Superconductivity in $\text{MgB}_2$ doped with $\text{Ti}$ and $\text{C}$

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Abstract

Measurements of the superconducting upper critical field, $H_{c2}$, and critical current density, $J_c$, have been carried out for $\text{MgB}_2$ doped with $\text{Ti}$ and/or $\text{C}$ in order to explore the problems encountered if these dopants are used to enhance the superconducting performance. Carbon replaces boron on the $\text{MgB}_2$ lattice and apparently shortens the electronic mean free path of $\text{MgB}_2$ and raising $H_{c2}$. Titanium forms precipitates of either $\text{TiB}$ or $\text{TiB}_2$ that enhance the flux pinning and raise $J_c$. Most of these precipitates are intra-granular in the $\text{MgB}_2$ phase. For samples containing both $\text{C}$ and $\text{Ti}$ doping, the $\text{C}$ appears to still replace $\text{B}$ in the $\text{MgB}_2$ lattice and the $\text{Ti}$ precipitates out as a boride. If approximately 0.5% $\text{Ti}$ and approximately 2% $\text{C}$ are co-deposited with $\text{B}$ to form doped boron fibers and these fibers are in turn reacted in $\text{Mg}$ vapor to form doped $\text{MgB}_2$, the resulting superconductor has $\mu_0H_{c2}(T = 0) \sim 25 \, T$ and $J_c \sim 10,000 \, \text{A/cm}^2$ at $5 \, \text{K}$ and $2.2 \, T$.

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I. INTRODUCTION

The performance of MgB$_2$ superconducting materials can be greatly enhanced by the addition of small amounts of carbon that will raise the upper critical magnetic field, $H_{c2}$, and the critical current density, $J_c$. Point defects like carbon that substitute for boron in the host lattice have been shown to raise $\mu_0H_{c2}(T = 0)$ from 16 T in pure MgB$_2$ to 32 T for a carbon level of $\sim 4\%$. At higher carbon contents, $\mu_0H_{c2}$ rises more slowly and eventually drops to about 25 T at $\sim 10\%$ carbon. Several different precipitate phases have been used to form small pinning sites in the MgB$_2$ lattice. For example, SiC, YB$_4$, TiB$_2$, and MgSi$_2$ have been added and show a rise of $J_c$ into the range of $10^6 A/cm^2$ at 10 K and self field with about 5% precipitate additions. In many of these experiments, either a powder-in-tube (PIT) process or a pressed and sintered pellet method have been used to form the precipitates for the synthesis.

In a different approach to sample preparation, a chemical vapor deposition, CVD, method can be used to co-deposit B together with a doping element to form long lengths of carbon doped boron fiber. Subsequent heat treatment in Mg vapor transforms the doped boron into doped MgB$_2$. Both the CVD and powder methods have advantages. The advantage of powder methods is that the diffusion lengths are comparable to the powder size giving relatively low reaction temperatures and short reaction times. The advantage of co-depositing the impurity with the B in a CVD process is that the impurity is mixed with the B on an atomic scale. Both Ti and C separately have been successfully doped into MgB$_2$ using these CVD methods.

The purpose of the work reported here is to study the combined C and Ti doping of MgB$_2$ to determine whether samples can be prepared with the combined benefits of both dopants, raising $\mu_0H_{c2}$ to the range of 30 T and raising $J_c$ values to the range of $10^4 A/cm^2$ at 20 K and 5 T. Two specific questions need to be addressed. Does the addition of Ti to the C-doped MgB$_2$ samples reported earlier reduce the amount of C in the MgB$_2$ lattice, possibly by forming TiC precipitates? In the presence of C, can the Ti precipitate size be maintained at $\sim 5 nm$ for high $J_c$ performance?
II. EXPERIMENTAL

