Study of superconducting and electromagnetic properties of un-doped and organic compound doped MgB2 conductors

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STUDY OF SUPERCONDUCTING AND ELECTROMAGNETIC PROPERTIES OF UN-DOPED AND ORGANIC COMPOUND DOPED MgB$_2$ CONDUCTORS

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UNIVERSITY OF WOLLONGONG

By

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Institute for Superconducting & Electronic Materials

Faculty of Engineering

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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.

Md Shahriar Al Hossain

2008
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ABSTRACT

In this thesis I emphasized on the organic compound doping (specially carbohydrate group, malic acid, C$_4$H$_6$O$_5$) and heat treatment effects on the superconducting properties of MgB$_2$. I also focused on the basic and fundamental properties of un-doped MgB$_2$ wires in different temperatures for comparison purpose. And finally I have proposed another new dopant which avoids some problems using carbohydrate in some aspects.

Firstly, I have studied the effects of sintering temperature on the phase transformation, lattice parameters, full width at half-maximum (FWHM), strain, critical temperature ($T_c$), critical current density ($J_c$) and resistivity ($\rho$) in MgB$_2$/Fe wires. All samples were fabricated by the in situ powder-in-tube method (PIT) and sintered within a temperature range of 650–900 °C. I have showed that why I have taken such sintering temperature range by analyzing with differential thermal analysis (DTA). The increased FWHM and decreased $T_c$ at low sintering temperature region suggested the smaller grain size and poor crystallinity. Strain values also higher at low sintering region. That's why it was observed that wires sintered at low temperature, 650 °C, resulted in higher $J_c$ up to 12 T. The best transport $J_c$ value reached 4200 A cm$^{-2}$ at 4.2 K and 10 T. This is related to the grain boundary pinning due to small grain size and poor crystallinity due to strain defects. On the other hand, wires sintered at 900 °C had a lower $J_c$ in combination with better crystallinity due to higher $T_c$.

The effect of carbohydrate doping on lattice parameters, microstructure, $T_c$, $J_c$, $H_{irr}$, and $H_{c2}$ of MgB$_2$ has been studied. In this work I used malic acid, C$_4$H$_6$O$_5$ as an example of
carbohydrates as an additive to MgB$_2$. We have described the advantages of carbohydrate doping include homogeneous mixing of precursor powders, avoidance of expansive nanoadditives, production of highly reactive C, and significant enhancement in $J_c$, $H_{irr}$, and $H_{c2}$ of MgB$_2$, compared to un-doped samples. The defects due to the C substitution into boron site lead to the enhancement of $H_{irr}$ and $H_{c2}$. The decrease of $a$-axis lattice parameter and reduction of $T_c$ indicates poor crystallinity due to C substitution. The microstructure was shown both for un-doped and doped samples which were well consistent with FWHM. The $J_c$ for MgB$_2$+30 wt% C$_4$H$_6$O$_5$ sample was increased by a factor of 21 at 5 K and 8 T without degradation of self-field $J_c$ due to C substitution into B sites.

During the evaporation process of the C$_4$H$_6$O$_5$ with B and solvent, freshly and highly reactive C is produced and C substitution for B can take place at the temperature same as the formation temperature of MgB$_2$. By using this chemical route I again evaluated the doping effects of C$_4$H$_6$O$_5$, from 0 to 30 wt% of the total MgB$_2$, on the lattice parameters, lattice strain, amount of carbon (C) substitution, microstructures, weight fraction of MgO, critical temperature ($T_c$), critical current density ($J_c$), and irreversibility field ($H_{irr}$) of a MgB$_2$ superconductor. The calculated lattice parameters show a large decrease in the $a$-axis lattice parameter for MgB$_2$ + C$_4$H$_6$O$_5$ samples from 3.0861(6) to 3.0736(1) Å, with even a 10 wt% addition. This is an indication of C substitution into boron sites, with the C coming from C$_4$H$_6$O$_5$, resulting in enhancement of $J_c$ and $H_{irr}$. Specifically, the $H_{irr}$ of the MgB$_2$ + C$_4$H$_6$O$_5$ samples prepared by the chemical solution route reached around 7 T at 20 K, with a $T_c$ reduction of only 1.5 K. In addition, the self-field $J_c$ of the MgB$_2$ +
C$_4$H$_6$O$_5$ samples was only slightly reduced at an additive level as high as 30 wt%. The interesting thing I found here is maximum C-substitution and the maximum enhancement of all the superconducting parameters up to 10 wt% addition, after that the improvement rate is saturated. From these data I can claim 10 wt% addition is enough for maximum C-substitution and enhancement of superconducting properties. However, residual oxygen after evaporation processing contributed to a large amount of MgO in our MgB$_2$ + 30 wt% C$_4$H$_6$O$_5$ samples. These problems can be further controlled by the amount of C$_4$H$_6$O$_5$ additive or different evaporation temperatures.

After the successful doping effects of C$_4$H$_6$O$_5$ into MgB$_2$, then I investigated the behavior of C$_4$H$_6$O$_5$ as a dopant with different sintering temperatures. All the samples were prepared by the chemical solution route. I report the carbon (C) substitution effects of MgB$_2$ + 10 wt% C$_4$H$_6$O$_5$ on the lattice parameters, critical temperature ($T_c$), upper critical field ($H_{c2}$), and irreversibility field ($H_{irr}$) as a function of sintering temperature in the range from 600 to 900 °C. The additive C$_4$H$_6$O$_5$ as the C source resulted in a small depression in $T_c$, but significantly increased the C substitution level, and hence improved the $H_{c2}$ and $H_{irr}$ performance at a low sintering temperature of 600 °C in conjunction with a short sintering period of 4 h. In addition, the low-temperature sintering process resulted in small grain size and higher impurity scattering compared to a pure MgB$_2$ superconductor which promotes the flux pinning significantly.

Very recently, I have chosen another solid hydrocarbon dopant named pyrene (C$_{16}$H$_{10}$) in to MgB$_2$. There are few reasons behind this decision. Firstly we know all the carbohydrates consist of carbon (C), hydrogen (H), and oxygen (O). During the
evaporation process of C$_4$H$_6$O$_5$, I noticed that the MgO amount is gradually increased with increasing doping level. So our group suggests such special solid hydrocarbon without O content which may reduce the MgO content within the matrix. In this work, we report on significantly enhanced $J_c$ in MgB$_2$ superconductor that was easily obtained by doping with a hydrocarbon, highly active C$_{16}$H$_{10}$, and using a sintering temperature as low as 600 °C. The processing advantages of the C$_{16}$H$_{10}$ additive include production of a highly active carbon C source, an increased level of disorder, and the introduction of small grain size, resulting in enhancement of $J_c$. 
CHAPTER 1:

1. INTRODUCTION

The Dutch physicist Heike Onnes discovered superconductivity in 1911. He observed that mercury cooled below 4.2 degrees Kelvin lost all of its electrical resistance. Onnes labeled this phenomena superconductivity [1]. Research into superconductivity is enjoying a renaissance. Physicists have discovered a wide variety of materials over the past ten years, including iron, single crystals of carbon-60, and even DNA, which that lose their electrical resistance at low temperatures.

Superconducting metals and alloys each have a characteristic transition temperature from normal conductivity to superconductivity called the critical temperature \((T_c)\). The resistivity of a material is exactly zero below the superconducting transition temperature. As there is no loss of electrical energy when superconductors carry electrical current, so relatively narrow wires made of superconducting materials can be used to carry huge currents. However, there is a particular maximum current that each of these materials can be made to carry, above which they stop being superconductors. If too much current is pushed through a superconductor, it will revert to the normal state, even though it may be below its transition temperature. The value of the critical current density \((J_c)\) is a function of temperature; i.e., the colder you keep the superconductor the more current it can carry.

An electrical current in a wire creates a magnetic field around the wire. The strength of the magnetic field increases as the current in the wire increases. Because superconductors are able to carry large currents without loss of energy, they are well suited for making strong electromagnets. When a superconductor is cooled below its transition temperature \((T_c)\) and the magnetic field is increased around it, the magnetic field forms part of the
environment of the superconductor. If the magnetic field is increased to a critical point, the superconductor will go to the normal resistive state.

The maximum value for the magnetic field at a given temperature is known as the critical magnetic field and is given the symbol $H_c$. Each of these parameters is very dependent on the other two properties. Maintaining the superconducting state requires that both the magnetic field and the current density, as well as the temperature, remain below the critical values, all of which depend on the material. For all superconductors, there exists a region of temperatures and magnetic fields within which the material is superconducting. Outside this region the material is normal. Once the transition from the normal state to the superconducting state occurs, external magnetic fields can't penetrate the superconductor. This effect is called the Meissner effect and has implications for making high speed, magnetically-levitated trains. It also has implications for making powerful, small, superconducting magnets for magnetic resonance imaging (MRI).

In 1958, Abrikosov divided superconductor materials into two groups by their behaviour in magnetic fields: *type-I* and *type-II* superconductors [2]. In type-II superconductors there are two critical fields, the lower critical field ($B_{c1}$) and the upper critical field ($B_{c2}$). 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. The diameter of the vortices is of the order of the coherence length of the superconductor, $\xi$. As the field increases towards $B_{c2}$, the flux totally penetrates the whole sample, and it returns to the normal state. When a type-I superconductor is placed in a weak external magnetic
field, the field penetrates the superconductor for only a short distance, which is called the penetration depth ($\lambda$).

When superconductors are to carry large currents, then these vortices must not move in response to magnetic fields and currents. Resistivity occurs when a vortex moves. Magnetic vortices can be effectively pinned at sites of atomic defects. Flux pinning occurs at such tiny defects in the crystalline structure of the superconducting material. Consider a magnet on top of a superconductor. If we imagine the magnetic field around the magnet in the form of lines of force, the superconductor repels the majority of the magnetic force lines, which support and levitate the magnet. A smaller portion of the lines of force become trapped in the defects in the superconductor matrix and are held in place. These trapped lines of force (flux pinning) are the reason why the magnet doesn't slide and fall off the superconductor.

In 1962 Brian Josephson showed that if there is a very thin (a few nanometers thick) electrically insulating film (a weak link) between two pieces of superconductor [3], then contrary to expectations, there will continue to be a flow of electrical current right through the insulator. This superconducting current is called a supercurrent. This phenomenon is a very visible manifestation of a quantum mechanical effect. This is very important for the superconductor applications point of view.

LTS (Low Temperature Superconductor) materials of interest have $T_c$'s grouped either around 10K (niobium metal and niobium alloys) or between 15K and 23 K (mostly niobium compounds). These metallic materials conduct electricity in all directions,
simplifying the fabrication of conductors. They are used predominantly in polycrystalline form and are capable of sustaining very high current densities.

In 1986, K.A Muller and J. G Bednorz [4] discovered a new family of materials that can conduct electricity with absolutely no resistance. Because these so-called superconductors work at much higher temperatures (HTS) than any previously identified superconductors, the discovery was considered one of the most important of that decade. Although the HTS have relatively high critical temperatures compared to the LTS, and some can be made superconducting by immersion in liquid nitrogen at 77 K, most of them are unsuitable for practical applications because of the weak-link effects [5]. The main component of the HTS devices already proves themselves is wire made with compounds of bismuth, strontium, calcium, copper, and oxygen. These materials are generically known as BSCCO (pronounced bisco). However, the high cost of using BSCCO looms as a serious obstacle to its wide use. That cost may come down through high-volume production of the wire and improvements in its performance. Still, even BSCCO manufacturers are looking for less expensive alternatives to the material.

In laboratories throughout the world, researchers are racing to develop wire from another high-temperature superconductor called yttrium barium copper oxide, or YBCO (pronounced ibco). YBCO wires may cost less than BSCCO ones. They are also expected to carry higher currents than BSCCO wires in the presence of the magnetic fields found in many types of equipment. If YBCO wire can be made in practical lengths, a challenge that arose as soon as YBCO was discovered in 1987, high-temperature superconductivity
may finally offer both costs that are low enough and performance that is high enough to make it a central technology of the 21st century, say many industry observers [6].

Although YBCO has quite a 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 than 10 degrees are not effectively transparent to current flow and act as strong barriers to current [7].

It bears observation that LTS technology was first utilized in purely performance-driven sectors, e.g., in science, research, and technological development (RTD), and in military applications. The next market area to open up was in medical applications, where competition from non-superconducting devices is weak. At present the largest market is for magnets in medical diagnosis, mostly in magnetic resonance imaging (MRI), and the overall market for components, systems and services, exceeding 4 billion euros in 2005, is almost all LTS-based. In the highly competitive field of magnetic separation for the clean-up of kaolin clay, LTS based magnets have totally displaced all alternative approaches on a cost effective basis. However, this penetration of the industrial manufacturing market place has not extended to other applications to date. Neither LTS nor HTS have so far been able to contribute substantially to highly cost-competitive commercial markets such as energy, information, communications, and transportation. Up until now, only slowly growing and, again, mainly performance-driven niche segments have emerged within these large markets, which are dominated by widely established, non-superconducting components [9].
The vast publicity arising from the discovery of high temperature superconductors in 1987 led many to the conclusion that we were about to enter a superconducting age. People may still remember the excitement about the huge business potentials and significant impacts on civilization. However, after 15 years, people are disappointed at the limited commercial applications. The key for many large-scale applications is the development of commercially viable superconducting wires.

Professor J. Akimitsu (Aoyama Gakuin University) announced the discovery of superconductivity in MgB$_2$ at 39 K on January 10, 2001, at a symposium on "Transition Metal Oxides" in Sendai, Japan. The compound consists of alternating layers of magnesium and boron. The crystal structure is also anisotropic [10], but to a lesser degree in comparison with high T$_c$ oxide superconductors. The absence of weak links is great news for wire processing [10,11]. It has been shown in the literature [10] that there is a need for uniaxial texture in order to obtain better superconducting performance than that of Nb$_3$Sn superconducting wires. However, there is no easy-cleavage layer in the case of Bi2212, and previous results in the literature did not show texture formation with the normal powder-in-tube deformation process for this material [12-17].

Paul Grant has shown the benefits of the low cost of MgB$_2$ [18], and S. Patnaik et al. [10] have calculated that uniaxial texture is necessary for superior properties compared to those of Nb$_3$Sn. Since MgB$_2$ does not have the weak-link problem, the powder structure will lead to low-cost high-performance superconducting wires prepared by the powder-in-tube method. It is expected that the MgB$_2$ superconducting wires will be the workhorse superconducting wires for low temperature applications [19].
MgB$_2$ is advantageous compared to other conventional metallic superconductors for applied superconductivity due to the significantly high transition temperature of 39 K [20], the low cost and high abundance of Mg and B, and the large coherence length. Doping with various elements or compounds, as well as optimization of synthesis conditions, has been found to be effective for enhancing the critical current properties for MgB$_2$ bulks and wires. C is one of the most effective dopants for such purposes, showing significant enhancement in the electromagnetic properties of MgB$_2$ [21-30]. Improvement of both the upper critical field ($H_{c2}$) and the critical current density ($J_c$) is essential to fully utilize MgB$_2$’s $T_c$ of 39K. Attempts to accomplish this have led to the introduction of numerous techniques, including ball milling [31, 32], chemical doping [22-30], and irradiation [33]. Among these, chemical doping is a simple and readily scalable technique.

Due to the relatively large coherence length and small anisotropy of MgB$_2$, the fluxoids to be pinned are string-like and could be pinned by inclusions and precipitates in the grains, which makes chemical doping very promising [25]. Among the large number of compounds used for chemical C doping into MgB$_2$, SiC is the most popular, being effective for enhancement of $J_c$ and the irreversibility field ($H_{irr}$), the field at which the Lorentz force, which causes flux vortices to move, exceeds the pinning force, under magnetic fields [22, 23, 29, 34]. However, the best high field $J_c$ values achieved were compromised by the reduction in self-field and low-field $J_c$. In most cases, samples are prepared by solid state mixing of the starting materials. It is important to emphasize the fact that achievement of homogeneous mixtures using solid state mixing is a considerable challenge, especially when nanosize precursors are used. Agglomeration of nano-
additives in the precursors is a common phenomenon. For various forms of C doping, the substitution of C for boron (B) cannot be achieved at the same temperatures as that of the MgB$_2$ formation reaction, due to their poor reactivity. In order to overcome these problems we proposed to use a carbohydrate such as DL malic acid (C$_4$H$_6$O$_5$) as the dopant, and this formed a considerable part of the research on which this thesis is based.

An outline of the thesis is given in the following. The significant advantages of carbohydrate doping are briefly discussed in Chapter 2, which contains a literature review. The simultaneous dual reaction mechanism explained in Chapter 2 promotes C substitution for B in the lattice and the inclusion of excess C within the grains, resulting in the enhancement of $J_c$, $H_{irr}$, and $H_{c2}$. Chapter 3 contains an explanation of the experimental methods used. I first discuss the fundamental and basic properties of MgB$_2$ wire samples in Chapter 4. I discuss the use of malic acid as a representative carbohydrate dopant in Chapter 5. I report on the MgB$_2$ superconductor bulk samples that were fabricated with malic acid doping and on the effects of the composition in wt%. Chapter 6 reports on a systematic investigation of the superconductivity of MgB$_2$ + C$_4$H$_6$O$_5$ samples prepared by using the chemical solution route. I have improved the reactivity and homogeneity of the doped samples by using this route. The lattice parameters, full width at half maximum (FWHM) of spectroscopy peaks, lattice strain, $T_c$, $J_c$, $H_{irr}$, $H_{c2}$, and microstructures are all presented in comparison with the un-doped reference MgB$_2$. Chapter 7 contains a systematic study of the effect of sintering temperature (from 600 °C to 900 °C) in malic acid doped MgB$_2$. We discovered a significant enhancement of $H_{c2}$ and $H_{irr}$ due to C substitution, even at the low sintering
temperature of 600 ºC. The largest $H_{c2}$ and $H_{irr}$ were found in a MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ sample sintered at 600 ºC for 4 hours.

Carbohydrate samples contain carbon (C), hydrogen (H) and oxygen (O). Although we conducted evaporation processing to eliminate the oxygen (O) content, the fraction of MgO due to included O from the carbohydrate increased gradually with increasing doping level. An important goal is to reduce the MgO fraction within the matrix and find a highly active C source that will be effective for enhancing the superconducting properties at lower sintering temperatures of ~600 ºC, the same as for MgB$_2$ formation.

In Chapter 8, we also suggest a different hydrocarbon, pyrene (C$_{16}$H$_{10}$), which has no oxygen content, as with this C source we may overcome the problems of increased formation of MgO, which we faced in carbohydrate doping. This is a colorless solid and consists of four fused benzene rings, resulting in a large, flat aromatic system. At around a temperature of 145-148 ºC, it decomposes separately, and then the highly active hydrogen that has been released may act as an oxygen getter at elevated temperature. In addition, it can be dissolved in a proper solution for homogeneous mixing. To clearly understand the $J_c$ behavior and superconductivity of MgB$_2$ using C$_{16}$H$_{10}$, the lattice parameters, the actual amount of C substituted, the lattice strain, MgO fraction, and transport $J_c$ were evaluated compared to pristine MgB$_2$/Fe wires.
References


6. http://findarticles.com/p/articles/mi_m1200/is_21_158/ai_68147219/pg_1


18. Paul M. Grant, Sleepless in Seattle, posted on High T<sub>c</sub> Update.


    **19**, 175 (2006)


32. A. Matsumoto, H. Kumakura, H. Kitaguchi, H. Hatakeyama, H. Yamada, and M.


34. S. X. Dou, V. Braccini, S. Soltanian, R. Klie, Y. Zhu, S. Li, X. L. Wang, and D.
CHAPTER 2

2. LITERATURE REVIEW

2.1 Introduction:

Magnesium diboride (MgB$_2$) has been known to scientists for approximately 50 years; however, no one had ever considered superconductivity in the material – whether it could conduct electrical current perfectly, without resistance, when cooled to temperatures near absolute zero.

That all changed in January 2001 when Jun Akimitsu of Aoyama Gakuin University in Tokyo publicized how he and his research team had discovered that MgB$_2$ becomes superconducting at 39 K, nearly twice the temperature of the current intermetallic superconductors in that time. This announcement had experimentalists around the world hurrying to duplicate and verify the Japanese findings.

MgB$_2$’s high critical temperature ($T_c$), simple crystal structure, large coherence lengths, high critical current densities ($J_c$), and high upper critical fields ($H_{c2}$), as well as the transparency of its grain boundaries to current gave promise that MgB$_2$ would be a high quality material for both large scale applications and electronic devices. MgB$_2$ has been fabricated in various forms bulk, single crystals, thin films, tapes and wires. A large number of published research results reveal the great interest of the research community in this newly discovered material. In this chapter, we will discuss the fundamental properties of MgB$_2$ superconductors and give an overview of research progress, recent markets and future prospects for this superconductor.
2.2 Why is MgB$_2$ so special?

