Development of superconducting magnesium diboride conductors

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DEVELOPMENT OF SUPERCONDUCTING MAGNESIUM DIBORIDE CONDUCTORS

A thesis submitted in fulfillment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

SAEID SOLTANIAN, B. Sc., M. Sc.

Institute for Superconducting & Electronic Materials

Faculty of Engineering

2004
DECLARATION

This is to certify that the work presented in this thesis was carried out by the candidate in the laboratories of the Institute for Superconducting and Electronic Materials (ISEM), at the University of Wollongong, NSW, Australia, and has not been submitted for a degree to any other institution for higher education.

Saeid Soltanian

2004
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The work in this thesis concentrates on the fabrication and characterization of MgB$_2$ superconducting bulk wire and tape. An overview of the research on MgB$_2$ superconductor during the last three years is also provided.

High transport and magnetic critical current density values above $10^5$ A/cm$^2$ have been obtained for metal-clad wires and tapes. Fe-clad MgB$_2$ tapes were fabricated using a powder-in-tube technique. The tape shows a sharp transition with a transition width $\Delta T_c$ of 0.2 K and a $T_{c0}$ of 37.5 K. An high transport critical current value of $1.7 \times 10^4$ A/cm$^2$ for both 29.5 K in 1 Tesla and 33 K in zero applied field has been achieved. The effects of sintering time and temperature on the formation and critical current densities of Fe-clad MgB$_2$ wires is also investigated. MgB$_2$ wires were sintered for different periods of time at predetermined temperatures. In contrast to the common practice of sintering for several hours, results show that there is no need for prolonged heat treatment in the fabrication of Fe/MgB$_2$ wires. A total time in the furnace of several minutes is enough to form nearly pure MgB$_2$. $J_c$ of $4.5\times10^5$ A/cm$^2$ in zero field and above $10^5$ A/cm$^2$ in 2 T at 15 K has been achieved for Fe/MgB$_2$ wires sintered for a short time. These findings substantially simplify the fabrication process, making it possible to have a continuous process for fabrication and reducing the costs for large-scale production of MgB$_2$ wires.

Ag and Cu clad MgB$_2$ wires were also fabricated using an in-situ reaction method. The effects of a shorter than usual sintering on the critical current densities of Ag and Cu clad MgB$_2$ wires were studied. For Ag clad wire $J_c$ is improved by more than two times after the short period sintering process. $J_c$ values of $1.2\times10^5$ A/cm$^2$ in zero field and above $10^4$ A/cm$^2$ in 2 T at 20 K have been achieved for Ag clad MgB$_2$ wire which is only sintered for a few minutes at 800 °C. However, a remarkable degree of reaction has been found between the superconducting cores and the sheath materials, leading to the formation of Cu$_2$Mg and Ag$_3$Mg for copper and silver clad wires, respectively. The results show that the short sintering causes less reaction between the magnesium and the sheath materials and markedly improves the critical current density. Our results also show that iron is still the best sheath material for MgB$_2$ superconductor wire and tape. Sixteen-filament stainless steel/Fe/MgB$_2$ wires were fabricated by the powder-in-tube method followed by groove rolling. Magnetic critical current densities of $3.4\times10^4$ A/cm$^2$
in 0.5 T and about $1.9 \times 10^5$ A/cm$^2$ in 1 T at 5 K were achieved. Results on transport $J_c$ of solenoid coils up to 100 turns fabricated with Cu-sheathed MgB$_2$ wires using a wind-reaction in-situ technique are reported. Despite the low density of the single core and some reaction between the Mg and the Cu-sheath, our results demonstrate that the decrease in transport $J_c$ with increasing length of MgB$_2$ wires is insignificant. Solenoid coils with diameters as small as 10 mm can be readily fabricated using a wind-reaction in-situ technique. The $J_c$ of coils is essentially the same as for straight wires. $J_c$ values of 133,000 A/cm$^2$ and 125,000 A/cm$^2$ at 4 K and self field have been achieved for small coil wound using Cu-sheathed tape and Cu-sheathed wire respectively. The results indicate that the MgB$_2$ wires have potential for large scale applications.

The effect of chemical doping on the superconductivity and critical current density of MgB$_2$ superconductor is investigated. Enhancements in the $J_c$ field performance as well as the irreversibility field were obtained due to chemical doping with both C and SiC nano-particles.

Doping MgB$_{2-x}$(SiC)$_{x/2}$ with $x = 0$, 0.2 and 0.3 and a 10 wt% nano-SiC doped MgB$_2$ sample, led to slight decrease in $T_c$ and significantly enhanced $H_{c2}$, $H_{irr}$ and $J_c$ at high magnetic fields. Compared to the non-doped sample, $J_c$ for the 10 wt% doped sample increased by a factor of 32 at 5 K and 8 T, 42 at 20 K and 5 T, and 14 at 30 K and 2 T. At 20 K, which is considered to be a benchmark operating temperature for MgB$_2$, the best $J_c$ for the doped sample was $2.4 \times 10^5$ A/cm$^2$ at 2 T, which is comparable to $J_c$ of the best Ag/Bi-2223 tapes. At 20 K and 4 T, $J_c$ was 36,000 A/cm$^2$, which is an order of magnitude higher than for the Fe/MgB$_2$ tape. Our results show that there are two distinguishable but closely related mechanisms: increase of $H_{c2}$ and improvement of flux pinning that control the performance of $J_c(H)$ in the samples. SiC-doping introduced many nano-scale precipitates and disorders at B and Mg sites, provoking a high resistivity of $\rho(40K) = 300 \, \mu\Omega\text{-cm} \ (RRR = 1.75)$ for the SiC-doped sample, leading to significant enhancement of both $H_{c2}$ and $H_{irr}$ with only minor effects on $T_c$. EELS and TEM analysis revealed impurity phases: Mg$_2$Si, MgO, MgB$_4$, BO$_x$, Si$_x$B$_y$O$_z$, and BC at a scale below 10 m and an extensive domain structure of 2-4nm domains in the doped sample which serve as strong pinning centers. The effect of nano-SiC doping on the critical current density and flux pinning of Fe/MgB$_2$ wires is also investigated. The depression of $T_c$ with increasing SiC doping level remained rather small. High level
SiC doping resulted in a substantial enhancement in the $J_c(H)$ performance. The transport $J_c$ for all the wires is comparable to the magnetic $J_c$ at higher fields despite the low density of the samples. The transport $I_c$ for the 10 wt% doped Fe/MgB$_2$ wire reached 675 A at 24 K and 1 T ($J_c = 140,000$ A/cm$^2$) and 500 A at 20 K and 2T ($J_c = 103,000$ A/cm$^2$). The transport $J_c$ for the 10 wt% SiC doped MgB$_2$ wire is 30 times higher than for the undoped wire. SiC doped MgB$_2$ polycrystalline samples were fabricated using different grain sizes (20 nm, 100 nm, and 37 µm) of SiC and different doping levels (0, 8, 10, 12, 15 wt%) in order to investigate the effect of the particle size of the starting SiC powder on the properties of samples. Results show that grain sizes of the starting precursors of SiC have a strong effect on the critical current density and its field dependence. The smaller the SiC grains are, the better the $J_c$ field performance is. Significant enhancement of $J_c$ and the irreversibility field $H_{irr}$ were revealed for all the SiC doped MgB$_2$ with additions up to 15 wt%. A $J_c$ as high as 20,000 A/cm$^2$ in 8 T at 5 K was achieved for the sample doped with 10 wt% SiC with a grain size of 20 nm. Results indicate that the nano-inclusions and substitution inside MgB$_2$ are responsible for the enhancement of flux pinning.

Polycrystalline MgB$_{2-x}C_x$ samples with $x=0.05$, 0.1, 0.2, 0.3, 0.4 nano-particle carbon powder were prepared using an in-situ reaction method under well-controlled conditions to limit the extent of C substitution. It was found that both the $a$-axis lattice parameter and the $T_c$ decreased monotonically with increasing doping level. However, for the sample doped with the highest nominal composition of $x=0.4$ the $T_c$ dropped only 2.7 K. The nano-C doped samples showed an improved field dependence of the $J_c$ compared with the undoped sample over a wide temperature range. The enhancement by C-doping is not as strong as for nano-SiC doped MgB$_2$. X-ray diffraction results indicate that C reacted with Mg to form nano-size Mg$_2$C$_3$ and MgB$_2$C$_2$ particles.

A study of ac susceptibility, magnetic shielding and the sample size effect is presented in Chapter 6. Systematic ac susceptibility measurements were performed on MgB$_2$ bulk samples. It is shown that the flux creep activation energy is a nonlinear function of the current density $U(J) \propto J^{-0.2}$, indicating a nonlogarithmic relaxation of the current density in this material. The dependence of the activation energy on the magnetic field is determined to be a power law $U(B) \propto B^{-1.33}$, showing a steep decline in the activation
energy with magnetic field, which accounts for the steep drop in the critical current density with magnetic field that is observed in MgB$_2$.

Magnetic shielding was investigated by means of transport critical current measurements for Fe-sheathed MgB$_2$ round wires. Strong magnetic shielding by the iron sheath was observed, resulting in a decrease in $I_c$ by only 15% in a field of 0.6 T at 32 K. In addition to shielding, interaction between the iron sheath and the superconductor resulted in a constant $I_c$ between 0.2 and 0.6 T. This was well beyond the maximum field for effective shielding of 0.2 T. This effect can be used to substantially improve the field performance of MgB$_2$/Fe wires at fields at least 3 times higher than the range allowed by mere magnetic shielding by the iron sheath. The dependence of $I_c$ on the angle between the field and the current showed that the transport current does not flow straight across the wire, but meanders between the grains.

The effect of sample size on the critical current density and the flux pinning of pure and SiC doped MgB$_2$ bulk samples has been investigated. At high fields a systematic degradation of magnetic $J_c$ and $H_{irr}$ was observed as the sample size decreased. However, $J_c$ remarkably increased on decreasing the sample volume at low magnetic fields below 1 T. The SiC doped samples show less sample size effect than the pure samples, indicating a larger n-factor and therefore a stronger pinning effect due to SiC doping.
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CHAPTER 1: INTRODUCTION

Superconductivity has been an exciting, fascinating and challenging topic for almost one century. This phenomenon was observed for the first time by a brilliant Dutch physicist, Heike Kamerlingh Onnes, a professor of physics at the University of Leiden, successfully liquefied Helium in 1908 and was subsequently able to reduce the temperature of liquid helium down to as low as 0.9 K. He had intended to measure the resistivity of metals as a function of temperature at very low temperatures. By measuring the resistivity of Mercury, as a high purity metal at the time, he found in 1911 that the electrical resistivity of Mercury abruptly dropped to zero, the lowest measurable value, when the sample was cooled below 4.2 K [1]. Onnes realized that the new phenomenon represented a new physical state and termed it the superconductive state. In 1913, he won a Nobel Prize in Physics for his research in this field. His further investigation showed that other metals such as tin and lead also enter the superconducting state if they are cooled below 3.8 K and 7.2 K, respectively [2]. The temperature at which the transition from the normal state to the superconducting state occurs was called the critical temperature \( T_c \). Onnes also observed that although it was possible to pass a huge electric current through the superconducting mercury sample, there was a threshold value for the current density above which the sample would return to the normal state [3]. This threshold value, which is extremely important for practical applications is called the critical current density \( J_c \). Moreover, Onnes also discovered that magnetic fields higher than \( H_c \), the critical magnetic field, can similarly destroy the superconducting state.

For many years the study of the low temperature properties of materials led to the observation of the superconductivity in many metals and alloys.

In 1933, Walther Meissner and his student Robert Ochsenfeld discovered an important magnetic property of superconductors. They observed that a magnetic field lower than \( H_c \) was suddenly expelled by superconductor specimens on cooling below \( T_c \) [4]. In other words, the material becomes fully diamagnetic in the superconducting state. This is called the Meissner effect and was found to be an intrinsic property of superconductors. It has been widely used for the testing the superconducting state. Due
to the Meissner effect, if an external magnetic field is applied to a sample which is in the superconducting state, an electric current is produced near the surface of sample, in such a way as to create a magnetic field that exactly cancels the external magnetic field.

In 1935, Fritz and Heinz London theoretically explained the Meissner effect by positing two groups of electrons in a superconducting material, the superconducting electrons and the normal state electrons. They employed the Maxwell equations to develop a set of electrodynamics equations, called the London equations [5]. According to the London equations, the magnetic field exponentially falls off with increasing distance from the surface of a superconducting sample. The characteristic decay length is called the London penetration depth ($\lambda$).

In 1950 V. Ginzburg and L. Landau developed a theoretical explanation for superconductors based on general symmetry properties [6]. Although the Ginzburg-Landau theory explained the macroscopic properties of superconductors, the microscopic properties remained unsolved.

Seven years later, three physicists at the University of Illinois in Urbana, John Bardeen, Leon Cooper and Robert Schrieffer, presented a theoretical explanation for the superconducting state [7]. This theory was widely accepted and is well known as the BCS theory. Based on this theory, despite the Coulomb repulsive forces between the electrons, due to distortion in the crystal structure (phonon mediation), slight attraction between pairs of electrons located near the Fermi surface leads to the production of bonded pairs of electrons, called Cooper pairs [8]. The size of a Cooper pair in a superconductor is known as the coherence length ($\xi$). The BCS theory explained superconductivity in the low temperature and low magnetic field regime. Soon after that, the BCS theory was extended and become useful for high magnetic fields as well [9].

Alexei Alekseevich Abrikosov theoretically investigated the properties of superconductors in external magnetic fields. In 1957 he discovered that superconducting materials can be separated into two groups, type-I and type-II superconductors [10]. His brilliant predictions were experimentally confirmed about three years later. In type-II superconductors there are two critical fields, the lower critical field ($B_{c1}$) and the upper critical field ($H_{c2}$). If the external magnetic field is lower than $B_{c1}$, the field is
completely expelled and the material behaves the same as a type-I superconductor. By increasing the field above $B_{c1}$ up to $B_{c2}$, the flux partially penetrates into the superconductor as vortices. As the field increases above $B_{c2}$, the flux totally penetrates the whole sample, and it returns to the normal state.

In 1962 Brian D. Josephson, a 22 years old British student at Cambridge University, predicted that via a tunneling process, electric current could flow between two superconducting materials separated by a thin (a few nano-meter thick) insulating layer or weak link [11]. Later, his prediction was experimentally confirmed and became known as the Josephson effect. This phenomenon is widely used in applications of superconductors.

A significant breakthrough was made in 1986 by Georg Bednorz and Alex Müller, at the IBM Laboratory in Rüschlikon, Switzerland, when they made a ceramic superconductor from lanthanum, barium, copper, and oxygen with a transition temperature of 35 K [12]. Subsequently, by substitution of yttrium for lanthanum another ceramic superconductor with a transition temperature of 92 K was discovered [13]. This was significant because it now became possible to use cheap liquid nitrogen as the refrigerant. Since the transition temperature of the material was considerably higher than those of the old superconductors, they called these materials the High Temperature Superconductors (HTS).

Further investigation led to the synthesis of a new Tl-Ca-Ba-Cu-O superconductor with a $T_c$ value of 120 K in 1988 [14]. In 1993 the mercury based oxide superconductor HgBa$_2$Ca$_2$Cu$_3$O$_8$ with a $T_c$ of 133 K was discovered [15]. By the partial substitution of thallium for mercury in this material, the $T_c$ value increased to 138 K for a superconductor with the nominal composition of Hg$_{0.8}$Tl$_{0.2}$Ba$_2$Ca$_2$Cu$_3$O$_{8+x}$ [16].

In terms of applications of high temperature superconductors in polycrystalline form, most efforts to date have been concentrated on two main groups of materials, YBCO [13] and BSCCO [17]. In the first group, YBa$_2$Cu$_3$O$_7$ (Y123) has a $T_c$ value of 93 K. The superconducting materials in the second group can be synthesized in three different phases, Bi$_2$Sr$_2$CuO$_x$ (Bi-2201), Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Bi-2212) and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (Bi-2223).
Although a single crystal of YBCO has quite an high critical current density and strong flux pinning, it was very soon confirmed that the polycrystalline form of this superconductor cannot be used due to weak links. Grain boundaries between grains that are misaligned by more that 10 degrees are not effectively transparent to current flow and act as strong barriers to current [18]. In the BSCCO group, so far Bi-2223 with a \( T_c \) value of 110 K has been the most promising compound. The grains in this material can be very well aligned by careful mechanical and thermal processing.

The discovery of superconductivity at 39 K in MgB\(_2\) was first announced by Prof. J. Akimitsu in Jan. 2001 at the Symposium on Transition Metal Oxides in Sendai, Japan and published in *Nature* [19]. For the first few months of 2001, groups all over the world attempted to understand the properties of this new intermetallic superconductor. \( T_c \) was interestingly high compared to the other binary superconductors, almost twice as high as the highest \( T_c \) previously reported, 23 K in Nb\(_3\)Ge. Such a high \( T_c \) attracted great interest in clarifying the mechanism of superconductivity in this material, since some theorists proclaimed that a transition temperature higher than 23 K was not possible [20]. On the other hand, although the transition temperature of MgB\(_2\) was only 39 K, indeed much lower than the \( T_c \) of 134 K attained by mercury based high-\( T_c \) superconducting cuprates (HTS), MgB\(_2\) superconducting wire and tape were quickly prepared by many groups. The biggest motivation to use MgB\(_2\) conductors for power applications is the cost of this superconductor [21]. Despite the low cost of cooling the HTS with liquid nitrogen, the available HTS conductors, made from BSCCO, consume a large amount of expensive silver, about 70% by volume [21]. However MgB\(_2\) is a quite simple compound made of relatively low cost elements. It also can be cooled to a practical temperature by inexpensive and readily available closed-cycle cryocooler systems. In addition, the large coherence length, low anisotropy, strong grain connectivity, and high critical current density of MgB\(_2\) make this superconductor a good candidate for practical applications.

In this thesis, we study the preparation and characterization of MgB\(_2\) superconductor bulk, wire and tape. Our main focus is on possible ways to improve its properties to push it toward practical applications. We have developed techniques to prepare high quality MgB\(_2\) samples. The standard powder-in-tube technique was used to prepare mono-and multi-filamentary wire and tape. Cu, Ag, Fe and stainless steel were used as
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Sheath materials. Fe appears to be the most suitable sheath material among them, not only because of less reaction with the superconducting core, but also because it partially shields the superconducting core against an external magnetic field. It was found that pure MgB$_2$ superconductor is not very suitable for practical applications due to low flux pinning and low upper critical field. The poor flux pinning in pure MgB$_2$ samples that leads to steep decreases in $J_c$ as the magnetic field increases was also confirmed by ac susceptibility measurements. However, we show that the high field critical current density, the upper critical field, and $H_{irr}$ can be improved by chemical doping. Both C and SiC nano-particle doping are shown to significantly improve the $J_c$ field performance, making the materials suitable for practical applications. We have also shown that the $H_{irr}$ and zero field $J_c$ are strongly dependent on the sample size in both pure and SiC-doped polycrystalline samples. However, SiC-doped sample show a much lower sample size effect compared to pure samples.

References.


CHAPTER 2: LITERATURE REVIEW

2-1 Introduction

Magnesium diboride is an old material, synthesized and very well known since 1954 [1]. The discovery of superconductivity at 39 K in MgB$_2$ was first announced by Prof. J. Akimitsu in Jan. 2001 at the Symposium on Transition Metal Oxides in Sendai, Japan. Soon after that many groups all over the world attempted to work on this this new intermetallic superconductor. From an experimental point of view, different aspects have been studied, such as preparation of this superconductor, including the preparation of samples in the form of bulk, wire, tape and thin film, as well as the characterization of samples. At the same time many groups have tried to theoretically explain the properties of this superconductor. Papers daily appear on the cond-mat website providing rapid communications between all groups. More than 900 papers have been submitted to the cond-mat website during the last three years. Also according to the ISI Current Contents Database, until Jan 2004 more than 1300 papers with the title or subject of MgB$_2$ or magnesium diboride have been published in the international journals. The large amount of published research results reveals the great interest of the research community in this newly discovered material. In this chapter we provide general information about this superconductor and present a brief overview of the research progress in this field.

2-2 Crystal Structure and Superconductivity in MgB$_2$

MgB$_2$ has a layered structure with the P6/mmm space group, as shown in Fig. 2-1. It contains graphite-type boron layers that are separated by hexagonal close-packed magnesium layers. Each magnesium atom is located at the center of hexagons of boron atoms. The hexagonal unit cell has the in plane and out of the plane lattice parameters of $a = 3.086$ Å and $c = 3.524$ Å, respectively. Both transport and magnetic measurements show that MgB$_2$ is a superconductor with a transition temperature of about 39 K Fig. 2.
Figure 2-1: The crystal structure of MgB$_2$.

Figure 2-2: Temperature dependence of the resistivity of MgB$_2$ under zero magnetic field [2]. Inset is the field dependence of the susceptibility under zero field cooling (ZFC) and field cooling (FC) conditions.
2-3 Overview of Progress on MgB₂

2-3-1 Superconducting Energy Gap

According to the BCS model the value of the superconducting gap is given by \( \Delta = 1.76 \) \( K_B T_c \) [3]. Taking the \( T_c \) value of 39 K into account, we obtain a value of \( \Delta = 5.9 \text{ meV} \) for MgB₂ superconductor. Soon after the discovery of MgB₂ superconductor, the energy band structure of this superconductor near the Fermi energy was theoretically calculated from first principles [4-13]. The band structure of this compound is shown in Fig. 2-3.

![Band structure of MgB₂ superconductor with the B \( p \) character. The radii of the gray and black circles are proportional to the B \( p_z \) and B \( p_{x,y} \) character respectively [4].](image)

An early scanning tunneling spectroscopy experiment by Karapetrov et al shows that the value of the superconducting gap in MgB₂ at 4.2 K is 5 meV [14] with a temperature dependence of the BCS form.

Rubio-Bollinger et al. also reported a tunneling spectroscopy experiment [15] in small grains of MgB₂ and a good fit to the BCS model with a gap value of 2 meV was
obtained. To explain such a large discrepancy from the expected value of 5.9 meV they supposed that this value was due to the deviation of the DOS at the surface of superconductor with respect to the bulk. Therefore they supposed that this value of gap corresponded to a critical temperature at the surface of about 13.2 K.

Further experimental studies with different techniques such as specific heat measurements, point contact spectroscopy, Raman spectroscopy, tunneling spectroscopy and Andreev reflection spectroscopy indicate that in contrast to the conventional superconductors, MgB$_2$ has two different sized superconducting gaps of about $\Delta(0) = 7$ meV for the $\sigma$ sheets and $\Delta(0) = 2$meV for the $\pi$ sheets [16-56]. The superconductor gaps decrease with temperature, and both gaps equally become zero at $T= T_c$ as is shown in Fig. 2-4. These results are also supported by theoretical studies [8, 57-60]. It has been shown that the Fermi surface of this compound consists of four bands, two $\sigma$-type two-dimensional cylindrical hole sheets and two $\pi$-type three-dimensional tubular networks [4, 61, 62] as is shown in Fig. 2-5. This Fermi surface topology is very well confirmed by de Hass-van Alphen experiments as well [63, 64].

![Figure 2-4: Temperature dependence of superconducting gaps in MgB$_2$. Vertical solid curves represent the distribution of the superconducting gap values at various temperatures from 4 K to 38 K [60].](image-url)
Chapter 2: Literature Review

Figure 2-5: The Fermi surface of the MgB$_2$ superconductor. The green and blue surface (holelike) comes from the bonding $p_{x,y}$ bands, the blue tubular network (holelike) from the bonding $p_z$ bands, and the red (electronlike) tubular network from the antibonding $p_z$ band. The last two surfaces touch at the K point [4].

2-3-2 Hall Effect

The first measurement to evaluate the longitudinal resistivity ($\rho_{xx}$) and Hall coefficient ($R_H$) of the polycrystalline MgB$_2$ sample by Kang et al. shows that $R_H$ is positive in this superconductor for all temperatures above $T_c$ [65], indicating that the charge carriers in MgB$_2$ are holes. According to their results $R_H$ decreases with decreasing temperature with the value of $R_H = 4.1 \times 10^{-11}$ m$^3$/C at 100 K (Fig. 2-6). They also showed that $Cot \theta_H$ is proportional to $T^{1.8}$ as shown in the inset of Fig. 2-6.

The hole carrier density calculated by this group at this temperature is $1.5 \times 10^{23}$ /cm$^3$, which is about one order of magnitude larger than the charge carrier density in Nb$_3$Sn [66] and about two orders of magnitude larger than YBa$_2$Cu$_3$O$_y$ [67] at the same temperature. An Hall coefficient measurement of a c-axis oriented thin film by the same group confirmed that holes are the charge carriers [68, 69] (Fig. 2-7). In addition, it was found that $Cot \theta_H$ linearly increases as a function of $T^2$ instead of $T^{1.8}$. However a deviation from linearity occurred in the temperature range below 130 K ($T^*$ in Fig. 2-7) [69].
Figure 2- 6: Hall coefficient at 5 K. Top inset is the cotangent of the Hall angle measured at 5 T. The curve shows a nearly $T^{1.8}$ behavior. Bottom inset is the temperature dependence of the $\rho_{xx}$ curve which shows an overall $T^2$ behavior and a sharp transition near $T_c$ [65].

Figure 2- 7: $R_H$ versus temperature of MgB$_2$ thin films at 5 T. Distinct temperature dependencies of the $R_H$ are evident below and above 130 K. The upper inset is the temperature dependence of Cot $\theta_H$ at 5 T. A clear $T^2$ law was observed above 130 K. The lower inset is a schematic diagram of the Hall-bar pattern. [68, 69]
More measurements by Kang et al. showed no Hall sign anomaly in the mixed state (Fig. 2-8) [68]. Other results reported by this group also indicated a universal scaling law of $\rho_{xy} \propto \rho_{xx}^{\beta}$ with $\beta \approx 2$ in the mixed state and $\rho_{xy}$ and $\rho_{xx}$ the longitudinal and Hall resistivities, respectively. These results were in agreement with the experimental results for Bi$_2$Sr$_2$CaCu$_2$O$_8$ single crystal [70] and Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ thin film [71]. It is also in agreement with the universal Hall scaling theory proposed by Vinokur et al. [72]. However, experimental results reported by Jin et al. showed an unusual Hall effect in the mixed state in superconducting MgB$_2$ films [73]. In contrast to Kang et al., Jin et al. observed a sign reversal in the measured Hall resistivity versus temperature over a wide range of applied magnetic field up to 8 T, as we can see in Figs. 2-9 and 2-10. An anisotropy in the normal state Hall effect was also observed in the MgB$_2$ single crystal by Eltsev et al. (Fig. 2-11) [74, 75]. They found a positive in-plane Hall constant (H parallel to the c axis) in agreement with the previous experiments, while they found that the out-of-plane Hall constant (H parallel to $ab$ plans) is negative, indicating n-type charge carriers.

![Figure 2-8](image_url)

Figure 2-8: $\rho_{xx}$ (a) and $\rho_{xy}$ (b) measured at applied current densities of $10^2$, $10^3$, and $10^4$ A/cm$^2$ and for $H=2$ and 5 T. No sign change was observed in the mixed-state, which is in contrast to the HTS case [68].
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Figure 2-9: Temperature dependence of $R_H$ ($H=8T$) of a MgB$_2$ film plotted on a logarithmic temperature scale. The sign change of $R_H$ in the mixed state can be clearly seen. The inset is the Hall angle $\cot \theta_H$ versus the temperature between $T_c$ and 300 K at $H=8$ T [73].

Figure 2-10: Temperature dependence of (a) $R_H$ and (b) longitudinal resistivity $\rho$ at $H=2$, 4, 6, and 8 T [73].
This result was in agreement with the numerical calculations of the independent Hall components of the resistivity tensor for MgB$_2$ performed by Eltsev et al. (Fig. 2-12) [76]. The anisotropy in the Hall coefficient can be explained as follow: as we saw earlier, the Fermi surface of MgB$_2$ consists of four bands, two hole-like $\sigma$-bands in the form of 2D cylindrical Fermi surfaces and two hole- and electron-like 3D $\pi$-bands [4, 8, 9]. In the in plane case ($H$ parallel to $c$), the hole-like carriers dominate the behavior of $R_{H}$, resulting in positive values of $R_{H}$. On the other hand when $H$ is parallel to the $ab$ plane (out-of-plane), the $\sigma$-bands become less important, and the electron-like carriers dominate the $R_{H}$ [75-77].
Figure 2-12: The numerical calculation of transport properties of MgB$_2$ as a function of doping in a rigid-band scheme [76].

