shown in Fig. 9. \( \omega_2 \) shifts to low frequency quickly with the graphene addition because of the strong tensile strain. The softness of \( E_{2g} \) mode was observed only in MgB\textsubscript{2}–SiC thin films due to tensile strain-induced bond-stretching, which resulted in a \( T_c \) as high as 41.8 K. Although \( \omega_2 \) modes are dominant in low graphene content samples, \( T_c \) drops slightly. This is in agreement with the energy gap behaviors because of the carbon substitution induced band filling and interband scattering. \( \omega_2 \) is marginal in G10 and vanishes in G20. \( \omega_3 \) shifts to high frequency slowly in low graphene content samples because the tensile strain has confined the lattice shrinkage. However, the tensile strain can not counteract the intensive carbon substitution effects when the graphene content is higher than 10 wt\% and \( \omega_4 \) takes the place of \( \omega_2 \). It should be noted that \( \omega_3 \) is not as dominant as \( \omega_2 \) in pure MgB\textsubscript{2} and \( \omega_4 \) is the strongest peak as in the other carbonaceous chemical doped MgB\textsubscript{2} due to lattice distortion. Furthermore, another peak \( \omega_5 \) has to be considered in G10 and G20 to fit the spectra reasonably. The Raman spectrum of G20 was separated from the mixed spectra of MgB\textsubscript{2} and MgB\textsubscript{2}C\textsubscript{2} based on their different scattering shapes: MgB\textsubscript{2} shows broaden and dispersed waves, while MgB\textsubscript{2}C\textsubscript{2} shows sharp peaks (Li, W. X. et al., 2008).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig9.png}
\caption{The typical spectrum of MgB\textsubscript{2} consisting of three broad peaks}
\end{figure}

The tensile strain was unambiguously detected in graphene-MgB\textsubscript{2} alloys made by diffusion process and the \( \pi \) energy gap was broadening with the graphene addition. The bond-stretching \( E_{2g} \) phonon mode splits into one soften mode due to the tensile strain and another harden mode due to the carbon substitution on boron sites. Although \( E_{2g} \) mode splitting have been observed in C doped MgB\textsubscript{2}, both the two peaks shift to higher frequency and this is the first time to observe the coexistence of two modes shifting to opposite directions. The \( T_c \) value does not show enhancement because of impurity scattering effects and carbon substitution. However, higher \( T_c \) values are expected in graphene-MgB\textsubscript{2} alloys processed by proper techniques or made of stabilized graphene.
2.3.4 Upper critical field and irreversibility field

Figure 10 shows the upper critical field, $H_{c2}$, and the irreversibility field, $H_{irr}$, versus the normalised $T_c$ for all the samples. It is noted that both $H_{c2}$ and $H_{irr}$ are increased by graphene doping. The mechanism for enhancement of $J_c$, $H_{irr}$, and $H_{c2}$ by carbon containing dopants has been well studied. The C can enter the MgB$_2$ structure by substituting into B sites, and thus $J_c$ and $H_{c2}$ are significantly enhanced due to the increased impurity scattering in the two-band MgB$_2$ (Gurevich, A., 2003). Above all, C substitution induces highly localised fluctuations in the structure and $T_c$, which have also been seen to be responsible for the enhancements in $J_c$, $H_{irr}$, and $H_{c2}$ by SiC doping.

Fig. 10. Upper critical field, $H_{c2}$, and irreversibility field, $H_{irr}$, versus normalised transition temperature, $T/T_c$, for all graphene doped and undoped MgB$_2$ samples (Xu, X. et al., 2010).

Furthermore, residual thermal strain in the MgB$_2$-dopant composites can also contribute to the improvement in flux pinning (Zeng, R. et al. 2009). In the present work, the C substitution for B (up to 3.7 at.%) graphene doping is lower, from the table 1, the change of the $a$-parameter is smaller, according to Avdeev et al result (Avdeev, M. et al., 2003), the level of C substitution, $x$ in the formula Mg(B$_{1-x}$C$_x$), can be estimated as $x = 7.5 \times \Delta(c/a)$, where $\Delta(c/a)$ is the change in $c/a$ compared to a pure sample. As both the $a$-axis and the $c$-axis lattice parameters determined from the XRD data showed little change within this doping range the level of carbon substitution is low at this doping level. This is in good agreement with the small reduction in $T_c$ over this doping regime. At 8.7 at% doping, there is a noticeable drop in the $a$-axis parameter, suggesting C substitution for B, which is also consistent with the reduction in $T_c$. The source of C could be the edges of the graphene sheets, although the graphene is very stable at the sintering temperature (850°C), as there have been reports of graphene formation on substrates at temperatures ranging from 870-1320°C (Coraux, J. et al., 2009). The significant enhancement in $J_c$ and $H_{irr}$ for G037 can not be explained by C substitution only.

2.3.5 Microstructure by TEM

The microstructure revealed by high resolution transmission electron microscope (TEM) observations show that G037 sample has grain size of 100-200 nm which is consistent with
value of the calculated grain size in table 1. The graphene doped samples have relatively higher density of defects compared with the undoped sample as shown in the TEM images of figure 11(a) and (c). The density of such defects is estimated to be 1/3 areas of TEM images, indicating high density in the doped samples. In figures 11(b) it should be noted that the order of fringes varies from grain to grain, indicates that the defect is due to highly anisotropic of the interface.