So what makes MgB$_2$ such an important research topic?

- So far, the $T_c$ of MgB$_2$ is the highest among the superconducting transition temperatures of all metallic compounds;
- Lower anisotropy than HTS superconductors;
- Large coherence length ($\xi = 50$ Å);
- Weak-link-free grain boundaries;
- High transport current densities ($J_c$) of the order of $10^6$ A/cm$^2$ and high upper critical magnetic field ($H_{c2}$) in the temperature range from 4.2 K to 25 K in bulk sample, as reported in [2] and [3];
- Another important reason to count MgB$_2$ as a promising potential contender for industrial applications at temperatures lower than 30 K is its economical material fabrication, since it does not require Ag for sheathing, unlike many other high $T_c$ superconducting tapes or wires [4]. HTSC wires are 70% silver [1], therefore costly.

2.3 Crystal and electronic structure of MgB$_2$

MgB$_2$ has the simple hexagonal AlB$_2$-type structure (space group P6/mmm), which is common among borides. The MgB$_2$ structure is shown in Figures. 2.1 and 2.2. It contains graphite-type boron layers, which are separated by hexagonal close-packed layers of magnesium. At room temperature, lattice parameters $a = b = 3.0851$ Å, $c = 3.5201$ Å have been reported [5]. The magnesium atoms are positioned at the centers of the hexagons formed by the boron atoms and donate their electrons to the boron planes.
Similar to graphite, MgB$_2$ shows evidence of a strong anisotropy in the B-B lengths: the distance between the boron planes is significantly longer than the in-plane B-B distance. Its transition temperature is almost twice as high as the highest $T_c$ among binary superconductors for Nb$_3$Ge, $T_c = 23$K. Making a comparison with other types of superconductors (Figure 2.2), one can note that MgB$_2$ may be the "ultimate and vital" low- $T_c$ superconductor with the highest critical temperature [6].

Figure 2.1. MgB$_2$ structure [6].
2.4 Superconducting mechanism in MgB$_2$

Immediately after the declaration of the breakthrough represented by superconductivity in MgB$_2$, the most significant question that was proposed was whether the origin of that superconductivity can be explained inside the conventional Bardeen, Cooper and Schrieffer (BCS) theory electron-phonon mechanism or requires a more exotic one. There are several experiments and speculative calculations that have been conducted to respond to this question. So far, the superconducting mechanism in this compound is mainly interpreted in terms of BCS-type phonon mediated pairing, based upon boron isotope effect and studies of the energy gap.
2.4.1 Isotope effect

Canfield’s group [17,18] initially claimed a large boron isotope effect, founded on the observation of the temperature dependent magnetization, resistance, and specific heat in Mg\textsuperscript{10}B\textsubscript{2} and Mg\textsuperscript{11}B\textsubscript{2} samples as shown in Figure 2.3 from Doan et al. [4]. The large boron isotope effect means that the vibrations of the boron atoms have a very vital responsibility for the superconductivity of MgB\textsubscript{2}, which is not an unusual mechanism, but a phonon mediated BCS one.

![Figure 2.3](image)

Figure 2.3 (a) Isotope shift as seen in magnetization (upper panel) and resistance (lower panel) [4].
Figure 2.3 (b). Temperature dependent specific heat of Mg$^{10}$B$_2$ (top) and Mg$^{11}$B$_2$ (bottom) in zero (filled circles) and 90 kG (open triangles) applied field. The arrows mark position of $T_c$ as determined from magnetization measurements [4]

2.4.2 Two-gap superconductivity of MgB$_2$

The unique property of MgB$_2$ superconductor is the presence of two independent superconductivity gaps with different sizes. Dou et al. [24] explained this phenomenon in detail from the large-scale applications point of view.

There have long been reports on the band structure of MgB$_2$ both before and after the breakthrough discovery of the superconductivity of MgB$_2$ [7-14], and it is now understood comprehensively.

Figure 2.4 (a) shows a golden hexagonal network, which is connected with the $\sigma$ bands, and the six green lobes above and below the boron planes, which are linked with the $\pi$ bands. Unlike conventional metallic bands, the $\sigma$ band has its charge concentrated along the B-B axes rather spread throughout the unit cell (Figure 2.4 (b)).
Please see print copy for Figure 2.4

Figure 2.4 Electronic structure of MgB$_2$ (a) the 2-D network of $\sigma$ bands and 3-D network of $\pi$ bands [16]; (b) Fermi surface of MgB$_2$. The vertical sections of cylinders at the corners are linked with the $\sigma$ bands; the more 3-D network of tunnels and caves in the center of the region is connected with the $\pi$ bands. [15].

The B honeycomb controls the electronic structure, which can be visualized as originating from $\sigma$ bonding inside the B planes and from $\pi$ bonding orbitals out of the plane. Inside the MgB$_2$ crystal the in-plane $\sigma$ orbitals guide to a corresponding 2-D $\sigma$ band, whereas the $\pi$ space charge expands both out-of-plane and in-plane to outline the 3-D $\pi$ band. This partly covalent structure of the MgB$_2$ crystal gives rise to the Fermi surface, with its two $\pi$ and $\sigma$ conduction bands. For dirty, single-band low temperature superconductors a renowned formula for the zero-temperature upper critical field $H_{c2}(0)$ is specified by the frequently quoted term:

$$H_{c2}(0) = 0.86T_c \left( -\frac{dH_{c2}}{dT} \right)_{T_c}$$  \hspace{1cm} (1)$$

It is well recognized that for single band superconductors both $H_{c2}(0)/T_c$ and the slope (- $dH_{c2}/dT)_{T_c}$ scale with the normal state resistivity $\rho$, and hence that (for fixed $T_c$) both the low temperature $H_{c2}$ and that near $T_c$ are given assistance simultaneously from an
enhancement of $\rho$. Equation (1) recommends an experimental method of attaining $H_{c2}(0)$ that can be accomplished at moderate fields, near $T_c$. Enhancement of $H_{c2}$ can be anticipated to track the increases in the resistivity, this phenomena has facilitated the design of low temperature superconductors over the years. For MgB$_2$, however, the straightforward rule has quantitative modifications, because the resistivity, $\rho$, depends on the electronic diffusivities $D_\pi$ and $D_\sigma$, which are linked with MgB$_2$’s two-band conductivity as follows [19]:

$$\frac{1}{\rho} = e^2 (N_{F\pi}D_\pi + N_{F\sigma}D_\sigma)$$

(2)

The introduction of such two diffusivities results in definite departures from the single-band predictions. In particular ($H_{c2}/T_c$) and ($-dH_{c2}/dT$)$_{Tc}$ respond separately to $D_\pi$ and $D_\sigma$, rather than jointly and in proportion to $1/D$. Therefore, while the higher impurity scattering is advantageous to $H_{c2}$ over the whole temperature range for both single-band and double-band superconductors, in the latter case it gives $H_{c2}(0)$ the chance to diverge away to very large values in response to strong decreases in either $D_\sigma$ or $D_\pi$.

The two-gap superconductivity has major implications for the applicability of MgB$_2$, as it is the low $H_{c2}$ which has mainly restricted the prospective industrial applications of clean MgB$_2$, for which $H_{c2}$ is even less than that of Nb-Ti. Significant efforts have thus been made to increase the $H_{c2}$. Using nanoparticle SiC doping into MgB$_2$, Dou’s group has achieved a record high upper critical field, $H_{c2}(0)$, in bulk materials [20]. Recently, using high field transport measurements, Braccini et al. have reported the achievement of record high upper critical fields ($H_{c2}$) for textured films [21]. This exceptional $H_{c2}$ enrichment to more than 74T for thin films is the positive effect of the two-gap superconductivity of MgB$_2$, which has been evidenced by many measurements and
calculations [22, 23]. There are three diverse impurity scattering channels in MgB$_2$ alloys: intraband scattering within each $\sigma$ and $\pi$ sheet and interband scattering between them. It is these multiple scattering channels which make it possible to enhance the $H_{c2}$ of MgB$_2$ to a much larger extent than in one-gap superconductors, not only by the typical raising of the normal state resistivity, $\rho$, as in low-temperature superconductors, but also by optimizing the relative weight of the $\sigma$ and $\pi$ scattering rates by selective substitution of boron or magnesium.

2.4.3 Anisotropy

Many groups also investigated the strong anisotropy effects on the current carrying capacity in superconductors. This anisotropy is occurred, as MgB$_2$ consists of a layered arrangement of Mg and B hexagonal sheets. For different fabrication configurations, the values of the anisotropic ratio $\gamma = H_{c2}/abl \ H_{c2}/c$ vary outstandingly. In Figure 2.5 [4], $\gamma$ obtaining values from 1.2 to 7 are observed. For deciding accurately the intrinsic degree of anisotropy in MgB$_2$, more experiments on larger single crystals are required.
Figure 2.5. Upper critical field anisotropy versus temperature for MgB$_2$ single crystals, wire and powders. Note that the $H_{c2}(T)$ data for MgB$_2$ bulk falls between the anisotropic dependencies of $H_{c2}(T)$ for $H//c$ and $H//ab$ [4]; reference names and numbers used in the figure’s legend according to [4].

Anisotropy is very essential both for the fundamental understanding of this material and for practical applications, strongly affecting the pinning and critical currents. The intrinsic degree of anisotropy in MgB$_2$ is still subject to controversy, with reports giving values ranging between 1.1 and 9. For textured bulk and partially oriented crystallites, the anisotropy ratio $\gamma = H_{c2} //ab/H_{c2} //c$ is reported to be between 1.1 and 1.7 [25, 26, 27]; for $c$-axis oriented films, it is 1.2 to 2 [28, 29, 30]; in single crystals, there are slightly larger values than in aligned powders or films, between 1.7 and 2.7 [31, 32, 33]; and finally, for powders, there are unpredictably large values, ranging from 5 to 9 [34, 35].
2.4.4 Coherence lengths

Buzea and Yamashita [6] reported a comparison between the values of the coherence lengths, the anisotropy parameter $\gamma$, and the upper critical field, as determined from experiments performed on aligned powders, thin films, single crystals, and randomly aligned powders, as can be seen in Table 2.1. In order to deduce the values of the anisotropic coherence lengths from the upper critical fields they used the anisotropic Ginzburg-Landau theory equations: for the magnetic field applied along the $c$-axis $H_{c2} \parallel c = \Phi_0/2\pi \xi_{ab}^2$, and for the magnetic field applied in the $ab$-plane $H_{c2} \parallel ab = \Phi_0/2\pi \xi_{ab} \xi_c$, where $\Phi_0$ is the flux quantum and $\xi_{ab}$, $\xi_c$ are the coherence lengths along the $ab$ plane and $c$-axis. The previous formulae are in the CGS system.

Overall, they reported that the coherence length values along the $ab$ plane range from $\xi_{ab}(0) = 3.7$ to $12.8$ nm and along the $c$-axis from $\xi_c(0) = 1.6$ to $5.0$ nm. Probably the most reliable data are for single crystals, with $\xi_{ab}(0) = 6.1 - 6.5$nm and $\xi_c(0) = 2.5 - 3.7$nm.

Please see print copy for Table 2.1

**Table 2.1.** Anisotropy of the upper critical field and coherence lengths inferred from experiments on aligned powders, thin films, single crystals, and randomly aligned powders [6]; reference names are used in this table according to [6].
2.4.5 Absence of weak links:

Evidence for the absence of weak links in MgB$_2$, is illustrated in Figure 2.6, as reported by Buzea and Yamashita [6]. The transport measurements in high magnetic fields of dense bulk samples yield very similar $J_c$ values to those from inductive measurements [36, 37]. This confirms that the inductive current flows coherently all the way through the sample, unaffected by grain boundaries. As a result the flux motion will decide the $J_c$ dependence on field and temperature. Jin et al. [38] found that some materials used as tubes or sheaths in the powder-in-tube (PIT) method dramatically reduce the critical current of MgB$_2$. Although MgB$_2$ itself does not show the weak-link effect, contamination does result in weak-link-like activities [6].

![Figure 2.6](image_url)

**Figure 2.6** Critical current density dependence on magnetic field and temperature. Data are taken from resistive and magnetic measurements [6,139].
2.5 Fabrication/Preparation of MgB$_2$ superconductors

It is still a technical challenge to prepare high quality superconducting MgB$_2$ samples for the production of superconductor electronic devices, even though polycrystalline MgB$_2$ is readily available on the market. A variety of sample preparation methods are discussed in this section: for example in-situ, ex-situ, mechanical alloying, hot and cold isostatic pressing, PIT methods for wires and tapes, and liquid infiltration method, etc. A severe common problem encountered with these fabrication techniques is the requirement for a high annealing temperature. This is because magnesium melts at about 600 °C, and at temperatures above this, both magnesium and boron are active in forming oxides. In Chapter 4, I report on the use of differential thermal analysis (DTA) of un-doped MgB$_2$ to determine the appropriate annealing temperature range. The formation of MgO and B$_2$O$_3$ has a detrimental effect on the superconducting properties of MgB$_2$, as reported by many groups, as discussed in a later section.

2.5.1 Bulk samples:

MgB$_2$ superconductor in a bulk form is important for determining basic physical and electrical properties. Bulk samples shaped as pellets are easier to prepare compared to other forms of MgB$_2$ samples, such as wires, tapes, films, single crystals, etc., and these pellets are useful for fundamental research. Different methods of bulk samples fabrication are explained in the following sections:

2.5.1.1 In-situ and ex-situ methods:

One of the advantages of MgB$_2$ fabrication is that commercial MgB$_2$ powder is already available from chemical suppliers, as it has been synthesized since the early 1950s.
However, sometimes the quality of MgB$_2$ powder that is commercially available is not as high as desirable. For example, MgB$_2$ commercial powders have wider transitions in the superconducting state [39] and slightly lower $T_c$ than the materials prepared in the laboratory from stoichiometric Mg and B powders [6]. Zhao et al [40], presents the $J_c$–$H$ curves of in-situ film that show a much weaker field dependence than those of ex-situ film, which is attributable to stronger flux pinning in the in-situ film. The small-grain (<100 nm) feature in Figure 2.7 and the high oxygen level detected in the in-situ annealed MgB$_2$ film may be decisive for the significant improvement of $J_c$, $H_{irr}$, and $H_{c2}$ [Figures. 2.8 & 2.9].

Please see print copy for Figure 2.7

**Figure 2.7.** Atomic force microscope (AFM) images (illuminated 3D mode) of the in-situ and ex-situ annealed MgB$_2$ films. (a) in-situ annealed film in 500× 500 nm$^2$ range, (b) ex-situ annealed film in 2 × 2 µm$^2$ range [40].
**Figure 2.8.** The critical current densities of the two types of MgB$_2$ film as calculated from $M$–$H$ loops. Solid symbols: *ex-situ* annealed film; open symbols: *in-situ* annealed film [40].

**Figure 2.9.** (a) Irreversibility lines, (IL) versus temperature curves for the *in-situ* and *ex-situ* annealed films. The data for an oxygen alloyed MgB$_2$ film [2] are put into the figure for comparison. (b) Upper critical fields versus temperature for the two films. The data for $c$-axis-oriented MgB$_2$ films from [10] are also shown in this figure [40].
Chen et al [41] also show the effects of *in-situ* and *ex-situ* Cu doping on MgB$_2$ bulk samples which were studied in the annealing temperature range of 600 ºC–900 ºC. MgO was found to be present in the *in-situ* samples and there was already some MgO present commercial MgB$_2$ powder. CuB$_{24}$ is the only compound produced by the reaction of Cu and B, and its existence can be seen in all the *in-situ* but only in some of the *ex-situ* samples. Multiple phases were observed (see Table. 2.2) in the *in-situ* samples even at low annealing temperatures. MgB$_2$ was formed at 600 ºC, which is still below the melting point of magnesium.

Recently, Kumakura et al. [416] reported that in the case of the *in-situ* method, a sub-micron Mg starting powder is quite effective for enhancing $J_c$. Some kinds of carbon compound additions to the starting powder introduce a carbon substitution for boron in the MgB$_2$ crystal and enhance $B_{irr}$. In general, *ex-situ*-processed MgB$_2$ tapes show lower $J_c$ than *in-situ* processed tapes. The key factor to obtain a high $J_c$ for an *ex-situ* tape is the high quality of the MgB$_2$ starting powder.

Please see print copy for Table 2.2

Table 2.2 Phase formation in the *in-situ* and *ex-situ* samples at different annealing temperatures [41]
2.5.1.2 Mechanical alloying (MA):

Mechanical alloying is a handy, simple, and useful processing technique from the performance point of view that is now being employed in the production of nanocrystals and/or nanoparticles from all material classes. Even though a range of mechanical alloying devices exist, a high-energy type ball mill is typically used to produce particles in the nanoscale size range. Reduction of particle size is achieved over time in the high-energy ball mill, as is a reduction in crystallite grain size, both of which reach minimum values after extended milling times (Above 400 rpm, milling is considered high energy ball milling). Grain sizes, as determined from standard X-ray diffraction techniques, are typically reported as a function of milling time; however, the actual particle sizes that result from milling, while assumed to be larger than the reported grain sizes for polycrystalline materials, often go unreported. Moreover, what are often reported as nanocrystals may not be such in the technical definition of the term (<10nm grain size), especially for polymeric materials, where grain sizes in excess of 100 nm are still being obtained. The performance of the MA depends on various factors such as the type of ball and jar, size of the ball, ball to powder ratio, speed and time of milling, type of media, etc. Particle agglomeration, where nanoparticles stick together because of attractive forces, is also a serious issue for long milling times. Finally, contamination from milling media (e.g., stainless steel vials and balls) is a serious problem that has not yet been thoroughly investigated. Despite these difficulties, MA is more widely used than ever and continues to be applied to the formation of nanoparticles and nanocrystalline structures in an ever-increasing variety of metals, ceramics, and polymers [42].
Very recently, Xu et al. [43] investigated MgB$_2$ bulk samples that contained, 96% B, that had been ball-milled for 12 hours in a toluene medium in comparison with one made from as-supplied commercial 96% B, with the results showing a significant enhancement in the high field $J_c$ (red color in Figure. 2.11) due to the small grain size, as confirmed by full width at half maximum (FWHM) values (Figure 2.10 (c)) and better reactivity particularly because the more numerous grain boundaries in the MgB$_2$ could be acting as strong flux pinning centers. Even though they used a medium that contained C in their experimental procedure, there were no apparent C substitution effects among the samples (as shown by the $a$-axis parameter in Figure 2.10 (a)). At least, the doping level of C is almost the same within a 12 h ball-milling time, but lattice strain increases due to defects that arise in increased ball-milling times (Figure 2.10 (d)).

Please see print copy for Figure 2.10

**Figure 2.10** Dependence on ball-milling time of (a) $a$- and $c$-axis lattice parameters, (b) $c/a$, (c) full-width at half-maximum (FWHM) of particular peaks, and (d) lattice strain of MgB$_2$ samples using different B [43].
Figure 2.11. The magnetic critical current density ($J_c$) for all MgB$_2$ samples as a function of external magnetic field at 5 and 20 K [43]. The numbers before the second B in the sample names give the boron ball-milling times in hours. B96S used as received 96% B.

Herrmann et al [44] systematically investigated the superconductivity of MgB$_{2-x}$C$_x$ bulk samples doped with nano-structured carbon. In this experiment, bulk samples were prepared by pressure assisted sintering using a mechanically alloyed precursor powder. Due to the very small grain size of the mechanically alloyed precursor (Figure 2.12), the bulk samples also showed a nanocrystalline microstructure, which, due to the high number of grain boundaries acting as pinning centers, supported critical current densities of $> 1 \times 10^4$ A cm$^{-2}$ at 8 T and 4.2 K (Figure 2.13). It has been shown previously that a sophisticated, high-energy treatment of the precursor powder by mechanical alloying (MA) can improve the superconducting properties of MgB$_2$ [45, 46, 47]. As reported earlier by Gruner et al. [48], it has been shown that pre-milled carbon with an enhanced reactivity is a very effective dopant under this treatment.
Figure 2.12. Grain size distribution of mechanically alloyed precursor powder obtained by statistical investigation (bottom panel) of a transmission electron microscope (TEM) image (top panel) in dark field mode [44]. The inset of the top panel shows the corresponding selected area electron diffraction (SAED) pattern.

Figure 2.13. Critical current density versus applied magnetic field for un-doped and carbon doped MgB$_2$ bulk samples at 4.2 and 20 K [44]
2.5.1.3 Hot (HIP) and Cold (CIP) isostatic pressing:

2.5.1.3.1 CIP:

Cold isostatic pressing (CIP) applies pressure from multiple directions for achieving greater uniformity of compaction (high-quality parts) and increased shape capability compared to uniaxial pressing.

There are two methods of carrying out isostatic pressing. In wet-bag isostatic pressing, powder is encased in a rubber sheath that is immersed in a liquid which transmits the pressure uniformly to the powder. In dry-bag isostatic pressing, rather than immerse the tooling in a fluid, the tooling itself is built with internal channels into which high-pressure fluid is pumped. Cross-sectional views of both types of CIP are illustrated in Figure 2.14.