2-3-3 Pressure Effect

Study of the superconducting properties under high pressure is one of the first experiments usually performed after the discovery of a new superconductor. The effect of pressure on the MgB$_2$ superconductor has been examined by many groups in terms of either change in the transition temperature or change in lattice parameters. Table 2-1 shows a summary of experimental results of the effects of pressure on the $T_c$ of MgB$_2$ superconductor [78]. As we can see, the experiments have been carried out at pressures as high as 44 GPa. Also, different materials such as He, Fluorinert, NaF and Silicon oil have been utilized as a pressure medium. The experimental results of a few groups are also presented in Fig. 2-13 [79]. It can be seen that $T_c$ monotonically decreases as the pressure is increased, with the measured $dT_c/dP$ values between $-0.35$ K/GPa [80, 81] and $-2$ K/GPa [82, 83]. However, a $dT_c/dP$ value of about $-1.1$ K/GPa is mostly confirmed by experiments. The reduction of $T_c$ under pressure is consistent with a BCS-type pairing interaction mediated by high-frequency boron-boron modes. This indicates that the reduction of the density of states at the Fermi energy, due to the contraction of B-B and B-Mg bonds, dominates the hardening phonon frequencies that can cause an increase in $T_c$ as external pressure is applied [79].
Table 2-1: Summary of the experimental results of the pressure effects on MgB$_2$ superconductor single crystal (first 5 rows) and polycrystalline (remaining rows) samples [78].

<table>
<thead>
<tr>
<th>$P_{\text{max}}$ (GPa)</th>
<th>$T_c(0)$ (K)</th>
<th>$(dT_c/dP)_0$ (K/GPa)</th>
<th>Measurement</th>
<th>Pressure medium</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
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<td>0.63, 23</td>
<td>38.24</td>
<td>-1.10(3)</td>
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<td>SC</td>
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<td>SC</td>
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<td>0.4</td>
<td>37.16</td>
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<td>SC</td>
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<tr>
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<td>SC</td>
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</tr>
<tr>
<td>1.4</td>
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<td>$\rho$ Fluorinert</td>
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</tr>
<tr>
<td>0.66</td>
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<td>PC</td>
<td>[84]</td>
</tr>
<tr>
<td>0.63</td>
<td>39.1</td>
<td>-1.09(4)</td>
<td>$\chi_{ac}^{11}B$</td>
<td>He</td>
<td>PC</td>
<td>[85]</td>
</tr>
<tr>
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<td>-1.11(3)</td>
<td>$\chi_{ac}^{11}B$</td>
<td>He</td>
<td>PC</td>
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<td>40.5</td>
<td>-1.12(3)</td>
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<td>PC</td>
<td>[85]</td>
</tr>
<tr>
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<td>37.5</td>
<td>-1.13</td>
<td>$\chi_{ac}$</td>
<td>He</td>
<td>PC</td>
<td>[86]</td>
</tr>
<tr>
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<td>-1.07</td>
<td>$\chi_{ac}$</td>
<td>He</td>
<td>PC</td>
<td>[87]</td>
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<tr>
<td>33</td>
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<td>-1.1</td>
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<td>PC</td>
<td>[88]</td>
</tr>
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<tr>
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</tr>
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<td>-1.6</td>
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<td>PC</td>
<td>[89]</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>37.3</td>
<td>-2</td>
<td>$\chi_{ac}$ 4:1 methanol/ethanol</td>
<td>PC</td>
<td>[83]</td>
<td></td>
</tr>
<tr>
<td>1.46</td>
<td>38.2</td>
<td>-1.36</td>
<td>$\rho$ 1:1 diphene/kerosene</td>
<td>PC</td>
<td>[90]</td>
<td></td>
</tr>
<tr>
<td>1.35</td>
<td>37.5</td>
<td>-1.9</td>
<td>$\rho$ Fluorinert</td>
<td>PC</td>
<td>[91]</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>38.3</td>
<td>-1.5(1)</td>
<td>$\chi_{dc}$ Kerosene/mineral oil</td>
<td>PC</td>
<td>[92]</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>39</td>
<td>-1.03</td>
<td>$\rho$ Fluorinert</td>
<td>PC</td>
<td>[93]</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>39</td>
<td>-1.1</td>
<td>$\chi_{dc}$</td>
<td>PC</td>
<td>[94]</td>
<td></td>
</tr>
<tr>
<td>7.6</td>
<td>37.5</td>
<td>-1.6(increasing)</td>
<td>$\chi_{ac}$ NaF</td>
<td>PC</td>
<td>[86]</td>
<td></td>
</tr>
<tr>
<td>7.6</td>
<td>37.5</td>
<td>-1.13(decreasing)</td>
<td>$\chi_{ac}$ NaF</td>
<td>PC</td>
<td>[86]</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>39</td>
<td>-1.20(9)</td>
<td>$\rho$ Steatite</td>
<td>PC</td>
<td>[95]</td>
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</tr>
<tr>
<td>33</td>
<td>35</td>
<td>-0.35 to -0.8</td>
<td>$\rho$ Steatite</td>
<td>PC</td>
<td>[80, 81]</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>38</td>
<td>-1.18(6)</td>
<td>$\chi_{dc}$ Silicon oil</td>
<td>PC</td>
<td>[95]</td>
<td></td>
</tr>
</tbody>
</table>

Changes in the crystal structure and lattice parameters of MgB$_2$ superconductor under pressure have been studied by many groups [81, 86, 93, 96-100]. Experimental results confirm that MgB$_2$ remains hexagonal and keeps its crystal structure even at high pressures up to 40 GPa [81]. It is also confirmed by all experimental results that an anisotropy in the compressibility of MgB$_2$ occurs, with the $c$-axis lattice parameter decreasing faster than the $a$-axis lattice parameter as the hydrostatic pressure increases, indicating that the Mg-Mg (in-plane) bonds are stronger than the Mg-B (out-of-plane) bonds (Fig 2-14) [79]. This anisotropy in the compressibility decreases with pressure as revealed in the inset of Fig. 2-14 [79, 81].

The differences in $dT_c/dP$ as well as in the compressibility values reported by different groups might be due to the different materials utilized in different experiments as the pressure medium, as we can see in Table 2-1 and Figs. 2-13 and 2-14 [78, 79].
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Figure 2-13: The pressure dependence of $T_c$ of the MgB$_2$ superconductor [79]. The legends indicate the pressure medium used by each author, Saito [91], Lorentz [87, 89], Tissen [83], Monteverde [80], Bordet [81], Schlachter [86], Tomita [84], Goncharov [100], and Deemyad [85].

Figure 2-14: The pressure dependence of the normalized lattice parameters of MgB$_2$ superconductor. The lattice parameters are normalized to zero pressure values [79]. The legends indicate the pressure medium used by each author, Prassides [98], Goncharov [100], Vogt [96], Schlachter [86], and Bordet [81]. Inset shows the pressure dependence of the ratio between the c-axis lattice parameters and a-axis lattice parameters [81].
2-3-4 Isotope Effect

An isotope effect on a superconductor transition temperature indicates the phonon mediation of superconductor coupling. MgB$_2$ is a special system with two elements which both have different isotope masses that can change $T_c$ due to substitution of different isotopes. For a single element superconductor, the isotope effect coefficient ($\alpha$) is defined as $\alpha = d \ln T_c / d \ln M$ or $T_c \propto M^\alpha$ [101, 102]. $M$ is an atomic mass, which is different for different isotopes of this superconductor.

For a multi-element superconductor the total isotope effect coefficient is the sum over the individual isotope effects for different masses $M_i$:

$$\alpha = \sum \alpha_i = \sum -\partial \ln T_c / \partial \ln M_i$$

Soon after the discovery of the MgB$_2$ superconductor, the effect of B isotopes on this superconductor was measured by Bud'ko et al. [103]. They found that measurements of both temperature dependent magnetization and specific heat reveal a 1 K shift in $T_c$ from 39.2 K for Mg$^{11}$B$_2$ to 40.2 K for Mg$^{10}$B$_2$ (Figs. 2-15 and 2-16). Also, using the above equation they calculated the boron isotope coefficient to be $\alpha_B = 0.26$ (3), where 3 indicates the error in the last decimal place. These results strongly support the idea that MgB$_2$ is a phonon mediated BCS superconductor.

![Figure 2-15: Magnetization divided by applied magnetic field as a function of temperature for Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ [103].](image)
Further studies of the isotope effects of both the Mg and B elements were performed by Hinks et al. [104]. They measured six different samples prepared using $^{10}$B, $^{11}$B, $^{24}$Mg, $^{25}$Mg and $^{26}$Mg isotopes. Fig. 2-17 shows the superconducting transition for the isotopically substituted MgB$_2$ samples reported by Hinks et al. [104]. According to their experimental results, the B isotope effect coefficient is $\alpha_B = 0.3$ (1), which was in good agreement with the measurements of Bud’ko et al. On the other hand, they found that Mg isotope has very little effect on $T_c$. $T_c$ increases by about 0.1 K on substitution of $^{24}$Mg with $^{26}$Mg. The estimated Mg isotope effect coefficient is $\alpha_{Mg} = 0.02$ (1). Therefore the total isotope effect is $\alpha_t = \alpha_B + \alpha_{Mg} = 0.32$. These results clearly indicate that the phonons involved in the superconductivity of MgB$_2$ are mainly B phonons, while Mg phonons make very little contribution to the overall pairing.

Figure 2-16: Temperature dependent specific heat of Mg$^{10}$B$_2$ and Mg$^{11}$B$_2$ in zero and 90 kG (filled circle and open triangles, respectively) applied magnetic field for temperatures near $T_c$. Arrows show the transition temperatures [103].
Figure 2-17: Superconducting transition for the MgB$_2$ samples substituted by Mg and B isotopes (reported by Hinks et al.) [104]. The magnetization for all samples is shown in (a) ("Mg indicates a sample with natural Mg). (b) and (c) show the small change in superconducting transition due to the substitution of Mg isotopes (the temperature scale is expanded).

The total isotope effect for MgB$_2$ is much lower than the expected value of 0.5 for a conventional BCS superconductor. Recent calculations [105] show that the reduced isotope effect can be due to the anharmonicity of the planar B optic mode. This idea was confirmed by Choi et al. [59]. By calculation of the isotopic-effect exponent coefficient from the anisotropic Eliashberg equation with anharmonic phonon frequencies, they obtained $\alpha_B = 0.32$ and $\alpha_{Mg} = 0.03$ which are very close to the experimental values. However without anharmonicity they obtained $\alpha_B = 0.46$ and $\alpha_{Mg} = 0.02$, indicating that the low isotope effect exponent coefficient is mainly due to phonon anharmonicity.
2-3-5 Fabrication of MgB$_2$ Thin Film

Superconducting films are important for electronics applications such as Josephson junctions and superconducting quantum interference devices (SQUID). Many groups have attempted to prepare MgB$_2$ thin films. However, the high sensitivity of Mg to oxidation, the high volatility of Mg and the large difference between the vapor pressures of Mg and B are the main obstacles to preparation of superconducting MgB$_2$ films.

MgB$_2$ thin films have been prepared using the different techniques as listed in Table 2-2. Pulsed laser deposition (PLD) seems to be the most common method for film fabrication among them. High quality films have been prepared using a one step preparation (in-situ) or a two step preparation (ex-situ) technique. Ex-situ techniques consist of deposition of amorphous B (or Mg-B composite) precursors on substrates, then heating the film in a rich Mg vapor. This method has been widely used and has been quite successful in growing high-quality films [106-112]. A few groups have also fabricated MgB$_2$ film using the in-situ or one step technique [113-116].

Each method has its benefits and disadvantages. The two step method gives good crystalline films and good superconducting properties, but cannot be used to fabricate Josephson junctions or multi-layer films. On the other hand, although the in-situ method gives films with poorer crystallinity and lower $T_c$, this method is applicable for multi-layer fabrication. The one step method gives films with a more smooth surface than films made via the two step method, but generally speaking, MgB$_2$ films have a rough surface morphology compared to YBa$_2$Cu$_3$O$_7$ thin films. Therefore, methods need to be improved to be suitable for electronic device applications. However, recently Zeng et al. [117] reported in-situ growth of high-quality MgB$_2$ thin films by using a newly developed technique of hybrid physical–chemical vapor deposition. This is expected to be a very promising growth technique in terms of applications for superconducting electronics.

Different substrates have been used for the deposition of MgB$_2$ thin films. Appropriate substrate selection is important in order to achieve better lattice matching and less reaction with the superconductor film. It has been reported that MgB$_2$ reacts with many common substrate materials such as Si, SiO$_2$, Al$_2$O$_3$, SiC and SrTiO$_3$, but no reaction
occurs with ZrO$_2$ and MgO [118]. To date, various substrates such as sapphire (Al$_2$O$_3$) – R and -C, SrTiO$_3$ (100) and (111), SiC (0001), LaAlO$_3$, MgO (100) and Si (100) and (111) have been used to prepare MgB$_2$ film. Al$_2$O$_3$ seems to be the most common substrate used to prepare high quality films. For this substrate, films prepared by Mg diffusion show higher $T_c$ with a sharper transition than other films[79]. Fig. 2-18 which is extracted from reference [79] shows the critical temperature of thin films prepared on different substrates.

![Figure 2-18: Critical temperature and critical temperature width for MgB$_2$ films deposited on different substrates. Figure is extracted from ref. [79]. Data are from the references: Al$_2$O$_3$ 1 [107, 111], 2 [109], 3 [106], 4, 8, 12 [112], 5 [119], 6, 10, 13 [111], 7 [120], 9, 14 [121], 11 [122], 14 [123]; SrTiO$_3$– 1,2,3 [108],4 [124]; Si-1,2 [112], 3,4 [125],5, 6, 7 [111], 8 [124]; MgO- [124] ; SiC [124].](image)

2-3-6 Fabrication of MgB$_2$ Single Crystal

The physical properties of a superconductor especially the anisotropy properties, have to be studied on a single crystal. Many groups have attempted to grow single crystals after the discovery of MgB$_2$ superconductor. However, the formation of MgO phase, the high
Table 2-2: Summary of the experimental results on MgB$_2$ superconductor thin film prepared by different techniques.

<table>
<thead>
<tr>
<th>Preparation technique</th>
<th>$T_c$ (K)</th>
<th>Substrate</th>
<th>Reference</th>
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<td>29-34</td>
<td>Al$_2$O$_3$</td>
<td>[126]</td>
</tr>
<tr>
<td>PLD</td>
<td>22-24</td>
<td>Si, SrTiO$_3$, MgO</td>
<td>[124]</td>
</tr>
<tr>
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<td>27</td>
<td>Si</td>
<td>[127]</td>
</tr>
<tr>
<td>PLD</td>
<td>31-36</td>
<td>SrTiO$_3$</td>
<td>[108]</td>
</tr>
<tr>
<td>PLD</td>
<td>36</td>
<td>Al$_2$O$_3$, MgO</td>
<td>[128]</td>
</tr>
<tr>
<td>PLD</td>
<td>25</td>
<td>MgO, Al$_2$O$_3$</td>
<td>[114]</td>
</tr>
<tr>
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<td>39</td>
<td>Al$_2$O$_3$</td>
<td>[106]</td>
</tr>
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</tr>
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1 electron-beam evaporation  
2 molecular beam epitaxy  
3 magnetron sputtering  
4 hybrid physical–chemical vapour deposition (HPCVD)  
5 multiple-target sputtering  
6 planar magnetron sputtering
reactivity of Mg in the vapor and melt phases with containers and flux materials, the low solubility of MgB$_2$ in Mg, and the high Mg vapor pressure and incongruent melting of Mg cause difficulties in the crystal growth procedure of MgB$_2$ [161, 162].

A thermodynamic analysis of the Mg-B system using the calculation of phase diagrams modeling technique is presented by Liu et al. [163]. They calculated three phase diagrams of temperature–composition (Fig. 2-19), pressure–composition (Fig. 2-20), and pressure–temperature (Fig. 2-21) for this superconductor based on the known data on the MgB$_2$, MgB$_4$ and MgB$_7$ phases. According to their results, MgB$_2$ is stable only under high Mg overpressure. If the Mg overpressure is too low MgB$_2$ tends to decompose to MgB$_4$ +Mg (gas) [163]. For example under 1 atm and 1 Torr pressure, MgB$_2$ is decomposed to MgB$_4$ and Mg gas at 1545 °C and 912 °C, respectively [161].

Figure 2-19: Temperature–composition phase diagrams of the Mg–B system under pressures of (a) 1 atm, (b) 1 Torr, and (c) 1 mTorr [163].
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Figure 2-20: Pressure–composition phase diagram of the Mg–B system at 850 °C.

Figure 2-21: The phase diagram (pressure–temperature) for the Mg:B atomic ratio $x_{Mg} / x_{B} > 1/2$. The thermodynamic stability window for the deposition of MgB$_2$ thin films is region of Gas+MgB$_2$ [163].

So far, two different methods have been developed to prepare sub-millimeter MgB$_2$ single crystal; one is crystal growth by encapsulation and the other is the high-pressure method. In this method a mixture of Mg and B is heated at high temperature up to 1700 °C in a closed metal container of stainless steel, Nb or Mo [164-166] under an Ar gas
pressure of $1<P_{Ar}<14kbar$. With this method, crystals have been made using techniques such as vapor transformation [167, 168], using a mixture of MgB$_2$ and other flux materials, i.e. Na [166], Mg [164, 165, 169-171], Cu[171, 172], and Al [171]. The other method is sintering at high-pressures and temperatures in BN[162, 171, 173-177] or Ta reaction cells[169]. For experiments in the Mg-B-N system, the BN powder is used as a source of boron and nitrogen. The powder is put in a BN container as a reaction cell and sintered under high pressure, mostly by using the cubic-anvil press as shown in Fig. 2-22 [171]. Fig. 2-23 shows optical microscope images of MgB$_2$ single crystal prepared using the BN system.

![Figure 2-22: a) The image of the cubic anvil apparatus including the hydraulic press to provide the necessary force. b) A schematic of the cubic anvil cell. Steel pieces are arranged so as to provide forces from all sides onto the sample located in the middle. A 400 A current passes through a graphite tube inside the pyrophylite cube to provide the heat. The sample is placed in a BN container which is located inside the graphite heater [171].](image)

![Figure 2-23: Optical microscope picture of MgB$_2$ single crystals prepared using the Mg-B-N system under high pressure. Scale size is 1 mm [162].](image)
2-3-7 Fabrication of MgB$_2$ Wire and Tape

Preparing and developing superconducting wires and tapes is essential for practical applications such as applications in the cable and magnet industries. MgB$_2$ superconductor wire was produced very soon after the discovery of this superconductor. The first wire was produced by Canfield et al. [178] by diffusing Mg vapor into boron fibers with a tungsten wire core. This wire showed a quite high $J_c$ value of above $10^5$ A/cm$^2$ at 5 K and zero field. The results were promising and many groups have attempted to make wires and tapes using different methods.

2-3-7-1 Preparation of Wire and Tape

Since MgB$_2$ is mechanically hard and brittle, it is impossible to directly draw it into a fine wire. Different techniques have been developed to prepare MgB$_2$ conductors. Although the powder in tube technique is widely used, other techniques have also been tried by a few groups. The powder-in-tube technique will be explained in detail in the next chapter. However, the continuous tube forming and filling technique (CTFF) will be explained in this chapter.

2-3-7-1-1 Powder in Tube Technique

The conventional powder-in-tube technique, using a metal tube as a stabilizer, has become a major method for the preparation of wires and tapes due to the relatively low cost and high quality of the products, as well as the suitability of this technique for large scale industrial production.

2-3-7-1-2 Continuous Tube Forming and Filling (CTFF) Technique

This technique has been used to prepare MgB$_2$ wires and tapes by the High-Tech Company in US. In fact it has been adapted to wire fabrication from pre-existing technologies used in the tobacco industry. In this technique, a continuous metal strip (Fe, Cu) is first produced as a sheath material. As the ribbon enters and moves through the tube shaping dies they gradually form it into a U shape as shown in the Fig. 2-24. After the powder is inserted, the closing dies gradually close off the tube. After the tube
has been closed, it passes through subsequent dies to reduce the diameter to a fine wire of approximately 2mm in diameter. Numerous long lengths of wire have been made using this technique.

**Figure 2-24: Schematic of apparatus for continuous tube forming and filling (CTFF) for MgB$_2$ wire and tape fabrication.**

### 2-3-7-2 Effect of the Sheath Material

Using the proper metal as a sheath material has been found to be critical in preparing high performance wire. Iron was found to be a suitable sheath material for MgB$_2$ wire [179] or tape [180-182] as Mg tends to react with many metals such as Cu and Ag even at temperatures lower than its melting point [181].

#### 2-3-7-2-1 WIRE

Iron has been widely used by many groups as a sheath material for wire [179, 181, 183-212]. However other metals, such as Cu [185, 195, 200, 206, 213-227], Ag [213, 215, 218, 220, 221, 223], Ni [189, 228-230], and Ta[195, 231] have also been used for this purpose. In addition multi-layers of metals or metallic alloys, such as stainless steel (SS) [185, 204, 215, 232-237], carbon steel (CS) [206], Fe/Cu [181, 188, 203, 219, 238], Fe/SS [186, 201, 239-241], NbZr [195], Cu/Ni [185, 206, 232], Cu/Ta [214, 242-244],
Ag/SS [213], Ta/Cu/SS [245], Nb/Cu/SS [239, 245], Ta/SS [186], and Nb/SS [186], have been reported by many groups as metal cladding for MgB$_2$ wire.

2-3-7-2-2 Tape

Fe is also most commonly used as a sheath material for MgB$_2$ superconducting tape [180, 182, 186, 188-190, 195, 197-199, 201, 206, 209, 211, 241, 246-254]. However, similar to the wire situation, other metals and alloys, such as Cu [195, 206, 215, 217, 219, 252, 255-259], Ag[215, 252, 257], SS [206, 215, 232, 258, 260-264], Ni [182, 189, 228, 257, 265-270], Ta[195], Nb[271], Fe/Cu[219, 272], Ni/Cu[206, 232, 258], NbZr[195], Fe/SS[186, 201], Ta/Cu[244, 273], Cu/NbZr[274], Monel[271], and CS[206, 275-277], have also been used as the metal cladding.

It was found that mechanical hardness of the sheath material results in densification as well as improving the grain connectivity in the superconducting core[185, 186, 206, 258, 277]. Therefore, hard sheath materials such as SS [186, 258] and CS [277] have been used. Experimental results reveal that critical current density and its field dependence are significantly enhanced due to the hardness of sheath materials.

Multi-filamentary wires and tapes are also prepared using different sheath materials [188, 191, 194, 198, 200, 203, 209, 229, 240, 274, 278].

2-3-7-3 Effect of the Precursor Material

In terms of precursor material, to prepare MgB$_2$ superconductor two different methods are mainly used. In the so-called *in situ* reaction method a mixture of Mg and B is used as a starting material. The mixture is packed into a metallic tube, and then MgB$_2$ is formed inside the tube by heat treatment. However, commercially available and pre-reacted MgB$_2$ powder is used as a starting material in the *ex situ* reaction method. The *in situ* reaction method is widely used both for wire [180, 187, 190, 191, 200, 207, 210, 211, 213, 218, 220, 221, 223-227, 238, 244, 248-250, 275, 279-281] and for tape [180, 187, 190, 191, 200, 207, 210, 211, 221, 238, 244, 248-250, 273, 275, 279, 280]. The *ex situ* reaction method is also used both for wire [194, 197, 199, 203, 207, 213, 219, 220, 222, 275, 282] and for tape [194, 197, 199, 203, 207, 219, 222, 231, 275]. Apart from
these methods a mixture of Mg\(^{+2}\)B and MgB\(_2\) was also used by Schlachter et al. to prepare wire and tape [208], as well as by Pan et al. [207].

In the *ex situ* reaction method it has been shown that the quality of the starting powder has a significant effect on the critical current density of Cu clad tape [256].

Fujii et al. used MgH\(_2\) instead of Mg as a precursor powder to prepare MgB\(_2\) tape. They claimed that the \(J_c\) values of the tapes prepared using mixture of MgH\(_2\) + B were about twice as large as those prepared using the mixture of Mg + B [251, 275, 276].

Using the pre-reacted powder, the influence of the initial MgB\(_2\) grain size on critical current density, upper critical and irreversibility fields has been studied by Flukiger et al. [198]. They employed ball milling to reduce the grain size of MgB\(_2\) starting material leading to an enhancement of \(J_c\) [198].

The porosity of samples has been one of the main weaknesses of MgB\(_2\) samples so far. Samples with higher mass density have been prepared using pre-reacted and very fine powders in the reaction *ex situ* technique [198] or by sintering under pressure (hot press technique) in the reaction *in situ* method [283-286]. The hot isostatic pressing (HIP) method has also been employed to make dense samples, resulting in improvements in the microstructure and superconducting properties of the material, thereby improving the \(J_c\) field performance [235, 287].

**2-3-7-4 Magnetic Shielding and ac Loss in Fe/MgB\(_2\) Conductors**

Studies on two other physical aspects of Fe sheath MgB\(_2\) superconductor, ie. magnetic shielding [183, 187, 192, 202, 205, 288] and ac loss [187, 288] have also been reported. Results indicate that the presence of Fe in MgB\(_2\)/Fe composite shields the superconductor core against an external field of 2 kOe; at higher fields a fixed \(\Delta H\) was observed (partial shielding) [183, 187]. It also results in suppression of ac loss due to shielding of the core against an externally applied field [187]. Therefore, using Fe as a sheath material may be beneficial for power applications.
2-3-7-5 Long Conductors and Coil

Ni coil [230] has been produced using ex situ reaction, and Cu coil [227] has been produced using the wind-reaction in situ technique (to be explained in chapter 4). Ni clad conductor in the shape of a helix about 1.5 m long and in a pancake shape about 2 m long have also been successfully prepared and measured by Grasso et al. [270]. These results confirm the suitability of this superconductor for practical applications.

2-3-7-6 Effect of Heat Treatment in MgB$_2$ Tape and Wire

On the one hand, heat treatment is an essential step in the in situ technique. For post annealing, a wide range of temperatures have been used, from as low as just above the Mg melting point [179, 227] to as high as 1100 °C [204]. It was found that even lower sintering temperatures of 500 °C [289] or 600 °C [225] are enough to form the MgB$_2$ phase if mechanically pre-alloyed powder is employed.

On the other hand, even in the ex situ reaction methods, post annealing is essential as it has been found to enhance the $J_c$ and its magnetic field performance [185, 194, 201, 204, 208, 229, 270, 277]. This enhancement is reported to be up to one order of magnitude [201, 208].

The effects of sintering time on the critical current density of MgB$_2$ wires prepared by the reaction in situ method have also been studied (it will be explained in chapter 4). We have found that prolonged heat treatment is not necessary in the fabrication of Fe clad wires. MgB$_2$ phase can be formed quickly. Several minutes sintering gives almost the same performance as a longer sintering time. This finding substantially simplifies the fabrication procedure for wire. Short sintering of wires with other sheath materials, such as Cu and Ag, avoid a high reaction rate between the magnesium powder and the sheath, resulting in an enhancement in $J_c$ (see Chapter 4).

2-3-7-7 Other Techniques Have Been Used for Preparation of MgB$_2$ Conductors

Other techniques, such as Reactive Liquid Mg Infiltration to make hollow wires as used by Giunchi et al. [278] and diffusion of magnesium vapor into boron fibers with
tungsten cores [178, 290-292], as well as the suspension spinning method [293, 294], were also tried by a few groups to prepare MgB$_2$ superconducting wire.

Two more different techniques, boron diffusion into Mg tape [295] and deposition of MgB$_2$ film on a Hastelloy tape buffered with an yttria-stabilized-zirconia layer [296], have also been used to prepare different types of MgB$_2$ tape.

**2-3-8 Chemical Doping**

Attempts have been made to accomplish substitutions in the MgB$_2$ superconductor lattice. Substitutions are important because they can lead to increases in $T_c$ or to the discovery of a related compound with higher $T_c$, or to enhancement in the physical properties by such means as producing pinning centers. They can also clarify the mechanism of superconductivity.

Many elements have been tried as substitutes for Mg or B, such as C [297-305], Al [306-311], Mn [309, 312], Zr [309, 313-315], Na [310, 316], Li [306, 316-318], Si [306, 319], Be [320], Ag [309, 310, 321], Ti [212, 244, 309, 315, 322, 323], Mg [324], B [324], Sn [325], Fe [309, 325, 326], Co [325, 326], F [327], Cu [309, 310, 328, 329], Mo [309], Ca [309, 310], Y [309], Pb [330], Ir [331], Zn [310], V [323], Nb [323] and O [108]. In addition to the above elements, many compounds have also been tried as dopants in MgB$_2$, such as SiC [193, 211, 251, 332-335], Y$_2$O$_3$ [336], WSi$_2$ [250], ZrSi$_2$ [250] and SiO$_2$ [251].

Although many of the above reports declared the Mg and B had been partially replaced by other elements, Cava et al. [337] have recently claimed that most of them are incorrect and that just three elements, C, Al and Mn are really substituted, while the others cannot meet the criteria for successful chemical doping.

Unfortunately, all chemical dopants lead to decreases in the $T_c$ value. It has been shown by many groups that C can substitute in the B position up to about $x=0.1$ in the MgB$_2$-$xCx$ composition. All reports show a serious decrease in the in-plane lattice parameter. There are some disagreements between the results in term of the rate of decrease in $T_c$, which is probably due to incomplete incorporation of C in different experiments. Al has also been found to be very well substituted in the Mg site. The higher the doping, the
larger the decreases in $T_c$ and the wider the transition. The decrease in $T_c$ is significant as at about $x=0.4$ in Mg$_{1-x}$Al$_x$B$_2$ the superconducting phase disappears [338]. Doping also leads to a contraction in both lattice parameters. However, the in-plane lattice parameter decreases faster than the out-of-plan lattice parameter as the doping level increases. It has also been found that there are two phases for doping levels between $x=0.1$ and $x=0.25$ having different $c$ axis lattice parameters with different AlB$_2$ base structures [337] (Fig. 2-25). In the case of Mn, it has been shown that the solubility of Mn in MgB$_2$ is very low; Mn can successfully substitute into the Mg site to the maximum value of 5%. The substitution causes a great suppression in $T_c$ at the rate of $dT_c/dx=-159$ [312].