Long lengths of doped boron fiber are prepared in a CVD apparatus similar to that used for commercial boron filament production. All of the materials reported here were deposited on a W fiber with an initial diameter of about 15µm. The W enters the reaction chamber moving at a few cm/s through a Hg seal into a long glass tube containing flowing H₂, BCl₃, CH₄, and TiCl₄. For Ti doping, H₂ is bubbled through liquid TiCl₄ to provide TiCl₄ molecules in the gas stream. Typically the BCl₃ flow rate was 3 l/min with the CH₄ and TiCl₄ flow rates adjusted for the desired doping levels. The diameter of the exiting doped B fibers were in the 75µm to 100µm range. The doped B fibers were cut to lengths of ∼3 cm and placed in a Ta tube with a Mg to B ratio of 1 : 1. The Ta was welded shut, sealed in a quartz tube, and heat treated in a box furnace for appropriate periods. Upon removal from the furnace, ampoules were quenched in water. Resistivity measurements are made by a four contact method using silver epoxy to make the electrical contacts. A Quantum Design PPMS system was used to make resistivity vs temperature, ρ vs. T, measurements up to 14 T. At higher fields, ρ vs. H measurements are made in a 32.5 T copper coil magnet at the National High Magnetic Field Laboratory at Florida State University. Magnetization measurements were made in a Quantum Design SQUID magnetometer with a magnetic field range of 5.5 T and JC was determined from the magnetization hysteresis using the Bean Model for cylindrical shell samples. A Philips CM30 transmission electron microscope (TEM) was employed for the microstructure characterization. Samples for the TEM were made using a crush-flow technique.

III. Ti-DOPING ONLY

In an earlier publication, we investigated a series of Ti-doped MgB₂ samples that were deposited on a commercial carbon coated SiC fiber substrate with a diameter of approximately 80 µm instead of the 15 µm diameter W substrate used here. The doped-MgB₂ layers ranged from about 4 µm to 10 µm thick. Flux pinning was excellent and gave JC over 10,000 A/cm² at 25 K and 1.3 T for a sample with an average doping of about 9%Ti. Unfortunately, there were problems with this approach to sample preparation. First, the diffusion of Mg into the B caused swelling and the MgB₂ pulled away from the substrate.
Second, the presence of a carbon coated substrate made the amount of C in the specimen uncertain. In addition, these samples had a rather inhomogeneous Ti distribution. There was a high Ti level near the SiC core and near the outer surface of the fiber. Transmission electron microscope (TEM) observations for one of these samples that had been reacted for 2 h at 950°C are shown in Fig. 1a. Results reveal a random distribution of precipitates scattered through the grain, ranging in size from 1 nm to 20 nm with a spacing about 5 times as large. Energy dispersive spectroscopy for a large portion of the grain in Fig. 1a, revealed that the Ti/Mg ratio was ∼ 5%. Selected area diffraction taken along the c-axis showed the prominent hexagonal pattern of MgB₂ with additional powder pattern rings arising from the titanium boride precipitates. The beam was then tipped off axis to show the rings more prominently. Indexing the rings revealed that the precipitates were TiB rather than TiB₂. These results differ from those found by Zhao and coworkers. They found that samples prepared by mixing powders of Mg, Ti, and B and reacting gave TiB₂ precipitates on the MgB₂ grain boundaries. This illustrates that different sample preparation methods can yield different types and locations of the precipitates. Both the precipitation of TiB throughout the grains and precipitation of TiB₂ on the grain boundaries seem to give enhanced flux pinning.

Samples with 15 µm diameter tungsten cores were prepared using three different TiCl₄ flow rates in the CVD reactor, 0.42 cc/min, 1.26 cc/min and 2.9 cc/min. After the CVD deposition, the fibers were reacted in Mg vapor to form Ti-doped MgB₂. Energy dispersive spectra (EDS) in a scanning electron microscope (SEM) was used to probe the uniformity of Ti distribution across the superconducting fiber and to measure the Ti to Mg ratio, [Ti]/[Ti + Mg]. Line scans in various regions of the sample show that the Ti level was uniform to about 10% of the average value. Multiple point scans and area scans in the EDS give average values of the [Ti]/[Ti + Mg] ratio, shown in Fig. 2 indicating that the percent Ti is roughly linearly related to the flow rate in the reaction chamber. Point scans, line scans, and large area raster scans were used for analysis. The large area raster scan shown by the open squares on Fig. 2 comprises the most data and are probably the most accurate measure of the Ti content. These three flow rates of 0.42 cc/min, 1.26 cc/min, and 2.9 cc/min, give 0.3%, 0.5% and 1.6% respectively for the [Ti]/[Ti + Mg] ratio.