Please see print copy for Figure 2.14

**Figure 2.14.** Cross-sectional view of dry CIP (left) and wet CIP (right) [432].
2.5.1.3.2 HIP:

Hot isostatic pressing (HIP) is used when great uniformity is required and where net-shape production (also of intricate and complex shapes) leads to economic advantages (e.g., metal alloys for aerospace applications and complex ceramic parts).

The process is analogous to CIP. The apparatus is a high-temperature furnace enclosed in a water-cooled autoclave capable of withstanding high pressures and providing a uniform hot-zone temperature (up to 2000ºC). The pressurization gas is argon or helium.

The sinter-HIP version of the process achieves improved strength and wear resistance in some ceramic or ceramic composite materials for cutting tools and other applications. Here the part is first sintered and then HIP is applied. The reduced porosity of HIP processed materials enables improved mechanical properties and enhanced workability. The HIP process reduces internal voids and creates clean, firm bonds and fine, uniform microstructures. These characteristics are not possible with welding or casting. The virtual removal of internal voids and densification of ceramic materials enhances part performance and improves fatigue strength. A schematic cross-sectional view of the HIP system used by ANSTO is illustrated in Figure 2.15.
Significantly improved $J_c$ at high fields was found in a HIP processed MgB$_2$ pellet, in comparison with its unprocessed counterpart, as is shown in Figure 2.16. Such enhancement is attributed to the removal of the porosity present in the MgB$_2$ pellet, resulting in better inter-grain connectivity. The scanning electron microscope (SEM) images in Figure 2.17 show the microstructural differences between HIP processed and unprocessed samples. The HIP process was also found to scatter and distribute the MgO uniformly from the grain boundaries where it existed in the unprocessed MgB$_2$ pellet, and to generate more dislocations in the pellets [49, 50].
Figure 2.16. Magnetic critical current density $J_c$ as a function of magnetic field $H$ for the un-HIP processed and unprocessed samples at 5 and 30 K. Both samples show nearly the same value of $J_c$ at self-field, but the differences between the samples increases with field, and the drop in $J_c$ at higher fields is very much faster in the unprocessed sample than in the HIP processed one [49].

Figure 2.17 SEM micrographs of MgB$_2$ samples (a) surface of the unprocessed sample and (b) surface of the HIP processed sample [49].
Liao et al. [51] reported from the TEM investigation of large areas of hot isostatically pressed wires and comparison with the structures of wires that were not subjected to isostatic pressing that less porosity seems to exist in the hot isostatically pressed wires than in the unpressed wires. Usually there are two kinds of areas in the hot isostatically pressed wires: dense areas and areas with porosity. They pointed out a typical example, shown in Figure 2.18(a), in which a dense area is marked with A, while an area with porosity is marked with B. Comparison at higher magnifications shows that the MgB$_2$ grain sizes in a dense area (Figure 2.18(b)) are normally smaller than those in an area with porosity (Figure 2.18(c)). They propose that using MgB$_2$ powders with finer grain sizes is an effective way to further increase the density of a wire prepared by the powder-in-tube technique and therefore to obtain better connectivity. The observation also indicates that diffusion-based mechanisms are important for densification of MgB$_2$, at least at the final stages of the densification. This density variation in the hot isostatically pressed wires agrees with the observed variation of elastic properties in hot isostatically pressed MgB$_2$ samples.
2.5.2 Wire and tape samples:

Since 2001 when MgB$_2$ was first reported to have a transition temperature of 39 K, conductor development has progressed to where MgB$_2$ superconductor wire in kilometer-long piece-lengths has been demonstrated in magnets and coils. Currently, work has started and is in-progress on demonstrating MgB$_2$ wire in superconducting devices for which the wire is also available commercially. MgB$_2$ superconductors and coils have the outstanding potential to be integrated into diverse commercial applications, such as,
magnetic resonance imaging (MRI), fault current limiters (FCL), transformers, motors, generators, adiabatic demagnetization refrigerators, magnetic separators, magnetic levitation applications, energy storage, and high energy physics applications, which benefit the community to a large extent. In this section we discuss the progress in MgB$_2$ conductor and coil development over the last several years.

2.5.2.1 Mg diffusion method:

One of the most interesting methods to increase the MgB$_2$ core density is the diffusion method [414] and [415]. Canfield first fabricated wires by exposing tungsten-core B filaments to Mg vapor [52]. Togano et al. fabricated a B/Fe–Mg composite tape and obtained a high-density MgB$_2$ layer by the diffusion reaction between the B layer and an Fe–Mg alloy sheet [415]. Although the $J_c$ values of this composite tape are below the $J_c$ values of PIT-processed tapes at the present stage, probably due to the oxidation of Mg, this diffusion method seems to be one of the key techniques for the enhancement of the $J_c$ values [452]. This work was quickly followed by reports pursuing powder-in-tube (PIT) approaches.

2.5.2.2 PIT method

To form the basis of long length superconductors, the powder-in-tube (PIT) technology has been extensively used, beginning with the low temperature superconductors NbTi and Nb$_3$Sn.

The common process of tape and wire fabrication is this powder-in-tube (PIT) process, [53-60], which is characterized by filling metallic tubes with powder and then drawing
them into wires and rolling them into tapes (Figure 2.19). Several methods have been reported in the literature so far for wire production. The \textit{in-situ} PIT technique is one of them, which consists of filling metallic tubes with elemental Mg and B powders, and subsequent deformation and heat-treatment [55, 56, 61].

\textbf{Figure 2.19.} Powder in tube (PIT) process for wires and tapes [433]
2.5.2.3 HIP processing:

Most of the research groups like to use the so-called PIT method to produce MgB₂ superconducting wires. This involves sheathing the MgB₂ powder in a tube of thin iron or some other material. In the beginning, this idea was not very successful, as the system was too porous to reach an acceptable critical current density. To overcome this problem researchers produced wires and formed them into coils, which they processed by hot isostatic pressing (HIP). This process brought the superconducting powders into close contact, reducing porosity, and enhancing the current carrying capacity by 45% compared to MgB₂ wires formed using traditional annealing methods.

Figure 2.20. The normalized pinning forces obtained from $I_c (B)$ measurements of MgB₂/Cu and MgB₂/Fe/Cu composites at 4.2 K [62].

Kovac et al [62] has improved the grain connectivity by cold isostatic pressing but it has a negative effect on pinning [Figure 2.20]. The fill factor, additional pressurization and/or composite geometry also influence the pressure stress in the MgB₂ core and so affect
pinning. In general, the high pressure improved inter-grain connectivity but reduced pinning within the high density two-axial rolling (TAR) deformed MgB$_2$ core. This effect can be different for lower density wires, e.g. deformed by drawing.

It was also found that the hot isostatic pressing operation induced more structural defects (which I have already discussed previously for bulk samples and presented some SEM-TEM images) that are beneficial in increasing the current carrying capacity, with higher current carrying capacity equating to thinner wires.

**2.5.2.4 Continuous Tube Filling and Forming (CTFF) method:**

Hypertech Research, Inc. employs a patented process, named the continuous tube filling and forming (CTFF) process [Figure 2.21] to make a new powder metallurgy version of superconductor wires. The illustration below shows a conceptual schematic diagram of the process. Wire begins with a metal strip made of Nb that is formed into a tube while being filled continuously with powder. Then the whole Nb tube with powder is put into another tube made of Monel. After double sheathing the tube is ready for drawing. Historically, all other manufacturers of superconductor wire use a batch process, which involves filling tubes of a fixed length with powder. This requires much larger tubes to obtain longer lengths of wire. This traditional method also involves more wire processing (drawing or extrusion) and thus incurs higher manufacturing costs.
The *in-situ* technique involves direct CTFF filling of the “tube” with elemental magnesium and boron powder and a consequent drawing process, followed by the heat treatment, during which the elements react to form MgB$_2$. The advantages of the *in-situ* process are simplicity of fabrication, lower reaction temperatures, and increased ease in adding dopants or other additives to the wire [63]. The lower reaction temperature is particularly important, as it helps to minimize the possibility of powder-barrier reactions [64].

### 2.5.2.5 Liquid infiltration method:

Recently Hur et al. [65] and Giunchi et al. [66] succeeded in the fabrication of high-$J_c$ MgB$_2$/Fe wires by applying the internal Mg diffusion (IMD) process [Figure 2.22] with a pure Mg core and SiC addition. According to the IMD process, a pure Mg rod with a 2 mm diameter was positioned at the center of a Fe tube, and the gap between the Mg and the Fe tube was filled with B powder or a powder mixture of B-(5mol%) SiC. The composite was cold worked into 1.2mm diameter wire and finally heat treated at...
temperatures above the melting point of Mg (~650 °C). Throughout the heat treatment, the liquid Mg infiltrated into the B layer and reacted with B to form MgB$_2$.

PIT processed wire normally shows a granular MgB$_2$ microstructure. In the IMD-processed wire, on the other hand, the MgB$_2$ layer is more closely packed, and the porosity in the MgB$_2$ layer is much smaller than that of the PIT processed wire shown in Figure 2.23. The 5mol% SiC doped IMD wire shows higher $J_c$ (Figure 2.24) and smaller field dependence of $J_c$ than the wires with no added SiC, suggesting that some C atoms substitute for B atoms in MgB$_2$ lattice, enhancing the upper critical field, $B_{c2}$.

After the discovery of MgB$_2$ superconductor, different types of fabrication processes were reported. Some of those processes and different forms of MgB$_2$ are summarized in Figure 2.25.

Please see print copy for Figure 2.22

**Figure 2.22** Schematic diagram of the fabrication process of MgB$_2$/Fe composite wire using the internal Mg diffusion (IMD) process [65].
**Figure 2.23** SEM images of the fractured cross-sections of MgB$_2$ cores in wires (a) 5 mol% SiC added IMD processed wire, heat treated at 700 °C for 1 hour; (b) PIT processed wire [65].

**Figure 2.24** Transport $J_c$ vs field curves at 4.2 K of pure and 5mol% SiC added IMD processed wire. The data on PIT processed wires are also shown for comparison [65].
2.5.3 Sheath materials for PIT:

Many groups have already studied the effects of the sheath materials on the superconducting properties of MgB$_2$ wires and tapes [6, 12, 51, 56, 57, 58, 59, 60, 61, 62, 67-138, 146, 147, 158, 192, 193, 299, 307, 316, 318, 324, 349, 360, 370, 371, 378, 402, 423]. Recently Kovac et al. [140] reported that single-core MgB$_2$ wires with Fe, Nb, and Ta sheaths were prepared by \textit{in-situ} and \textit{ex-situ} powder-in-tube processes.
Figure 2.26. $J_c(B)$ dependences (a) for *in-situ* MgB$_2$ wires sintered at temperatures ranging from 500 °C to 750 °C, and (b) for *ex-situ* wires sintered at 950 °C [140]

Comparable $J_c(B)$ characteristics have been attained for *in-situ* wires with Fe, Nb, and Ta sheaths, but very low $J_c$ was measured for Nb- and Ta-sheathed *ex-situ* wires compared to those with an iron sheath. They have found that the best $J_c(B)$ performance was for Nb-sheathed *in-situ* wire, but the worst $J_c(B)$ performance (by two orders of magnitude or lower) was obtained for *ex-situ* wire. They proposed that these differences should be attributed mainly to extensive crack generation in the *ex-situ* Nb-sheathed MgB$_2$ during wire formation, which cannot be repaired by the final heat treatment. Instead of this, possible boron infiltration into the sheath material at annealing temperatures above 750 °C could account for the noticeable decrease in the critical current. The experiments presented have shown that the best $T_c$ and $J_c$ can be obtained for iron-sheathed *ex-situ* wires, but the highest $J_c$ with an Nb sheath can be obtained for *in-situ* wires. The highest $T_c$ of *in-situ* wires was found for a Ta sheath. The best MgB$_2$ core homogeneity was achieved for an iron-sheathed *in-situ* wire, as well as by the *ex situ* route.
2.5.4 Effect of starting materials on the superconductivity:

2.5.4.1 Mg precursor powder:

2.5.4.1.1 Properties of Mg

Mg is a grayish-white, fairly tough metal. Mg is available in several forms including chips, granules, powder, rods, foil, sheets, turnings, and ribbons. Mg tarnishes slightly in air, and finely divided Mg readily ignites upon heating in air and burns with a dazzling white flame. Normally Mg is coated with a layer of oxide, MgO, which protects Mg from air and water.

2.5.4.1.2 Size of Mg powder

The quality of the starting Mg powder, such as its purity and particle size, has been demonstrated to play an important role in determining the superconducting properties of MgB$_2$. Using the finest or nanometer sized Mg powder is effective for enhancing the critical current. Yamada et al. has verified that the replacement of commercial Mg powder with nanometer-size Mg powder [144,145] is effective in enhancing the reaction between Mg and B, and thus leads to a better grain connectivity and hence, the $J_c$ enhancement. He showed that the transport $J_c$ values of the un-doped and 10 mol% SiC-doped tapes fabricated from nanometer-size Mg powder reached 90 and 250 A/mm$^2$ at 4.2 K and 10 T, respectively. However, the nanometer-size Mg powders reported previously are definitely expensive, compared to the commercial Mg powder. The use of an ultra-fine Mg and B powder mixture prepared by ball milling also successfully improved the grain connections and increased the $J_c$ values [146, 147].
Figure 2.27. Transport critical current densities versus applied magnetic field at 20 K for MgB$_2$/Fe tapes prepared with 10 µm size Mg and high purity boron powders. The heat-treatment temperature was 700 °C [148].

If we could find any cheaper and finer Mg powder for the fabrication of MgB$_2$, the total production cost could be decreased significantly. The Ma group used slightly cheaper but finer 10 µm size spherical Mg powder as a precursor, so that the Mg could react more uniformly and quickly with the B powder. Thus the uniformity of the fabricated MgB$_2$ was improved and the grain size of the MgB$_2$ was decreased, hence $J_c$ increased, as shown in Figure 2.27 which is better than Yamada’s result [148].

2.5.4.1.3 Mg deficiency:

All the MgB$_2$ samples after heat treatment (>650 °C) are naturally Mg deficient, because, it is well known that Mg is extremely volatile at high temperatures. For that reason, it is simply predictable that some Mg easily vanishes during the fabrication process of the sample. That is to say, the prepared samples are generally Mg deficient. Nevertheless,
Mg, as the other constitutional element, is a very reactive element. Mg powder has a large surface area, and it oxidizes easily throughout the powder production, storage and handling so MgO is formed with air even before mixing with boron powder. We will discuss the effects of MgO on MgB$_2$ superconducting properties in a later section.

Almost all of the reports on Mg precursor have only paid attention to the Mg stoichiometry effect, but there has been no detailed report on the effects of the purity of Mg on the critical current density and transition temperature [149-153]. However, up to now, all the reports on effects on the critical temperature fluctuate extensively, which most likely is due to the diverse fabrication conditions and the starting precursor. In general, Mg deficiency degrades the critical temperature. X. Z. Liao et al. reported that Mg deficiency introduced significant strain into the crystalline lattice of MgB$_2$ [154]. Jiang et al. proved that Mg deficiency was also found to improve the high-field $J_c$ for MgB$_2$/Fe in-situ wire [155].

2.5.4.1.4 Excess Mg:

Lezza et al. did not find any effect on either $J_c$ or $B_{c2}$ by the addition of 5% Mg into MgB$_2$ powder [156]. However, when developing devices for high-field applications recent results have indicated that preparing MgB$_2$ samples with a slight excess of Mg might not be advantageous [157]. Nevertheless, excess Mg has been reported to prevent the problems of Mg deficiency and remove the micro-cracks that would otherwise be present, and thus enhancing the connectivity in MgB$_2$ wires [158]. The samples prepared by mechanical alloying with an Mg surplus show a high critical temperature ($T_c$), high $J_c$, $1.53 \times 10^6$ A/cm$^2$ at 7.5 K in self-field, and a homogeneous and uniform microstructure [159]. Recently, Zeng et al. [160] have investigated the effect of excess Mg on the crystal
structure and on the magnetic and transport superconducting properties of MgB$_2$, compared with normal MgB$_2$ samples. The excess Mg in the precursor assists oxygen incorporation into the MgB$_2$ lattice, reduces the detrimental MgO content in the system, improves the connectivity, and thus significantly enhances the critical current density and upper critical field. The enhancements in $J_c$, $H_{irr}$, and $H_{c2}$ are strongly dependent upon the sintering temperature. The maximum enhancement in the low-field $J_c$ was achieved in the 10% Mg excess samples sintered at 750 °C, while the 10% Mg excess sample sintered at 650 °C had the best $H_{irr}$ and $H_{c2}$. Susner et al. investigated the effect of both doping and excess Mg on the superconducting properties of MgB$_2$. They reported that at temperatures below 20 K, excess Mg + SiC doping performed best, while above 20 K, excess Mg without SiC gave better transport properties. [161]

**2.5.4.1.5 MgH$_2$ instead of Mg:**

Kumakura’s group has systematically studied the effects of the Mg on the superconducting properties. They achieved twice as large $J_c$ by using MgH$_2$ as the Mg source compared to samples prepared using a mixture of Mg + B powders [162-176].

**2.5.4.2 B precursor powder:**

**2.5.4.2.1 Properties of Boron powder:**

Boron is a non-metallic element and exists naturally as 19.9% $^{10}$B isotope and 80.1% $^{11}$B isotope. Eleven isotopes of boron are known. High-purity crystalline boron may be prepared by the vapor phase reduction of boron trichloride or tribromide with hydrogen on electrically heated filaments. Impure, or amorphous, boron, a brownish-black powder,
can be obtained by heating the trioxide with magnesium powder. Boron of 99.9999% purity has been produced and is available commercially. At standard temperatures boron is a poor electrical conductor, but it is a good conductor at high temperatures [177].

2.5.4.2.2 Purity of Boron precursor:

Recently, W. Haßler et al. [178] revealed that the \( T_c \) and the microstructure of MgB\(_2\) tapes are correlated with oxygen impurities and the grain size of the B precursor powder. They also proved that the nominal purity of boron specified by the suppliers was not satisfactory for the characterization of the boron precursor powder, as the information only considers metallic impurities. Jiang et al. [179] also demonstrated that MgO phase can be significantly reduced in the MgB\(_2\) by removing the B\(_2\)O\(_3\) through boron purification.

Many groups [136, 180] had already reported that samples made from crystalline boron powders have around an order of magnitude lower \( J_c \) compared to those made from amorphous precursors. The samples made from amorphous B contain far fewer Mg(B)–O phases than crystalline B, despite the fact that the amorphous B contains more B\(_2\)O\(_3\) [180]. Xu et al. [181] studied the influence of the amorphous boron powder on the superconducting properties; MgB\(_2\) bulk samples were prepared using 96% and 99% pure commercial boron powder as well as 92% commercial boron powder after a purification process. The results showed that the original 96% and the purified 92% powders have larger particle size compared to the pure 99% boron powder, which leads to reduced
magnetic critical current densities (Figure 2.28), but they at least improved the critical current values by using the purified 92% boron powders compared to original 96% boron.

Figure 2.28. Normalized volume pinning force ($F_p$) as function of the applied field at (a) 5 K and (b) 20 K, for the different samples [181].

However, more recently he showed [data has already shown in previous section] that the reactivity of 96% B powder can be improved by using ball-mill processing, leading to enhanced magnetic critical current density, $J_c$, compared to the original 96% B powder. The MgB$_2$ made using low grade 96% B powder could be particularly beneficial for industrial applications because of its low material cost [43]. High purity 99% boron is
very expensive these days, so researchers are still trying to find cheaper alternatives which can properly compete with costly 99% boron.

2.6 Fundamental properties of MgB$_2$ superconductors:

2.6.1 Critical parameters:

2.6.1.1 Critical temperature ($T_c$):

Again, superconductivity, that means, the loss of electrical resistivity of a material below a critical temperature ($T_c$), is still being considered one of the most fascinating phenomena in condensed matter science. However, a literature survey showed that superconductivity near 39 K in MgB$_2$ was completely unexpected compared to other boron-based compounds, which had more expectations attached to them. However, so far there have been no reports of any other diboride-based material that is superconducting at temperatures comparable to that of MgB$_2$. A comparison of the superconducting properties in diboride systems can be found in [6]. Many factors, such as material synthesis conditions, crystal structure, crystal defects, strain, chemical composition, doping, external pressure, irradiation by energetic ions, the presence of a magnetic field, etc., can affect the critical temperature of a superconductor in a different ways. Vinod et al. reported $T_c$ against different parameters, and Figures 2.29 and 2.30 show some of them [182].
Figure 2.29. Variation of $T_c$ of MgB$_2$ with doping level for various dopants. Data for the graphs are taken from the references given in brackets [182]; the reference numbers shown in the figure legend according to [182].