In contrast to doping with elements, a slight reduction of $T_c$ has been found in the samples doped with large amount of SiC, Y$_2$O$_3$, WSi$_2$, ZrSi$_2$ and SiO$_2$. Also, the $J_c$ values of samples doped with these compounds were significantly enhanced in high magnetic fields and increases in $H_{irr}$ and $H_{c2}$ occurred, a promising development for practical applications.

Figure 2-25: Partial collapse of the spacing between the boron layers in Mg$_{1-x}$Al$_x$B$_2$. The figure shows variation of the in-plane (a) and between-plane (c) lattice parameters as a function of aluminium concentration. In the two-phase region, c-axis values for both phases are shown [337, 338].
2.3.9 Critical Fields

MgB\textsubscript{2} is a type II superconductor, therefore two different critical field have to be measured.

2-3-9-1 Upper Critical Field ($H_{c2}$)

To have a potential application, it is essential to have a high $H_{c2}$, as it shows the ability of superconductor to sustain superconductivity at high magnetic fields. A wide range of $H_{c2}$ values has been reported for different samples so far. Even for the same sample there are two different values for $H_{c2}$ due to anisotropy in this superconductor. For clean single crystal samples, relatively low values of the upper critical fields about $H_{c2}^{\parallel ab} (0) \approx 18$ T and $H_{c2}^{\perp ab} (0) \approx 3.5$ T have been reported parallel and perpendicular to the $ab$ plan, respectively [174, 339-343]. However, the higher value of the upper critical fields varies considerably up to about $H_{c2} \approx 29$ T for bulk samples containing impurities [344, 345] and up to about $H_{c2}^{\parallel ab} (0) \approx 48$ T for thin film according to recent measurements [344, 346, 347]. Such high values of $H_{c2}$ also suggest that MgB\textsubscript{2} is a suitable candidate for practical applications.

2-3-9-2 Lower Critical Field ($H_{c1}$)

By characterizing single and polycrystalline MgB\textsubscript{2} superconductors, different values of the lower critical field ranging between $H_{c1} (0) \approx 150$ Oe to 480 Oe have been reported [79, 164, 348-351]. However, according to recent measurements in a high purity single crystal sample, the lower critical field has been found to be $H_{c1}^{\parallel ab} (5K) \approx 120$ mT and $H_{c1}^{\perp ab} (5K) \approx 250$ mT [342].

2.3.10 Penetration Depth

Using the data for the lower critical field, the value of the penetration depth can be calculated, ranging between 85-203 nm [79] with the average value of $\lambda \sim 140$ nm [340, 352]. However, recent measurements in a high purity single crystal sample shows the penetration depth to be $\lambda_{ab} (0) \approx 22\pm 2$ nm and $\lambda_c (0) \approx 100\pm 10$ nm [342].
2-3-11 Coherence Length

In the CGS system the coherence length can be calculated using \( H_{c2} \) as \( \xi^2 = \frac{\Phi_0}{2\pi H_{c2}} \) \[353\]. Using the value of \( H_{c2} \), \( \xi(0) \) has been estimated to be \( \sim 5 \) nm in polycrystalline samples \[178\]. Considering the different values of \( H_{c2} \) in single crystal, the values of the coherence length have been reported to be \( \xi_{ab}(0) \approx 7 \) nm and \( \xi_c(0) \approx 4 \) nm for aligned MgB\(_2\) crystallites, using the \( \xi_{ab}^2(0) = \frac{\Phi_0}{2\pi H_{c2}^{ab}} \) and \( \xi_{ab} \xi_c = \frac{\Phi_0}{2\pi H_{c2}^{ab}} \) formulas \[354\]. However, different values of \( \xi_{ab}(0) = 10 \pm 0.2 \) nm and \( \xi_c(0) = 5 \pm 0.2 \) nm were recently reported for single crystal, which are relatively higher than other values in the literature \[342\].

2-3-12 Mean Free Path

The electronic mean free path can be roughly calculated from the experimental data of resistivity (\( \rho \)) and carrier density, as well as the average Fermi velocity, using the classical Drude model. The value of \( l \) is estimated to be approximately 60 nm\[178\] for high purity polycrystalline samples and 80 nm for single crystal samples \[33\].

2-3-13 Anisotropy

The study of anisotropy is important for practical applications as well as for understanding the physical properties. The layered structure of MgB\(_2\) results in an anisotropy property in the superconducting parameters. Many groups have measured the anisotropy parameter by using either the upper critical field \( \gamma = H_{c2}^{ab} / H_{c2}^{ab} = \xi_{ab} / \xi_c \) or the critical current density \( \gamma = J_c^{ab} / J_c^c \).

2-3-13-1 Anisotropy in MgB\(_2\) Powder

The anisotropy in \( H_{c2} \) has been measured for MgB\(_2\) powder. The very large values of \( \gamma = 6 \) \[355\] and \( \gamma = 6-9 \) \[356\] were determined using different techniques.
2-3-13-2 Anisotropy in Bulk MgB$_2$

A small, but distinct anisotropy of the upper critical field $\gamma = H_{c2}^{\parallel ab} / H_{c2}^{\perp ab} = 1.2$ was found for hot deformed and high density samples [357-359]. However an upper critical field anisotropy of $\gamma = 1.7$ as well as an almost temperature independent ratio $J_{c}^{ab} / J_{c}^{c}$ similar to 1.5 were found in an aligned bulk MgB$_2$ crystallite sample [354, 360].

2-3-13-3 Anisotropy in MgB$_2$ Thin Film

Different values of the anisotropy parameter were found for MgB$_2$ thin film samples. Different values of $\gamma = 1.8-2$ [347], 1.2-1.8 [135], 1.4-1.8 [136], 1.25 [346], 2 [361] and 3 [132] have been reported for the upper critical field anisotropy. By measuring the critical current density $\gamma = 2.55$ was determined from the scaling behavior of $J_c$ [362].

2-3-13-4 Anisotropy in MgB$_2$ Single Crystal

In single crystal samples a wide range for the anisotropy parameter from $\gamma = 2$ to $\gamma = 6$ has been reported by many groups [164, 165, 170, 171, 174, 175, 339, 341-343, 363-372]. Although many people found a constant anisotropy parameter over the temperature range measured [339, 342, 363], despite the anisotropic Ginzburg-Landau theory that predicts temperature independent anisotropy, it has been found by many groups that $\gamma$ is temperature dependent and decreases with increasing temperature [171, 174, 343, 365-368, 371].

2-3-13-5 Anisotropy in MgB$_2$ Tape

It has been found from x-ray diffraction studies, that $c$-axis texturing appears in the core of MgB$_2$ tapes during the cold working procedure [198, 199, 206, 215, 228, 258, 275]. This texturing increases with the sheath strength [215, 258] and has been found to be larger in tapes made by the ex situ technique than in tapes made by the in situ technique [275]. The anisotropy ratio was determined to be 1.3 for $H_{c2}$ parallel and perpendicular to the surface of the tape [198, 199]. However an unusual larger anisotropy factor of 10 was also reported by Kumakura et al. [258].
2-3-14 Strong Grain Connectivity

It has been confirmed by transport and magnetic measurements that unlike the HTS superconductors [373, 374], MgB$_2$ does not show any weak links, therefore grain boundaries are highly transparent to current flow [375, 376]. This is an advantage of MgB$_2$ compared to the HTS superconductors so far as practical applications are concerned, since high values of critical current density have been observed in MgB$_2$ thin film, bulk, and tapes and wires with no weak links.

Fig. 2-26 reveals the temperature dependence of $J_c$ at different magnetic fields [377]. A good agreement between the $J_c$ values obtained by transport measurements and the magnetic $J_c$ values estimated from hysteresis loops using the Bean model confirms inductive current flows throughout the sample with no grain boundary barrier.

![Figure 2-26: Temperature dependence of the critical current density of polycrystalline MgB$_2$ sample for H = 0.5, 1, 2, 3, and 5 T. The values for $J_c > 10^3$ A/cm$^2$ were estimated from magnetic measurements, while those for $J_c < 10^3$ A/cm$^2$ were estimated from transport measurements [377].](Image)
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CHAPTER 3: EXPERIMENTAL PROCEDURE

3-1 Sample Preparation

3-1-1 Preparation of Bulk MgB₂

Polycrystalline samples of MgB₂ were prepared through the conventional solid state reaction using a reaction *in-situ* process. High purity powders (99%) of magnesium (-325 mesh) and amorphous boron (-325 mesh) were used as starting materials. The precursor powders were weighed out according to the nominal atomic ratio and well mixed through grinding using a mortar and pestle. The powders were pressed into pellets 10 mm in diameter and 2-3 mm in thickness using a uniaxial hydraulic press. The pellets were sealed in Fe tubes, then heat treated at different temperature ranged between 680 °C to 950 °C. Wide range of sintering time were used from a few minutes to 2h. In order to get the pure phase and suitable results different sintering time and temperature have been used for different experiment. Heat treatment performed in flowing high purity Ar under the ambient pressure using the tube furnace. This was followed by a furnace cooling to room temperature. A temperature profile for the preparation of MgB₂ bulk sample is shown in the Fig. 3-1. Bar-shaped samples in a few millimeter size were cut and dry polished from the sintered pellets.

![Temperature profile](image)

*Figure 3-1: Schematic drawing of the thermal treatment used in the preparation of MgB₂ samples.*
3-1-2 Fabrication of MgB₂ Wire and Tape

3-1-2-1 Fabrication of Wire and Tape Using the Powder-in-Tube Technique

During this work Fe, Cu and Ag-clad MgB₂ wires were prepared using a standard powder-in-tube (PIT) method. The procedure is mainly consists of three steps.

I. Preparing the precursor powder and packing the powder into a metal tube.

II. Mechanical deformation process to make green wire or tape.


In the first step two different powders were used. In the experiments using the ex situ reaction technique, commercially available powder supplied by Alfa Aesar was employed. However, in situ reaction technique was used in the most of the experiments. For these experiments, powders of magnesium and amorphous boron (both in 99% purity and –325 mesh) with the stoichiometry of MgB₂ were well mixed using an agate mortar and pestle. The mixed powder was then loaded into a metal tubes. The tubes used in the experiments have an outside diameter (OD) of 6-9 mm, a wall thickness of 0.5-1.5 mm, and a length of about 10 cm depending on the experiment. One end of the tube was sealed either by a piece of lead or by a piece of aluminum. The tubes were filled in and packed with mixed powders. The remaining ends were crimped mechanically.

Mechanical deformation is the second step. Each tube was drawn to the final diameter of about 1.3 mm. Drawing was carried out by passing the tube through the conical hole of successive round dies at a speed of a few cm/s. For tape making, the thin wire was cold rolled to the flat tape with a thickness of 300-600 µm.

Apart from the above procedure two axial groove rolling was used to prepare the Stainless Steel sheath square wire. A deformation rate of no more than 15% per pass was used in the whole mechanical deformation procedure.
Sintering the wires and tapes were carried out using a tube furnace by a similar procedure to the heat treatment of pellet samples. Different sintering times and sintering temperatures were used and will be explained for each experiment separately. Fig. 3-2 shows the preparation procedure for single filament MgB$_2$ tape.

### 3-1-2-2 Fabrication of Multifilament MgB$_2$ Wire

To prepare the multifilament wire, numbers of single filament wires with a length of about 10-15 cm were cut from the as drawn wire. This was followed by bundling and restacking the wires, then inserting them into new metal tubes. This tube was then mechanically deformed to a thin wire and heat treated in a similar way to the single wire. Fig. 3-3 shows the fabrication procedure for multifilament tape. The detailed experiments will be presented later.

### 3-2 Sample Characterization

#### 3-2-1 X-ray Diffraction Pattern (XRD) Technique

The X-ray diffraction pattern technique is the fastest and most convenient method for microstructure characterization of MgB$_2$ superconductor. This technique has been widely employed to examine the microstructure, phase formation, and study of the
Chapter 3: Experimental Procedure

Figure 3-3: The fabrication procedure of the multifilament tape.

texture, as well as calculation of the lattice parameters. The X-ray examination were carried out using two different instruments: Philips PW1730 and MAC MO3XHF. Both machines were fully automated and configured in a Bragg-Brentano focusing geometry, with a $\theta$-2$\theta$ optics. In all X-ray investigations, monochromatized CuK\textalpha radiation from a normal focus X-ray tube was used, having wavelengths $\lambda_{K\alpha 1}=1.5405$ Å and $\lambda_{K\alpha 2}=1.5443$ Å. For the X-ray study of powders and pellets, the samples were ground using a mortar and pestle. For study and phase analysis of MgB\textsubscript{2} tapes or wires, the metal sheaths were mechanically removed simply by dry polishing the sheath to expose the core. A chemical compound or new phase can be determined if the volume ratio exceeds a few percent and if the grain sizes are larger than 1 µ. Peaks were indexed using Bragg’s law of $2d\sin\theta = n\lambda$, where $n$ is an integer, $\lambda$ is the radiation wavelength $\theta$ is the diffraction angle and $d$ is the distance between the reflecting parallel planes with same (hkl) Miller’s indices. The average grain size can be semi-quantitatively estimated, as the average crystallite is proportional to the width of a reflection peak at half maximum intensity (FWHM) [398, 399]. The lattice parameters were calculated by indexing the peaks using the Rietveld refinement method.

3-2-2 Scanning Electron Microscopy (SEM) and Optical Microscopy (OM)

A direct observation of microstructure as well as the investigation of morphology can be made using the SEM and OM. The SEM was equipped with Electron Dispersive
Analysis (EDS) attachments. The scanning electron microscopy was performed using secondary electron and back-scattered electron (BSE) detectors. The resolution of the optical microscope is 1 µm. However SEM can provide useful information on the structure in the sub-micron range. Specimens were prepared by cold mounting the wires and tapes in the Strues Epofix epoxy resin. The polishing procedure was applied after about 24 h to allow the resin to cure. SiC grinding papers of 600, 800, 1200 and 2400 mesh were used followed by polishing with 5 µm, 3 µm and 1 µm diamond paste. Water cannot be used as a lubricant due to the reaction of MgB$_2$ with water; therefore to avoid this, Struers blue lubricant was used during the polishing process. A thin layer of gold with a thickness of about 300 Å was deposited on the specimens mounted in resin.

3.2.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy permits a direct observation and characterization of fine microstructure. The TEM images were obtained at the University of New South Wales and the Nanyang Technological University of Singapore. Two different instruments were employed for TEM examination: a Philips CM200 Field Emission Gun Transmission Electron Microscope and a JEOL 3010 High Resolution Transmission Electron Microscope (HRTEM). Specimens were prepared by pulverizing the powder with mortar and pestle, then dispersing it in ethanol. The suspension was then pipetted on to holey-carbon coated copper grids.

3.2.5 Magnetic Measurements

3.2.5-1 AC Susceptibility Measurements

To study the electromagnetic properties of superconductors, a method consisting of generating a harmonically varying magnetic field to probe the sample and registering the magnetic response of the sample, is widely used [400]. The ac susceptibility measurement is one of the common experiments of this type.

A schematic diagram of the instrument for ac susceptibility is shown in Fig. 3-4. For measurement, a piece of MgB$_2$ in the normal state is placed in a system of coils,
consisting of a large coil for dc magnetic field control, a smaller coil for the ac magnetic field, and pick-up coils which can detect the magnetic response of the specimen. A harmonic magnetic field \( (H_{ac}) \) is produced by the ac coil. According to the Faraday’s law, the induced voltage in the pick-up coils is:

\[
V = -\frac{d\varphi}{dt}
\]

(3-1)

Where \( \varphi \) itself consist of two terms due to \( H_{ac} \), as well as the specimen response, \( \varphi = \varphi_{ext} + \varphi_s \). In order to eliminate the \( \varphi_{ext} \), the pick-up coil set consists of two identical coils, wound in an opposite direction and connected in series together. As long as the sample is in the normal state, the ac magnetic field penetrates the whole sample. When the normal-superconductor transition occurs, the magnetization of the specimen changes due to flux exclusion, therefore \( \varphi \) changes as \( \varphi_s = MA \). Here, \( A \) is the cross-sectional area of specimen. Since \( \chi = dM/dH \), it follows:

\[
\frac{d\varphi}{dt} = A \frac{dM}{dH} \frac{dH}{dt} = \chi A \frac{dH}{dt}
\]

(3-2)

Therefore the voltage induced in the pick-up coil is proportional to the susceptibility of sample:

\[
V = -A\chi \frac{dH}{dt}
\]

(3-3)

Then, any change in the sample susceptibility gives a change in the voltage across the pick-up coil, and this change can be detected by a Lock-in Amplifier.

In this work, the ac susceptibility of MgB\(_2\) samples was measured using the Quantum Design Physical Property Measurement System (PPMS) with a sensitivity of up to \( 10^{-8} \) emu. More details as well as experimental results are presented in the subsequent chapters.
3-2-5-2 DC Magnetization Measurements

DC magnetization measurements were carried out on MgB$_2$ samples using the Quantum Design Physical Property Measurement System (PPMS). In order to measure the absolute value of the dc magnetization, a dc field was applied to the sample, and the sample was moved through the entire detection coil. The pick-up coil detects a waveform signal versus the position of the sample. The dc magnetization was then extracted by fitting the detected signal with the known waveform signal.

![Figure 3-4: A schematic diagram of the instrument for ac susceptibility.](image)

$J_c$ can be calculated from the measured magnetic hysteresis loop assuming that $J_c \propto \Delta M$, where $\Delta M$ is the width of the hysteresis loop (Fig. 3-5). $\Delta M$ can be calculated using the relation $\Delta M = M^+ - M^-$, where $M^+$ and $M^-$ are positive and negative branch of hysteresis loop, respectively. The calculation of $J_c$ from the dc magnetization is based on the critical state model [401], applied to a finite sample and usually called the “modified Bean model”. For a bar shaped sample, the magnetic critical current density can be calculated using the following relation [402]:
\[ J_c = \frac{20\Delta M}{a \left(1 - \frac{a}{3b}\right)} \quad (4-3) \]

In this relation, \( a \) and \( b \) are the dimensions of sample in cm, perpendicular to the magnetic field direction with \( a < b \). \( J_c \) and \( \Delta M \) are in A/cm\(^2\) and in emu/cm\(^3\), respectively.

For a cylindrical sample parallel to the magnetic field, \( J_c \) can be calculated as:

\[ J_c = 30 \frac{\Delta M}{d}, \]

where \( d \) is the diameter of the cylinder in cm.

\[ \text{Figure 3-5: Magnetic hysteresis loop showing the width of the magnetic hysteresis loop (\( \Delta M \)).} \]

### 3-2-6 Transport Measurements

Transport measurements of MgB\(_2\) samples were carried out using the so-called four probe technique. This method consists of attaching four contacts to the sample. The two outermost contacts are for the current \( (I) \) and the two inner contacts are for the voltage \( (V) \). As the current passes through the sample, a voltage is generated which is proportional to the resistivity. At the normal-superconducting transition, the voltage drops down to a level which is lower than the noise level of the measuring instrument. In the case of critical current \( (I_c) \) measurements, the standard value of 1 \( \mu \)V/cm was
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used as a criterion for $I_c$. Therefore, $I_c$ is arbitrarily defined as the value of the current which produces a voltage drop of 1 µV between two voltage contacts separated by 1 cm. In different experiments, contacts were attached to the sample using different materials such as silver epoxy, Woods alloy, or by low temperature soldering with Sn:Pb 50:50 in order to make low resistance contacts. Particular care was taken with the current contacts. Details of the transport measurements are presented in further chapters.

References

2. Ionescu, M., *Growth and characterization of Bi-2212 crystals and improvement of Bi-2212/Ag superconducting tapes*, in ISEM. 1997, University of Wollongong: Wollongong.
CHAPTER 4: PREPARATION AND CHARACTERIZATION OF MgB$_2$ WIRE AND TAPE

4-1 Preparation and Characterization of Fe/MgB$_2$ Wire

4-1-1 Introduction

Efforts have been made to fabricate MgB$_2$ wires since the discovery of superconductivity at 39 K in this material [19]. A number of techniques have been developed to improve the processing parameters for achieving high critical current densities [198, 201, 233, 252, 277, 291, 315]. Among these, the powder-in-tube (PIT) process appears most promising and practically feasible. Some metals and alloys have been found to be suitable for sheath materials in the PIT process. Iron and its alloys in particular have been found to be non-poisoning to MgB$_2$ [201, 315, 403]. High transport critical current densities have been reported for Fe and Fe alloy clad-MgB$_2$ wires by some groups [201, 252, 315].

Heat treatment is applied in most PIT processes used for the fabrication of MgB$_2$. The times and temperatures that have been used so far for fabricating MgB$_2$ pellets and wires/tapes range from less than an hour to more than 48 h at sintering temperatures from 600 to 1000 °C. All the heat treatments must be under high purity Ar protection from oxidation. High $J_c$ metal-sheathed MgB$_2$ tapes without any heat treatment were reported using the pre reacted powder [277]. This process has advantages over those with heat treatment as it substantially simplifies the process and hence reduces the cost for wire fabrication. However, the sheath materials need to be of very high hardness in order to densify the MgB$_2$ core. High toughness metal is easily broken during the cold drawing and rolling process, and very careful and delicate design and control are mandatory [252, 294]. Furthermore, as MgB$_2$ is very brittle, it would be a formidable task to overcome the cracking problem for long length production without heat treatment.
In order to further improve and simplify the fabrication processes, we have carried out a systematic study on the effects of sintering time on MgB\(_2\) formation and \(J_c\). In this section we present the fabrication procedure as well as the characterization of the Fe-clad MgB\(_2\) wire. The effects of sintering time and temperature on the phase formation and critical current density of Fe-clad MgB\(_2\) wires will also be explained. MgB\(_2\) wires were fabricated using the powder-in-tube process and sintered for different periods of time at predetermined temperatures. In contrast to the common practice of sintering for several hours, the present results show that there is no need for prolonged heat treatment in the fabrication of Fe-clad MgB\(_2\) wires. A total time in the furnace of several minutes is enough to form nearly pure MgB\(_2\) phase with high performance characteristics. The results on \(T_c\), \(J_c\) and \(H_{irr}\) convincingly show that the samples which were only sintered for 3 minutes have quite good performances. In fact, the \(J_c\) field performance for the most rapidly sintered sample is as good as for all the other samples. \(J_c\) of \(4.5 \times 10^5\) A/cm\(^2\) in zero field and above \(10^5\) A/cm\(^2\) in 2 T at 15 K has been achieved for the best Fe-clad MgB\(_2\) wires. As a result of such a short sintering there is no need for using high purity argon protection and it is possible to carry out the heat treatment in a much less protective atmosphere or in air. These findings substantially simplify the fabrication process, making it possible to have a continuous process for fabrication and reducing the costs for large-scale production of MgB\(_2\) wires.

### 4-1-2 Experimental Details

The Fe/MgB\(_2\) wire was prepared using the powder-in-tube technique. Powders of magnesium (99%) and amorphous boron (99%) were used as starting materials. The pure Fe tube has 8mm OD, 1.5 mm wall thickness and 10 cm long. The composite tube was drawn from 8 mm to 1.5 mm diameter. Short wire samples of about 2 cm in length were sealed in a small Fe tube and then heat treated at 750 °C for 30 min in flowing high purity Ar. Due to a strong shielding effect from the Fe sheath metal [200, 203], bare cores were used for the magnetic characterization. Cylindrical bars of MgB\(_2\) core were obtained by removing the Fe sheath mechanically.
4-1-3 Results and Discussion

4-1-3-1 Phase Formation and Microstructure

Fig. 4-1 shows XRD patterns recorded from the core of the Fe-clad MgB$_2$ wire after the iron sheath was mechanically removed. The sample is revealed to be single phase with a small amount of MgO (<5%).

![XRD patterns](image)

**Figure 4-1:** XRD patterns recorded from the core of the Fe-clad MgB$_2$ wire after the iron sheath was mechanically removed.

Fig. 4-2 shows the more accurate XRD pattern obtained with Rietveld analysis. It also shows a small amount of MgO. The peaks can be very well indexed with the space group $P6/mmm$. SEM examination revealed that the grain size in the superconducting core is smaller than 1 micron. An optical image of a cross-section of a sample is shown in Fig. 4-3. There is a well-defined interface between the Fe sheath metal and the MgB$_2$ core. No reaction has been found between the sheath and the superconductor. The core is very porous in agreement with the mass density of sample, which is only 1.3 g/cm$^3$, suggesting that the performance of wire could be further improved if the density of the wires can be increased.
4-1-3-2 Superconductivity and Critical Current Density

Fig. 4-4 shows the transition temperature ($T_c$) for a core sample determined by the ac susceptibility (real part and imaginary part) measurements. The $T_c$ onset for the sample ($\sim 38.3$ K) is almost the same as that reported by a number of groups. The sample also showed a sharp transition with a transition width of less than 1 K.

Figure 4-2: Rietveld analysis of MgB$_2$ powder. The powder was prepared by grinding the superconducting core of Fe/MgB$_2$ wire.

Figure 4-3: A typical optical microscope image of the transverse cross-section for a Fe/MgB$_2$ wire sample.
Chapter 4: Preparation and Characterization of MgB$_2$ Wire and Tape

Figure 4- 4: AC susceptibility of the core of the Fe-clad MgB$_2$ wire after the iron sheath was mechanically removed.

Measurements of the $M$-$H$ loops at different temperatures were carried out on the bare cylindrical bar samples. A typical $M$-$H$ loop of a MgB$_2$ wire sample is shown in Fig. 4-5. We can see that a typical flux-jumping pattern is present for temperatures below 15 K. This flux jumping was first observed in an MgB$_2$ bulk samples [404] but occurs in thin films samples as well [405]. The flux jumping has been directly visualized using magneto-optical imaging techniques and explained in terms of phenomena associated with rapid flux penetration[405, 406]. The critical current density was calculated from the $M$-$H$ loops using the Bean critical model. $J_c$ versus magnetic field up to 8 Tesla for Fe/MgB$_2$ wire sample at 5 K, 10 K, 15 K, 20 K, 25 K, and 30 K is presented in Fig. 4-6. It should be noted that $J_c$ of $4.5 \times 10^5$ A/cm$^2$ at 15 K and zero field has been achieved. Because of the flux jumping, the $J_c$ below 15 K cannot be measured.

Figure 4- 5: $M$-$H$ loop for Fe/MgB$_2$ wire sample at different temperatures: 5 K, 10 K, 15 K, 20 K, 25 K, and 30 K.
4-1-3-3 Effect of the Sintering Time

In order to further improve and simplify the fabrication processes of Fe/MgB$_2$ wire, we have carried out a systematic study on the effect of sintering time on MgB$_2$ formation and $J_c$. Short wire samples of about 2 cm in length were sealed in a small Fe tube and then directly heated at a preset temperature ($T_{\text{max}}$) for 3-32 minutes in flowing high purity Ar or nitrogen, or in air (when a very short sintering time is used). This is then followed by a quench in liquid nitrogen.

![Field dependence of $J_c$ of Fe/MgB$_2$ wire sample at different temperature 5 K, 10 K, 15 K, 20 K, 25 K, and 30 K.](image)

Fig. 4-7 shows the real temperature of the samples as a function of time, starting from when the wires were loaded into a hot tube furnace held at a constant temperature $T_{\text{max}}$ of 745, 840, and 900 °C. It shows that only a short time (2-3 min.) is required for the samples to reach $T_{\text{max}}$, and that the higher the $T_{\text{max}}$, the shorter the time. Six samples, which were heat treated at different $T_{\text{max}}$, are illustrated and the removal time indicated by open circles as shown in Fig. 4-7. Samples 1, 5 and 6 were removed from the furnace after 3 minutes, having experienced only a few seconds at $T_{\text{max}}$. Samples 2-4 were removed after sintering for 6, 15, and 32 minutes, respectively. The surface of the Fe tube used to seal the wires was slightly oxidized after sintering in air. However, the MgB$_2$/Fe wire samples sealed inside the Fe tube were as fresh as before sintering.
regardless of the time at $T_{max}$ and regardless of the atmosphere. A longer sintering time only gives rise to more severe surface oxidation of the outside Fe tube.

Figure 4-7: The real temperature of the samples as a function of time, after the wires were loaded into a hot tube furnace held at a constant temperature $T_{max}$.

Figure 4-8: XRD patterns recorded from the powdered core of the Fe-clad MgB$_2$ wire samples after the iron sheath was mechanically removed.
4-1-3-3-1 Effect of the Sintering Time on the Phase Formation and Microstructure

XRD results show that all the samples have almost the same phase purity (above 90% MgB$_2$). Fig. 4-8 shows XRD patterns recorded from the core of the Fe/ MgB$_2$ wires (samples 1, 4 and 5) after the iron sheath was mechanically removed. It is clear that sample 5 has the same high phase purity as sample 4, even though it was only heat treated for 3 min.