Because these Ti doped samples were deposited on a 15 µm diameter W wire and had a 76 µm outer diameter, these fibers require much longer times or higher temperatures to
fully form the $MgB_2$ phase than the 4 to 10 $\mu m$ $B$ layers of the earlier work. Therefore, temperatures of 1000 to 1200°C were often used. A sample with 0.5%$Ti$ reacted for 72 h at 1000°C were found to be 95% reacted using polarized light in an optical microscope. A TEM micrograph of this sample, Fig. 1b, shows precipitates that are much larger than in Fig. 1a. In this figure, the sweeping shaded areas arise from the underlying holey carbon support. In this micrograph, the beam has been tilted to emphasize areas of dense dislocations as shown, for example, in the top center of the micrograph. Many of the precipitates were 50 to 200 $nm$ in diameter. Selected area diffraction indicated the precipitates were $TiB_2$ and had c-axes coaxial with the $MgB_2$ grains in which they were imbedded. For a sample with 0.5%$Ti$ plus 2.1%$C$, the sample was fully reacted after 48 h at 1200°C and shows the 20 to 100 $nm$ diameter precipitates of Fig. 1c. Again the large precipitates here are $TiB_2$ with the c-axis parallel to the c-axis of the $MgB_2$ grain in which it is imbedded.

Another series of samples having 0.3%, 0.5% and 1.6% $Ti$ were all reacted at 1100°C for 48 h and studied in the TEM. For 0.3%$Ti$, the precipitate size is less than 50 $nm$ and widely spaced. For 0.5%$Ti$, the precipitate size ranges from 20 to 80 $nm$. For 1.6%$Ti$, the precipitate size ranges from 20 to 100 $nm$ and the density of precipitates is correspondingly higher. All of these samples show $J_c$ values higher than pure $B$, but lower than shown by the sample of Fig. 1a.

Magnetization data, shown in Fig. 3, indicate that the suppression of $T_c$ with $Ti$ doping depends on the temperature at which the $MgB_2$ forms. Samples reacted at 1000°C for 72 h have magnetization curves similar to pure $MgB_2$ except that they are shifted to lower temperature by about 1 $K$. The 0.3%$Ti$ and 1.6%$Ti$ are nearly identical whereas the 0.5%$Ti$ sample is a bit lower. The depression is not monotonic in $Ti$ content, and the results on Fig. 3 probably represent true scatter in the data. The cause of the suppression in $T_c$ is not understood. If the $Ti$ all precipitates as $TiB$ or $TiB_2$ and no $Ti$ is incorporated in the $MgB_2$ lattice, then it might be expected that the suppression of $T_c$ might be rather small and arise from lattice strains induced by the precipitates or other defects in the $MgB_2$. It is also possible that some $Ti$ atoms replace $Mg$ in the $MgB_2$ lattice and reduce the superconducting interaction in that way. Further study is going to be needed to determine which variables contribute to this suppression in $T_c$.

At 1100°C for 48 h, the suppression of $T_c$ behavior in Fig. 3b is similar to Fig. 3a except that the downward shift of $T_c$ is somewhat larger. At 1200°C for 24 h, shown in Fig. 3c,
the suppression of $T_c$ is very large and increases monotonically with Ti content. Because the $4\pi M$ vs. $T$ curves are not always monotonic in the Ti content, a new series of samples were made at 1100°C to check reproducibility. The data for the two sets of samples with the same Ti content differed by as much as 0.5 K. With these large TiB$_2$ precipitates, there are some as yet uncontrolled parameters.

An X-ray study of the shift in the MgB$_2$ a-axis lattice constant was undertaken to look for a connection between the lattice constant and the amount of impurity. For the case of carbon,

\[4\pi M vs. T\]

the a-axis lattice constant contracts linearly with increasing $C$, as shown by Fig. 4, while the c-axis remains essentially unchanged as reported by several authors.\footnote{4} For the case of Ti, the picture is more complicated. As shown in Fig. 4, the a-axis contracts with increasing Ti, but there is considerable scatter in the data and the amount of change in the a-axis may depend on the temperature at which the MgB$_2$ is formed. An additional sample with 4.7 cc/min flow rate of TiCl$_4$ (2.4%Ti) and reacted at 1200°C for 12 h is shown by the open square of Fig. 4. The apparent flat region of the a-axis lattice parameter between 0.5% and 2.4% Ti as shown by the open squares would appear to indicate that a solubility limit has been reached for Ti in MgB$_2$ at about 0.5% Ti.