Figure 2.30. Variation of $T_c$ of MgB$_2$ with variation in (a) the $a$ axis, (b) the $c$ axis and (c) the volume under irradiation, pressure or doping. Data for the graphs are taken from the references given in brackets [182]; the reference numbers shown in the figure legend according to [182].
2.6.1.2 Critical current density ($J_c$)

Researchers have produced the first microscopic images of a superconducting material near the critical current, the exact point at which it loses its ability to carry current without electrical resistance. In an applied magnetic field, a superconductor is permeated by a dense array of "magnetic vortices", swirling whirlpools of electric current. At and above the critical current, these vortices can move around and form intriguing patterns. Understanding the nature of magnetic vortex patterns is very important, because they control the flow of current through superconductors.

According to Nguyen et al. [4], the critical current density in MgB$_2$ depends on many factors, such as geometry, fabrication technique, heat-treatment procedure, quality and particle size. This is illustrated in Table 2.3 [183], which presents a comparison of $J_c$ for MgB$_2$ tape, wire, and film which was attained by different groups at the temperatures of 20 K and 4.2 K. In zero field and a temperature of 20K, the highest $J_c$ reaches 7x10$^6$ Am/cm$^2$, as reported by Moon et al. [184] for MgB$_2$ film. Such high current carrying capacity points strongly to the high potential of MgB$_2$ for industrial applications at the boiling point of H at atmospheric pressure (20.3K). Compare to film, the critical current density in tape and wire is smaller, but still very high, $J_c \approx 5x10^5$ Am/cm$^2$ in 0 T and 20 K [61].
Table. 2.3 Critical current densities in different MgB$_2$ tapes, wires and films for various magnetic fields and temperatures [4]; the reference names and numbers shown in the figure legend according to [4].

The conclusion can be drawn from Buzea and Yamashita’s [6] review that, unlike in HTS, $J_c$ (T, H) in MgB$_2$ is determined by its pinning properties and not by weak link effects. These pinning properties are strongly field dependent, becoming rather poor in modest magnetic fields. In dense bulk samples, the microscopic current density is practically identical to the intra-granular $J_c$ measured in dispersed powders [36], therefore the current is not limited by grain boundaries [185].
Recently the Dresden group has reported the highest $J_c$ (10,000 A cm$^{-2}$ at 14 T) in high field in a PIT tape sample that was made by high-energy ball milling. They presented this record $J_c$ data at the EUCAS’07 conference, as shown in Figure 2.31.

2.6.1.3 Upper critical field ($H_{c2}$)

$MgB_2$ is a type-II superconductor, so it is necessary to analyse both $H_{c1}$ and $H_{c2}$. Values of the upper critical field, $H_{c2}$, play an important role in practical applications of superconductors and are usually derived from magnetoresistivity measurements. Like $J_c$, $H_{c2}$ in $MgB_2$ also depends on many factors. Figure 2.32 presents the highest values for $MgB_2$ in different geometries. In the film configuration, $H_{c2}$ was found experimentally by Jung et al. [28] to be highest, up to 32T at temperature less than 1K. Also in film, Patnaik [30] reported a 40T $H_{c2}$, obtained by extrapolating the $H_{c2}$ (T) curve to very low temperature.
Gurevich et al. [430] have reported very high upper critical fields, up to 50 T, for MgB$_2$ thin film with high resistivity. They found a correlation between the resistivity and $H_{c2}$, and showed that the enhancement of $H_{c2}$ can be explained in the framework of the two-gap superconductivity in MgB$_2$, which provides an opportunity for further enhancement of $H_{c2}$ by tuning the impurity scattering.

2.6.1.4 Lower critical field ($H_{c1}$)

The lower critical field values for MgB$_2$ are situated between 25 and 48mT. The data on anisotropic $H_{c1}/ab$ and $H_{c1}/c$ measured using single crystals [32] does not encompass the values for bulk [186-189], suggesting that the data for single crystal is not accurate. The values of the penetration depth deduced from the lower critical field data range between
85 and 203 nm [6]. According to the recent measurements in a high purity single crystal sample, $H_{c1}$ has been found to lie between 120 mT and 250 mT [190].

2.6.1.5 Irreversibility field ($H_{irr}$)

$H_{irr}$ is the field at which the bulk current density goes to zero. The knowledge of the irreversibility line is important in potential applications, as non-zero critical currents are limited by magnetic fields below this line. Grasso et al. [191], using an ex-situ powder method to make MgB$_2$ tapes, found $H_{irr}$ to be just slightly higher than 12 T for a field perpendicular to the tape face. An anisotropy factor of about 1.4 in $H_{irr}$ has been reported for tapes (with the parallel orientation being higher than the perpendicular one [70]), indicating that rolling partially aligns the Mg and B planes parallel to the broad face of the tapes. Flukiger et al. [192], using the ex-situ technique, found $H_{c2}$s of 11.9 and 15.1 T at 4 K for $H_{\perp}$ and $H_{//}$ (with a tape anisotropy of 1.3). $H_{irr}$s of 8 and 10.4 T were measured at 4 K for $H_{\perp}$ and $H_{//}$ respectively. Ball milling of MgB$_2$, also extensively employed by Flukiger [183], was seen to increase $H_{irr}$ and $J_c$. The Kumakura group [193] investigated the use of SiO$_2$ and SiC in the in-situ process, finding that they were effective in considerably improving $J_c$, as well as enhancing $H_{irr}$ substantially. Sumption et al. reported on the $H_{irr}$ and flux pinning in MgB$_2$ with and without SiC [194].

Yamamoto et al. [195] reported that $H_{irr}$ can be enhanced by degradation of crystallinity, due to a low temperature solid-solid reaction. Eom et al. [196] made a dirty film with FWHM > 1°, resulting in an enhancement of $H_{c2}$ to ~50 T. In addition, Lee et al. [197] reported that a clean single crystal with FWHM ~0.06° had the only low $H_{c2}$, ~20 T.
The $H_{irr}$s extrapolated at zero temperature range between 6 and 12 T for MgB$_2$ bulk, films, wires, tapes, and powders, as illustrated in Figure 2.33 [6]. A significant improvement of the irreversibility line, accompanied by a very large $J_c$ between $10^6$ and $10^7$ A/cm$^2$ at 4.2 K and 1 T, has been reported in MgB$_2$ thin films with lower $T_c$ [30, 196, 29]. These results give further encouragement to the development of MgB$_2$ for high current applications.

Please see print copy for figure 2.33

**Figure 2.33.** Irreversibility field versus temperature for different geometries of MgB$_2$ (bulk, film, wire and powder) [6]; the reference names and numbers shown in the figure legend according to [6]
2.7 Chemical doping effects:

Pristine MgB$_2$ appears to not be very interesting for applications, due to the poor flux pinning and low $J_c$, $H_{c2}$, and $H_{irr}$ values. A significant enhancement of the critical current density in MgB$_2$ can be achieved through chemical doping with various kinds of material. To take advantage of its $T_c$ of 39 K, enhancements of both the upper critical field ($H_{c2}$) and $J_c$ are essential. Attempts to accomplish this have invoked the introduction of numerous techniques, including chemical doping [20, 215, 216, 224, 229, 238, 248, 254, 255, 399, 419, 420, 421], irradiation [422], and various thermo-mechanical processing techniques [50, 183, 423, 424]. Chemical doping is a simple and readily scalable technique.

Since MgB$_2$ has a relatively large coherence length and small anisotropy, the fluxoids to be pinned are string-like and amenable to pinning by inclusions and precipitates in the grains. This opens a window to the success of chemical doping in this material.
2.7.1 C-source doping:

A significant enhancement of critical current density ($J_c$) in MgB$_2$ can be achieved through chemical doping with carbon (C) containing composites or compounds, such as SiC, C, B$_4$C, carbon nanotubes (CNT), hydrocarbons, carbohydrates, etc. The C can enter the MgB$_2$ structure by substituting into boron (B) sites, and thus $J_c$ and $H_{c2}$ are significantly enhanced due to the increased impurity scattering in the two-band MgB$_2$. Several groups have already studied the effects of C doping on the superconductivity in MgB$_2$. Nano-SiC doping was the first report on nanodoping of MgB$_2$ that gave improvements in $J_c$ that were significant enough to be commercially viable [226-228]. Mickelson et al. first discovered B$_4$C as a suitable C source [218], and Ribeiro et al. [220] also reported that B$_4$C has high potential as a C source, because during the decomposition of B$_4$C, highly active C particles are formed.

However, they showed that higher sintering temperature and longer sintering time is required. Dou et al [228] reported enhanced superconducting properties of C doped MgB$_2$ from using SiC as a C source, with only a low temperature (~ 650 °C) sintering procedure required.

Table 2.5 shows the significant enhancement of $J_c$, $H_{c2}$, $H_{irr}$, flux pinning, vortex pinning, and connectivity in MgB$_2$ bulks, wires, and tapes from doping with the various kinds of C-sources that have already been investigated and reported in different journals.
Table 2.5 Reported C-sources as dopants.

<table>
<thead>
<tr>
<th>Type of C-source</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C and nano-C</td>
<td>198-217</td>
</tr>
<tr>
<td>B₄C</td>
<td>218-225</td>
</tr>
<tr>
<td>SiC</td>
<td>226-240</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>247-260</td>
</tr>
<tr>
<td>Carbon nanohorn</td>
<td>261</td>
</tr>
<tr>
<td>Diamond</td>
<td>241-243</td>
</tr>
<tr>
<td>Graphite</td>
<td>244-246</td>
</tr>
<tr>
<td>Polymers (PCS &amp; PVA)</td>
<td>262-264</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>265-268</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>269-276, 425</td>
</tr>
<tr>
<td>Carbides</td>
<td>277, 278</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>279</td>
</tr>
<tr>
<td>Silicon Oil</td>
<td>280</td>
</tr>
</tbody>
</table>

2.7.2 Single element dopants:

Some elements, both metal and non-metal, can substitute into Mg sites, and some can substitute into B sites. There is a long list of metals/non-metals as dopants used in MgB₂ which have been reported in different journals. Not all the single element dopants have positive effects on $J_c$ in MgB₂ superconductors.
Table 2.6 Reported single elements as dopants.

<table>
<thead>
<tr>
<th>Type of Metal/Non-Metal</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>284-293</td>
</tr>
<tr>
<td>Li</td>
<td>334-336</td>
</tr>
<tr>
<td>Si</td>
<td>334,337</td>
</tr>
<tr>
<td>Zn</td>
<td>324</td>
</tr>
<tr>
<td>Cu</td>
<td>295-306</td>
</tr>
<tr>
<td>Be</td>
<td>338</td>
</tr>
<tr>
<td>Mn</td>
<td>330,331</td>
</tr>
<tr>
<td>Nb</td>
<td>381</td>
</tr>
<tr>
<td>Ti</td>
<td>313-323</td>
</tr>
<tr>
<td>Fe</td>
<td>307-309</td>
</tr>
<tr>
<td>Co</td>
<td>340,341</td>
</tr>
<tr>
<td>Ni</td>
<td>387</td>
</tr>
<tr>
<td>Zr</td>
<td>325-329</td>
</tr>
<tr>
<td>Na</td>
<td>332,333</td>
</tr>
<tr>
<td>Ag</td>
<td>281-283</td>
</tr>
<tr>
<td>Mg</td>
<td>339</td>
</tr>
<tr>
<td>B</td>
<td>339</td>
</tr>
<tr>
<td>Sn</td>
<td>340</td>
</tr>
<tr>
<td>Mo</td>
<td>330</td>
</tr>
<tr>
<td>Ca</td>
<td>330,332</td>
</tr>
<tr>
<td>Y</td>
<td>330</td>
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<tr>
<td>Pb</td>
<td>343</td>
</tr>
<tr>
<td>Ir</td>
<td>344</td>
</tr>
<tr>
<td>V</td>
<td>345</td>
</tr>
<tr>
<td>O</td>
<td>196</td>
</tr>
<tr>
<td>Au</td>
<td>386</td>
</tr>
<tr>
<td>Cd</td>
<td>294</td>
</tr>
<tr>
<td>La</td>
<td>310-312</td>
</tr>
<tr>
<td>Ta</td>
<td>346</td>
</tr>
<tr>
<td>Hf</td>
<td>347,348</td>
</tr>
<tr>
<td>W</td>
<td>348</td>
</tr>
<tr>
<td>F</td>
<td>342</td>
</tr>
<tr>
<td>In</td>
<td>349,350</td>
</tr>
<tr>
<td>Bi</td>
<td>390</td>
</tr>
</tbody>
</table>
2.7.3 Other compound dopants:

There are many oxides, silicides, borides, and hydrides that have been used in MgB\textsubscript{2} as dopants.

2.7.3.1 Oxides:

Table 2.7 Reported oxides as dopants.

<table>
<thead>
<tr>
<th>Type</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>351,352</td>
</tr>
<tr>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>353</td>
</tr>
<tr>
<td>Dy\textsubscript{2}O\textsubscript{3}</td>
<td>354</td>
</tr>
<tr>
<td>Ho\textsubscript{2}O\textsubscript{3}</td>
<td>355</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>356</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>357-359</td>
</tr>
<tr>
<td>MgO</td>
<td>360-364</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>365-367</td>
</tr>
<tr>
<td>ZnO\textsubscript{2}</td>
<td>368</td>
</tr>
<tr>
<td>Y\textsubscript{2}O\textsubscript{3}</td>
<td>369</td>
</tr>
<tr>
<td>Tb\textsubscript{4}O\textsubscript{7}</td>
<td>389</td>
</tr>
</tbody>
</table>

2.7.3.2 Silicides:

Table 2.8 Reported silicides as dopants.

<table>
<thead>
<tr>
<th>Type</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrSi\textsubscript{2}</td>
<td>370-372, 374</td>
</tr>
<tr>
<td>WSi\textsubscript{2}</td>
<td>370-373</td>
</tr>
<tr>
<td>Mg\textsubscript{2}Si</td>
<td>372,375,376</td>
</tr>
<tr>
<td>MoSi\textsubscript{2}</td>
<td>377</td>
</tr>
</tbody>
</table>

2.7.3.3 Borides and hydrides:

Table 2.9 Reported borides and hydrides as dopants.

<table>
<thead>
<tr>
<th>Type</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB\textsubscript{2}</td>
<td>379,380,371</td>
</tr>
<tr>
<td>Nb\textsubscript{2}B\textsubscript{2}</td>
<td>381,382</td>
</tr>
<tr>
<td>TiB\textsubscript{2}</td>
<td>383,384</td>
</tr>
<tr>
<td>WB</td>
<td>378</td>
</tr>
<tr>
<td>ZrH\textsubscript{2}</td>
<td>385</td>
</tr>
</tbody>
</table>
2.8 Dual reaction model:

Last year (2007), Dou et al. [231] proposed a very interesting model, which they called the dual reaction model, based on the following factors to explain the mechanism behind the enhancement of electromagnetic properties due to C-doping.

Factors:

1. It has already been reported and confirmed by many research groups that carbon partially substitutes into boron sites and causes disorder, contributing to the enhancement of $H_{c2}$ and $J_c(H)$ in all forms and from all sources.

2. For un-doped and C-doped MgB$_2$ samples, a lower sintering temperature has a major beneficial effect on $J_c(H)$ and $H_{c2}$. Grain boundary scattering plays a significant role at low sintering temperatures, when the grain size is small, as claimed by Yamamoto et al. [391]. As a result, a higher concentration of impurity precipitates, larger resistivity, and higher $J_c$ and $H_{c2}$ are the consequences of a low processing temperature. The beneficial effects of a low heat-treatment temperature on un-doped and C-doped MgB$_2$ will also be discussed in Chapter 4 and Chapter 7.

3. Although the disorder is introduced in completely different ways for pure, nano-carbon, and nano-SiC-doped samples, there is a correlation observed between the $J_c(H)$ and $H_{c2}$. The improvement of $J_c(H)$ in the MgB$_2$ doped samples can be mainly attributed to the enhancement of $H_{c2}$. What is more interesting is that the residual resistivity ratio (RRR = $\rho_{300K}/\rho_{40}$) which shows the ‘quality’ of the sample, attains a lower value when $J_c(H)$ and $H_{c2}$ are the highest. According to Kiuchi et al. and Yamamoto et al., the improvement of $J_c(H)$ at high field can be
achieved by enhancement of the upper critical field due to charge carrier scattering by grain boundaries and C substitution [391,392].

Based on these features, the dual reaction model also provides an understandable viewpoint from which to evaluate and clarify all future doping efforts towards advancing the performance of MgB$_2$ in high and self magnetic field. Although one would expect that carbide compounds like TiC and NbC would have a similar effect to SiC, the enhancement of $J_c$ by these dopants is much less significant compared to SiC doping. In fact, TiC and NbC have shown little effect on the $T_c$ and $J_c$ of MgB$_2$ [393] at temperatures below 950 °C. This is because TiC and NbC do not react with Mg or B at the MgB$_2$ formation temperature, thus no fresh reactive C is available to be incorporated into the MgB$_2$ lattice during its formation. On the other hand, the non-C-containing dopants, such as Si [395] and the silicides [394], showed little enhancement of $J_c(H)$ of MgB$_2$, which is due to the absence of any substitution effects, although enhanced grain boundary pinning might occur with low sintering temperatures, as for SiC. Based on the dual reaction model, Dou et al. assessed and categorized a broad range of dopants in terms of benefit to enhancement of $J_c(H)$, $H_{c2}$, and $H_{irr}$. Table 2.10 illustrates the dopant categories and explains why these dopants show positive or negative effects on superconducting and electronic properties [231, 396].
Table 2.10 Assessment of dopants according to the dual reaction model.

<table>
<thead>
<tr>
<th>Category</th>
<th>Typical dopants</th>
<th>C-substitution</th>
<th>Effect on $J_c (H)$, $H_{c2}$ and $H_{irr}$</th>
<th>Reaction</th>
<th>Sintering temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-1</td>
<td>SiC, Carbohydrates</td>
<td>Partial C-substitution</td>
<td>Positive</td>
<td>Highly reactive with fresh C</td>
<td>Same formation temperature as MgB$_2$</td>
</tr>
<tr>
<td>Cat-2</td>
<td>nano-C, CNT, B$_4$C</td>
<td>Partial C-substitution</td>
<td>Positive</td>
<td>Moderate reaction</td>
<td>Higher formation temperature than MgB$_2$</td>
</tr>
<tr>
<td>Cat-3</td>
<td>Si and silicides</td>
<td>No C-substitution</td>
<td>Positive</td>
<td>Moderate reaction</td>
<td>Same formation temperature as MgB$_2$</td>
</tr>
<tr>
<td>Cat-4</td>
<td>BN, MgO</td>
<td>No substitution</td>
<td>Positive &amp; Negative</td>
<td>No reaction</td>
<td>Higher sintering temperature</td>
</tr>
</tbody>
</table>

During my PhD study, I conducted extensive theoretical and experimental research on organic compound (mainly carbohydrate) doping (category 1 (Cat-1) in Table 2.10) into MgB$_2$. As the malic acid which is under carbohydrate is my main research topic, I would like to discuss carbohydrate doping into MgB$_2$ in further detail.

2.9 Why are carbohydrates special compared to other dopants?

Among the various forms of C-containing dopants that have already been discussed in the previous section, SiC doping has achieved a record high in-field $J_c (B)$, $H_{c2}$, and irreversibility ($H_{irr}$) in MgB$_2$ [20, 229, 290] These record high properties have been confirmed and verified by many research groups, and the performance records remain unbroken up to now. It is true that the best high field $J_c$ values were reached in SiC doped
MgB$_2$ wires, but this was also compromised by the poor performance in self and low field. It is common that nanosize precursor particles are expensive, and it was these nanoparticle precursors that were chosen for the doping process, which also creates a great challenge to achieving homogenous distribution within the matrix materials through solid state mixing. There are always agglomerates of nano-additives in the precursors. For various forms of C doping, the substitution of C for boron (B) cannot be achieved at the same temperatures as that of the MgB$_2$ formation reaction, so it is impossible to produce highly reactive fresh C for a proper substitution effect. Hydrocarbons such as benzene have been used for C substitution [265]. However, the C substitution level is limited by the high volatility of these compounds.

In order to overcome these problems our team first proposed to use a carbohydrate, such as DL-malic acid (C$_4$H$_6$O$_5$), as the dopant. The significant advantages of carbohydrate doping are:

(1) Carbohydrates are readily available and cheaper than expensive nano-additives.

(2) Carbohydrates can be dissolved in a solvent, so that the solution can form a slurry with B powder. After evaporating the solvent, the carbohydrate forms a coating on the B powder surfaces, giving a highly uniform mixture.

(3) The carbohydrates in the mixture melt at lower temperatures and decompose at temperatures below the formation temperature of MgB$_2$, hence producing highly reactive and fresh C on the atomic scale, as well as a reducing reagent, carbon monoxide, which may convert boron oxide to B, reducing the impurities in B powder.