SEM examination revealed that the grain size is smaller than 1 micron, and the homogeneity appears to be the same for all the samples. The optical images of cross sections of samples are similar to what has been shown in Fig. 4-3. There is a well-defined interface between the Fe sheath metal and the MgB$_2$ core. It should also be noted that the density of the wire sample is only 1.3 g/cm$^3$, suggesting that $J_c$ could be further improved if the density of the wires can be increased.

4-1-3-3-1 Effect of the Sintering time on the Superconductivity, Critical Current Density and Irreversibility Field

Transition temperatures, $T_c$, and transition widths, $\Delta T_c$, for the 3-15 minute treated samples are all very similar. In fact, $T_c$ is almost the same (~ 38 K) for all the samples, while there is only a small difference in $\Delta T_c$, which decreases with increasing heating time from 3-15 min for samples 1-3 sintered at 745 °C (Fig 4-9).

![Figure 4-9: Temperature dependence of the real part of the ac susceptibility.](image-url)
Measurements of the \( M-H \) loops at different temperatures were carried out on the bare cylindrical bar samples. \( J_c \) versus magnetic field up to 6 Tesla for three samples at 10 K, 15 K, 20 K, and 30 K is shown in Fig. 4-10. Note that \( J_c \) of \( 4.5 \times 10^5 \) A/cm\(^2\) at 15 K and zero field has been achieved for sample 4. Again the \( J_c \) below 15 K cannot be measured because of the flux jumping. For \( T_{\text{max}} = 745 \, ^\circ\text{C} \), the \( J_c \) increases as the sintering time increases from 3 to 15 min. Fig. 4-11 shows the \( J_c \) versus sintering temperature for samples 1, 5 and 6 which were all treated for 3 min. Sample 1, sintered for 3 minutes at 745 \( \, ^\circ\text{C} \), has a markedly lower \( J_c \) than the other samples, probably due to poor grain connectivity. However, if \( T_{\text{max}} = 840 \, ^\circ\text{C} \), the \( J_c \) of the wire treated for just 3 minutes (sample 5) is as good as that of a wire treated for 15 min. at 745 \( \, ^\circ\text{C} \). Furthermore, \( J_c \) field performance of the sample sintered at \( T_{\text{max}} = 840 \, ^\circ\text{C} \) for 3 min. is the best out of all the samples, as evidenced by the crossover (indicated by arrows) of \( J_c-H \) curves in higher fields as shown in Fig. 4-10.

Fig. 4-12 shows the comparison of \( J_c \) at 20 K for both zero field and 3 T for sample wires sintered for different times. We can see that the \( J_c \) is as high as \( 3 \times 10^5 \) A/cm\(^2\) at 20 K zero field for samples 2-5. Noted that \( J_c \) for the 3 min sintered sample 5 is the same as for samples 2-4 which were sintered for 6 min to 32 min. For further comparison, \( J_c \) data from a Fe-clad MgB\(_2\) tape (described in the next section) are also shown in Fig. 4-12. The sample was prepared by 3 h heating to 800 \( ^\circ\text{C} \), holding for 1 h, and then slow cooling down to room temperature. It can be seen that the \( J_c \) and field dependence of the wire samples which were sintered for only a very short time are almost as good as the \( J_c \) and field performance of this reference tape.

![Figure 4-10: Field dependence of \( J_c \) at different temperatures for samples 3, 4 and 5.](image-url)
Figure 4-11: \( J_c \) versus sintering temperature of \( T_{\text{max}} \) for samples 1, 5 and 6 which were all sintered for 3 minutes.

Table 4-1: Fabrication conditions and \( J_c \) for all the samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>( T_{\text{max}} ) (°C)</th>
<th>Time*</th>
<th>( J_c ) (A/cm(^2))</th>
<th>15 K, 0T</th>
<th>20 K, 0T</th>
<th>30 K, 0T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>745</td>
<td>3 min.</td>
<td>1.5 \times 10^5</td>
<td>1.1 \times 10^5</td>
<td>3.2 \times 10^4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>745</td>
<td>6 min</td>
<td>2.7 \times 10^5</td>
<td>2.7 \times 10^5</td>
<td>6.5 \times 10^4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>745</td>
<td>15 min</td>
<td>4.5 \times 10^5</td>
<td>3.5 \times 10^5</td>
<td>1.3 \times 10^5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>745</td>
<td>32 min</td>
<td>3.5 \times 10^5</td>
<td>2.8 \times 10^5</td>
<td>9.8 \times 10^4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>840</td>
<td>3 min</td>
<td>3.7 \times 10^5</td>
<td>2.9 \times 10^5</td>
<td>1.1 \times 10^5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>900</td>
<td>3 min</td>
<td>-</td>
<td>3.0 \times 10^5</td>
<td>1.0 \times 10^5</td>
<td></td>
</tr>
</tbody>
</table>

*Samples were quenched in liquid nitrogen after a total sintering time in a furnace with predetermined \( T_{\text{max}} \).

Table 4-2: Comparison of \( J_c \) values.

<table>
<thead>
<tr>
<th>( J_c ) (A/cm(^2)) at 25 K, 1 T</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB(_2) wire (Sample 4, this work)</td>
<td>5.9 \times 10^4</td>
</tr>
<tr>
<td>MgB(_2) (HP synthesised pellet)</td>
<td>1.6 \times 10^4</td>
</tr>
<tr>
<td>Bi2223/Ag tape</td>
<td>2.9 \times 10^5</td>
</tr>
<tr>
<td>Bi2212/Ag tape</td>
<td>2.5 \times 10^3</td>
</tr>
</tbody>
</table>
Figure 4-12: \( J_c \) as a function of real sintering time at different \( T_{\text{max}} \). \( J_c \) data (closed circles) for a normally sintered MgB\(_2\)/Fe tape is also shown for comparison.

\( J_c \) of sample 4, a typical short-sintered MgB\(_2\) wire is compared with good quality \( J_c \) Bi2212/Ag and Bi2223/Ag tapes at 25 K and 1 T [408, 409] (Table 4-2). The \( J_c \) of a MgB\(_2\) pellet prepared using Mg+2B powders and sintered at 850 °C for 1 h under a pressure of 45 kbar [407] (HP synthesised MgB\(_2\) pellet) is also shown in the table. It can be seen that our short-sintered sample 4 has a lower \( J_c \) than for the Bi2223/Ag tape at 25 K and 1 T, but it has a higher \( J_c \) than the HP synthesised MgB\(_2\) pellet, and \( J_c \) is more than one order of magnitude higher for the Bi2212/Ag tapes.

Figure 4-13: Irreversibility line for all the samples.
Fig. 4-13 shows the irreversibility fields ($H_{irr}$) versus temperature for all the samples. $H_{irr}$ was determined from $J_c$-$H$ curves using the criterion of 100 A/cm$^2$. We can see that all the samples, except sample 1, have approximately the same $H_{irr}$.

### 4-1-4 Summary

Fe/MgB$_2$ wire has been prepared using the powder-in-tube and reaction \textit{in situ} techniques. The effect of sintering time and temperature on the formation and critical current densities of Fe-clad MgB$_2$ wires has been investigated. It was found that there is no need for prolonged heat treatment in the fabrication of Fe-clad MgB$_2$ wires. A total sintering time of several minutes is enough to form nearly pure MgB$_2$. The $T_c$, $J_c$ and $H_{irr}$ results show convincingly that the samples which were sintered for 3 minutes have quite high performance characteristics. These findings substantially simplify the fabrication process and can reduce the costs for large-scale production of MgB$_2$ wires.
Chapter 4: Preparation and Characterization of MgB₂ Wire and Tape

4-2 Preparation and Characterization of Fe/MgB₂ Tape

4-2-1 Introduction

The high critical current density values observed in bulk samples, regardless of the degree of grain alignment [395], are an advantage for making wires or tapes with no degradation of $J_c$, in contrast to the degradation due to grain boundary induced weak-links, which is a common and serious problem in cuprate high temperature superconductors. In polycrystalline bulk MgB₂ samples, critical current densities of $10^4$ to $10^5$ A/cm² at 4.2 K have been reported by several groups [368, 404, 410-413]. However, the fabrication of metal clad MgB₂ tapes or wires will be essential to meet the requirements of most such high current applications. Mechanical deformation during the tape making process can increase the density of the superconducting core as well as inducing pinning centres.

For tape fabrication, it is necessary to find a suitable sheath material for MgB₂ which does not degrade the superconductivity. So far, several metal-clad MgB₂ tapes or wires have been fabricated with sheath materials such as Nb [291], Cu, Ag, and Ni [233, 277], as well as Fe. For example, a transport $J_c$ of $10^4$ A/cm² at 4.2 K has been obtained for Ag/MgB₂ using pre-reacted MgB₂ without any heat treatment [233]. In fact any sort of heat treatment caused a degradation of $J_c$. A high transport $J_c$ of $10^5$ A/cm² at 4.2 K has been achieved for an unsintered Ni/MgB₂ tape [277]. Relatively high $J_c$ values were obtained for Cu clad MgB₂ tapes which were sintered for long time (48 h) at 620 °C [233]. For critical current optimization the proper choice of metal cladding material is essential since the Mg component of the compound tends to react with many metals such as Cu or Ag during sintering or reaction at temperatures around 900-1000 °C. In a detailed study of material compatibility, Jin et al [201] noted that whereas admixtures as high as 5 mol% of powdered Y, Mo, Cu, Ag, and Ti, to the MgB₂ powder prior to ribbon-forming and sintering at 900 °C seriously degraded the $J_c$, the presence of the same amount of Fe powder decreased $J_{c,4.2K}$ only from $1.8 \times 10^5$ to $1.5 \times 10^5$ A/cm² at 0.5 T and not at all at 1.25 T. It has been established that Mg and Fe have meager mutual solubility (about 0.01% Fe in Mg at its M.P. and 0.2 at.% Mg in Fe [414]). This and the
above results suggest that the processing of Mg+B or MgB2 powders in an Fe tube would be accompanied by little contamination and only slight degradation of $J_c$, and even then only in fields below about 1 T.

Most of the transport $J_c$ results reported for MgB2 wires and tapes are limited to 4.2 K so far. To take advantages of the relatively high $T_c$ of 39 K for MgB2 superconductor it is essential to have high $J_c$ values at temperatures above 20 K. For example, the boiling point of hydrogen at atmospheric pressure is 20.13 K, so that it is possible to use liquid hydrogen or cold hydrogen gas as a cryogen for cooling MgB2 wires. This requires that the MgB2 wires have sufficiently high $J_c$ values at around 25 K. In this section we present the fabrication of pure Fe clad MgB2 tapes with a high transport $J_c$ above $10^4$ A/cm$^2$ at 30 K and 1 T and $I_c$ greater than 150 A.

### 4-2-2 Experimental Details

Standard powder-in-tube methods were used for the Fe clad MgB2 tape. The as drawn wire was cold rolled to a ribbon over many steps. Several short samples 2 cm in length were cut from the ribbon. These pieces were then sintered in a tube furnace at 750 K for 30 min in flowing Ar gas. The mass loss after sintering is very small, less than 1%.

### 4-2-3 Results and Discussion

#### 4-2-3-1 Microstructures

Scanning electron microscopy (SEM) photomicrographs for the Fe clad tape after sintering are shown in Fig. 4-14. The picture on the left is a typical transverse cross section of an Fe clad tape. It clearly shows that the MgB2 core presents a homogeneous cross section. The picture on the right is the longitudinal cross-sectional micrograph showing good core homogeneity. Fig. 4-15 presents the high magnification microstructure of the core surface after mechanically removal of the Fe sheath material. This micrograph shows a porous microstructure with a clusters of grains of about 100 µm in size. Our results showing large grain sizes are very different from those seen in the reported Cu/Fe/MgB2 tape which was made using reacted MgB2 powders with a
starting grain sizes of 3 µm. The final grain size was significantly reduced to 120 nm due to the occurrence of substantial grain refinement during the wire fabrication process [201].

Figure 4-14: SEM image for a typical transverse (a) and a longitudinal (b) cross-section

4-2-3-2 Transport Properties

The critical current of the Fe clad MgB$_2$ tape was measured by the standard four-probe method. The sample used for the measurement has a length of 20.5 mm and a width of 3 mm. The MgB$_2$ core cross-section in this sample is similar to that shown in Fig. 4-14. Its average dimensions are $2.1 \times 0.45 \text{ mm}^2$. Therefore, the core cross-section is about $9.45 \times 10^{-3} \text{ cm}^2$. The current and voltage contacts were soldered with Wood’s alloy (giving a current contact resistance lower than 10 mΩ), and the distance between the voltage contacts was 7.5 mm.

Figure 4-15: High magnification microstructure of the core surface after the top Fe sheath material has been removed mechanically.
Figure 4-16: R-T curves for Fe/MgB$_2$ tape measured in fields of 0, 4, and 9.5 kOe in the EO and FO orientation.

The temperature dependence of the resistance ($R$-$T$) was measured using an AC current (frequency 18.4 Hz, $I=1$ mA). Fig. 4-16 shows $R$-$T$ measured at zero field over a wide temperature range from 300 to 10 K. It shows a sharp transition with a width, $\Delta T_c$, of 0.2 K and a $T_{c0}$ of 37.8 K. We also measured $R$-$T$ around the transition temperature with applied fields of 4 kOe and 9.5 kOe directed perpendicular to the sample axis and (a) parallel to the broad sample face (the “edge-on” or EO orientation) or (b) perpendicular to it (“face-on”, FO). As a result of differences in the degree of magnetic screening (see below) the field-induced decreases in $T_c$ were larger for the EO orientation than for the FO orientation.

Critical current measurements were made using a pulse method, with the current pulse linearly rising from zero to maximum current. The pulse duration was 20 ms for $T>33$ K and 10 ms for $T<30$ K. The voltage was amplified and recorded on a digital storage oscilloscope together with the voltage across a standard resistor, giving the current flowing through the sample. The temperature of the sample holder was monitored during the measurement with a gold-chromel thermocouple, showing a temperature rise after a pulse of approximately 0.2 K at currents higher than 150 A (the next pulse was applied after the temperature had fallen to denoted values). We estimate that the temperature rise of the sample itself was somewhat higher, but that just means that the critical current obtained is underestimated.
Although the above mentioned procedure for critical current measurements enables the determination of $I_c$ with the 1 $\mu$V/cm criterion, there were two problems: 1) the current pulse causes magnetization of the iron cladding, which gives a spurious voltage signal $V_m$ superimposed on the voltage of the superconductor $V_s$. Since $V_m$ was appreciable in fields $B<0.4$ T, $I_c$ in these fields was determined as the current at which the overall voltage starts to increase above the decaying $V_m$. However, the error in $I_c$ determination is 10% at most, and because of heating, the real $I_c$ is probably higher than the results obtained (especially at lower fields); 2) magnetization depends on the field direction. For that reason, we measured $I_c$ for both field directions (denoted on the figures in the same way as for resistance measurements) at 35 K.

The critical currents measured at temperatures above 29 K and in fields up to 1 T are shown in Fig. 4-17. Again as a result of differences in magnetic screening (see below) $I_{c,FO}$ for a given applied field was greater than $I_{c,EO}$. The critical current, $I_c$, increased from 10 to 164 A as the temperature decreased from 36.4 to 30 K, and changes of $I_c$ with field were smooth for 32 and 30 K. The critical current density $J_c$ is calculated using the calculated core cross section of $9.45 \times 10^{-3}$ cm$^2$, and its value is shown on the right axis of Fig. 4-17. We can see that the Fe clad MgB$_2$ has a very high transport $J_c$ of above $10^4$ A/cm$^2$ for fields $<0.5$ T at 33.2 K and for fields $< 0.8$ T at 32 K. The highest $J_c$ is about $1.7 \times 10^4$ A/cm$^2$ at 29.5 K and 1 T.

![Figure 4-17: Field dependence of $I_c$ (left axis) and $J_c$ (right axis) at different temperatures with fields perpendicular and parallel to the tape plane.](image)
4-2-3-3 Magnetic Critical Current Density

Magnetic measurements ($M$-$H$ loops) were carried out on a superconducting quantum interference device (SQUID, Quantum Design PPMS 9 T) magnetometer. In order to avoid a large magnetic signal from the Fe clad tape, we measured a MgB$_2$ core with dimensions of $0.78 \times 3.95 \times 0.32 \text{mm}^3$ taken from one of the Fe-clad tapes. All magnetic measurements were performed in the FO orientation. The magnetic critical current densities were derived from the Bean model: $J_c = 20\Delta M / a(1 - a/3b)$ and are summarized in Fig. 4-18, where $J_c(T)$ curves at $B=0$ T, 1 T, 2 T are plotted.

![Figure 4-18: Temperature dependence of $J_c$ at different applied magnetic fields perpendicular to the tape plane (FO orientation).](image)

The magnetic critical current density at $B=0$ T and $T=35$ K is about $1.38 \times 10^4$ A/cm$^2$, which is higher than the transport $J_c$ (see fig. 4-17). This is understandable because the transport critical current density was underestimated due to either the heating of the sample or the fast swapping rate of the applied current.

4-2-3-4 Magnetic Screening

Genenko et al. [415] have proposed the use of a surrounding high-permeability medium to enhance a superconductor’s transport current density, and Majoris et al [416] have proposed magnetic screening by surrounding ferromagnetic sheaths as a possible way of decreasing transport AC loss in multifilamentary strands. Applicability of the screening
principle to both high-\(T_c\) and low-\(T_c\) superconductors has been pointed out and its benefits to applications such as power transmission and fault-current limitation suggested [416]. But since Fe or low-alloy steels seem suitable cladding materials for the processing of powder-in-tube MgB\(_2\) strand both from mechanical and chemical-compatibility standpoints, the resulting wires automatically become ideal candidates upon which to explore and exploit the properties of magnetic screening.

In an Fe-clad wire the influence of magnetic screening can be gauged by comparing its superconductive properties in the sheath-on and sheath-off conditions, provided sheath removal can be successfully achieved without damage to the underlying superconductor. In the case of a rectangular tape screening information can be obtained by comparing its magnetically influenced properties in the FO and EO orientations as in Figs. 4-16 and 4-17, both of which indicate that screening is more effective when the tape is in the FO orientation. Consider Fig. 4-17, for example. This shows that rotating the sample from FO to EO in an applied field of 0.6 T is equivalent to increasing the internal field by 0.13 T. So far, we have not been able to use these data to deduce the actual shielding factors, \(S = \frac{H_{\text{applied}}}{H_{\text{internal}}}\), of the tapes concerned in spite of the existence of some published information on screening by rectangular cylinders [417]. Finally we note that in the context of magnetization measurement an equivalent sheath-off/sheath-on comparison can be achieved using data acquired at 40 K and below \(T_c\).
respectively, as in Fig. 6. The 15K $M-H$ loop for an Fe-clad round wire (from the same stock as the tape) is depicted in Fig. 19. That of the superconductive core itself, inset, is obtained by numerically subtracting the $M-H$ loop for the Fe sheath as measured at 40 K. Evidently partial screening takes place throughout an applied field range of $\pm 0.6$ T and complete shielding within $\pm 0.06$ T.

4-2-4 Summary

Fe-clad MgB$_2$ tapes fabricated by PIT techniques and sintered in pure Ar at 800 °C for 1 h at ambient pressure show a superconducting core with large clusters of grains with a size of about 100 µm. They have a sharp transition with a transition width $\Delta T_c$ of 0.2 K and $T_c^0$ at 37.8 K. A transport critical current density of $1.7 \times 10^4$ A/cm$^2$ for both 29.5 K in 1 T and for 33 K in null field has been obtained.

The Fe or low-alloy steel cladding material that seems necessary for successful PIT processing, both from the mechanical- and chemical-compatibility standpoints, also provides magnetic screening, the benefits of which (depending on applied field strength and materials permeability) can be higher $I_c$ and lower ac loss. In low magnetic fields wherein the relative permeability of the sheath material is large the shielding can be very effective, but becomes weaker as the sheath approaches magnetic saturation. It has been pointed out previously [416] that magnetic screening by surrounding ferromagnetic sheaths should decrease transport ac loss in both high-$T_c$ and low-$T_c$ multifilamentary strands and improve the performances of superconductive devices such as power transmission lines and fault-current limiters. Finally we note that the ferromagnetic sheath may have an additional benefit quite apart from screening. In precision field dipole magnets a considerable departure from field uniformity accompanies the use of superconducting strand with its inherent (“persistent-current”) magnetization. Among the several techniques available for canceling out the effects of superconductor magnetization [418] is strand coating with a ferromagnetic layer [419-421].
4-3 Preparation and Characterization of Cu/MgB\textsubscript{2} and Ag/MgB\textsubscript{2} Wire

4-3-1 Introduction

As explained in the last section some metals and alloys have been found to be suitable for sheath materials in the PIT process. Iron and its alloys in particular have been found to be not only non-poisoning to MgB\textsubscript{2} [199-201, 315, 403] but also capable of providing magnetic screening to reduce the effect of external applied magnetic fields on the critical current [200, 203, 315]. A high transport $J_c$ on the order of $10^4$-$10^5$ A/cm\textsuperscript{2} at 20 K and 4.2 K has been reported for Cu/Fe/MgB\textsubscript{2} tapes where reacted MgB\textsubscript{2} powders were used as the core conductor and sintered at 900-1000 °C for 0.5 h out of a total heat treatment time of more than 3 h, including the initial heating [404]. Recently Fe and Ni clad wire have been fabricated with quite high $J_c$ values of $2.3 \times 10^5$ A/cm\textsuperscript{2} at 4.2 K and 1.5 T in a Ni/MgB\textsubscript{2} tape and $10^4$ A/cm\textsuperscript{2} at 4.2 K and 6.5 T in a Fe/MgB\textsubscript{2} tape [202]. By using unreacted Mg+2B powders and sintering at 800 °C for 1 h, Fe clad MgB\textsubscript{2} tapes with a high transport $J_c$ above $10^4$ A/cm\textsuperscript{2} at 30 K and 1 Tesla and $I_c$ greater than 150 A also have been successfully fabricated as explained in the previous sections.

Although the high toughness materials have some benefits in achieving high-density samples, these materials are usually very hard to mechanically deform. They are also easily broken. Therefore, easily deformable silver and copper can be better alternatives for sheath materials, especially for some applications such as superconducting magnets, if high critical current density can be achieved. Ag and Cu-clad MgB\textsubscript{2} tapes using in-situ and ex-situ reactions have already been prepared. A magnetic $J_c$ value of above $10^4$ A/cm\textsuperscript{2} has been reported by Glowacki et al. at 5 K and low magnetic field for Cu clad MgB\textsubscript{2} wire, which was sintered at 620 °C for 48 h [233]. They have also reported relatively higher $J_c$ values for Cu clad MgB\textsubscript{2} wire that was heat-treated at 700 °C for 1h [238]. In section 4-1 we have shown that the MgB\textsubscript{2} superconducting phase can be formed in a very short time at any temperature above the melting point of magnesium.
Just a few minutes of heat treatment is enough to achieve high quality Fe/MgB$_2$ wires with a high $J_c$ value of $4.5 \times 10^5$ A/cm$^2$ at 15 K and 1 T.

As it has been reported that Ag and Cu react with Mg [238], it is proposed that a shorter sintering time would decrease the reaction of Mg with Ag and Cu sheath materials and lead to some improvements in wire performance. In this section we present the fabrication procedure as well as the characterization of the Ag and Cu sheathed MgB$_2$ superconductor wire. We also study the effect of short period sintering on the $J_c$ of Ag and Cu/MgB$_2$ wires and compare these results with the performance of Fe/MgB$_2$ wire that was also prepared with the short sintering.

4-3-2 Experimental Details

The powder-in-tube method was used to fabricate Ag and Cu clad MgB$_2$ wires using an in-situ reaction method. Powders of magnesium (99%) and amorphous boron (99%) with the stoichiometry of MgB$_2$ were well mixed. The pure Ag and Cu tubes had an outside diameter (OD) of 8 mm, a wall thickness of 1 mm, and were 10 cm long. The fabrication procedure has been explained previously. Short length Ag and Cu-clad wire samples about 2 cm in length were sintered using the fast formation method as described in section 4-1-3-3. One of the Ag-clad samples was also sintered by the normal longer sintering.

For the short sintering, Ag and Cu-clad wire samples were sealed in a small Fe tube and then directly heated at a preset temperature of 800 °C for 6 minutes in flowing high purity Ar. This was then followed by a quench in liquid nitrogen. In the normal sintering case, one Ag-clad MgB$_2$ sample was sealed in a small Fe tube and then sintered in a sealed tube furnace in flowing high purity Ar. In this case, the temperature was increased at a heating ramp rate of 600 °C/h to 800 °C, then furnace cooled down to room temperature without any holding period at 800 °C.

Fig. 4-20 shows the real temperature of the normally sintered sample as a function of time. The inset shows the average temperature variation of the fast sintered samples with time, starting from when the samples were loaded into a hot tube furnace held at a constant temperature of 800 °C.
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Figure 4-20: Real temperature that sample has experienced as a function of time for normal sintered sample. The inset shows the time variation of the average real temperature of the short sintered sample, starting from when the wires were loaded into a hot tube furnace held at a constant temperature of 800 °C.

Fig. 4-20 reveals that for the normal sintering case, the sample experienced temperatures higher than 660 °C, which is the magnesium melting point, for about 77 minutes. We thus called this sample the long time-sintered (LS) sample. However, for the fast formation case, this period is only a few minutes (about 4.5 min.) and we call these samples short-time sintered (SS) samples. The surface of the Fe tubes used to seal the wires was slightly oxidized after sintering. However, the MgB$_2$ wire samples sealed inside the Fe tubes were as fresh as before sintering.

By opening the wires and removing the superconductor cores mechanically, X-ray diffraction of the internal surface of the Ag and Cu sheath materials can be performed. The dc field dependence of the magnetization was measured using the PPMS (Quantum Design) between 5 K and 35 K at different dc fields up to 6 T. For magnetic characterization of Fe clad wire, bare cores were used because of the strong shielding effect of the Fe sheath metal as explained in the last section. Cylindrical bars of MgB$_2$ core were obtained by mechanically removing the Fe sheath. Ac susceptibility was measured with the amplitude and frequency of the excitation field 1 Oe and 117 Hz, respectively, using the same instrument.
4-3-3 Result and Discussion

The XRD pattern of a typical MgB$_2$ core separated from the Ag and Cu-clad wires is shown in Fig. 2. It can be seen that the result is relatively single MgB$_2$ phase with a slight amount of MgO (<5%) and MgB$_4$. In order to study the reaction between the core and the sheath material at the interface, XRD patterns of the internal surface of the Ag and Cu were obtained after the cores were removed mechanically. The temperature dependence of ac susceptibility for Fe, Ag and Cu-clad samples is shown in the inset of Fig. 4-21. It shown that all samples have a $T_c$ of about 38 K.

The XRD results are shown in Fig. 4-22. The patterns have been recorded from the internal surface of the sheaths of Ag and Cu-clad MgB$_2$ wire samples when the superconducting core was mechanically removed. It shows that magnesium has reacted
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Figure 4-22: XRD patterns recorded from the internal surface of the sheath of Ag and Cu-clad MgB$_2$ wire samples when the superconducting core was mechanically removed.

Figure 4-23: Scanning electron microscope image of a transverse cross-section of SS Cu-clad MgB$_2$ wire sample using back scattered electron imaging.

with the sheath materials and formed Cu$_2$Mg and Ag$_3$Mg phases on the internal sheath surfaces of the Cu and Ag-clad wires, respectively. The unknown peaks that were not matched with PDF database lines are indicated by question marks. For Fe-clad wire
there was not any clear evidence for any reaction between Mg or B and Fe. These results are in agreement with our results in the last sections.

Fig. 4-23 presents a magnified view of a transverse cross section of SS Cu-clad wire using SEM back scattered electron imaging. A well-defined reacted layer about 40 µm in thickness can be clearly seen. It is due to the reaction of magnesium and copper at high temperature in agreement with the XRD pattern (Fig. 4-22). The diffusion of magnesium into the copper sheath is clear in Fig. 4-24, which shows the Electron Dispersive Spectroscopy (EDS) surface analysis result. The magnesium concentration in the central part of the superconductor core is higher than in the area close to the copper sheath. The reacted layer in the SS Ag-clad wire is also about 25 µm (Fig. 4-25). However as we can see in Fig. 4-26, the reacted layer in the LS Ag-clad wire is much thicker, about 90 µm. So increasing the sintering time increases the magnesium deficiency and consequently causes a deficiency in MgB$_2$ phase in the superconducting core. Longer sintering times could thus lead to a lower $J_c$ in the wire.
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Measurements of the $M-H$ loops at different temperatures were carried out on the Cu, Fe and Ag-clad wires. A typical $M-H$ loop of an SS Ag-clad wire sample is shown in Fig. 4-27. We can see that a typical flux-jumping pattern is present for temperatures below 15 K. This flux jumping has been also observed in MgB\textsubscript{2} bulk samples [404].