For the case of Ti additions only, samples with an 1100°C for 48 h reaction temperature are used to illustrate the changes in superconducting properties. The values of $H_{c2}$ measured up to 9 $T$ for the three different Ti concentrations are slightly lower than for pure MgB$_2$ as shown on Fig. 5. As was found for values of $4\pi M$ vs. $T$ curves in Fig. 3b, the 0.5% Ti sample has the largest suppression of $T_c$ and the largest suppression of $H_{c2}$.

As shown by Fig. 6, the $J_c$ values at 20 K for these three Ti concentrations are enhanced by about a factor of 10 at fields, up to about 1.5 $T$. There is very little difference in $J_c$ as the Ti level is raised from 0.3%Ti to about 1.6%Ti. Values of $J_c$ drop through 1 kA/cm$^2$ at about 1.5 $T$ even though $\mu_0H_{c2}$ is above 6 $T$ at 20 K for these three samples as shown in Fig. 5.

IV. COMBINED Ti AND C DOPING

All the samples reported here for the combined doping were reacted at 1200°C to ensure full conversion to the MgB$_2$ phase. The $C$ content is determined from the CH$_4$ flow rate in the CVD chamber and previous results.\footnote{4} For a sample with 0.5%Ti plus 2.1%C shown in
Fig. 1c, the precipitates are 20 to 100 nm in diameter and selected area diffraction shows
the precipitates to be $TiB_2$ with the c-axis parallel to the c-axis of the $MgB_2$ grain in which
they are imbedded. In this micrograph, the beam is tilted so that the dislocations are not
so apparent, but they are there. These precipitates of Fig. 1c are similar to those in Fig.
1b, but in contrast to the $TiB$ precipitates of Fig. 1a.

An X-ray analysis of the combined $Ti$ and $C$ doping is illustrated in Fig. 7. The c-axis
lattice parameter from the (002) peak essentially does not change with $Ti$ and $C$ addition.
The a-axis lattice parameter contracts in a regular way as shown by the (110) peak of Fig. 7.
The 0.5% $Ti$-only peak moves to higher angle than the pure $MgB_2$ peak by about 0.11 degree
as shown by the heavy dotted line. The 2.1% $C$-only peak shifts out from the pure $MgB_2$
peak by about 0.22 degree as shown by the light dotted line. And, the 0.5% $Ti$+2.1% $C$
peak shifts out from the pure $MgB_2$ peak by about 0.29 degree as shown by the heavy solid
line. Roughly speaking, the decrease in a-axis lattice parameter is additive for $Ti$ and $C$
doping at this level.

As was reported earlier,[4] the $4\pi M$ vs. $T$ curves and the resulting $T_c$ values are depressed
monotonically with increasing $C$ content as shown by the open squares and solid circles of
Fig. 8. If an additional 0.5% $Ti$ is added to each of these $C$ concentrations, the combined
suppression of $T_c$ is roughly additive. As shown in Fig. 8, the addition of 2.1% $C$ to $MgB_2$
suppressed $T_c$ by about 2 K and the addition of 2.1% $C$ plus 0.5%$Ti$ suppressed $T_c$ by about
6 K.

Values of $\mu_oH_{c2}$ in samples with the combined doping shown in Fig. 9 by the open circles
are very similar to values for $C$ doping only reported previously[4] as shown by the solid
symbols. The solid triangles were taken with $R$ vs. $T$ measurements and the solid circles
were taken at the National High Magnetic Field Laboratory as $R$ vs. $H$ measurements. For
the combined $Ti$ and $C$ doped samples there was considerable rounding at the high field
end of the $R$ vs. $H$ transitions. The two open circles represent two different definitions of
$\mu_oH_{c2}$, the lower being a linear extrapolation of the long linear region of $R$ vs. $H$ up to
the normal state, and the upper open circle being the field where the resistivity reaches
the normal state value within the noise. The addition of a few percent $C$ to the $Ti$ doped
samples substantially raises $\mu_oH_{c2}$ (open circles) to values comparable to values for carbon
only (solid symbols).