(4) Because of the high reactivity of the freshly formed C, the C substitution for B can take place at the same temperature as the formation temperature of MgB$_2$. 
2.9.1 Why does malic acid show better performance than other carbohydrates?

2.9.1.1 Properties of malic acid (C\textsubscript{4}H\textsubscript{6}O\textsubscript{5})

The physical and chemical properties of C\textsubscript{4}H\textsubscript{6}O\textsubscript{5} can be found in the reference [397]. Fujishige et al. [398] reported on the thermal decomposition of C\textsubscript{4}H\textsubscript{6}O\textsubscript{5}, indicating an important path to motivate work on the mechanism of the chemical solution route with malic acid doping for MgB\textsubscript{2}, which will be described later in Chapter 6.

Carbohydrates, malic acid (C\textsubscript{4}H\textsubscript{6}O\textsubscript{5}) in this case, normally consist of carbon (C), oxygen (O), and hydrogen (H), so that the O can easily react with Mg to form MgO, which may enhance the vortex pinning, but also strongly degrades the connectivity, if it is present between MgB\textsubscript{2} grains, as seen in O-contaminated MgB\textsubscript{2}. [179, 425] Even though oxygen (O) is present in the C\textsubscript{4}H\textsubscript{6}O\textsubscript{5}, we proposed that C\textsubscript{4}H\textsubscript{6}O\textsubscript{5}, as an organic reagent, could introduce homogeneous mixing through a chemical solution route [Chapter 6]. In addition, due to the fact that most C\textsubscript{4}H\textsubscript{6}O\textsubscript{5} decomposes at temperatures below the formation temperature of MgB\textsubscript{2}, highly reactive and fresh C on an atomic scale could be introduced. Hence, we also reported that C substitution for B could take place at as low a temperature as the formation temperature of MgB\textsubscript{2} [Chapter 7]. Other groups [269, 271, 272, 274, 425] have already followed our route and confirmed the enhancement of superconducting and electromagnetic properties by different types of carbohydrate doping. Zhou et al [269] showed both high and self-field improvement from sugar doping into MgB\textsubscript{2}. I also [273] reported that a significant improvement in the superconducting properties, in this case without the chemical solution route, could be attributed to the lattice distortion due to the C substitution for boron, with the C coming from another
carbohydrate, namely tartaric acid (C$_4$H$_6$O$_6$). These findings suggest that C$_4$H$_6$O$_6$ is also a promising C source for MgB$_2$, with excellent $J_c$ properties under high field. The Ma group [271, 272, 425] also reported that improvements in $J_c$-$B$ performance from stearic acid, maleic acid (C$_4$H$_4$O$_4$), and maleic anhydride (C$_4$H$_2$O$_3$) doped MgB$_2$ tapes could be attributed to a high density of flux pinning centers and an increase in $H_{c2}$ due to C substitution for boron. Jun et al. [274] prepared C$_4$H$_6$O$_5$ doped MgB$_2$ wires and found improved superconducting properties.

### 2.10 Flux pinning:

Flux pinning is the phenomenon where magnetic flux lines do not move (become trapped, or “pinned”), in spite of the Lorentz force acting on them inside a current-carrying type II superconductor, such as MgB$_2$. The phenomenon cannot occur in type I superconductors, since these cannot be penetrated by magnetic fields (Meißner-Ochsenfeld effect).

The flux pinning is important and enormously interesting in applied superconductivity. The atomic or crystal defects, dislocations, grain boundaries, voids, point defects, strains, twin planes, inhomogeneities, and second phases present in any real superconductors are effective pinning sites. The flux pinning can be improved to maximize $J_c$ in practical conductors by tailoring various parameters of the superconductor.

Katsura et al. [403] reported that in un-doped MgB$_2$, a greater area of grain boundary due to smaller grain size is considered to be the most probable source of the dominant pinning centres. Recently, this idea was encouraged by results on electron-beam deposited thin films, which have very high $J_c$ and characteristic angular dependences of $J_c$ [400].
Although TEM studies on un-doped [401] and C-doped [399] MgB$_2$ have revealed the existence of $\zeta$-scale intragrain impurities which would act as pinning centres, such impurities are only observed in “well-grown” MgB$_2$ crystals, which usually have relatively low $J_c$. Therefore, similar intragrain microstructure cannot be expected in polycrystalline wires and tapes with applicable $J_c$ properties, since they have much smaller grain sizes [402] than those.

SiC, one of the best reported dopants so far, results in a large number of nanosized (5–30 nm) dislocations within the MgB$_2$ grains [405, 406], and these dislocations can strongly pin the flux lines. When SiC reacts with liquid Mg and amorphous B at the sintering temperature, the nanoparticles of SiC will act as nucleation sites to form MgB$_2$ and other non-superconducting phases such as Mg$_2$Si; BC, un-reacted Si, and other reaction products can be included within the grains as inclusions [404, 405, 406]. These highly dispersed reaction-induced products also contribute to the flux pinning [405, 406]. Some of the C from SiC may substitute for B atoms and create disorder at the boron planes. This will result in increased $\sigma$ band scattering and hence an increase in $H_{c2}$, as reported by Vinod et al. [417].

2.11 MgO formation and its effects:

Many groups have already studied the effects of MgO on the superconducting properties of MgB$_2$. Kovac et al. [407] reported on the effects of MgO content in commercial MgB$_2$ powders on the $J_c$ properties of ex-situ PIT processed MgB$_2$ wires. They also claimed that by increasing the amount of MgO, the inter-grain connectivity was worsened, but that well distributed and smaller sized MgO particles improved the flux pinning ability. MgO
has been shown to lead to isotropic pinning in films deposited in oxygen atmospheres [408], but the adverse effect of excess oxide phases at grain boundaries results in a degradation of grain connectivity.

Jiang et al. [409] also verified that nanosized MgO particles are effective for enhancing the magnetic and transport \( J_c \) of MgB\(_2\) wires. They observed that when the doping content was \( \leq 1.25 \) wt %, the critical temperature \( T_c \) was not significantly changed, but further increasing the doping content of nano-MgO led to a drastic drop in \( T_c \). The \( J_c \) enhancement was obtained within a doping amount of \( \leq 5 \) wt % but with the optimum doping content being at 1.25 wt\%. This result confirmed that the grain connectivity and flux pinning ability of MgB\(_2\) superconductor are very sensitive to the level of MgO phase. A negotiation between the inter-grain connectivity and the introduction of pinning centers into MgB\(_2\) superconductor might be obtained by optimizing the MgO content. The transport and magnetic \( J_c \) results are shown in Figures 2.34 and 2.35, respectively.
**Figure 2.34.** Field dependence of the transport $J_c$, properties of MgB$_2$/Fe tapes with various amounts of MgO nanoparticle addition. The measurements were performed at 4.2 K and with the field parallel to the tape surface [409].

**Figure 2.35.** Field dependence of the magnetic $J_c$, properties of MgB$_2$/Fe tapes with various amounts of MgO nanoparticle addition at 5, 20, and 30 K [409].
Recently Kim et al. [410] explained the mechanism of MgO formation by interpretation of the Gibbs free energy. The main reason for the formation of MgO within MgB$_2$ is likely to be because Mg in air could act as a potential O getter. That is, a small amount of MgO is already present in the starting materials. Reducing exposure to O plays an important role in improving this system, because formation of the oxide phase can result in secondary phases.

2.12 Market and future prospects for MgB$_2$

It has already been proven that MgB$_2$ material has potential in the race with the existing superconductors for industrial applications, in particular in the field of medical technology, where superconducting MRI magnets are used.

Based on the use of MgB$_2$ conductors, a well known company, ASG Superconductors, has started to design an open MRI magnet well in advance of the expected industrialization of the superconductor. On the other hand, this work allowed the possibility to start winding the first double pancake magnet just a few weeks after the production of the conductor by Columbus Superconductors in its first real and usable length, as reported by Braccini et al. [411].

MgB$_2$ is economical for practical applications, and the cost/performance ratio for MgB$_2$ is much lower than those for other superconductors [412, 413], as both Mg and B, and the sheath materials used are inexpensive. MgB$_2$ is also suitable for specific lightweight applications, such as in space applications, because its density is 2.6 g cm$^{-3}$, much lower than those of other superconductors and ordinary copper. Hyper Tech Research Inc, Columbus Superconductors, and others have already developed long lengths of multifilamentary MgB$_2$ conductors with high $J_c (H)$ values.
In fact MgB$_2$ has already proven its potential as the next generation high field magnetic material and as a strong competitor for the currently used NbTi and Nb$_3$Sn conductors. Table 2.11 shows a comparison of different types of superconductors based on different performance factors, as reported by Iwasa et al. [418]. Besides the magnet applications, MgB$_2$ conductors have potential uses in superconducting transformers, rotors, and transmission cables at temperatures of around 25 K, at fields of 1 T [417]. In the last two years, MgB$_2$ compound has demonstrated the potential to approach solid industrial development. Several long lengths of conductor have already been produced and delivered to customers by different manufacturers. A large bore MRI magnet, operating in a cryogen-free environment at 20 K, was built and successfully tested. Figure 2.37 shows the future road map of MgB$_2$ in various aspects. This indicates that MgB$_2$ will become one of the primary actors in the future market for superconducting materials [411].
Table 2.11 Parameter specifications: MgB₂, BSCCO, and NbTi [418].

Figure 2.37. Road map for MgB₂ wire development and commercial MgB₂ magnets [418].
References:


[388] www.hypertechresearch.com


[393] S.X. Dou et al., unpublished data.


[426] \url{http://marketplace.seeport.com/profile/view/40}


[431] \url{http://www.ansto.gov.au/__data/assets/pdf_file/0019/10099/HIP_Applicationsv33.pdf}

[432] \url{http://www.kobelco.co.jp/p109/05/p165e.htm}

[433] \url{http://www.techtra.pl/graph/PiT.jpg}
CHAPTER 3

3. EXPERIMENTAL PROCEDURE

3.1 Preparation of bulk sample

Polycrystalline MgB$_2$ samples doped with different level of malic acid (C$_4$H$_6$O$_5$) were prepared through a reaction in-situ process. The selected amount of C$_4$H$_6$O$_5$ (99%), from 0 to 30 wt % of total MgB$_2$ was mixed with an appropriate amount of B (99%) powder in toluene (C$_7$H$_8$, 99.5%). The toluene was taken as to make the concentration of 0.37 (M). Since the decomposition temperature of C$_4$H$_6$O$_5$ was at around 150 °C, his slurry was dried in vacuum oven for 2 hours at the temperature of 150 °C so that the B powder particles were coated by the C coming from C$_4$H$_6$O$_5$. This uniform composite was grinded, then mixed with an appropriate amount of Mg (99%) powder and grinded again. The thus-obtained powders with and without C$_4$H$_6$O$_5$ were put into a pressure die with the inner diameter of 13 mm and pressed into pellets under the pressure of 8 MPa. The precursor pellets were sealed inside iron tubes and sintered at 600 °C for 30 minutes to 4 hours and 650 °C to 900 °C for 30 minutes with heating rate of 5°C/min in flowing argon gas until the furnace cooled down to room temperature. The heat treated samples are cut from each pellet into a rectangular shape with the same dimensions of 1×2×3 and polished before the measurements.

3.2 Preparation of un-doped and doped wire samples

MgB$_2$/Fe monofilament wire was fabricated by the *in situ* PIT process. Mg (99%) and B (99%) powders were used as starting materials with the composition of MgB$_2$. Powder preparation for the pyrene (C$_{16}$H$_{10}$)/Fe doped wires is same as bulk sample preparation.
process described in section 3.1. The mixed powders were packed into an iron (Fe) tube with a length of 140 mm. The Fe tube had an outer diameter (O.D.) of 10 mm and inner diameter of 8 mm. The packing process was carried out in air. Both ends of the tubes were sealed with aluminium pieces. The composites were drawn to an O.D. of 1.42 mm. Drawing process was carried out by passing the tube through the conical hole of successive round dies at a speed of a few cm/s. A deformation rate of no more than 15% per pass was used in the whole mechanical deformation process. In case of tape making short wire samples (4 cm each), were cold rolled to the flat tape with the thickness of 500 µm and 3 mm width. All the samples were properly sealed with Fe tubes or Zr foil to avoid the oxidation. The fabricated wires were sintered at a range of temperatures from 600 (for 4 hrs) to 900 ºC for 30 min under high purity argon (Ar) gas and then cooled in the furnace. The heating rate was 5 ºC/min.

3.3 Sample characterization

3.3.1 X-ray diffraction

Microstructure, phase formation and texture analysis are easily examined by the X-ray diffraction (XRD). The crystal structure was refined with the aid of the program Jade (ver. 5.0). The crystal structures, such as lattice parameters, unit cell volume, c/a values, lattice strain, and weight fraction of MgO, were refined with the aid of the different types of program such as FullProf, Jade (ver. 5.0), Reitica, Powder4 etc. The lattice strain values were calculated from the slope and the crystallite size from the intercept in a plot of the calculated full width at half maximum (FWHM) x cos θ against sin θ. All these parameters can be calculated based on the raw data from XRD. In my research work I used the XRD instrument named Philips PW1730. In this diffratometer, CuKα radiation
with wavelength of 1.5405 Å was used to index the peak by the Bragg’s law from 15-70° (2-theta). The block diagram of XRD is shown in Figure 3.1.

![Figure 3.1. Schematic of an X-ray powder diffractometer [5]](Please see print copy for Figure 3.1)

The full-widths at half maximum (FWHM) can be determined by TRACES™ 6.3.0 software for three main indexed peaks (100, 110, 002) observed in the studied samples. According to the Scherrer equation, an increased FWHM value also indicates that the grain size has decreased as follows:

\[ D_p = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta} \]

where \( D_p \) is crystal size, \( \lambda \) is wavelength, \( \beta_{1/2} \) is the FWHM, and \( \theta \) is the peak position. From this equation, the crystal size is easily calculated as a function of peak width (FWHM). It is noted that Si powder was used as an internal standard to calculate these parameters.
3.3.2 Scanning electron microscopy (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm. The field emission gun (FEG) SEM can able to provide more clear highly magnified pictures.

Please see print copy for Figure 3.2

Figure 3.2 Spectroscopy data is often portrayed as a graph plotting counts vs. energy. The peaks correspond to characteristic elemental emissions [6].
The SEM is equipped with Energy Dispersive X-ray spectroscopy (EDS/EDX) attachment. EDS is an analytical tool predominantly used for chemical characterization shown in Figure 3.2. It is used to determine the energy spectrum of X-ray radiation to characterize the elemental composition of the samples area as well as few cubic micrometers.

3.3.3 Differential Thermal Analysis (DTA)

DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. This differential temperature is then plotted against time, or against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference. By DTA, we can estimate the sintering range of any sample.

Please see print copy for Figure 3.3
Figure 3.3: Schematic illustration of a DTA cell [1].

DTA may be defined formally as a technique for recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

3.3.4 Measurements of $T_c$, $J_c$, $H_{c2}$, $H_{irr}$

$T_c$ of the samples was defined as the onset temperature at which diamagnetic properties were observed. In addition, $H_{c2}$ and $H_{irr}$ were defined as $H_{c2}=0.9R(T_c)$ and $H_{irr}=0.1R(T_c)$ from the resistance ($R$) versus temperature ($T$) curve (5 mA ac). The magnetization ($M$) of the samples was measured at 5 and 20 K using a Physical Properties Measurement System (PPMS, Quantum Design) in a time-varying magnetic field up to 8.5 T with sweep rate of 50 Oe/s. The magnetic $J_c$ was derived from the width of the magnetization loop using Bean’s model [2]. For comparison all the samples for $J_c$ were made to the same size ($1 \times 2.25 \times 3.35$ mm$^3$) because there is a sample size effect for MgB$_2$ [3, 4].

The transport $I_c$ measurement was characterized by the standard four-point probe method with the criterion of 1 $\mu$V/cm. $J_c$ was obtained by dividing $I_c$ by the cross section of the MgB$_2$ core.
Reference


2.  C. P. Bean, Rev. Mod. Phys. 36, 31-36 (1964)


5.  Materials.binghamton.edu/labs/xray/xray.html

CHAPTER 4

4. THE EFFECTS OF SINTERING TEMPERATURE ON THE SUPERCONDUCTIVITY IN MgB$_2$/Fe WIRES

4.1 Introduction

MgB$_2$ superconductor is one of the best candidates for the fabrication of conductors and is competitive with other superconductors, such as Nb-based, Bi-based, and Y-based materials, for the reasons that I have already described in Chapter 2. The research community’s great interest relates to the fabrication of MgB$_2$ conductor in lengths $>$1 km and in stabilized form [1–3]. However, to make MgB$_2$ more viable in real application, the critical current density ($J_c$) of MgB$_2$ conductor must be raised considerably at 20 K. The intragranular $J_c$ and upper critical field ($H_{c2}$) of MgB$_2$ bulk may already be higher than those of NbTi and Nb$_3$Sn superconductors [4, 5], but further enhancement of intergranular $J_c$ has still remained a topic of great scientific and technological interest. For example, the presence of secondary phases or lattice defects limits the current path of MgB$_2$ locally [6]. Various factors, such as poor connectivity between superconducting grains and chemical heterogeneity at the grain boundaries affect the intergranular $J_c$ in polycrystalline MgB$_2$ [7]. The source of weak links could be poor crystallinity, as well as porosity within the MgB$_2$ matrix [8–10]. It is the major challenge for the MgB$_2$ research community to overcome the major intergrain connectivity limitations of MgB$_2$ so as to raise $J_c$ as a whole. In this chapter, therefore, I fabricated MgB$_2$/Fe wire by using the powder-in-tube (PIT) method sintered samples at different temperatures and then
analysed the strong correlations among phase transformation, lattice parameters, full width at half maximum (FWHM), $T_c$, $J_c$ and resistivity ($\rho$).

### 4.2. Experimental procedure

MgB$_2$/Fe wire was fabricated by the *in situ* PIT process. The detailed procedures for making wires have also been reported elsewhere [11]. Mg (99%) and B (99%) powders were used as starting materials with the composition of MgB$_2$. The mixed powders were packed into an iron (Fe) tube with a length of 140 mm. The Fe tube had an outer diameter (O.D.) of 10 mm and an inner diameter of 8 mm. The packing process was carried out in air. Both ends of the tubes were sealed with aluminium pieces. The composites were drawn to an O.D. of 1.42 mm. The fabricated wires were sintered at a range of temperatures from 650 to 900 °C for 30 min under high purity argon (Ar) gas and then cooled in the furnace. The heating rate was 5 °C/min. All the samples were characterized by various measurements, including differential thermal analysis (DTA), x-ray diffraction (XRD), $T_c$ and transport critical current ($I_c$). A PW1730 x-ray diffractometer with Cu Kα radiation was used to determine the phase and crystal structure of all the samples. The $a$- and $c$-lattice parameters were obtained from Rietveld refinement. The strain values were estimated by using an isotropic model [12]. $T_c$ was defined as the onset temperature at which diamagnetic properties were observed. The transport $I_c$ measurement was characterized by the standard four-point probe method with the criterion of 1 $\mu$V/cm. $J_c$ was obtained by dividing $I_c$ by the cross-sectional area of the MgB$_2$ core.
4.3 Results and discussion

4.3.1 Differential Thermal Analysis to obtain the proper sintering range:

[Image: Differential thermal analysis (DTA) for MgB$_2$/Fe wire and bare Fe.]

Figure 4.1. Differential thermal analysis (DTA) for MgB$_2$/Fe wire and bare Fe.

I evaluated the DTA results shown in Figure 4.1 for MgB$_2$/Fe wire and bare Fe to decide the proper sintering range. I used the same heating rate, 5 ºC/min in Ar gas, in order to maintain identical sintering conditions for the samples. For the MgB$_2$/Fe (Mg + 2B + Fe) sample, there were two exothermal peaks and two endothermal peaks, while the Fe had only one endothermal peak. In the case of the first exothermal peak (peak 1 in the Figure 4.1), this is related to the reaction between melting B$_2$O$_3$ and Mg, i.e. Mg reacts with
B\textsubscript{2}O\textsubscript{3} to form MgO. The reason for the existence of B\textsubscript{2}O\textsubscript{3} is because the surface of the commercial B powder has partially oxidized. From XRD (not shown), we observed that there were B\textsubscript{2}O\textsubscript{3} peaks (2\(\theta\) ~ 14.6° and 27.8°) in the B powder. The second exothermal peak (peak 2) could be associated with MgB\textsubscript{2} formation. On the other hand, the broadened endothermal peak (indicated by 3) at around 750 °C for Fe is probably related to the Curie temperature of bare Fe. The second endothermal peak (indicated by 4) at around 910 °C is due to the formation of Fe\textsubscript{2}B at the interface between the core and the sheath. We concluded that the MgO formation starts from 425 °C, that the MgB\textsubscript{2} phase starts to form at 575 °C and then finishes at 640 °C, and that the Fe\textsubscript{2}B phase forms above 910 °C when a heating rate of 5 °C /min is used. As a result, we found the appropriate sintering range to be 650–900 °C for MgB\textsubscript{2}/Fe conductor.