The critical current density was calculated from the $M-H$ loops using the Bean critical model. The field dependence of $J_c$ for three samples of Cu and Ag-clad wires at 10 K, 20 K and 30 K are shown in Fig. 4-28. The field dependence of Fe clad wire at 20 K and 30 K is also shown. As we can see, Fe-clad wire has the highest $J_c$ and the best $J_c$-field
dependence among all samples at 20 K and 30 K. It should be noted that a $J_c$ of $1.3 \times 10^5$ A/cm$^2$ at 20 K and zero field has been achieved for the SS Ag-clad sample. It is not possible to exactly measure the $J_c$ at low fields at temperatures below 15 K due to the flux jumping. As we can see the $J_c$ in the SS sample is more than two times higher than for the LS sample due to less reaction between the superconducting core and sheath material.

Figure 4-27: M-H loop of the SS Ag-clad MgB$_2$ wire sample at different temperatures.

Figure 4-28: Field dependence of $J_c$ at 5 K, 20 K and 30 K for Ag, Cu and Fe clad wires.
LS Ag-clad wire has the lowest $J_c$ at low fields over the entire temperature range. Although the SS Cu-clad wire has a higher $J_c$ than the LS Ag-clad wire at low field, the $J_c$-field performance of this sample is not as good as for the LS Ag-clad sample. The LS Ag-clad sample has a slightly higher $J_c$ than SS Cu-clad wire at high fields over the entire temperature range, probably due to poor grain connectivity in the Cu-clad wire.

![Graph showing $J_c$ vs. $H_{dc}$ for different samples.](image)

**Figure 4-29:** The comparison between $J_c$ field dependence of our SS Cu-clad MgB$_2$ wire and the Cu-clad wires which were reported by Glowacki et al. [14,15] at 5 K.

The field dependence of $J_c$ for the SS Cu-clad wire was compared with the results which were reported by Glowacki et al. [233, 422], as is shown in Fig. 4-29. As we can see, the $J_c$ of wire that was sintered at 700 °C for 1h is about two times higher than for wire that was sintered at 620 °C for 48 h. Our SS Cu-clad wire, which was sintered at 800 °C for 6 min, has better $J_c$-field performance than wire that was sintered at 620 °C for 48 h. It even has better $J_c$-field performance at low field (less than 4 T) than wire that was sintered at 700 °C for 1 h. The slightly inferior performance of our SS Cu-clad wire at high fields is probably because the longer sintering time in the 700 °C sample caused stronger grain connectivity.

Fig. 4-30 shows the irreversibility field ($H_{irr}$) versus temperature for all the samples. $H_{irr}$ was determined from $J_c$ – $H$ curves using the criterion of 100 A/cm$^2$. We can see that the copper clad wire has the lowest $H_{irr}$ for the whole temperature range. The SS Ag-clad wire also has a higher $H_{irr}$ than the LS wire over the whole temperature range. Fe
has the highest $H_{irr}$ among all the samples. As we can see, the differences between the $H_{irr}$ values are increased by decreasing the temperature.

![Irreversibility lines for all the samples.](image)

**4-3-4 Summary**

In this section we have investigated the effects of sintering time and temperature on the critical current densities of Cu, Ag and Fe-clad MgB$_2$ wires. It was found that a short heat treatment in the fabrication of Cu and Ag clad MgB$_2$ wires can markedly enhance the critical current density. A total sintering time of several minutes is enough to form nearly pure MgB$_2$ with high performance characteristics. SEM microanalysis, $J_c$ and $H_{irr}$ results show that the Cu and Ag clad MgB$_2$ wires samples which were sintered for 6 minutes are better than those sintered for longer times. $J_c$ of $1.2 \times 10^5$ A/cm$^2$ in zero field and above $10^4$ A/cm$^2$ in 2 T at 20 K have been achieved for the SS Ag-clad MgB$_2$ wire.
4-4 Fabrication and Critical Current Density in 16-Filament Stainless Steel/Fe/MgB₂ Square Wire

4-4-1 Introduction

As we explained in the previous sections the powder-in-tube (PIT) method seems the most promising for practical applications of MgB₂ wires or tapes. Fe and some of its alloys have been found to be suitable for this purpose [200, 203]. Grasso et al. showed that MgB₂ tape or wire can be made from pre-reacted commercially available powder without any heat treatment [277]. Furthermore Suo et al. showed that the critical current density of pre-reacted powder can be improved by a final heat treatment [202]. It has been also shown that increases in the \( J_c \) of tapes or wires result from the use of high toughness sheath materials due to mechanical densification of the superconducting core [265]. A 7-filament Cu-Ni/MgB₂ wire prepared by Kumakura et al. [252] had a transport \( J_{c,4.2K} \) of about \( 3 \times 10^4 \, \text{A/cm}^2 \) in self field and \( 10^4 \, \text{A/cm}^2 \) at 1 T. They had used pre-reacted powder and no further heat treatment was applied. An 18-filament Cu/NbZr/MgB₂ tape fabricated by Liu et al. [294] exhibited a transport \( J_{c,10K} \) of about \( 8 \times 10^4 \, \text{A/cm}^2 \) in self field and \( 1.36 \times 10^4 \, \text{A/cm}^2 \) at 1T. They used an in-situ reaction method, sintering samples at 600-1000 °C for 1-10 h. To prepare dense and compact multifilament wire we used Fe and stainless steel (SS) as a sheath material. In this section we report on the preparation and properties of a 16-filament MgB₂ square wire.

4-4-2 Experimental Details

The SS/Fe/MgB₂ wires were prepared using a standard PIT method. Commercially available MgB₂ powder (Alfa Acer) was loaded into an 8cm long pure Fe tube with an outside diameter of 5 mm and a wall thickness of 0.5 mm. The tube was groove rolled to wire with a square cross section of about 1.5 mm on each side and a length of 50 cm. An empty SS tube was groove rolled to prepare a square cross section tube with a 6 mm inside dimension (each side) and a length of 8 cm. Four pieces of the Fe-clad wire, each about 8 cm in length, were stacked inside this tube which was then groove rolled to a 4-filament wire about 2mm in outside dimension. Fig. 4-31 presents an SEM back
scattered electron image of a transverse cross section of the 4-filament SS/Fe/MgB₂ wire. A well-defined Fe sheath layer fully covered by an SS layer can be clearly seen.

![Image of a transverse cross-section of a 4-filament SS/Fe/MgB₂ wire](image1)

**Figure 4-31:** Scanning electron microscope image of a transverse cross-section of 4-filament SS/Fe/MgB₂ wire sample using back scattered electron imaging.

Four pieces of the 4-filament SS/Fe/MgB₂ wire each about 10 cm in length were again stacked inside another SS tube and groove rolled to a tough, high density, 16-filament wire about 2-3 mm in dimension (Fig. 4-32). Fig. 4-32 is an SEM image of a transverse cross section of the 16-filament SS/Fe/MgB₂ wire.

![Image of a transverse cross-section of a 16-filament SS/Fe/MgB₂ wire](image2)

**Figure 4-32:** Scanning electron microscope image of a transverse cross-section of 16-filament SS/Fe/MgB₂ wire sample.
Several samples about 2.5 cm long were cut and sintered at 950 °C in flowing high purity Ar. Fig. 4-33 is an SEM image of a superconducting core from the 16-filament SS/Fe/MgB$_2$ wire after sintering. Highly packed grains with an average grain size of about 300 nm can be seen.

![Figure 4-33: High magnification Scanning Electron Microscope image of a superconducting core for 16-filament SS/Fe/MgB$_2$ wire sample. The mark indicates 1 micron.](image)

A sample about 6 mm long was taken from the middle of each wire for magnetic measurement. The dc field dependence of the magnetization was measured by VSM using an applied field sweep amplitude of 17 kOe and a temperature range of 4.2 to 40 K, the latter temperature being just above the $T_c$ of MgB$_2$. In order to obtain the $M$-$H$ loops for the superconductor itself, the Fe contribution (the measurement results at 40 K) was subtracted away from the total $M$-$H$ loop [200, 207]. In the other words, the Fe magnetic contribution was electrically removed. Separate measurement of a small Fe sample sufficed to verify that ($M$-$H$)$_{\text{sheath}}$ itself was practically temperature independent within the temperature range of 4 to 40 K, validating the subtraction procedure over the temperature range of interest.

Magnetization loops for the 16-filament wire were measured from 4.2 K to 40 K at 2.5 K temperature intervals. A typical $M$-$H$ loop for a wire sample, with and without the Fe signal, is shown in Fig. 4-34.
4-4-3 Results and Discussion

Fig. 4-35 depicts a representative set of temperature-dependent loops after electrical removal of the sheath material. The paramagnetic slope evident at high temperature is due to the presence of stainless steel. Magnetic $J_c$s were calculated using the conventional semi-Bean critical-state approach.

The temperature dependences of magnetic $J_c$ of the 16-filament SS/Fe/MgB$_2$ wire at fields of 5 kOe and 10 kOe are shown in Fig. 4-36. At 5 K, $J_c$s of $3.4 \times 10^5$ A/cm$^2$ in 5 kOe and $2.4 \times 10^5$ A/cm$^2$ in 10 kOe were obtained. The transport $J_c$ temperature dependence of an 18-filament Cu/NbZr/MgB$_2$ wire [252] in self field and 10 KOe are also included in the figure, as well as the transport $J_c$ at 4.2 K of 7-filament Cu-Ni/MgB$_2$ wire [294] in self field and 10 kOe. It should be noted that a $J_c$,10K values of $2.3 \times 10^5$ A/cm$^2$ at 5 kOe and $1.3 \times 10^5$ A/cm$^2$ at 10 kOe have been achieved for the 16-filament SS/Fe/MgB$_2$ wire sample. Fig. 4-36 shows that the $J_c$ of our wire at 10 K and 10 kOe is considerably higher than that of the 18-filament Cu/NbZr/MgB$_2$ tape which had been prepared using unreacted powder and sintered at 600-1000 °C for 1-10 h.

Figure 4-34: A typical $M-H$ loop of 16-filament SS/Fe/MgB$_2$ wire sample.
Chapter 4: Preparation and Characterization of MgB$_2$ Wire and Tape

Figure 4-35: $M$-$H$ loops of 16-filament SS/Fe/MgB$_2$ wire sample at different temperatures, with the Fe contribution was removed.

Figure 4-36: Temperature dependence of magnetic $J_c$ of 16-filament SS/Fe/MgB$_2$ wire sample at 0.5 and 1 T. The figure includes the temperature dependence of the transport $J_c$ of 18-filament Cu/NbZr/MgB$_2$ tape sample at 0 and 1 T that is extracted from Liu et al. [294]. The temperature dependences of critical current density $J_c$ of 7-filament Cu-Ni/MgB$_2$ wire at 0 and 1 T and 4.2 K that are extracted from Kumakura et al. [252] is also included.
4-4-4 Summary

Sixteen-filament stainless steel/Fe/MgB$_2$ wires were fabricated by the powder-in-tube method followed by groove rolling and heat treatment at 950 °C. The wires were characterized using SEM, and vibrating sample magnetometry. High strength sheath material results in a dense superconducting core and relatively high critical current density. Magnetic critical current densities of 3.4×10$^5$ A/cm$^2$ in 0.5 T and about 1.9×10$^5$ A/cm$^2$ in 1 T at 5 K were achieved.
4-5 Transport Critical Current of Solenoidal MgB$_2$/Cu Coils Fabricated Using a Wind-Reaction *in situ* Technique

### 4-5-1 Introduction

Since the discovery of the 39 K superconductor, MgB$_2$ [19], significant advances has been achieved in the fabrication of various forms of MgB$_2$. In particular, intensive efforts have been made in improving the critical current density ($J_c$) in various metal sheathed MgB$_2$ wires. High $J_c$ of $10^5$ – $10^6$ A/cm$^2$ at 4 K to 30 K for MgB$_2$ wires and good performance of $J_c$ in magnetic field have been reported by several groups [200-202, 233, 265, 277, 404, 423]. However, the results reported thus far have been largely limited to short samples several centimetres long. In contrast, long Bi-based HTS wires with high $J_c$ were reported within several months time after discovery of the Bi-HTS compound [424]. For large scale applications it is essential to fabricate this material into long wires and coils. The critical challenge that remains is how much the $J_c$ deteriorates with increasing length of the wire and whether one can wind the wire into a coil without appreciable loss of $J_c$. In this section, we report the fabrication and transport critical current of solenoidal MgB$_2$/Cu coils fabricated using a wind-reaction in-situ technique.

### 4-5-2 Experimental Details

Standard powder-in-tube methods were used for Cu-Fe or Cu clad MgB$_2$ tapes. The pure Cu or Fe tubes had an outside diameter (OD) of 10 mm, a wall thickness of 1 mm, and a length of 12 cm. One end of the tube was sealed, and the tube was filled in with magnesium (99% purity) and amorphous boron (99%) with the stoichiometry of MgB$_2$. The composite was drawn to 0.5, 0.7 and 1 mm diameter wires several meters long. Some wires were further rolled to ribbon over many steps. Several short samples 2 cm in length were cut from the wires and ribbons. The green wires were wound onto a ceramic tube 8 mm in diameter with both ends fixed to slots at the end of the ceramic
tube. Several coils were prepared using this procedure, and one of the coils has 100 turns and was wound using 3-meter long Cu-sheathed MgB$_2$ wire. These coils and some straight pieces of wires and tapes were then sintered in a tube furnace at temperatures within a range of 650-750 °C for 10 min. A high purity argon gas flow was maintained throughout the sintering process.

Short pieces of wires 4 mm and 30 mm long were used for magnetic and transport critical current measurements using the four probe method. For longer wire samples up to 300 mm, a number of voltage contacts were made at different distances to determine the variation of $I_c$ with length. For the 100 turn coil two voltage contacts were made at a distance of 2 meters apart with the current contacts at the end of the coil. Transport measurements of the voltage versus current ($V-I$) were performed by a standard 4-probe, DC method. The measurements were performed in liquid helium. Current contacts were soldered onto the samples at least 1cm away from the voltage contacts, to allow for the heat created at the current contacts to dissipate into the liquid helium before it reached the part of the sample between the voltage contacts. The current was switched on and off gradually, to avoid damage to the sample due to the mechanical shock resulting from a fast change in the current. Each point in $V-I$ was taken within 10 seconds, to avoid heating the sample. Magnetic measurements were performed by a Quantum Design PPMS magnetometer. Magnetic hysteresis loops were used to obtain the field dependence of the critical current density at each of the temperatures measured, by employing the critical state model. The sweep rate of the field was 50 Oe/s. The magnetic field was always applied along the sample.

4-5-3 Results and Discussions

Figure 4-37 displays 10 mm diameter MgB$_2$ coils of 100 turns, wound using 3 meters of Cu-sheathed single core wire and heat-treated at 700 °C for 10 min. The coils are reasonably flexible and can be stretched by 20% and bent to an angle of 30° after heat treatment without degradation in $I_c$. Figure 4-38 shows photomicrographs of transverse and longitudinal cross-sections of a 100 turn solenoid coil (Coil-4). It is seen that the interface between the Cu and the MgB$_2$ core is very smooth. Although there is thin layer of MgCu formed during sintering the reaction between the Cu and the Mg is not very
Figure 4-37: The appearance of two 10 mm diameter MgB₂ coils of 100 turns, wound using 3 meters of Cu-sheathed single core wire and a 10 mm diameter coil of 10 turns. These coils were heat-treated at 700 °C for 10 min.

serious as a short reaction time (10min) and low sintering temperatures (750 °C) were used.

Figure 4-38: Photomicrographs of the transverse (a) and longitudinal (b) cross-sections of the 100 turn coil-4. The scale bars represent about 300 µm.
Table 4-3 lists the parameters for samples in the form of straight wires and coils with Cu-sheaths. These results show very interesting features. Compare wire-1 and coil-1 which are made from the same green wire. The $J_c$ is the same for both cases, indicating that (a) winding the wire into a 10 mm diameter coil does not degrade $J_c$ and (b) the increase in distance between the two voltage contacts from 13mm to 100mm did not cause a reduction in $J_c$. The $J_c$ results obtained from the straight wire (wire-2) and the 100 turn coil (coil-4) further indicate that there is no evidence of significant length dependence of $J_c$. For the sample wire-2, the critical current was not reached due to the limitations of contact heating. But the $I_c$ for all three contact distances exceeds 100 A. The 6 turn coil (coil-2) and 5 turn coil (coil-3) were wound using thinner Cu-sheathed wire (OD = 0.5mm) and tape respectively. Because their core density is relatively higher, respective $J_c$ values of 125,000 A/cm$^2$ and 133,000 A/cm$^2$ at helium temperature and self field has been achieved, suggesting that density is one of the critical factors to influence $J_c$.

Table 4-3: List of various samples with description and measurement results of $J_c$.

<table>
<thead>
<tr>
<th>Designation of samples</th>
<th>Sample description</th>
<th>Distance between voltage contacts (D, mm)</th>
<th>MgB$_2$ Core diameter (mm)</th>
<th>$I_c$ (A)</th>
<th>$J_c$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire-1</td>
<td>30mm MgB$_2$/Cu straight wire</td>
<td>13</td>
<td>0.45</td>
<td>105</td>
<td>66,000</td>
</tr>
<tr>
<td>Wire-2</td>
<td>200mm long MgB$_2$/Fe-Cu straight wire</td>
<td>37</td>
<td>0.6</td>
<td>&gt;100</td>
<td>&gt;35,300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>0.6</td>
<td>&gt;100</td>
<td>&gt;35,300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>0.6</td>
<td>&gt;100</td>
<td>&gt;35,300</td>
</tr>
<tr>
<td>Wire Coil-1</td>
<td>5 turn MgB$_2$/Cu coil, 10mm OD</td>
<td>100 (3 turns)</td>
<td>0.45</td>
<td>&gt;101</td>
<td>&gt;63,500</td>
</tr>
<tr>
<td>Wire Coil-2</td>
<td>6 turn MgB$_2$/Cu coil, 10mm OD</td>
<td>140 (4 turns)</td>
<td>0.32</td>
<td>100</td>
<td>125,000</td>
</tr>
<tr>
<td>Tape Coil-3</td>
<td>5 turn MgB$_2$/Cu coil, 10mm OD</td>
<td>100 (3 turns)</td>
<td>0.055</td>
<td>&gt;73</td>
<td>&gt;133,000</td>
</tr>
<tr>
<td>Wire Coil-4</td>
<td>100 Turn MgB$_2$/Cu solenoid, 10mm OD</td>
<td>35 (1 turn)</td>
<td>0.45</td>
<td>72</td>
<td>45,300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000 (63 turns)</td>
<td>0.45</td>
<td>73</td>
<td>45,900</td>
</tr>
</tbody>
</table>

Figure 4-39 shows the characteristics of the voltage – current curves ($V$-$I$) for the 100 turn solenoid coil with two voltage contacts at distance of 35 mm (1 turn) and 2 meters (63 turns) apart. Despite possible inhomogeneity along the length and the low density of the core, the same value of $J_c$ for the two very different voltage contact distances clearly indicates that the deterioration of $J_c$ with increasing length of MgB$_2$ wires is insignificant. It should be pointed out that the measurement for the voltage contact distance of 35 mm was performed after several cycles of the coil between helium temperature and room temperature due to the needed to change the contact position. It is
expected that the cycling could cause some degradation in $J_c$ as the density of the single core is low. Furthermore, a solenoid coil with 100 turns passing 73 A will generate a self-field of about 80 mT which will slightly reduce the $I_c$. So, the $J_c$ for the 35mm contact distance should be higher than that with the 2 meters contact distance. Compared to sample wire-1 which was made from the same batch of green wire the $J_c$ for the 35 mm contact distance would not be higher than that of wire-1. If the density of the wire core can be improved the thermal cycling would not have detrimental effects as has been demonstrated for Fe-sheathed wire [203].

![Figure 4-39: The voltage–current curves ($V$-$I$) for the 100 turn solenoid coil with two voltage contacts at a distance of 35 mm (1 turn) and 2 meters (63 turns). The two current contacts were soldered at the end of each side of the solenoid coil for the latter case.](image)

Note also from Figure 4-39 that the $V$-$I$ curve for the contact distance of 35 mm shows a steep increase at the critical current 72 A while the voltage for the large contact distance increases more gradually. For the former the $V$-$I$ characteristics beyond the critical current are dominated by the Cu sheath while in the latter case, there are still large segments of the coil remaining superconducting when a small section becomes normal. It is unclear that what kind of voltage criteria should be used to determine the $I_c$ for the Cu-sheathed MgB$_2$ wire at this stage. In our measurements we use the same standard to determine the $I_c$ for short straight wire and for the solenoid coils. This means that the criterion for the 100 turn solenoid coil is about 0.005 $\mu$V/cm, compared with common criterion of 1 $\mu$V/cm used in HTS wires. If we apply the 1 $\mu$V/cm criterion to the 100 turn coil the $I_c$ will be about 200 A, estimated by extrapolating the $V$-$I$ curve.
cause huge heating over normal sections of coil. Thus, the 1 µV/cm criterion may be applicable to the metal sheathed MgB₂ wire.

4-5-4 Summary

In this section, we report the results of transport $J_c$ of solenoid coils up to 100 turns fabricated with Cu-sheathed MgB₂ wires using a wind-reaction in-situ technique. Despite the low density of the single core material and some reaction between Mg and Cu-sheath, our results demonstrate that the decrease in transport $J_c$ with increasing length of MgB₂ wires is insignificant. Solenoid coils with diameters as small as 10 mm can be readily fabricated using a wind-reaction in-situ technique. The $J_c$ of coils is essentially the same as for straight wires. A $J_c$ of 133,000 A/cm² and 125,000 A/cm² at 4 K and self field has been achieved for a small coil wound using Cu-sheathed tape and Cu-sheathed wire respectively. These results indicate that MgB₂ wires have a great potential for large scale applications.

References


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CHAPTER 5: EFFECT OF CHEMICAL DOPING ON THE CRITICAL CURRENT DENSITY AND FLUX PINNING OF MgB₂

5-1 Enhancement of the Critical Current Density and Flux Pinning of Superconductor MgB₂ by Nanoparticle SiC Doping

5-1-1 Introduction

High $J_c$ values at a level of $10^5$ A/cm² to $10^6$ A/cm² at 20 K to 30 K for MgB₂ wires and tapes have been presented in previous chapter. Many groups have attempted to improve the critical current density in this superconductor as it has a lower $H_{c2}$ and $H_{irr}$ than the commercial low temperature superconductors Nb₃Sn and NbTi. Despite the strong link grain boundary effects on critical current density [1], the $J_c$ drops rapidly with increasing magnetic field due to poor flux pinning. Therefore, extensive research has been done on introducing pinning centers into this superconductor.

Various mechanical deformation processes have been used either to improve the density or to introduce defects, resulting some improvements in $J_c(H)$ in hot-pressed bulk, wires and tapes [2-10]. Because the MgB₂ lattice structure is rather rigid and the number of elements in the structure is only two, the density of defects, if any, introduced by mechanical deformation is too low to provide effective pinning.

Effective pinning centers has been induced by high energy ion irradiation of MgB₂ powder [11] or by oxygen alloying in MgB₂ thin films [10]. Producing pinning centers via chemical doping is another effective method and more practical compared to physical techniques. Several attempts have been made to improve flux pinning using chemical doping. The results for doping into MgB₂ reported so far are limited to

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addition rather than substitution. Additives appear to be ineffective for improving pinning at high temperatures. Zhao et al., and Feng et al. have doped MgB$_2$ with Ti and Zr, showing an improvement of $J_c$ at low temperatures, attributable to the sintering aid effect of these additives [12, 13]. However, there is no evidence for improved pinning at temperatures above 10 K as the $J_c$ drops off rapidly with increasing field ($H_{irr} \approx 4$ T at 20 K). Wang et al. doped MgB$_2$ using Y$_2$O$_3$ nanoparticles [14]. Their results showed a significant improvement of the irreversibility field ($H_{irr} = 11.5$ T) at 4.2 K for the doped sample due to the introduction of highly dispersed inclusions such as YB$_4$. However, the improvement in $H_{irr}$ at 20 K is insignificant for the doped samples. Cimerle et al. found that doping with a small amount of Li, Al and Si produced some increase in $J_c$, but there was no improvement in $H_{irr}$ [15] because single element doping degrades $T_c$ dramatically at high doping levels.

Recently, using high field transport measurements, Gurevich et al. have reported the achievement of record high upper critical fields ($H_{c2}$) for high resistivity films and untextured bulk polycrystals [16]. They found that enhancements to the resistivity have a strong influence on $H_{c2}$. The observed remarkable $H_{c2}$ enhancement to almost 50 T is a consequence of the two-gap superconductivity of MgB$_2$, which offers special opportunities for further $H_{c2}$ increased by tuning the impurity scattering. In this section we present chemical doping with nanoparticle SiC into MgB$_2$ by means of transport and magnetic measurement evaluations in combination with TEM observations on the nanoscale-SiC doped MgB$_2$. We will show that SiC doping can significantly enhance $J_c$ in high fields without a reduction in low field $J_c$ and only a slight reduction in $T_c$. The results demonstrate that nanoparticle SiC doping in MgB$_2$ induced intra-grain defects as effective pinning centres, which are largely responsible for the improved performance of $J_c(H)$ over a wide range of temperatures.

5-1-2 Experimental Details

MgB$_2$ pellet samples were prepared by an in-situ reaction method, which was described in detail previously. Powders of magnesium (99% pure) and amorphous boron (99% pure) were well mixed with SiC nano-particle powder (with a particle size of 10 nm to 100 nm) with the atomic ratio of MgB$_2$-x(SiC)$_{x/2}$, where $x = 0, 0.2, \text{ and } 0.3$. A sample with 10 wt% of SiC addition to MgB$_2$ was also made. Pellets 10 mm in diameter and 2
mm in thickness were made from these powders. Heat treatment was performed at a temperature of 800 °C for 30 min.

The magnetization of samples in magnetic fields up to 9 T was measured using a PPMS (Quantum Design) at the University of Wollongong and up to 14 T using the vibrating sample magnetometer (VSM) at the University of Wisconsin at Madison. The resistivity versus temperature curves \( \rho(T) \), were measured in magnetic fields up to 9 T by a four probe method at a current density of about 1 A/cm\(^2\) using the 9 T PPMS (Quantum Design) at the University of Wisconsin at Madison. All the samples were cut to the same size of 0.56×2.17×3.73 mm\(^3\) from as-sintered pellets. A magnetic \( J_c \) was derived using a Bean model. An empirical magnetic irreversibility field \( (H_{irr}) \) was defined as the field at which \( J_c \) falls to 100 A/cm\(^2\). The critical temperature \( (T_c) \) was obtained as the onset of the diamagnetic transition in magnetic ac susceptibility measurements. An high-resolution transmission electron microscope (HRTEM) was employed to characterize the morphology of the samples. Electron energy loss spectroscopy (EELS) [17] was obtained using a JEOL-3000F field emission STEM/TEM, equipped with a Schottky field-emission source operated at 300 keV.

### 5-1-3 Results and Discussion

Fig. 5-1 shows XRD patterns for the SiC doped and non-doped samples. The XRD pattern for the non-doped sample reveals about 5% MgO, besides MgB\(_2\) as the main phase. Doped samples consist of MgB\(_2\) as the main phase, with Mg\(_2\)Si as the major impurity phase (crosses in Fig. 5-1) as well as small amounts of MgO and MgB\(_4\).
Chapter 5: Effect of Chemical Doping on the Critical Current Density and Flux Pinning of MgB$_2$

Figure 5-1: XRD patterns for the undoped and SiC-doped samples.

Fig. 5-2 shows an SEM image of the MgB$_2$ + 10 wt% SiC sample. As we can see, the sample is very porous, consistent with the low mass density of the sample, about 1.3 g/cm$^3$ which is about 50% of the mass density of a fully dense sample. This suggests that $J_c$ could be further improved if the density of the sample can be increased. Large numbers of spherical holes with a size of about 10-15 µm are uniformly distributed in the superconducting matrix, as can be seen in this image. The holes can be attributed to voids that were left by the melting magnesium particles. A very similar microstructure was found for all the samples without any significant differences. Further SEM examination revealed that the MgB$_2$ matrix consists of sub-micron grains with average grain sizes of less than 100 nm, and the homogeneity appears to be the same for all the samples with different doping levels.
Fig. 5-3 shows the transition temperature ($T_c$) and transition width $\Delta T_c$ for the doped and undoped samples determined by ac susceptibility measurements. The $T_c$ onset for the undoped sample (~38.2 K) is almost the same as that reported by a number of groups. It shows also a sharp transition with the transition width of less than 1 K. For the doped samples, the $T_c$ decreases with increasing doping level. It is striking to note that despite the high doping level, the $T_c$ only drops about 0.8 K with 10 wt% of SiC doping. In contrast, $T_c$ is depressed to about 22 K for C doped MgB$_2$ with the nominal stoichiometry of Mg(B$_{0.8}$C$_{0.2}$)$_2$ synthesized from Mg and B$_4$C [18]. These results suggest that there is only a small fraction, if any, of C substituted for B in our samples.

Fig. 5-4 shows the $J_c(H)$ curves for MgB$_2$ doped and undoped samples at 5 K, 20 K, and 30 K. Note that all the $J_c(H)$ curves for doped samples show a crossover with the undoped samples at higher fields. Although SiC doping caused a slight reduction of $J_c$ in low fields, it is important to note that the $J_c$ for the doped samples drops with increasing field much more slowly than for the undoped ones.
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Compared to the non-doped sample, \( J_c \) for the 10 wt% doped sample increased by more than one order of magnitude at high magnetic fields. Although all the doped samples show considerably better \( J_c(H) \) performance compared to the undoped sample, Fig. 5-4 shows that the sample doped with 10 wt% SiC has slightly better performance than the other samples.