Values of $J_c$ for a series of samples reacted at 1200°C are shown in Fig. 10. For the
combined 2.1% $C + 0.5\% Ti$ sample at 5 $K$, the $J_c$ curve crosses 1 $kA/cm^2$ at about 3.2 $T$ shown by the solid circles. The 1.1% $C + 0.5\% Ti$ sample at 5 $K$ crosses 1 $kA/cm^2$ at 2.6 $T$, as shown by the open circles. The 0.5%$Ti$ only sample has the highest low field $J_c$ values and crosses 1 $kA/cm^2$ at 2.3 $T$. A pure $MgB_2$ sample at measured at 5 $K$ is shown by the solid squares. It is not shown here, but the the combined 2.1% $C + 0.5\% Ti$ sample at 20 $K$, the $J_c$ curve crosses 1 $kA/cm^2$ at about 1.5 $T$.

To summarize, the addition of $C$ to raise $H_{c2}$ and the addition of $Ti$ to form precipitate pinning centers are roughly independent of one another for the samples reported here. Carbon doped $MgB_2$ shows a rapid rise in $\mu_o H_{c2}(T = 0)$ from 16 $T$ for pure $MgB_2$ to 25 $T$ for $\sim 2.1\%$ added carbon. With both 2.1% $C$ and 0.5% $Ti$ the sample retains a $\mu_o H_{c2}(T = 0)$ of $\sim 25 T$ and no evidence for the formation of $TiC$ was seen. The addition of $Ti$ enhances $J_c$ substantially in the magnetic field range of 2.5 to 3.5 $T$, as shown in Fig. 10.

Much work needs to be done to optimize the the $C$ and $Ti$ levels and the processing to raise $J_c$ at high fields. For low reaction temperatures and short times to form the $MgB_2$ phase, $TEM$ data show that the precipitates are intra-granular and randomly oriented particles ranging in size from 1 to 20 $nm$. For higher reaction temperatures in the range from 1000 to 1200 $^\circ C$, the precipitates are much larger. The precipitates are usually intra-granular $TiB_2$ particles coplanar with the $MgB_2$ host that range from 50 $nm$ to 200 $nm$ in size. Coarsening of the $TiB_2$ precipitates at high temperatures and long times is clearly a problem. In magnetic fields from zero to 1 $T$, the addition of carbon to $Ti$-doped $MgB_2$ gives relatively little change in $J_c$, but in the 3 to 4 $T$ range, carbon additions clearly enhance $J_c$. A very practical problem is that the addition of either $C$ or $Ti$ slows down the rate at which the $B$ fibers transform to the $MgB_2$ phase. For high $J_c$ values, it is helpful to react at low temperatures to give small $MgB_2$ grains and to prevent the $Ti$ precipitate coarsening. Some method is needed to overcome these slow reaction rates, probably the use of fine powders to keep the reaction time short and the reaction temperatures low. It would be desirable to make doped boron powders so that the diffusion lengths can be much smaller and the reaction temperatures lower.
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FIGURE CAPTIONS

Fig. 1 TEM micrograph of MgB$_2$ with 5%Ti reacted 950$^\circ$C-2 h, C coated SiC substrate. 
b) MgB$_2$ with 0.5%Ti reacted 1000$^\circ$C-72 h, W substrate. c) MgB$_2$ with 0.5%Ti + 2.1%C reacted 1200$^\circ$C-48 h, W substrate.

Fig. 2 Percent Ti in MgB$_2$ sample as a function of the TiCl$_4$ flow rate in the CVD apparatus.

Fig. 3 Magnetization transitions for 3 different Ti levels at a) 1000$^\circ$C, b) 1100$^\circ$C and 1200$^\circ$C.

Fig. 4 Comparison of change in a-axis lattice constant for both Ti and C doping.

Fig. 5 $H_{c2}$ for MgB$_2$ doped with Ti only.

Fig. 6 Enhancement of $J_c$ with Ti additions.

Fig. 7 X-ray data for the (002) and (110) peaks for pure B, 0.5% Ti, 2.1%C, and 0.5%Ti + 2.1%C.

Fig. 8 Comparison of C + Ti doping with C only.

Fig. 9 $H_{c2}$ for combined C + Ti doping (open symbols) compared to C only doping (solid symbols).

Fig. 10 Enhancement of $J_c$ for combined Ti and C additions. The Ti only curve was reacted 1200$^\circ$C 12h. The Ti plus C samples were reacted at 1200$^\circ$C 48h.
This figure "Fig1.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/0411531v1
Fig. 4

- Ti 1200°C
- Ti 1100°C
- Ti 1000°C

C 1200°C