4.3.2 Analysis of the lattice parameters and MgO formation
Figure 4.2. (a) Lattice parameters and (b) weight fractions of MgB$_2$ and MgO with different sintering temperatures.

The lattice parameters (a) and the weight fractions of MgB$_2$ and MgO (b) with different sintering temperatures are shown in Figure 4.2. We observed that both $a$- and $c$-axis lattice parameters did not change within the heat treatment range of 650–900 °C within the accuracy of error. That is, the XRD spectra did not show any peak shifting in our samples which are not shown here. It is to be noted that the weight fraction of MgO is also remained constant, ~10%, with different sintering temperatures. This is because most
MgO is not formed by the reaction of B$_2$O$_3$ but was introduced externally, i.e. the possibility of MgO formation can be attributed to both: (1) the presence of MgO in the starting powder as Mg could act as an oxygen getter in air, $2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s)$; and (2) the reaction of melted B$_2$O$_3$ at around 450 °C with Mg to form MgO, $3\text{Mg}(s) + \text{B}_2\text{O}_3(s) \rightarrow 3\text{MgO}(s) + 2\text{B}(s)$. Of these, the former is responsible for a much greater contribution to MgO formation within MgB$_2$. This is because Mg is a very active material that is very easy to oxidize in air [13]. In this case, MgO particles may be present at the grain boundary between MgB$_2$ grains, resulting in depression of the $J_c$ of the whole conductor. Thus, starting powders with high purity are important for the superconducting properties. These observations can be further supported by the weight fraction of MgO for a sample sintered at 1000 °C (not shown). We observed that the weight fraction of MgO was still ~10% with this even higher sintering temperature. Fe$_2$B was observed as a new secondary phase, ~6%. However, the weight fraction of MgB$_2$ further decreased to 84%. This indicates that most MgO was coming from the starting material. There is a reaction with the already formed MgB$_2$ and the Fe sheath at >900 °C [14–16].

**4.3.3 Analysis of the $T_c$, FWHM and lattice strain**
Figure 4.3. Critical temperature ($T_c$) and full width at half-maximum (FWHM) of the (110) peak against sintering temperature.

The $T_c$ and FWHM of MgB$_2$ (110) peak against sintering temperature are shown in Figure 4.3. Among the various XRD peaks, the FWHM of (110) is related to the in-plane crystallinity. According to Williamson–Hall, the strain and grain size can affect the FWHM value [17]. So far as strain is concerned, there are actually two types of strain in samples, micro-strain and macro-strain. The micro-strain varies from one grain to another on the microscopic scale, resulting in non-uniformity, which produces peak broadening. On the other hand, macrostrain is uniform, and its uniform effects can produce peak shifting. The former is due to the contribution of defects inside grains, and the latter is due to the substitution of elements such as C into B sites. The analysis of FWHM can provide considerable information on the crystallite size and micro/lattice strain that is present in the specimen.
It was observed that the behaviour of $T_c$ had an opposite trend from FWHM. The FWHM decreased as the sintering temperature increased. According to Scherrer’s formula, the FWHM value is inversely proportional to grain size. On the other hand, $T_c$ increased, that is, there was better crystallinity or fewer defects. Improvement of crystallinity accompanies better grain connectivity of the MgB$_2$ grains. On the other hand, the significant depression of crystallinity for MgB$_2$ sintered at 650 ºC originates from disorder in the crystal lattice, which is caused by various lattice defects such as intragranular precipitates and unreacted Mg.

\[ \text{\textbf{Figure 4.4.}} \text{ Analysis of the micro- and macro-strain with diffraction line.} \]
Figure 4.5 shows the behaviour of strain with different sintering temperatures. We observed that the strain decreased, unlike the $T_c$ behaviour, as the sintering temperature increased. This is probably related to the defects within grains as mentioned above. That is, improvement of crystallinity due to grain growth may reduce defects within samples. As a result, we observed that there is a strong correlation between strain and $T_c$. Note that the sample sintered at 650 °C achieved a higher $J_c$ (Figure 4.6), even though the sample sintered at 650 °C had a relatively higher strain value, ~0.58%. This also indicates that various defects trapped within MgB$_2$ grains might act as flux pinning centres.
6.3.4 Analysis of the superconducting properties

![Graph showing transport $J_c(B)$ of MgB$_2$/Fe wires sintered at different temperatures.]

**Figure 4.6.** Transport $J_c(B)$ of MgB$_2$/Fe wires sintered at different temperatures.

The transport $J_c(B)$ of MgB$_2$/Fe wires sintered at different temperatures is shown in Figure 4.6. As the sintering temperature increased to 900 °C, $J_c$ values significantly decreased. Note that the $J_c(B)$ slopes of wires sintered within the temperature range of 650–800 °C did not show any significant differences. Clearly, 650 °C is the optimum sintering temperature among our Fe sheathed MgB$_2$ wire samples. The $J_c$ value reached 4200 A cm$^{-2}$ at 4.2 K and 10 T. The estimated $H_{irr}$ at 4.2 K with a criterion of $J_c \sim 100$ A cm$^{-2}$ was 15.8 T from extrapolation. These results are slightly higher than those of other groups, even for wires made from MgH$_2$ and B mixtures [18, 19]. On the other hand, the wire sintered at 900 °C is expected to show better $J_c$ under low field, even if $J_c$ values are low under high field. This better performance at low field may be related to good connectivity due to grain growth and reduced defects.
Table 4.1 illustrates the measured \( \rho \) values, residual resistivity ratios (RRR, \( \rho(300\, K)/\rho(40\, K) \)) and active crosssectional area fraction (\( A_F \)) for MgB\(_2\)/Fe wires with different sintering temperatures. To measure the \( \rho \), the Fe sheath of the MgB\(_2\)/Fe wire was removed. We observed that \( \rho \) at 300 K decreased as the sintering temperature increased. This is related to the better crystallinity of MgB\(_2\) phase due to additional grain growth, as mentioned above. Specifically, the relatively lower \( \rho \) near 300 K may be related to higher density and better inter-granular connection. On the other hand, \( \rho \) behaviour near 40 K is probably related to the intra-granular defects since, as the temperature decreases, the phonon contribution to \( \rho \) also decreases. The defects inside grains may have still affected the \( \rho \) at 40 K [20]. These observations can be further supported by the \( \Delta \rho \) and RRR behaviour. It is well known that relatively high values of the RRR indicate good sample quality.

The connection factor, \( A_F \), was also evaluated by the resistivity phonon term according to Rowell analysis [20]. We observed that \( A_F \) of a sample sintered at 900 °C was slightly larger than that at 650 °C. \( A_F \) values ranged from as low as 0.21 to as high as 0.26 depending on which sintering temperature was selected. However, \( A_F \) of all our samples still had a smaller value. This indicates that there are some current obstacles, MgO,

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \rho_{40, K} ) (( \mu \Omega , \text{cm} ))</th>
<th>( \rho_{300, K} ) (( \mu \Omega , \text{cm} ))</th>
<th>( \Delta \rho (\rho_{300, K} - \rho_{40, K}) )</th>
<th>RRR</th>
<th>( A_F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>650 °C/30 min</td>
<td>41.8</td>
<td>77.3</td>
<td>35.5</td>
<td>1.85</td>
<td>0.21</td>
</tr>
<tr>
<td>700 °C/30 min</td>
<td>36.7</td>
<td>71.1</td>
<td>34.4</td>
<td>2.01</td>
<td>0.21</td>
</tr>
<tr>
<td>800 °C/30 min</td>
<td>27.3</td>
<td>56.4</td>
<td>29.1</td>
<td>2.06</td>
<td>0.25</td>
</tr>
<tr>
<td>900 °C/30 min</td>
<td>24.8</td>
<td>53.4</td>
<td>28.6</td>
<td>2.46</td>
<td>0.26</td>
</tr>
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</table>
between MgB₂ grains, resulting in depression of connectivity. As a result, the MgO fraction decrease in the starting material would be a key point to further improve the self-field $J_c$ of MgB₂.

### 4.4. Summary

We observed that sintering the wire at low temperature, 650 °C, resulted in higher $J_c$ up to 12 T at 4.2 K and lower $T_c$. The best transport $J_c$ value reached 4200 A cm⁻² at 4.2 K and 10 T. This significant behaviour for the MgB₂ samples can be explained by the depression of crystallinity as grain size decreases. Note that the sample sintered at 650 °C achieved the highest $J_c$, even though this sample had a relatively higher strain value, ~0.58%, and a higher $\rho$ which indicate that various defects within grains could act as flux pinning centres.
References


CHAPTER 5

5. CARBOHYDRATE (C₄H₆O₅) DOPING TO ENHANCE THE ELECTROMAGNETIC PROPERTIES OF MgB₂ SUPERCONDUCTORS

5.1 Introduction:

A significant enhancement in the electromagnetic properties of MgB₂ has been achieved through doping with various forms of carbon (C) which I already discussed in chapter 2. To take advantage of its $T_c$ of 39 K [1], enhancements of both the upper critical field ($H_{c2}$) and $J_c$ are essential. Attempts to accomplish this have invoked the introduction of numerous techniques including chemical doping [2–6], irradiation [7], and various thermo-mechanical processing techniques [8, 9]. Among the numerous forms of C-containing dopants, Dou group has achieved a record high in-field $J_c (B)$, $H_{c2}$, and irreversibility ($H_{irr}$) in MgB₂ by SiC doping [2]. Many MgB₂ groups have confirmed and reproduced these record high properties and reported in many papers [2, 5, 10, 11]. However, the best high-field $J_c$ values at 5 K achieved in the SiC doped MgB₂ wires but the self-field and low-field $J_c$ at 20 K were not much improved. With nano-SiC there are always agglomerates of nanoadditives in the precursors. Various forms of C doping already reported but with most of them the C substitution for boron (B) cannot be achieved at the same temperatures as that of the MgB₂ formation reaction due to their poor reactivity.
In order to overcome these problems I proposed to use a carbohydrate such as DL-malic acid (C$_4$H$_6$O$_5$) as the dopant. I already discussed the significant advantages of carbohydrate over other C sources in chapter 2. The simultaneous dual reactions promote C substitution for B in the lattice at the same temperature as the formation temperature of MgB$_2$ and the inclusion of excess C within the grains, resulting in the enhancement of $J_c$, $H_{irr}$, and $H_{c2}$.

In this chapter, therefore, I used malic acid as a representative of carbohydrate dopant. I fabricated MgB$_2$+ C$_4$H$_6$O$_5$ samples with different addition levels. The lattice parameters $T_c$, $J_c$, $H_{irr}$, $H_{c2}$, and microstructures are presented in comparison with the un-doped reference MgB$_2$.

5.2 Experimental:

MgB$_2$ pellets were prepared by an in situ reaction process with the addition of C$_4$H$_6$O$_5$. The selected amount of C$_4$H$_6$O$_5$ (99%), from 0 to 30 wt % of total MgB$_2$ was mixed with an appropriate amount of B (99%) powder in toluene (C$_7$H$_8$, 99.5%). The toluene was taken as to make the concentration of 0.37 (M). Since the decomposition temperature of C$_4$H$_6$O$_5$ was at around 150 °C, this slurry was dried in vacuum oven for 2 hours at the temperature of 150 °C so that the B powder particles were coated by the C coming from C$_4$H$_6$O$_5$. This uniform composite was then mixed with an appropriate amount of Mg (99%) powder. These mixed powders were ground, pressed, and then sintered at 900 °C for 30 min under argon gas. The crystal structures were analyzed by means of x-ray diffraction analysis (Philips PW-1730). Lattice parameters were estimated from Rietveld refinement of the x-ray diffraction patterns using the Reitica software package, within the accuracy of calculation. $T_c$ of the samples was
defined as the onset temperature at which diamagnetic properties were observed. In addition, $H_{c2}$ and $H_{irr}$ were defined as $H_{c2}=0.9R(T_c)$ and $H_{irr}=0.1R(T_c)$ from the resistance ($R$) versus temperature ($T$) curve (5 mA ac). The magnetization ($M$) of the samples was measured at 5 and 20 K using a Physical Properties Measurement System (PPMS, Quantum Design) in a time-varying magnetic field up to 8.5 T with sweep rate of 50 Oe/s. The magnetic $J_c$ was derived from the width of the magnetization loop using Bean’s model. For comparison all the samples for $J_c$ were made to the same size ($1 \times 2.25 \times 3.35$ mm$^3$) because there is a sample size effect for MgB$_2$ [13, 14].

5.3 Result and Discussion:

5.3.1 Analysis of lattice parameters and crystallinity in doped samples:

<table>
<thead>
<tr>
<th>Malic acid (C$_4$H$_6$O$_5$) amount (wt %)</th>
<th>Lattice parameters</th>
<th>Actual C (%) in MgB$_{2-x}C_x$</th>
<th>$T_c$ (K)</th>
<th>$\rho_{40}$ K ($\mu\Omega$ cm)</th>
<th>$\rho_{300}$ K ($\mu\Omega$ cm)</th>
<th>$H_{irr}^*$ (T) (20 K)</th>
<th>$J_c$ (A cm$^{-2}$) Self-field (20 K)</th>
<th>$J_c$ (A cm$^{-2}$) 8 T (5 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.0835(5)</td>
<td>3.5217(5)</td>
<td>37.6</td>
<td>34.5</td>
<td>73.5</td>
<td>5.4</td>
<td>$3.9 \times 10^5$</td>
<td>$0.1 \times 10^4$</td>
</tr>
<tr>
<td>10</td>
<td>3.0751(6)</td>
<td>3.5268(3)</td>
<td>0.0380</td>
<td>35.8</td>
<td>90.2</td>
<td>146.5</td>
<td>$3.5 \times 10^5$</td>
<td>$2.3 \times 10^4$</td>
</tr>
<tr>
<td>20</td>
<td>3.0746(4)</td>
<td>3.5229(7)</td>
<td>0.0404</td>
<td>35.7</td>
<td>83.8</td>
<td>146.2</td>
<td>$3.5 \times 10^5$</td>
<td>$2.7 \times 10^4$</td>
</tr>
<tr>
<td>30</td>
<td>3.0731(9)</td>
<td>3.5214(7)</td>
<td>0.0460</td>
<td>35.8</td>
<td>79.6</td>
<td>131.9</td>
<td>$4.0 \times 10^5$</td>
<td>$2.6 \times 10^4$</td>
</tr>
</tbody>
</table>

*Extrapolation from measured lattice parameters (Ref. 12).

Table 5.1. Measured data for un-doped MgB$_2$ and MgB$_{2+x}$ C$_4$H$_6$O$_5$ samples with different addition levels. $H_{irr}$* was calculated from the standard criterion of $J_c$ (100 A cm$^{-2}$).

Table 5.1 shows the measured data for the un-doped MgB$_2$ and MgB$_{2+x}$ C$_4$H$_6$O$_5$ samples with different addition levels. The lattice parameters calculated from XRD show a large decrease in the $a$-axis parameter with 10 wt % C$_4$H$_6$O$_5$ and a small further drop in $a$ with increasing C$_4$H$_6$O$_5$ addition level, but no change in the $c$-axis parameter. This is an indication of the C substitution for B. The actual C substitution level can be estimated
from the $a$-axis change [12]. It should be noted that the net C percentage addition is only 36% of the C$_4$H$_6$O$_5$ addition. The actual C substitution levels of 1.9–2.3 at % of B at three doping levels are clearly higher than those with other forms of C dopants, which is attributable to the high reactivity of fresh C released from the decomposition of C$_4$H$_6$O$_5$ at low temperature. The increase in sintering temperature improves both the crystallinity and the C substitution for B. The former will increase $T_c$, while the latter will decrease $T_c$. As a compromise, these two opposing factors result in a high level of C substitution for B with a relatively small drop in $T_c$. The high-field $J_c$’s of the MgB$_2$ + C$_4$H$_6$O$_5$ samples were much higher than that of the un-doped MgB$_2$. Specifically, it should be noted that the self-field $J_c$ of MgB$_2$+ C$_4$H$_6$O$_5$ samples was not reduced at addition levels as high as 30 wt % C$_4$H$_6$O$_5$; hence the connectivity between MgB$_2$ grains was not affected by addition with C$_4$H$_6$O$_5$. Although there is a possibility of the formation of H$_2$O during sintering due to the decomposition of C$_4$H$_6$O$_5$, there was no degradation in self-field $J_c$, even for 30 wt % C$_4$H$_6$O$_5$ added to MgB$_2$. This may be attributable to the fact that the decomposition products, C and CO, of C$_4$H$_6$O$_5$ reduced B$_2$O$_3$ and hence increased the effective cross section of the superconductor.

5.3.2 Analysis of the superconducting and electronic properties:
Figure 5.1. Superconducting properties of un-doped MgB$_2$ and MgB$_2$ + C$_4$H$_6$O$_5$ samples with different addition levels: (a) Magnetic field dependence of $J_c$ in all samples at 20 and 5 K; (b) field dependence of the volume pinning force, $F_p=J_cB$, of all samples at 20 K. The $F_p$ is normalized by the maximum volume pinning force $F_{p,\text{max}}$. 

$J_c$ (A cm$^{-2}$) vs. $B$ (T)

$F_p/F_{p,\text{max}}$ vs. $B$ (T)
Figure 5.2. Normalized temperature dependence of $H_{irr}$ and $H_{c2}$ for un-doped and C$_4$H$_6$O$_5$ doped samples. $H_{c2}$ and $H_{irr}$ were defined as $H_{c2}=0.9 \ R(T_c)$ and $H_{irr}=0.1 \ R(T_c)$ from the $R$ vs $T$ curve.

Figure 5.1(a) shows the magnetic field dependence of $J_c$ in all samples at 20 and 5 K. It should be noted that $J_c$ values in high field were increased by more than an order of magnitude. For example, the $J_c$ value of $2.5 \times 10^4 \ A \ cm^{-2}$ at 5 K and 8 T for MgB$_2$+30 wt% C$_4$H$_6$O$_5$ sample is higher than that of the un-doped MgB$_2$ by a factor of 21. In addition, there was no $J_c$ degradation in self-field for the MgB$_2$+30 wt% C$_4$H$_6$O$_5$ sample. These findings can be further supported by the flux pinning results. Figure 5.1(b) plots the field dependence of the volume pinning force, $F_p=J \times B$, of all samples at 20 K. The $F_p$ is normalized by the maximum volume pinning force $F_{p,\text{max}}$. The flux pinning for the MgB$_2$+ C$_4$H$_6$O$_5$ samples was significantly higher than that of the un-doped one at $B>1.5$ T. This result indicates that the $F_p(B)$ of MgB$_2$+ C$_4$H$_6$O$_5$ samples was improved by the C
substitution effect and nano-C inclusions within the grains. The normalized temperature
dependence of $H_{irr}$ and $H_{c2}$ for all samples is shown in Fig. 5.2. Significantly enhanced
$H_{irr}$ and $H_{c2}$ for MgB$_2$+ C$_4$H$_6$O$_5$ samples were observed, suggesting that C substitution
into B sites results in an enhancement in $H_{irr}$ and $H_{c2}$. The steeper slopes of $H_{irr}$ for MgB$_2$
+ C$_4$H$_6$O$_5$ samples exceeded $H_{c2}$ of un-doped MgB$_2$ below a temperature of 22 K. The
resistivities $\rho$ for the un-doped and MgB2+ C$_4$H$_6$O$_5$ samples are 34 and 80–90 $\mu\Omega$-cm at
40 K, respectively, as shown in Table 5.1. The increased resistivity for MgB$_2$+ C$_4$H$_6$O$_5$
samples indicates the increased impurity scattering as a result of C substitution into B
sites.

5.3.3 Comparison of microstructure in un-doped and doped samples:
FEG-SEM images for (a) un-doped MgB$_2$, (b) MgB$_2$ +10 wt% C$_4$H$_6$O$_5$, and (c) MgB$_2$+30
wt% C$_4$H$_6$O$_5$ are shown in Fig. 5.3. The un-doped MgB$_2$ sample appears inhomogeneous,
consisting of crystalline grains from several tens of nanometers in size to 500 nm. The
morphology of the MgB$_2$+10 wt% C$_4$H$_6$O$_5$ sample was refined to smaller, denser, and
more homogeneous grains compared to the un-doped MgB$_2$ one. The grain refinement by
10 and 20 wt % C$_4$H$_6$O$_5$ additions is supported by the full width at half maximum
(FWHM) results for all the peaks, as shown in Figure 5.4. As the doping level further
increases to 30 wt %, however, grains appear to have a bar/plate shape, with their width
up to 150 nm and length up to 400 nm, in a well connected grain network (Fig. 5.3(c)).
Figure 5.3. Photographs from FEG-SEM: (a) un-doped MgB₂, (b) MgB₂ + 10 wt% C₄H₆O₅, and (c) MgB₂ + 30 wt% C₄H₆O₅.
Figure 5.4. FWHM as a function of the amount of C$_4$H$_6$O$_5$. MgB$_2$ (100), (101), (002), and (110) correspond to $2\theta$ ~ 33.6°, 42.5°, 52.0°, and 60.0°, respectively.