Fig. 5-5 shows a comparison of \( J_c(H) \) for the 10 wt% SiC doped sample at 20 K with data reported in literature. \( J_c \) for this sample exhibits better field performance and higher values of \( J_c \) in high fields than any other element doped samples [12, 14] and better than the undoped tape [19]. Our SiC doped MgB\textsubscript{2} samples are even better than thin film MgB\textsubscript{2}, which has exhibited one of the strongest reported flux pinning with high \( J_c \) in high magnetic fields. At 20 K, the best \( J_c \) for the 10wt% SiC doped sample was \( 10^5 \) A/cm\(^2\) at 3 T, which exceeded \( J_c \) of the state-of-the-art Ag/Bi-2223 tapes. At 20 K and 4 T, \( J_c \) was 36,000 A/cm\(^2\), which is twice as high as for the MgB\textsubscript{2} thin films [10] and an order of magnitude higher than for the state-of-the-art Fe/MgB\textsubscript{2} tapes [19].

Figure 5-3: Transition temperature (\( T_c \)) for the doped and undoped samples determined by ac susceptibility measurements (real part).
Figure 5-4: $J_c(H)$ curves for MgB$_2$ doped (crosses, dashed and dotted lines for MgB$_2$ + 10 wt% SiC, MgB$_{1.6}$(SiC)$_{0.1}$, and MgB$_{1.7}$(SiC)$_{0.15}$ respectively) as well as undoped samples (solid lines) at 5 K, 20 K, and 30 K.

Figure 5-5: A comparison of magnetic $J_c(H)$ at 20 K for the 10 wt % SiC-doped sample and for samples that were doped with Ti and Y$_2$O$_3$ as well as a thin film with strong pinning and Fe/MgB$_2$ tape. Inset: temperature dependence of the irreversibility field for SiC-doped MgB$_2$ with different SiC content (triangles and squares) and for previously prepared doped MgB$_2$ (round symbols).

The temperature dependence of $H_{irr}$ for nano-SiC doped MgB$_2$, as well as for the pellets and tapes reported previously in the literature (round symbols), is shown in the inset to Fig 5-5. Apparently, $H_{irr}$ for x=0 overlaps with $H_{irr}$ for the previous samples, even though the latter had significantly smaller values of $J_c$. Doping with SiC significantly
improved $H_{irr}$. For example, $H_{irr}$ for SiC doped samples reached 7.3 T at 20 K, compared to 5.7 T for the non-doped one. This is consistent with improvement of field dependence of $J_c$ with the doping. Because $H_{irr}$ for the undoped control sample (x=0) is the same as for the previously reported samples, the improvement of $J_c(H)$ occurred indeed because of the SiC doping and not because of improved sintering of MgB$_2$.

Given the ease of production of SiC-doped MgB$_2$, our results significantly strengthen the position of MgB$_2$ as a competitor to more expensive conventional superconductors and HTS. This is because SiC doping is easily achievable and results in strong improvement of flux pinning. In the present study, the density of the pellet samples is still very low, only about 1.3 g/cm$^3$. Thus, still higher $J_c$ can be achieved by improving the density.

In order to confirm the results and check the reproducibility of samples, as well as achieving better understanding of the underlying mechanism responsible for the improvement in $J_c(H)$, more samples were made by doping with 10 wt% addition of SiC nano particles. The pure and doped samples have been measured in the Applied Superconductivity Center, University of Wisconsin in Madison.

Fig. 5-6 shows the resistivity versus temperature between 30 K to 300 K, for doped and undoped samples, obtained by four probe transport measurements. The onset $T_c$ of the undoped sample was 37.5 K. For the 10 wt% SiC-doped sample, $T_c$ decreased only by 0.6 K, consistent with the previous results. It should be note that the resistivities of the two samples are very different. The doped sample has a larger resistivity than the undoped sample over the whole temperature range. For example at 40 K, $\rho$ is 90 $\mu\Omega$cm for the undoped sample and 300 $\mu\Omega$cm for the doped sample. However the undoped sample has a lower residual resistivity ratio (RRR) than the doped sample. Both doped and undoped samples were prepared using a reaction in-situ method, and they both have a low density, about 50% of theoretical density. Thus, the porosity is about the same for both samples and should not be the reason for the significant difference in the resistivity. However these results are understandable as the doped sample contains a large amount of impurity.
Figure 5-6: Resistivity versus temperature between 30 K to 300 K, for doped and undoped samples, extracted from four probe transport measurements.

Figure 5-7: Resistivity versus temperature curves $\rho(T)$ for the undoped sample in different magnetic fields up to 9 T.

Figure 5-8: Resistivity versus temperature curves $\rho(T)$ for the SiC-doped sample in different magnetic fields up to 9 T.
Figs. 5-7 and 5-8 show the resistivity versus temperature curves $\rho(T)$ for the undoped (Fig. 5-7) and the SiC-doped (Fig. 5-8) samples at different magnetic fields up to 9 T. The doped sample has stronger superconductivity than the undoped, as is shown explicitly in the figures. The transition becomes broad with increasing field. The broadening of the transition for the undoped sample is more pronounced than for the nano-SiC doped sample at high field. It is also evident that the $T_c$ was depressed much more severely with increasing applied field in the undoped sample (Fig. 5-7) than in the nano-SiC doped sample (Fig. 5-8), indicating that nano-SiC doping enhanced the flux pinning in the MgB$_2$.

Figs. 5-9 and 5-10 show the magnetic field dependence of $J_c$ at 4.2 K, 10 K, 20 K and 30 K for the undoped and doped samples respectively, calculated from the dc magnetization measurements using the VSM. Note that all the $J_c(H)$ curves for doped samples show a much slower drop with increasing field compared to the undoped sample over all the measured temperature ranges, which is consistent with the previous results. The $J_c$ for the nano-SiC doped sample is greater than 10,000 A/cm$^2$ at 4.2 K and 10 T, 10 K and 8 T, and 20 K and 5 T, respectively.

Figs. 5-11 and 5-12 display the comparison between the $J_c(H)$ values at 4.2 K and 20 K for the undoped and SiC-doped samples. The $J_c$ for the doped sample increased by more than one order of magnitude at 4.2 K and above 10 T, compared to that for undoped samples. The $J_c$ for the doped sample also increased by an order of magnitude at 20 K and 5 T compared to the undoped samples. At 20 K, the best $J_c$ for the 10 wt% SiC doped sample achieved $10^5$ A/cm$^2$ at 3 T which again exceeded those of the state-the-art Ag/Bi-2223 tapes and 36,000 A/cm$^2$ at 4 T, which is double that of the thin film and an order of magnitude high than those of the Fe/MgB$_2$ tapes [19].
Figure 5-9: Magnetic field dependence of $J_c$ at 4.2 K, 10 K, 20 K and 30 K for the undoped MgB$_2$ sample.

Figure 5-10: Magnetic field dependence of $J_c$ at 4.2 K, 10 K, 20 K and 30 K for the SiC doped MgB$_2$ sample.

Figure 5-11: The comparison between $J_c(H)$ of the undoped and SiC-doped samples at 4.2 K.
Irreversibility fields ($H_{irr}$) for both the doped and undoped samples are shown in Fig. 5-13. The irreversibility line for the doped sample is higher than for the undoped sample over the whole temperature range. Doping with SiC significantly improved $H_{irr}$. For example, the $H_{irr}$ for the SiC doped sample reached 12 T and 7.5 T, compared to 8.8 T and 5.5 T for the undoped one at 10 K and 20 K, respectively.

Fig. 5-14 shows the temperature dependence of the upper critical field $H_{c2}$ determined from the resistance transition curves in Figs. 5-7 and 5-8 at a temperature where the
resistivity is 90% of the value of the resistive transition. We note that $H_{c2}(T)$ is improved for the nano-SiC doped sample. This is in agreement with the Gurevich et al. results that found the higher $H_{c2}$ for films and untextured bulk polycrystals with higher resistivity [16]. Since $H_{c2}$ should be directly tied to $\rho$ it is clear that the effect of impurities must be considered to be affecting the derived values of resistivity, which are not directly interpretable as being representative of the scattering in the samples. This problem will be discussed below in connection with the effect of impurity on flux pinning.

![Graph of $H_{c2}(T)$ as a function of temperature for the undoped and the 10 wt% SiC doped sample.](image)

Figure 5-14: The upper critical field (90% of the resistive transition) as a function of the temperature for the undoped and the 10 wt% SiC doped sample.

The TEM images showed a high density of dislocations and a large number of ~10nm inclusions inside the grains (Fig. 5-15 top and bottom right). EDS analysis of the grains revealed the presence of uniformly distributed Mg, B, C, Si and O (inset to Fig. 5-15 top). TEM examination revealed that there are a number of impurity phases in the form of nano-meter size inclusions inside and in between the grains in the nano-SiC doped sample. These impurities include Mg$_2$Si, MgB$_4$ and MgO detected by XRD analysis, and unreacted SiC, amorphous BO$_x$, Si$_x$B$_y$O$_z$ and BC detected by using the EELS technique. TEM images also show that the grain size of MgB$_2$ is smaller than 100nm. The Z-contrast image [20-22] of the nano-SiC doped sample, which shows a typical MgB$_2$ crystal in the [100] orientation, is presented in Fig. 5-15 as well (bottom left). EDX analysis shows that the Mg:Si ratio is identical across the entire sample, indicating that the phase distribution is globally homogeneous. However, nano-scale impurity phases of MgB$_4$ and MgO are present within the grains. The presence of oxygen within
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...the grains is consistent with the results obtained from an oxygen alloyed thin film with strong pinning and a resistivity of 220 µΩcm [10].

Recent work on SiC-doped MgB₂ single crystal grown under high pressure (30 kbar) and high temperature (1900-1950°C) showed there was only C substitution for B with no Si detected in the crystals. These authors revealed that the C substitution for B is as high as 16%, the highest level of substitution in all the C-doping studies so far, which leads to a depression in $T_c$ from 39 K to 9 K [23]. There is a clear trend for C substitution in MgB₂ to depress $T_c$ in the literature data as well [24-27]. The higher the sintering temperature is, the larger the proportion of C that is substituted for B in MgB₂. As we used relatively lower sintering temperatures, ~800 °C, the C substitution for B is expected to be lower. In the SiC doped sample, it is therefore possible that the C substitution is at 1-3%, which is believed to be quite reasonable from literature on C substitution in terms of depression of $T_c$. However the level of C substitution could not be readily identified so far.

In addition to the high concentration of nano-inclusions, there are structural defects observed in the nano-SiC doped sample by Li et al. [28]. This kind of nano-domain structure may be the result of a small proportion of C substituted for B.

Nano-particle SiC doping into MgB₂ has a special features compared to all other doping reported so far. In this case, not only the extent of enhancement in $J_c(H)$ is very large, by more than an order of magnitude above certain fields, but also the enhancement of $J_c(H)$ occurred in all the temperatures ranges up to $T_c$, in contrast to most of the other doping studies, which have been effective in enhancing $J_c(H)$ only within low temperature ranges. Also in contrast to previous work on doping for improving $J_c$, SiC doping has no densification effect, as evidenced by the fact that the density of the doped samples is quite low and independent of the doping level.

According to two-gap superconductivity theory, the nano SiC doping could lead to two different scattering channels. First, the partial C substitution for B or the formation of alloying between B and Si, B and C and B and O in the close vicinity of B sites causes disorder on B sites which will result in *in-plane* $\sigma$ scattering. The alloying phases such as BC, BO₃ and SiBO₃ detected by the EELS analysis have dimensions well below 10nm. Their scattering will lead to an increase in $dH_c/dT$ at temperatures near $T_c$. The
higher $H_{c2}$ at higher temperatures contributes to the enhancement of $J_c(H)$ at higher temperatures for the SiC doped samples. Second, the formation of nano-domain structures is due to the variation of Mg-B spacing which in turn causes disorders at B and Mg sites. These nano-domains with a size of 2-3nm are also well below the 8-10 nm coherence length of MgB$_2$. These extensive nano-domain defects could result in strong in-plane and out-of-plane scatterings and contribute to the increase of resistivity and $H_{c2}$ in a wide temperature regime. This accounts for the enhancement of $J_c(H)$ over a wide temperature range for the SiC doped samples.

![TEM images showing the intragrain dislocations and nanoparticle inclusions within MgB$_2$ grains](image1.png)

![EDS element analysis of MgB$_2$ grains of doped sample](image2.png)

Figure 5-15: TEM images showing the intragrain dislocations and nanoparticle inclusions within MgB$_2$ grains (top and bottom right). Inset: EDS element analysis of MgB$_2$ grains of doped sample.

On the other hand, the additional impurities at nano-scale introduced by SiC doping can serve as strong pinning centers to improve flux pinning within a certain field region.
This is clearly demonstrated by the superior $J_c - H$ performance of the SiC doped samples.

The potential pinning centers induced by SiC doping include inclusions such as the highly dispersed MgSi$_2$, BC, BO$_x$ and SiBO$_x$ which are all at a scale below 10nm, match the coherence length very well and can act as strong pinning centers. Some large impurity particles such as unreacted SiC would not be effective pinning centers but would act to reduce superconducting volume and thus should be eliminated in order to further improve the zero field $J_c$. In addition, the nano-domain defects at a scale of 2-3 nm in an extensive network would provide very effective collective pinning at all temperatures up to $T_c$.

5-1-4 Summary

In summary, we have demonstrated that the critical current density, irreversibility field and flux pinning properties of MgB$_2$ in bulk form can be significantly improved by a readily achievable and economically viable chemical doping with SiC, paving the way for MgB$_2$ to potentially replace the current market leader, Nb-Ti. The nano-scale SiC doping into MgB$_2$ enhances both $H_{c2}$ and flux pinning through multiple scattering channels. Alloying at B and Mg sites due to C substitution and the formation of nano-domain structures will cause strong scattering over a wide range of temperatures, leading to enhancement in $H_{c2}$. A high concentration of various nano-scale impurity phases results in high resistivity, a low residual resistivity ratio, and a large irreversibility field and upper critical field with modest $T_c$ reduction. The highly dispersed nano-scale precipitates MgSi$_2$, BC, BO$_x$, SiBO$_x$ and the extensive domain structures on a scale well below 10 nm serve as strong pinning centres. Large particle impurities such as unreacted SiC (>100 nm) increase resistivity, reduce the superconducting volume and do not help with the improvement of either flux pinning or $H_{c2}$ and therefore should be eliminated. The doping with SiC enhances the critical current density, the irreversibility field and the upper critical field in a manner that helps make MgB$_2$ potentially competitive with both low and high-$T_c$ superconductors.
5-2- Transport Critical Current Density in Fe-Sheathed Nano-SiC Doped MgB$_2$ Wires

5-2-1 Introduction

It has been shown that Fe is suitable sheath for fabrication of MgB$_2$ wire using a powder-in-tube method [7, 8] as demonstrated in the previous chapter. However, the $J_c$ performance of wires remains unsatisfactory for many applications due to the poor pinning ability of this material. In the previous section, we showed that chemical doping with nano-particle SiC into MgB$_2$ can significantly enhance $J_c$ in high fields with only slight reduction in $T_c$. This finding suggested that possible substitution of C for B in MgB$_2$ induced intra-grain defects as well as an high density of nano-inclusions as effective pinning centres, responsible for the improved performance of $J_c(H)$ over a wide range of temperatures. However, all the critical current densities presented in the previous section were limited to magnetic measurements. As the materials are far from optimum and the sample density was only about 50% of the theoretical value the current in such a porous material is highly percolative. The major concern is whether the material can carry a large transport $J_c$. In this section, we study the effect of the nanometer-size SiC doping on the transport critical current density and its magnetic field dependence for MgB$_2$ wires. Our results reveal that the nanometer size SiC-doped MgB$_2$/Fe wires can carry very high transport $I_c$ and $J_c$ in the applied magnetic fields. SiC doped MgB$_2$ is very promising for many applications, as this chemical doping is a readily achievable and economically viable process to introduce effective flux pinning.

5-2-2 Experimental Details

Standard powder-in-tube methods were used for the Fe clad MgB$_2$ tape. Powders of magnesium (99%) and amorphous boron (99%) were well mixed with 0 and 10 wt% of SiC nanoparticle powder (size of 10 nm to 20 nm) and thoroughly ground. The pure Fe tube had an outside diameter (OD) of 10 mm, a wall thickness of 1 mm, and was 10 cm long. The wire preparation procedure has been explained earlier. Short samples 2 cm in
length and 1.4 mm in diameter were sintered in a tube furnace at 800 °C for 30 min. A high purity argon gas flow was maintained throughout the sintering process. Transport current was measured using pulse DC method. Because the critical current for these wires was hundreds of amperes, the transport measurements had to be performed by a pulse-method, to avoid heating. A pulse of current was obtained by discharging a capacitor through the sample, a coil of thick copper wire and a non-inductive resistor connected in series. The current was measured via the voltage drop on the non-inductive resistor of 0.01 Ohm. With a proper choice of coil, the current reached its maximum value (700 A) within 1 ms. The voltage developed on the sample was measured simultaneously with the current, using a 2-channel digital oscilloscope. Because both channels of the oscilloscope had the same ground, the signal from the voltage taps was first fed to a transformer preamplifier (SR554). This decoupled the voltage taps from the resistor used for measuring the current, thereby avoiding creation of ground loops and parasitic voltages in the system, as well as of an additional current path in parallel to the sample. The transformer amplified the voltage 100 times, improving the sensitivity of the experiment. Magnetic field was produced by a 12 T superconducting magnet. Sample mounting allowed for orienting the field either perpendicular to the wire, or parallel to it. In the later case, the field was also parallel to the current passing through the sample. The sample was placed into a continuous flow helium cryostat, allowing a control of temperature to better than 0.1 K. The magnetization of samples was also measured using a PPMS (Quantum Design). The samples were in the form of bars cut from pellets which were processed under the same conditions as the wires, as explained in the previous chapter. A magnetic $J_c$ was derived from the height of the magnetization loop using Bean’s model.

5-2-3 Results and Discussion

Fig. 5-16 shows the transition temperature ($T_c$) for the doped and undoped samples determined by ac susceptibility measurements. The $T_c$ obtained as the onset of magnetic screening for the undoped sample was 37.6 K. For the 10 wt% SiC doped sample, the $T_c$ was decreased by only 0.7 K. In contrast, the $T_c$ was depressed by almost 7 K for 10% C substitution for B in MgB$_2$ [27].
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Figure 5-16: Critical transition temperature ($T_c$) measured using magnetic susceptibility versus temperature for pure MgB$_2$ and 10wt% SiC doped MgB$_2$/Fe wires

As explained in the previous section, this suggests that the higher tolerance of $T_c$ to SiC doping in MgB$_2$ is attributable to the low level of C substitution.

Fig. 5-17 shows a typical $V$-$I$ characteristic for the 10 wt% SiC doped MgB$_2$/Fe wire. It should be noted that the self-field of the current pulse induced a voltage in the voltage taps, which gave a background voltage. It was easy to distinguish the voltage created by the superconductor on this background, because the voltage developed very abruptly when the current reached the value of $I_c$. It is interesting to note that the total current that the SiC doped wire can carry reached 665 A at 24 K and 1.1 T. Due to the limitations of our power source all the $I_c$ measurements were limited to a maximum 700 A.

Figure 5-17: $I$-$V$ curves for 10 wt% SiC doped MgB$_2$/Fe wire. $I_c = 665$ A at 24 K and 1.1 T.
Fig. 5-18 shows the $J_c(H)$ curves for the undoped and the 10 wt% SiC-doped MgB$_2$ samples at 5 K, 10 K, and 30 K. Note that all the $J_c(H)$ values for 10 wt% SiC doped MgB$_2$/Fe wire are significantly higher than for the undoped sample at higher fields. The transport $I_c$ for the 10 wt% doped MgB$_2$/Fe reached 140,000 A/cm$^2$ at 24 K and 1 T and 103,000 A/cm$^2$ at 20 K and 2 T ($J_c$). The transport $J_c$ for the 10 wt% SiC doped MgB$_2$ wire increased by a factor of 6 at 5 K and 9 T and 20 K and 5 T respectively, compared to the undoped wire. These results indicate that SiC doping strongly enhances the flux pinning of MgB$_2$ in magnetic fields.

The enhancement of pinning by SiC doping is also evident from the pinning force density versus magnetic field results shown in Fig. 5-19. The volume pinning force density of 5.5 GN/m$^3$ at 20 K is comparable to that of NbTi at 4.2 K. Although the maximum pinning force density only has a little shift to higher field the pinning force density for the SiC doped MgB$_2$/Fe wire is clearly greater than for the undoped wire at fields above 1.5 T.
Fig. 5-20 shows a comparison of the transport $J_c$ with the magnetic $J_c$. Although there are quite different voltage standards for measuring the transport and magnetic $J_c$, due to steep characteristics, results are expected to be similar for both methods. The transport $J_c$ for the wires is comparable to the magnetic $J_c$ at higher fields despite the low density of the samples and percolative nature of the current. Fig. 5-20 also shows a comparison of the transport $J_c(H)$ behaviour for 10 wt% SiC doped MgB$_2$/Fe wire at 20 K with the thin film [8] and the Fe-sheathed MgB$_2$ tape [7] reported previously.
We see the $J_c$ for the 10 wt% SiC doped wire is 30 times higher than one of the best transport $J_c$ reported in Fe-MgB$_2$ tape and better than the strongly pinned thin film (magnetic $J_c$ for the thin film).

Fig. 5-21 shows the $J_c(H)$ versus temperature for 10 wt% SiC doped wire at 1 T, 2 T and 4 T. With SiC doping, we can achieve $J_c$ values from 50,000 A/cm$^2$ to 150,000 A/cm$^2$ over a temperature range between 15 K and 25 K and a field range of 2 T to 5 T under the total current supply limit of 700 A. Nevertheless, these results demonstrate that nano-SiC doping into MgB$_2$/Fe wire makes a number of applications practical, including MRI, moderate magnets, magnetic windings for energy storage, magnetic separators, transformers, levitation, motors and generators. Furthermore, the SiC substituted MgB$_2$/Fe wire is much more attractive from the economic point of view. The main cost for making MgB$_2$ conductors will be the high purity B. Because C and Si are abundant, inexpensive and readily available, by doping the superconductor with SiC, the overall cost for making MgB$_2$ conductors will be reduced. Furthermore, SiC doping has already been shown to enhance flux pinning, a significant benefit.

![Figure 5-21: $J_c(H)$ versus temperature for the 10 wt% SiC doped MgB$_2$ wire at 1 T, 2 T and 4 T.](image)

The TEM image (Fig. 5-22) shows a high density of dislocations and massive nanometer size inclusions inside the grains, consistent with the previous section. The density of the present Fe-sheathed MgB$_2$ wires is still very low, only about 1.2 to 1.3 g/cm$^3$. Thus, a higher $J_c$ and better flux pinning can be achieved by further optimization of the processing conditions, as well as further improving the density of samples.
5-2-4 Summary

Nano-SiC doped MgB$_2$/Fe wires were fabricated using a powder-in-tube method and a reaction in-situ process. The depression of $T_c$ with increasing SiC doping level remained rather small. The transport $J_c$ for all the wires is comparable to the magnetic $J_c$ at higher fields despite the low density of the samples and the percolative nature of current. We have further demonstrated that a very high transport critical current and current density of Fe-sheathed MgB$_2$ wires can be achieved by a readily achievable and economically viable chemical doping with nano-SiC. $J_c$ values over 100,000 A/cm$^2$ at 5 K and 5 T and 20 K and 2 T are comparable to NbTi and HTS respectively. High performance SiC doped MgB$_2$ wires will have a great potential to replace the current market leaders, Nb-Ti and HTS, for many practical applications at 5 K to 25 K up to 5 T. There is a plenty of room for further improvement in $J_c$ as the density of the current samples is only about 50%.

Figure 5- 22: TEM image for the 10 wt% SiC doped MgB$_2$/Fe wire.
5-3 Effect of Grain Size and Doping Level of SiC on the Superconductivity and Critical Current Density in MgB$_2$ Superconductor

5-3-1 Introduction

We have shown in the previous sections a significant improvement of $J_c$, $H_{irr}$ at both high and low temperatures in nano-SiC doped MgB$_2$ bulk samples with only a slight reduction of $T_c$. It has been shown that nano-inclusions, as well as possible substitution in the crystal lattice, lead to this significant improvement. The objective of this section is to study the grain size effect of the precursor SiC on the superconductivity and flux pinning and to further investigate the enhancement in $J_c$ field performance. It was found that the particle size of SiC plays a critical role in controlling the reaction between Mg$^{+2}$B and SiC resulting in both substitution and nano-inclusions.

5-3-2 Experimental Details

MgB$_2$ pellet samples used in the present study were prepared by an in-situ reaction method, which has been described in detail previously. Magnesium (99%) and amorphous boron (99%) were well mixed with commercial SiC (0, 8, 10, 12, 15 wt%). Powders having three different grain sizes were used: a very fine powder with particle sizes smaller than 20 nm (powder 1), powder 2 which has particle sizes ranging up to 300 nm and powder 3, a coarse crystalline SiC with particle sizes around 35 µm. These particle sizes were determined by TEM and SEM and will be explained in the next section. Pellets 10 mm in diameter and 2 mm in thickness were prepared by sintering at 800 ºC for 30 min in flowing high purity Ar. The magnetization of samples was measured using a PPMS (Quantum Design). Samples in the form of bars were cut from the as-sintered pellets. All the samples have the same size ($0.56\times2.17\times3.73$ mm$^3$). A magnetic $J_c$ was derived from the height of the magnetization loop ($M$-$H$) using the Bean Model.
5-3-3 Results and Discussions

5-3-3-1 Effect of Grain Sizes of SiC

Fig. 5-23 shows the XRD patterns for the three different SiC powders used in this work. It can be seen that there are no diffraction peaks for powder 1, indicating that this powder is amorphous. Powders 2 and 3 show diffraction peaks, indicative of their crystalline natures. Powder 3 gives a strong diffraction intensity as well as sharp peaks in agreement with its bigger particle size. On the other hand, powder 2 shows a few peaks, which are wider than the equivalent peaks for powder 3, especially the $2\theta = 33.7'$ and $38'$ peaks that are very wide with low intensity. This XRD pattern indicates that powder 2 contains a wide range of particle sizes.

![XRD pattern of the starting SiC powders with different grain sizes.](image)

Figure 5-23: The XRD pattern of the starting SiC powders with different grain sizes.

Figs. 5-24 to 5-26 show TEM images of powders 1 and 2 (Figs. 5-24 and 5-25) as well as a SEM image of powder 3 (Fig. 5-26). We can see that the grains of SiC in powder 1 are very fine with almost the same grain size of about 10 nm to 20 nm, (Fig. 5-24). On the other hand it can be clearly seen that powder 2 contains grains with a wide range of grain sizes from about 10 nm to about 300 nm (Fig. 5-25), consistent with its XRD pattern. The SiC particles in powder 3 are almost uniform crystalline grains with an average size of about $37 \mu m$ (Fig. 5-26).
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The XRD patterns of the samples after reaction as well as the reference MgB$_2$ sample are shown in Fig. 5-27. All three samples were doped with 10 wt % SiC. Mg$_2$Si is the main impurity phase for the sample that was made using powder 1 (sample a), in agreement with previous results. However, we can still see some un-reacted SiC in the samples that were made using powders 2 and 3, samples b and c, respectively. In addition, no Mg$_2$Si was found in sample c. This means that only part of the SiC takes part in the reaction with Mg and B and becomes doped into MgB$_2$.

![Figure 5-24: TEM image of starting powder 1. Powder contains almost uniform particles with an average grain size of 10 nm to 20 nm.](image)

![Figure 5-25: TEM image of starting powder 2. Powder contains different particles with a wide range of grain sizes from 10 to 300 nm.](image)
Figure 5-26: SEM image of starting powder 3. Powder contains almost uniform particles with an average grain size of 35 µm.

Figure 5-27: XRD patterns of MgB$_2$ samples doped with 10 wt % of different SiC powders as well as the reference sample.

Fig. 5-28 shows an SEM image of sample c which was made using crystalline SiC powder (Powder 3). Big grains of un-reacted SiC can be easily seen in the MgB$_2$ matrix, which is in agreement with its XRD pattern. This means that the coarse SiC powder is very stable and did not react with Mg+B. Therefore; little or no substitution for B by Si and C can be expected. However, for very fine SiC powder substitutions take place as Mg$_2$Si was formed. This is the big difference in the phases of samples.
made with coarse and fine powder. This difference is responsible for the significant difference in $J_c$ field dependence shown below. However, this pattern does not show that all the SiC powder was consumed in sample a.

AC susceptibility measurement results for all samples are presented in Fig. 5-29. $T_c$ values of about 37.65K, 37.5K, 37K and 36.25K were found for the reference sample, sample c, sample b and sample a respectively. The small change in $T_c$ for such a large amount (10 wt%) of added material confirms the results presented in the previous section. Also, we can see that the smaller grain size leads to lower $T_c$, which is understandable, as smaller grains can react more readily than larger ones.