Fig. 11. (a) TEM image showing the defects with grains of the G037 sample with order of fringes varies between grains. Defects and fringes are indicated by arrow, and (b) HRTEM image of fringes. TEM images show large amount of defects and fringes can be observed in the graphene doped sample G037. (c) TEM image of the undoped sample for reference (Xu, X. et al., 2010).
Similar fringes have been reported in the MgB\textsubscript{2} (Zeng, R. et al. 2009), where these fringes were induced by tensile stress with dislocations and distortions which were commonly observed in the areas. As the graphene doped samples were sintered at 850°C for 10 hrs, the samples are expected to be relatively crystalline and contain few defects. Furthermore, as already shown above the C substitution level is low in graphene doped samples. Thus, the large amount of defects and amorphous phases on the nanoscale can be attributed to the residual thermal strain between the graphene and the MgB\textsubscript{2} after cooling because the thermal expansion coefficient of graphene is very small while that for MgB\textsubscript{2} is very large and highly anisotropic. The large thermal strain can create a large stress field, and hence structure defects and lattice distortion. These defects and distortions on the order of the coherence length, $\xi$, can play a role as effective pinning centres that are responsible for the enhanced flux pinning and $J_c$ in the graphene doped MgB\textsubscript{2}. The thermal strain-induced enhancement of flux pinning has also been observed in the SiC-MgB\textsubscript{2} composite as there is a noticeable difference in thermal expansion coefficient between MgB\textsubscript{2} and SiC (Coraux, J. et al., 2009).

3. Conclusion

In conclusion, the effects of graphene doping on the lattice parameters, $T_c$, $J_c$, and flux pinning in MgB\textsubscript{2} were investigated over a range of doping levels. By controlling the processing parameters, an optimised $J_c(B)$ performance is achieved at a doping level of 3.7 at.%. Under these conditions, $J_c$ was enhanced by an order of magnitude at 8 T and 5 K while $T_c$ was only slightly decreased. The strong enhancement in the flux pinning is argued to be attributable to a combination of C substitution for B and thermal strain-induced defects. Also, the evidence from collective pinning model suggests the $\delta T_c$ pinning mechanism rather than the $\delta l$ pinning for the graphene doped MgB\textsubscript{2} contrary to most doped MgB\textsubscript{2}. The strong enhancement of $J_c$, $H_{c2}$, and $H_{irr}$ with low levels of graphene doping is promising for large-scale MgB\textsubscript{2} wire applications.

Tensile strain effects on superconducting transition temperature ($T_c$) was observed in graphene-MgB\textsubscript{2} alloys to pursue high $T_c$ in multi-gap superconductors. The enhancement of energy gap for $\Omega$-band indicates the weak rescale of density of state on Fermi surface. The $E_{2g}$ mode split into two parts: one dominant soften mode responding to tensile strain and another harden mode responding to carbon substitution effects. The existence of soften $E_{2g}$ mode in bulk samples suggests that modified graphene-MgB\textsubscript{2} alloys are the potential candidates for the high performance superconducting devices.

The effects of graphene doping in MgB\textsubscript{2}/Fe wires were also investigated. At 4.2K and 10T, the transport $J_c$ was estimated to be for the wire sintered at 800°C for 30 minutes, the doped sample is almost improved as one order, compared with the best un-doped wire sample. The strong enhancement of the temperature dependence of the upper critical field ($H_{c2}$) and the irreversibility field ($H_{irr}$) is found from the resistance ($R$) - temperature ($T$). But the calculated active cross-sectional area fraction ($A_F$) represents the connectivity factor between adjacent grains is lower, which is the main factor to improve transport $J_c$ in limitation. It should mention that in recently research activity, two groups can improve the mass density and the grain connectivity very well. One is the internal Mg diffusion processed (IMD) multi-filamentary wire, which is developed by Togano (Hur, J. M. et al., 2008). The other one is the cold high pressure densification (CHPD) in-situ MgB\textsubscript{2} wire by Flukiger 18. If can
combine these methods with the graphene doping, the strong enhancement of $J_c$, $H_{c2}$, and $H_{irr}$ with low levels of graphene doping is promising for large-scale MgB$_2$ wire in industrial applications.

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5. References


Soltanian, S. et al. (2005). High transport critical current density and large $H_{c2}$ and $H_{irr}$ in nanoscale SiC doped MgB$_2$ wires sintered at low temperature. *Superconductor Science & Technology*, Vol 18, No. 5, pp. 658-666, ISSN 0953-2048


This book is a collection of the chapters intended to study only practical applications of HTS materials. You will find here a great number of research on actual applications of HTS as well as possible future applications of HTS. Depending on the strength of the applied magnetic field, applications of HTS may be divided in two groups: large scale applications (large magnetic fields) and small scale applications (small magnetic fields). 12 chapters in the book are fascinating studies about large scale applications as well as small scale applications of HTS. Some chapters are presenting interesting research on the synthesis of special materials that may be useful in practical applications of HTS. There are also research about properties of high-Tc superconductors and experimental research about HTS materials with potential applications. The future of practical applications of HTS materials is very exciting. I hope that this book will be useful in the research of new radical solutions for practical applications of HTS materials and that it will encourage further experimental research of HTS materials with potential technological applications.

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