Consistent with the FEG-SEM image is the decrease in FWHM for the 30 wt % doped sample (Fig. 5.4) although the average FWHM values for all peaks are still bigger than those of the un-doped sample. The FEG-SEM image suggests that at higher addition levels C$_4$H$_6$O$_5$ may act as a sintering aid to improve the crystallinity. The grain growth should not improve the electromagnetic properties. However, this effect may be offset by the increase in C substitution level, the reduction in resistivity (Table 5.1), and improvement in grain connectivity. This is well evidenced by the fact that the self-field $J_c$ of the MgB$_2$+30 wt% C$_4$H$_6$O$_5$ sample was enhanced while the improved in-field $J_c$, $H_{\text{irr}}$, and $H_{c2}$ were maintained, as shown in Figures 5.1 and 5.2.
5.4 Summary:

Carbohydrate doping results in a small depression in $T_c$ but significantly increases the C substitution level, reduces the impurities, and hence improves $J_c$, $H_{irr}$, and $H_{c2}$ performances at all the operating temperatures and over the entire field range. This finding opens a direction for the manufacture of nano doped materials using the carbohydrate solution route, which solves the agglomeration problem, avoids the use of expensive nano additives, and achieves improved performance properties.
References:


CHAPTER 6

6. SYSTEMATIC STUDY OF MgB$_2$ + C$_4$H$_6$O$_5$ SUPERCONDUCTOR PREPARED BY THE CHEMICAL SOLUTION ROUTE

6.1 Introduction:

We have already investigated in previous chapters that carbon (C) can enter the MgB$_2$ structure by substituting for boron (B), which leads to increased impurity scattering in the two-band MgB$_2$, and hence significantly increases $J_c$ and the upper critical field ($H_{c2}$). Due to the agglomeration of nano-sized dopant particles, un-reacted C remains in the MgB$_2$ matrix and reacts with magnesium (Mg) or B powders, resulting in the formation of impurity phases. To overcome these properties, it is necessary to study the homogeneity of mixing as well as the activity of the reactions between B and C materials so as to achieve a full reaction. The various methods have been studied by many groups. Mickelson et al [1] first reported that B$_4$C was considered to be one of the more reactive C-containing compounds because free C was liberated from B$_4$C. To further improve the high field $J_c$ performance, however, using the B$_4$C compound meant that a higher sintering temperature was needed, up to 800 °C [2]. Dou et al [3] studied the effects of SiC doping on MgB$_2$ superconductor to overcome the same problems. Even though SiC was much more effective at enhancing the $J_c$ at a low sintering temperature (<650 °C), there were agglomerations of nanoparticles in the MgB$_2$ matrix, resulting in blocking of current flow. C and CNT as dopants also needed a higher sintering temperature ~900 °C.
for C substitution. In addition, because of their high aspect ratio, the CNTs were much more easily entangled [4], reducing homogeneity.

In chapter 4 [5], we have shown the possibility of using carbohydrate as a C source for MgB$_2$. For these reasons, the additive effects of C$_4$H$_6$O$_5$ on the MgB$_2$ superconductivity were further evaluated systematically. Because of the high reactivity of freshly formed C from sources such as SiC, C substitution for B can take place at the same temperature as the formation temperature of MgB$_2$. The C$_4$H$_6$O$_5$ can be dissolved in a proper solvent and evaporated at a temperature of $\sim 150$ °C, so that the solution can form a slurry with B powder. After evaporation of the solvent, the C forms an encapsulating coating on the B powder surfaces or disperses in the matrix, giving a highly uniform mixture. This finding solves the agglomeration problem and avoids the use of expensive nano additives.

We again fabricated MgB$_2$ superconductor with C$_4$H$_6$O$_5$ included using this chemical solution route. The lattice parameters, lattice strain, amount of C substitution, microstructures, weight fraction of MgO, critical temperature ($T_c$), $J_c$, and irreversibility field ($H_{irr}$) are presented in comparison with those for the un-doped reference MgB$_2$.

6.2. Experimental procedure

The fabrication process has already been discussed in the section 5.2 of chapter 5. All samples were characterized by x-ray diffraction (XRD) and field emission gun-scanning electron microscopy (FEG-SEM). The crystal structures, such as lattice parameters, unit cell volume, $c/a$ values, lattice strain, and weight fraction of MgO, were refined with the aid of the program FullProf. The lattice strain values were calculated from the slope and the crystallite size from the intercept in a plot of the calculated full width at half maximum (FWHM) $\times$cos $\theta$ against sin $\theta$. $T_c$ was defined as the onset temperature at
which diamagnetic properties were observed. The magnetization was measured at 20 K using a Physical Properties Measurement System (PPMS, Quantum Design) in a time-varying magnetic field up to 8.5 T. The magnetic $J_c$ was derived from the width of the magnetization loop using Bean’s model. In addition, the $H_{irr}$ was defined with a $J_c$ criterion of 100 A cm$^{-2}$.

6.3. Results and discussion

6.3.1 Analysis of lattice parameters and unit cell volume

![Graph showing a-axis, c-axis, unit cell volume, and c/a values versus amount of malic acid.](image)

**Figure 6.1.** (a) a-axis lattice parameter, (b) c-axis lattice parameter, (c) unit cell volume, and (d) c/a values of MgB$_2$ + C$_4$H$_6$O$_5$ samples calculated from Rietveld refinement.
Figure 6.1 shows the lattice parameters, unit cell volume, and \( c/a \) values of MgB\(_2\) + C\(_4\)H\(_6\)O\(_5\) samples calculated from Rietveld refinement. All XRD measurements were performed on ground MgB\(_2\). It was observed that the lattice parameters and volume decreased monotonically as the amount of C\(_4\)H\(_6\)O\(_5\) additive increased to 10 wt\%. This changed behaviour is attributed to the C substitution into B sites, because of the size difference between B and C ions. Beyond that point all parameters remained unchanged within the accuracy error. What is interesting is that it only required \( \sim 10 \) wt\% of C\(_4\)H\(_6\)O\(_5\), i.e., even though the amount of C\(_4\)H\(_6\)O\(_5\) additive further increased to 20 or 30 wt\%, the lattice parameters did not change any more. This point is important because it limits the parameter space in the MgB\(_2\) structure to only 10 wt\% C\(_4\)H\(_6\)O\(_5\). The \( a \)-axis lattice parameter significantly decreased from 3.0861(6) to 3.0736(1) Å. However, the lattice parameters and the volume had opposite trends from \( c/a \).

### 6.3.2 Analysis of C-substitution and strain effect

From the results of Lee et al [6] and Kazakov et al [7], we can, indirectly, estimate the actual amount of the C contributed for our MgB\(_2\) + C\(_4\)H\(_6\)O\(_5\) samples. These values were estimated from the dependence of the \( a \)-axis lattice parameter as determined by single crystal XRD. The value was calculated to be \( x \sim 0.0172 \) to 0.0304 in the composition of Mg \( (B_{1-x}C_x)_2 \) as can be seen in Figure 6.2 (a). The calculated results are strongly correlated with lattice strain (Figure 6.2 (b)). As far as strain is concerned, there are actually two types of strain in the sample which I already mentioned in chapter 4.
Figure 6.2. (a) Actual amount of C substitution ($x$) in the composition of Mg($B_{1-x}C_x$)$_2$ and (b) lattice strain with amount of C$_4$H$_6$O$_5$ additive.

From Figure 6.2 (b), it should be noted that the lattice strain values of C doped samples were slightly higher than that of the pristine MgB$_2$. This can be attributed to the C substitution in the structure and un-reacted C inside grains.
Figure 6.3. The $a$-axis lattice parameter versus actual C substitution ($x$) in Mg(B$_{1-x}$C$_x$)$_2$.

Figure 6.3 shows the $a$-axis parameter versus actual C substitution ($x$) in the Mg(B$_{1-x}$C$_x$)$_2$ for MgB$_2$ + C$_4$H$_6$O$_5$ samples. From our $a$-axis data, we extract the following relationship:

$$a = 3.08616 - 0.43958x$$

(1)

where $x$ is the C content from Mg( B$_{1-x}$C$_x$)$_2$. That is, C substitution strongly affects the $a$-axis parameter of the MgB$_2$ structure. Specifically, from the Avdeev et al [8] results, the level of C substitution, $x$ in the composition of Mg(B$_{1-x}$C$_x$)$_2$, can be easily estimated as $x = 7.5 \times \Delta (c/a)$, where $\Delta (c/a)$ is the change in $c/a$ compared to a pristine sample. That is, the actual C substitution level is related to $c/a$. 

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6.3.3 Analysis of the grain morphology using micro-structure

Figure 6.4. Field emission gun-scanning electron microscopy (FEG-SEM) images of (a) un-doped MgB$_2$, (b) MgB$_2$+10 wt% C$_4$H$_6$O$_5$ and (c) MgB$_2$+30 wt% C$_4$H$_6$O$_5$.

Figure 6.4 shows FEG-SEM images of (a) un-doped MgB$_2$, (b) MgB$_2$+10 wt% C$_4$H$_6$O$_5$, and (c) MgB$_2$+30 wt% C$_4$H$_6$O$_5$. All of the samples showed similar granular microstructures. However, the un-doped MgB$_2$ sample appears inhomogeneous and has
poor connectivity, consisting of grains from several tens of nanometres in size to 500 nm. As the additive level increased to 10 wt%, the grain morphology of the sample was refined to more homogeneous grains (100–200 nm) and better connectivity. In the case of MgB$_2$ + 30 wt% C$_4$H$_6$O$_5$, however, it again appears inhomogeneous, consisting of grains from 100 nm in size to 1000 nm. This may be attributed to the excess C dopant, i.e., the parameter space is limited to 10 wt% C$_4$H$_6$O$_5$ as mentioned above. The excess C is present as second phases in the MgB$_2$. What is interesting is that grains for MgB$_2$ + 30 wt% C$_4$H$_6$O$_5$ appeared to have a bar shape in the local parts.

![Figure 6.5](image)

**Figure 6.5.** Field emission gun-scanning electron microscopy (FEG-SEM) image of MgB$_2$ + 30 wt% C$_4$H$_6$O$_5$ with inhomogeneous microstructures.

Figure 6.5 shows a FEG-SEM image of MgB$_2$ + 30 wt% C$_4$H$_6$O$_5$ with low magnification (×5000). As can be seen in the Figure 6.5, there were holes in local areas, with sizes of 1–5 µm. We suggest the possibility that trapped gas such as carbon monoxide is being released during heat treatment processing. From differential thermal analysis (not
shown), there were other endothermal peaks of $\text{C}_4\text{H}_6\text{O}_5$ up to 300 °C, even though the decomposition temperature for $\text{C}_4\text{H}_6\text{O}_5$ was about 140–150 °C. These problems can be further controlled by varying the amount of $\text{C}_4\text{H}_6\text{O}_5$ additive or by different evaporation temperatures.

6.3.4 Formation of MgO increased with increasing doping level

To explore the possibility that the formation of MgO is due to residual oxygen (O), we also calculated the weight fractions of MgB$_2$/Mg (B$_{1-x}$C$_x$)$_2$ and MgO with different amounts of $\text{C}_4\text{H}_6\text{O}_5$ additive. As the amount of $\text{C}_4\text{H}_6\text{O}_5$ increased, it was expected that the weight fraction of MgO would increase, as can be seen in Figure 6.6.

![Figure 6.6](image)

**Figure 6.6.** Weight fractions of MgB$_2$/Mg (B$_{1-x}$C$_x$)$_2$ and MgO with different amounts of $\text{C}_4\text{H}_6\text{O}_5$ additive.

Specifically, the MgO fraction was estimated to be 16.5 wt% in the MgB$_2$ + 20 wt% $\text{C}_4\text{H}_6\text{O}_5$ sample. This is probably because residual O after evaporation processing reacts with Mg. However, the MgO fraction in the 5 or 10 wt% samples did not show any
differences compared to un-doped MgB$_2$. It should be noted that un-doped MgB$_2$ had MgO of 6.6 wt% even though there was no use of C$_4$H$_6$O$_5$ + C$_7$H$_8$ during the sample preparation. This indicates that the precursor Mg powder was already oxidized [9].

6.3.5 Analysis of the superconducting properties

Figure 6.7. Critical temperature ($T_c$) behaviour with different amounts of C$_4$H$_6$O$_5$ additive. The inset shows that $T_c$ broadening occurred for all MgB$_2$ + C$_4$H$_6$O$_5$ samples.

Figure 6.7 shows the $T_c$ behaviour of all samples with different amounts of C$_4$H$_6$O$_5$ additive. The estimated values were 37.6, 37.0, 35.8, 35.7, and 35.8 K, respectively. What is surprising is that the $T_c$ of the MgB$_2$ + C$_4$H$_6$O$_5$ samples remained unchanged, except for that of MgB$_2$+5wt% C$_4$H$_6$O$_5$ among the additive samples. The C$_7$H$_8$ used in this experiment is believed to be related to the saturated $T_c$ behaviour. This is probably because a large fraction of the C$_4$H$_6$O$_5$ does not take part in the substitution reaction and
directly evaporates with C$_7$H$_8$ under this specific experimental condition. We should consider the possibility of a C$_7$H$_8$ effect [10]. In the inset, we also observe that $T_c$ broadening occurred for all of the MgB$_2$ + C$_4$H$_6$O$_5$ samples. This could be associated with degradation of crystallinity due to C substitution, which is consistent with the results on the lattice parameter and lattice strain.

**Figure 6.8.** Irreversibility field ($H_{irr}$) dependence as a function of the amount of C$_4$H$_6$O$_5$ additive. The $H_{irr}$ values were defined by a critical current density ($J_c$) criterion of 100 A cm$^{-2}$. The inset shows $J_c$ of all MgB$_2$ + C$_4$H$_6$O$_5$ samples at 20 K.

The $H_{irr}$ dependence as a function of the amount of C$_4$H$_6$O$_5$ additive is shown in Figure 6.8. The $H_{irr}$ values were defined by a $J_c$ criterion of 100 A cm$^{-2}$. The $H_{irr}$ of the MgB$_2$ + C$_4$H$_6$O$_5$ samples reached around 7 T at 20 K. As can be seen in the Figure 6.8, $H_{irr}$ is strongly correlated with the amount of C substitution, which results in increasing lattice strain and $\Delta T_c (T_{c,\text{onset}} - T_{c,\text{zero}})$ for MgB$_2$. Specifically, it should be noted that the self-field $J_c$ of the MgB$_2$ + C$_4$H$_6$O$_5$ samples in the inset was slightly changed at an additive level as high as 30 wt%. In addition, $J_c$ and $H_{irr}$ were almost the same for the samples.
with 10 and 30 wt%. This effect may be offset by the grain of bar shape due to excess C₄H₆O₅. As a result, this finding opens a direction for the manufacture of nanodoped materials using the C₄H₆O₅ + C₇H₈ solution, which solves the agglomeration problem, avoids the use of expensive nanoadditives, and achieves improved performance properties such as $J_c$, $H_{irr}$, and $H_{c2}$.

6.4 Summary

We systematically investigated the superconductivity of MgB₂ + C₄H₆O₅ samples prepared by using the chemical solution route. All superconductor properties, such as lattice parameters, lattice strain, amount of C substitution, microstructures, weight fraction of MgO, $T_c$, $J_c$, and $H_{irr}$, were sensitive to the amount of C₄H₆O₅ additive. The lattice parameters decreased monotonically within the accuracy errors as the amount of C₄H₆O₅ additive increased to 10 wt%. When the amount of C₄H₆O₅ additive was further increased to 20 wt%, the lattice parameters did not change any more. This means that the parameter space in the MgB₂ structure is limited to only 10 wt% C₄H₆O₅ additive. These observations were further supported by the results on $c/a$, lattice strain, $T_c$, and $H_{irr}$, which are related to the limited carbon (C) substitution into B. Specifically, the $H_{irr}$ of the MgB₂ + C₄H₆O₅ samples prepared by the chemical solution route reached around 7 T at 20 K with a $T_c$ reduction of only 1.5 K. In addition, the self-field $J_c$ of the MgB₂ + C₄H₆O₅ samples was slightly changed at an additive level as high as 30 wt%. As a result, only a small fraction of C₄H₆O₅ (~10 wt%) is required as a C source for our MgB₂ superconductor.
References


CHAPTER 7

7. SIGNIFICANT ENHANCEMENT OF $H_{c2}$ and $H_{irr}$ IN MgB$_2$ + C$_4$H$_6$O$_5$ BULKS AT THE LOW SINTERING TEMPERATURE OF 600 °C

7.1 Introduction:

In previous chapters, we have already shown that $J_c$ enhancement by more than one order of magnitude in high magnetic field can be achieved with only a slight reduction in $T_c$ for MgB$_2$ + C$_4$H$_6$O$_5$ [1] sintered at 900ºC. To further explore the potential as a C source of C$_4$H$_6$O$_5$, low temperature sintering also has significant advantages for commercial MgB$_2$ conductors such as MgB$_2$ + SiC. Recently, Fujii et al. [2] prepared Fe-containing tape samples at the low temperature of 600ºC using MgH$_2$ instead of Mg powder. Mg freshly decomposed from MgH$_2$ below 600ºC can be easily reacted with B for MgB$_2$ formation. The $H_{c2}$ and $H_{irr}$ enhancement at low sintering temperature is crucial for selection of various sheath materials and reduction of production costs. For these reasons, C$_4$H$_6$O$_5$ is one of the main candidate materials for low sintering temperature processing at 600ºC, as this C source can be fully decomposed at temperatures as low as 300ºC. In this chapter, therefore, I have systematically studied the $H_{c2}$ and $H_{irr}$ at different sintering temperatures in the range from 600 to 900ºC, and we have found the largest $H_{c2}$ and $H_{irr}$ for MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ sample sintered at 600ºC for 4 hours.
7.2 Experimental:

MgB$_2$ pellets were prepared by an *in-situ* process with the addition of 10 wt% C$_4$H$_6$O$_5$. The fabrication processing is described in previous chapters. All samples were sintered in a tube furnace at temperatures ranging from 650 to 900°C for 30 min, and at 600 °C for 30min, 2 hours, and 4 hours under high purity argon gas. The heating rate was 5 °C/min$^{-1}$. All samples were characterized by X-ray diffraction (XRD), field emission gun-scanning electron microscopy (FEG-SEM), $T_c$, $H_{irr}$, and $H_{c2}$. The lattice parameters were obtained from Rietveld refinement. $T_c$ was defined as the onset temperature at which diamagnetic properties were observed. In addition, $H_{c2}$ and $H_{irr}$ were defined as $H_{c2} = 0.9R(T_c)$ and $H_{irr} = 0.1R(T_c)$ from the resistance ($R$) versus temperature ($T$) curve. Details of the sample compositions, heat treatment conditions, and measured superconducting properties of all the un-doped and MgB$_2$ + 10 wt% C$_4$H$_6$O$_5$ samples are given in Table 7.1.

7.3 Result and discussion:

Figure 7.1 shows the XRD patterns of all the samples produced at different sintering temperatures. It was observed that the un-doped MgB$_2$ and MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples sintered at 650 to 900°C seemed to be well developed MgB$_2$ with a small amount of MgO. The inset of Figure 7.1 also shows the MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples sintered at 600°C for 30 min, 2 hours and 4 hours. In the 600°C for 30 min sample, peaks of un-reacted Mg due to the low sintering temperature and insufficient time were observed.
Figure 7.1. The X-ray diffraction patterns for referenced un-doped MgB$_2$ sintered at 650°C and MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples sintered from 650 to 900°C. Inset is the MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples sintered at 600°C for 30 min, 2 hours, and 4 hours, respectively.