![SEM image of sample c after reaction. The large grains of un-reacted SiC can be easily seen in the MgB$_2$ superconductor.](image)

Figure 5-28: SEM image of sample c after reaction. The large grains of un-reacted SiC can be easily seen in the MgB$_2$ superconductor.

![Ac susceptibility, $\chi$, [emu] vs. Temperature, T[K].](image)

Figure 5-29: The ac susceptibility of MgB$_2$ samples doped with 10 wt % of different SiC powders as well as the reference sample at different temperatures.
$J_c$ versus field at 30, 20 and 5 K are plotted in Fig. 5-30. The performance of the $J_c$ field dependence was improved by decreasing the grain sizes of the SiC precursor powder. The finer the SiC powders, the better the $J_c$ field dependence is. For the coarse powders (-400 mesh), the $J_c$ field dependence is slightly better than for the MgB$_2$ reference sample due to limited reaction between the particles, which can react with Mg+B. The resultant impurities or remaining SiC can embed in the MgB$_2$ grains acting as pinning centers. For sample a, $J_c$ value of about 20000 A/cm$^2$ was achieved at 5 K and 8 T, which is more than one order of magnitude higher than that of the MgB$_2$ reference sample at the same field and temperature. TEM results show that there are large numbers of nano-inclusions embedded inside the MgB$_2$ grains. This is because the SiC is very fine, so that it can be readily form as inclusions inside the MgB$_2$ grains and substitute in the lattice during the formation of MgB$_2$ as explained in previous sections. However, the crystalline SiC powders may distribute themselves around grain boundaries acting as weak links due to their poor chemical activity.

![Figure 5-30: The $J_c$ field dependence of MgB$_2$ samples doped with 10 wt % of different SiC powders as well as the reference sample at different temperatures of 5, 20 and 30 K.](image)

**5-3-3-2 Effect of SiC Doping Levels**

As the very fine powders of SiC (20 nm) produce the best results, we can use this fine powder to study the effect of the amount of SiC on the flux pinning in the SiC-doped MgB$_2$ samples in order to optimize the addition of SiC. Samples with SiC weight % of 0, 8, 10, 12, and 15 were studied in this work. The XRD patterns show that there is
almost no difference in phase purity, with only an increase of Mg$_2$Si when SiC increases. $T_c$ also changed only slightly in all the samples. The $J_c$ field dependence at different temperatures is shown in Fig. 5-31. It can be seen that all the SiC doped samples have almost the same $J_c$ values as a function of field and temperature at all the doping levels studied. However, it seems that the sample doped by 10 wt% SiC has slightly better performance, compared to the MgB$_2$ reference sample. This means that the MgB$_2$ is very tolerant to the amount of SiC.

![Figure 5-31: The $J_c$ field dependence of MgB$_2$ samples doped with SiC weight % of 0, 8, 10, 12, 15 at 5 K and 20 K.](image)

**5-3-4 Summary**

SiC doped MgB$_2$ polycrystalline samples were fabricated by in-situ reaction using different grain sizes (20 nm, 100 nm, and 37 microns) of SiC and different doping levels (0, 8, 10, 12, 15 wt %). Grain sizes of the precursor SiC have a strong effect on the critical current density and its field dependence. The smaller the SiC grains are, the better the $J_c$ field performance and $H_{irr}$ is. It was found that very fine SiC powder plays an important role in the reaction between Mg+B and SiC. Significant enhancement of $J_c$ and $H_{irr}$ were revealed for all the SiC-doped MgB$_2$ with added levels up to 15 wt%. A $J_c$ value as high as 20,000 A/cm$^2$ in 8 Tesla and 5 K was achieved for the sample doped with 10 wt% SiC having a grain size of about 20 nm. The high performance of the nano-SiC doped MgB$_2$ superconductor will have great potential for practical applications.
5-4 Effect of Nano-Carbon Particle Doping on the Flux Pinning Properties of MgB$_2$ Superconductor

5-4-1 Introduction

The effect of C-doping on superconductivity in MgB$_2$ compound has been studied by several groups [23-27, 29-32]. The results on C solubility and the effect of C-doping on $T_c$ reported so far vary significantly from no substitution to 16% of B substituted by C, while the decrease in $T_c$ ranged up to 30 K at the highest substitution level [18, 23, 33, 34]. The significant differences among the studies on C-substitution are attributable to the fabrication techniques and precursor materials used. It appears that lower sintering temperatures (e.g. 700 °C) and short sintering times result in an incomplete reaction and hence lower C solubility in MgB$_2$. The mixing procedure applied to the precursor materials may also contribute to inhomogeneity in the final product. It is difficult to precisely determine the C solubility in the lattice, as the lattice parameters can also be affected by the change of stoichiometry in MgB$_2$, because excess C extracts Mg and B to form MgB$_2$C. Recently, Ribeiro et al. used Mg and B$_4$C as precursors to synthesize C doped MgB$_2$ by sintering at 1200 °C for 24 hours [33]. Their samples appeared to be homogeneous. A neutron diffraction study confirmed that the most likely solubility of C in MgB$_2$ is around 10% of B positions [34]. This gives a large drop in both $T_c$ (=22K) and the $a$-axis lattice parameter.

The studies on C doping into MgB$_2$ have thus far only focused on the effect on superconductivity. From the applications point of view, the effect of C doping on the flux pinning properties is also important. In this section, we explain the effects of C doping on the flux pinning and critical current density in MgB$_2$. It is clear from previous works that complete substitution causes a drastic depression in $T_c$, which is very undesirable for improving $J_c$ at high temperatures. In order to explore the potential applications of MgB$_2$ at around 20 K or above, it is essential to maintain the $T_c$ and, at the same time, to enhance the $J_c$ performance in magnetic fields. Therefore, we
designed synthesis conditions that limit the degree of C substitution, but can introduce effective pinning centers into MgB$_2$.

5-4-2 Experimental Details

Polycrystalline samples of MgB$_{2-x}$C$_x$ were prepared through a reaction in-situ process as explained earlier. High purity powders of magnesium (99%), amorphous boron (99%) and carbon nano-particles (with a particle size of about 20 nm) were weighed out according to the nominal atomic ratio of MgB$_{2-x}$C$_x$ with $x = 0, 0.05, 0.1, 0.2, 0.3, 0.4$ and well mixed through grinding. The heat treatment was performed at 770 °C for 30 min in flowing high purity Ar. An un-doped sample was also made under the same conditions for use as a reference sample. The magnetization was measured using a PPMS (Quantum Design). The magnetic $J_c$ was calculated from the height $\Delta M$ of the magnetization loop ($M-H$) using the Bean model. The $T_c$ was determined by measuring the real part of the ac susceptibility at a frequency of 117 Hz and an external magnetic field of 0.1 Oe. $T_c$ was defined as the onset of the diamagnetism.

5-4-3 Results and Discussion

Fig. 5-32 shows the XRD patterns of MgB$_{2-x}$C$_x$ samples for $x=0, 0.05, 0.1, 0.2, 0.3$ and 0.4 as well as the XRD pattern of the starting C powder. An Si standard was used for all runs. It can be seen that there are no diffraction peaks for C powder, indicating that this powder is amorphous. Thus, there is no peak related to C in the XRD patterns of the C-doped samples, and the amount of the un-reacted C powder is not clear. The undoped samples consist of a main phase, MgB$_2$, with minor phases of MgO (<5%) and MgB$_4$. In the C-doped samples extra peaks appear as impurity phases. These peaks can be indexed as Mg$_2$C$_3$ and Mg$_2$B$_2$C$_2$, and they increase as the doping level increases.

More accurate XRD examinations were performed to evaluate the lattice parameters. The XRD patterns are shown in Fig. 5-33. Note that the position of the (100) peak shifts continuously to higher angles with increasing C doping level, indicating a decrease in the a-axis lattice parameter. However the position of the (002) peak remains unchanged with increasing C-doping level, indicating that C-doping does not affect the c axis.
Figure 5-32: XRD patterns of MgB$_{2-x}$C$_x$ composition for x=0, 0.05, 0.1, 0.2, 0.3 and 0.4 as well as the XRD pattern of the starting C powder.

Figure 5-33: The (100) and (002) (inset) Bragg reflections for MgB$_{2-x}$C$_x$ composition with x= 0, 0.05, 0.1, 0.2, 0.3, and 0.4

The changes in crystal lattice parameters deduced from the x-ray diffraction patterns of the samples as well as the lattice parameters extracted from the previously published studies by Maurin et al. [25] and Avdeev et al. [34] are shown in Fig. 5-34. As can be seen, the in-plane (a axis) lattice parameter decreases monotonically as the C doping level decreases from 3.087Å to 3.076Å at x=0 and x=0.4 respectively. This is
understandable because the average size of the C ion (0.077 nm) is smaller than the B (0.082 nm). However, we are unable to see any significant change in the inter layer (c-axis) lattice parameter. This is in agreement with recent work, indicating that carbon is substituted in the boron honeycomb layer and does not change the interlayer distance in the MgB2 crystal. However, the change in the a lattice parameter even for x=0.4 is considerably less than the a axis contraction from 3.085 to 3.052 due to 10% carbon doping [34]. This indicates that the carbon powder in our samples is only partially substituted in the B position due to the low sintering temperature and short sintering time. The C mostly reacted with Mg and B to form Mg2C3 and MgB2C2 or remained in an un-reacted form.

Fig. 5-35 shows the transition temperature ($T_c$) for the doped and undoped samples determined by ac susceptibility measurements. The $T_c$ onset for the undoped sample (~38.5 K) is almost the same as that reported by a number of groups. For the doped samples, the $T_c$ decreases with increasing doping level. Despite the large amount of non-superconducting phases present, the $T_c$ only drops slightly, 2.7 K at a high C doping level of x=0.4 (which represents 20% C doping). This result is in contrast to the previously reported results in which the $T_c$ was depressed about 17 K in the 10% C
substituted sample, as we can see in the inset of Fig. 5-35 [34]. Once again, these results suggest that only a small amount of C powder was substituted in the B position in our samples, consistent with the lattice contraction. Because the C doping has little effect on the $T_c$, the partial substitution and partial addition of nano-carbon particles may enhance flux pinning over a wide range of temperatures.

Fig. 5-36 (a-d) shows the $J_c(H)$ curves for MgB$_2$ doped and undoped samples at 5 K, 10 K, 20 K and 30 K. It should be noted that at 5 K, 10 K and 20 K, all the $J_c(H)$ curves for doped samples show a crossover with the undoped sample at higher fields except for the sample doped with $x=0.4$ at 20 K. Because the C doping reduces $T_c$, only the $J_c(H)$ curve for the C-doped sample with $x=0.05$ shows the crossover with the undoped sample at 30 K.

Fig. 5-37 shows the irreversibility field, $H_{irr}$ versus temperature for all the doped and undoped samples. Here, we defined $H_{irr}$ as the field where $J_c$ drops to 100 A/cm$^2$. The improvement in $H_{irr}$ for all the C doped samples is consistent with the $J_c(H)$. 

**Figure 5-35:** AC susceptibility (real part) vs. magnetic field for different nominal C content $x$ for MgB$_{2-x}C_x$. The inset shows the $T_c$ changes with $x$ for the same composition including for $x=0.1$, reported by Ribeiro et al. [18].
Figure 5- 36: The $J_c$ field dependence of MgB$_{2-x}$C$_x$ composition for $x=0$, 0.05, 0.1, 0.2, 0.3 and 0.4 at 5 K, 10 K, 20 K and 30 K.

Figure 5- 37: Irreversibility lines for MgB$_{2-x}$C$_x$ composition for $x=0$, 0.05, 0.1, 0.2, 0.3 and 0.4.
In order to understand the mechanisms for the enhancement of flux pinning in the nano-C doped samples a TEM study was performed. Fig. 5-38 shows a typical TEM image for the C-doped sample at $x=0.05$ (Fig. 7(a)) and $x=0.1$ (Fig. 7(b)). Note that the MgB$_2$ grains are approximately 100–200 nm long and 50-100 nm wide. It is evident that although the doping levels of $x=0.05$ and $x=0.1$ are well below the C solubility limit, there are noticeable amounts of precipitates which may be unreacted C and the impurity phases Mg$_2$C$_3$ and MgB$_2$C$_2$. These precipitates are uniformly distributed within the matrix and have a diameter of 5nm to 10nm. Many are included in the grains as fine inclusions. The density and amount of these inclusions increase with increasing doping level. The size of these inclusions matches the coherence length of MgB$_2$ very well. Thus, it is believed that the high density of nano-inclusions is responsible for the enhanced flux pinning in the C-doped samples.

In previous sections, we presented the effect of nano-SiC doping into MgB$_2$. Compared to the un-doped sample, $J_c$ for the 10wt% SiC-doped sample increased by more than an order of magnitude in higher magnetic fields. It was also confirmed that nano-Si particle doping shows a pinning enhancement, but not as strong as with SiC [35]. Fig. 5-39 compares the normalized $J_c(H)$ and $H_{ irr}$ for nano-SiC, nano-Si [35] and nano-C doped MgB$_2$ at 20 K. Note that C and Si doping gave almost the same level of enhancement over the undoped sample, while SiC-doped MgB$_2$ remained the best of all the forms of MgB$_2$.

![Figure 5-38: TEM images for C doped MgB$_{2-x}$Cx composition at $x=0.05$ (a) and 0.1 (b).](image-url)
Chapter 5: Effect of Chemical Doping on the Critical Current Density and Flux Pinning of MgB$_2$

Figure 5-39: A comparison of $J_c(H)$ and $H_{irr}$ for SiC, C and Si doped MgB$_2$.

5-4-4 Summary

The effect of C doping on lattice parameters, $T_c$, $J_c$ and flux pinning in MgB$_2$ was investigated under the conditions of limited C substitution for B. It was found that both the $a$-axis lattice parameter and the $T_c$ decreased monotonically with increasing doping level. For the sample doped with the highest nominal composition of $x=0.4$ the $T_c$ dropped only 2.7 K. The nano-C-doped samples showed an improved field dependence of the $J_c$ over a wide temperature range compared with the undoped sample. X-ray diffraction and TEM studies indicate that C reacted with Mg to form Mg$_2$C$_3$ and MgB$_2$C$_2$ with nano-dimensions. Nano-particle inclusions and substitution, both observed by transmission electron microscopy, are proposed to be responsible for the enhancement of flux pinning in high fields.

References

Chapter 5: Effect of Chemical Doping on the Critical Current Density and Flux Pinning of MgB$_2$


6-1 Flux Dynamics of MgB$_2$ Superconductor by ac Susceptibility Measurement

6-1-1 Introduction

The critical current density, one of the most important parameters in considering superconductors for practical applications, has been determined to be quite high in MgB$_2$ as we have shown in the last chapters. Although the zero field values of $J_c$ are quite exciting compared to the high temperature superconductors, we have seen in previous chapters that they decrease rapidly with the applied magnetic field. The critical current density is determined by the pinning properties of the sample as well as by the flux motion, because the motion of the vortices over pinning centres (flux creep) in the superconductor induces dissipation and reduces the critical current density $J_c$. It is the flux creep that sets the limiting critical current density in superconductors. It is thus essential to study the activation energy against flux motion, in order to understand the underlying mechanism resulting in the rapid decreasing relationship between the critical current density and magnetic field, and therefore to enhance the current carrying capacity of this material. In this section, we investigate the flux creep activation energy in MgB$_2$, and determine its dependence on the current density, the magnetic field, and the temperature by measuring the real $\chi'(T)$ and imaginary $\chi''(T)$ parts of the ac susceptibility at different ac field amplitudes, frequencies and dc magnetic fields. The irreversibility line is obtained using the third harmonic ac susceptibility technique.
6-1-2 Experimental Details

All measurements were performed on a MgB$_2$ bulk sample ($T_c$ = 38.6 K, $\Delta T_c$ < 1 K by ac susceptibility in an ac field of 1 G and frequency 117 Hz). The sample preparation has been explained in the previous chapters. A sample with dimension of 2.18 $\times$ 2.76 $\times$ 1.88 mm$^3$ was cut from the as-sintered pellet. Phase purity was determined by XRD and grain size by SEM. The ac susceptibility measurements were carried out using a Quantum Design PPMS.

6-1-3 Results and Discussion

Figure 6-1 shows the effects of the dc magnetic field $B_{dc}$ on the ac susceptibility of the MgB$_2$ bulk sample. As $B_{dc}$ is increased from 0.5 T to 3 T, the transition temperature shifts to lower temperatures and the transition width broadens. Although the transition width is slightly changed from about 3 K at 0.5 T to 6 K at 3 T, the transition temperature is greatly depressed by the dc field from about 35 K at 0.5 T to 27 K at 3 T, while in Y-Ba-Cu-O, the depression in $T_c$ is quite small [1, 2]. As the transition temperature under a dc magnetic field is an indication of the irreversibility line (IL), this result indicates that the IL in the pure MgB$_2$ bulk sample is rather low in the $H$-$T$ plane, as has been obtained by dc magnetization measurements [3, 4] and confirmed by our results explained in previous chapters. The inset of Fig. 6-1 shows the IL of the MgB$_2$ sample determined by the onset temperature of the ac susceptibility at high frequency and low ac field amplitude, which is higher than the ILs obtained by dc measurements [1, 2]. The reason is that the IL determined by ac measurement is frequency and ac field amplitude dependent. This has been discussed in detail by Deak et al. [5].

Typical $\chi'(T)$ and $\chi''(T)$ curves for the MgB$_2$ bulk sample at $B_{dc}$=1 T are shown in Fig. 6-2. The frequency $f$ =1117 Hz, and different ac field amplitudes $B_{ac}$ are indicated in this figure. As $B_{ac}$ is increased, the transition shifts to lower temperatures accompanied by an increasing transition width. The effects of the frequency on the ac susceptibility of this MgB$_2$ sample is shown in Fig. 6-3. In contrast to the effects of $B_{ac}$, the transition shifts to higher temperatures and the transition width broadens as $f$ is increased. All the characteristics shown in Figs. 6-1 to 6-3 for the MgB$_2$ sample are similar to what have
been observed in high temperature superconductors [1, 2] and predicted from theoretical calculations [6]. This is understandable, because ac susceptibilities at different dc magnetic fields, ac field amplitudes and frequencies reflect a common phenomenon, i.e. flux dynamics in type-II superconductors.

Figure 6-1: $\chi'(T)$ and $\chi''(T)$ curves of the MgB$_2$ bulk sample at $B_{ac}=1$ G, $f = 1117$ Hz, and $B_{dc} = 0.5, 1, 2, 3$ T. Inset shows the irreversibility line (solid line is just a guide to the eye).

Figure 6-2: $\chi'(T)$ and $\chi''(T)$ curves of the MgB$_2$ sample at $B_{dc} = 1$ T, $f = 1117$ Hz and $B_{ac} = 0.1, 0.5, 1, 2, 5, 10, 15$ G (from right to left).
A measurement of the superconducting transition by means of the ac susceptibility \( \chi = \chi' + i\chi'' \) typically shows a sharp decrease in the real part of the susceptibility \( \chi' \), just below the critical temperature \( T_c \), a consequence of diamagnetic shielding, and a peak in the imaginary part of the susceptibility \( \chi'' \), representing losses. The peak in \( \chi'' \) will occur when the flux front reaches the centre of the sample. It follows that the position of the peak in \( \chi'' \) will also strongly depend on temperature, dc field, ac field amplitude and frequency. The criterion for the peak in \( \chi'' \) is [7]:

\[
U(T_p, B_{dc}, J)=U(T_p)U(B_{dc})U(J)=k_B T_p \ln \frac{1}{f_{\text{peak}}t_0}
\]

where the time scale \( t_0 = 4\pi\mu_0 H_{ac}^2 / \rho_0 J^2(\omega) \) [7], \( \rho_0 \) is the prefactor in the Arrhenius law \( \rho = \rho_0 \exp[-U(J)/K_B T] \), \( T_p \) is the peak temperature in the \( \chi''(T) \) curve and \( k_B \) is the Boltzmann constant.

It has been shown [6] by numerical calculation that during the penetration of the ac magnetic field into a superconductor, the magnetic field profile can be regarded as a straight line. Therefore, at the peak temperature, the current density can be approximated as

\[
J = \frac{H_{ac}}{d}
\]

where \( d \) is the sample size.

Since

\[
\frac{U(T)}{K_B T} U(J, B_{dc}) = -\ln(f) - \ln(t_0)
\]

a plot of - \( \ln f_{\text{peak}} \) versus \( U(T_p)/k_B T_p \) should be a straight line with the slope of \( U(J, B_{dc}) \).

We can derive the current density dependence of the activation energy \( U(J) \) by varying the ac amplitude and then using equation (6-2) to determine the current density. Using the ac method the usual difficulty in conventional relaxation measurements of having
only a very limited time window (1~10^4 s) can be overcome by extending the latter to smaller values of 10^{-5}~10^{-3} s (\(f=100 \text{ kHz -1 kHz}\)) [1, 2].

In order to account for the explicit temperature dependence of the activation energy, we choose a form of temperature scaling function

\[ U(T) = [1 - (T / T_x)^2]^2 \]  \hspace{1cm} (6-4)

where \(T_x=36.3, 34.3, 31.5, 29.1 \text{ K}\) for \(B_{dc}=0.5, 1, 2, 3 \text{ T}\), respectively, is a characteristic temperature, which is taken from the irreversibility line. \(U(T)\) changes slightly with temperature for \(T \ll T_x\) and drops rapidly as \(T\) approaches \(T_x\). A detailed discussion on choosing the function \(U(T)\) has been given by McHenry et al. [8].

![Figure 6-3: \(\chi'(T)\) and \(\chi''(T)\) curves of the MgB\(_2\) sample at \(B_{dc} = 0.5 \text{ T}, B_{ac} = 2 \text{ G}, \) and \(f=17, 51, 117, 351, 1117, 3331, 9999 \text{ Hz}\) (from left to right).](image)

Fig. 6-4 shows \(-\ln f_{peak} \) versus \(U(T_p) / k_B T_p\) curves at \(B_{dc} = 0.5 \text{ T}\) and various current densities. The experimental data can be fitted very well by straight lines [Eq. (6-3)], shown as solid lines in Fig. 6-4. We can then derive the activation energy \(U(J, B_{dc} = 0.5 \text{ T})\) at other dc magnetic fields have also been derived, and the results are summarized in Fig. 6-5, where the activation energy \(U(J) \propto U(J, B_{dc}) \times B^{1.3}\) is plotted as a function of the current density for the MgB\(_2\) bulk sample at various dc magnetic fields. As can be seen from Fig. 6-5, we have obtained a
universal curve $U(J)$ by scaling the data by $B^{1.3}$. The slight scattering at low current density may result from the field-dependent critical current density $J_c(B)$. Note that $B_{dc}$ has been changed to $J$ by using Eq. (6-2), where $d$ is the sample size rather than the grain size, because it has been reported [3] that current flow in MgB$_2$ is strongly linked. The current density $J$ obtained here is also very close to what has been derived using magnetization measurements [9].

Figure 6-4: $-\ln f_{peak}$ versus $U(T_p)/k_B T_p$ of the MgB$_2$ sample at various current densities indicated by different symbols. Solid lines are linear fits calculated from Eq. (3).

From the best fit of the data in Fig. 6-5, we derived the current density dependent activation energy $U(J) \propto J^{-0.2}$, which is highly non-linear. This result suggests that the $I-V$ curve of MgB$_2$ should also be highly non-linear, because using the Arrhenius rate equation, we have $E = Bv_0 \exp[-U(J)/k_B T] \propto \exp(-J^{-\mu})$. Non-linear $I-V$ characteristics have been experimentally observed in MgB$_2$ [10]. On the other hand, the relaxation of the current density or the magnetization can be derived from equation (6-1) as $J(t) \propto [\ln(t/t_0)]^{-1/\mu}$, which is also a non-linear function of $\ln(t/t_0)$.
Figure 6-5: Activation energy $U(J) \sim U(J, B_0) \times B_1.3$ as a function of the current density for the MgB$_2$ sample at various dc magnetic fields. Solid line is the fitting curve $U(J) \sim J^{0.2}$.

As can be seen from equation (6-3), we can also derive the activation energy as a function of the dc magnetic field $U(B)$ by fixing the current density $J$. The results are summarized in Fig 6-6, where the activation energy $U(B) \propto U(J, B_0) \times J^{0.21}$ is plotted as a function of the magnetic field for the MgB$_2$ sample at various current densities. As can be seen from Fig. 6-6, by scaling the data by $J^{0.21}$, we have also obtained a universal curve. This current density dependence is consistent with the one derived in Fig. 6-5. Since the scaling factor $B_0$ [see Eq. (6-5) below] for $B$ is current density independent, we can see that the scaling of $U(B)$ is much better than that of $U(J)$ shown in Fig. 6-5. The solid line in Fig. 6-6 is a fit to the power law $U(B) \propto B^{-1.33}$. The obtained $U(B)$ is also consistent with the one derived from scaling in Fig. 6-5. The self-consistent scaling of $U(J,B)$ shown in Fig. 6-5 and Fig. 6-6 suggests that the separation of the activation energy $U(J,B,T)$ to $U(J)U(B)U(T)$ in Eq. (6-1) is quite reasonable. The final expression for the temperature-, field- and current density-dependent activation energy is given by

$$U(T, B, J) = U_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \left( \frac{B}{B_0} \right)^{-n} \left( \frac{J_0}{J} \right)^{\mu} \right]$$

(6-5)

where, $U_0$, $B_0$ and $J_0$ are scaling values, and the exponents $n$ and $\mu$ are determined to be 1.33 and 0.2 respectively.
As for the magnetic field dependence of the activation energy, a $B^I$ dependence has been previously derived using the Anderson-Kim model of the activation energy combined with the Ginzburg-Landau expressions for the coherence length, thermodynamic critical field, depairing critical current density, etc. [11, 12]. Such a $B^I$ dependence has been observed in a La$_{1.86}$Sr$_{0.14}$CuO$_4$ single crystal with weak pinning centres by McHenry et al. [8]. For YBa$_2$Cu$_3$O$_x$ samples with strong pinning centres, such as twin planes, stacking faults or Y$_2$BaCuO$_5$ inclusions, a $U(B)\sim B^{-0.5}$ has been derived by both ac susceptibility [2] and dc magnetization measurements [13, 14].

On the other hand, for the new superconductor MgB$_2$ we find a $U(B)\propto B^{-1.33}$ dependence showing that the activation energy decreases even faster with increasing magnetic field, compared to weakly pinning high temperature superconducting La$_{1.86}$Sr$_{0.14}$CuO$_4$ single crystal. The weakening of the activation energy with increasing magnetic field is probably the reason why the critical current density drops steeply as the magnetic field increases, as has been observed by dc magnetization measurements [3, 4, 15, 16].

Figure 6-6: Activation energy $U(J)\propto U(J, B_{dc})\times J^{0.21}$ as a function of the magnetic field for the MgB$_2$ sample at various current densities. The solid line is the fitting curve $U(J)\propto B^{-1.33}$.
6-1-4 Summary

In summary, a systematic ac susceptibility measurements have been performed on a MgB$_2$ bulk sample. The magnetic-field- and current-density-dependent flux creep activation energy has been determined to be $U(J, B) \propto J^{-0.2} B^{-1.33}$. Compared to high-temperature superconductors $U(B) \propto B^{-1}$ for a weakly pinned La$_{1.86}$Sr$_{0.14}$CuO$_4$ single crystal and $U(B) \propto B^{-0.5}$ for strongly pinned YBa$_2$Cu$_3$O$_x$, the steeply declining dependence $U(B) \propto B^{-1.33}$ results in a steep drop in $J_c$ with magnetic field and suggests that pinning in pure MgB$_2$ is quite weak, as can also be seen from the low irreversibility field.
6-2 Improvement of Critical Current in Fe/MgB₂ Superconducting Wires by a Ferromagnetic Sheath

6-2-1 Introduction

As we saw in the previous chapters, Fe sheathed MgB₂ wire is currently one of the most promising conductors for practical application. In addition to providing a medium for obtaining MgB₂ in a chemical reaction at high temperature and ensuring the mechanical strength of the wires, iron is a ferromagnetic material which can be utilized to magnetically shield the superconductor from the external field. This could be very effectively employed for decoupling the superconducting filaments in a multifilamentary MgB₂/Fe wires, substantially lowering the AC loss in the wires. Majoros et al. theoretically predicted that magnetic shielding could lead to a decrease in transport AC loss [17]. A model by Genenko et al.[18] predicted either a suppression or enhancement of the loss-free transport current of a superconducting strip in magnetic surroundings. Earlier measurements [19] indicated the existence of magnetic shielding in MgB₂/Fe tapes, suppressing the ac loss. In chapter 4 we have also shown that the critical current density of Fe/MgB₂ tape can be affected by magnetic shielding. In this section, we present more detailed measurements of the field dependence of transport \( J_c \), influenced by magnetic shielding and the interaction between the Fe sheath and the superconductor in round MgB₂/Fe wires.

6-2-2 Experimental Details

Fe/MgB₂ wire samples were prepared through the powder in tube and reaction in situ techniques. Measurements were performed on three superconducting round wires The zero field critical current density \( (J_{c0}) \) at 32 K as well as the dimensions of the samples are given in Table 6-1. The critical temperature of all the samples obtained from the measurements of magnetic ac susceptibility was found to be almost 38.5 K. The mass density of the samples was almost the same for all the samples within experimental uncertainty (5%), about 60%. However, we expect S3 to have slightly higher mass density because it was drawn to the smaller diameter and had the highest value of \( J_{c0} \) as
can be seen in Table 6-1. SEM images showed that all three samples had the same average grain size of about 100nm.

Voltage-current characteristics were measured using a 6 milliseconds long pulse of current. The current was swept at a constant rate, with the maximum current 250 A. The signal from the voltage taps was filtered by a low-pass filter and pre-amplified by a SR560 preamplifier. The current through the wire was measured via the voltage drop on a non-inductive resistor, connected in series to the wire and current source. Both voltage and current signals were fed into a digital oscilloscope. The measured data were transferred into a computer for analysis. Using a high enough cut-off frequency of the low-pass filter prevented distortions of the voltage signal and the phase shift between the current and voltage signals.

The measured MgB$_2$/Fe wire was placed in a continuous flow cryostat, with temperature control better than 0.1 K. The cryostat was placed in an electromagnet on a rotating base, enabling the angle between the field and long axis of the wire to be changed. Measurements were limited to the temperature range between 32 and 35 K, due to the limitations of the current source. $V(I)$ measurements showed a very sharp increase in the voltage at the critical current ($I_c$).

**6-2-3 Results and Discussion**

Figure 6-7 shows the angular dependence of $I_c$ for S1, at 33.7 K and 400 mT. The $\theta = 90^\circ$ represents the magnetic field perpendicular to the long (cylindrical) axis of the wire. As we can see, critical current shows a maximum value of 99 A for $\theta = 90^\circ$. The $I_c$ value is decreased by about 75% of its maximum value within 30$^\circ$. However, for the remaining 60$^\circ$, only a negligible change in $I_c$ was observed (Fig. 6-7). These measurements helped to accurately align the field into a perpendicular orientation. Fig. 6-8 shows the temperature dependence of $I_c$ for S1 in zero field. The zero field critical current value ($I_{c0}$) decreased almost linearly with temperature between 32 and 36 K, at a rate of 46.4 A/K. For higher temperatures, $I_{c0}$ decreased more gradually, approaching zero at about 38.5 K.
Table 6-1: Dimensions of the samples measured; $d_o$, $d_i$, and $l$ are outer diameter, inner diameter and length, respectively. $J_{c0}$ is the critical current density in zero external field, at a temperature of 32 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_o$ (mm)</th>
<th>$d_i$ (mm)</th>
<th>$l$ (mm)</th>
<th>$J_{c0}$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1.50</td>
<td>0.85</td>
<td>14</td>
<td>38,700</td>
</tr>
<tr>
<td>S2</td>
<td>1.52</td>
<td>0.95</td>
<td>14</td>
<td>21,000</td>
</tr>
<tr>
<td>S3</td>
<td>1.30</td>
<td>0.65</td>
<td>13</td>
<td>53,300</td>
</tr>
</tbody>
</table>

The magnetic field dependence of $I_c$ for sample S3 at 32 K is shown in Fig. 6-8. The solid and open symbols correspond to $\theta = 90^\circ$ and $\theta = 0^\circ$, respectively. In the latter case, the field is parallel to the long wire axis, and therefore to the current. The solid line shows the value of the self-field produced by the critical current at the surface of the superconducting core. For $\theta = 0^\circ$, $I_c$ does not change with the field up to about 0.03 T (open symbols in Fig. 6-9). For higher fields, an exponential decrease in $I_c$ is obtained: $I_c = I_{c0} \exp(-H/H_0)$. For all the samples measured, $H_0 \approx 0.35$ T at 32 K.

Figure 6-7: Angular dependence of critical current for Fe/MgB$_2$ wire sample S1 at 33.7 K and 0.4 T.
Figure 6- 8: Temperature dependence of critical current in zero field for Fe/MgB₂ wire sample S1. Inset is the critical current density versus temperature for this sample. Lines are just guides to the eye.

For \( \theta = 90^\circ \), the field dependence of \( I_c \) is the same as for \( \theta = 0^\circ \) with \( H > 0.6 \) T. However, for \( 0.2 \) T < \( H < 0.6 \) T, there is a plateau in \( I_c(H) \), where \( I_c \) decreases with the field by less than 5% of \( I_{c0} \) (Figure 6-9). For \( H < 0.2 \) T, \( I_c \) decreases with the field by about 20% of \( I_{c0} \). The inset to Fig. 6-9 shows that the experimental points for the two field orientations overlap by adding 0.38 T to the parallel field.

Figure 6- 9: Field dependence of critical current for sample S3 at 32 K. The solid and open symbols are for perpendicular and parallel field (i.e. \( \theta = 90^\circ \) and \( 0^\circ \)), respectively. The solid line is the self-field produced on the surface of the superconductor by the critical current. Inset: The same, with 380 mT added to the parallel field.
The same results were obtained for the other samples measured, except for the difference in $I_{c0}$ and the field by which $I_c(H)$ for $\theta = 0^\circ$ had to be shifted to obtain overlapping with $I_c(H)$ for $\theta = 90^\circ$ (Inset to Fig. 6-9). The values of this field for S1 and S2 were 0.39 T and 0.33 T, respectively.

The results shown in Fig. 6-9 are affected by the magnetic shielding due to the Fe sheath, as well as by the interaction between the sheath and superconductor. To identify the effects of shielding only, the field inside and outside the sheath was measured, with the MgB$_2$ removed. This was performed by inserting tiny pick-up coils into the sheath and using an external ac magnetic field with frequencies between 20 and 60 Hz, and a field amplitude up to 0.6 T. The length of the coils corresponded to the distance between the voltage contacts when measuring $I_c(H)$. Comparing the results for different frequencies, we found that the dynamic effects (eddy currents) were negligible below 30 Hz.

Fig. 6-10 shows the magnetic field inside the Fe sheath against the external magnetic field for $\theta = 90^\circ$ (open symbols). The solid symbols were measurements with the sheath removed from the pick-up coil ($H_{in}=H_{out}$) and the solid line shows theoretical shielding for an infinite cylinder of the same dimensions and magnetic susceptibility as our Fe sheath [20].

For $H<0.2$ T, the shielding from the external field was almost total, with $H_{in}=0.04 \, H_{out}$ at 0.2 T (Fig. 6-10). For higher fields, the shielding rapidly weakened and for $H>0.4$ T the entire external field additional to 0.4 T was passed through the Fe sheath, i.e. $H_{in}$ against $H_{out}$ was parallel to the data with no shield for $H>0.4$ T. These measurements are in good quantitative agreement with calorimetric measurements of ac loss in a similar MgB$_2$/Fe wire [19]. However, the measured shielding is better than that given by the analytical expression for an infinite cylindrical shield of the same thickness and magnetic permeability [20] (solid line in Fig. 6-10). Still, extrapolation of the experimental results to high fields is in agreement with the theoretical prediction. The discrepancy at low fields is probably due to the finite length of the measured sheath.

The inset to Fig. 6-10 shows the measured shielding for $\theta = 0^\circ$. The dashed line represents $H_{in}=H_{out}$. The shielding was almost total for $H<0.02$ T. For $H>0.025$ T, the
entire field higher than 0.025 T was passed through the shield. The hysteresis was due to magnetic hysteresis of the iron.

\[ \text{I}_c(H) \text{ for } \theta = 90^\circ \] can be explained by the shielding effect. The initial plateau is a consequence of complete shielding from the external field. Above 0.025 T, \( \text{I}_c(H) \) is the same as with no shield, except for about 0.025 T which is screened out by the shield. The same is obtained for \( \theta = 90^\circ \) and \( H > 0.6 \) T, except that the value of the screened-out field is about 0.3 T (Fig. 6-10). However, \( \text{I}_c(H) \) for \( H < 0.6 \) T cannot be explained by simple screening. Instead of the expected constant \( \text{I}_c \) with the external field fully screened out for \( H < 0.2 \) T, \( \text{I}_c \) actually decreases with the field (Fig. 6-9). For 0.2 T \( < H < 0.6 \) T, \( \text{I}_c \) decreases very little with field (Fig. 6-9), despite the full penetration of field through the Fe sheath (Fig. 6-10).

Overlapping of \( \text{I}_c(H) \) for \( \theta = 0^\circ \) and \( \theta = 90^\circ \) above 0.6 T (Inset to Fig. 6-9) shows that the current does not flow through the wires in a straight line. If that were the case, \( \text{I}_c(H) \) corrected for the shielding of the iron sheath would differ for the two orientations of the field. This is because \( \text{I}_c(H) \) is defined by the Lorentz-like force on magnetic vortices [21]. This force is proportional to \( H \times \sin \theta \). Therefore, for \( \theta = 0^\circ \), Lorentz force would always be zero and \( \text{I}_c \) would not depend on the field. This is in contrast to the experimental results in the Inset to Fig. 6-9. These results suggest that the current

\[ \begin{align*}
\text{H parallel to wire} & \\
\text{H perpendicular to wire}
\end{align*} \]

Figure 6-10: The magnetic field inside the iron sheath, \( H_{in} \), plotted against the external field, \( H_{out} \), for perpendicular field, \( \theta = 90^\circ \) (open symbols). When the iron sheath is removed, \( H_{in} = H_{out} \) (solid symbols). The solid line shows theoretical \( H_{in} \) against \( H_{out} \). Inset: \( H_{in} \) against \( H_{out} \) for a parallel field, \( \theta = 0^\circ \) (solid symbols). The dashed line shows \( H_{in} = H_{out} \) for parallel field.
meanders between the superconducting grains, resulting in a variation of local $\theta$. Averaging over the whole sample volume gives the same $I_c(H)$ for $\theta = 90^\circ$ and $0^\circ$ after shifting of $I_c(H)$ by 0.38 T along $H$-axis (the shift is needed to account for the shielding by the iron sheath). The decrease in $I_c$ for $H<0.2$ T cannot be ascribed to weak links, because such a decrease was not also observed for the case $\theta = 0^\circ$ (Fig. 6-9).

6-2-4 Summary

In conclusion, transport critical current ($I_c$) was measured for Fe-sheathed MgB$_2$ round wires. A critical current density of $5.3 \times 10^4$ A/cm$^2$ was obtained at 32 K. Strong magnetic shielding by the iron sheath was observed, resulting in a decrease in $I_c$ by only 15% in a field of 0.6 T at 32 K. In addition to shielding, interaction between the iron sheath and the superconductor resulted in a constant $I_c$ between 0.2 and 0.6 T. This was well beyond the maximum field for effective shielding of 0.2 T. This effect can be used to substantially improve the field performance of MgB$_2$/Fe wires at fields at least 3 times higher than the range allowed by mere magnetic shielding by the iron sheath. The dependence of $I_c$ on the angle between the field and the current showed that the transport current does not flow straight across the wire, but meanders between the grains.
6-3 Effect of Sample Size on the Magnetic Critical Current Density in Nano-SiC Doped MgB$_2$ Superconductors

6-3-1 Introduction

Improving the critical current density ($J_c$) is one of the most important issues so far as applications are concerned. Results presented in chapter 5 show that SiC doped MgB$_2$ superconductor is one of candidates for high field applications. In contrast to the direct transport $J_c$ measurements used for tapes and wires, for bulk samples one has to calculate magnetic $J_c$ from the dc magnetization using the Bean model. It has been shown that magnetic $J_c$ strongly depends on the sample size [22]. In contrast to the high $T_c$ superconductor materials [23] it was observed that in pure MgB$_2$ bulk samples $H_{irr}$ decreased as the sample volume decreased. Due to the dependence of $J_c$ on sample size, for a reliable comparison of $J_c$ values derived from magnetic measurements, sample size has to be carefully taken into account. Some explanations have been presented to explain this behavior. Jin et al. suggested a linear dependence of the activation energy on the $J_c$ and gave an explanation for the $J_c$ dependence on the sample size [24]. They proposed that in a cylindrical MgB$_2$ sample, vortices are remarkably rigid in small samples up to 1mm long, while they behave as individual segments for longer samples. Horvat et al. qualitatively explain this phenomenon by considering the different coupling between the grains at different length scales [22]. Very recently Qin et al. established a new model to explain this effect [25]. Based on this model the magnetic $J_c$ depends on sample size as $J_c \propto R^{\frac{1}{n}}$ where R is the radius of a cylindrical sample and $n$ is the $n$-factor characterizing the $E$-$J$ curve $E = E_c (J / J_c)^r$. They proposed that the low $n$ factor at high magnetic fields is the reason for the significant sample size effect for pure MgB$_2$ superconductors. As the nano-SiC doped sample exhibited much stronger flux pinning than the pure MgB$_2$, we intend to investigate the size effect in the strong pinning samples and compare them with pure MgB$_2$ samples. A detailed study with the aim of further understanding the sample size effect in both pure and doped MgB$_2$ superconductor is presented in this section.
6-3-2 Experimental Details

Two groups of polycrystalline MgB$_2$ and MgB$_2$ +10% SiC samples were synthesized from high purity Mg and B and nano-SiC powders using the Hot Isostatic Pressing (HIP) method. An MgB$_2$ pellet was prepared by reacting magnesium and boron powders at 850°C under isostatic pressure of 150 MPa for 1 hour. The magnetization was measured over a temperature range of 5 K to 30 K using the Quantum Design PPMS. Bar shaped samples were cut and dry polished from each pellet for magnetic measurements. The shiny polished surface was golden and black for the pure and doped samples respectively. The sample volume was decreased about 75% through sawing and dry polishing after each measurement. To avoid any geometrical effect on the results each dimension reduced by a factor of about 0.35% (i.e. the ratio of a:b:c remains constant) before each subsequent measurement. The sample information is presented in Table 6-2. The magnetic measurements were performed by applying the magnetic field parallel to the longest sample axis. The magnetic $J_c$ was calculated using the Bean model. The $T_c$ was determined to be 38.6 K and 37.5 K for the pure and doped samples respectively using the ac susceptibility measurement. A small bar shaped sample of the same size as sample 4, was directly cut from the same batch and given a $J_c$ measurement. No significant difference was found between the results for this sample and for sample 4, indicating that the repeated polishing and measurements had no effect on the samples.

Table 6-2: The dimensions of samples prepared for magnetic measurements. Each dimension was reduced by about 35% before each subsequent measurement. The magnetic field was applied parallel to the c axis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Undoped</th>
<th>Doped</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (mm)</td>
<td>b (mm)</td>
</tr>
<tr>
<td>1</td>
<td>1.07</td>
<td>3.27</td>
</tr>
<tr>
<td>2</td>
<td>0.7</td>
<td>2.12</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>1.34</td>
</tr>
<tr>
<td>4</td>
<td>0.29</td>
<td>0.85</td>
</tr>
</tbody>
</table>
6-3-3 Results and Discussion

The field dependence of $J_c$ for SiC doped and undoped MgB$_2$ samples at 5 K, 20 K and 30 K for samples of different sizes are presented in Fig. 6-11 and Fig. 6-12 respectively. It can be clearly seen that in both doped and undoped samples the $J_c$ field performance strongly depends on the sample size. At high field, $J_c$ significantly decreased as a function of the magnetic field as the sample size decreased. On the other hand, the low field $J_c$ increased as the sample size decreased in both pure and doped samples. These changes in either low fields or in high fields are stronger in the lower temperature regime. Flux jumping was observed in both pure and doped samples but flux jumps occurred at higher fields for bigger samples. Flux jumping was also found to be less serious in the doped samples. For sample 1 flux jumping was observed up to 3.9 T for the doped sample, but in the pure sample flux jumping can be seen even at 5 T. Flux jumping also occurred in the pure samples 1 and 2 at 20 K, but no flux jumping was observed in the doped samples at 20 K.

Figure 6-11: Magnetic $J_c$ field dependence of MgB$_2$ + 10% SiC samples of different sizes (Table 6-2) at 5 K, 20 K and 30 K.
Figure 6- 12: Magnetic $J_c$ field dependence of pure MgB$_2$ samples of different sizes (Table 6-2) at 5 K, 20 K and 30 K.

The ratio of $J_{c1}/J_{c4}$ for samples 1 and 4 between 5 T and 8.5 T for both pure and doped samples at 5 K are presented in Fig. 6-13. For both samples the larger the sample, the higher the $J_{c1}/J_{c4}$ ratio. However, the sample size dependence is much more pronounced in the undoped sample. At 6.5 T and 5 K $J_{c4}$ is lower than $J_{c1}$ by a factor of 1.8 for the doped samples. However, under the same conditions, $J_{c4}$ is more than one order of magnitude lower than $J_{c1}$ in the pure samples. The $J_c$ field dependences of the doped samples at low magnetic fields and 20 K are shown in the inset of Fig. 6-13. As we can see, the zero field $J_c$ increases as the sample size decreases. However, the differences between the $J_c$ values of all the samples are reduced by increasing the magnetic field. The $J_c$ field dependence curve of sample 1 crosses over the $J_c$ curves of the smaller samples at a magnetic field of about 1 T. The same behavior was also found in the pure samples.

The dependence of the irreversibility field $H_{irr}$ on the volume of pure and doped samples at 20 K is shown in a semi-logarithmic plot in Fig. 6-14. $H_{irr}$ was determined from $J_c$–$H$ curves using the criterion of 100 A/cm$^2$. Some points for the pure samples were extracted from reference [4]. As we can see, $H_{irr}$ decreases logarithmically as the
sample volume decreases. The irreversibility field $H_{irr}$ versus the sample volume is plotted in the inset with linear scaling, showing a gradual saturation behavior as the sample volume increases. Almost the same trend was found at other temperatures as well.

![Graph showing the ratio of $J_{c1}/J_{c4}$ between 50000 Oe and 85000 Oe for both pure and doped samples at 5 K. The $J_e$ field dependence of doped sample at low magnetic fields at 20 K is shown in the inset.](image1)

**Figure 6-13:** The ratio of $J_{c1}/J_{c4}$ between 50000 Oe and 85000 Oe for both pure and doped samples at 5 K. The $J_e$ field dependence of doped sample at low magnetic fields at 20 K is shown in the inset.

![Graph showing the dependence of $H_{irr}$ samples on the sample volume of pure and doped MgB$_2$ at 20 K in a semi-logarithmic plot. $H_{irr}$ versus the volume with linear scaling is shown in the inset.](image2)

**Figure 6-14:** The dependence of $H_{irr}$ samples on the sample volume of pure and doped MgB$_2$ at 20 K in a semi-logarithmic plot. $H_{irr}$ versus the volume with linear scaling is shown in the inset.
Fig. 6-15 shows the dependence of the zero field critical current ($J_{c0}$) on the sample volume of pure and doped samples at 20 K and 30 K. Some points for pure samples were extracted from reference [4]. All $J_{c0}$ values were normalized to the $J_{c0}$ value of the biggest sample. Over all temperature ranges the smaller samples had a higher $J_{c0}$. For pure samples the normalized $J_{c0}$ increases slightly as the sample volume decreases down to 7 mm$^3$, followed by a faster increase for smaller sample volumes. $J_{c0}$ can also be very well scaled for both 20 K and 30 K with the same curve. However for doped samples, $J_{c0}$ increases more gradually than for the pure samples as the sample size decreases. Moreover the $J_{c0}$ values for 20 K and 30 K cannot be scaled using the same curve. The difference between the normalized $J_{c0}$ values for 20 K and 30 K is increased by decreasing the volume. The lower the temperature is, the faster $J_{c0}$ increases. The absolute value of $J_{c0}$ versus the sample volume for pure and doped samples at 20 K is plotted on a logarithmic scale in the inset. The curves can be fitted as an exponential decay function as is shown in the figure (lines).

Figure 6-15: The dependence of the zero field $J_c$ ($J_{c0}$) on the sample volume of pure and doped samples at 20 K and 30 K. In the inset the dependence of $J_{c0}$ on the volume at 20 K is plotted on a logarithmic scale.
Based on Qin’s method we have plotted \( \ln(J_c) \) versus \( \ln[ab/(a+b)] \) for the doped samples at 20 K and at 3 T, 4 T, 5 T, and 6 T in Fig. 6-16. Similar curves at 5 K and 30 K for different magnetic fields are presented in the insets of this figure. The solid lines are the best linear fittings between \( \ln(J_c) \) and \( \ln[ab/(a+b)] \). The inverses of the slopes give the \( n \) factors. Calculated \( n \) factors for the SiC doped samples are shown in Fig. 6-17 at 5 K, 20 K and 30 K. The \( n \) factors of pure samples are also included as open squares and open triangles for 5 K and 20 K respectively. The solid lines are just guides to the eye.

As the \( n \)-factor is the exponent characterizing the \( E-j \) curve \( E = E_c(j/j_c)^n \), a large \( n \)-factor will lead to a sharp \( E-j \) curve. On the other hand, the \( n \)-factor can be calculated as \( n = U_0/kT \) [25], where \( U_0 \) is the energy scale for the current density dependent activation energy \( U(j) = U_0 \log(j/j_c) \) with \( k \) the Boltzmann constant. Therefore a large \( n \) indicates a stronger pinning effect. Moreover, the dependence of the current density on the sample size has been derived to be \( j \propto R^{1/n} \), indicating that a large \( n \) will give rise to less sample size dependence. It can be seen from Fig. 6-16 that the \( n \)-factors of the doped samples are much higher than those of the pure samples, indicating that strong pinning centers have been introduced into the MgB\(_2\) samples by means of SiC doping.

**Figure 6-16:** The sample size dependence of \( J_c \) for doped MgB\(_2\) samples at 20 K. The same dependence is plotted in the insets for 5 K and 30 K. The solid lines are linear fits to the data.
Chapter 6: Study of ac Susceptibility, Magnetic Shielding and Sample Size Effect in MgB$_2$ Superconductor

Fig. 6-17 also explains the observed lesser sample size effect in the SiC doped samples shown in Figs. 1–3.

![Figure 6-17: The $n$ factor versus applied magnetic field for the doped MgB$_2$ samples at 5 K, 20 K and 30 K (solid symbols). The $n$ factor of pure samples are also included (open symbols). The solid lines are only guides to the eye.](image)

6-3-4 Summary

In conclusion we have studied the sample size effect in pure and SiC doped MgB$_2$ samples and derived the $n$-factors for both samples. The doped samples show a larger $n$-factor and less sample size dependence, indicating a stronger pinning effect by SiC doping in MgB$_2$ samples. The irreversibility field $H_{irr}$ was found to increase with increasing sample volume as a logarithmic function. The zero field $J_c$ decreased with decreasing sample volume as an exponential decay function. A systematic shift in the pinning force density was found in both pure and doped samples as the sample volume decreased.
References


Chapter 6: Study of ac Susceptibility, Magnetic Shielding and Sample Size Effect in MgB₂ Superconductor


CHAPTER 7: CONCLUSION

Fe-clad MgB$_2$ tapes made by powder-in tube technique show a superconducting core with large clusters of grains about 100 µm in size. They reveal a sharp transition with a transition width $\Delta T_c$ of 0.2 K and transition temperature $T_{c0}$ of 37.5 K. A transport critical current density of $1.7 \times 10^4$ A/cm$^2$ for both 29.5 K in 1 T and for 33 K in null field has been obtained. The effects of sintering time and temperature on the critical current densities of Cu, Ag and Fe-clad MgB$_2$ wires have been also investigated. It was found that a short time heat treatment in the fabrication of Cu and Ag clad MgB$_2$ wires can markedly enhance the critical current density. A total sintering time of several minutes is enough to form nearly pure MgB$_2$ with high performance characteristics. The Cu and Ag clad MgB$_2$ wire samples which were sintered for 6 minutes are better than those sintered for longer times. $J_c$ of $1.2 \times 10^5$ A/cm$^2$ in zero field and above $10^4$ A/cm$^2$ in 2 T at 20 K have been achieved for Ag-clad MgB$_2$ wire sintered for a short period of time. Moreover, it is evident that long MgB$_2$ wires and solenoid coils can be fabricated using the wind-reaction in-situ technique with little $J_c$ degradation over the entire length, paving the way for design and fabrication of the magnetic windings and magnets which are the central element for many large scale applications.

We demonstrated that a very high critical current density can be achieved by a readily achievable and economically viable chemical doping with nano-C or nano-SiC. By studying the SiC doped samples, it was found that there are two closely related but distinguishable mechanisms: $H_{c2}$ and flux pinning that jointly control the performance of $J_c(H)$. Nano-scale SiC doping into MgB$_2$ enhances both $H_{c2}$ and flux pinning. Alloying at B and Mg sites due to C substitution and the formation of nano-domain structures will cause strong scattering over a wide range of temperatures, leading to enhancement in $H_{c2}$. A high concentration of various nano-scale impurity phases results in high resistivity, a low residual resistivity ratio and a large irreversibility field and upper critical field with modest $T_c$ reduction. The highly dispersed nanoscale precipitates MgSi$_2$, BC, BO$_x$, and SiBO$_x$ and the extensive domain structures at a scale well below 10 nm both serve as strong pinning centres. Large particle impurities such as
unreacted SiC (>100nm) increase resistivity, reduce superconducting volume and do not help the improvement of either flux pinning or $H_{c2}$. They should therefore be eliminated. The doping with SiC gives enhancements to the critical current density, the irreversibility field and the upper critical field in a manner that helps make MgB$_2$ potentially competitive with both low and high-$T_c$ superconductors. In Fe-sheathed MgB$_2$ wire we have further demonstrated that $J_c$ field performance can be significantly improved by nano-SiC doping. $J_c$ values over 100,000 A/cm$^2$ at 5 K and 5 T and 20 K and 2 T were obtained for Fe clad wire, comparable to both NbTi and HTS. High performance SiC doped MgB$_2$ wires will have a great potential to replace the current market leaders, Nb-Ti and HTS, for many practical applications at 5 K to 25 K up to 5 T. It was also found that the grain sizes of the precursor SiC have a strong effect on the critical current density and its field dependence. The smaller the SiC grains are, the better the $J_c$ field performance and $H_{irr}$ is. It was found that very fine SiC powder plays an important role in the reaction between Mg+B and SiC. Significant enhancements of $J_c$ and $H_{irr}$ were revealed for all the SiC-doped MgB$_2$ with added levels up to 15 wt%. A $J_c$ value as high as 20,000 A/cm$^2$ in 8 Tesla and 5 K was achieved for the sample doped with 10 wt% SiC, which had grain sizes of about 20 nm. The high performance of the nano-SiC doped MgB$_2$ superconductor will have great potential for practical applications

The effect of nano-particle C doping on the lattice parameters, $T_c$, $J_c$ and flux pinning in MgB$_2$ was investigated as well. It was found that both the $a$-axis lattice parameter and the $T_c$ decreased monotonically with increasing doping level. For the sample doped with the highest nominal composition of $x=0.4$ the $T_c$ dropped only 2.7 K. The nano-C-doped samples showed an improved field dependence of the $J_c$ over a wide temperature range compared with the undoped sample. X-ray diffraction and TEM studies indicate that C reacted with Mg to form Mg$_2$C$_3$ and MgB$_2$C$_2$ with nano-dimensions. Nano-particle inclusions and substitution, both observed by transmission electron microscopy, are proposed to be responsible for the enhancement of flux pinning in high fields. Although a significant improvement in MgB$_2$ performance has been obtained by nano-SiC and C doping, there is still no evidence for Si doping whether in Mg or B sites. It is still not clear whether substitution or inclusion is the more effective way to improve the properties of samples. More work is necessary to elucidate the mechanism of flux pinning in the doped samples. There is also a lot of room for further study of nano
particle doping effects on the mechanical properties and stability of samples exposed to water. It is also needs to be pointed out that the fabrication process needs to be optimized in order to achieve better performance for practical applications.

In the final part of the thesis, we performed systematic ac susceptibility measurements on a MgB$_2$ bulk sample. The magnetic-field- and current-density-dependent flux creep activation energy has been determined to be $U(J, B) \propto J^{-0.2} B^{-1.33}$. Compared to high-temperature superconductors ($U(B) \propto B^{-1}$ for a weakly pinned La$_{1.86}$Sr$_{0.14}$CuO$_4$ single crystal and $U(B) \propto B^{-0.5}$ for strongly pinned YBa$_2$Cu$_3$O$_y$), the steeply declining dependence $U(B) \propto B^{-1.33}$ results in a steep drop in $J_c$ with magnetic field and suggests that pinning in MgB$_2$ is quite weak. We also demonstrate by direct transport measurements of $I_c$ that an iron sheath can be used as a very effective magnetic shield with MgB$_2$ superconducting wires. The initial decrease in $I_c$ with field and the plateau in intermediate fields is a newly observed effect, originating in an interaction between the Fe sheath and the superconductor. Better understanding of this effect can lead to extending the plateau to higher fields and improving the field performance of MgB$_2$/Fe wires further. It was also shown that the current path in the wires meanders between the grains.

The sample size effect in pure and SiC doped MgB$_2$ samples has been studied, and the n-factor for both samples was also derived. The doped samples show a larger n-factor and less sample size dependence, indicating a stronger pinning effect by SiC doping in MgB$_2$ samples. The irreversibility field $H_{irr}$ was found to increase with increasing sample volume as a logarithmic function. The zero field $J_c$ also decreased with decreasing sample volume. More work is needed to clearly understand the mechanism underlying this effect.
Publication During the PhD Study