As the sintering time further increased to 4 hours, however, the un-reacted Mg peak was significantly reduced, and it almost disappeared when the sintering temperature was gradually increased. Specifically, MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples processed at 600°C for 4 hours had larger full width at half maximum (FWHM) values than those other samples, as described in Table 7.1. This indicates that small grains and imperfect crystallinity exist in samples processed at low sintering temperatures. Yamamoto *et al.*
reported that $H_{irr}$ can be enhanced by degradation of crystallinity due to a low temperature solid-solid reaction. Eom et al. [4] made a dirty film with FWHM $> 1^\circ$, resulting in an enhancement of $H_{c2}$ to $\sim 50$ T. In addition, Lee et al. [5] reported that a clean single crystal with FWHM $\sim 0.06^\circ$ had the only low $H_{c2}, \sim 20$ T. That is, low crystallinity is primarily responsible for larger $H_{irr}$ and $H_{c2}$. On the other hand, FWHM values decreased with increasing sintering temperature, which is attributable to the improvement of crystallinity. Improvement of crystallinity also accompanies better grain connectivity of the MgB$_2$, resulting in increased density [6]. It is to be noted that FWHMs of MgB$_2 + 10$wt% C$_4$H$_6$O$_5$ samples are relatively larger than those of un-doped MgB$_2$ over the whole sintering range. This result is related to the lattice disorder due to C substitution into B sites. The resistivities $\rho$ for un-doped MgB$_2$ and MgB$_2 + 10$wt% C$_4$H$_6$O$_5$ samples sintered at different sintering temperatures were 25–42 and 90–137 $\mu\Omega$cm at 40 K, respectively, as shown in Table 7.1. The increased $\rho$ for MgB$_2 + 10$wt% C$_4$H$_6$O$_5$ samples also indicates the increased impurity scattering as a result of C substitution into B sites.
### Table 7.1. Measured data for un-doped MgB$_2$ and 10wt% C$_4$H$_6$O$_5$ samples with different sintering conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering conditions</th>
<th>Lattice parameters (Å)</th>
<th>Actual C substitution (x) in Mg(B$_{1-x}$C$_x$)$_2$</th>
<th>$\rho_{40\text{ K}}$ (µΩ cm)</th>
<th>$T_c$ (K)</th>
<th>FWHM of (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-doped 650ºC x 30min</td>
<td>3.0857  3.5270</td>
<td></td>
<td>41.8</td>
<td>36.80</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>Un-doped 900ºC x 30min</td>
<td>3.0851  3.5260</td>
<td></td>
<td>24.8</td>
<td>38.10</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>MgB$_2$ + C$_4$H$_6$O$_5$ 600ºC x 4 hour</td>
<td>3.0749  3.5240</td>
<td>0.0232</td>
<td>137.1</td>
<td>33.57</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Mg B$_2$ +C$_4$H$_6$O$_5$ 650ºC x 30min</td>
<td>3.0753  3.5237</td>
<td>0.0224</td>
<td>116.6</td>
<td>33.38</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>MgB$_2$ + C$_4$H$_6$O$_5$ 700ºC x 30min</td>
<td>3.0722  3.5189</td>
<td>0.0293</td>
<td>88.9</td>
<td>34.74</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>MgB$_2$ + C$_4$H$_6$O$_5$ 800ºC x 30min</td>
<td>3.0734  3.5205</td>
<td>0.0266</td>
<td>94.8</td>
<td>34.79</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>MgB$_2$ + C$_4$H$_6$O$_5$ 900ºC x 30min</td>
<td>3.0764  3.5231</td>
<td>0.0198</td>
<td>90.2</td>
<td>35.03</td>
<td>0.55</td>
<td></td>
</tr>
</tbody>
</table>

*Extrapolation from measured lattice parameter (Ref. 7).*

**Figure 7.2.** SEM images for MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples sintered at (a) 600ºC for 4 hours and (b) 650ºC for 30 min.
These observations can be further supported by the microstructures. FEG-SEM images for MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples sintered at (a) 600 and (b) 650ºC are shown in Figure 7.2. All the samples showed similar granular microstructures. However, the sample sintered at 600ºC appears inhomogeneous and has poor connectivity, consisting of grains from several tens of nanometers in size to 300 nm. As the sintering temperature further increased to 650ºC, the grain morphology of the sample was refined to more homogeneous grains (100-200 nm) and better connectivity after melted Mg. Even though FWHM values between both samples did not show much difference, the poorer crystallinity of the sample sintered at 600ºC can be attributed to the solid-solid reaction.

![Figure 7.3](image_url)

**Figure 7.3.** Temperature dependence of normalized (a) $H_{ir}$ and (b) $H_{c2}$ for MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples as a function of sintering temperature.
The temperature dependence of $H_{irr}$ and $H_{c2}$ for all the un-doped and MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ samples sintered at different sintering temperatures are shown in Figure 7.3. We observed that $H_{irr}$ and $H_{c2}$ were depressed systematically as the sintering temperature increased to 900 °C. This indicates that degradation of crystallinity at low temperature can be the driving force for larger $H_{irr}$ and $H_{c2}$, as mentioned above. In addition, the significant C substitution into B sites at a sintering temperature as low as 600°C may induce disorder on the lattice sites, which can lead to the enhancement of the $H_{irr}$ and $H_{c2}$. That is, there are two effects, poor crystallinity and C substitution, which may be responsible for the significantly enhanced $H_{irr}$ and $H_{c2}$ for the MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ sample sintered at 600 °C.

Figure 7.4. Temperature dependence of normalized $H_{c2}$ for the MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ sample sintered at 600°C for 4 hours. The $H_{c2}$ for other C doped samples are also shown for comparison (Ref. 9).
What is interesting is that fresh C coming from C₄H₆O₅ can enter into B sites easily, even with sintering at 600°C for 4 hours, as shown in Table 7.1. The a-axis lattice parameter, decreased from 3.0851 Å for a well developed un-doped sample sintered at 900°C for 30 min to 3.0749, 3.0753, 3.0722, 3.0734, 3.0764 Å for MgB₂ + 10wt% C₄H₆O₅ samples sintered at 600°C for 4 hours and 650, 700, 800, and 900 °C for 30 min, respectively. Even though there were some fluctuations in the changing a lattice parameter in samples with different sintering temperatures, the amount of C substitution seemed to be saturated, with the average x ~ 0.0242 in the Mg(B₁₋ₓCₓ)₂, at all sintering temperatures [7]. In general, the shrinkage of the a-axis is attributed to the substitution of C for B. That is, significant C substitution can be achieved for MgB₂ + 10wt% C₄H₆O₅, even with a low sintering temperature regime. On the other hand, the c-axis lattice parameter remained unchanged. Thus MgB₂ + C₄H₆O₅ samples produces highly reactive C, allowing it to achieve relatively higher C substitution levels at lower temperature, compared to nano-C, B₄C, and carbon nanotube [8]. In Figure 7.4, it is shown that significantly enhanced \( H_{c2} \) has been found in an MgB₂ + C₄H₆O₅ sample compared to different kinds of C doped samples [9]. The steeper slopes of \( H_{c2} \) of MgB₂ + 10wt% C₄H₆O₅ exceeded \( H_{c2} \) of other referenced samples. Based on these results, active C freshly released from C₄H₆O₅ can easily enter into B sites at the same temperature as MgB₂ formation.
7.4 Summary:

In summary, C₄H₆O₅ has again proved to be an attractive C source dopant like SiC for enhancing $H_{irr}$ and $H_{c2}$ in a way that is compatible with low temperature sintering for a short period of time. The quality of the MgB₂ + 10wt% C₄H₆O₅ samples are attributable to the high level of C substitution into B sites and the induction of smaller grain size at sintering temperature as low as 600°C. This result is consistent with results on the $a$-axis lattice parameter, $T_c$, FWHM, microstructures, and actual C substitution. As a result, the very cheap C₄H₆O₅ dopant is one of most significant potential C sources for commercial MgB₂ superconductor.
References:


CHAPTER 8

8. INFLUENCE OF DISORDER ON THE IN-FIELD $J_c$ OF MgB$_2$ WIRES USING HIGHLY ACTIVE PYRENE (C$_{16}$H$_{10}$)

8.1 Introduction

In chapters 5, 6 and 7, I reported on the C source possibilities of carbohydrate (malic acid, C$_4$H$_6$O$_5$) doping through a chemical solution route to achieve homogeneous mixing. The advantages of the chemical solution route using various carbohydrates have now been confirmed by other groups [1-3]. However, our understanding of the cause of the significantly enhanced $J_c$ and $B_{irr}$ has still remained unclear due to the complicated reactions involved. In addition, although we conducted evaporation processing to eliminate the oxygen (O) content, the fraction of MgO due to included O from the carbohydrate increased gradually with increasing doping level. [4] If we can reduce the MgO fraction within the matrix and find a highly active C source that will be effective at lower sintering temperatures 600 °C, the same as for MgB$_2$ formation, we speculate that the resulting high disorder due to C substitution, as well as strong flux pinning due to the small crystalline size, can have simultaneous positive effects on the infield $J_c$. A higher sintering temperature is usually necessary for most of the other C sources, leading to crystalline growth and worse pinning [5]. The use of low temperature processing is also crucial as it allows selection of various sensitive sheath materials and the reduction of production costs. Although Yamada et al. [6] prepared Fe sheathed tape samples by using a liquid aromatic hydrocarbon together with ball milling, it is very difficult to control the composition during ball milling because of its volatile properties. In this chapter,
therefore, I suggested a different hydrocarbon, pyrene (C\textsubscript{16}H\textsubscript{10}), which has no oxygen content, as the C source. This is a colorless solid and consists of four fused benzene rings, resulting in a large, flat aromatic system. At around a temperature of 145–148 °C, it decomposes into benzene (C\textsubscript{6}H\textsubscript{6}), other hydrocarbons, and C. The released fresh C enables the improvement reactivity. In addition, it can be dissolved in a proper solution for homogeneous mixing. To clearly understand the \( J_c \) behavior and superconductivity of MgB\textsubscript{2} using C\textsubscript{16}H\textsubscript{10}, the lattice parameters, the actual amount of C substituted, the lattice strain, the MgO fraction, and the transport \( J_c \) were evaluated and compared to pristine MgB\textsubscript{2}/Fe wires.

8.2 Experimental

Magnesium (Mg, 99%), boron (B, 99%), and pyrene (C\textsubscript{16}H\textsubscript{10}, 98%) powders were used as starting materials. The mixed powders were packed into a Fe tube, which was then drawn to an outer diameter of 1.42 mm. The fabricated wires were sintered at different temperatures within a wide range from 600 to 800 °C for 30 min to 4 h under high purity argon gas and then cooled in the furnace. The heating rate was 5 °C min\(^{-1}\). All the measurements have been done in a similar way as I mentioned in the chapter 4.
8.3 Result and discussion

8.3.1 Doping effect of C$_{16}$H$_{10}$ on lattice parameter, lattice strain and MgO formation

![Graph showing results](image)

**Figure 8.1.** (a) The $a$-axis lattice parameter, (b) lattice strain, and (c) fraction of MgO/Mg for pristine MgB$_2$ and MgB$_2$+ C$_{16}$H$_{10}$/Fe wires as a function of the amount of pyrene. All wire samples were sintered at 650 °C for 30 min. The solid line show a linear fit to the data.

Figure 8.1(a) shows the calculated results for pristine MgB$_2$ and MgB$_2$+ C$_{16}$H$_{10}$/Fe wires as a function of the amount of pyrene, C$_{16}$H$_{10}$. All wire samples were sintered at 650 °C for 30 min. We observed that the $a$-axis parameter of MgB$_2$+ C$_{16}$H$_{10}$/Fe wires decreased gradually with increasing amounts of C$_{16}$H$_{10}$. The shrinkage of the $a$-axis lattice parameter can be attributed to the substitution of C with small atomic size, which causes disorder in the MgB$_2$ structure that can potentially change the properties of MgB$_2$ [5, 7].

What is interesting is that C substitution into B sites took place even at the low sintering
temperature of ~650 °C. To further clarify the effects of C substitution, we calculated the lattice strain of the structure as a function of the amount of C$_{16}$H$_{10}$, as can be seen in Fig. 8.1 (b). Lattice strain is usually an interesting parameter for quantifying disorder. Estimated strain values at different doping levels showed the opposite trend to the changes in the $a$-axis parameter. This indicates that more C substitution has introduced higher disorder into the MgB$_2$ structure. However, the MgO fraction does not increase with increasing doping level. Figure 8.1(c) shows the calculated MgO fraction of pristine MgB$_2$ and of MgB$_2$ + C$_{16}$H$_{10}$/Fe wires on the basis of Rietveld refinement. At the very least, the MgO fraction for MgB$_2$+10 wt% C$_{16}$H$_{10}$/Fe wires is less than or similar to that found in the pristine MgB$_2$ under our experimental conditions. Thus, the MgO effect on the degradation of $J_c$ is negligible.

8.3.2 Sintering temperature effect on lattice parameter and C-substitution
Figure 8.2. (a) The $a$-axis lattice parameter, (b) $c$-axis lattice parameter, and (c) actual amount of carbon (C) substitution ($x$) in the composition of Mg(B$_{1-x}$C$_x$)$_2$ for pristine MgB$_2$ and MgB$_2$+10 wt% C$_{16}$H$_{10}$/Fe wires as a function of sintering temperature. The wire samples were sintered at 600 °C for 4 h, 620 °C for 1 h, 650 °C for 30 min, 700 °C for 30 min, 800 °C for 30 min, respectively. The solid line show a linear fit to the data.

Figure 8.2 shows the calculated results for pristine MgB$_2$ and MgB$_2$+10 wt% C$_{16}$H$_{10}$/Fe wires as a function of sintering temperature. The wire samples were sintered at 600 °C for 4 h, 620 °C for 1 h, 650 °C for 30 min, 700 °C for 30 min, and 800 °C for 30 min, respectively. What is surprising is that the $a$-axis parameter of MgB$_2$+10 wt% C$_{16}$H$_{10}$/Fe wires showed a slight increasing trend from 3.0684 to 3.0724 Å with increasing sintering temperature (Fig. 8.2(a)). However, this is not an ordinary phenomenon. For example, common C additives, such as C, SiC, and carbon nanotube (CNT), can achieve much more C substitution into the MgB$_2$ structure as the sintering temperature further increases, resulting in a reduced $a$-axis parameter and enhanced $B_{\text{irr}}$ and $J_c$ [8]. The $c$-axis parameter also mimics the change in the $a$-axis parameter (Fig. 8.2(b)). Obviously, a low sintering temperature can give rise to higher disorder in the MgB$_2$ structure, leading to broadening of the diffraction peaks. This implies combined effects of crystalline size reduction and increased lattice strain. Specifically, the crystalline size in MgB$_2$ superconductor sample can be attributed to the number of grain boundaries. Based on changes in the $a$-axis parameter, the actual amount of C substitution can be estimated by comparing the calculated value with that of a single crystal. The actual C substitution [7] for the sample sintered at 600 °C was about $x \sim 0.03913$ in the composition of Mg(B$_{1-x}$C$_x$)$_2$. As a result, the maximum C substitution level can be easily achieved at a low sintering temperature of 600 °C under our experimental conditions (Fig. 8.2 (c)). At this temperature, the much greater amount of C substituted on the B sites introduces
strong electron scattering centers that reduce the electron mean free path and, thus, could significantly enhance $B_{irr}$. [5]

8.3.3 Analysis of transport $J_c$ in $C_{16}H_{10}$ doped MgB$_2$

![Figure 8.3](image)

**Figure 8.3** Transport critical current density ($J_c$) of pristine MgB$_2$ and MgB$_2$+10 wt% $C_{16}H_{10}$/Fe wires as a function of applied magnetic field and sintering temperature.

Figure 8.3 shows the transport $J_c$ of pristine MgB$_2$ and MgB$_2$+10 wt% $C_{16}H_{10}$/Fe wires sintered within a temperature range of 600 to 800 °C. The $J_c$ of the MgB$_2$+10 wt% $C_{16}H_{10}$/Fe wires gradually decreased as the sintering temperature increased. This is because grain boundaries are likely to be acting as the predominant pinning centers [9]. In addition, the amount of C substitution decreased with increasing sintering temperature. Note that $J_c$ of the MgB$_2$+10 wt% $C_{16}H_{10}$/Fe wires was higher than that of the pristine MgB$_2$ wire under magnetic field from 7 to 12 T. Transport $J_c$ did not show any large differences among the MgB$_2$+10 wt% $C_{16}H_{10}$ wire samples. As a result, the MgB$_2$+10
wt% C$_{16}$H$_{10}$/Fe wire sintered at 600 °C showed better $J_c$ performance, compared to samples doped with other forms of C and sintered at a similar temperature. [8]
8.4 Summary

In summary, using pyrene, C\textsubscript{16}H\textsubscript{10}, is also effective for enhancing $J_c$ of MgB\textsubscript{2} superconductor, even at sintering temperatures as low as 600 °C. Specifically, the $J_c$ of the sample sintered at 600 °C for 4 h was $\approx$10 000 A cm$^{-2}$ at 10 T and 4.2 K. In addition, the MgO fraction for MgB\textsubscript{2}+10 wt\% C\textsubscript{16}H\textsubscript{10} /Fe wires was less than or similar to that found in the pristine MgB\textsubscript{2} under our experimental conditions. The advantages of using C\textsubscript{16}H\textsubscript{10} include the production of highly active C due to the decomposition of the pyrene and the introduction of small grain size due to low temperature sintering, resulting in enhancement of $J_c$. 
References


CHAPTER 9

9. CONCLUSION:

We have systematically studied the effect of heat treatment temperature on the phase formation, lattice parameters, critical temperature \( T_c \), full width half maximum (FWHM), critical current density \( J_c \) and resistivity \( \rho \) in the pristine MgB\(_2\)/Fe wires. DTA results gave us the idea about the optimum heat treatment condition and all the samples were fabricated by \textit{in-situ} PIT and sintered within the temperature range of 650–900 °C according to the DTA analysis. I observed that smaller grain size due to higher FWHM values and poor crystallinity due to decreased \( T_c \) found at low sintering temperature samples. So the best transport \( J_c \) value reached 4200 A cm\(^{-2}\) at 4.2 K and 10 T at 650 °C. The samples sintered at 650 °C have relatively higher strain value and higher \( \rho \) which indicates that various defects within grains could act as pinning centers.

I have already discussed a lot about the reason why I used the carbohydrate (malic acid, C\(_4\)H\(_6\)O\(_5\), in this case) as a doping into MgB\(_2\). We have shown carbohydrate doping results in a small depression in \( T_c \) but significantly increase the C substitution level. When compared to the un-doped MgB\(_2\) as a reference sample, it was found that the C substitution for B could enhance the pinning property such as an improvement of \( J_c \), upper critical field \( (H_{c2}) \) and irreversibility field \( (H_{irr}) \) in a high-field regime. Smaller, denser and more homogeneous grains in MgB\(_2\)+ 10wt\% C\(_4\)H\(_6\)O\(_5\) samples enhance the critical current. The improvement of the \( H_{c2} \) and \( H_{irr} \) at a heat-treatment temperature of 900 °C can be attributed to the increase of the flux pinning by more C substitution.
We used the toluene (C_7H_8) as a solvent in C_4H_6O_5 doped MgB_2 for uniform and homogeneous mixing. Samples are prepared by using this chemical solution route and superconducting properties are systematically studied. It is found that lattice parameters, lattice strain, amount of C substitution, T_c, J_c, and H_{irr} are sensitive to the amount of C_4H_6O_5 additive. The lattice parameters, T_c decreased monotonically as the amount of C_4H_6O_5 additive increased to 10 wt%. Amount of C-substitution, lattice strain, H_{irr} increased to maximum level at 10 wt% addition of C_4H_6O_5. When the amount of C_4H_6O_5 additive was further increased to 20 wt% or 30 wt%, the lattice parameters and other superconducting properties became saturated. This means that the parameter space in the MgB_2 structure is limited to only 10 wt% C_4H_6O_5 additive. As a result, only a small fraction of C_4H_6O_5 (~ 10 wt%) is required as a C source for our MgB_2 superconductor.

SiC is still the best C-source for enhancing the superconducting properties even at very low sintering temperature and short sintering time. This motivated me to work further on the effect of sintering temperature in C_4H_6O_5 doped MgB_2 superconductor. I already proved the quality of C_4H_6O_5 as a dopant and in this study I also found the high level of C substitution into B sites and the induction of smaller grain size at a sintering temperature as low as 600 °C. This result is consistent with results on the a-axis lattice parameter, T_c, FWHM, microstructures, and actual C substitution. As a result, the very cheap C_4H_6O_5 dopant is one of the most significant potential C sources for commercial MgB_2 superconductor. This finding opens a direction for the manufacture of nano-doped materials using the carbohydrate chemical solution route, which solves the agglomeration
problem, avoids the use of expensive nanoadditives, and achieves improved performance properties at low sintering temperature and short sintering period.

The complicated chemical solution route and increased MgO formed in increased doping level of C₄H₆O₅ were the problems I faced using the carbohydrate doping. That’s why, in last work in my thesis, I proposed another new organic dopant, called pyrene (C₁₆H₁₀) which has no oxygen (O) content. I have shown that the MgO fraction for MgB₂+10 wt% C₁₆H₁₀/Fe wires was less than or similar to that found in the pristine MgB₂ under my experimental conditions. Fresh and highly active C was produced by using solid-solid mixing rather than the complicated chemical solution route and contributed to improve the superconducting properties. Increased level of defects and introduction of smaller grain size due to low temperature sintering, resulting the enhancement of pinning centers and hence J_c.
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